SYNTHESIS AND CHARACTERIZATION OF COPOLYMERS BASED ON
2,3,4,5,6-PENTAFLUOROSTYRENE

A Dissertation
Presented to
The Graduate Faculty of The University of Akron

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

Marta Paz Pazos
December, 2005
SYNTHESIS AND CHARACTERIZATION OF COPOLYMERS BASED ON
2,3,4,5,6-PENTAFLUOROSTYRENE

Marta Paz Pazos

Dissertation

Approved:  
Advisor  
Dr. Coleen Pugh

Advisor  
Department Chair  
Dr. Mark D. Foster

Committee Chair  
Dr. William J. Brittain

Committee Chair  
Dean of the College  
Dr. Frank N. Kelley

Committee Member  
Dr. Stephen Cheng

Committee Member  
Dean of the Graduate School  
Dr. George R. Newkome

Committee Member  
Dr. Wayne L. Mattice

Committee Member  
Dr. Peter L. Rinaldi

Accepted:

Department Chair

Dr. Mark D. Foster

Dean of the College

Dr. Frank N. Kelley

Dean of the Graduate School

Dr. George R. Newkome
ABSTRACT

2,3,4,5,6-Pentafluorostyrene (PFS) was polymerized in the presence of a solution of polybutadiene (PB) in tetrahydrofuran using benzoyl peroxide as the radical initiator at 50, 60, 80 °C. The products were graft copolymers of poly(2,3,4,5,6-pentafluorostyrene) (PPFS) into PB. The copolymerizations follow typical free radical polymerization kinetics and behavior, with the rate of propagation proportional to the monomer concentration and the square root of the initiator concentration. Gel permeation chromatography (GPC) equipped with two detectors (UV and refractive index) has allowed us to determine conversion of the monomer, graft efficiency, graft ratio and graft frequency of the grafted products obtained at different temperatures and initiator concentrations, without the need of purification and/or isolation of the final graft copolymer. Conversion of the monomer and graft ratio increase and grafting frequency decreases with increasing temperature and initiator concentration. The grafting efficiencies and grafting ratios are consistent with a system that terminates mainly by combination and whose graft sites are generated by hydrogen abstraction of allylic radicals by initiator primary radicals. Pure graft copolymers were isolated by extracting unreacted PB into hexanes and PPFS homopolymer generated as a side-product into acetone. The similarity of the glass transition temperatures of the PPFS
grafts and the corresponding extracted PPFS homopolymers confirms that their lengths are approximately equal.

We also attempted to react PFS with PB by an ene reaction, which would result in PB modified with perfluorinated rings connected to the PB backbone through a two carbon spacer. However, we were not able to perform the modification either with PB or with model compounds. One of the reactions tested was PFS with β-pinene, which resulted in the copolymerization of them. The copolymer products are composed of isolated units of β-pinene randomly distributed between blocks of PFS segments, as evidenced from their copolymer reactivity ratios and their glass transitions.

PFS was also copolymerized in bulk with styrene (at 70 and 25 °C), 1-vinyl naphthalene (at 70 and 25 °C) and 2-vinyl naphthalene (at 70 °C). In all the systems investigated the copolymer reactivity ratios are indicative of copolymerization with strong tendency to alternation. NMR spectroscopy shows evidence for this alternation by both new resonances and shifting of resonances present in the homopolymers. In addition, their thermal behavior is consistent with that of alternating copolymers. They exhibit only one glass transition, at a temperature greater than the weighted average of the glass transitions of the two homopolymers. The alternation tendency and thermal behavior of the copolymers are attributed to strong interactions developed between perfluorinated aromatic rings and regular aromatic hydrocarbons.
DEDICATION

I would like to dedicate this dissertation to all those people who, some way or another, have helped me supported and believed in me, especially to my husband, Jeffrey Schroeder. Without him, this trip would have been a lot more difficult.
ACKNOWLEDGEMENTS

In all the years I spent at the University of Akron (and some of the preceding ones), as a graduate student, there have been many events, stories, circumstances that have surrounded the work in the lab, the reading articles, the classes, the tests, the “cumes”… All of them have contributed a little bit to making this possible. I am now taking the opportunity to thank all those people that have taken part in them, so here is the list of some of them (there is really no room for all of them).

I would like to start with my advisor, Dr Coleen Pugh. Someone asked me not that long ago what it was that I had enjoyed the most in grad school. I answered that working for her, and I really meant it. I thank her for her dedication, her willingness to discuss, her ability to get the best out of a student, her constructive criticism, and for how much I have learnt from her. I never thought that a person that has not been in the field for more than 45 years could know so much about polymer science.

My mother, Mercedes, who is always there, when I most need a mother, despite of not always being so happy with my decisions. I would also like to thank her for having a contagious strength and perseverance that make you want to get to the end, even if it is just for her.
Also my sister, Silvia, who has taught me that things with a smile always taste better, and she certainly is the only person guaranteed to get it out of me. Thanks for being so proud of your little sister, for thinking so highly of me. I guess that in this sense I would like to include Carlos, my brother in law.

Senen, my father. There are certainly a lot of things I should acknowledge him for, but two of them seem more worthwhile to mention. First, for his love to science in general and polymer physical chemistry in particular, which made him my role model. And also for being the person who encouraged me the most to cross the puddle and pursue my doctorate.

Dr. Arturo Lopez-Quintela, my advisor as an undergraduate, who very well understood me when I was going through a rough patch, and had the patience to never give up on me. Thanks also to Manuel Faraco, who got me out of the rough patch and handed me the tools and taught me the mechanisms not to fall in it again.

Dr. Javier De Abajo, Dr. Jose de la Campa and Dr. Angel Lozano, my advisors and mentor in my brief stay in the Institute of Polymer Science in Madrid. I owe them my first true polymer synthesis, and small molecules too, experience. I am also extremely grateful to them for being so responsive every time I have contacted them. It is so nice to know that you can count on such great scientists.

Angela, Belen, Tatiana, Encarna, Oscar, who no matter what, when or where have always been my friends, and who continuously remind me of the
reasons why I always considered friendship so important.

The incredible Foundation “Pedro Barrie de la Maza”, which does amazing things for the sons and daughters of Galicia, where I was born and grew up. They chose me to be the recipient to one of the graduate scholarships that allowed me to come to the University of Akron, and to the Fulbright Commission, who also took care of my admission and some other important stuff.

My good friends in grad school, who made the first years a fun experience and helped me not to feel like at home so far away from mine. To Becky, for being such a great friend, and have treated me as family. I also extend my thanks to her parents, Mr. Mike and Mrs. Marlene Sawayda. Thanks also to Paul, not only for being a great friend but also very helpful with academic stuff. And Goran, for his ability to make anyone laugh, or at least try.

There are few people who have also contributed or helped me with some of the work I include in this dissertation. Drs. Rinaldi and Dudipala, from the Chemistry Department at The University of Akron, who helped me with most of the NMR spectroscopy work I include in this dissertation. Dr. Harwood, for always being receptive with my questions and requests anytime I had any. Dr. Brittain, for allowing us to use his lab for the synthesis of a monomer. Brian Mirous, for the measurements of the contact angles, and Dr. Taschner for his help with optical rotation measurements.

There are also several members in the Pugh group I am grateful to. Andrea, not only for holding my hand in my first (and sometimes second) steps in
the lab, but also for being a good friend to always count on, especially when I needed a reminder of why I was here in the first place. Thanks also to Mike (Rubal), for his continuous help in everything I asked him for. I would also like to thank Adam for his patience and receptiveness in my first mentoring experience. He made it a lot more enjoyable than I ever thought it would be.

Luca Fontana, Fred Good and Dan Sand, from Ashland Inc. They gave me the first job out of school (which gave more sense to all the effort put into), and were very understanding when I needed to finish my doctoral degree requirements once I had already started.

Mr. Jeffrey and Mrs. Marlene Schroder. They have shown continuous interest, excitement and have been so very proud of their daughter in law. Thanks also for having made me feel all the time like part of the family, like a true daughter.

And last, my husband, Jeffrey Schroeder, deliberately for the end; whom I thank for his continuous support, encouragement and understanding. But especially for always believing that I could do it, even when I only wanted to give it up. Thanks sincerely, Jeffrey.
TABLE OF CONTENTS

LIST OF TABLES ........................................................................................................ xix
LIST OF FIGURES ..................................................................................................... xxiv
LIST OF SCHEMES .................................................................................................. xxxiii

CHAPTERS

I. INTRODUCTION ..................................................................................................... 1

II. LITERATURE REVIEW .......................................................................................... 4

2.1 Fluorinated Polymers ......................................................................................... 4

   2.1.1 General Considerations on Fluorinated Polymers ...................................... 4

   2.1.2 Fluorinated Polymers Containing Aliphatic Fluorocarbons ....................... 6

      2.1.2.1 Fluoroplastics .......................................................................................... 6

      2.1.2.2 Fluoroelastomers .................................................................................. 9

      2.1.2.3 Fluorinated Polyurethanes .................................................................. 9

      2.1.2.4 Polyfluoroacrylates ............................................................................. 10

      2.1.2.5 Perfluoropolyethers ............................................................................ 10

   2.1.3 Aromatic Fluorocarbons and their Polymers ............................................. 11

      2.1.3.1 2,3,4,5,6-Pentafluorostyrene .............................................................. 11
2.1.3.2 Polymerization of 2,3,4,5,6-Pentafluorostyrene ...................... 12
  2.1.3.2.1 Conventional Radical Polymerization ............................. 12
  2.1.3.2.2 Other polymerization methods ...................................... 18
2.1.3.3 Poly(2,3,4,5,6-pentafluorostyrene) .................................... 20
  2.1.3.3.1 Spectroscopic Properties of Poly(2,3,4,5,6-
           pentafluorostyrene) ......................................................... 21
  2.1.3.3.2 Solubility and Solution Properties of Poly(2,3,4,5,6-
           pentafluorostyrene) ........................................................ 22
  2.1.3.3.3 Thermal Properties of Poly(2,3,4,5,6-
           pentafluorostyrene) ........................................................ 23
2.1.3.4 Copolymers of 2,3,4,5,6-Pentafluorostyrene and Styrene .......... 25
  2.1.3.4.1 Spectroscopy of the Copolymers of 2,3,4,5,6-
           Pentafluorostyrene and Styrene ..................................... 25
  2.1.3.4.2 Solubility of the Copolymers of 2,3,4,5,6-
           Pentafluorostyrene and Styrene ...................................... 26
  2.1.3.4.3 Thermal Properties of the Copolymers of 2,3,4,5,6-
           Pentafluorostyrene and Styrene .................................... 27
2.1.4 Commercial Applications of Poly(2,3,4,5,6-Pentafluorostyrene)
  and its Derivatives ......................................................................... 28
2.2 Interactions between Aromatic Hydrocarbons and Aromatic
  Fluorocarbons ................................................................................... 30
  2.2.1 Binary Complex of Hexafluorobenzene and Benzene and
           Methylated Benzenes .......................................................... 32
  2.2.2 Other Binary Complexes ...................................................... 35
  2.2.3 Interactions between Aromatic Rings: Crystal Structures ........... 36
  2.2.4 Applications Using Aromatic Hydrocarbon Aromatic
           Fluorocarbon Interactions ..................................................... 39
2.3 Graft Copolymers ........................................................................ 41
2.3.1 General Considerations of Graft Copolymers.................................41
    2.3.1.1 Radical Graft Polymerization..................................................42
    2.3.1.2 Redox Initiated Graft Polymerization......................................43
    2.3.1.3 Anionic Graft Polymerization..................................................44
    2.3.1.4 Cationic Graft Polymerization.................................................44
2.3.2 Grafting Polybutadiene....................................................................44
    2.3.2.1 Graft Copolymers of Polybutadiene with Styrene.......................45
    2.3.2.2 Graft Copolymers of Polybutadiene with Other Monomers .........46
2.4 Modification of Polybutadiene by Ene Reaction..................................48
    2.4.1 The Ene Reaction. Important Considerations.............................48
    2.4.2 Modification of Polybutadiene (and other Elastomers) by Ene Reaction........................................................................50
2.5 Polymerization of β-Pinene...................................................................57
    2.5.1 Importance of β-Pinene in Polymer Science.................................57
    2.5.2 Polymers of β-Pinene by Cationic Polymerization......................57
    2.5.3 Polymers of β-Pinene by Radical Polymerization.......................60
2.6 Thermal Properties of Polymer Blends and Copolymers .......................61
    2.6.1 Thermal Properties of Polymer Blends.........................................61
    2.6.2 Thermal Properties of Copolymers..............................................63
III. EXPERIMENTAL..................................................................................64
    3.1 Materials.........................................................................................64
        3.1.1 Polymers....................................................................................64
        3.1.2 Monomers and Reagents for Monomer Syntheses......................64
3.1.3 Reagents for other Syntheses ................................................................. 65
3.1.4 Initiators and Inhibitors ........................................................................ 66
3.1.5 Solvents ................................................................................................... 66

3.2 Techniques .................................................................................................. 67
3.2.1 NMR Spectroscopy ................................................................................. 68
3.2.2 Gel Permeation Chromatography ........................................................... 68
3.2.3 Differential Scanning Calorimetry ............................................................ 69
3.2.4 Contact Angles ...................................................................................... 69
3.2.5 Optical Rotations .................................................................................... 70

3.3 Homopolymerization of 2,3,4,5,6-Pentafluorostyrene .................................. 70

3.4 Grafting Polybutadiene with 2,3,4,5,6-Pentafluorostyrene ............................... 71
3.4.1 Synthesis of Polybutadiene Grafted with 2,3,4,5,6-Pentafluorostyrene ............... 71
3.4.2 Calculation of Monomer Conversion and Grafting Parameters by UV Detected Gel Permeation Chromatography .................................................. 72
3.4.3 Calculation of Monomer Conversion Gravimetrically .............................. 74
3.4.4 Purification and Isolation of Polybutadiene Grafted with 2,3,4,5,6-Pentafluorostyrene .......................................................... 75

3.5 Ene Reaction of 2,3,4,5,6-Pentafluorostyrene with Polybutadiene and Model Compounds ..................................................................................... 76
3.5.1 Tosylation of Oleyl Alcohol ..................................................................... 76
3.5.2 Reduction of p-Toluenesulfonyl 9-Octadecene-1-ol .................................. 77
3.5.3 Attempted Ene Reaction with Model Compounds ..................................... 77
3.5.4 Attempted Ene Reaction with High Molecular Weight Polybutadiene ......... 78
3.5.5 Attempted Ene Reaction with Low Molecular Weight Polybutadiene ................................................................. 79

3.6 Arene Complexes ................................................................. 80

3.6.1 1,2,3,4,5-Pentamethylycyclopentadiene ($C_p^*$) ................... 80
3.6.2 $C_p^*$RuCl$_2$ ........................................................................... 81
3.6.3 $[C_p^*$RuOMe$_2$] ................................................................. 82
3.6.4 Attempted Synthesis of the Arene Complex with 2,3,4,5,6-
Pentafluorostyrene ....................................................................... 82

3.7 Copolymerization of β-Pinene and 2,3,4,5,6-Pentafluorostyrene ........ 82

3.7.1 Copolymerization of 2,3,4,5,6-Pentafluorostyrene and β-Pinene in Solution and in Bulk ................................................. 82
3.7.2 Copolymerization of 2,3,4,5,6-Pentafluorostyrene and β-Pinene. Determination of Reactivity Ratios ........................................ 83
3.7.3 Monomer Conversion .............................................................. 84
3.7.4 Copolymer Composition .......................................................... 85

3.8 Copolymerization of Styrene and 2,3,4,5,6-Pentafluorostyrene ...... 87

3.8.1 Copolymerization of Styrene and 2,3,4,5,6-Pentafluorostyrene at 70 °C ............................................................. 87
3.8.2 Copolymerization of Styrene and 2,3,4,5,6-Pentafluorostyrene at 25 °C ............................................................. 88
3.8.3 Monomer Conversion .............................................................. 88
3.8.4 Copolymer Composition .......................................................... 90
3.8.5 Homopolymerization of Styrene .............................................. 91
3.8.6 Homopolymerization of 2,3,4,5,6-Pentafluorostyrene ............... 92

3.9 Copolymerization of 2-Vinyl Naphthalene and 2,3,4,5,6-
Pentafluorostyrene ........................................................................ 93
3.9.1 Copolymerization of 2-Vinyl Naphthalene 2,3,4,5,6-
Pentafluorostyrene at 70 °C.................................................................93

3.9.2 Monomer Conversion and Copolymer Composition...............94

3.9.3 Synthesis of Poly(2-Vinyl Naphthalene) ...............................95

3.10 Copolymerization of 1-Vinyl Naphthalene and 2,3,4,5,6-
Pentafluorostyrene ..............................................................................97

3.10.1 Synthesis of 1-Vinyl Naphthalene...........................................97

3.10.2 Homopolymerization of 1-Vinyl Naphthalene.........................99

3.10.3 Copolymerization of 1-Vinyl naphthalene and 2,3,4,5,6-
Pentafluorostyrene at 70 °C.................................................................99

3.10.4 Copolymerization of 1-Vinyl naphthalene and 2,3,4,5,6-
Pentafluorostyrene at 25 °C.................................................................100

3.10.5 Monomer Conversion and Copolymer Composition...............101

3.11 Blends of Polystyrene and Poly(2-Vinyl Naphthalene) with
Poly(2,3,4,5,6-pentafluorostyrene) .......................................................102

3.12 Attempted Synthesis of 1-Vinyl Pyrene........................................102

3.12.1 Synthesis of 1-Bromo Pyrene...................................................102

3.12.2 Attempted Synthesis of 1-Vinyl Pyrene ....................................103

IV. GRAFT COPOLYMERIZATION OF 2,3,4,5,6-PENTAFLUOROSTYRENE
ONTO POLYBUTADIENE ....................................................................106

4.1 Synthesis of Poly(2,3,4,5,6-pentafluorostyrene) ..........................106

4.2 Grafting of 2,3,4,5,6-Pentafluorostyrene onto Polybutadiene ..........110

4.2.1 Synthesis of Graft Copolymers of 2,3,4,5,6-Pentafluorostyrene
onto Polybutadiene ...........................................................................110

4.2.2 Monomer Conversion ................................................................118

4.2.3 Grafting Parameters Characterizing the Graft
Copolymerizations..............................................................................122
4.2.4 Length of the Grafted Poly(2,3,4,5,6-pentafluorostyrene) Chains ................................................................. 129

4.3 Isolation of Grafted Copolymers of 2,3,4,5,6-Pentafluorostyrene onto Polybutadiene ................................................................. 134

4.4 Thermal Behavior of Poly(butadiene-\textit{graft}-pentafluorostyrene) .......... 141

4.5 Elemental Analysis of Poly(butadiene-\textit{graft}-pentafluorostyrene) ......... 143

V. ENE REACTIONS OF 2,3,4,5,6-PENTAFLUOROSTYRENE ONTO POLYBUTADIENE ....................................................................................... 145

5.1 Introduction ............................................................................................ 145

5.2 Attempted Reaction of 2,3,4,5,6-Pentafluorostyrene with High Molecular Weight Polybutadiene ................................................................. 146

5.3 Attempted Reaction of 2,3,4,5,6-Pentafluorostyrene with Low Molecular Weight Polybutadiene ........................................................................ 151

5.4 Attempted Reaction of 2,3,4,5,6-Pentafluorostyrene with Model Compounds ......................................................................................... 155

5.4.1 Synthesis of 9-Octadecene ..................................................................... 155

5.4.2 Attempted Model Reactions of 2,3,4,5,6-Pentafluorostyrene with 1-Decene, 1-Octadecene and 9-Octadecene ............................................. 156

5.4.3 Attempted Model Reactions of 2,3,4,5,6-Pentafluorostyrene with \(\beta\)-Pinene ............................................................................................................. 159

5.5 Attempted Synthesis of Arene Complexes ............................................. 161

5.5.1 Synthesis of the Ligand .......................................................................... 161

5.5.2 Attempted Synthesis of the Arene Complex ......................................... 162

VI. COPOLYMERIZATION OF 2,3,4,5,6-PENTAFLUOROSTYRENE WITH \(\beta\)-PINENE ........................................................................................................ 164

6.1 Introduction ................................................................................................. 164

6.2 Copolymerization of 2,3,4,5,6-Pentafluorostyrene with \(\beta\)-Pinene .......... 164
6.3 Reactivity Ratios in the Copolymerization of 2,3,4,5,6-
Pentafluorostyrene with β-Pinene..............................................................165

6.4 Molecular Weight of the Copolymers.....................................................175

6.5 Thermal Behavior of the Copolymers......................................................177

6.6 Optical Activity and Surface Energy of the Copolymers.......................180

VII. COPOLYMERIZATION OF STYRENE AND VINYL AROMATIC
HYDROCARBONS WITH 2,3,4,5,6-PENTAFLUOROSTYRENE. ...............184

7.1 Introduction .............................................................................................184

7.2 Copolymerization of Styrene with 2,3,4,5,6-Pentafluorostyrene ..........184

7.2.1 Copolymerization of Styrene with 2,3,4,5,6-Pentafluorostyrene.  
Determination of Reactivity Ratios..............................................................184

7.2.2 NMR Spectroscopy of the Copolymers..............................................196

7.2.3 Molecular Weight and Thermal Behavior of the Copolymers .........209

7.3 Copolymerization of 2-Vinyl Naphthalene with 2,3,4,5,6-
Pentafluorostyrene .......................................................................................213

7.3.1 Copolymerization of 2-Vinyl Naphthalene with 2,3,4,5,6-
Pentafluorostyrene. Determination of Reactivity Ratios ......................214

7.3.2 Molecular Weight and Thermal Behavior of the Copolymers .........220

7.4 Copolymerization of 1-Vinyl Naphthalene with 2,3,4,5,6-
Pentafluorostyrene .......................................................................................225

7.4.1 Synthesis of 1-Vinyl Naphthalene......................................................225

7.4.2 Copolymerization of 1-Vinyl Naphthalene with 2,3,4,5,6-
Pentafluorostyrene. Determination of Reactivity Ratios ......................225

7.4.3 Molecular Weight and Thermal Behavior of the Copolymers .........236

7.5 Blends of Polystyrene and Poly(2-Vinyl Naphthalene) with  
Poly(2,3,4,5,6-pentafluorostyrene) ..............................................................239

7.6 Attempted Synthesis of 1-Vinyl Pyrene...............................................245
VIII. SUMMARY ..................................................................................................................247
REFERENCES AND NOTES ..............................................................................................254
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Some fluoropolymers and their structure and properties</td>
<td>6</td>
</tr>
<tr>
<td>2.2</td>
<td>Reactivity ratios of 2,3,4,5,6-pentafluorostyrene in radical copolymerization</td>
<td>18</td>
</tr>
<tr>
<td>2.3</td>
<td>Glass transition temperatures ($T_g$) of fluoropolymers</td>
<td>24</td>
</tr>
<tr>
<td>2.4</td>
<td>Reactivity ratios and their products for copolymerization of styrene ($M_1$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>and pentafluorostyrene (PFS, $M_2$) under radical or anionic conditions</td>
<td>26</td>
</tr>
<tr>
<td>4.1</td>
<td>Comparison of poly(2,3,4,5,6-pentafluorostyrene) synthesized with</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>different initiator amounts</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>Experimental conditions of the five different graft copolymerizations of</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,3,4,5,6-pentafluorostyrene (PFS) onto polybutadiene (PB). First number</td>
<td></td>
</tr>
<tr>
<td></td>
<td>in experiment name corresponds to the temperature ($^\circ$C) of the</td>
<td></td>
</tr>
<tr>
<td></td>
<td>experiment and the second corresponds to the amount of initiator</td>
<td></td>
</tr>
<tr>
<td></td>
<td>expressed as mol% of benzoyl peroxide initiator used relative to PB units;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>increase of temperature observed on horizontal and initiator on vertical</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>Comparison of monomer conversion determined gravimetrically and</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>from gel permeation chromatography (GPC) injections directly from the</td>
<td></td>
</tr>
<tr>
<td></td>
<td>grafting reactions of polybutadiene (PB) with pentafluorostyrene (PFS)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>in tetrahydrofuran using benzoyl peroxide (BPO) as the initiator. Results</td>
<td></td>
</tr>
<tr>
<td></td>
<td>for GPC values are average of three measurements. Gravimetical results</td>
<td></td>
</tr>
<tr>
<td></td>
<td>were performed twice. First three rows correspond to an increase in the</td>
<td></td>
</tr>
<tr>
<td></td>
<td>initiator concentration at constant temperature ($T=60 , ^\circ$C), and</td>
<td></td>
</tr>
<tr>
<td></td>
<td>second three rows correspond to those experiments at constant BPO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>concentration (5% mol relative to PB) with an increase in the temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>121</td>
</tr>
</tbody>
</table>
4.4 Variation of the grafting efficiency (defined by equation 3.2) of pentafluorostyrene (PFS) as a function of time in graft copolymerizations of polybutadiene (PB) and PFS in tetrahydrofuran in the presence of benzoyl peroxide (BPO) as the initiator. Mean values and standard deviations from gel permeation chromatography injections of copolymerizations performed in triplicate..............................124

4.5 Variation of the grafting ratio (defined by equation 3.3) of pentafluorostyrene (PFS) as a function of time in graft copolymerizations of polybutadiene (PB) and PFS in tetrahydrofuran in the presence of benzoyl peroxide (BPO) as the initiator. Mean values and standard deviations from gel permeation chromatography injections of copolymerizations performed in triplicate..............................125

4.6 Grafting parameters characterizing the poly(butadiene-graft-pentafluorostyrene)s (PB-g-PPFS) produced in the graft copolymerizations of poly(butadiene) (PB) with pentafluorostyrene (PFS) in tetrahydrofuran using benzoyl peroxide (BPO) as the initiator. Mean values and standard deviations from copolymerizations performed in triplicate................................................................................ 130

4.7 Number-average molecular weights \((M_n)\) and polydispersities \((pdi=M_w/M_n)\) of ungrafted poly(pentafluorostyrene) (PPFS) homopolymer measured by direct gel permeation chromatography (GPC) injections of the graft copolymerizations of poly(butadiene) (PB) and pentafluorostyrene (PFS) in tetrahydrofuran (THF) in the presence of benzoyl peroxide (BPO) as the initiator. Mean values and standard deviations from copolymerizations performed in triplicate.........................................................131

4.8 Solubility of 20 mg polybutadiene (PB), poly(pentafluorostyrene) PPFS, and poly(butadiene-graft-pentafluorostyrene) (PB-g-PPFS) in 20 mL solvent after 6 h at room temperature. Number-average molecular weights \((M_n)\) and polydispersity index \((pdi = M_w/M_n)\) determined by gel permeation chromatography relative to polystyrene: PB used for grafting, \(M_n = 3.85 \times 10^5\), \(pdi = 3.51\); PPFS, \(M_n = 2.28 \times 10^4\), \(pdi = 1.80\) (mean of UV & RI detectors); PB-g-PPFS-60/5, \(M_n = 2.45 \times 10^5\), \(pdi = 1.63\) (mean of UV & RI detectors), grafting efficiency \(= 0.097\), grafting ratio \(= 0.268\). +++ = soluble, + = partially soluble, - = insoluble ...............136
4.9 Comparison of the amount of poly(2,3,4,5,6-pentafluorostyrene) (PPFS) homopolymer generated in the graft copolymerizations of polybutadiene (PB) with pentafluorostyrene (PFS) at final conversion with that extracted with acetone at room temperature. Graft copolymerizations performed in triplicate in tetrahydrofuran using benzoyl peroxide as the initiator; 24-36 h extractions to constant weight loss. Only one of each of the three set of samples was purified...

4.10 Comparison of the glass transition temperatures ($T_g$), of the grafts of poly(butadiene-$\textit{graft}$-pentafluorostyrene)s (PB-$g$-PPFS) and the corresponding poly(2,3,4,5,6-pentafluorostyrene) (PPFS) homopolymers extracted with acetone. $T_g$s determined by differential scanning calorimetry; mean of values from second and third heat at 10 oC/min. PB-$g$-PPFS produced at final conversion (60 h) in the grafting reactions of polybutadiene (PB) with pentafluorostyrene (PFS) in tetrahydrofuran using benzoyl peroxide (BPO) as the initiator

4.11 Comparison of the elemental compositions of the poly(butadiene-$\textit{graft}$-pentafluorostyrene)s (PB-$g$-PPFS) with those calculated from the grafting ratios (GR) and grafting frequencies (GF.) PB-$g$-PPFSs produced at final conversion (60 h) in the grafting reactions of PB with PFS in tetrahydrofuran using benzoyl peroxide as the initiator; performed in triplicate. After purification by extraction with hexanes (12 h) and acetone (36 h.) GR determined from eq. 3.3 and GF determined from equation 3.4

6.1 Results of the copolymerizations of equimolar amounts of 2,3,4,5,6-pentafluorostyrene with $\beta$-pinene

6.2 Comonomer conversion for the radical copolymerization of pentafluorostyrene (PFS) with $\beta$-pinene (PIN) for 2 h in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator and 1,3-dichlorobenzene as an internal standard

6.3 Data used to determine the reactivity ratios of pentafluorostyrene (PFS, $M_1$) and $\beta$-pinene (PIN, $M_2$) in their radical copolymerization for 2 h in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator

6.4 Number-average molecular weights ($M_n$) and polydispersities (pdi=$M_w/M_n$) measured by gel permeation chromatography in tetrahydrofuran (THF) and toluene of the copolymers produced by radical copolymerizations of pentafluorostyrene (PFS) and $\beta$-pinene (PIN) for 2 h in bulk at 70 °C with benzoyl peroxide (1 mol%) as the initiator
6.5 Dependence of the glass transition temperature ($T_g$) of poly(pentafluorostyrene-co-β-pinene)s on their copolymer composition and number-average degree of polymerization ($DP_n$) ..................................................178

6.6 Dependence of the specific Rotations ($[\alpha]^{25}_D$) of poly(pentafluorostyrene-co-β-pinene)s on their compositions and concentration of the solution ...........................................................................181

6.7 Static contact angles ($\theta_s$) of films of poly(2,3,4,5,6-pentafluorostyrene) (PPFS) and poly(pentafluorostyrene-co-β-pinene)s (PFS-co-PIN) films on silicon wafers.................................................................................................................183

7.1 Comonomer conversions for the radical copolymerization of styrene (Sty) and 2,3,4,5,6-pentafluorostyrene (PFS) in bulk at 70 °C for 25 min. using benzoyl peroxide (1 mol%) as the initiator ................................................187

7.2 Data used to determine the reactivity ratios of styrene ($Sty$, $M_1$) and pentfluorostyrene ($PFS$, $M_2$) in their radical copolymerization for 25 min in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator .......188

7.3 Comonomer conversions for the radical copolymerization of styrene (Sty) with 2,3,4,5,6-pentafluorostyrene (PFS) for 2.5 h in bulk at 25 °C using t-butyl peroxy pivalate (1 mol%) as the initiator ......................193

7.4 Data used to determine the reactivity ratios of styrene ($Sty$, $M_1$) and pentfluorostyrene ($PFS$, $M_2$) in their radical copolymerization in bulk for 2.5 h at 25 °C using t-butyl peroxy pivalate (1 mol%) as the initiator ...194

7.5 Number-average molecular weights ($M_n$) and polydispersities ($pdi=M_w/M_n$) measured by gel permeation chromatography in tetrahydrofuran of the copolymers produced by radical copolymerizations of styrene (Sty) and pentfluorostyrene (PFS) for 25 min in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator and in bulk for 2.5 h at 25 °C using t-butyl peroxy pivalate (1 mol%) as the initiator .................................................................210

7.6 Dependence of the glass transition temperature ($T_g$) of poly(styrene-alt-pentafluorostyrene)s on their copolymer composition and number-average degree of polymerization ($DP_n$). The copolymers were synthesized by radical copolymerization of styrene and pentafluorostyrene (PFS) in bulk at either 70 °C for 25 min using benzoyl peroxide (BPO) as the initiator or at 25 °C for 2.5 h using t-butyl peroxy pivalate as the initiator .................................................................211
7.7 Comonomer conversions for the radical copolymerization of 2-vinyl naphthalene (2-VN) with 2,3,4,5,6-pentafluorostyrene (PFS) for 30 min in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator .................. 215

7.8 Data used to determine the reactivity ratios of 2-vinyl naphthalene (2-VN, M₁) and 2,3,4,5,6-pentafluorostyrene (PFS, M₂) in their radical copolymerization in bulk for 30 min at 70 °C using benzoyl peroxide (BPO, 1 mol%) as the initiator ........................................................................................................ 216

7.9 Number-average molecular weight ($M_n$), polydispersity index (pdi), degree of polymerization ($DP_n$), and glass transition temperature ($T_g$) of poly(2-vinyl naphthalene-alt-pentafluorostyrene)s (poly(2VN-alt-PFS)) as a function of the molar amount (%) of 2-vinyl naphthalene (2-VN) in the copolymer .................................................................................................................................. 221

7.10 Number-average molecular weight ($M_n$), polydispersity index (pdi), degree of polymerization ($DP_n$), and glass transition temperature ($T_g$) of poly(2-vinyl naphthalene)s obtained under different conditions .......... 222

7.11 Comonomers conversion for the radical copolymerization of 1-vinyl naphthalene (1-VN) with 2,3,4,5,6-pentafluorostyrene (PFS) in bulk for 2.5 h at 70 °C using benzoyl peroxide (1 mol%) as the initiator ............... 228

7.12 Data used to determine the reactivity ratios of 1-vinyl naphthalene (1-VN, M₁) and pentafluorostyrene (PFS, M₂) in their radical copolymerization in bulk for 2.5 h at 70 °C using benzoyl peroxide (1 mol%) as the initiator .......................................................... 229

7.13 Comonomers conversion for the radical copolymerization of 1-vinyl naphthalene (1-VN) with 2,3,4,5,6-pentafluorostyrene (PFS) in bulk for 7 h at 25 °C using $t$-butyl peroxo pivalate (1 mol%) as the initiator .......... 233

7.14 Data used to determine the reactivity ratios of 1-vinyl naphthalene (1-VN, M₁) and pentafluorostyrene (PFS, M₂) in their radical copolymerization in bulk for 7 h at 25 °C using $t$-butyl peroxo pivalate (1 mol%) as the initiator and $n$-butyl acetate as an internal standard .......... 234

7.15 Number-average molecular weight ($M_n$), polydispersity index (pdi) and glass transition temperature ($T_g$) of poly(1-vinyl naphthalene-alt-pentafluorostyrene)s synthesized by radical copolymerization of 1-vinyl naphthalene (1-VN) and 2,3,4,5,6-pentafluorostyrene (PFS) in bulk for 2.5 h at 70 °C using benzoyl peroxide (1% mol) as the initiator .......... 237
7.16 Glass transition temperature ($T_g$) of the blends of polystyrene (PS, $DP_n = 204$), poly(2,3,4,5,6-pentafluorostyrene) (PPFS, $DP_n = 250$) and poly(2-vinyl naphthalene) (P2-VN, $DP_n = 80$) as a function of their composition.
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Surface electrostatic potential of hexafluorobenzene and benzene</td>
<td>33</td>
</tr>
<tr>
<td>2.2</td>
<td>Phase diagram for the system hexafluorobenzene-benzene. $X_F$ is the mole fraction of the hexafluorobenzene</td>
<td>34</td>
</tr>
<tr>
<td>3.1</td>
<td>Calibration of the gel permeation chromatography UV detector at 254 nm for poly(2,3,4,5,6-pentafluorostyrene) (number-average molecular weight, $M_n = 10.2 \times 10^3$, polydispersity index, $pdi = 1.56$) as a function of concentration in tetrahydrofuran</td>
<td>74</td>
</tr>
<tr>
<td>3.2</td>
<td>$^1$H NMR Spectra of the polymerization mixture for the experiment PFS-co-PIN-5/5 before and after copolymerization. 1,3-Dichlorobenzene resonance (7.40 ppm) as internal standard. Polymerization time 2 h</td>
<td>86</td>
</tr>
<tr>
<td>3.3</td>
<td>$^1$H NMR spectrum of copolymer from experiment PFS-co-PIN-5/5 synthesized at 70 °C with benzoyl peroxide as initiator (1 mol%). The peaks under label “b” are due to all protons in the copolymer except from the vinyl proton of the β-pinene units, which corresponds to resonance labeled as “a”. Peak marked with an asterisk is due to residual CHCl$_3$ from deuterated solvent and with two asterisks is due to residual water also in the NMR solvent</td>
<td>87</td>
</tr>
<tr>
<td>3.4</td>
<td>$^1$H NMR spectra of the polymerization mixture for the experiment Sty-$alt$-PFS-5/5 before and after copolymerization. Internal standard $n$-butyl acetate (peak “c”). Copolymerization time 25 min</td>
<td>89</td>
</tr>
<tr>
<td>3.5</td>
<td>$^1$H NMR spectrum of the copolymer from experiment Sty-$alt$-PFS-5/5 synthesized at 70 °C with benzoyll peroxide as initiator (1 mol%). The peaks under label “b” are due to all protons in the backbone of the copolymer and resonances labeled as “a” correspond to aromatic protons of styrene units of the copolymer. Resonance marked with an asterisk is due to residual CHCl$_3$ from deuterated solvent and with two asterisks is due to residual water also in the solvent</td>
<td>90</td>
</tr>
</tbody>
</table>
4.1 Gel permeation chromatography UV detector (254 nm) responses of samples taken at 0 and 24 h from the grafting reaction of polybutadiene (PB) with pentafluorostyrene (PFS) in the presence of 5 mol% benzyol peroxide (BPO) in tetrahydrofuran at 60 °C. Reaction composition: 0.36 M PB, 0.70 M PFS, 18 mM BPO

4.2 UV-detected (254 nm) gel permeation chromatography responses of samples taken every 12 h from the grafting of poly(butadiene) (PB) with pentafluorostyrene (PFS) in tetrahydrofuran at 60 °C in the presence of benzyol peroxide (BPO) (5 mol% relative to PB). Experiment name: PB-γ-PFS-60/5. Reaction composition: 0.36 M PB, 0.70 M PFS, 18 mM BPO. Arrow indicates increasing copolymerization time

4.3 2,3,4,5,6-Pentafluorostyrene (PFS) monomer conversion at 50, 60 and 80 °C in tetrahydrofuran in the presence of polybutadiene (PB) and benzyol peroxide (BPO) (5 mol% relative to PB) as initiator as a function of copolymerization time. Monomer conversions determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS, 18 mM of BPO); mean values and standard deviations presented from triplicate experiments

4.4 2,3,4,5,6-Pentafluorostyrene (PFS) monomer conversion at 60 °C in tetrahydrofuran in the presence of polybutadiene (PB), using 2.5, 5 and 10 mol% benzyol peroxide (BPO) (relative to PB repeat units) as initiator as a function of copolymerization time. Monomer conversions determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS, 18 mM of BPO); mean values and standard deviations presented from triplicate experiments

4.5 Dependence of the initial rate of polymerization ($R_p = -d[M]/dt$) as a function of the product of the monomer concentration ([M]) and the square root of the initiator concentration ($[I]^{1/2}$) in the graft copolymerization of polybutadiene (PB) with pentafluorostyrene (PFS) in tetrahydrofuran using 2.5, 5 and 10 mol% benzyol peroxide (BPO) (relative to PB) as the initiator at 60 °C. $R_p$ was determined from triplicate measurements of the conversion of PFS by UV-detected gel permeation chromatography

4.6 Pentafluorostyrene (PFS) grafting efficiency (GE) at 60 °C in tetrahydrofuran using 2.5, 5 and 10 mol% benzyol peroxide (BPO) (relative to polybutadiene (PB)) as initiator as a function of copolymerization time. GE determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS, 18 mM of BPO); mean values and standard deviations presented from triplicate experiments
4.7 Pentfluorostyrene (PFS) grafting efficiency (GE) at 50, 60 and 80 °C in tetrahydrofuran (THF) in the presence of polybutadiene (PB) and benzoyl peroxide (BPO) (5 mol% relative to PB) as initiator as a function of copolymerization time. GE was determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS, 18 mM of BPO); mean values and standard deviations presented from triplicate experiments .................................................................126

4.8 Pentfluorostyrene (PFS) grafting ratio at 60 °C in tetrahydrofuran using 2.5, 5 and 10 mol% benzoyl peroxide (BPO) as initiator relative to polybutadiene (PB) repeat units as a function of copolymerization time. Determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS, 18 mM of BPO); mean values and standard deviations presented from triplicate experiments .................................................127

4.9 Pentfluorostyrene (PFS) grafting ratio at 50, 60 and 80 °C in tetrahydrofuran in the presence of polybutadiene (PB) and benzoyl peroxide (BPO) (5 mol% relative to PB) as initiator as a function of copolymerization time. Determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS, 18 mM of BPO); mean values and standard deviations presented from triplicate experiments .....128

4.10 Number average molecular weight ($M_n$) of grafts of poly(pentfluorostyrene) (PPFS) at 60 °C of poly(butadiene-$\text{graft}$-pentfluorostyrene) (PB-$g$-PPFS) synthesized in tetrahydrofuran in the presence of polybutadiene (PB) and benzoyl peroxide (BPO, 2.5, 5 and 10 mol% relative to PB) as initiator as a function of copolymerization time. PPFS chains length determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS; 9.0, 18 and 36 mM of BPO); mean values and standard deviations presented from triplicate experiments. Assumed that length of the grafted PPFS is same as length of ungrafted PPFS ........................................133

4.11 Number average molecular weight ($M_n$) of grafts of poly(pentfluorostyrene) (PPFS) at 50, 60 and 80 °C of poly(butadiene-$\text{graft}$-pentfluorostyrene) (PB-$g$-PPFS) synthesized in tetrahydrofuran in the presence of polybutadiene (PB) and benzoyl peroxide (BPO, 5 mol% relative to PB) as initiator as a function of copolymerization time. PPFS chains length determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS, 18 mM of BPO); mean values and standard deviations presented from triplicate experiments. Assumed that length of the grafted PPFS is same as length of ungrafted PPFS .................................................................134

xxvii
4.12 $^1$H NMR (300 MHz) spectra in CDCl$_3$ of: (a) Crude poly(butadiene-
graft-pentafluorostyrene) (PB-g-PPFS-60/5), (b) poly(butadiene) (PB)
exttracted from PB-g-PPFS-60/5 using hexanes; (c) poly(2,3,4,5,6-
pentafluorostyrene) extracted from PB-g-PPFS-60/5 using acetone;
d) pure PB-g-PPFS-60/5 graft copolymer after extractions. * = residual protonated solvent. PB number average molecular weight: $M_n$
= 3.45 x 10$^5$ (mean of UV & RI detectors), polydispersity index: pdi =
$M_w/M_n = 2.63$, grafting ratio = 0.268, grafting frequency = 588, 4.41
PPFS grafts of $DP_n = 46.5$ per PB chain.................................................140

4.13 Dependence of the glass transition temperatures ($T_g$s) of
poly(2,3,4,5,6-pentafluorostyrene) (PPFS) grafts of poly(butadiene-
graft-pentafluorostyrene)s (PB-g-PPFS)s and the corresponding PPFS
homopolymers extracted from the graft copolymers with acetone as a
function of the PPFS degree of polymerization ($DP_n$). PB-g-PPFS graft
copolymers produced by copolymerization of 2,3,4,5,6-
pentafluorostyrene (PFS) with polybutadiene (PB) in THF in the
presence of benzoyl peroxide (BPO); 0.36 M PB, 0.70 M PFS, 2:1
PFS:PB repeat units; 2.5, 5, 10 mol% BPO relative to PB repeat units;
50, 60 or 80 °C ..........................................................................................143

5.1 Gel permeation chromatography (GPC) UV detector (254 nm)
responses of samples taken at 0 and 36 h from the reaction of
polybutadiene (PB) and pentafluorostyrene (PFS) at 210 °C for 36 h.
Number average molecular weight of the reaction product $M_n = 1.25$ x
10$^5$, polydispersity index pdi = 4.6. PB GPC$_{PSi} M_n = 3.85$ x 10$^5$, pdi =
3.51; 96% 1,4-cis, 3.5% 1,4-trans and 0.5% 1,2-vinyl content ...............150

5.2 Refractive index detected gel permeation chromatography of
unreacted low molecular weight polybutadiene (PB). Number average
molecular weight PB $M_n = 4.30$ x 10$^3$, polydispersity index pdi = 2.6;
75% 1,4-cis, 24% 1,4-trans and 1.0% 1,2-vinyl content according to the
supplier ....................................................................................................152

5.3 Refractive index detected gel permeation chromatography of reaction
mixture of low molecular weight polybutadiene (PB) and 2,3,4,5,6-
pentafluorostyrene at 180 °C for 4 days. Number-average molecular
weight PB $M_n = 4.30$ x 10$^3$, polydispersity index pdi = 2.6; 75% 1,4-cis,
24% 1,4-trans and 1.0% 1,2-vinyl content according to the supplier.
Reaction mixture $M_n = 6.70$ x 10$^3$, pdi = 10.8.............................................153
5.4 Refractive index (RI) detected gel permeation chromatography of product of the reaction of molecular weight polybutadiene (PB) and 2,3,4,5,6-pentafluorostyrene at 180 °C for 4 days, after extraction with acetone for 24 h. PB number-average molecular weight $M_n = 4.30 \times 10^3$, polydispersity index pdi = 2.6; 75% 1,4-cis, 24% 1,4-trans and 1.0% 1,2-vinyl content according to the supplier. Product $M_n = 4.95 \times 10^3$, pdi = 4.3; RI detector ................................................................. 154

5.5 UV detected gel permeation chromatography of product of the reaction of molecular weight polybutadiene (PB) and 2,3,4,5,6-pentafluorostyrene at 180 °C for 4 days, after extraction with acetone for 24 h. PB number-average molecular weight $M_n = 4.30 \times 10^3$, polydispersity index pdi = 2.6; 75% 1,4-cis, 24% 1,4-trans and 1.0% 1,2-vinyl content according to the supplier. Product $M_n = 9.70 \times 10^3$, pdi = 7.2; UV detector .......................................................................................... 154

6.1 $^1$H NMR spectra of: 1) poly(2,3,4,5,6-pentafluorostyrene); 2) poly(pentafluorostyrene-co-β-pinene)-9/1 (poly(PFS-co-PIN)-9-1), with 98% 2,3,4,5,6-pentafluorostyrene (PFS); 3) poly(PFS-co-PIN)-5/5, with 86% PFS; 4) poly(PFS-co-PFS)-1/9 with 58% PFS. Peaks marked with * are due to residual CHCl$_3$ .................................................................................. 169

6.2 Finemann-Ross plot (equation 6.1) used to determine the reactivity ratios $r_1 = k_{11}/k_{12}$, and $r_2 = k_{22}/k_{21}$ in the radical copolymerization of 2,3,4,5,6-pentafluorostyrene (M$_1$) and β-pinene (M$_2$) for 2 h in bulk at 70 °C with benzoyl peroxide (1 mol%) as the initiator ...................................................... 172

6.3 Kelen-Tüdos plot (equation 6.6) used to determine the reactivity ratios $r_1 = k_{11}/k_{12}$, and $r_2 = k_{22}/k_{21}$ in the radical copolymerization of 2,3,4,5,6-pentafluorostyrene (M$_1$) and β-pinene (M$_2$) for 2 h in bulk at 70 °C with benzoyl peroxide (1 mol%) as the initiator ...................................................... 172

6.4 Dependence of the number-average degree of polymerization ($DP_n$) as a function of the composition of the copolymers, synthesized by radical copolymerization of pentafluorostyrene and β-pinene for 2 h in bulk at 70 °C using 1 mol% benzoyl peroxide as the initiator ........................................ 177

6.5 Dependence of the glass transition temperature ($T_g$) of the poly(pentafluorostyrene-co-β-pinene)s as a function of the amount of 2,3,4,5,6-pentafluorostyrene (PFS). The copolymers were synthesized by the radical copolymerization of PFS and β-pinene for 2 h in bulk at 70 °C using 1 mol% of benzoyl peroxide as the initiator ........................................ 179
7.1 Finemann-Ross plot (equation 6.1) used to determine the reactivity ratios \( k_1 = k_{11} / k_{12} \) and \( k_2 = k_{22} / k_{21} \) in the radical copolymerization of styrene (M₁) and 2,3,4,5,6-pentafluorostyrene (M₂) in bulk for 25 min. at 70 °C with benzoyl peroxide (1 mol%) as the initiator .........................189

7.2 Kelen-Tüdos plot (equation 6.6) used to determine the reactivity ratios \( k_1 = k_{11} / k_{12} \) and \( k_2 = k_{22} / k_{21} \) in the radical copolymerization of styrene (M₁) and 2,3,4,5,6-pentafluorostyrene (M₂) in bulk for 25 min. at 70 °C with benzoyl peroxide (1 mol%) as the initiator .........................189

7.3 Finemann-Ross plot (equation 6.1) used to determine the reactivity ratios \( k_1 = k_{11} / k_{12} \) and \( k_2 = k_{22} / k_{21} \) in the radical copolymerization of styrene (M₁) and 2,3,4,5,6-pentafluorostyrene (M₂) for 2.5 h in bulk at 25 °C using \( t \)-butyl peroxycarboxylate (1 mol%) as the initiator .....................195

7.4 Kelen-Tüdos plot (equation 6.6) used to determine the reactivity ratios \( k_1 = k_{11} / k_{12} \) and \( k_2 = k_{22} / k_{21} \) in the radical copolymerization of styrene (M₁) and 2,3,4,5,6-pentafluorostyrene (M₂) for 2.5 h in bulk at 25 °C using \( t \)-butyl peroxycarboxylate (1 mol%) as the initiator .....................195

7.5 \(^1\)H NMR spectra of 1) polystyrene; 2) poly(2,3,4,5,6-pentafluorostyrene); 3) poly(styrene-alt-pentafluorostyrene)-3/7, 40% styrene; 4) poly(styrene-alt-pentafluorostyrene)-5/5, 54% styrene; 5) poly(styrene-alt-pentafluorostyrene)-7/3, 68% styrene. Peak marked with an asterisk corresponds to residual CHCl₃ ........................................197

7.6 Quantitative \(^{13}\)C NMR spectra of 1) polystyrene; 2) poly(2,3,4,5,6-pentafluorostyrene); 3) poly(styrene-alt-pentafluorostyrene)-3/7, 40% styrene; 4) poly(styrene-alt-pentafluorostyrene)-5/5, 54% styrene; 5) poly(styrene-alt-pentafluorostyrene)-7/3, 68% styrene. Resonance at 78.0 ppm due to solvent CHCl₃ ..................................................199

7.7 Quantitative \(^{13}\)C NMR spectra of 1) polystyrene; 2) poly(2,3,4,5,6-pentafluorostyrene); 3) poly(styrene-alt-pentafluorostyrene)-3/7, 40% styrene; 4) poly(styrene-alt-pentafluorostyrene)-5/5, 54% styrene; 5) poly(styrene-alt-pentafluorostyrene)-7/3, 68% styrene. Resonance at 78.0 ppm due to solvent CHCl₃. Spectrum shows only area between 100 and 160 ppm ..................................................200

7.8 \(^{19}\)F NMR spectra of: 1) poly(2,3,4,5,6-pentafluorostyrene), 2) poly(styrene-alt-pentafluorostyrene)-5/5, 54% styrene; 3) poly(styrene-alt-pentafluorostyrene)-1/9, 35% styrene .................................................201
7.9 Expanded hetero nuclear single quantum coherence experiment (HSQC) of poly(styrene-alt-pentafluorostyrene-5/5), with 54% mol of styrene. The copolymer was synthesized by the radical copolymerization of styrene and pentafluorostyrene in bulk at 70 ºC for 25 min using benzoyl peroxide (1 mol%). The spectrum shows only the area between 21.6 and 52.2 ppm (horizontal axis) and 0.80 and 3.60 ppm (vertical axis), which corresponds to backbone area..............205

7.10 Nuclear overhauser effect spectroscopy (NOESY). NOESY full spectrum of poly(styrene-alt-pentafluorostyrene-5/5), with 54% mol of styrene. The copolymer was synthesized by the radical copolymerization of styrene and pentafluorostyrene in bulk at 70 ºC for 25 min using benzoyl peroxide (1 mol%) ..........................................................207

7.11 Nuclear overhauser effect spectroscopy (NOESY) expanded spectrum of poly(styrene-alt-pentafluorostyrene-5/5), with 54% mol of styrene. The copolymer was synthesized by the radical copolymerization of styrene and pentafluorostyrene in bulk at 70 ºC for 25 min using benzoyl peroxide (1 mol%) ........................................................................208

7.12 Plot of the glass transition temperature (T_g) of poly(styrene-alt-pentafluorostyrene) as a function of the 2,3,4,5,6-pentafluorostyrene (PFS) content. T_g's are determined by differential scanning calorimetry, mean of values from 2nd and 3rd heat at 10 ºC/min ...........................................213

7.13 Finemann-Ross plot (equation 6.1) to determine the reactivity ratios (k_1 = k_{11} / k_{12} and k_2 = k_{22} / k_{21}) in the radical copolymerization of 2-vinyl naphthalene (M_1) and 2,3,4,5,6-pentafluorostyrene (M_2) for 30 min in bulk at 70 ºC using benzoyl peroxide (1 mol%) as the initiator .................217

7.14 Kelen-Tüdos plot (equation 6.6) to determine the reactivity ratios (k_1 = k_{11} / k_{12} and k_2 = k_{22} / k_{21}) in the radical copolymerization of 2-vinyl naphthalene (M_1) and 2,3,4,5,6-pentafluorostyrene (M_2) for 30 min in bulk at 70 ºC using benzoyl peroxide (1 mol%) as the initiator .................218

7.15 1H NMR spectra of 1) poly(pentafluorostyrene), 2) poly(2-vinyl naphthalene); 3) poly(2-vinyl naphthalene-alt- pentafluorostyrene)-5/5, with 58 mol % of 2-vinyl naphthalene. Resonances marked with an asterisk correspond to residual CHCl_3 from solvent.................................219
7.16 Plot of glass transition temperature ($T_g$) as a function of the degree of polymerization ($DP_n$) for several poly(2-vinyl naphthalene)s. $T_g$s were determined by differential scanning calorimetry; mean of values from 2$^{nd}$ and 3$^{rd}$ heat at 10 °C/min. $DP_n$ values determined by gel permeation chromatography relative to polystyrene standards..............222

7.17 Plot of glass transition temperature ($T_g$) as a function of the degree of polymerization (1/$DP_n$) for several poly(2-vinyl naphthalene)s. $T_g$s were determined by differential scanning calorimetry; mean of values from 2$^{nd}$ and 3$^{rd}$ heat at 10 °C/min. $DP_n$ values determined by gel permeation chromatography relative to polystyrene standards.............223

7.18 Plot of the glass transition temperature ($T_g$) of the poly(2-vinyl naphthalene-alt-pentafluorostyrene)s as a function of the pentafluorostyrene (PFS) molar amount. $T_g$s were determined by differential scanning calorimetry; mean of values from 2$^{nd}$ and 3$^{rd}$ heat at 10 °C/min ..............................................................................................224

7.19 Finemann-Ross plot (equation 6.1) used to determine the reactivity ratios ($k_1 = k_{11} / k_{12}$ and $k_2 = k_{22} / k_{21}$) in the radical copolymerization of 1-vinyl naphthalene (M$_1$) with 2,3,4,5,6-pentafluorostyrene (M$_2$) for 2.5 h in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator........230

7.20 Kelen-Tüdos plot (equation 6.6) used to determine the reactivity ratios ($k_1 = k_{11} / k_{12}$ and $k_2 = k_{22} / k_{21}$) in the radical copolymerization of 1-vinyl naphthalene (M$_1$) and 2,3,4,5,6-pentafluorostyrene (M$_2$) for 2.5 h in bulk at 70 °C using benzoyl peroxide (BPO, 1 mol%) as the initiator ....230

7.21 $^1$H NMR Spectra of 1) poly(2,3,4,5,6-pentafluorostyrene), 2) poly(1-vinyl naphthalene), 3) poly(1-vinyl naphthalene-alt-pentafluorostyrene)-5/5, with 57 mol% of 1-vinyl naphthalene. Resonances marked with an asterisk corresponds to residual CHCl$_3$.......231

7.22 Finemann-Ross plot (equation 6.1) used to determine the reactivity ratios ($k_1 = k_{11} / k_{12}$ and $k_2 = k_{22} / k_{21}$) in the radical copolymerization of 1-vinyl naphthalene (M$_1$) and 2,3,4,5,6-pentafluorostyrene (M$_2$) for 7 h in bulk at 25 °C using t-butyl peroxy pivalate (1 mol%) as the initiator......235

7.23 Kelen-Tüdos plot (equation 6.6) used to determine the reactivity ratios ($k_1 = k_{11} / k_{12}$ and $k_2 = k_{22} / k_{21}$) in the radical copolymerization of 1-vinyl naphthalene (M$_1$) and 2,3,4,5,6-pentafluorostyrene (M$_2$) for 7 h in bulk at 25 °C using t-butyl peroxypivalate (1 mol%) as the initiator........236

xxxii
7.24 Plot of the glass transition temperature \( (T_g) \) of the poly(1-vinyl naphthalene-\textit{alt}-pentafluorostyrene)s as a function of the molar amount (\%) of pentafluorostyrene (PFS). \( T_g \)s were determined by differential scanning calorimetry (DSC), mean of values from 2\textsuperscript{nd} and 3\textsuperscript{rd} heat at 10 °C/min ......................................................... 238

7.25 Differential scanning calorimetry thermograms of blends of polystyrene (PS, \( DP_n = 204 \)) and poly(2,3,4,5,6-pentafluorostyrene) (PPFS, \( DP_n = 250 \)) prepared by radical polymerization initiated by benzoyl peroxide (1 mol\%) at 70 °C. The traces correspond to the second heating scan. Glass transition temperature \( (T_g) \) values mean of values from 2\textsuperscript{nd} and 3\textsuperscript{rd} heat at 10 °C/min ......................................................................................... 240

7.26 Plot of the glass transition temperature \( (T_g) \) of the blends of polystyrene \( (DP_n = 204) \) and poly(2,3,4,5,6-pentafluorostyrene) (PPFS, \( DP_n = 250 \)) as a function of the molar amount of PPFS in the blend. Glass transition temperature \( (T_g) \) values mean of values from 2\textsuperscript{nd} and 3\textsuperscript{rd} heat at 10 °C/min ......................................................................................... 241

7.27 Differential scanning calorimetry thermograms of a blended and non-blended sample of polystyrene \( (DP_n = 204) \) and poly(2,3,4,5,6-pentafluorostyrene) \( (DP_n = 250) \) prepared by the radical polymerization initiated by benzoyl peroxide (1 mol\%) in bulk at 70 °C for 25 min .......... 242

7.28 Differential scanning calorimetry thermograms of blends of poly(2-vinyl naphthalene) \( (P2-VN, DP_n = 80) \) and poly(2,3,4,5,6-pentafluorostyrene) (PPFS, \( DP_n = 250 \)) prepared by radical polymerization initiated by benzoyl peroxide (1 mol\%) at 70 °C. The traces correspond to second heating scan. Glass transition temperature \( (T_g) \) values mean of values from 2\textsuperscript{nd} and 3\textsuperscript{rd} heat at 10 °C/min ......................................................................................... 243

7.29 Plot of the glass transition temperature \( (T_g) \) of the blends of poly(2-vinyl naphthalene) \( (DP_n = 80) \) and poly(2,3,4,5,6-pentafluorostyrene) (PPFS, \( DP_n = 250 \)) as a function of the molar amount of PPFS in the blend. Glass transition temperature \( (T_g) \) values mean of values from 2\textsuperscript{nd} and 3\textsuperscript{rd} heat at 10 °C/min......................................................................................... 244
## LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>13</td>
</tr>
<tr>
<td>2.2</td>
<td>14</td>
</tr>
<tr>
<td>2.3</td>
<td>15</td>
</tr>
<tr>
<td>2.4</td>
<td>16</td>
</tr>
<tr>
<td>2.5</td>
<td>48</td>
</tr>
<tr>
<td>2.6</td>
<td>50</td>
</tr>
<tr>
<td>2.7</td>
<td>50</td>
</tr>
<tr>
<td>2.8</td>
<td>53</td>
</tr>
<tr>
<td>2.9</td>
<td>54</td>
</tr>
<tr>
<td>2.10</td>
<td>55</td>
</tr>
<tr>
<td>2.11</td>
<td>56</td>
</tr>
</tbody>
</table>
2.12 Isomers of pinene.................................................................57

2.13 Mechanism of the cationic polymerization of β-pinene catalyzed by AlCl₃. a) Initiation, b) propagation and c) termination..........................59

4.1 Synthesis of poly(2,3,4,5,6-pentafluorostyrene) by radical polymerization of 2,3,4,5,6-pentafluorostyrene using benzoyl peroxide as the initiator in tetrahydrofuran solution ..................................................107

4.2 Synthesis of poly(butadiene-graft-pentafluorostyrene) by radical copolymerization of 2,3,4,5,6-pentafluorostyrene in the presence of polybutadiene \( (M_n = 1.25 \times 10^5, \text{pdi} = 4.6; \ 96\% \ 1,4\text{-cis}, \ 3.5\% \ 1,4\text{-trans} \) and 0.5% 1,2-vinyl content; \( \text{GPC}_{PS} \ M_n = 3.85 \times 10^5, \text{pdi} = 3.51 \) ) in tetrahydrofuran using benzoyl peroxide as the initiator. Grafting is shown only on the 1,4-cis repeat units due to their high concentration.....111

4.3 Proposed elementary reactions for the graft copolymerization of Polybutadiene with 2,3,4,5,6-pentafluorostyrene using benzoyl peroxide as the initiator .................................................................113

5.1 Proposed ene reaction between pentafluorostyrene with polybutadiene (PB.) Only 1,4-cis units were considered due to abundance. The two possible products are displayed. High molecular weight PB number average molecular weight: \( M_n = 1.25 \times 10^5, \text{pdi} = M_w/M_n = 4.6, 96\% \) 1,4-cis (y), 3.5%, 1,4-trans (x) and 0.5% 1,2-vinyl (z) content according to the supplier: Goodyear; gel permeation chromatography relative to polystyrene standards \( \text{GPC}_{PS} \ M_n = 3.85 \times 10^5, \text{pdi} = 3.51, \) mean of UV and RI detectors. Low molecular weight PB \( M_n = 3.00 \times 10^3, 75\% \) 1,4-cis, 24% 1,4-trans and 1.0% 1,2-vinyl content according to the supplier: Aldrich. \( \text{GPC}_{PS} : M_n = 4.30 \times 10^3, \text{pdi} = 2.85, \) RI detector ..........147

5.2 Synthesis of 9-octadecene..........................................................156

5.3 Attempted ene reaction of pentafluorostyrene (PFS) with model compounds 1-decene \((x = 6)\) and 1-octadecene \((x = 14)\).................................157

5.4 Attempted ene reaction of pentafluorostyrene with 9-octadecene ...........157

5.5 Attempted ene reaction of pentafluorostyrene with β-pinene .................159

5.6 Multi-step synthesis of the ligand \([C_p^*\text{RuOMe}]_2\) by a) Synthesis of 1,2,3,4,5- pentamethylcyclopentadiene \((C_p^*\) ), b) reaction of \( C_p^* \) with \( \text{RuCl}_3, 3\text{H}_2\text{O} \) to form the ligand intermediate \( C_p^*\text{RuCl}_2 \) and c) reaction of \( C_p^*\text{RuCl}_2 \) with potassium carbonate........................162
5.7 Attempted synthesis of a ruthenium arene complex of PFS and 1,2,3,4,5-pentamethylcyclopentadiene..............................................................163

6.1 Synthesis of poly(pentafluorostyrene-co-β-pinene) by radical copolymerization of pentafluorostyrene (PFS) with β-pinene at 70 °C using benzyol peroxide (BPO) as the initiator. The copolymerization was carried either in bulk or in tetrahydrofuran (THF) solution......................165

6.2 Proposed elementary reactions in the radical copolymerization of pentafluorostyrene and β-pinene for 2 h in bulk at 70 °C using benzyol peroxide as the initiator.............................................................................174

7.1 Synthesis of poly(styrene-alt-pentafluorostyrene) by radical copolymerization of styrene (M₁) and 2,3,4,5,6-pentafluorostyrene (M₂) at 70 °C for 25 min using 1 mol% benzyol peroxide as the initiator .........................................................185

7.2 Proposed elementary reactions in the radical copolymerization of styrene and 2,3,4,5,6-pentafluorostyrene in bulk for 25 min at 70 °C using benzyol peroxide (1% mol) as the initiator ..............................................................190

7.3 Synthesis of poly(styrene-alt-pentafluorostyrene) by radical copolymerization of styrene (M₁) and 2,3,4,5,6-pentafluorostyrene (M₂) at 25 °C for 2.5 h using benzyol peroxide (1 mol%) as the initiator ........... 192

7.4 Homolytical cleavage of t-butyl peroxyl pivalate at 25 °C .......................209

7.5 Copolymerization of 2-vinyl naphthalene (M₁) and 2,3,4,5,6-pentafluorostyrene (M₂) in bulk for 30 min at 70 °C using benzyol peroxide (BPO, 1 mol%) as the initiator ..............................................................214

7.6 Synthesis of 1-vinyl naphthalene .......................................................................225

7.7 Copolymerization of 1-vinyl naphthalene (M₁) and pentafluorostyrene (M₂) in bulk for 2.5 h at 70 °C using benzyol peroxide (BPO, 1 mol%) as the initiator..............................................................227

7.8 Copolymerization of 1-vinyl naphthalene (M₁) and 2,3,4,5,6-pentafluorostyrene (M₂) for 7 h in bulk at 25 °C with t-butyl peroxyl pivalate (1 mol%) as the initiator ........................................................................232

7.9 Synthesis of 1-bromo pyrene .............................................................................245

7.10 Synthesis of pyrenyl magnesium bromide.....................................................246

xxxvi
Fluorinated polymers have many desirable properties, including low surface energies, high thermal, chemical and oxidative resistance, and low refractive index.\(^1\) Although polymers based on aliphatic fluorocarbons are the most commonly used, those based on aromatic fluorocarbons have at least some of the same outstanding properties. Furthermore, aromatic hydrocarbons develop interactions with aromatic fluorocarbons in contrast to their aliphatic counterparts.\(^2\) Hexafluorobenzene, a perfluorinated aromatic compound, forms a 1:1 complex with several aromatic hydrocarbons such as benzene,\(^2\) 2-methyl naphthalene\(^2\) and 1-methyl naphthalene.\(^3\) These interactions have been used for solid-state polymerization,\(^4\) liquid crystals\(^5\) and self-organizing aggregates used for optoelectronics.\(^6\)

New polymeric materials can be produced by the modification of existing materials either by polymer analogous reactions or by graft copolymerization. We attempted to modify polybutadiene (PB) with 2,3,4,5,6-pentafluorostyrene (PFS), which is a perfluorinated aromatic compound, by graft copolymerization or by ene reaction. The resulting modified products should combine the properties of rubbers and fluoropolymers, and the interactions developed with one of the
most commonly used fillers in the rubber industry, carbon black, should be improved due to the interactions between the perfluorinated rings and the polyaromatic surface of the filler.

A graft copolymer has a backbone of one polymer and branches of another polymer, and it is often synthesized by the polymerization of the monomer that will constitute the grafts in the presence of a solution or melt of the backbone polymer and an initiator.\(^7\) We have polymerized PFS in the presence of a solution of PB and a radical initiator, investigating the dependence of the polymerization on the temperature and initiator concentration.\(^8\)

An ene reaction is a substituting addition of a compound with a double bond (enophile) to an olefin with an allylic hydrogen (ene).\(^9\) PB has been modified with maleic anhydride,\(^10\) acrylates,\(^11\) triazoline-diones,\(^12\) and acyclic azocarboxylates\(^13\) following an ene mechanism. There are no literature examples of ene reactions involving PFS, or any other styrene derivative. Based on relative electron affinities PFS should be almost as reactive as maleic anhydride towards PB in an ene reaction. However, we have not been successful in this modification. One of the drawbacks of the ene reaction is its high activation energy, and therefore the requirement of very high temperatures to attain desirable degrees of modification.\(^9\) Lewis acids have been used to lower this activation energy in reactions involving a carbonyl group attached to the double bond; this lowers the required reaction temperature. These Lewis acids have a vacant orbital that can complex with the lone pair on the carbonyl oxygen present in common enophiles and make their double bond more electrophilic.\(^9\) In analogy, we wanted to
produce an arene complex with PFS to lower the electron density of the double bond and increase its reactivity toward the ene reaction.

In an attempt to test the ability of PFS as an enophile we reacted it with β-pinene, which is the most reactive ene compound toward an ene reaction. This resulted in a radical copolymerization. The copolymers combine the low surface energy characteristic of fluoropolymers with optical activity due to the presence of a chiral center. We also determined their reactivity ratios in the radical copolymerization.

In order to correlate the interactions developed between hydrocarbon and perfluorinated aromatic rings, we also copolymerized PFS with several monomers having one or two aromatic rings, including styrene, 2-vinyl naphthalene and 1-vinyl naphthalene. We determined their reactivity ratios in radical copolymerization and analyzed the final copolymer products to investigate the effect of the interactions between the two types of rings on the structure and properties of the resulting products.
CHAPTER II
LITERATURE REVIEW

2.1 Fluorinated Polymers.

2.1.1 General Considerations on Fluorinated Polymers.

The International Organization for Standardization (ISO) definition of fluorinated polymers or fluoropolymers is a polymer made from monomers containing one or more atoms of fluorine and their copolymers with other monomers, provided the copolymer has a higher amount of fluorinated monomer.\(^\text{14}\) They are a rather unique group of polymeric materials, characterized for having very special application and performance properties. These properties include good to outstanding resistance to aggressive chemicals (including acids, bases, organic solvents and petroleum and its derivatives); unique dielectric properties (low dielectric constants and dissipation factors), good release properties and antisticking behavior, low friction coefficient, high optical clarity and low refractive index, low flammability, high thermal and oxidative stability, low water absorptivity and low surface energies. Due to their inert nature, fluoropolymers are among the safest synthetic materials. Some of the factors contributing to the characteristics of fluoropolymers are: strong bond between C and F atoms (116 kcal/mol vs. 99 kcal/mol of a C-H
bond, 84 kcal/mol of a C-O bond, 83 kcal/mol of a C-C bond, 78 kcal/mol of a C-Cl bond, 66 kcal/mol of a C-Br bond, and 57 kcal/mol of a C-I bond),\(^1\) shielding of the carbon chain by the fluorine atoms, low interchain forces present in most cases, and high melting points as a consequence of their crystalline behavior.\(^1,15\) However, fluoropolymers exhibit several weaknesses, including high processing temperatures (which translates into high processing cost) and poor solubility in common organic solvents, which precludes proper characterization.

There are two main classifications of fluorinated polymers: (1) by the degree of fluorination, including partially fluorinated and totally fluorinated,\(^16,17\) and (2) by their ability to crystallize, including fluoroplastics and fluoroelastomers. Fluoroplastics are semicrystalline materials that melt at temperatures above 150 °C. In contrast, fluoroelastomers are amorphous materials with glass transition temperatures (\(T_g\)) below 0 °C. They can be crosslinked into stable networks to maintain their elastomeric properties.\(^18\) Due to their exceptional properties, fluoropolymers are the choice in applications requiring a high performance (coatings, aerospace, aeronautics, optics) and despite their high cost, they are undergoing an increasing demand.

Two distinct routes are generally followed to obtain fluorine-containing polymers: first, by the polymerization of suitable monomers having one or more fluorine atoms; and second, by the chemical modification of non-fluorinated polymers. While the first method is the most commonly practiced, the second method allows the preparation of novel fluorinated materials for which there are
no commercially available and/or easily synthesized monomers.\textsuperscript{19,20} Table 2.1 summarizes some of the most common commercial fluoropolymers.

Table 2.1. Some fluoropolymers and their structure and properties.\textsuperscript{1}

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Abbreviation</th>
<th>Structure</th>
<th>Melting Point. (° C)</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (tetrafluoroethylene)</td>
<td>PTFE</td>
<td>-CF$_2$-CF$_2^-$</td>
<td>327</td>
<td>2.1</td>
</tr>
<tr>
<td>Poly (vinylidene fluoride)</td>
<td>PVDF</td>
<td>-CH$_2$-CF$_2^-$</td>
<td>168</td>
<td>8.8</td>
</tr>
<tr>
<td>Poly (vinyl fluoride)</td>
<td>PVF</td>
<td>-CF$_2$-CHF$-$</td>
<td>200</td>
<td>7.7</td>
</tr>
<tr>
<td>Poly (chlorotrifluoroethylene) Fluorinated Ethylene Propylene Copolymer..</td>
<td>PCTFE</td>
<td>-CF$_2$-CFCl$-$</td>
<td>211</td>
<td>2.5</td>
</tr>
<tr>
<td>Ethylene and Tetrafluoroethylene Copolymer.</td>
<td>PFEP</td>
<td>-CF$_2$-CF$_2^-$</td>
<td>271</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>PETFE</td>
<td>-CH$_2$-CH$_2^-$</td>
<td>260</td>
<td>2.6</td>
</tr>
</tbody>
</table>

2.1.2 Fluorinated Polymers Containing Aliphatic Fluorocarbons.

2.1.2.1 Fluoroplastics.

Aliphatic fluoropolymers are, in their simplest form, polymers of saturated hydrocarbons in which the hydrogen atoms have been replaced totally or partially by fluorine atoms. The discovery that tetrafluoroethylene readily undergoes polymerization, to produce poly(tetrafluoroethylene) (PTFE), is considered the origination of fluoropolymer chemistry.\textsuperscript{21} PTFE was first commercialized by Dupont under the name of Teflon\textsuperscript{®} and is still considered one of the most chemically and thermally stable polymers on the market. It has a very high melt viscosity (due to the high molecular weights that PTFE achieves) and a very high
melting point (340 °C when the crystallinity is about 90%).) Some other commercially important fluorine-containing polymers include poly(vinyl fluoride), poly(chlorotrifluoroethylene), poly(vinylidene fluoride), copolymers of tetrafluoroethylene with hexafluoropropylene (FEP copolymer, often viewed as PTFE with an occasional CF$_3$ attached), copolymers of ethylene and tetrafluoroethylene (ETFE copolymer), and poly(2,2-bisfluoromethyl-4,5-difluoro-1,3-dioxole) (PDD, copolymer commercialized by Dupont under the name of Teflon AF®, which has the lowest refractive index known for any solid organic polymer.$^{15,17}$) In most cases, copolymerization disrupts the crystalline structure present in PTFE, which translates into a lower melting point.

The mechanical properties of these fluorinated polymers and copolymers depend greatly on whether they are fully fluorinated or they contain hydrogen atoms in their structure. The latter are normally twice as stiff and have about 1.5 times the strength of fully fluorinated polymers. This is a direct consequence of the attractive forces developed between the bulky -CF$_2$- of one chain and the smaller -CH$_2$- of the adjacent chains. In contrast, fully fluorinated polymers have greater elongations and their service temperatures are higher.$^{15}$

Many other properties are a direct consequence of the structure of these polymers and whether they are crystalline or amorphous. Amorphous fluorinated polymers are generally copolymers in which the introduction of a second monomer, which may be fully or partially fluorinated, has disrupted the crystalline lattice. Their solubility in selected fluorinated solvents is enhanced and they can
therefore be fully characterized and processed as solutions for specialty coatings and films.

All fluorinated materials are UV resistant due to the strong C-F bond, which is resistant to pure photolysis, and the absence of light-absorbing chromophores. Crystalline fluoropolymers have much lower clarity (poor optical properties) than those unable to crystallize.\textsuperscript{15}

All aliphatic fluoropolymers have outstanding chemical resistance to acids, alkalis and organic solvents. However, partially fluorinated materials are less chemically resistant than perfluorinated materials and their performance is worse under extreme temperatures.\textsuperscript{18}

PTFE has very good insulating properties. The very low dielectric strength of this polymer is a result of a very symmetrical chain structure in which all of the C-F bonds (dipoles) are equally balanced. However, the new amorphous polymers, such as Teflon AF\textsuperscript{®}, have even better insulating properties.

A large amount of these materials is used in electrical and electronic applications, with major use for insulation for military and aerospace equipment. The chemical industry is another destination of these fluoropolymers, which are used to fabricate gaskets, lined pipe, seals, molded packing, laboratory equipment, and compression-molded parts. Because of their low friction coefficient, they are also used in sliding bearing pads in static and dynamic load supports. Films are used in solar-collector windows because of the excellent weather resistance, high transparency and light weight. Fabric and metal coatings are also destinations of these materials. Fluoropolymer tubing is being
used for supplying high purity gases. In general, applications requiring high temperature performance, high thermal and chemical resistance and good electrical properties are suitable for these fluorinated polymers and copolymers based on aliphatic structures.\textsuperscript{1,15}

2.1.2.2 Fluoroelastomers.

Fluoroelastomers are synthetic copolymers suitable for applications in hostile environments, with broad service temperature ranges and aggressive chemical contact. Fluorocarbon elastomers are the most common. They are classified into fluorocarbon elastomers based on vinylidene (VDF) and perfluoroelastomers, which derive from tetrafluoroethylene (TFE). In order to obtain amorphous structures from monomers that homopolymerize into highly crystalline structures, they must be copolymerized with the right monomer(s) and in the right feed compositions.\textsuperscript{22} VDF-based elastomers were developed first and are still the most important commercially available fluoroelastomers; despite their high cost, VDF-based elastomers are preferred over many other specialty rubbers. Fluoroelastomers have a very high resistance to high temperatures and to aggressive chemicals, properties that can be mostly related to the high energy of the C-F bond and the enhanced strength of the C-C and C-H bonds due to the presence of fluorine atoms.\textsuperscript{23}

2.1.2.3 Fluorinated Polyurethanes.\textsuperscript{1,15}

Polyurethanes are materials with a wide range of physical and chemical properties that can be obtained from combinations of the affordable and commercially available polyisocyanates and polyols. Tuning of the composition
and formulation results in block, comb, or random materials that may take any physical form, from brittle glasses to elastomers.

Fluorination of these materials enhances their chemical, thermal, hydrolytic and oxidative stability. They also become more permeable to oxygen, more biocompatible and their surfaces are less attractive to strenuous non-desired substances.

2.1.2.4 Polyfluoroacrylates.\textsuperscript{1,15}

The products of polymerization and copolymerization of fluoroalkyl acrylates and fluoroalkyl methacrylates have the most practical use. The presence of fluorine atoms in polyacrylates imparts a combination of good optical and mechanical properties with high heat resistance and thermal stability. Their low surface energy makes these fluoropolymers ideal for coatings for repellant textiles and fibers. The largest volume of the production of this kind of polymers is for textile coatings.\textsuperscript{24,25,26}

2.1.2.5 Perfluoropolyethers.\textsuperscript{15}

Perfluoropolyethers (PFPEs) are a class of fluoropolymers having low molecular weights, with a structure that contains only fluorine, carbon and oxygen. This peculiar composition makes them useful for extreme conditions such as oxidizing environments and aggressive chemical exposure. They exhibit liquid-phase behavior over a temperature range between −100 °C and 400 °C. They may exhibit liquid behavior over the largest temperature range of any materials. They are used as lubricants for computer hard disks (where minimum head/disk interfacial wear friction is required), as high temperature greases and
as vacuum pump oils. Due to their lyophobic and hydrophobic behavior, they are also used in cosmetic applications.

2.1.3 Aromatic Fluorocarbons and their Polymers.

2.1.3.1 2,3,4,5,6-Pentafluorostyrene.

2,3,4,5,6-Pentafluorostyrene (PFS) was prepared for the first time by Nield, Stephens and Tatlow\(^2^7\) in the United Kingdom, and by Pummer and Wall\(^2^8\) in the United States. Nield et al.\(^2^7\) reacted pentafluorobenzene with bromine in ether with aluminum bromide as a catalyst. The resulting product, bromopentafluorobenzene, was reacted with magnesium (activated with iodine) in dry ether in order to create the Grignard reagent: pentafluorophenylmagnesium bromide. This reagent was converted into 1-(pentafluorophenyl)ethanol by reaction with acetaldehyde followed by protonation with dilute hydrochloric acid. The alcohol was dehydrated by heating with phosphoric oxide and a small quantity of quinol to obtain the PFS. Wall et al.\(^2^9\) first synthesized PFS by making the 1-(pentafluorophenyl)ethanol in the same way as described above. The alcohol was dehydrated in this case by passing it through a glass tube containing aluminum oxide pellets at 350 °C with the help of nitrogen gas. In 1963 Wall et al. also synthesized PFS starting from hexafluorobenzene, which was converted into 2,3,4,5,6-pentafluoro-\(\alpha\)-methylstyrene by reaction with isopropenyllithium. Reaction of 2,3,4,5,6-pentafluoro-\(\alpha\)-methylstyrene with vinyllithium resulted in a low yield of PFS; the product was mainly unreacted hexafluorobenzene.\(^2^9\) PFS is now commercially
available from several suppliers; PFS and 4-fluorostyrene are the only fluorinated styrenes that can be purchased.

PFS is a clear colorless liquid at room temperature, with a boiling point of 62-63 °C at 50 mm Hg and 142-143 °C at 760 mm Hg; density of 1.406 g/cm³ and refractive index, nD²⁰ = 1.4445-1.4465. It is flammable and has a flash point of 34 °C. It is stable under normal temperatures and pressures, although it may decompose producing carbon monoxide, carbon dioxide and hydrogen fluoride.

Pryor and Huang reported for the first time the radical-initiated polymerization of PFS in 1969. Many other methods to polymerize and copolymerize PFS with several vinyl monomers have been reported. A detailed explanation of the most relevant methods is reported in the following section.

2.1.3.2 Polymerization of 2,3,4,5,6-Pentafluorostyrene.

2.1.3.2.1 Conventional Radical Polymerization.

Scheme 2.1 shows the main reactions involved in the polymerization of PFS following a radical mechanism. Pryor and Huang studied in detail the radical polymerization of PFS initiated with 2,2’-azobisisobutyronitrile (AIBN). They studied the kinetics of this polymerization with density measurements, finding that the rate of initiation was \( R_i = 11.8 \times 10^{-6} \text{ sec}^{-1} \). Considering that in bulk \( R_i = 2kdf \) (in which \( k_d \) is the decomposition constant of the initiator and \( f \) is the efficiency of that initiator, defined as the amount of radicals formed that successfully initiate monomer), and taking the value of \( k_d = 1.13 \times 10^{-5} \text{ sec}^{-1} \) at 60 °C, a value for \( f \) of 0.52 was found, which is comparable to that of the AIBN-initiated polymerization of 4-fluorostyrene (\( f=0.55 \)).
Initiation

\[ \text{I}_2 \xrightarrow{\Delta} 2 \text{I}^- \]

\[ \text{I}^- + \text{F} \xrightarrow{} \text{F} \]

Propagation

\[ \text{F} \xrightarrow{} \text{F} \]

Termination

\[ \text{F} \xrightarrow{} \text{F} \]

Scheme 2.1. Polymerization of 2,3,4,5,6-pentafluorostyrene by radical initiation.\textsuperscript{30}

They also determined the polymerizability (1/\(\delta\)) of the monomer, which is defined as \(1/\delta = k_p / (2k_t)^{0.5}\) (in which \(k_t\) is the termination rate constant), finding that the value for PFS at 60 °C of 0.0385 is comparable to that for styrene (0.0333)\textsuperscript{33}; but different to the polymerizability of methyl methacrylate (0.147)\textsuperscript{34}, and vinyl acetate (0.430)\textsuperscript{35}. The transfer constants to several solvents were also
calculated for the polymerization of PFS. While the radical from PFS is as selective toward benzylic hydrogens as the polystyryl radical, the radicals from PFS undergo less transfer to ketones. This is ascribed to a more electron-withdrawing substituent of the PFS monomer. Furthermore, the transfer constant to monomer is lower for PFS than for styrene. Comparison of molecular weights determined osmometrically with those determined using tritium-labeled AIBN indicates that termination occurs mainly by combination.

Pure thermally-initiated polymerization of PFS was also studied and compared to the mechanism accepted for styrene.\textsuperscript{30,36} Scheme 2.2 shows the mechanism for the pure thermal initiation of styrene, involving the formation of a Diels-Alder dimer of styrene followed by a molecule-assisted transfer of a hydrogen atom from the dimer to a styrene molecule.\textsuperscript{37}

\begin{center}
\textbf{Scheme 2.2. Thermally-initiated polymerization of styrene.}\textsuperscript{37}
\end{center}
Although the initiation rate for this self-initiated polymerization is much slower than that for the radical polymerization using an initiator like AIBN, it is far from negligible. In fact, styrene and its derivatives are the only monomers that have proved to undergo pure thermal self-initiation.\textsuperscript{37}

The rate of the thermal-initiated polymerization of PFS is lower than that for styrene. If the same mechanism were followed, it would involve the formation of an analogous Diels-Alder type dimer (Scheme 2.3), with the consequent transfer of a fluorine atom to PFS. However, the fluorinated dimer is produced in a very low yield if any at all. If it is formed it must be quite unreactive, in contrast to the very reactive styrene dimer. Besides, the observed chain transfer constant of bulk PFS is very low, and this includes transfer from any fluorinated dimer that may be present. Therefore, the only possibility would be if the fluorinated dimer transferred a fluorine atom to any possible radical species present.

\begin{equation}
2 \text{CH}_2=\text{CH} + \text{R} \rightarrow \text{F}_2\text{C}_2\text{H}_4\text{F} + \text{R-F}
\end{equation}

\textbf{Scheme 2.3.} Diels-Alder dimerization of 2,3,4,5,6-pentafluorostyrene followed by abstraction of a fluorine atom. \textit{R}• represents any possible radical species present.\textsuperscript{36}
The thermal-initiated polymerization of PFS cannot proceed through the same mechanism as that of styrene. If the fluorinated dimer is formed, the only way it could initiate polymerization of PFS is if there is another radical present in the medium, which can abstract a fluorine atom from the dimer.

The proposed mechanism for the thermal initiation of PFS included the formation of a 1,4-diradical, which converts into a more active propagating species: a monoradical by abstraction of a hydrogen atom (Scheme 2.4). Isotope effect studies confirm that the monomer cannot be the hydrogen donating species, so the final proposed mechanism includes the formation of the 1,4-diradical and subsequent abstraction of a hydrogen atom from a chain transfer agent (impurity, polymer, etc.) to form a propagating monoradical.

![Diagram of proposed mechanism for thermal initiation of PFS polymerization]

Scheme 2.4. Proposed mechanism for the thermal initiation of the radical polymerization of 2,3,4,5,6-pentafluorostyrene.$^{36}$

Since that 1969 study, many other authors have reported the polymerization and copolymerization of PFS following a radical mechanism initiated by AIBN,$^{38,39,40,41,42,43,44}$ benzoyl peroxide (BPO),$^{42}$ 4,4’-azobis(4-cyanopentanoic acid) (ABCPA)$^{45,46}$ and ultraviolet radiation.$^{47}$
PFS has been radically copolymerized with several vinyl monomers, such as styrene,\textsuperscript{30,39,40,41,44,45,46} methyl methacrylate,\textsuperscript{30} butadiene,\textsuperscript{48} isoprene,\textsuperscript{48} glycidyl methacrylate,\textsuperscript{41,42} and 1-(4-nitrophenyl)-2-(4-[[2-(methacryloyloxy) ethyl]ethylamino]-phenyl) diazene.\textsuperscript{42} The parameters \( r_1 \) and \( r_2 \) are the monomer reactivity ratios, which are defined as the ratio of the rate constant for a reactive propagating species adding its own type of monomer to the rate constant of addition of the other monomer. The values of the reactivity ratios can be correlated to the structure of the resulting copolymer. Thus, if the product \( r_1 r_2 \) approaches 0, then an alternating copolymer results; if this product \( r_1 r_2 \) is close to 1, then the sequence of the two monomers in the copolymer will be random; and if \( r_1 r_2 \) is much greater than 1, then the copolymer backbone will be composed of alternating blocks of each of the monomers.\textsuperscript{49} There have been several attempts to correlate the structure with the reactivity ratios of the monomers involved in a copolymerization. A better understanding in this area would allow predicting monomer reactivity ratios and the structure of copolymers that have not been synthesized yet. A useful correlation was proposed by Alfrey and Price in 1947,\textsuperscript{50} in which they proposed that the rate constant for a radical \( M_1^\cdot \) to react with a monomer \( M_2 \) would follow the expression shown in equation (eq.) 2.1.

\[
k_{f2} = P_1 Q_2 \exp (-e_1 e_2)
\]

Eq. 2.1

\( P_1 \) measures the resonance stabilization of radical \( M_1^\cdot \) and \( Q_2 \) measures the resonance stabilization of \( M_2^\cdot \), and \( e_1 \) and \( e_2 \) measure the polarity of the monomers \( M_1 \) and \( M_2 \) respectively. For reference, styrene was arbitrarily assigned a Q value of 1, and the more stabilized by resonance a monomer is, the
higher the Q value it shows. Analogously, the reference value for the polarity parameter e is \(-0.80\), arbitrarily chosen for styrene. Monomers having electron-withdrawing substituents have a positive value of e, and monomers having a very negative value of e have electron donating substituents.\(^{49}\)

Table 2.2 shows the reported reactivity ratios found in the literature for the radical copolymerization of PFS with several common vinyl monomers, and the values of Q and e for those same monomers. Pryor and Huang\(^{30}\) reported the Q and e values of PFS to be 0.69 and 0.74, respectively.

Table 2.2. Reactivity ratios of 2,3,4,5,6-pentafluorostyrene in radical copolymerization.

<table>
<thead>
<tr>
<th>M(_1)</th>
<th>M(_2)</th>
<th>(r_1^a)</th>
<th>(r_2^a)</th>
<th>(r_1r_2^a)</th>
<th>Q(_2^b)</th>
<th>e(_2^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFS</td>
<td>Styrene</td>
<td>0.22</td>
<td>0.43</td>
<td>0.09</td>
<td>1.00</td>
<td>-0.80</td>
</tr>
<tr>
<td>PFS</td>
<td>Methyl Methacrylate</td>
<td>0.99</td>
<td>0.98</td>
<td>0.89</td>
<td>0.78</td>
<td>0.40</td>
</tr>
<tr>
<td>PFS</td>
<td>Butadiene</td>
<td>0.50</td>
<td>1.01</td>
<td>0.50</td>
<td>1.70</td>
<td>-0.50</td>
</tr>
<tr>
<td>PFS</td>
<td>Isoprene</td>
<td>0.43</td>
<td>8.50</td>
<td>3.68</td>
<td>1.00</td>
<td>-0.55</td>
</tr>
</tbody>
</table>

\(^a\) Values from reference 30 (first two rows) and reference 48 (last two rows). Copolymerization carried out in bulk at 60 °C, with AIBN as initiator.

\(^b\) Values from reference 37.

2.1.3.2.2 Other polymerization methods.

Nishimura et al. reported the anionic polymerization of PFS, as well as its copolymerization with styrene, following an anionic mechanism.\(^{51}\) PFS shows a large positive value of e (related to the electron withdrawing character of the substituent of the monomer, Table 2.2), and therefore it should be easily polymerized anionically. They synthesized polymers by initiating PFS with
anionic initiators of relatively low nucleophilicity, such as pyridine, in contrast to styrene, which can only be polymerized with highly nucleophilic initiators, such as $n$-C$_4$H$_9$Li. Anionic propagation of PFS is more controlled than that of styrene. This is due to the lower electron-density of the propagating PFS carbanion because of the electron-withdrawing effect of the fluorine atoms. The copolymerization of PFS with styrene initiated by $n$-C$_4$H$_9$Li showed similar alternating behavior of that initiated by AIBN, with similar reactivity ratios: $r_1 = 0.33$ (styrene) and $r_2 = 0.43$ (PFS) (vs. 0.43 and 0.22 respectively for radical copolymerization using AIBN as initiator). In a later publication, Nishimura et al. reported the copolymerization of PFS with 1,3-divinylbenzene ($m$-DVB) and 1,4-divinylbenzene ($p$-DVB). The resulting products were soluble copolymers with crosslinkable groups. The copolymerization times were much longer than those required for the copolymerization of styrene with both isomers of DVB, and in contrast to the styrene system in which $p$-DVB is more reactive than $m$-DVB, $m$-DVB is much more reactive than $p$-DVB, as evidenced by the amount of PFS found in each copolymer system.

PFS has also been polymerized by $\gamma$-irradiation at atmospheric pressure, chemical vapor deposition, plasma polymerization, and plasma enhanced chemical vapor deposition. The last three techniques allow for the synthesis of thin films, which have low dielectric constants.

Atom radical transfer polymerization (ATRP) is a new polymerization technique that allows for control of the polymerization, and results in well-defined compositions and/or architectures of the resulting products. Since it is a radical
polymerization technique, it can be used for a wide range of monomers and does not require extremely pure, oxygen free and extra dry conditions, in contrast to living ionic polymerizations. Jankova and Hvilsted reported the first polymerization and copolymerization of PFS following an ATRP mechanism.\textsuperscript{60} The yields were high at 110 °C and the rate of propagation was fast, which is probably due to the electron-withdrawing character of the fluorine atoms. Polymerization is controlled since the apparent polymerization rate is first order in monomer and the molecular weight increases linearly with conversion. They also polymerized styrene from a PPFS macroinitiator and PFS from a PS macroinitiator, obtaining block copolymers of PFS and styrene in both cases. ATRP was also used to make triblock copolymers based on central poly(ethylene glycol) or poly(ethylene glycol-co-propylene glycol) blocks with PPFS outer blocks.\textsuperscript{61} Diblock copolymer brushes containing PFS (outer blocks) were synthesized by surface-initiated ATRP from silica substrates.\textsuperscript{62} Also, ATRP was used to prepare linear, branched and arborescent PFS brushes, from a 4-vinylbenzyl chloride inimer that was immobilized on hydrogen terminated silica surfaces.\textsuperscript{63}

2.1.3.3 Poly(2,3,4,5,6-pentafluorostyrene).

PPFS is a white powdery solid, electrostatically charged with a reported density as measured by pycnometry of 1.5499 g/cm\textsuperscript{3}.\textsuperscript{30} Since the first reported syntheses, there have been many synthetic studies employing several polymerization techniques and reports on its properties. PPFS is now commercially available, either as a homopolymer or copolymerized with glycidyl
methacrylate. The following sections explain some of its properties and its main uses.

2.1.3.3.1 Spectroscopic Properties of Poly(2,3,4,5,6-pentafluorostyrene).

Very far infrared spectroscopy (close to microwave) absorption measurements show that PPFS exhibits a low frequency of collisions as expected from the great mass and quadrupole moments of the perfluorinated aromatic rings.64

UV spectroscopy of PPFS was carried out by Su.44 He compared the absorption and emission spectra of PPFS to those of PS. Although the absorption spectra of both homopolymers are identical, their fluorescence spectra are not the same, due to the lack of excimer emission by PPFS. O’Connor et al. reported the photophysics of PPFS and compared them to polystyrene, and to model compounds, like pentafluorotoluene and hexafluorobenzene.38,65 The UV emission spectra of a PPFS film and that of a dilute solution of PPFS in ethyl acetate were the same as the UV emission spectra of a dilute solution of pentafluorotoluene in pentane. These emission spectra lack the vibronic structure found for PS and benzene. The features of the emission spectra of pentafluorotoluene do not depend on the concentration of the solution, and both pentafluorotoluene solution and PPFS film emission spectra show no bands below 290 nm, contrary to PS film emission spectra. They explained that the bands with no structure in the emission spectra of both PPFS film and pentafluorotoluene solution are not due to excimer formation (in agreement with what was reported by Su44) but to an excited-state conformation
that is significantly distorted from the initially excited ground-state conformation. Thus, as opposed to PS and poly(4-fluorostyrene), PPFS shows no excimer formation. The lack of excimer formation for PPFS was explained as due to Coulombic interactions between perfluorinated rings, which prevents two rings (the chromophores) from coming close enough to form an excimer.\textsuperscript{42}

2.1.3.3.2 Solubility and Solution Properties of Poly(2,3,4,5,6-pentafluorostyrene).

Polymeric materials intended for surface coating or thin films are normally prepared from solution. Therefore, it is very important to investigate their solubility and solution properties of these polymers.

PPFS is soluble in methyl ethyl ketone, methyl isobutyl ketone, tetrahydrofuran (THF), ethyl acetate, and fluorobenzene; slightly soluble in pyridine, acetone, methyl isopropyl ketone, and chlorobenzene; and insoluble in benzene, toluene, iodobenzene, bromobenzene, carbon tetrachloride, chloroform, carbon disulfide, methanol, ethanol, ether, tetralin, dioxane, decalin, cyclohexane, hexane, heptane, and 1,2-dichlorobenzene.\textsuperscript{30} A later study\textsuperscript{60} reported that PPFS synthesized by ATRP is soluble in fluorobenzene, methyl ethyl ketone, THF, xylene, methyl isobutyl ketone, ethyl acetate, and chloroform; slightly soluble in dimethoxyethane; and insoluble in hexafluorobenzene, carbon tetrachloride, 1,2-dichlorobenzene, toluene, hexachloroacetone, and hexafluoro-2-propanol. The only disagreement found was solubility in chloroform, attributed to differences in molecular weight of the PPFS used.\textsuperscript{60}

As part of his doctoral research, Su studied the solution properties of PPFS prepared by radical polymerization of PFS using AIBN as the initiator, either in
bulk or in methyl ethyl ketone solution.\textsuperscript{44} The second virial coefficient determined by static light scattering\textsuperscript{66} in THF at 30°C was $3.15 \times 10^{-6}$, and the refractive index increment determined in the same manner was 0.0433. From intrinsic viscosity measurements he also reported the Mark-Houwink constant $a$ calculated from equation 2.2, in which $[\eta]$ is the intrinsic viscosity, $M$ is the molecular weight and $K$ and $a$ are the Mark-Houwink parameters, in different solvents to range from 0.505 to 0.711 as the solvent quality changes from poor to good. He reported that hexafluorobenzene and methyl isobutyl ketone were good solvents for PPFS, and that ethyl acetate and THF were poor solvents.

$$[\eta] = K M^a$$ \hspace{1cm} \text{Eq. 2.2}

Swelling measurements of crosslinked PPFS, prepared with varying amounts of divinylbenzene and AIBN as the initiator, were used to determine the solubility parameter of crosslinked PPFS in THF, which Su reported to be approx. 8.2 (cal/cm$^3$)$^{1/2}$. The root-mean-square radius of gyration of PPFS, which measures the unperturbed chain dimensions of a polymer in solution of a theta solvent as determined by static light scattering, was greater than that of PS having the same degree of polymerization. Therefore, the polymer chains of PPFS are more extended than those of PS.\textsuperscript{44}

2.1.3.3.3 Thermal Properties of Poly(2,3,4,5,6-pentafluorostyrene).

One of the most unique properties of fluoropolymers is their thermal and oxidative stability. The glass transition temperatures ($T_g$s) of several fluorine-containing polymers are listed in Table 2.3.\textsuperscript{67} Introduction of fluorine atoms in the main chain results in higher the $T_g$s than side group substitution. PPFS,
prepared by the self-initiated polymerization of PFS, was more thermally stable and more resistant to photooxidation than PS.\textsuperscript{68,69}

Table 2.3. Glass transition temperatures ($T_g$) of fluoropolymers.\textsuperscript{67}

<table>
<thead>
<tr>
<th>Structure</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CF$_2$-CF$_2$-</td>
<td>152</td>
</tr>
<tr>
<td>-CH$_2$-CHCF$_3$-</td>
<td>27</td>
</tr>
<tr>
<td>-CH$_2$-CH$_6$F$_5$-</td>
<td>105</td>
</tr>
<tr>
<td>-CF$_2$-CF$_6$F$_5$-</td>
<td>194</td>
</tr>
<tr>
<td>-CF$_2$-CF$_6$H$_5$-</td>
<td>202</td>
</tr>
</tbody>
</table>

Su studied the thermal degradation of PPFS determined using thermogravimetric analysis (TGA), under an inert atmosphere of nitrogen.\textsuperscript{44} The degradation temperature for 1% weight loss of PPFS was lower (420 °C) than that for PS (511 °C). However, the decrease in molecular weight of a PS sample after being held at 350 °C was greater than that of PPFS. He concluded that the PS chains undergo random scission at relatively low temperatures, although the volatiles only become evident at a much higher temperature. In contrast, PPFS chains undergo chain scission at a higher temperature, but the unzipping process is faster so the volatiles become evident at lower temperatures. Jankova and Hvilsted\textsuperscript{60} observed that the degradation temperature for 10% weight loss of PPFS and PS are 436 and 379 °C, respectively, for samples with a number-average molecular weight of 1.14 x 10$^4$ and 1.00 x 10$^4$ Dalton, respectively. They also found that the thermal stability of PPFS prepared by ATRP was higher
than that of PPFS prepared either thermally (396 °C) or by conventional radical polymerization (423 °C), all of which are higher than the thermal degradation temperature of PS. Therefore, they found that the PPFS degradation temperature is higher than that of PS, which disagrees with Su’s report.

Su\textsuperscript{44} also reported the infinite molecular weight $T_g$ of PPFS as 107 °C, which is higher than that reported by Jankova and Hvilsted\textsuperscript{60} 101.2 °C. Although this last value is also an infinite molecular weight $T_g$, the highest molecular weight used in the thermal studies was ten times lower than that used by Su. Lemieux \textit{et al.}\textsuperscript{45,46} reported that the $T_g$ of PPFS is 108 °C, for a polymer with a molecular weight in the same range as that examined by Su.

2.1.3.4 Copolymers of 2,3,4,5,6-Pentafluorostyrene and Styrene.

The copolymerization of styrene and PFS by a conventional radical mechanism was studied by Pyror and Huang\textsuperscript{30} and by Su\textsuperscript{44} and by an anionic mechanism by Nishimura.\textsuperscript{52} The reported reactivity ratios and the product of them are compiled in Table 2.4. The copolymerization of styrene and PFS tends to alternate when copolymerized radically and anionically. The block copolymerization of PFS and styrene was carried out by ATRP by polymerization of PFS from a styrene macroinitiator or vice versa.\textsuperscript{60}

2.1.3.4.1 Spectroscopy of the Copolymers of 2,3,4,5,6-Pentafluorostyrene and Styrene.

The fluorescence emission spectra of the copolymers of 2,3,4,5,6-pentafluorostyrene and styrene (poly(styrene-co-PFS)) were identical to the spectrum of PPFS. There is no excimer formation, and no emission from styrene
was detected due to an energy transfer from phenyl rings to perfluorinated phenyl rings.\textsuperscript{41}

Table 2.4. Reactivity ratios and their products for copolymerization of styrene (M\textsubscript{1}) and pentafluorostyrene (PFS, M\textsubscript{2}) under radical or anionic conditions.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>r\textsubscript{1} \textsuperscript{a}</th>
<th>r\textsubscript{2} \textsuperscript{a}</th>
<th>r\textsubscript{1}r\textsubscript{2} \textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Radical\textsuperscript{a}</td>
<td>0.43</td>
<td>0.22</td>
<td>0.09</td>
</tr>
<tr>
<td>Anionic\textsuperscript{b}</td>
<td>0.33</td>
<td>0.43</td>
<td>0.14</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Copolymerization carried at 60 °C, in bulk, with AIBN as initiator. Reference 30.

\textsuperscript{b} Reference 51.

O’Connor \textit{et al.}\textsuperscript{39} also studied the emission spectra of films made of the copolymers resulting from the copolymerization of PFS and styrene initiated by AIBN, observing a dependence of the intensity of the emitted light with the amount of PFS present in the copolymer. Small amounts of PFS result in significant quenching of the excimer emission of PS. The absorption spectra of metalloporphyrins immobilized in films of poly(styrene-co-PFS) are the same for both the film and the toluene solution, demonstrating that there are no interactions between the copolymer and the metalloporphyrins.\textsuperscript{40}

2.1.3.4.2 Solubility of the Copolymers of 2,3,4,5,6-Pentafluorostyrene and Styrene.

The solubilities of several block copolymers of styrene and PFS prepared by ATRP were studied.\textsuperscript{60} An increased amount of styrene in the copolymers increased their solubility in chloroform and methylene chloride but decreased their solubility in ethyl acetate. O’Connor \textit{et al.}\textsuperscript{39} reported the spin-cast films of
poly(styrene-co-PFS) from a solution of ethyl acetate, which was a good solvent for them.

Su reported that the copolymers of PFS and styrene synthesized by conventional radical polymerization are soluble in both benzene and hexafluorobenzene, which are non-solvents for PPFS and PS respectively.\textsuperscript{44}

2.1.3.4.3 Thermal Properties of the Copolymers of 2,3,4,5,6-Pentafluorostyrene and Styrene.

Su reported the thermal degradation behavior of copolymers of PFS and styrene prepared by radical copolymerization.\textsuperscript{44} The degradation temperature of several copolymers, defined by the temperature at which the copolymers suffer a 1% weight loss, and determined by TGA, was between those of the homopolymers, and increased as the amount of PFS increased until it leveled off after 50% PFS. The molecular weight of the copolymers after being held at 350 °C indicated that no chain scission occurs in them, contrary to both PPFS and PS. Therefore, the degradation mechanism of the copolymers must not be the same as that for the homopolymers, as he reported. The thermal stability of the copolymers is a consequence of stable PFS linkages and attractive interactions between the two types of aromatic rings.

Jankova and Hvilsted\textsuperscript{60} reported the thermal degradation determined by TGA of several block copolymers of PFS and styrene prepared by ATRP, and of a copolymer prepared by the conventional radical polymerization of PFS and styrene. The degradation temperature of a block copolymer with 42% PFS is 27 °C lower than that of the PPFS homopolymer and 30 °C higher than that of PS.
Even a relatively small amount of PFS improved the thermal stability of the PS block. The degradation temperature of a statistical copolymer with a higher molecular weight than that of the block copolymers was also lower than the degradation temperature of PPFS.

The $T_g$s of copolymers of PFS and styrene prepared by conventional radical polymerization initiated by AIBN were 105 °C for three copolymers containing 32.2, 52.8, and 68.1 mol% of styrene, and molecular weights of $1.38 \times 10^5$, $1.14 \times 10^5$ and $0.83 \times 10^5$ Dalton, respectively. Therefore in this study, the $T_g$s of the copolymers were independent of the composition of the copolymers for that molecular weight range.44

2.1.4 Commercial Applications of Poly(2,3,4,5,6,-Pentafluorostyrene) and its Derivatives.

Fluorinated polymers have many desirable properties (Section 2.1.1), including low surface energy, high optical clarity, low refractive index, and high UV, thermal and chemical stabilities.1,15 Fluoropolymers based on aromatic fluorocarbons also have very interesting properties that make them potentially important for commercial applications. PPFS forms films with low surface energies,55 as determined by high water contact angles.62 In fact, the critical surface tension of PPFS is similar to that of other aliphatic fluoropolymers.70

PFS is used in fabrication of hydrogels to make contact lenses for continuous wear, with improved wettability and oxygen permeability. These hydrogels were made from copolymers of siloxane, methacrylates, and PFS.71,72,73
PFS was used to make magnetic electrophoretic toners, for document generation, which showed minimized smearing of image.\textsuperscript{74} Copolymers of PFS and glycidyl methacrylate were subsequently crosslinked by contact printing and developed by wet etching, producing high quality ridge waveguides with smooth surfaces.\textsuperscript{41,75} Low loss polymeric optical waveguide materials for optical devices were made of a terpolymer of PFS, styrene, and glycidyl methacrylate for the cladding and buffer layers, and a terpolymer of PFS, styrene and 4-hydroxystyrene for the guiding layer.\textsuperscript{76} Particles used to separate nucleic acids were made using fluoropolymers containing PFS.\textsuperscript{77} The surface of the particles present unusual polarity that is beneficial in performing chromatographic separations. Polymeric materials containing PFS were made into adsorbent particles by high shear reaction with a porogen.\textsuperscript{78} The resulting particles meet all of the characteristics necessary for the stationary phase of high performance liquid chromatography. Films of PPFS, made by plasma enhanced chemical vapor deposition, were designed to be used as antireflective polymeric coatings.\textsuperscript{58,79} Films having low dielectric constants were made by pulsed plasma polymerization of PFS,\textsuperscript{57} and films made of copolymers of PFS and styrene were used to immobilize oxygen sensors.\textsuperscript{40} Copolymers of styrene and PFS have a higher permeability to oxygen than that of PS homopolymer. PPFS was also used to coat pigment particles for displays, due to its transparency and good mechanical properties.\textsuperscript{80} Copolymers of styrene and PFS made from the controlled radical copolymerization of the two types of monomers were used for
marine antifouling materials.\textsuperscript{81} PFS was used as a comonomer or modified as 4-hydroxytetrafluoro styrene to make materials for lithography.\textsuperscript{82,83,84}

2.2 Interactions between Aromatic Hydrocarbons and Aromatic Fluorocarbons.

Fully fluorinated aliphatic or alicyclic fluorocarbons are generally immiscible with aliphatic or alicyclic hydrocarbons, contrary to what the simplest molecular theories of liquid mixtures would predict. The excess Gibbs free energy of these mixtures is so largely positive that on cooling the solution demixes at upper critical temperatures above room temperature. Before aromatic fluorocarbons became commercially available, mixtures of aromatic fluorocarbons and aromatic hydrocarbons were predicted to behave the same as their aliphatic counterparts.\textsuperscript{85} However, in 1960, Patrick and Prosser\textsuperscript{2} showed that hexafluorobenzene and benzene form an equimolar molecular complex, contrary to what was predicted. They develop very strong interactions, contrary to their aliphatic counterparts.

Fenby and Scott\textsuperscript{86} studied the heats of mixing of several binary systems of two aromatic compounds varying the levels of fluorination. Three parameters contribute to the heat of mixing, which differ both in sign and in their dependence on the composition of the mixture. These contributions are: a physical interaction, which is positive in sign and typical of mixtures of hydrocarbons and fluorocarbons; a chemical interaction, which is negative in sign and comes from the formation of the charge transfer complex; and a specific interaction between matching H and F atoms. The binary complex will be more likely formed if the $\pi$
system of the aromatic hydrocarbon is a stronger donor and the $\pi$ system of the aromatic fluorocarbon is a stronger acceptor (i.e. has more fluorine atoms).

Andrews et al.$^{87}$ studied the enthalpies of mixing between hexafluorobenzene and several alicyclic and aromatic hydrocarbons over a small range of temperatures and in some cases over a whole range of compositions. They found that for the system composed of hexafluorobenzene and benzene, the plot of the excess enthalpies ($H^E$) of mixing vs. the molar fraction of benzene in the mixture is a curve with negative $H^E$ at all compositions except from the regions in which the fluorocarbon amount is minimum, in which there is a positive maximum that decreases as the temperature of the mixture increases. Their results agreed with those reported by Fenby and Scott,$^{86}$ except for the absolute value of $H^E$. The complex formed is more stable with a greater substitution of the hydrocarbon by alkyl groups. Two major factors increase the stability of the complexes: the increased donor character of the hydrocarbon upon alkyl substitution (as explained above), and the lower spherical symmetry of the most substituted ones. Alkyl substitution has a greater effect on the stability of the complexes formed with aromatic hydrocarbons than with aliphatic ones, due to an electrostatic interaction of the C-F bond dipole to the hydrocarbon $\pi$-quadrupole. This interaction causes a face-to-face configuration of the hydrocarbon and fluorocarbon that allows them to interact more strongly than in other configurations, which are not angle dependent. They concluded that although charge transfer is an important factor, the predominant one governing the excess thermodynamic heat is the shape of the hydrocarbon.
The gas-liquid critical temperatures of fluorocarbon-hydrocarbon mixtures as a function of their composition were later studied, and the results related to interaction parameters. The thermodynamic parameters indicated that the strength of the molecular interactions was greatest in the case of aromatic fluorocarbon + aromatic hydrocarbon. The major factor governing the interactions developed between the two types of molecules was the relative shapes of the component molecules. The interactions increase with an increased deviation from spherical symmetry of the shape of the molecule.

2.2.1 Binary Complex of Hexafluorobenzene and Benzene and Methylated Benzenes.

Patrick and Prosser in 1960 were the first to find strong interactions between aromatic hydrocarbons and their fluorinated counterparts. They observed that a solid was formed upon mixing benzene and hexafluorobenzene. The solid-forming process was investigated by following the freezing points of mixtures of known compositions of benzene and hexafluorobenzene. The freezing point diagram shows a maximum melting point of 23.4 °C for the equimolar mixture of the two. Since benzene and hexafluorobenzene have similar melting points of 5.4 and 5.0 °C respectively, the higher melting point of an equimolar mixture shows evidence of a 1:1 molecular complex, which is regarded as the electron-donor-acceptor or charge-transfer type. The inductive effect of the fluorine atoms, responsible for the higher ionization potential of hexafluorobenzene than that of benzene, makes the fluorinated rings have an electron acceptor character. Complexes of the charge transfer type are generally
characterized by a charge transfer spectrum, observed for the complex between benzene and trinitrobenzene in the region 2800-3400 Å, in which there are no bands in the charge transfer spectra of the single components. Unfortunately no bands appeared in the region of 2300-3000 Å for the complex between benzene and hexafluorobenzene, attributed to the low concentrations of the complex in the measurements.

The theoretical electrostatic potential map of benzene reveals concentrations of negative potential above and below the molecular plane, and a ring of positive potential in the plane focused on the hydrogen atoms. HFB has a reversed charge distribution. Figure 2.1 shows these two types of rings and their reversed charge distribution as modeled by Hahn. While benzene is electron rich in the centre of the ring, the high electronegativity of the fluorine atoms attracts that charge towards the edges.

![Figure 2.1. Surface electrostatic potential of hexafluorobenzene and benzene.](image)

89
The complete phase diagram for the complex between benzene and HFB, first reported by Patrick and Prosser,\(^2\) was fully investigated by Duncan and Swinton (Figure 2.2).\(^9^0\) A maximum appears at 23 °C, for the equimolar complex.

![Phase Diagram](image)

Figure 2.2. Phase diagram for the system hexafluorobenzene-benzene. \(X_F\) is the mole fraction of the hexafluorobenzene.\(^9^0\)

Swinton\(^9^1\) explained, in a review chapter, that the melting point and therefore the stability of the complexes increased upon increase of the degree of alkyl substitution of the aromatic hydrocarbon. This could be due to either an increase in the electron-donating ability of the hydrocarbon upon alkyl substitution or an increase in the packing ability in the mixed crystal lattice of the complex. The crystal structures of the complexes are difficult to determine due to the high molecular motion of these complexes, even at low temperatures, and a
higher tendency of the fluorocarbon than that of the hydrocarbon to evaporate. However, the crystal structures of a few complexes of hexafluorobenzene with several aromatic hydrocarbons were determined. These indicate an alternation of the molecules stacking along a vertical axis, with a small displacement of the centers of the molecules along this axis. The spacing between the molecules was such that the distance between F and H atoms was much smaller than normal van der Waals values. The IR spectra also showed evidence of complexation: hexafluorobenzene dissolved in cyclohexane showed an absorption band, which was decreased in wavelength and increased in intensity when HFB was dissolved in benzene. These data demonstrated an enhanced intermolecular interaction between aromatic hydrocarbons and fluorocarbons.

2.2.2 Other Binary Complexes.

Patrick and Prosser\(^2\) reported the formation of another complex between hexafluorobenzene and mesitylene, with a melting point of 34 °C, which is stable enough to crystallize from ether. Hexafluorobenzene formed a similar complex with 2-methylnaphthalene,\(^2\) which also crystallizes from ether and has a melting point of 56 °C. (Mesitylene and 2-methylnaphthalene melt at –45 °C and 32 °C respectively.) Pentafluorobenzene also forms equimolar complexes with some aromatic hydrocarbons, including benzene. This complex has two incongruent melting points, one at an equimolar composition and the other with 2 moles of benzene and three of pentafluorobenzene.\(^92\)
The phase diagram (solid-liquid) for hexafluorobenzene and naphthalene (melting point = 81 °C) was reported by McLaughlin and Messer. The equimolar complex had a melting point of 98 °C. The solid-liquid phase diagram of hexafluorobenzene and 1-methylnaphthalene was studied in 1983. A 1:1 complex was formed with a melting point of 100 °C, which is much higher than that of the single components (5.0 °C and –22 °C, respectively).

A 1:1 mixture of perfluorotriphenylene and triphenylene forms a complex that has a melting point of 250-252 °C, which is higher than the individual compounds (109 and 199 °C, respectively). Based on this result, Weck et al. studied the solid state structure by X-ray diffraction of the crystals grown from a 1:1 mixture of perfluorotriphenylene and triphenylene, which showed a columnar arrangement in which the two components of the mixture are stacked in an alternating fashion. The attraction forces developed between the two types of molecules are strong enough to induce marked changes in both molecules.

2.2.3 Interactions between Aromatic Rings: Crystal Structures.

The solid-state structure of a 1:1 molecular complex between benzene and hexafluorobenzene was investigated using X-ray diffraction. The crystal structure was with molecular pairs alternating the benzene and hexafluorobenzene rings packed in a face-to-face manner, with a distance between molecules of 3.5 and 3.7 Å, which is very different from the packing of the pure solids, in which the aromatic rings are perpendicular to each other. Persistence of the complexes in the liquid state is demonstrated on the basis of
thermodynamic data (Section 2.2.1), and from detailed X-ray and neutron scattering.\textsuperscript{97}

A theoretical study\textsuperscript{98} of the 1:1 complex was proposed based on a simple electrostatic model, which indicated that the dimer was mainly formed through quadrupole-quadrupole interactions and that the most stable molecular arrangement was that in which both aromatic rings were parallel to each other. The stability of the systems composed of benzene and either hexafluorobenzene or pentafluorobenzene was studied by using pseudopotential calculations including electron correlation. For the benzene : hexafluorobenzene complex, the minimum in the interaction energy curve was located at 3.70 Å, consistent with the experimental data. These results suggest that the interaction energy value from the theoretical calculations, -4.33 kcal/mol, was reliable. The other complex studied, benzene : pentafluorobenzene, had similar results but with the minimum in the energy curve located at a slightly larger distance (3.75 Å) and a smaller interaction energy (-3.49 kcal/mol). Both the electron correlation and the electrostatic contribution determined the stability between the complexes, and both factors are critical to determine the minimum in the energy curve. These theoretical results were compared with experimental ones obtained from enthalpies of association measurements taken for various systems composed by a fluorinated aromatic ring hexafluorobenzene, pentafluorobenzene and tetrafluorobenzene and an aromatic hydrocarbon benzene (one ring), toluene (one ring with a methyl substituent) and naphthalene or methylnaphthalene (two fused rings, one of them with a methyl substituent).\textsuperscript{99} They correlated those
enthalpy values with the electrostatic energy for the system studied, which is in turn the main contribution in the enthalpy changes observed upon mixing. For those systems composed of interacting molecules that have an opposite sign of their respective quadrupole moments, the most stable arrangement is face-to-face. Systems composed of molecules having same-sign quadrupole moments arrange in a perpendicular manner.

Collings et al.\textsuperscript{100} determined the X-ray crystal structures of several 1:1 complexes prepared with hexafluorobenzene and several arene compounds: naphthalene, anthracene, phenathrene, pyrene and triphenylene. The solid-state structures of these complexes contain mixed stacks of alternating parallel aromatic hydrocarbon and hexafluorobenzene molecules, which is a very different situation to the packing of the pure components (usually perpendicular arrangements). Based on \textit{ab initio} calculations, the packing mode was mainly governed by electrostatic interactions.

Therefore, there is still controversy in the nature of the interactions that lead to the formation of stable complexes between perfluorinated aromatic compounds and regular aromatic hydrocarbons. While some authors support the idea that they are mainly due to a charge transfer,\textsuperscript{2,85,98,100} other claim that they come mainly from quadrupole-quadrupole interactions,\textsuperscript{86,87,99} and therefore they are van de Waals or dispersion interactions. The first hypothesis is now more largely accepted. While the distance measured for these complexes corresponds to that found for regular van der Waals contacts, the energy of the
interactions between the two types of rings is in the order of a weak hydrogen bond (stronger than dispersion or van der Waals).\textsuperscript{98,99}

2.2.4 Applications Using Aromatic Hydrocarbon Aromatic Fluorocarbon Interactions.

The chemistry of non-covalent intermolecular interactions or supramolecular chemistry has been intensively studied due to its importance in many areas.\textsuperscript{101} In particular, interactions between aromatic units are of crucial importance in determining the structures and properties of assemblies in chemistry, biology and material science. For example, arene-arene interactions contribute to the stabilization of DNA,\textsuperscript{102} and they are involved in the recognition events and tertiary structure of proteins.\textsuperscript{103} Aromatic interactions are responsible for the aggregation between porphyrins and macrocycles in solution,\textsuperscript{104} which is important in events of molecular recognition both in the solid and in the liquid state.\textsuperscript{105,106,107}

Coates \textit{et al.}\textsuperscript{4} reported the solid-state photodimerization and photopolymerization of several monoolefins and diolefins substituted with phenyl and perfluorophenyl groups. The alternating stacking first seen for the complex between hexafluorobenzene and benzene is a general supramolecular motif, and the geometry of crystallization is directed by the face-to-face interaction of phenyl-perfluorophenyl groups. The resulting arrangement leads to distances between the centers of the phenyl rings short enough to allow photocycloaddition
in the solid-state (and therefore photodimerization and photopolymerization) of the phenyl and perfluorophenyl substituted mono- and diolefins.

Dai et al.\textsuperscript{5} studied the liquid crystal behavior of a series of 1,4-bis(phenylethynyl)benzenes with different levels of fluorination. The interactions between perfluorinated rings and regular aromatic moieties cause the molecules to stack along an axis in an alternating fashion with equal spacing between all molecules along that stacking axis. The molecules form sheets very close to a planar geometry. The complexes formed between those molecules with interacting phenyl moieties exhibit a greater liquid crystalline range, with a higher temperature of isotropization compared to either of their constituents. Liquid crystallinity was promoted by mixing molecules containing fluorinated and non-fluorinated rings, which showed no tendency to individually form liquid crystals. This suggests that the intermolecular stacking interactions were present in the liquid crystalline state and responsible for it.

Weck et al.\textsuperscript{95} reported the liquid crystalline behavior of the complex formed between perfluorotriphenyl and a chiral ether derivative of triphenylene. The first indication that the complex was formed was the change in color from white to light yellow upon mixing. The UV spectrum of the complex also had a band that was absent in the spectra of the single components. The complex also had different transition temperatures than those detected for the single compounds. Optical polarized microscopy and X-ray diffraction were used to assign the mesophase of the 1:1 complex to a highly ordered columnar alignment.
Self-organizing aggregates of large aromatic chromophores suitable for optoelectronic applications were made using the directing effect of phenyl-perfluorophenyl interactions. The effect of fluorination on molecular and solid-state properties will eventually help understand the relation between molecular connectivity and optical behavior of organic solids.

2.3 Graft Copolymers.

2.3.1 General Considerations of Graft Copolymers.

In 1933 Houtz and Askins observed that a dead polymer increased its molecular size in the presence of growing polymer chains. Later, Flory and Mayo proposed that growing polymer molecules could undergo chain transfer reactions with polymer molecules resulting in branched vinyl polymers.

The definition of a graft copolymer is a copolymer containing a long sequence of one monomer (referred as the "backbone polymer") and one or more branches ("grafts") of long sequences of another monomer. Graft copolymerization allows new materials by modifying existing polymers. Graft copolymers are very important technological materials, since they combine or improve the properties of several existing polymers. In blends and composites they greatly improve their interfacial region, helping them achieve better processability and mechanical properties. The graft copolymers act as a polymeric surfactant locating at the interface of the blend phases, resulting in a kinetic and thermodynamic stabilization.

Although the most common method for synthesizing graft copolymers involves radical polymerization, other methods, such as ionic, have increased in
the past years. The following sections explain the most important methods to obtain graft copolymers.

2.3.1.1 Radical Graft Polymerization.

The monomer to be grafted onto the polymer backbone is polymerized radically in the presence of a dissolved or molten polymer, and a radical initiator. Usually the final product of a graft copolymerization will contain the following species: homopolymer of the monomer not grafted; homopolymer of the backbone that has not been attacked by the free radicals; and the graft copolymer, which has the polymer backbone and grafts of the monomer being polymerized. The simultaneous generation of both homopolymer and graft copolymer is due to competitive reactions of homopolymeric radicals and backbone polymeric radicals towards monomer molecules.\(^7,^{113}\)

Polymer radicals, which will initiate graft copolymerization, are formed by abstraction of hydrogen (or other labile atom present in the polymer backbone) by either primary initiator radicals or propagating radicals from the homopolymerization of the monomer.\(^7,^{113}\) Huang and Sundberg reported a detailed kinetic analysis describing the graft copolymerization mechanism based on this assumption.\(^{113}\) The activity of the free radicals and the backbone structure were the two controlling factors in the mechanism of the grafting copolymerization. The efficiency of the incorporation of the monomer to the grafted chains depends on the initiation mechanism of the graft site and on the mode of termination of the formed polymer chain (combination or disproportionation). Their kinetic analysis allowed the calculation of several
grafting parameters and their dependency upon monomer, initiator and backbone concentrations, and could be applied to several systems with different grafting mechanisms.

Although this method of preparing graft copolymers yields a mixture of graft copolymer with the two homopolymers, many important commercial systems are prepared this way: HIPS (high impact PS, which is styrene polymerized in the presence of polybutadiene (PB)); ABS (acrylonitrile and styrene polymerized in the presence of PB); and MBS (methyl methacrylate and styrene polymerized in the presence of PB).

Polymer radicals can also be prepared by irradiation of a polymer-monomer mixture with ionizing radiation. Most grafting radiation reactions are performed in a heterogeneous media. The polymer swells (but does not dissolve) by the monomer, and the monomer-swollen polymer is irradiated while immersed in excess monomer. The product is composed of the same three species as in the chain transfer induced grafting polymerization. One example of this method is the graft copolymerization of polyethylene with styrene, resulting in poly(ethylene-\textit{graft}-styrene), which generally involves very little homopolymerization of styrene compared to the amount of grafted copolymer formed.\textsuperscript{114}

2.3.1.2 Redox Initiated Graft Polymerization.

Redox initiation is a very efficient method to initiate graft copolymerization. Polymers containing hydroxy pendant groups undergo redox-initiated grafting reactions with cerium salts.\textsuperscript{115} The main advantage of this method is that
minimum homopolymerization occurs since only polymer radicals are formed. The drawback of this process is that the polymer backbone must have the necessary groups to be initiated in a redox process.

2.3.1.3 Anionic Graft Polymerization.

Polymeric anions can be obtained by metallation of the polymer (like 1,4-PB) by treating it with a strong base (t-butyllithium or polyamides with sodium.) The anions can initiate the polymerization of monomers like styrene, acrylonitrile and ethylene oxide. Anionic graft copolymerization has also been achieved from polymers having carboxylate pendant groups.

2.3.1.4 Cationic Graft Polymerization.

Reaction of a polymer having chlorine atoms with diethylaluminum chloride (a Lewis acid) results in a carbenium ion containing polymer. This can cationically initiate the polymerization of isobutylene, tetrahydrofuran and other monomers, resulting in a graft copolymer.

2.3.2 Grafting Polybutadiene.

In the late 1940s the rubber modification of PS and poly(styrene-co-acrylonitrile) became of industrial interest. Since then there has been increased interest in studying the mechanism of grafting PB with several monomers and the final properties of the resulting products. Graft copolymers based on PB have been commonly used in polymer technology as impact modifiers.
2.3.2.1 Graft Copolymers of Polybutadiene with Styrene.

Poly(butadiene-\textit{graft}-polystyrene) is one of the most investigated graft copolymers made from PB. It is used as a mixture with elastomeric PB dispersed in a matrix of polystyrene, called high impact polystyrene or HIPS.\textsuperscript{7}

Amos \textit{et al.}\textsuperscript{120} described the preparation of styrene-modified PB. PB is soluble in styrene, in which it forms a homogeneous solution. Upon agitation (key factor in obtaining a useful final product) and heating of the solution, styrene polymerized. The monomer was grafted onto the rubber during the polymerization process. Also, Blanchette and Nielsen\textsuperscript{121} reported the graft copolymerization of PB dissolved in styrene, and separated the final products by extraction techniques.

Chopey\textsuperscript{122} suggested that the graft polymerization onto PB proceeded by chain transfer from the polymeric radical (growing polystyryl radicals) to the rubber backbone. This was contradicted by Gesner,\textsuperscript{123} who observed that the growing polystyryl chains did not react with the rubber, but that the grafting sites were formed by direct interaction with the primary initiator radicals.

Brydon \textit{et al.}\textsuperscript{124} studied the radical-induced graft copolymerization of styrene onto PB in benzene at 60 °C, using BPO as the radical initiator. They determined the grafting efficiency, which is defined as the proportion of styrene grafted onto the PB relative to the amount homopolymerized. The maximum grafting efficiency values achieved were around 30\%, and depended on the ratio of PB to styrene in the mixture. The grafting copolymerization of styrene followed conventional free radical copolymerization kinetics, with the rate of propagation
first-order in monomer and one half-order in initiator. AIBN was unable to induce this graft copolymerization. The low reactivity of the AIBN radical to abstract an H from the PB backbone to form a polymeric radical was explained in terms of resonance stability of the primary radical formed from AIBN.\textsuperscript{125}

In 1994 Huang and Sundberg\textsuperscript{126} presented a new method to follow the grafting copolymerization of styrene onto PB, initiated radically by BPO. This new method used a gel permeation chromatograph equipped with refractive index (RI) and UV detectors to determine the composition of samples withdrawn directly from the copolymerization medium. The grafting efficiencies were around 20\%, and they also calculated other grafting polymerization parameters, such as grafting ratio (defined as the ratio of the mass of grafted polymer to mass of backbone polymer), the monomer conversion, the graft frequency (number of repeat units on the backbone between two consecutive grafting points), and the molecular weight of the grafts. Their method allowed the characterization of the grafting copolymerization of styrene onto PB without the need to purify the polymer mixture or separate the final copolymer product from residual monomer and homopolymer byproduct before analysis, as required by most other analytical methods. In a later publication,\textsuperscript{127} the authors confirmed the inability of AIBN to create polymeric radicals from the PB backbone, and the inability to initiate graft copolymerization of styrene onto PB.

2.3.2.2 Graft Copolymers of Polybutadiene with Other Monomers.

Huang and Sundberg\textsuperscript{113,126} also studied the graft copolymerization of benzyl methacrylate and acrylate monomers onto PB. The mechanism of grafting of
methacrylate monomers onto PB is similar to that of the grafting of styrene, with the grafting sites formed by primary radicals from the initiator. However, the polymethacrylate propagating radicals are slightly more reactive than the polystyryl radicals and grafting did take place when AIBN was used as an initiator, albeit in very small quantities. Grafting readily took place when AIBN was used as the initiator for the radical graft copolymerization of benzyl acrylate onto PB. The polyacrylate radicals are reactive enough to abstract the allylic hydrogens to form the grafting sites. The graft copolymerization with benzyl acrylate was more effective with AIBN than with BPO.

Bigrift terpolymers were prepared from PB by consecutive radical grafting of methylmethacrylate and styrene.\textsuperscript{112} These have a compatibilizer effect for blends of polystyrene and poly(vinyl chloride), which are incompatible polymers.

Chen \textit{et al.}\textsuperscript{128,129} prepared a graft copolymer of HIPS grafted with maleic anhydride by melt mixing the two components in the presence of a radical initiator. The product was miscible with the precursor HIPS and used as a compatibilizing agent for blending HIPS with a polyamide. The mechanism for this compatibilization was the reaction of the anhydride groups with the amide of the polyamide.

The graft copolymerization of styrene and acrylonitrile onto PB has been studied since as early as 1956.\textsuperscript{130} This process leads to the very commercially important product ABS, which has been extensively studied and applied ever since.
2.4 Modification of Polybutadiene by Ene Reaction.

2.4.1 The Ene Reaction. Important Considerations.

An ene reaction is the thermal reaction of an alkene having an allylic hydrogen (the “ene” compound) with a compound containing a double bond (the “enophile”) to form a new bond by migration of the double bond on the “ene” compound and the shift of the hydrogen (Scheme 2.5). Hoffman\(^9\) defined it as “the indirect substituting addition of a compound with a double bond (enophile) to an olefin with an allylic hydrogen (ene)”. The ene reaction is a very simple and versatile reaction with the advantage of being “clean” and not producing anything other than the “ene” adduct. However, the ene reaction has a very high activation energy, which limits its synthetic utility due to the very high temperatures required. Mechanistically, the ene reaction is related to the better known “Diels-Alder” reaction which will proceed more readily when the enophile has electron-withdrawing substituents and the ene component is substituted by electron-donating groups.

![Scheme 2.5. General mechanism of the ene reaction.](image)

Although it depends on the particular reaction and the enophile used, generally the relative reactivity of monoolefins as ene components is 1,1-
disubstituted > trisubstituted > tetrasubstituted >> monosubstituted or 1,2-disubstituted. A primary allylic hydrogen is abstracted more readily than secondary and tertiary allylic hydrogens. Terminal alkenes are less reactive as ene components than internal and, for 1,2-disubstituted monoolefins, cis are less reactive than trans.

The natural compound β-pinene is the most reactive compound on an ene reaction towards enophiles. It forms ene adducts with maleic anhydride, dimethyl maleate and fumarate, methylenemalonic ester, butyl glyxolate and benzyn.

One of the most widely used enophiles is maleic anhydride, which is an alkene in which the carbon-carbon double bond is substituted by the very electronegative anhydride group. Other alkenes used as enophiles are α,β-unsaturated ketones, esters, and nitriles.

“Azo” compounds (compounds having a nitrogen-nitrogen double bond) are more reactive as enophiles than alkenes, capable of reacting with ene compounds under relatively mild conditions to complete conversions. Some “azo” compounds commonly used as enophiles are acyclic azocarboxylate and 4-phenyl-1,2,4-triazoline-3,5-dione (Scheme 2.5), which has been called “record enophile” due to its ability to react smoothly with a wide variety of “enes” at room temperature.

Carbonyl compounds, such as ketones and carbonyl cyanides, can also react as enophiles in an ene reaction. The reaction between formaldehyde and olefins is of industrial interest.
Scheme 2.6. Structure of most reactive enophiles toward an ene reaction.

The most widely used solvents in ene reactions are those having a high boiling point, due to the high temperatures required. Dichlorobenzene and nitrobenzene are among the most common used.

Lewis acids have been used as catalysts for the ene reaction since they can complex with ketones, aldehydes or esters (regular groups present in enophile structures), making their double bond more electron deficient and thereby lowering the activation energy of the ene reaction to a synthetically useful process. The Lewis acids used most as catalysts are aluminum trichloride, ethyl aluminum dichloride and zinc dichloride (Scheme 2.7).\textsuperscript{9,131}

Scheme 2.7. Ene reactions with and without Lewis acids.\textsuperscript{9}

2.4.2 Modification of Polybutadiene (and other Elastomers) by Ene Reaction.

Polydiienes can be modified by changing the steric and electrostatic characteristics of the chain and adding a new functionality to the chain. A
reaction successfully accomplishes a chemical modification if it satisfies the following criteria:

a. Temperature: Low enough not to produce side reactions such as chain scission and crosslinking.

b. Flexibility: The chemical reaction must provide the desired properties without affecting the functionality added to the polymer backbone.

c. Attainable Degree of Modification: The conversion of the reaction must be high enough to modify the polymer backbone to a desired degree.

d. Singularity of the reaction: The modification does not have any side reaction that can affect the physical properties of the polymer backbone, such as depolymerization and crosslinking.

Generally, an ene reaction is a modification pathway that allows for the intrusion of the desired reactant with no side reactions. The introduced functionality generally remains intact, ready for further reaction. The main drawback of the ene reaction is its high activation energy and the high temperatures required for the desired degrees of modification. These temperatures are normally close to the temperatures at which depolymerization occurs. However, PB and other elastomeric polymers such as natural rubber (NR) and synthetic poly(isobutylene) (PI) have also been modified by ene reactions with several enophiles.

Schultz et al. modified PB by ene reaction with isopropyl azodicarboxylate (IAD) at 80°C. They reacted IAD with four different PBs: high 1,4 cis; high 1,4 trans; mixed 1,4 cis and trans; and 1,2 (Scheme 2.8), establishing the structure-
property and structure-reactivity relationships. High 1,4-substituted PB was more reactive in the ene reaction with IAD than with the homologous 1,2-substituted PB. The structure of modified 1,2-PB exhibited a random distribution of the functionality, while the modified high 1,4-PB was blocky in character and exhibited a multiphase morphology. The modification of PB by IAD took place by an ene mechanism, albeit some evidence of a free radical process was present, especially in the case of the 1,2-PB, since this is more prone to radical reactions. To achieve similar conversions on the 1,2-PB as the 1,4-PB counterpart longer time was required. The modification efficiency (ME) is the ratio of IAD incorporated in the modified PB vs. the initial IAD. ME is related to the grafting efficiency (GE) used to characterize graft copolymerizations (Section 2.3.2). The maximum MEs were for the case of reaction of IAD onto high 1,4-trans PB (around 93%), and the time to achieve similar modification levels for the 1,2 backbones was five times that for the modification of the 1,4-PB, opposed to the general reactivities of alkenes in an ene reaction reported by Snider. The glass transition temperature of modified 1,4-PB increased with ME increase until two transitions emerged, due to the blocky modification of 1,4-PB. The glass transition temperature of modified 1,2 backbone increased upon increase of the ME. Two transitions were not recorded.
Scheme 2.8. Ene reaction of isopropyl azodicarboxylate (IAD) with all several polybutadiene structures.\textsuperscript{13}

Butler and Williams\textsuperscript{133} studied the modification of several polydienes, including random cis-trans-PB, cis-PB, cis-PI, and random styrene-butadiene copolymer, with 4-substituted-1,2,4-triazoline-3,5-diones (called “record enophile” due to its high tendency to react with ene compounds\textsuperscript{9}). The advantage of these enophiles is the versatility of substitution of the triazolinediones on the 4-position, allowing introduction of different groups in the modification. The ene reactions with 4-methyl and 4-phenyl-1,2,4-triazoline-3,5-diones were performed at room temperature using THF and benzene as solvents, achieving MEs up to 93%. ME values were highest when reaction was in THF (a better solvent for modified
PBs) and when the enophile was 4-phenyl substituted IAD. The softening points of the modified polymers were higher than those of the unmodified ones and the higher the ME, the higher the softening point. All of the modified products were soft, white powders, whose solubility depended on the degree of modification. The modifying groups were very polar and had hydrogen bonding sites, which strongly influenced the properties of the final products such as the thermal behavior, solubility, viscosity and tensile properties.

Champbell et al.\textsuperscript{134} synthesized graft copolymers of PI with polystyrene by reacting azodicarboxylate-functional polystyrene with PI (natural or synthetic), following an ene reaction (Scheme 2.9). The functionalized polystyrene reacts with PI either in solution at 60° C for several days or in bulk at 90° C. The maximum grafting efficiencies were on the order of 76% when synthetic PI was used and 55% if the backbone was NR. The products showed microphase separation, and their physical properties depended on the total amount of PS in the product.

\begin{equation}
\begin{align*}
\text{CH}_3 - \text{CH}_2 - \text{C} = \text{C} - \text{CH}_3 + \text{ROOC} - \text{COO} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH} & \rightarrow \text{CH}_3 - \text{CH}_2 - \text{C} = \text{C} - \text{CH}_2 - \text{NH} - \text{C} = \text{O} - \text{COO} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH} \\
\end{align*}
\end{equation}

Scheme 2.9. Synthesis of graft copolymer by ene reaction of poly(isoprene) with polystyrene-modified azodicarboxylate.

Mallakpour et al.\textsuperscript{12} modified narrow molecular weight PB (prepared by anionic polymerization) with 4-phenyl-1,2,4-triazoline-3,5-dione via an ene
reaction at room temperature to conversions of 5, 10 and 15%. The functionalized polymers were reacted with an acid chloride derivative of L-leucine to form optically active polymers by replacement of N-H by an optically active group. This reaction (Scheme 2.10) is an example of how the products of an ene reaction products can further react to achieve other ones with products different properties.

Scheme 2.10. Synthesis of optically active polybutadiene (PB) by (a) ene reaction of 1,4-cis PB with 4-phenyl-1,2,4-triazoline-3,5-dione and (b) reaction of modified PB with an acid chloride derived from N-phthaloyl-L-leucine and thionyl chloride.\textsuperscript{12}

Lawson et al.\textsuperscript{10} prepared ultrahigh impact rubber-toughened polycaprolactams. They modified partially hydrogenated PB with maleic anhydride and the ene adducts contained varying amounts of succinic anhydride pendant groups. The modification reactions were performed either in solution or in bulk, and the maximum levels of modification attained were around 1.5% by weight of final product. Typical reaction temperatures used were between 170 and 200 °C, with shorter reaction times required for higher temperatures. The
pendent groups provided a grafting site for reaction with an amino group of the polycaprolactam forming an imide group (Scheme 2.11).

Scheme 2.11. Synthesis of grafted partially hydrogenated 1,4-trans polybutadiene (PB) by (a) ene reaction of PB with maleic anhydride, and (b) reaction of PB with polyamide.$^{10}$

The reaction of low molecular PB (oligomeric oils) with stearyl acrylate was also studied.$^{11}$ The product shows side-chain crystallization, evidenced from the viscosity measurements above and below the crystallization temperatures. The temperatures used to achieve desired yields were between 180 and 220 °C, which are higher than those required for the reaction between PB and maleic anhydride to obtain similar degrees of modification.
2.5 Polymerization of β-Pinene.

2.5.1 Importance of β-Pinene in Polymer Science.

α- and β-Pinenes (Scheme 2.12) are terpenes, which are a class of hydrocarbons derived from isoprene produced by many plants. They are bicyclic natural compounds, and constitute the major components in the composition of

\[ \text{α-pinene} \quad \text{β-pinene} \]

Scheme 2.12. Isomers of pinene.

turpentine, obtained from pine gum distillation. Pinene homopolymers are polyterpene (or terpenic) resins, which are low molecular weight polymers. They are thermoplastics that vary from viscous liquids to hard materials and are stable to UV irradiation and heat. They are important commercial products used in adhesive, sealant, wax coating and casting industries. They are often used in the food packaging industry due to their chemical and thermal stabilities, and lack of toxicity.\(^{135,136}\)

2.5.2 Polymers of β-Pinene by Cationic Polymerization.

Polymerization of β-pinene was first reported by Thomas,\(^{137}\) who found a resinous reaction product when a terpene hydrocarbon was polymerized in the presence of aluminum chloride and an aromatic compound, by a cationic mechanism. Contrary to what Thomas believed, the aromatic compound does not play any role other than solvent in the cationic polymerization of terpenes.\(^{138}\)
Since then, the homopolymerization of pinenes and their copolymerization with several other monomers (styrene, \( p \)-methylstyrene, tetrahydrofuran) following a cationic mechanism initiated by Lewis acids has been extensively studied.\textsuperscript{139,140,141,142,143,144,145,146,147} The mechanism of the cationic polymerization of \( \beta \)-pinene is well-known.\textsuperscript{143,144,145,146,147} The initiator is a proton, formed by the interaction of a Lewis acid with any residual water present in the reaction. The proton adds to the double bond of the \( \beta \)-pinene, and the four-membered ring of the bicyclic structure opens to form a stable tertiary carbenium ion (a ring of 6 members) that reacts with the monomer to propagate the chain (Scheme 2.13). Termination occurs by transfer of a proton to monomer, forming a terminal exo unsaturation. Aluminum chloride has been the most used catalyst in the cationic polymerization of \( \beta \)-pinene. Aluminum chloride is a very reactive catalyst, which requires very low reaction temperatures. Alkylaluminum chlorides are not so reactive and do not require such conditions, which makes them more useful in synthetic processes.\textsuperscript{145,146,148,149}

The resulting products of the cationic homopolymerization of \( \beta \)-pinene are very low molecular weight polymers. The molecular weight decreases with increasing polymerization temperature.\textsuperscript{145}

Cationic polymerization of \( \beta \)-pinene has been used to synthesize end-functionalized polymers\textsuperscript{143,144} and block copolymers\textsuperscript{144} by sequential monomer addition (cationic polymerization is a living polymerization).
Scheme 2.13. Mechanism of the cationic polymerization of β-pinene catalyzed by AlCl₃. a) Initiation, b) propagation and c) termination.

Khan and Yousufzai¹⁵⁰ copolymerized β-pinene with styrene cationically in the presence of using aluminum trichloride at 10⁰ C. The copolymerization was faster in benzene than in toluene and produced higher molecular weight copolymers for the same feed compositions.¹⁵⁰ Kennedy and Chou¹⁵¹
copolymerized β-pinene with isobutylene cationically in the presence of ethyl aluminum dichloride. The resulting copolymers were vulcanizable materials with a random monomer distribution on the backbone. Depending on the composition of the copolymer these were glassy or rubbery, and were resistant to ozone.

2.5.3 Polymers of β-Pinene by Radical Polymerization.

Very little has been reported on the radical homo and copolymerization of terpenes in general and pinenes in particular. Although β-pinene is much more reactive in a cationic polymerization, α- and β-pinene have similar reactivities in radical polymerizations. Only oligomers (degree of polymerization ≈ 4.5) result when homopolymerized in the presence of a radical initiator such as AIBN.\textsuperscript{148,150}

β-Pinene reacts with dienophiles such as maleic anhydride to give an “ene” product.\textsuperscript{152} However, in the presence of a radical initiator, maleic anhydride and β-pinene undergo copolymerization.\textsuperscript{153} Maslinska-Solich and Rudnicka\textsuperscript{154} studied the radical copolymerization of those two monomers initiated by AIBN and BPO. They believed that the reaction proceeded via the formation of a 1:1 charge-transfer complex, resulting in a 1:1 alternating copolymer. However, the rate of copolymerization increased with the amount of maleic anhydride in the feed, which contradicts the usual observation in alternating copolymerizations, in which the maximum rate occurs at an equimolar feed composition. This was attributed to absorption of the maleic anhydride monomer by the copolymer as it formed. IR spectroscopic analysis of the resulting copolymers showed
alternation. The yield of the copolymers obtained using BPO as initiator was higher than using AIBN.

The radical copolymerization of β-pinene with styrene and methyl methacrylate initiated with AIBN was used to obtain pinene polymers with a higher molecular weight than those obtained by the cationic homopolymerization of β-pinene. The copolymers were solid powders with a weight average molecular weight between $1.6 \times 10^4$ and $2.5 \times 10^4$ Daltons. In contrast, when β-pinene was homopolymerized by AIBN the products were waxy solids or viscous oils having a weight average molecular weight around 850.

The mechanism of the radical copolymerization was such that a primary radical from the thermal cleavage of the initiator adds to the β-pinene monomer forming a secondary radical, which rearranges into a tertiary D-limonene radical before propagating with additional comonomer.

2.6 Thermal Properties of Polymer Blends and Copolymers.

Copolymer synthesis offers the possibility to alter the properties of a polymer by introducing a second repeat unit into the structure. Polymer blends combine the properties of different polymers through a physical mixture of existing ones. No synthesis of a new polymer is required.

2.6.1 Thermal Properties of Polymer Blends.

A polymer blend is a mixture of polymers. The miscibility and therefore stability of the formed blend are controlled by thermodynamic factors, and therefore depend on the nature of the polymers and the composition of the
mixture. In general, a blend is a compatible mixture if its physical properties do not show the individual transitions of its components.\textsuperscript{155} One of the most popular methods to investigate the miscibility of a blend is to determine its thermal behavior. The existence of one $T_g$ indicates that the blend is miscible, and in contrast, the existence of more than one transition indicates that the structure is a multiphase, with no full miscibility.

The thermal properties of blends of poly(2,6-dimethylphenylene oxide) (PPO) and PS have been determined.\textsuperscript{156,157} All blends show one transition between those of the homopolymers and increases with the amount of PPO (highest $T_g$ component) in the blend. The transitions of the blends are broader than those of the pure components, due to localized concentration fluctuations in the blends.\textsuperscript{158} Also, the relaxation process of the polymers is the same when blended. Formation of a $\pi$-cation complex from the interaction of methyl groups of PPO with aromatic groups of PS is the most accepted theory to explain miscibility of these blends.\textsuperscript{155,156,157,159,160,161} In contrast PPO is incompatible with poly($p$-chlorostyrene),\textsuperscript{162} evidenced from the detection of two transitions for the blends of the two polymers with different compositions. The blends of PPO with several statistical copolymers of styrene and $p$-chlorostyrene are miscible when the copolymer is richest in styrene.\textsuperscript{161}

Blends of poly(vinylphenol) and poly(vinylpyrrolidone) are fully miscible, as evidenced from the existence of only one transition over the entire composition range. The $T_g$ is higher than those of the single components.\textsuperscript{163,164} Hydrogen bonding is responsible for this miscibility. Unlike the interactions developed
between PPO and PS, hydrogen bonding is a strong interaction that causes a positive deviation of the $T_g$s of the blends.

2.6.2 Thermal Properties of Copolymers.

Copolymerization is used to alter physical properties such as crystallinity and flexibility. The $T_g$ of alternating and statistical copolymers generally falls in between those of the two homopolymers. The behavior of block copolymers is different, since the blocks show their own independent thermal and structural characteristics.$^{165}$

However, copolymers of vinylphenol and vinylpyrrolidone (poly(PVPh-co-PVP)) exhibit single transitions higher than those of the homopolymers and than that of a blend with the same composition.$^{166}$ The strong hydrogen bonding between the comonomers is responsible for the increased $T_g$ in the copolymers.
CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Polymers.

High molecular weight polybutadiene (PB, \( M_n = 1.25 \times 10^5 \), \( \text{pdi} = M_w/M_n = 4.6 \), 96% 1,4-cis, 3.5% 1,4-trans and 0.5% 1,2-vinyl content according to the supplier: Goodyear; GPC_{PS} \( M_n = 3.85 \times 10^5 \), \( \text{pdi} = 3.51 \), mean of UV and RI detectors) was used as received. Low molecular weight polybutadiene (PB, Aldrich, \( M_n = 3.00 \times 10^3 \) (determined by VPO), 75% 1,4-cis, 24% 1,4-trans and 1.0% 1,2-vinyl content according to the supplier; GPC_{PS} \( M_n = 4.30 \times 10^3 \), \( \text{pdi} = 2.85 \), RI detector).

3.1.2 Monomers and Reagents for Monomer Syntheses.

Bromine (Aldrich, reagent grade), 1,3-bis(diphenylphosphino)propane nickel (II) chloride (NiCl_2(dppp), Strem, 99%), 1-bromonaphthalene (Acros, 97%) and iodine (Johnson Mathey, 98%) were used as received. Acetaldehyde (commercially available, 99%) was distilled from calcium hydride. Magnesium turnings (Acros, 98%) were ground with a mortar and dried under vacuum at temperatures between 100 and 140 °C overnight (15 h).
2,3,4,5,6-Pentafluorostyrene (PFS, Acros or Oakwood 97%) was passed through a short column of basic activated alumina to remove inhibitor immediately before polymerizations and copolymerizations, and used as received for ene reactions. (1S, 5S)-6,6-Dimethyl-2-methylenebicyclo[3.1.1]heptane (l)-β-pinene (Aldrich 99 %) was distilled under reduced pressure (boiling point (bp) 60 °C / 20 mm Hg). Pyrene (Acros, 99%) was recrystallized from boiling ethanol. Styrene (Aldrich, 98%) was passed through a short column of basic activated alumina to remove inhibitor immediately before each use. Vinyl bromide (Aldrich, 95%) was dried by passing through a drying tube containing calcium chloride and phosphorous pentoxide. 2-Vinyl naphthalene (2-VN, Acros, 97%) was recrystallized from ethanol and water (85:15 v/v) below 25 °C and stored at <5 °C.

3.1.3 Reagents for other Syntheses.

Calcium chloride and calcium hydride were commercially available and used as received. 1-decene (Lancaster, > 95%), lithium wire (Alfa Aesar, in oil, 2% sodium), magnesium sulfate (EMD, ACS grade), 1-octadecene (Aldrich, 90%), potassium hydroxide (Fisher, ACS certified), sodium bicarbonate (Mallinckrodt, ACS certified), sodium tetraborohydride (Sigma, 99%) and ruthenium (III) chloride hydrate (Strem, 99.9%) were used as received. Potassium carbonate (Riedel-De Häen, 99%) was either dried under vacuum at 140 °C for 10 h or used as received. 2-Bromo-2-butene (Acros, 98%, mixture of cis and trans) was purified by passing through a small column of basic alumina. Ethyl acetate (EM Science, 99.8%) was distilled from calcium hydride. 9-Octadencen-1-ol (oleyl
alcohol, Acros, 70%, 100% was distilled under reduced pressure (bp = 150 °C/ 5 mm Hg). \( p \)-Toluenesulfonyl chloride (Acros, 99%) was recrystallized from ethyl ether. Triethylamine (EM Science, 97%) was distilled from potassium hydroxide (bp = 89 °C/ 760 mm Hg). Hydrochloric acid (1.0 M, calculated) was made by dissolving 10 mL of commercially available concentrated HCl (Fisher, aqueous concentrate) in 100 mL of water.

3.1.4 Initiators and Inhibitors.

\( t \)-Butyl peroxy pivalate (Johnson Mathey, 75% in mineral oil), 2,6-di-\( t \)-butyl-\( p \)- cresol (butylated hydroxytoluene, BHT, Aldrich ≥ 99.8%) and 1,4- dihydroxybenzene (hydroquinone, Acros 99%) were used as received. Azobis(isobutyronitrile) (AIBN, Johnson Mathey, 99%) was recrystallized from methanol below 40 °C and stored in a freezer at <-10 °C. Benzoyl peroxide (BPO, Acros, 85%) was recrystallized from chloroform and methanol (25:75 v/v) below 25 °C and stored in a freezer at <-10 °C.

3.1.5 Solvents.

The following solvents used to carry out precipitations, solubility tests, column chromatography and extractions were commercially available and were used as received: acetone, acetonitrile, benzene, \( n \)-butyl acetate, carbon tetrachloride, chloroform, dichloromethane, cyclohexanone, 1,2-dichlorobenzene, 1,3-dichlorobenzene, N,N-diethylamide, dimethylformamide, dimethylsulfoxide, ethyl acetate, hexanes, methyl acetate, methyl ethyl ketone, nitrobenzene, 1,1,2,2-tetrachloroethane, 1,2,4-trichlorobenzene, 1,1,1-trichloroethane, 1,1,2-
trichloro-2,2,1-trifluoroethane, α,α,α-trifluorotoluene, tetrahydrofuran, toluene, σ-xylene.

Carbon tetrachloride (Aldrich, 98%) was distilled from calcium hydride. Diethyl ether (EM Science, reagent grade) was distilled from purple sodium benzophenone ketyl under N₂. Dimethyl sulfoxide (DMSO, Fisher, reagent grade) was distilled from calcium hydride and stored over molecular sieves. Hexanes were washed with 5% HNO₃ in H₂SO₄, neutralized with dilute aqueous sodium bicarbonate and water, stored over calcium chloride, and then distilled from purple sodium benzophenone ketyl under N₂. Methanol (EM Science, reagent grade) was either distilled from calcium hydride or used as received. Methylene chloride was washed with 10% HNO₃ in H₂SO₄, neutralized with dilute aqueous sodium bicarbonate and water, stored over calcium chloride, and then distilled from calcium hydride under N₂. Nitrobenzene (Acros, > 99%) was distilled from calcium hydride. Tetrahydrofuran (THF, EM Science, reagent grade) was dried by distillation from purple sodium benzophenone ketyl under N₂ for the polymerizations, and from LiAlH₄ for GPC measurements and GPC sample preparations. Toluene (EM Science, HPLC grade) was distilled from purple sodium benzophenone ketyl.

3.2 Techniques.

All reactions were performed under a N₂ atmosphere using a Schlenk line unless noted otherwise. Activated basic alumina (Aldrich, 150 μm mesh size, 58
Å pore size) and silica gel (Sorbent Technologies, 63-200 µm mesh size, 60 Å pore size) were used for column chromatography.

3.2.1 NMR Spectroscopy.

$^1$H (300 MHz) and $^{13}$C (75 MHz) NMR spectra ($\delta$, ppm) were recorded on a Mercury 300 spectrometer. All $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$, and the resonances were measured relative to residual solvent resonances and referenced to tetramethylsilane. $^{19}$F NMR (297 MHz) spectra were recorded on either a Mercury 300 or a Gemini 300. $^{19}$F NMR spectra were recorded in either $n$-butyl acetate (using either acetone-d$_6$ or dimethyl sulfoxide-d$_6$ to lock the signal) or in CDCl$_3$ and referenced to trifluoroacetic acid. Quantitative $^{13}$C (97 MHz) spectra were recorded on an INOVA 400 spectrometer, in 10 mm probes-tubes, dissolving 250-300 mg of polymer in 3-4 mL of CDCl$_3$. Singlet: s, doublet: d, triplet: t, quartet: q, multiplet: m.

Gradient heteronuclear multiple bond correlation experiment (gHMBC) spectra were recorded on an INOVA 400, and nuclear Overhauser effect spectroscopy (NOESY) were recorded on a UNITY-INOVA 750.

3.2.2 Gel Permeation Chromatography.

Molecular weights relative to linear polystyrene (Aldrich) were determined by gel permeation chromatography (GPC) at 35 °C using either THF or HPLC grade toluene as solvent (1.0 mL/min), a set of 50, 100, 500, $10^4$ and linear (50-10$^4$) Å Styragel 5 µm columns, a Waters 410 differential refractometer (RI) and/or a
Waters 486 tunable ultraviolet/visible (UV/Vis) detector set at 254 nm. All molecular weight values reported are mean values from RI and UV detectors, unless otherwise noted.

3.2.3 Differential Scanning Calorimetry.

A Perkin-Elmer Pyris 1 differential scanning calorimeter was used to determine the thermal behavior of all pure graft copolymers and recovered PB and PPFS homopolymers, after they were dried overnight in-vacuo at room temperature. Their glass transition temperatures (T_g's), were read as the middle of the change in heat capacity. All heating and cooling rates were 10 °C/min. Transition temperatures were calibrated using indium and benzophenone standards. When required, large amounts of samples (grafted copolymers) were loaded into the differential scanning calorimetry (DSC) sample pans by melting the copolymers in the sample pans under a N_2 atmosphere, and adding more copolymer as necessary.

3.2.4 Contact Angles.

Contact angles were determined using a Rame Hart NRL-100 contact angle goniometer equipped with an environmental chamber and tilting base mounted on a vibrationless table (Newport Co.) A 10 μL droplet of deionized water was placed on the surface of a film and the static contact angle was measured 30 s after the water droplet was dropped. Each reported value is the average of four independent measurements. Sample films to measure surface
properties were made as follows. A drop of a solution of copolymer in THF (0.2% w/v) was deposited on a silicon wafer and spread tilting the wafer in all directions, followed by evaporation of the solvents at room temperature overnight.

3.2.5 Optical Rotations.

Optical rotation measurements of THF solutions of the copolymers were made using a JASCO digital polarimeter, model DIP-360, equipped with a Glan-Thompson prism and a sodium lamp that emits at 589 nm. Specific rotations were measured of known concentration solutions of the copolymers in THF, using a 100 mm (optical path) cell, which holds 5 mL of solution. The response speed was 4°/s, and the integration time 5 s.

3.3 Homopolymerization of 2,3,4,5,6-Pentafluorostyrene.

Low molecular weight PPFS was synthesized for NMR analysis as follows. A solution of PFS (0.39 g, 2.0 mmol) and BPO (0.19 g, 0.80 mmol) in THF (14 mL) was degassed in a Schlenk tube by five freeze-pump-thaw cycles. After stirring at 75 °C for 48 h, the polymerization solution was precipitated in methanol (75 mL), collected and dried in-vacuo overnight at room temperature to yield 33 mg (86%) of PPFS as a white, electrostatic powder; \( M_n = 3725 \), pdi = 1.34. \(^1\)H NMR: 2.00 (broad s, \(\text{CH}_2\text{CHAr}\)), 2.40 (broad s, mr + rr \(\text{CH}_2\text{CHAr}\)), 2.75 (broad s, mm \(\text{CH}_2\text{CHAr}\)). \(^{13}\)C NMR: 32.0 (sharp s, \(\text{CH}_2\text{CHAr}\)), 37.0 (broad m, \(\text{CH}_2\text{CHAr}\)), 115.0 (sharp s, aromatic C1), 138.0 (d, aromatic C2 and C6), 140.0 (d, aromatic C4), 145.0 (d, aromatic C3 and C5). \(^{19}\)F NMR: -162.0 (sharp s, C3-F), -154.4 (sharp s, C4-F), -143.0 (broad s, C2-F).
Medium molecular weight PPFS was synthesized in 83% yield to calibrate the GPC UV detector response using 5 mol% BPO in THF (0.14 mM PFS, 7.0 x 10^{-2} mM BPO) at 75 °C; $M_n = 1.02 \times 10^4$, pdi = 1.56.

Higher molecular weight PPFS was also synthesized in 73% yield for solubility tests using 1 mol% BPO in THF (0.14 mM PFS, 1.4 x 10^{-3} mM BPO) at 75 °C; $M_n = 2.28 \times 10^4$, pdi = 1.80.

3.4 Grafting Polybutadiene with 2,3,4,5,6-Pentafluorostyrene.

3.4.1 Synthesis of Polybutadiene Grafted with 2,3,4,5,6-Pentafluorostyrene.

The graft copolymerizations were performed in triplicate and followed as a function of time as in the following example. A solution of PB (0.29 g, 5.0 mmol repeat units) in dry THF (15 mL) was degassed by five freeze-pump-thaw cycles and stirred at 50 °C for 15 h to dissolve PB. PFS (2.1 g, 10 mmol) and BPO (6.5 mg, 0.25 mmol) were added to the PB solution. The polymerization solution was divided into five glass tubes sealed to round bottom flasks, with four tubes containing 1.5 mL each, and the final tube containing 5 mL solution. The polymerization solutions were again degassed by four freeze-pump-thaw cycles. The glass tubes were then sealed under vacuum using a torch, and placed in an oil bath at 60 °C. After stirring at 60 °C, the first four polymerizations were quenched at successive 12 h periods by immersing each tube into ice water before breaking the neck of the tube, withdrawing an aliquot (0.5 mL) for GPC analysis, and precipitating the remaining solution into a N$_2$-saturated solution of BHT in methanol (1% w/v, 5 mL); the GPC aliquots were diluted with dry THF containing 0.5% (w/v) of BHT (1 mL). The last tube was quenched after 60 h,
and 4 mL of the polymerization solution was precipitated into 50 mL of the N\textsubscript{2}-saturated solution of BHT in methanol (1% w/v). Each precipitate was collected and dried in-vacuo overnight at room temperature to yield 26 mg, 48 mg, 63 mg, 70 mg, and 297 mg from tubes 1-5, respectively. All samples contained the graft copolymer poly(butadiene-\textit{graft}-pentafluorostyrene), PPFS homopolymer and up to a trace amount of unreacted PB homopolymer.

3.4.2 Calculation of Monomer Conversion and Grafting Parameters by UV Detected Gel Permeation Chromatography.

The UV detector tuned at 254 nm of the chromatograph was calibrated with solutions of known concentration of PPFS in THF (same as used in the chromatograph) using 50 µL injections. Figure 3.1 shows that the relationship between the intensity (total area under the peak in arbitrary units) of the UV detector response at 254 nm and PPFS concentration is linear. Since PB has a very small absorbance in the UV detector relative to that of PPFS, the composition of the grafted copolymers and the amount of PPFS homopolymer formed could be determined for a solution of known concentration (g/L) of crude product sample. UV-detected GPC traces taken at 12 h of copolymerization and beyond show two peaks, the first (at lower elution volume or higher molecular weight) due to the absorbance of PPFS grafted onto PB and the second peak (at higher elution volume or lower molecular weight) corresponding to the homopolymer of PFS formed during the experiment. Integrating these peaks and applying the calibration, the weight of grafted PPFS and PPFS homopolymer were calculated, which in turn were used in the calculations of the conversion of
the PFS monomer and other grafting parameters. The PFS conversion was calculated by dividing the total amount of PPFS formed (both grafted and homopolymer) by the initial amount of monomer, as in equation (eq.) 3.1.

\[
\text{monomer conversion} = \frac{\text{mass PPFS in graft copolymer} + \text{mass PPFS homopolymer}}{\text{initial mass of PFS used}} \quad \text{Eq. 3.1}
\]

We also determined three grafting parameters from the UV-detected GPC traces of each aliquot taken every 12 h from the copolymerizations. The grafting efficiency (GE, in units of g PPFS / g PFS) is defined as the weight percentage of polymerized monomer that is grafted, and can be determined as the mass of PPFS that is grafted (integral of high molecular weight peak) divided by the total mass of PPFS produced (sum of integrals of both peaks on GPC chromatogram) (eq. 3.2).

\[
\text{GE} = \frac{\text{mass PPFS in graft copolymer}}{\text{mass PPFS in graft copolymer} + \text{mass of PPFS homopolymer}} \quad \text{Eq. 3.2}
\]

The grafting ratio (GR, in units of g PPFS / g PB) is the average mass of PPFS grafts per mass of backbone polymer. It is determined as the amount of grafted PPFS (calculated as the integral of the high molecular weight peak) divided by the amount of PB injected in the chromatograph (eq. 3.3).

\[
\text{GR} = \frac{\text{mass PPFS in graft copolymer}}{\text{mass PB backbone}} \quad \text{Eq. 3.3}
\]

The grafting frequency (GF) is defined as the average number of backbone repeat units between two consecutive graft points, and therefore can be calculated by dividing the average number of repeat units in the PB backbone \((DP_n \text{ relative to polystyrene})\) by the number of grafted PPFS chains (calculated
from the mass of grafted PPFS in the first peak and the average molecular weight of the PPFS grafts) per PB backbone chain (calculated from the mass of PB injected and the starting PB’s GPCPSI-determined molecular weight, $M_n = 3.85 \times 10^5$) (eq. 3.4).

$$GF = \frac{DP_{n, PB}}{\text{number of grafted PPFS chains}}\left(\frac{\text{number of PB backbone chains}}{\text{number of grafted PPFS chains}}\right)$$

Eq. 3.4

Figure 3.1. Calibration of the gel permeation chromatography UV detector at 254 nm for poly(2,3,4,5,6-pentafluorostyrene) (number-average molecular weight, $M_n = 10.2 \times 10^3$, polydispersity index, $pdi = 1.56$) as a function of concentration in tetrahydrofuran.

3.4.3 Calculation of Monomer Conversion Gravimetrically.

All crude samples were weighed after drying overnight in-vacuo. To determine the conversion, the amount of polymer backbone was subtracted from
the weight of crude sample and that amount (which should correspond to the
total PPFS produced) was divided by the initial PFS mass.

\[
\text{monomer conversion} = \frac{\text{mass crude product} - \text{mass PB backbone}}{\text{initial mass of PFS used}}
\]

Eq. 3.5

3.4.4 Purification and Isolation of Polybutadiene Grafted with 2,3,4,5,6-
Pentafluorostyrene.

In order to purify the crude product and isolate the graft copolymer from the
unreacted PB and / or PPFS homopolymer formed, we first performed solubility
tests of PB and PPFS homopolymers in a several solvents. Homopolymer (20
mg) was immersed in 20 mL of solvent for 6 h. Hexanes and acetone were the
best solvents for extraction of unreacted PB and non-grafted PPFS, respectively.

The graft copolymers were isolated from the two homopolymers by extracting
out any unreacted PB (<5% recovered) using hexanes, and extracting out PPFS
(56-71 wt%) homopolymer using acetone, both at room temperature. For
example, part of the final sample from the above polymerization (0.25 g) was
dispersed in hexanes (50 mL) for 24 h. The undissolved sample was collected in
a fritted glass funnel, dried overnight in-vacuo at room temperature, and then
dispersed in acetone (50 mL) for 36 h. The undissolved sample was again
collected, and dried overnight in-vacuo at room temperature to yield 78 mg (93%)
of poly(butadiene-graft-pentafluorostyrene) as a slightly rubbery but brittle, white
electrostatic solid. \(^1\)H NMR: 2.00 (broad s, CH\(_2\)CHAr), 2.10 (s, CH\(_2\)CH=), 2.40
(broad s, CH\(_2\)CHAr), 5.40 (s, CH\(_2\)CH=). \(^{19}\)F NMR: -163.5 (broad s, C3-F), -
156.0 (broad s, C4-F), -141.0 (broad s, C2-F).
In this case, no PB was isolated from the hexanes filtrate after rotary evaporation. The extracted PPFS was isolated from the acetone filtrate by removing approximately half of the solvent by rotary evaporation, and then adding methanol to the concentrate until it was turbid (20 mL methanol). The mixture was allowed to settle overnight (16 h) at 5 °C, and the precipitate was collected and dried in-vacuo to yield 0.12 g (71% recovered) of PPFS as a white powdery electrostatic solid; $M_n = 9.15 \times 10^3$, $pdi = 1.60$. $^1H$ NMR spectroscopy confirmed the absence of PB homo- and copolymers: 2.00 (broad s, $CH_2CHAr$), 2.40 (broad s, mr + rr $CH_2CHAr$), 2.75 (broad s, mm $CH_2CHAr$). $^{19}F$ NMR: -162.0 ppm (sharp s, C3-$F$), -154.0 ppm (sharp s, C4-$F$), -143.0 (broad s, C2-$F$).

3.5 Ene Reaction of 2,3,4,5,6-Pentafluorostyrene with Polybutadiene and Model Compounds.

3.5.1 Tosylation of Oleyl Alcohol.

Tosylated oleyl alcohol ($p$-toluenesulfonyl 9-octadecene-1-ol) was synthesized in 53.6-78.0% yield as in the following example. A solution of oleyl alcohol (5.26 g, 20.0 mmol) in methylene chloride (40 mL) was added dropwise to a solution of $p$-toluenesulfonyl chloride (4.74 g, 25.0 mmol) and triethylamine (1.52 g, 15.0 mmol) in methylene chloride (75 mL). The reaction mixture was stirred for 5 days at room temperature, after which it was poured into 100 mL of water and stirred for approx. 10 min. The aqueous phase was extracted four times with methylene chloride (50 mL each). The combined organic layers were washed three times with water (80 mL each time) and then with 25 % w/v aqueous sodium bicarbonate (80 mL). The solvent was removed by rotary
evaporation and the product was left for 4 days in 50 mL of 2.5 % w/v aqueous sodium bicarbonate. The product was extracted three times with methylene chloride (75 mL each), which gave 6.45 g of oleyl tosylate after removal of the methylene chloride by rotary evaporation. $^1$H NMR: 0.90 (sharp t, $CH_3CH_2$) 1.25 (sharp m, $CH_3(CH_2)_5$), 1.60 (sharp t, $CH_2CH_2O\text{SO}_2$), 2.00 (broad s, $CH_2CH_=$), 2.20 (sharp s, $C_6H_4CH_3$), 4.00 (sharp t, $CH_2\text{SO}_2$), 5.25 (broad s, $CH=CH$), 7.35 (sharp d, 2 aromatic H ortho to $CH_3$, $\text{OSO}_2C_6H_2H_2\text{CH}_3$), and 7.80 (sharp d, 2 aromatic H ortho to $\text{OSO}_2$, $\text{OSO}_2C_6H_2H_2\text{CH}_3$).

3.5.2 Reduction of $p$-Toluenesulfonyl 9-Octadecene-1-ol.

Sodium tetraborohydride (0.80 g, 20 mmol) was stirred in DMSO at 60 °C for 15 h. A solution of $p$-toluenesulfonyl 9-octadecene-1-ol (4.30 g, 11.0 mmol) was added dropwise to it and stirred for 8 h at 55 °C. This solution was extracted three times with hexanes (40 mL each), and the combined hexanes portions were washed three times with water (30 mL each) and dried over magnesium sulfate overnight. Extraction solvent was removed by rotary evaporation to yield 1.97 g (78.2% conversion) of crude 9-octadecene. The crude product was distilled under reduced pressure (bp = 165 °C / 5 mm Hg) in the presence of hydroquinone to yield 1.01 g (39.2%) of the final pure product. $^1$H NMR: 0.90 (sharp t, $CH_3CH_2$, 6 H), 1.30 (m, $CH_3(CH_2)_5$, 12 H) 2.00 (broad m, $CH_2CH_=$, 4 H), 5.35 (broad s, $CH=\$, 2 H).

3.5.3 Attempted Ene Reaction with Model Compounds.

We attempted an ene reaction between PFS and 1- and 9-octadecene, and 1-decene, both in bulk and using a solvent. For the reaction in bulk, either 1- or
9-octadecene (0.60 g, 2.4 mmol) or 1-decene (0.34 g, 2.4 mmol) were poured into a glass tube sealed to a round bottom flask with PFS (0.46 g, 2.4 mmol) and BHT (52.8 mg, 0.24 mmol) to prevent oligomerization and/or oxidation of the alkene. 1,3-Dichlorobenzene was also added to the mixture (17.6 mg, 0.12 mmol) as internal standard. The reaction mixture was degassed by three freeze-pump-thaw cycles and the tube was flame-sealed under vacuum. Then the mixture was stirred for 7 days at temperatures between 140 and 220 °C. $^1$H NMR spectra were taken of the reaction mixture before and after reaction. The vinyl resonance of 1-octadecene or 1-decene at 5.80, or 9-octadecene at 5.40 ppm, was normalized by dividing its integral by the integral of H2 resonance of 1,3-dichlorobenzene at 7.40 ppm. Comparing the values of the normalized integrals before and after reaction allowed us to observe any possible changes taking place. Similar comparison was done for PFS, by normalizing the integral of the resonance at 6.70 ppm (sharp m, =CH) with the integral of H2 of 1,3-dichlorobenzene at 7.40 ppm.

For the experiment in solution, 1,2-dichlorobenzene (0.70 g, 4.8 mmol) or nitrobenzene (0.70 g, 5.7 mmol) was added to the reaction mixture as both a solvent and an internal standard. The experiment was carried out and monitored as above.

3.5.4 Attempted Ene Reaction with High Molecular Weight Polybutadiene.

For the reaction with high molecular weight PB in solution, PB (0.13 g, 2.4 mmol repeat units) and 1,3-dichlorobenzene (0.70 g, 4.8 mmol) were degassed in a Schlenk tube by three freeze-pump-thaw cycles and the solution was stirred
overnight for 15 h at 80 °C. The solution was poured into a round bottom glass reactor and PFS (0.46 g, 2.4 mmol) and BHT (52.8 g, 0.24 mmol) were added to it. After degassing again by three freeze-pump-thaw cycles, the tube was flame-sealed under vacuum and the reaction was placed in an oil bath at 180 °C for 7 days. For the reaction in bulk, PB (0.13 g, 2.4 mmol repeat units), PFS (0.46 g, 2.4 mmol), BHT (52.8 mg, 0.24 mmol) as antioxidant, and 17.6 mg of 1,3-dichlorobenzene (0.12 mmol) as internal standard were poured into a glass tube sealed to a round bottom flask. The contents were degassed (three freeze-pump-thaw cycles) and the tube was flame-sealed under vacuum, after which the tube was placed in an oil bath at 180 °C for 7 days. 1H NMR spectra of the PB was taken before reaction and of the product.

3.5.5 Attempted Ene Reaction with Low Molecular Weight Polybutadiene.

To carry out the reaction with low molecular weight PB, PB (0.13 g, 2.4 mmol repeat units), PFS (0.46 g, 2.4 mmol), BHT (52.8 mg, 0.24 mmol) as antioxidant, and 17.6 mg of 1,3-dichlorobenzene (0.12 mmol) as internal standard for reaction in bulk, were poured into a glass tube sealed to a round bottom flask. The mixture was stirred until complete mixing was achieved, and a small aliquot was taken for 1H NMR analysis. The reaction mixture was then degassed by three freeze-pump-thaw cycles and flame-sealed under vacuum. The reaction mixture contained in the sealed tube was stirred for 4 days at 180 °C. The tube was then broken and an aliquot was taken for 1H NMR analysis. The vinyl resonance of PB =CH at 5.40 ppm (broad s) was normalized with respect to the H2 of 1,3-dichlorobenzene resonance at 7.40 ppm. Normalized peaks before and after
stirring reaction mixture were compared to observe any possible changes. The PFS conversion was monitored as above. Reaction product is a viscous white thick fluid.

In order to isolate the possible ene reaction product, 70 mg of it was immersed in 5 mL of acetone for 24 h to extracted out any PPFS. The solvent was decanted off and the product was dried in vacuum for 14 h producing 55.5 mg of product.

3.6 Arene Complexes.

3.6.1 1,2,3,4,5-Pentamethylcyclopentadiene (C₅⁺).

Crude 1,2,3,4,5-pentamethylcyclopentadiene (C₅⁺) was synthesized in 33-68% yield as follows. Lithium wire (2.5 g, 0.35 mol) was cut into small pieces (approx. 1/6 in.) under a N₂ atmosphere in a drybox, and put into 50 mL of diethyl ether contained in a three-neck round bottom flask, and stirred for 10 min. 2-Bromo-2-buten (25 mL, 0.18 mol) in 200 mL of diethyl ether was added to it dropwise over 45 min., putting the mixture at a temperature <0 °C every 5 min. to avoid excessive heating of the reaction. The mixture was then stirred for 5 h at room temperature. A reflux condenser and an addition funnel were attached to the flask and the reaction was taken outside of the drybox. The addition funnel was charged with ethyl acetate (10 mL, 0.10 mol) in 50 mL of diethyl ether, which was added dropwise to the mixture above very slowly. The reaction was stirred for 16 h at room temperature and poured into an aqueous solution of ammonium chloride (30% w/v, 600 mL). The aqueous layer was then extracted three times with diethyl ether (100 mL each) and all combined organic layers were
concentrated to approx. 75 mL by rotary evaporation, after drying over magnesium sulfate for 2 h. p-Toluenesulfonyl chloride (1.62 g, 11.5 mmol) was stirred in 75 mL of diethyl ether and the concentrate from the previous reaction was added to this solution as quickly as possible from an addition funnel. The mixture was stirred for 5 h, after which the reaction mixture was washed three times with saturated aqueous sodium bicarbonate (100 mL each). The combined aqueous portions were extracted three times with diethyl ether (100 mL each). The combined organic portions were dried over magnesium sulfate for two hours and solvent was removed by rotary evaporation. The crude product was passed through a silica gel column using methylene chloride as eluant. The solvent was removed by rotary evaporation to give 9.25 g (68.0 mmol) of C₇p*. The crude product (2.0 g, 14.7 mmol) was degassed by three freeze-pump-thaw cycles, followed by distillation under reduced pressure (bp = 52 °C / 10 mm Hg) to give 0.50 g (25.2% yield) of pure C₇p*. ¹H NMR: 1.00 (sharp d, CH₂CH₂(CH₃)₄, 1.80 (sharp d, CH₃CH₂CH₂(CH₃)₄, 2.50 (broad m, CH). 3.6.2 C₇p*RuCl₂.

C₇p* (0.35 g, 2.5 mmol) was added dropwise from an addition funnel to a solution of ruthenium (III) chloride hydrate (0.20 g, 0.76 mmol) in 10 mL of previously distilled methanol, and the mixture was refluxed for 12 h. The reaction mixture was taken into a N₂-atmosphere drybox and left for 8 h at -20 °C. The resulting brown crystalline solid was collected and washed several times with hexanes to yield 0.12 g (47 %) of Cp*RuCl₂. ¹H NMR: 4.90 (broad s, CH₃, 5 H) in
CDCl$_3$, 6.00 (broad s, CH$_3$, 5 H) in CH$_2$Cl$_2$ with two drops of CDCl$_3$ to lock spectrum.

3.6.3 [C$_p$*RuOMe]$_2$.

C$_p$*RuCl$_2$ (0.11 g, 0.30 mmol) was dissolved in methanol (3 mL) inside of a N$_2$-atmosphere drybox, and potassium carbonate (0.18 g, 1.3 mmol) was added. The reaction mixture was stirred at room temperature for 24 h, after which the reaction mixture was decanted from the unreacted potassium carbonate to another flask. The methanol was evaporated in-vacuo and the product recovered with diethyl ether (5 mL). Solvent was partially removed in-vacuo and left for 7 days at < -5 ºC to yield 22 mg (4.1 x 10$^{-2}$ mmol) of product. $^1$H NMR : 1.60 (broad s, C$_p$*), 3.70 (broad m, OMe).

3.6.4 Attempted Synthesis of the Arene Complex with 2,3,4,5,6-Pentafluorostyrene.

We mixed 22 mg (4.1 x 10$^{-2}$ mmol) of [C$_p$*RuOMe]$_2$ contained in 88 mg of diethyl ether with 10 mg of PFS (5.1 x 10$^{-2}$ mmol) and a drop of concentrated HCl. The mixture was left to react for 3 days at room temperature in an inert atmosphere.

3.7 Copolymerization of β-Pinene and 2,3,4,5,6-Pentafluorostyrene.

3.7.1 Copolymerization of 2,3,4,5,6-Pentafluorostyrene and β-Pinene in Solution and in Bulk.

PFS and β-pinene were first polymerized in solution as follows. PFS (0.58 g, 3.0 mmol), β-pinene (0.48 g, 3.0 mmol) and BPO (1.15 mg, 0.06 mmol) in THF (7.0 mL) were mixed in a Schlenk tube. The mixture was degassed by 5 freeze-
pump-thaw cycles and placed in an oil bath at 70 °C for 20 h. The polymerization tube was immersed in ice water to quench the polymerization and then the mixture was poured into methanol (100 mL). After cooling for 15 h at < -10 °C, the copolymer precipitate was filtered and dried in-vacuo overnight at room temperature to yield 0.11 g (10% yield) of an off-white electrostatic solid. $M_n = 5.5 \times 10^3$, $\text{pdi} = 1.36$. Copolymer composition determined by $^1\text{H}$ NMR spectroscopy 87 mol % PFS, 13 mol% β-pinene.

The copolymerization in bulk was carried out similarly. The mixture was quenched by immersing the tube in ice water, 2 mL of THF were added to the mixture and this was poured into 100 mL of methanol. After precipitation, filtering and drying, 0.12 g (12% yield) of an off-white electrostatic solid were recovered: $M_n = 4.9 \times 10^3$, $\text{pdi} = 1.55$. Copolymer composition determined by $^1\text{H}$ NMR spectroscopy 85 mol % PFS, 15 mol% β-pinene.

3.7.2 Copolymerization of 2,3,4,5,6-Pentafluorostyrene and β-Pinene. Determination of Reactivity Ratios.

The copolymerizations were performed using monomer feed compositions from 0.1 to 0.9 mol % PFS and 0.9 to 0.1 mol % β-pinene as in the following examples. For feed compositions from 0.3 to 0.9 mol % PFS: PFS (0.44 g, 2.2 mmol), β-pinene (0.31 g, 2.2 mmol) and BPO (1.1 mg, 45 µmol) were mixed with 1,3-dichlorobenzene (7.5 mg, 51 µmol) used as internal standard. A small aliquot of the polymerization mixture was taken for NMR measurement. The rest of the solution was then poured into a glass tube sealed to a round bottom flask, and subsequently degassed by four freeze-pump-thaw cycles. The glass tube
was then flame-sealed under vacuum and placed in an oil bath at 70 °C for 2 h. The tube was then immersed in ice water to quench the polymerization before breaking the neck of the tube. A small aliquot was taken for NMR analysis before adding THF (1 mL) to the remaining solution. The THF-diluted polymerization mixture was added dropwise to an Erlenmeyer flask containing 10 mL methanol. After cooling for 20 h at <-10 °C, the copolymer precipitate was filtered and dried in-vacuo overnight at room temperature to yield 18 mg (4.2%) of an off-white electrostatic solid. \( M_n = 3.72 \times 10^3 \), \( \text{pdi} = 1.54 \), 86% mol% PFS, 14% \( \beta \)-pinene.

For feed compositions 0.1 to 0.2 mol % PFS: PFS (0.17 g, 0.9 mmol), \( \beta \)-pinene (0.49 g, 3.6 mmol) and BPO (1.1 mg, 0.04 mmol) were mixed with 1,3-dichlorobenzene (7.5 mg, 0.05 mmol) used as an internal standard. Copolymerization was then carried out as above. After breaking the tube and taking a small aliquot for NMR analysis and the rest of the polymerization mixture was purified by column chromatography using silica gel as the stationary phase and THF/hexanes (1:1) as the eluant. The first fraction contained the unreacted monomers and the second fraction contained the copolymer product, which was precipitated in methanol after removing half of the solvent by rotary evaporation. After cooling for 48 h at <-10 °C, the copolymer product was filtered and dried in-vacuo overnight at room temperature to yield 2.7 mg (<1%) of an off-white waxy solid. \( M_n = 2.82 \times 10^3 \), \( \text{pdi} = 1.43 \), 69 mol% PFS, 31 mol% \( \beta \)-pinene.
3.7.3 Monomer Conversion.

$^1$H NMR spectroscopy was used to determine the monomer conversion with 1,3-dichlorobenzene as the internal standard. Figure 3.2 shows stacked $^1$H NMR spectra taken from the copolymer mixture of the PFS-co-PIN-5/5 experiments at $t=0$ and at $t=2$ h. In order to determine the conversion of β-pinene, the integral of the $CH_2$=R resonance (labeled a) at 4.60 ppm (sharp d) was normalized relative to the integral of the aromatic H2 resonance (c on Figure 3.2) at 7.40 ppm (sharp s) of 1,3-dichlorobenzene in the NMR spectra taken before and after polymerization. The same applies when determining the conversion of PFS but using the $CH_2$=CH resonance (peak b) integral at 6.70 ppm (sharp m). The conversion is given by equation 3.6.

$$\text{% Conversion} = \frac{\text{normalized integral before reaction} - \text{normalized integral after reaction}}{\text{normalized integral before reaction}} \times 100$$ \hspace{1cm} \text{Eq. 3.6}

3.7.4 Copolymer Composition.

Figure 3.3 shows the $^1$H NMR spectrum of the copolymer PFS-co-PIN-5/5. Peak “a” at 5.15 ppm (broad s, C=CH$CH_2$) corresponds to the vinyl proton of the β-pinene unit. Peaks in the alkyl region labeled “b” (0.50-2.10) correspond to the PFS unit resonances (3 H) overlapped with the non-vinyl β-pinene resonances (15 H). The integral for 1 proton of the β-pinene unit can be known from peak “a” ($H_{(PIN)}$, equation 3.7). Multiplying this amount by fifteen and subtracting it from the integral of all the alkyl resonances labeled “b”, we obtain the integral
corresponding to the PFS unit, which can be normalized by dividing it by three 
\( H_{(PFS)} \), equation 3.8).

\[
H_{(PIN)} = \text{integral peak "a"} \\
H_{(PFS)} = \frac{1}{3} \left[ \text{(integral peaks "b")} - 15 \times \text{(integral peak "a")} \right]
\]

Eq. 3.7

Eq. 3.8

\[ t = 0 \ h \]

\[ t = 2 \ h \]

Figure 3.2. \(^1\)H NMR Spectra of the polymerization mixture for the experiment PFS-co-PIN-5/5 before and after copolymerization. 1,3-Dichlorobenzene resonance (7.40 ppm) as internal standard. Polymerization time 2 h.

Therefore \(^1\)H NMR spectroscopy of the copolymers provides us with the relative amounts of PFS (eq. 3.9) and PIN units in the copolymer (eq. 3.10). The composition of the copolymer is then given by equations 3.9 and 3.10.

\[
\% \text{PFS} = \frac{H_{(PFS)}}{H_{(PFS)} + H_{(PIN)}} \times 100
\]

Eq. 3.9

\%

\[
\% \text{PIN} = 100 - \% \text{PFS}
\]

Eq. 3.10

The percentage yield of the recovered polymer was determined from the weight of the recovered copolymer and its composition (determined as explained above) using equation 3.11.
% Yield = \frac{\text{weight copolymer} \times 100}{\text{initial weight PFS} \times \frac{\% \text{ PFS in copolymer}}{100} + \text{initial weight PIN} \times \frac{\% \text{ PIN in copolymer}}{100}}

\text{Eq. 3.11}

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]

\[ \text{Eq. 3.11} \]
thaw cycles. The glass tube was then flame-sealed under vacuum and placed in an oil bath at 70 °C for 25 min. The tube was immersed in ice water to quench the polymerization before breaking the neck of the tube. A small aliquot was taken for NMR analysis before adding THF (1 mL) to the remaining solution. The THF-diluted polymerization mixture was added dropwise to methanol (15 mL) contained in an Erlenmeyer flask. After leaving for 20 h at room temperature, the polymer precipitate was filtered and dried in-vacuo overnight at room temperature to yield 13.2 mg (6.0% yield) of a white electrostatic solid. $M_n = 4.71 \times 10^4$, $pdi = 2.30$; 57 mol% styrene, 43 mol% PFS.

3.8.2 Copolymerization of Styrene and 2,3,4,5,6-Pentafluorostyrene at 25 °C.

The copolymerizations were performed using monomer feed (mol %) compositions from 0.1 to 0.9 mol% PFS and 0.9 to 0.1 mol% styrene as in the following example. Styrene (0.21 g, 2.0 mmol), PFS (0.39 g, 2.0 mmol), and $t$-butyl peroxo pivalate (10 mg, 0.040 mmol) were mixed with $n$-butyl acetate (7 mg, 0.06 mmol) used as internal standard. The polymerizations were carried out as above, except that $t$-butyl peroxo pivalate was used as the initiator instead of BPO. The monomers and internal standard mixture were cooled in an ice bath prior to addition of the initiator, and subsequently degassed by four freeze-pump-thaw cycles. The copolymerization time was 2.5 h. After work-up and leaving for 20 h at < 5 °C, the polymer precipitate was filtered and dried in-vacuo overnight at room temperature to yield 0.55 mg (< 1%) of a white electrostatic solid.

3.8.3 Monomer Conversion.
\(^1\)H NMR spectroscopy was used to determine the PFS and styrene conversion using \(n\)-butyl acetate as the internal standard. Figure 3.4 shows stacked \(^1\)H NMR spectra taken of the copolymer mixture of the PFS-co-styrene-5/5 experiment at \(t=0\) and at \(t=25\) min. To determine the conversion of styrene, the integral of the resonance at 5.25 ppm (\(CH_2=\), sharp d, labeled “b” on figure 3.4) was normalized relative to the integral of the resonance at 4.10 ppm of \(n\)-butyl acetate (\(CH_2OCOCH_3\), sharp t, “c” in Figure 3.4) divided by two, in the NMR spectra taken before and after polymerization.

The same applies when determining the conversion of PFS: the integral of the resonance at 6.10 ppm (\(CH_2=\), sharp d, labeled “a” in Figure 3.4) was normalized the same way as above. The conversion of both monomers is given by equation 3.6.

Figure 3.4. \(^1\)H NMR spectra of the polymerization mixture for the experiment Sty-\(alt\)-PFS-5/5 before and after copolymerization. Internal standard \(n\)-butyl acetate (peak “c”). Copolymerization time 25 min.
Figure 3.5. $^1$H NMR spectrum of the copolymer from experiment Sty-alt-PFS-5/5 synthesized at 70 °C with benzoyl peroxide as initiator (1 mol%). The peaks under label “b” are due to all protons in the backbone of the copolymer and resonances labeled as “a” correspond to aromatic protons of styrene units of the copolymer. Resonance marked with an asterisk is due to residual CHCl$_3$ from deuterated solvent and with two asterisks is due to residual water also in the solvent.

3.8.4 Copolymer Composition.

Figure 3.5 shows the $^1$H NMR spectrum of the copolymer PFS-co-styrene-5/5. The two broad resonances in the aromatic area (6.60 ppm, aromatic H2 and H6; and 7.05 ppm, aromatic H3, H4 and H5) correspond to the aromatic protons of the styrene units in the copolymer (labeled “a” in Figure 3.5). Dividing the integral of the resonances “a” by five, the normalized value for the styrene units was obtained ($H_{(STYR)}$, equation 3.12). In order to obtain the normalized value for PFS units ($H_{(PFS)}$, equation 3.13), the normalized value for styrene units was multiplied by three (since there are three alkyl H for each monomer), and this value was subtracted to the integral of the resonances located between 1.30 and
2.80 (labeled “b”, which correspond to the alkyl H of both monomers), and subsequently divided by three.

\[ H_{(STYR)} = \frac{1}{5} \] (integral peak “a”)

\[ H_{(PFS)} = \frac{1}{3} \left[ (\text{integral peaks “b”}) - 3 \times H_{(STYR)} \right] \]

The composition of the copolymers is given by equations 3.14 and 3.15.

\[ \% \text{ PFS} = \frac{H_{(PFS)}}{H_{(PFS)} + H_{(STYR)}} \times 100 \]

\[ \% \text{ STYR} = 100 - \% \text{ PFS} \]

The percentage yield of the recovered polymer was determined from the weight of the recovered copolymer and its composition (determined as explained above) using the following expression, similar to determination of the yield of the copolymers PFS-co-PIN (previous Section).

\[ \% \text{ Yield} = \frac{\text{weight copolymer}}{\text{initial weight PFS} \times \text{\% PFS in copolymer} + \text{initial weight Sty} \times \text{\% Sty in copolymer}} \times 100 \]

3.8.5 Homopolymerization of Styrene.

Low molecular weight polystyrene was synthesized for NMR analysis as follows. A solution of styrene (0.21 g, 2.0 mmol) and BPO (0.19 g, 0.80 mmol) in THF (14 mL) was degassed in a Schlenk tube by five freeze-pump-thaw cycles. After stirring at 70 °C for 48 h, the polymerization solution was precipitated in methanol (75 mL), collected and dried in-vacuo overnight at room temperature to
yield 0.15 g (71 %) of polystyrene as a white powder; $M_n = 3.1 \times 10^3$, pdi = 1.67. $^1$H NMR: 1.50 (broad s, CH$_2$CHAr), 1.95 (broad s, mm + mr + rr CH$_2$CHAr). $^{13}$C NMR: 41.0 (sharp s, CH$_2$CHAr), 44.0 (broad m, CH$_2$CHAr), 126.0 (s, aromatic C4), 128.5 (two overlapped s, aromatic C2, C6, C3 and C5), 146.0 (m, aromatic C1).

Medium molecular weight polystyrene was synthesized for thermal analysis as follows. Styrene (3.03 g, 28.9 mmol) and BPO (69.9 mg, 0.290 mmol) were degassed in a round bottom glass tube by four freeze-pump-thaw cycles. After degassing, the tube was flame-sealed under vacuum and stirred at 70 °C for 25 min. The polymerization was quenched in an ice water bath before breaking the neck of the tube. THF (approx. 5 mL) was added and the solution was precipitated in methanol (25 mL), collected and dried in-vacuo overnight at room temperature to yield 0.35 g (11 %) of polystyrene as a white powder; $M_n = 2.12 \times 10^4$, pdi = 1.89.

3.8.6 Homopolymerization of 2,3,4,5,6-Pentafluorostyrene.

PPFS for thermal analysis was synthesized as follows. PFS (1.50 g, 7.77 mmol) and BPO (18.5 mg, 0.0760 mmol) were degassed in a round bottom glass tube by four freeze-pump-thaw cycles. After degassing, the tube was flame-sealed under vacuum and put in an oil bath at 70 °C for 25 min. The polymerization was quenched in an ice water bath before breaking the neck of the tube. THF (approx. 3 mL) was added and the solution was precipitated in methanol (25 mL), collected and dried in-vacuo overnight at room temperature to yield 0.17 g (12 %) of PPFS as a white powder; $M_n = 4.85 \times 10^4$, pdi = 1.68.
3.9 Copolymerization of 2-Vinyl Naphthalene and 2,3,4,5,6-Pentafluorostyrene.

3.9.1 Copolymerization of 2-Vinyl Naphthalene and 2,3,4,5,6-Pentafluorostyrene at 70 °C.

The copolymerizations were performed using monomer feed compositions from 0.4 to 0.9 mol % PFS and 0.6 to 0.1 mol % 2-vinyl naphthalene (2-VN) as in the following example. 2-VN (0.23 g, 1.5 mmol), PFS (0.29 g, 1.5 mmol), and BPO (7.3 mg, 0.030 mmol) were mixed with n-butyl acetate (7.5 mg, 0.050 mmol) used as internal standard. A small aliquot of the polymerization mixture was taken for NMR analysis. The rest of the mixture was then poured into a glass tube sealed to a round bottom flask, and subsequently degassed by four freeze-pump-thaw cycles. The glass tube was then flame-sealed under vacuum and placed in an oil bath at 70 °C. After 30 min the tube was immersed in ice water to quench the polymerization before breaking the neck of the tube. A small aliquot was taken for NMR analysis before adding THF (1 mL) to the remaining solution. The THF-diluted polymerization mixture was warmed on a hot plate set at 70 °C for approx. 2 min and added dropwise to previously-warmed methanol (10 mL) contained in an Erlenmeyer flask. The precipitate was collected after settling for 20 h at room temperature and dried in-vacuo overnight at room temperature to yield 12.7 mg (4.9%) of an off-white electrostatic solid.

The copolymerizations were performed using monomer feed compositions from feed compositions of 0.1 to 0.3 mol % PFS and 0.9 to 0.7 mol % 2-VN as in the following example. 2-VN (0.32 g, 2.10 mmol), PFS (0.17 g, 0.90 mmol) and n-butyl acetate (7.50 mg, 0.05 mmol) were poured into a glass tube sealed to a
round bottom flask, and subsequently evacuated. Vacuum was stopped and the mixture was stirred in an oil bath at 70 °C until the contents melted. A small aliquot was taken for $^1$H NMR analysis and BPO (7.30 mg, 0.03 mmol) was then added. The polymerization mixture was degassed by four freeze-pump-thaw cycles and the tube was flame-sealed under vacuum. The rest of the polymerization was carried out as above to yield 25.6 mg of a white electrostatic solid (9.7% yield). In some cases, the copolymer product was contaminated with 2-VN. To purify the product, the copolymer was dissolved in the minimum amount of THF (approx. 5 mg/mL), and precipitated into 10 mL of methanol. Yields after this sort of purification were below 2%.

3.9.2 Monomer Conversion and Copolymer Composition.

The PFS monomer conversion was calculated exactly the same way as explained in Section 3.8.3. To determine the conversion of 2-VN, the integral of the resonance at 5.30 ppm ($CH_2=$) was normalized with respect to the integral of the resonance at 4.10 ppm of $n$-butyl acetate ($CH_2OCOCH_3$, sharp t, “c” in Figure 3.4) divided by two, in the NMR spectra taken before and after polymerization. Equation 3.6 was used to calculate the conversion of both monomers.

The composition of the copolymers was determined by the same procedure described in section 3.8.4. In order to determine the $^1$H NMR integral normalized for one proton of the 2-VN units in the copolymer ($H_{(2VN)}$), the integral of the resonances between 6.20 and 7.90 ppm was divided by seven. The normalized integral for the protons belonging to the PFS unit $H_{(PFS)}$ was determined as stated
in equation 3.13, but substituting $H_{(STYR)}$ for $H_{(2VN)}$. The composition of the copolymers was given by equations 3.17 and 3.18.

$$\%\ PFS = \frac{H_{(PFS)}}{H_{(PFS)} + H_{(2-VN)}} \times 100$$  \hspace{1cm} \text{Eq. 3.17}

$$\%\ 2-VN = 100 - \%\ PFS$$  \hspace{1cm} \text{Eq. 3.18}

3.9.3 Synthesis of Poly(2-Vinyl Naphthalene).

In order to investigate the dependence of the thermal behavior of poly(2-vinyl naphthalene) (P2-VN) on the degree of polymerization, P2-VNs with various molecular weight were synthesized.

Low molecular weight P-2VN was synthesized as follows. 2-VN (0.31 g, 2.0 mmol) and BPO (24 mg, 0.10 mmol) were degassed in a round bottom glass tube by five freeze-pump-thaw cycles, and the tube was flame-sealed under vacuum. After stirring at 70 °C for 48 h, THF (approx. 4 mL) was added after breaking the neck of the tube and the polymerization mixture was precipitated in methanol (25 mL), collected and dried in vacuo overnight at room temperature to yield 48.5 mg (32.3 %) of P-2VN as a white electrostatic powder; $M_n = 3300$, $pdi = 2.67$. $^1$H NMR: 1.60 (broad s, $CH_2CHAr$), 1.90 (broad s, mm + mr + rr $CH_2CHAr$), 6.40 (broad s, aromatic H1, H3), 7.30 (broad s, aromatic H4, H6, H8, H9), 7.60 (broad s, aromatic H7).

Medium molecular weight P-2VN was synthesized as follows. 2-VN (0.31 g, 2.0 mmol) and BPO (4.8 mg, 0.020 mmol) were degassed in a round bottom glass tube by five freeze-pump-thaw cycles, and the tube was flame-sealed under vacuum. After stirring at 70 °C for 30 min, THF (approx. 4 mL) was added
after breaking the neck of the tube and the polymerization mixture was precipitated in methanol (25 mL), collected and dried in-vacuo overnight at room temperature to yield 39.0 mg (12.6 %) of P2VN as a white electrostatic powder; \( M_n = 1.24 \times 10^4 \), pdi = 2.61.

Medium molecular weight P2-VN was also synthesized in THF solution as follows. A solution of 2-VN (0.31 g, 2.0 mmol) and BPO (4.8 mg, 0.020 mmol) in THF (14 mL) was degassed in a Schlenk tube by five freeze-pump-thaw cycles. After stirring at 70 °C for 24 h, the polymerization solution was precipitated in methanol (75 mL), collected and dried in-vacuo overnight at room temperature to yield 59.0 mg (19.0 %) of P2-VN as a white electrostatic powder; \( M_n = 2.77 \times 10^4 \), pdi = 2.93.

High molecular weight P2-VN was synthesized as follows. 2-VN (0.31 g, 2.0 mmol) and BPO (2.4 mg, 0.0098 mmol) were degassed in a round bottom glass tube by five freeze-pump-thaw cycles, and the tube was flame-sealed under vacuum. After stirring at 70 °C for 24 h, THF (approx. 4 mL) was added after breaking the neck of the tube and the polymerization mixture was precipitated in methanol (25 mL), collected and dried in-vacuo overnight at room temperature to yield 48.5 mg (32.3 %) of P2-VN as a white electrostatic powder; \( M_n = 5.39 \times 10^4 \), pdi = 2.30.

3.10 Copolymerization of 1-Vinyl Naphthalene and 2,3,4,5,6-Pentafluorostyrene.

3.10.1 Synthesis of 1-Vinyl Naphthalene.

Magnesium (2.25 g, 94.0 mmol) and a few small crystals of iodine were put in a 3-neck round bottom flask, equipped with a reflux condenser and an addition
funnel. 1-Bromonaphthalene (15.0 g, 72.5 mmol) in diethyl ether (50 mL) was added dropwise for approx. 30 min. Reflux started at the beginning of the addition and after approx. 2 h reflux stopped and the reaction mixture became a lump that incorporated all of the solvent. More diethyl ether (40 mL) was added and the reaction flask was immersed in an oil bath set at 50 °C. After stirring the reaction mixture for 4 more h, a small aliquot was taken and a drop of aqueous HCl (2.0 M) was added. The 1H NMR spectrum of the aliquot showed only naphthalene: 7.40 (sharp m; H2, H3, H6, H7) and 7.80 (sharp m; H1, H4, H5, H8), which demonstrates that the reaction was complete, and all 1-bromonaphthalene was converted into naphthyl magnesium bromide.

The solution was degassed by two freeze-pump-thaw cycles and taken into a N2 atmosphere in a dry box, where toluene (90 mL) was added and the reaction mixture was heated until complete dissolution. The solution was decanted into a glass sleeve custom made to fit the bottom part of a Parr® reactor, and NiCl2(dppp) (0.19 g, 0.36 mmol) was added to the reaction mixture. The Parr® reactor was assembled as indicated by the manufacturer, and taken out of the dry box. The reaction mixture was purged with N2 for approx. 5 min, and the reactor bottom was then immersed in a liquid N2 filled Dewar until the temperature of the mixture as recorded by the reactor thermometer was < -50°C. The reactor was connected to a cylinder containing vinyl bromide and this was added to the reaction mixture (17.4 g, 109 mmol), measuring the amount of vinyl bromide added into the reactor by the weight difference of the cylinder. Once the addition was completed, the Dewar filled with liquid N2 was removed, and the
reaction was allowed to warm to room temperature (max. temperature recorded = 23 °C) and stirred for 23 h.

To work up, the reaction was purged for 5 min with N₂ and the Parr® reactor was opened to air to evaporate the excess of unreacted vinyl bromide. After that time it was poured into a beaker containing 100 mL of aqueous HCl (1.0 M) and stirred for 30 min. The two phases were separated and the organic layer was washed three times with aqueous HCl (1.0 M) (100 mL each), and then washed with 1.0 % w/v aqueous sodium bicarbonate until the washings were neutral as determined with pH paper (two times, 100 mL each). All aqueous portions were combined and extracted three times with diethyl ether (75 mL each) and all combined organic layers were dried over magnesium sulfate overnight. The solution was filtered and the diethyl ether and most of the toluene were removed by rotary evaporation. The rest of the toluene was removed by trap-to-trap distillation, applying full vacuum to the Schlenk line and heating the remaining solution in an oil bath at 65 °C. The crude product (dark yellow viscous liquid) was purified by subliming off naphthalene side product. Once naphthalene was removed, the product was further purified by column chromatography using silica as the stationary phase and chloroform as eluant, followed by distillation under reduced pressure (bp = 80 °C/ 0 mm Hg), with a short path distillation head, running hot water through the condenser¹⁶⁷ to yield 6.98 g (62.5%) of 1-vinyl naphthalene (1-VN) as a clear viscous liquid. ¹H NMR: 5.50 and 5.90 (CH₂=CHAr, sharp d), 7.50 (CH₂=CHAr and aromatic H5, H6, H7; slightly
broadened m), 7.70 (aromatic H4, sharp d), 7.85 (aromatic H8, sharp d), 7.95 (aromatic H3, sharp d), 8.20 (aromatic H2, sharp d).

3.10.2 Homopolymerization of 1-Vinyl Naphthalene.

Poly(1-vinyl naphthalene) (P1-VN) was synthesized as follows. 1-VN (0.31 g, 2.0 mmol) and BPO (4.8 mg, 0.020 mmol) were degassed in a round bottom glass tube by five freeze-pump-thaw cycles, and the tube was flame-sealed under vacuum. After stirring at 70 °C for 2.5 min, THF (approx. 4 mL) was added after breaking the neck of the tube and the polymerization mixture was precipitated in methanol (25 mL), collected and dried in-vacuo overnight at room temperature to yield 23.0 mg (7.4 %) of poly(1-vinyl naphthalene) as a white electrostatic powder; \( \text{GPC}_{\text{PSI}} M_n = 5.05 \times 10^3 \), \( \text{pdi} = 2.58 \). \(^1\)H NMR: 1.45 (broad s, CH\textsubscript{2}CHAr), 2.85 (broad s, mm + mr + rr CH\textsubscript{2}CHAr), 6.25 (broad s, aromatic H9), 7.45 (broad m, aromatic H2, H3, H4, H6, H7, H8).

3.10.3 Copolymerization of 1-Vinylnaphthalene and 2,3,4,5,6-Pentafluorostyrene at 70 °C.

The copolymerizations were performed using monomer feed compositions of 0.1 to 0.9 mol % PFS and 0.9 to 0.1 mol % 1-VN as in the following example: 1-VN (0.23 g, 1.5 mmol) PFS (0.29 g, 1.5 mmol), and BPO (7.3 mg, 0.030 mmol) were mixed with \( n \)-butyl acetate (7.5 mg, 0.050 mmol) used as internal standard. A small aliquot of the polymerization mixture was taken for NMR analysis. The rest of the mixture was then poured into a glass tube sealed onto a round bottom flask, and subsequently degassed by four freeze-pump-thaw cycles. The glass tube was then flame-sealed under vacuum and placed in an oil bath at 70 °C.
After 2.5 h the tube was immersed in ice water to quench the polymerization before breaking the neck of the tube. A small aliquot was taken for NMR analysis before adding THF (1 mL) to the remaining solution. The THF-diluted polymerization mixture was warmed up on a hot plate set at 70 °C for approx. 2 min and added dropwise to an Erlenmeyer flask containing 10 mL methanol, previously warmed on a hot plate set at 70 °C for 5 min. After 20 h at room temperature, the precipitate was collected and dried in-vacuo overnight at room temperature to yield 15.9 mg (6.2 %) of an off-white electrostatic solid. $M_n = 7.06 \times 10^3$, pdi = 1.62.

3.10.4 Copolymerization of 1-Vinylnaphthalene and 2,3,4,5,6-Pentafluorostyrene at 25 °C.

The copolymerizations were performed using monomer feed compositions from 0.1 to 0.9 mol % PFS and 0.9 to 0.1 mol % 1-VN as in the following example. 1-VN (0.23 g, 1.5 mmol), PFS (0.29 g, 1.5 mmol), and n-butyl acetate (7.0 mg, 0.06 mmol) used as internal standard were mixed and a small aliquot was taken for NMR analysis. The rest of the mixture was then poured into a glass tube sealed onto a round bottom flask and cooled in an ice bath. $t$-Butyl peroxy pivalate (15.0 mg, 0.06 mmol) was then added and the mixture was degassed by four freeze-pump-thaw cycles. The glass tube was then flame-sealed under vacuum and placed in an oil bath at 25 °C. After 7 h the tube was immersed in ice water to quench the polymerization before breaking the neck of the tube. A small aliquot was taken for NMR analysis before adding THF (1 mL) to the remaining solution. The THF-diluted polymerization mixture was warmed
on a hot plate set at 70 °C for approx. 2 min and added dropwise to an
Erlenmeyer flask containing 10 mL methanol, previously warmed on a hot plate
set at 70 °C for 5 min. After 20 h at < 5 °C, the precipitate was collected and
dried in-vacuo overnight at room temperature to yield 0.80 mg (1.8 %) of an off-
white electrostatic powder.

3.10.5 Monomer Conversion and Copolymer Composition.

The PFS conversion was determined as explained in section 3.8.3. To
determine the conversion of 1-VN, the integral of the resonance at 5.45 ppm
(CH$_2$=CHAr) was normalized relative to the integral of the resonance at 4.10 of n-
butyl acetate (CH$_3$(CH$_2$)$_2$CH$_2$OCOCH$_3$, sharp t, “c” on figure 3.4) divided by two,
in the NMR spectra taken before and after polymerization. Equation 3.6 was
used to calculate conversion of both monomers.

In order to determine the composition of the copolymers, the same procedure
was carried out as in section 3.8.4. In order to determine the $^1$H NMR integral
normalized for one proton of the 1-VN units in the copolymer (H$_{(1VN)}$), the integral
of the resonances between 6.20 and 7.90 ppm was divided by seven. The
normalized integral for the protons belonging to the PFS unit H$_{(PFS)}$ was
determined as stated in equation 3.13, but substituting H$_{(STYR)}$ for H$_{(1VN)}$. The
composition of the copolymers was given by equations 3.19 and 3.20.

\[
\% \text{PFS} = \frac{H_{(PFS)}}{H_{(PFS)} + H_{(1-VN)}} \times 100 \quad \text{Eq. 3.19}
\]

\[
\% \text{1-VN} = 100 \cdot \% \text{PFS} \quad \text{Eq. 3.20}
\]
3.11 Blends of Polystyrene and Poly(2-Vinyl Naphthalene) with Poly(2,3,4,5,6-pentafluorostyrene).

Blends of the two homopolymers were made as follows. PS (21 mg, 0.20 mmol repeat units) and PPFS (40 mg, 0.20 mmol repeat units) were dissolved in 2 mL of THF and stirred for 30 min. The solution was left for an additional 45 min without stirring and methanol (5 mL) was added to the solution as quickly as possible. The blends were allowed to precipitate at room temperature for 4 h, filtered and dried overnight under vacuum at room temperature, to yield 38 mg (92 %) of the blend.

A blend of polystyrene and PPFS was also made by Su’s procedure. Polystyrene (20 mg, 0.19 mol repeat units), and PPFS (37 mg, 0.19 mol repeat units) were dissolved in THF (5.8 mL), stirred for 26 h covered. The solvent was left to evaporate and the blend was dried in the vacuum oven until constant weight (two periods of 24 h each), to yield 41 mg (87 % yield) of the blend.

3.12 Attempted Synthesis of 1-Vinyl Pyrene.

3.12.1 Synthesis of 1-Bromo Pyrene.

Pyrene (5.50 g, 27.2 mmol) was dissolved in carbon tetrachloride (25 mL) contained in a 3-neck round bottom flask equipped with a reflux condenser and an addition funnel, which was placed in an oil bath set at 80 °C. From the addition funnel a solution of bromine (4.30 g, 26.9 mmol) in carbon tetrachloride (10 mL) was added dropwise. The pyrene solution started to reflux when the bromine solution was added. The mixture was stirred for 25 h at 80 °C, and filtered from a precipitate formed during that time. We previously observed that dibromopyrene is insoluble in carbon tetrachloride, and therefore we discarded
the solid precipitate formed, which was identified as the dibrominated derivative. The filtered solution was washed three times with water (20 mL each) and dried overnight over magnesium sulfate. The solvent was removed after filtration by rotary evaporation to recover a light brown solid that was recrystallized in ethanol. The first crop yielded 2.90 g (38.2%) of a yellow crystalline solid. $^1$H NMR: 8.00 (aromatic H4, H5, sharp m); 8.05 (aromatic H7, H9, two overlapped sharp d); 8.20 (aromatic H3, H6, H8, H10, overlapped sharp m); 8.40 (aromatic H2, sharp d). The second crop contained a large amount of unreacted pyrene and therefore it was not be used in following steps.

3.12.2 Attempted Synthesis of 1-Vinyl Pyrene.

Magnesium (300 mg, 12.5 mmol) and a few small crystals of iodine were put in a 3-neck round bottom flask, equipped with a reflux condenser and an addition funnel. 1-Bromopyrene (1.99 g, 9.80 mmol) in THF (10 mL) was added dropwise. Since the reaction did not activate spontaneously with the first drops added (no reflux started), the mixture was heated with a heat gun until reflux was obtained and was maintained. Addition took a total of approx. 15 min. After 30 min after the addition was completed the reflux stopped and the reaction flask was immersed in an oil bath set at 70 °C. After stirring the reaction mixture for 6 more h, a small aliquot was taken and a drop of water was added to it. $^1$H NMR of the aliquot showed only pyrene: 7.84 (broad t, H1 and H6), 7.87 (broad d; H3, H4, H8 and H9), and 8.25 (broad t, H2, H5, H7, and H10), which demonstrated that the reaction was complete, and all 1-bromopyrene was converted into pyrenyl magnesium bromide. The $^1$H NMR resonances were shifted toward
lower field and appeared broader and with different splitting than those of pyrene. However, there was no presence of bromopyrene resonances (at 8.40 ppm) in the spectrum. The solution was degassed by two freeze-pump-thaw cycles and taken into a N\textsubscript{2} atmosphere in a dry box, where toluene (20 mL) was added and the reaction mixture was heated until complete dissolution. The solution was poured into a glass sleeve custom made to fit the bottom part of a Parr\textsuperscript{®} reactor, and NiCl\textsubscript{2}(dppp) (26 mg, 0.050 mmol, 0.5 mol% with respect to Grignard reagent) was added to the reaction mixture. The Parr\textsuperscript{®} reactor was assembled as indicated by the manufacturer, and taken out of the dry box. Reaction mixture was purged with N\textsubscript{2} for approx. 5 min, after which reactor bottom was immersed in a liquid N\textsubscript{2} filled Dewar until the temperature of the mixture as recorded by the reactor thermometer was < -50°C. The reactor was connected to cylinder containing vinyl bromide and this was added to the reaction mixture (2.10 g, 19.8 mmol), measuring the amount of vinyl bromide added into the reactor by the weight difference of the cylinder. Once addition was completed, the Dewar filled with liquid N\textsubscript{2} was removed, and the reaction was allowed to warm up to room temperature (max. temperature recorded = 23 °C) and stirred for 23 h. The reaction was purged for 5 min with N\textsubscript{2} and the Parr\textsuperscript{®} reactor was opened to air to evaporate the excess of unreacted vinyl bromide. After that time it was poured into a beaker containing 50 mL of aqueous HCl (1.0 M) and stirred for 30 min. The two phases were separated and the organic layer was washed three times with aqueous HCl (1.0 M) (25 mL each), and then with aqueous sodium bicarbonate (1.0 % w/v) until the washings were neutral (two times, 40 mL each).
The aqueous layers were combined and extracted three times with diethyl ether (25 mL each) and the combined organic layers were dried over magnesium sulfate overnight. The solution was filtered and the THF, diethyl ether and most of the toluene were removed by rotary evaporation. The rest of the toluene was removed by trap-to-trap distillation. $^1$H NMR shows pyrene: 8.02 (sharp t, H1 and H6), 8.10 (sharp s; H3, H4, H8 and H9), and 8.20 (sharp d, H2, H5, H7, and H10). The same reaction was tried using a different amount of NiCl$_2$(dppp) (93 mg, 0.17 mmol; 1.5 mol% with respect to Grignard reagent) and stirred at room temperature for 5 days. The result was the same.

Since no reaction was observed with the previous method, we tried a different route. 1-Bromopyrene was converted into pyrenyl magnesium bromide by reaction with magnesium in THF, as explained above. The reaction was complete as observed by $^1$H NMR (only pyrene present after protonation). The pyrenyl magnesium bromide solution was degassed and taken into a drybox. Acetaldehyde (0.68 g, 15 mmol) in 1.15 mL THF was cooled below 20 °C and added dropwise to Grignard reagent mixture. The mixture was stirred letting it warm to room temperature or heating it up to 45 °C. After 10 and 45 min aliquots were taken for $^1$H NMR analysis. This showed pyrene (8.02 (sharp t, H1 and H6), 8.10 (sharp s; H3, H4, H8 and H9), and 8.20 (sharp d, H2, H5, H7, and H10)) and acetaldehyde (2.15 (sharp s, CH$_3$CHO), 9.85 (sharp s, CH$_3$CHO), besides THF (solvent) (1.90 (sharp t, CH$_2$CH$_2$O), 3.85 (sharp t CH$_2$CH$_2$O). After 15 h $^1$H NMR showed only pyrene and THF.
CHAPTER IV
GRAFT COPOLYMERIZATION OF 2,3,4,5,6-PENTAFLUOROSTYRENE ONTO POLYBUTADIENE

4.1 Synthesis of Poly(2,3,4,5,6-pentafluorostyrene).

We synthesized three different molecular weight PPFS samples to characterize their properties. Scheme 4.1 outlines the synthesis of PPFS, using THF as the solvent and BPO as the initiator. We used THF since it is a fairly good solvent for PPFS and has a fairly low chain transfer. The chain transfer constants for the thermal AIBN-initiated polymerization of PFS are 1.53 x 10^{-4} and 1.61 x 10^{-4} respectively. We found that BPO is a more efficient initiator than AIBN for the homopolymerization of PFS. Pryor and Huang\textsuperscript{18} showed that the initiator efficiency of AIBN at 60 °C is f=0.29 in THF and f=0.52 in bulk. The maximum conversions reported for the polymerization in THF were 26%, which were much lower than those achieved in this work using BPO as the initiator.

Table 4.1 summarizes the results for the homopolymerizations of PFS in bulk and in THF with different initiator concentrations. As expected, the conversion of the monomer decreased and the molecular weight increased with a decreased amount of initiator used.
Scheme 4.1. Synthesis of poly(2,3,4,5,6-pentafluorostyrene) by radical polymerization of 2,3,4,5,6-pentafluorostyrene using benzoyl peroxide as the initiator in tetrahydrofuran solution.

Also the polydispersity indices (pdi) were between 1.34 and 1.80, as expected for termination by combination\textsuperscript{30} for the PPFS radicals. The polymerization in bulk gave a much lower conversion and a higher pdi.

Table 4.1. Comparison of poly(2,3,4,5,6-pentafluorostyrene) synthesized with different initiator amounts.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Solvent</th>
<th>[BPO] x 10\textsuperscript{-3} (M)</th>
<th>(M_n) x 10\textsuperscript{-3} \textsuperscript{a}</th>
<th>pdi \textsuperscript{a}</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPFS-LMW</td>
<td>THF</td>
<td>56</td>
<td>3.72</td>
<td>1.34</td>
<td>86</td>
</tr>
<tr>
<td>PPFS-MMW</td>
<td>THF</td>
<td>7.0</td>
<td>10.2</td>
<td>1.56</td>
<td>83</td>
</tr>
<tr>
<td>PPFS-HMW</td>
<td>THF</td>
<td>1.4</td>
<td>22.8</td>
<td>1.80</td>
<td>73</td>
</tr>
<tr>
<td>PPFS-BULK</td>
<td>-</td>
<td>14</td>
<td>8.50</td>
<td>6.67</td>
<td>39</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Number-average molecular weight (\(M_n\)), weight-average molecular weight (\(M_w\)) and polydispersity (pdi = \(M_w/M_n\)) determined by gel permeation chromatography relative to polystyrene using mean of RI and UV detectors.

The low molecular weight PPFS was synthesized for NMR analysis in order to assign the spectra of the copolymers and the recovered polymers after extraction. The \(\textsuperscript{1}H\) NMR spectrum of PPFS is similar to that of free-radically synthesized polystyrene in the aliphatic region, except that the resonances are
shifted downfield by approximately 0.5 ppm. Both free-radically synthesized and atactic polystyrene exhibit broad resonances at approximately 1.5 ppm due to $CH_2$, and at approximately 2.0 due to $CH$. In contrast, the $CH$ mm triad resonance of isotactic polystyrene appears as a well-defined pentad at approximately 2.2 ppm, and the $CH$ rr triad resonance of syndiotactic polystyrene appears as a well-defined pentad at approximately 1.9 ppm. Both free-radically synthesized polystyrene (atactic) and isotactic polystyrene that has been epimerized to stereochemical equilibrium exhibit less intense resonances, apparently due to the mm triads, as down-field shoulders on the mr + rr $CH$ resonance at 2.0 ppm. Therefore, while atactic polystyrene shows only two resolved resonances in the area between 1.0 and 2.5 ppm, the downfield resonance of the PPFS in $^1$H NMR is a broad singlet that is well-resolved from the other two broad resonances, and therefore it shows three resonances. This spectrum is also nearly identical to that of PPFS produced by atom-transfer radical polymerization, whose propagating radicals undergo primarily reversible termination with bromine radical, rather than termination by combination as in this conventional radical polymerization; i.e. the resonance at 2.75 ppm should not be due to $CH(Ar)-CH(Ar)$ resulting from termination by combination. Therefore, we have assigned the well-resolved $^1$H NMR resonances of PPFS at 2.0, 2.4 and 2.75 ppm to $CH_2$, mr + rr $CH$, and mm $CH$ respectively.

The $^{13}$C NMR spectrum of PPFS is similar to that of free radical synthesized PS. It has a sharp resonance at 32.0 ppm due to $CH_2CHAr$ and a broad multiplet due to $CH_2CHAr$ at 37.0 ppm. The alkyl region of the spectrum has the same
resonances as that of PS, but shifted upfield by 8.0 ppm. In both the PPFS and PS $^{13}$C NMR spectra, the $\text{CH}_2$ resonances are sensitive to the tacticity of the polymer. In the aromatic area, the $^{13}$C NMR spectrum of PPFS showed one sharp singlet at 115.0 ppm, which corresponds to the ipso aromatic carbon (C1) and three doublets centered at 138.0, 140.0 and 145.0 ppm, corresponding to the carbon atoms 2 and 6, 4, and 3 and 5 respectively. These resonances are doublets due to spin-spin coupling between bonded carbon and fluorine nuclei, since the spectra were not collected with carbon-fluorine decoupling.

The $^{19}$F NMR spectrum of PPFS showed three resonances corresponding to the three types of fluorine nuclei present in the polymer. The resonance corresponding to the fluorine atoms closest to the backbone (i.e. attached to aromatic carbons 2 and 6) appear as a broad singlet, while the other resonances are sharp singlets. The proximity of these fluorine nuclei to the polymer backbone is reflected by their broadened resonances. The $^{19}$F NMR spectrum of PPFS is very similar to that of the PFS monomer, all three resonances are very sharp.

The medium molecular weight PPFS ($M_n=10.2 \times 10^3$, $\text{pdi}=1.56$) was used to calibrate the UV detector of the gel permeation chromatograph used to follow this graft copolymerization. We made solutions of different concentrations of PPFS in THF, starting with the highest concentration and diluting to half of the concentration until five solutions were made. The area under the peak on the UV detector was determined with the software and these values were plotted against the concentration of the different solutions. The data points in Figure 3.1 are
linear with a positive slope and an intercept at the origin of the coordinates system. This is a direct consequence of Beer’s law, which states that concentration is directly proportional to absorbance.

The highest molecular weight PPFS ($M_n=22.8 \times 10^3$, $\text{pdi}=1.80$) was used to determine the solubility of PPFS in several solvents in order to isolate the final copolymer products by extractions.

4.2 Grafting of 2,3,4,5,6-Pentafluorostyrene onto Polybutadiene.

4.2.1 Synthesis of Graft Copolymers of 2,3,4,5,6-Pentafluorostyrene onto Polybutadiene.

We grafted copolymers PFS onto PB by polymerizing PFS in the presence of a solution of PB in THF, a good solvent for PB and a fairly good solvent for PPFS with a low chain transfer, using BPO as the radical initiator (Scheme 4.2.) We also attempted this copolymerization using AIBN as the initiator. However, this resulted in a negligible amount of graft copolymer. This phenomenon is consistent with the graft copolymerization of styrene onto PB, with neither polystyryl radicals nor AIBN radicals being capable of abstracting an allylic hydrogen to create a grafting site.$^{113,124,126,127}$

In analogy to the graft copolymerization of styrene, poly(pentafluorostyryl) radicals were not reactive enough to abstract an allylic hydrogen from the PB backbone in order to initiate the graft copolymerization. This fact helped us elucidate the elementary reactions occurring in the graft copolymerization, which are shown in Scheme 4.3.
Scheme 4.2. Synthesis of poly(butadiene-\textit{graft}-pentafluorostyrene) by radical copolymerization of 2,3,4,5,6-pentafluorostyrene in the presence of polybutadiene ($M_n = 1.25 \times 10^5$, pdi = 4.6; 96% 1,4-\textit{cis}, 3.5% 1,4-\textit{trans} and 0.5% 1,2-vinyl content; GPC$_{PS_t}$ $M_n = 3.85 \times 10^5$, pdi = 3.51) in tetrahydrofuran using benzoyl peroxide as the initiator. Grafting is shown only on the 1,4-\textit{cis} repeat units due to their high concentration.

The primary radicals formed from the homolytic cleavage of BPO both initiate polymerization of PFS and abstract a hydrogen atom from the PB backbone forming an allyl radical. Therefore, primary radicals from dissociation of BPO rather than propagating poly(pentafluorostyryl) radicals generate most of the grafting sites. This allyl radical initiates the homopolymerization of PFS, producing a grafted growing radical chain. Since allyl radicals have the same reactivity as benzyl radicals, both should react with PFS in graft initiation and propagation, respectively. Poly(pentafluorostyryl) radicals terminate by combination,$^{30}$ to produce both graft copolymer and ungrafted PPFS homopolymer. The grafted and free PPFS chains should grow and terminate at the same rate since they are in the same conditions of radicals concentration, temperature and pressure. Therefore, the average length of the grafts and the ungrafted PPFS homopolymer should be equal. The possibility of crosslinking
coupling of two growing grafted chains is very low due to the high dilution conditions of these copolymerizations and was not included. We did not include any other chain transfer reactions, such as chain transfer to monomer, polymer and or solvent in this scheme.

We initially performed this copolymerization in a single Schlenk tube equipped with a rubber septum, from which aliquots were withdrawn periodically with a syringe and needle for chromatographic analysis. The problem with this technique was that the rubber septum was permeable to oxygen due to swelling, especially at the highest temperature used (i.e. 80 °C), which caused low conversion of the monomer and lower molecular weight of the grafts and homopolymer. We then tried single-use polymerization tubes that were sealed under vacuum. The problem with the flame-sealed tubes was the polymer (PB, PPFS or grafted copolymer) climbed the neck of the reactor and precipitated in the cooler regions such that they were unavailable for further reaction. This occurred primarily in the lowest temperature (i.e. 50 °C) reactions. Both systems led to poor reproducibility of the results. We then used round bottom glass reactors sealed to a glass tube, which were degassed and sealed under vacuum. Every tube was used for only one analysis, minimizing the introduction of oxygen in the copolymerization medium. The attachment of the round bottom flask enabled continuous stirring of the mixture, thereby avoiding precipitation of polymer in the neck.
Scheme 4.3. Proposed elementary reactions for the graft copolymerization of polybutadiene with 2,3,4,5,6-pentafluorostyrene using benzoyl peroxide as the initiator.
We carried out the graft copolymerization under five different experimental conditions to yield the graft copolymers poly(butadiene-\textit{graft}-pentafluorostyrene). In all of them, the concentration of PB backbone (0.36 M repeat units), PFS monomer (0.70 M) and solvent were constant. We investigated the copolymerization at three different temperatures, maintaining constant BPO concentration (18 mM, 5 mol% relative to PB units concentration), which corresponded to the series of experiments labeled PB-g-PPFS-50/5, PB-g-PPFS-60/5 and PB-g-PPFS-80/5. We also investigated the effect of the initiator concentration at a constant temperature of 60 °C, which were the experiments labeled PB-g-PPFS-60/2.5, PB-g-PPFS-60/5 and PB-g-PPFS-60/10. Table 4.2 displays how the compositions of the five different experimental conditions were designed to study the effect of these two variables on the copolymerizations.

Table 4.2. Experimental conditions of the five different graft copolymerizations of 2,3,4,5,6-pentafluorostyrene (PFS) onto polybutadiene (PB). First number in experiment name corresponds to the temperature (°C) of the experiment and the second corresponds to the amount of initiator expressed as mol% of benzoyl peroxide initiator used relative to PB units; increase of temperature observed on horizontal and initiator on vertical.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-g-PFS-60/2.5</td>
<td>T = 60 °C</td>
<td>2.5% BPO</td>
</tr>
<tr>
<td>PB-g-PFS-50/5</td>
<td>T = 50 °C</td>
<td>5.0% BPO</td>
</tr>
<tr>
<td>PB-g-PFS-60/5</td>
<td>T = 60 °C</td>
<td>5.0% BPO</td>
</tr>
<tr>
<td>PB-g-PFS-80/5</td>
<td>T = 80 °C</td>
<td>5.0% BPO</td>
</tr>
<tr>
<td>PB-g-PFS-60/10</td>
<td>T = 60 °C</td>
<td>10% BPO</td>
</tr>
</tbody>
</table>
We used in our study the method previously proposed by Huang and Sundberg to follow the graft copolymerization of styrene onto PB. The advantage of this method is the ability to follow the graft copolymerization and determine all of the characterization parameters described without separating and/or purifying the final copolymer product, which is a procedure that normally leads to experimental error and low reproducibility of the results. Aliquots were taken directly from the polymerization medium, diluted in the presence of a radical inhibitor to stop the reaction, and injected into a gel permeation chromatograph equipped with two detectors: an RI and a tunable UV-vis detector set at 254 nm (UV region). The method takes an advantage of the fact that PB does not absorb significantly in the UV-vis region relative to the strong absorbance shown by PPFS.

![Detector Response](image)

**Figure 4.1.** Gel permeation chromatography UV detector (254 nm) responses of samples taken at 0 and 24 h from the grafting reaction of polybutadiene (PB) with pentafluorostyrene (PFS) in the presence of 5 mol% benzoyl peroxide (BPO) in tetrahydrofuran at 60 °C. Reaction composition: 0.36 M PB, 0.70 M PFS, 18 mM BPO.
Figure 4.1 shows the UV-detected GPC chromatogram of samples taken at the beginning (t=0 h) and after 24 h for one of the experiments under the conditions of PB-g-PPFS-60/5. The GPC chromatogram corresponding to the beginning of the reaction showed no absorbance peaks, which demonstrates that PB does not absorb at 254 nm relative to the absorbance of PFS. At the beginning of the process, there was no PPFS present, only PB and PFS monomer, which elutes at a higher volume (lower molecular weight) than the range displayed in the figure. After 24 h of reaction, the GPC chromatogram showed two well-defined peaks. At this time the polymerization of PFS has already taken place. The first peak corresponds to the graft copolymer, and its appearance is due to the the PPFS grafts and not the backbone. (PB does not absorb in the UV detector compared to the PPFS.) The second peak at higher elution volume and therefore at a lower molecular weight, corresponds to the PPFS homopolymer.

In order to confirm that the first peak of the chromatogram taken at 24 h is not due to any other possibility such as oxidation, we repeated the experiment without an initiator. The chromatograms showed no peaks, which also demonstrates that PFS does not polymerize by thermal initiation.

The molecular weight of the first peak is higher, albeit similar, to that of the PB homopolymer and the RI chromatogram showed that same peak with a higher intensity due to the ability of PB to absorb in this detector (similar ratio of areas should be observed between the two peaks if it was only homopolymer). Therefore, the first peak must be due to the absorbance of the grafts and not to higher molecular weight homopolymer.
The two peaks were very well resolved, and therefore we did not need any curve fitting and/or band deconvolution, as was previously reported necessary.\textsuperscript{110} In fact, if we used a ratio of PB to PFS of 1:1 instead of the 1:2, the resolution was not as good.

![Figure 4.2. UV-detected (254 nm) gel permeation chromatography responses of samples taken every 12 h from the grafting of poly(butadiene) (PB) with pentafluorostyrene (PFS) in tetrahydrofuran at 60 °C in the presence of benzoyl peroxide (BPO) (5 mol\% relative to PB). Experiment name: PB-g-PFS-60/5. Reaction composition: 0.36 M PB, 0.70 M PFS, 18 mM BPO. Arrow indicates increasing copolymerization time.](image)

Figure 4.2 presents the superimposed UV-detected traces of the graft copolymerization of PFS on PB at 60 °C, with 5\% mol BPO (PB-g-PPFS-60/5) for aliquots taken every 12 h of the graft copolymerization. They all showed two well-defined peaks, whose area increased with time up to a point at which the formation of PPFS, either grafted or free, leveled off, as demonstrated by the constant area of the peaks. Using the calibration of the UV detector response for
PPFS concentration and the amount of sample injected, the amounts of grafted copolymer and free PPFS were calculated from the areas under the peaks.

![Graph showing monomer conversion](image)

Figure 4.3. 2,3,4,5,6-Pentafluorostyrene (PFS) monomer conversion at 50, 60 and 80 °C in tetrahydrofuran in the presence of polybutadiene (PB) and benzoyl peroxide (BPO, 5 mol% relative to PB) as initiator as a function of copolymerization time. Monomer conversions determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS, 18 mM of BPO); mean values and standard deviations presented from triplicate experiments.

4.2.2 Monomer Conversion.

We used equation 3.1 to determine the monomer conversion for each set of three experiments by the GPC UV-detected method, by calculating the amount of PPFS formed from the area of the two peaks and the calibration curve. The monomer conversion was determined every 12 h. Figure 4.3 shows the effect of the temperature on the GPC-determined monomer conversions, using a constant amount of initiator of (5% mol of BPO relative to PB repeat units). Figure 4.4
presents the effect of increased initiator concentration at a constant temperature of 60 °C.

![Graph](image)

Figure 4.4. 2,3,4,5,6-Pentafluorostyrene (PFS) monomer conversion at 60 °C in tetrahydrofuran in the presence of polybutadiene (PB), using 2.5, 5 and 10 mol% benzoyl peroxide (BPO) (relative to PB repeat units) as initiator as a function of copolymerization time. Monomer conversions determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS, 18 mM of BPO); mean values and standard deviations presented from triplicate experiments.

As expected, the maximum conversions achieved increased with both increasing initiator concentration and increasing temperature due to the increasing concentration of primary radicals. In all the cases, the monomer conversion leveled off after 24 or 36 h, except at the highest temperature. At 80 °C, the maximum monomer conversion was achieved before 12 h; we therefore took the first aliquot from the PB-g-PPFS-80/5 experiment at 6 h.
Table 4.3 summarizes the average values of the monomer conversions for each set of triplicate experiments as a function of time, and compares them to the monomer conversions values determined gravimetrically, which are as the average of two experiments each. The gravimetric values were determined by precipitation of the final product at every 12 h, followed by recovery of the product and determination of the amount of PPFS produced (grafted and homopolymer) by the difference between the total weight of the final product and the known amount of PB backbone present in the sample. The conversions determined from the GPC method are slightly higher than those determined gravimetrically, which always includes unavoidable mechanical losses and incomplete precipitation of the final products.

We determined the initial rates of polymerization for the copolymerizations at 60 °C. Figure 4.5 presents the initial rate of polymerization \( R_p = -d[M]/dt \) as a function of the product of the monomer concentration \([M]\) and the square root of the initiator concentration \([I]^{1/2}\) at 60 °C. Although our data has only three initiator concentrations, the linear dependence of \( R_p \) vs \([M][I]^{1/2}\) demonstrates that the homo- and copolymerization of PFS follows typical radical polymerization kinetics.
Table 4.3. Comparison of monomer conversion determined gravimetrically and from gel permeation chromatography (GPC) injections directly from the grafting reactions of polybutadiene (PB) with pentafluorostyrene (PFS) in tetrahydrofuran using benzoyl peroxide (BPO) as the initiator. Results for GPC values are average of three measurements. Gravimetrical results were performed twice. First three rows correspond to an increase in the initiator concentration at constant temperature (T=60 °C), and second three rows correspond to those experiments at constant BPO concentration (5% mol relative to PB) with an increase in the temperature.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Conversion (%) Method</th>
<th>Copolymerization Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>GPC</td>
<td>-</td>
<td>6.2</td>
</tr>
<tr>
<td>PB-g-PPFS-60/2.5</td>
<td>Gravimetrically</td>
<td>-</td>
</tr>
<tr>
<td>GPC</td>
<td>-</td>
<td>11.5</td>
</tr>
<tr>
<td>PB-g-PPFS-60/5</td>
<td>Gravimetrically</td>
<td>-</td>
</tr>
<tr>
<td>GPC</td>
<td>-</td>
<td>15.6</td>
</tr>
<tr>
<td>PB-g-PPFS-60/10</td>
<td>Gravimetrically</td>
<td>-</td>
</tr>
<tr>
<td>GPC</td>
<td>-</td>
<td>6.5</td>
</tr>
<tr>
<td>PB-g-PPFS-50/5</td>
<td>Gravimetrically</td>
<td>-</td>
</tr>
<tr>
<td>GPC</td>
<td>-</td>
<td>11.5</td>
</tr>
<tr>
<td>PB-g-PPFS-60/5</td>
<td>Gravimetrically</td>
<td>-</td>
</tr>
<tr>
<td>GPC</td>
<td>15.9</td>
<td>53.9</td>
</tr>
<tr>
<td>PB-g-PPFS-80/5</td>
<td>Gravimetrically</td>
<td>15.0</td>
</tr>
</tbody>
</table>
Figure 4.5. Dependence of the initial rate of polymerization \( R_p \) as a function of the product of the monomer concentration ([M]) and the square root of the initiator concentration \([I]^{1/2}\) in the graft copolymerization of polybutadiene (PB) with pentfluorostyrene (PFS) in tetrahydrofuran using 2.5, 5 and 10 mol\% benzoyl peroxide (BPO) (relative to PB) as the initiator at 60 °C. \( R_p \) was determined from triplicate measurements of the conversion of PFS by UV-detected gel permeation chromatography.

4.2.3 Grafting Parameters Characterizing the Graft Copolymerizations.

We used the GPC UV-detected method proposed by Huang and Sundberg\textsuperscript{126} to calculate the PFS grafting efficiency (GE) and the PFS grafting ratio (GR) from the values of the integrated areas of the peaks in the UV chromatograms, after converting them with the calibration for PPFS concentration, and applying equations 3.2 and 3.3 respectively. Tables 4.4 and 4.5 show respectively the average GE and GR values for each time and triplicate GPC UV-detected experiments.

The GE is the ratio between the amount of monomer incorporated into the grafts and the total amount of monomer consumed (sum of monomer in grafts +
monomer in free homopolymer chains). Therefore the GE relates to the competition between allyl radicals (leading to grafted chains) and benzyl radicals (leading to the formation of free homopolymer chains) initiating the polymerization of PFS.

Figures 4.6 and 4.7 plot the data in Table 4.4 showing the effect on GE of increased initiator concentration at constant temperature of 60 °C, and the effect on GE of increased temperature at constant initiator concentration of 5% mol of BPO (relative to PB repeat units), respectively.

Figure 4.6. Pentafluorostyrene (PFS) grafting efficiency (GE) at 60 °C in tetrahydrofuran using 2.5, 5 and 10 mol% benzoyl peroxide (BPO) (relative to polybutadiene (PB)) as initiator as a function of copolymerization time. GE determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS, 18 mM of BPO); mean values and standard deviations presented from triplicate experiments.
Table 4.4. Variation of the grafting efficiency (defined by equation 3.2) of pentfluorostyrene (PFS) as a function of time in graft copolymerizations of polybutadiene (PB) and PFS in tetrahydrofuran in the presence of benzoyl peroxide (BPO) as the initiator. Mean values and standard deviations from gel permeation chromatography injections of copolymerizations performed in triplicate.

<table>
<thead>
<tr>
<th>Experiment a</th>
<th>Copolymerization Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td>PB-g-PPFS-60/2.5</td>
<td>0.092 ± 0.101 ± 0.083 ± 0.080 ± 0.077 ±</td>
</tr>
<tr>
<td></td>
<td>0.004</td>
</tr>
<tr>
<td>PB-g-PPFS-60/5</td>
<td>0.103 ± 0.099 ± 0.099 ± 0.098 ± 0.097 ±</td>
</tr>
<tr>
<td></td>
<td>0.002</td>
</tr>
<tr>
<td>PB-g-PPFS-60/10</td>
<td>0.085 ± 0.079 ± 0.063 ± 0.065 ± 0.060 ±</td>
</tr>
<tr>
<td></td>
<td>0.009</td>
</tr>
<tr>
<td>PB-g-PPFS-50/5</td>
<td>0.103 ± 0.097 ± 0.094 ± 0.102 ± 0.105 ±</td>
</tr>
<tr>
<td></td>
<td>0.016</td>
</tr>
<tr>
<td>PB-g-PPFS-60/5</td>
<td>0.103 ± 0.099 ± 0.099 ± 0.098 ± 0.097 ±</td>
</tr>
<tr>
<td></td>
<td>0.002</td>
</tr>
<tr>
<td>PB-g-PPFS-80/5</td>
<td>0.078 ± 0.080 ± 0.078 ± 0.075 ± 0.071 ± 0.070 ±</td>
</tr>
<tr>
<td></td>
<td>0.007</td>
</tr>
</tbody>
</table>

a First number in the experiment name corresponds to the copolymerization temperature (°C); second number corresponds to the mol% of BPO initiator used relative to PB repeat units.
Table 4.5. Variation of the grafting ratio (defined by equation 3.3) of pentfluorostyrene (PFS) as a function of time in graft copolymerizations of polybutadiene (PB) and PFS in tetrahydrofuran in the presence of benzoyl peroxide (BPO) as the initiator. Mean values and standard deviations from gel permeation chromatography injections of copolymerizations performed in triplicate.

<table>
<thead>
<tr>
<th>Experiment $^a$</th>
<th>Copolymerization Time (h)</th>
<th>6</th>
<th>12</th>
<th>24</th>
<th>36</th>
<th>48</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-g-PPFS-60/2.5</td>
<td>0.040 ± 0.075 ± 0.150 ± 0.161 ± 0.154 ±</td>
<td>0.011</td>
<td>0.008</td>
<td>0.012</td>
<td>0.003</td>
<td>0.009</td>
<td></td>
</tr>
<tr>
<td>PB-g-PPFS-60/5</td>
<td>0.083 ± 0.173 ± 0.251 ± 0.268 ± 0.268 ±</td>
<td>0.021</td>
<td>0.010</td>
<td>0.019</td>
<td>0.006</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>PB-g-PPFS-60/10</td>
<td>0.095 ± 0.181 ± 0.183 ± 0.213 ± 0.214 ±</td>
<td>0.030</td>
<td>0.074</td>
<td>0.014</td>
<td>0.013</td>
<td>0.051</td>
<td></td>
</tr>
<tr>
<td>PB-g-PPFS-50/5</td>
<td>0.047 ± 0.110 ± 0.135 ± 0.164 ± 0.170 ±</td>
<td>0.009</td>
<td>0.032</td>
<td>0.014</td>
<td>0.011</td>
<td>0.021</td>
<td></td>
</tr>
<tr>
<td>PB-g-PPFS-60/5</td>
<td>0.083 ± 0.173 ± 0.251 ± 0.268 ± 0.268 ±</td>
<td>0.021</td>
<td>0.010</td>
<td>0.019</td>
<td>0.006</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>PB-g-PPFS-80/5</td>
<td>0.088 ± 0.305 ± 0.318 ± 0.309 ± 0.297 ± 0.279 ±</td>
<td>0.006</td>
<td>0.030</td>
<td>0.008</td>
<td>0.014</td>
<td>0.032</td>
<td>0.015</td>
</tr>
</tbody>
</table>

$^a$ First number in the experiment name corresponds to the copolymerization temperature (°C); second number corresponds to the mol% of BPO initiator used relative to PB repeat units.
Huang and Sundberg reported that grafting systems that terminate by combination and in which the grafting site is created by chain transfer of the primary initiator radical show increased GE with monomer conversion. Therefore there should be an increase in GE with the monomer conversion and in turn with time (Section 4.3.) However, the GE either decreased with increased time or did not vary with time within experimental error.

![Grafting Efficiency Graph](image)

Figure 4.7. Pentafluorostyrene (PFS) grafting efficiency (GE) at 50, 60 and 80 °C in tetrahydrofuran (THF) in the presence of polybutadiene (PB) and benzoyl peroxide (BPO) (5 mol% relative to PB) as initiator as a function of copolymerization time. GE was determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS, 18 mM of BPO); mean values and standard deviations presented from triplicate experiments.

GE seemed to decrease with increasing temperature at least when comparing the results at 60 and 80 °C. The effect of initiator concentration at a constant temperature was not very consistent, which indicates that GE does not depend on this variable. According to Huang and Sundberg\textsuperscript{120} this characterizes a
system whose graft site is initiated by primary initiator radicals and whose propagating radicals terminating by combination.

The grafting ratio (GR) measures the amount of grafted PFS in the final copolymer product, averaged over all of the PB chains, included those that may not have been grafted. Figures 4.8 and 4.9 plot the data in Table 4.5 and show the effects of initiator concentration and temperature, respectively.

![Diagram of grafting ratio vs. time](image)

**Figure 4.8.** Pentafluorostyrene (PFS) grafting ratio at 60 °C in tetrahydrofuran using 2.5, 5 and 10 mol% benzoyl peroxide (BPO) as initiator relative to polybutadiene (PB) repeat units as a function of copolymerization time. Determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS, 18 mM of BPO); mean values and standard deviations presented from triplicate experiments.

GR values increase steadily with time. The GR increases markedly with temperature and with initiator concentration, at least from 2.5 to 5 mol % of BPO relative to PB repeat units.
Table 4.6 summarizes all of the grafting parameters, including the GE from Table 4.5 averaged over time, and the maximum GR from Table 4.5. The GEs are never higher than 12%, and seem to decrease with increasing temperature, at least when comparing the values at 60 and 80 ºC. They also do not seem to depend on the initiator concentration.

The increased amount of primary radicals formed with both increasing initiator concentration and temperature has an important effect on the GR. An increase of the temperature from 50 to 80 ºC almost doubles the GR value. An increase of the initiator concentration from 2.5 to 5 mol% relative to PB backbone repeat units produces as similar doubling effect. A further increase to 10% mol
of BPO had little or almost no effect on the GR value. The maximum GR values were never higher than 32%.

The grafting frequency and, in turn, the number of PPFS grafted chains per PB backbone may be calculated provided the lengths of the grafts are known. The grafting frequency (equation 3.4) can also be calculated if the length of the grafts is known. As discussed above, the lengths of the grafted and ungrafted PPFS chains should be equal under dilute conditions since the initiating sites have similar reactivities, and the two types of chains are in similar environments and should therefore propagate and terminate by combination at similar rates. Table 4.6 summarizes the presumed lengths of the PPFS grafts, the resulting number of grafted PPFS chains per PB backbone, and therefore the grafting frequency from each copolymerization. It demonstrates that the number of grafts increases with increasing polymerization temperature and increasing initiator concentration due to the greater amount of radicals generated, and that the average number of backbone repeat units (grafting frequency) between grafts decreases.

4.2.4 Length of the Grafted Poly(2,3,4,5,6-pentafluorostyrene) Chains.

We assumed that the length of the grafts was the same as the length of the ungrafted PPFS chains. Table 4.7 summarizes the number-average molecular weight values of the ungrafted PPFS chains obtained by direct injections done every 12 h of the graft copolymerizations in the gel permeation chromatograph and the pdi values.
Table 4.6. Grafting parameters characterizing the poly(butadiene-graft-pentafluorostyrene)s (PB-g-PPFS) produced in the graft copolymerizations of poly(butadiene) (PB) with pentafluorostyrene (PFS) in tetrahydrofuran using benzoyl peroxide (BPO) as the initiator. Mean values and standard deviations from copolymerizations performed in triplicate.

<table>
<thead>
<tr>
<th>Experiment a</th>
<th>Average PFS Grafting Efficiency b</th>
<th>Maximum PFS Grafting Ratio c</th>
<th>Number of Grafted PPFS Chains per PB Backbone</th>
<th>PFS Grafting Frequency d</th>
<th>DPn of PPFS grafts e</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-g-PPFS- 60/2.5</td>
<td>0.087 ± 0.009</td>
<td>0.161 ± 0.003</td>
<td>1.82 ± 0.03</td>
<td>1424 ± 24</td>
<td>62.9 ± 6.0</td>
</tr>
<tr>
<td>PB-g-PPFS- 60/5</td>
<td>0.099 ± 0.002</td>
<td>0.268 ± 0.011</td>
<td>4.41 ± 0.21</td>
<td>588 ± 28</td>
<td>46.5 ± 1.0</td>
</tr>
<tr>
<td>PB-g-PPFS- 60/10</td>
<td>0.070 ± 0.011</td>
<td>0.214 ± 0.051</td>
<td>5.70 ± 0.52</td>
<td>454 ± 41</td>
<td>28.7 ± 0.7</td>
</tr>
<tr>
<td>PB-g-PPFS- 50/5</td>
<td>0.100 ± 0.004</td>
<td>0.170 ± 0.021</td>
<td>2.13 ± 0.20</td>
<td>1217 ± 114</td>
<td>72.2 ± 2.6</td>
</tr>
<tr>
<td>PB-g-PPFS- 60/5</td>
<td>0.099 ± 0.002</td>
<td>0.268 ± 0.011</td>
<td>4.41 ± 0.21</td>
<td>588 ± 28</td>
<td>46.5 ± 1.0</td>
</tr>
<tr>
<td>PB-g-PPFS- 80/5</td>
<td>0.075 ± 0.004</td>
<td>0.318 ± 0.008</td>
<td>4.90 ± 0.10</td>
<td>519 ± 16</td>
<td>43.3 ± 2.0</td>
</tr>
</tbody>
</table>

a First number in the experiment name corresponds to the copolymerization temperature (°C); second number corresponds to the mol% of BPO initiator used relative to PB repeat units.
b Defined by equation 3.2, mean of values in Table 4.4
c Defined by equation 3.3, maximum values in Table 4.5
d Defined by equation 3.4.
e Number average degree of polymerization (DPn) of grafted PPFS assumed to be equal to ungrafted PPFS from graft copolymerization injection at 60 h, as determined by GPC relative to PS standards, averaged over triplicate experiments.
Table 4.7. Number-average molecular weights ($M_n$) and polydispersities (pdi=$M_w/M_n$) of ungrafted poly(pentafluorostyrene) (PPFS) homopolymer measured by direct gel permeation chromatography (GPC) injections of the graft copolymerizations of poly(butadiene) (PB) and pentafluorostyrene (PFS) in tetrahydrofuran (THF) in the presence of benzoyl peroxide (BPO) as the initiator. Mean values and standard deviations from copolymerizations performed in triplicate.

<table>
<thead>
<tr>
<th>Experiment a</th>
<th>$M_n \times 10^3$ and (pdi) as a function of Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td>PB-g-PPFS-60/2.5</td>
<td>14.7 ± 13.7 ± 13.3 ± 12.3 ± 12.2 ± 0.62 1.47 0.58 0.76 0.81</td>
</tr>
<tr>
<td></td>
<td>(1.67 ± 1.57 ± 1.57 ± 1.54 ± 1.56 ± 0.01) (0.04) (0.01) (0.03) (0.02)</td>
</tr>
<tr>
<td>PB-g-PPFS-60/5</td>
<td>12.2 ± 10.7 ± 10.5 ± 9.83 ± 8.87 ± 1.04 0.65 0.30 0.29 0.35</td>
</tr>
<tr>
<td></td>
<td>(1.67 ± 1.49 ± 1.62 ± 1.81 ± 1.71 ± 0.12) (0.05) (0.01) (0.03) (0.01)</td>
</tr>
<tr>
<td>PB-g-PPFS-60/10</td>
<td>7.90 ± 6.53 ± 6.00 ± 5.73 ± 5.57 ± 2.00 1.01 0.78 0.15 0.21</td>
</tr>
<tr>
<td></td>
<td>(1.54 ± 1.65 ± 1.73 ± 1.68 ± 1.73 ± 0.10) (0.07) (0.02) (0.08) (0.01)</td>
</tr>
</tbody>
</table>

a First number in the experiment name corresponds to the copolymerization temperature (°C); second number corresponds to the mol% of BPO initiator used relative to PB repeat units for experiments carried at 60 °C in the presence of BPO 2.5, 5 and 10 mol% relative to PB repeat units.
Table 4.7. (Continuation)

<table>
<thead>
<tr>
<th>Experiment  (a)</th>
<th>(M_n \times 10^{-3}) and ((\text{pdi})) as a function of Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td>PB-(g)-PPFS-50/5</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>18.8 ±</td>
</tr>
<tr>
<td></td>
<td>2.60 ±</td>
</tr>
<tr>
<td></td>
<td>(1.57 ±</td>
</tr>
<tr>
<td></td>
<td>0.01)</td>
</tr>
<tr>
<td>PB-(g)-PPFS-60/5</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>12.2 ±</td>
</tr>
<tr>
<td></td>
<td>1.04 ±</td>
</tr>
<tr>
<td></td>
<td>(1.67 ±</td>
</tr>
<tr>
<td></td>
<td>0.12)</td>
</tr>
<tr>
<td>PB-(g)-PPFS-80/5</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>11.7 ±</td>
</tr>
<tr>
<td></td>
<td>0.76 ±</td>
</tr>
<tr>
<td></td>
<td>(1.62 ±</td>
</tr>
<tr>
<td></td>
<td>0.02)</td>
</tr>
</tbody>
</table>
Figure 4.10. Number average molecular weight ($M_n$) of grafts of poly(pentafluorostyrene) (PPFS) at 60 °C of poly(butadiene-graft-pentafluorostyrene) (PB-g-PPFS) synthesized in tetrahydrofuran in the presence of polybutadiene (PB) and benzoyl peroxide (BPO, 2.5, 5 and 10 mol% relative to PB) as initiator as a function of copolymerization time. PPFS chains length determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS; 9.0, 18 and 36 mM of BPO); mean values and standard deviations presented from triplicate experiments. Assumed that length of the grafted PPFS is same as length of ungrafted PPFS.

Figure 4.10 presents the length of the initiator concentration increase at a constant temperature of 60 °C. Figure 4.11 plots the length of the grafted chains vs. time increasing the temperature at a constant initiator concentration (5 mol% relative to PB repeat units.) The molecular weight decreases with time as a consequence of the decrease in the monomer to initiator concentration ratio as a radical polymerization proceeds.\textsuperscript{172} Increasing the number of primary radicals, due to an increased temperature and/or initiator concentration, decreases the
length of the grafts. The pdi values are all between 1.54 and 1.88, corresponding to polymers that terminate primarily by combination.\(^{172}\)

![Figure 4.11. Number average molecular weight ($M_n$) of grafts of poly(pentafluorostyrene) (PPFS) at 50, 60 and 80 °C of poly(butadiene-\textit{graft}-pentafluorostyrene) (PB-\textit{g}-PPFS) synthesized in tetrahydrofuran in the presence of polybutadiene (PB) and benzoyl peroxide (BPO, 5 mol% relative to PB) as initiator as a function of copolymerization time. PPFS chains length determined by UV-detected gel permeation chromatography (0.36 M PB, 0.70 M PFS, 18 mM of BPO); mean values and standard deviations presented from triplicate experiments. Assumed that length of the grafted PPFS is same as length of ungrafted PPFS.]

4.3 Isolation of Grafted Copolymers of 2,3,4,5,6-Pentafluorostyrene onto Polybutadiene.

The GPC UV-detected method is a very useful analytical method to follow and characterize the entire copolymerization process and to observe the effect of varying the temperature and/or the initiator concentration. However, to study the properties of the graft copolymer products it was necessary to separate the graft copolymer from the PB and PPFS homopolymers present in the final product mixture.
One of the biggest challenges was to find a good solvent system for separating the components of the final product mixture. Table 4.8 summarizes our solubility tests of PPFS, the PB homopolymer used throughout this study, and one of the purified graft copolymers (PB-g-PPFS-60/5), whose solubility was initially tested on the crude (unpurified) product (or mixture of products). However, the crude product solubility is similar to that of PPFS, which was the major component of this final products mixture, and therefore we report the solubility of the purified final copolymer product.

There are several solvents that provide selective dissolution of one of the homopolymers without dissolving the graft copolymer and/or the other homopolymer. For example, acetone and \( \alpha,\alpha,\alpha \)-trifluorotoluene selectively dissolve PPFS without dissolving either PB or the graft copolymer. We chose acetone due to low its cost and high volatility. Benzene, carbon tetrachloride, chloroform, 1,2-dichlorobenzene and hexanes are candidates for selectively extracting PB without dissolving PPFS or the graft copolymer. Hexanes was the most appropriate due to its low cost, high volatility and availability.

We were able to isolate the graft copolymers from up to a trace amount (< 5%) of unreacted PB and a large amount of the PPFS homopolymer byproduct, respectively, by extracting the crude products with hexanes at room temperature for 6 h periods to constant weight (generally 24 h), and then with acetone at room temperature for 12 h periods to constant weight (generally 36 h).
Table 4.8. Solubility of 20 mg polybutadiene (PB), poly(pentafluorostyrene) (PPFS), and poly(butadiene-*graft*-pentafluorostyrene) (PB-*g*-PPFS) in 20 mL solvent after 6 h at room temperature. Number-average molecular weights ($M_n$) and polydispersity index (pdi = $M_w/M_n$) determined by gel permeation chromatography relative to polystyrene: PB used for grafting, $M_n = 3.85 \times 10^5$, pdi = 3.51; PPFS, $M_n = 2.28 \times 10^4$, pdi = 1.80 (mean of UV & RI detectors); PB-*g*-PPFS-60/5, $M_n = 2.45 \times 10^5$, pdi = 1.63 (mean of UV & RI detectors), grafting efficiency = 0.097, grafting ratio = 0.268. +++ = soluble, + = partially soluble, - = insoluble.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>PB</th>
<th>PPFS</th>
<th>PB-<em>g</em>-PPFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Benzene</td>
<td>+++</td>
<td>-(^a)</td>
<td>-(^a)</td>
</tr>
<tr>
<td>n-Butyl Acetate</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>CCl(_4)</td>
<td>+++</td>
<td>-</td>
<td>-(^b)</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>+(^a)</td>
<td>-</td>
<td>-(^a)</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>+++</td>
<td>-</td>
<td>+(^a)</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>+(^a)</td>
<td>+++</td>
<td>+(^b)</td>
</tr>
<tr>
<td>1,2-Dichlorobenzene</td>
<td>+++</td>
<td>-</td>
<td>-(^b)</td>
</tr>
<tr>
<td>N,N-Diethylacetamide</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dimethylsulfoxide</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>-</td>
<td>+++</td>
<td>+(^a)</td>
</tr>
<tr>
<td><strong>Hexanes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>-</td>
<td>-</td>
<td>-(^b)</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
<td>-(^c)</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>Methyl Sulfoxide</td>
<td>-</td>
<td>-</td>
<td>-(^b)</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) swells
\(^b\) disperses
\(^c\) dissolves if heated
Table 4.8. (Continuation.)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>PB</th>
<th>PPFS</th>
<th>PB-g-PPFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,2,4-Trichlorobenzene</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,1,2-Trichloro-2,2,1-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Trifluoroethane</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>α,α,α-Trifluorotoluene</td>
<td>-</td>
<td>+++</td>
<td>-</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>+++</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>Toluene</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>σ-Xylene</td>
<td>+++</td>
<td>+++</td>
<td>+</td>
</tr>
</tbody>
</table>

In contrast to the trace amounts of unreacted PB homopolymer, up to 80% of the PPFS in the graft copolymerization mixtures was homopolymer. Table 4.9 summarizes the results obtained for the maximum conversions as determined by the two methods, the amount of PPFS homopolymer present in the final products and the amount of PPFS homopolymer extracted from the crude graft copolymers after acetone extraction, expressed in percentage weight loss. These two values agree well. However, the amount of PPFS isolated from the extract by precipitation is less than 75%, and generally decreased with decreasing molecular weight of PPFS. However, the molecular weight of the recovered PPFS is only slightly higher than that of the PPFS homopolymer measured by direct injection of the copolymerization mixtures into the GPC. This small increase is probably due to incomplete precipitation of the lowest molecular
weight portions. The pdi values of the extracted PPFS are between 1.51 and 1.66, consistent with termination primarily by combination.\textsuperscript{30,172}

Table 4.9. Comparison of the amount of poly(2,3,4,5,6-pentafluorostyrene) (PPFS) homopolymer generated in the graft copolymerizations of polybutadiene (PB) with pentafluorostyrene (PFS) at final conversion with that extracted with acetone at room temperature. Graft copolymerizations performed in triplicate in tetrahydrofuran using benzoyl peroxide as the initiator; 24-36 h extractions to constant weight loss. Only one of each of the three set of samples was purified.

<table>
<thead>
<tr>
<th>Experiment a</th>
<th>Monomer Conversion (%)</th>
<th></th>
<th>Fraction Crude Sample that is Homopolymer (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>GPC</td>
<td>Gravimetrically</td>
</tr>
<tr>
<td>PB-(g)-PPFS-60/2.5</td>
<td>28.4 ± 0.96</td>
<td>22.3</td>
<td>61.7</td>
</tr>
<tr>
<td>PB-(g)-PPFS-60/5</td>
<td>39.3 ± 1.96</td>
<td>39.0</td>
<td>73.8</td>
</tr>
<tr>
<td>PB-(g)-PPFS-60/10</td>
<td>50.1 ± 3.10</td>
<td>43.1</td>
<td>75.7</td>
</tr>
<tr>
<td>PB-(g)-PPFS-50/5</td>
<td>22.7 ± 1.50</td>
<td>19.3</td>
<td>58.3</td>
</tr>
<tr>
<td>PB-(g)-PPFS-60/5</td>
<td>39.3 ± 1.96</td>
<td>39.0</td>
<td>73.8</td>
</tr>
<tr>
<td>PB-(g)-PPFS-80/5</td>
<td>56.2 ± 3.25</td>
<td>56.5</td>
<td>80.3</td>
</tr>
</tbody>
</table>

\(a\) First number in the experiment name corresponds to the copolymerization temperature \((\degree\text{C})\); second number corresponds to the mol\% of BPO initiator used relative to PB repeat units.
<table>
<thead>
<tr>
<th>Experiment a</th>
<th>Graft Copolymer Weight Loss After Extraction (%)</th>
<th>Fraction PPFS Homopolymer Recovered b (wt%)</th>
<th>Extracted PPFS Homopolymer b $M_n \times 10^{-3}$ (pdi)c</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-g-PPFS-60/2.5</td>
<td>68.0</td>
<td>72.5</td>
<td>12.3 (1.66)</td>
</tr>
<tr>
<td>PB-g-PPFS-60/5</td>
<td>69.0</td>
<td>71.0</td>
<td>10.4 (1.60)</td>
</tr>
<tr>
<td>PB-g-PPFS-60/10</td>
<td>71.0</td>
<td>52.0</td>
<td>5.73 (1.51)</td>
</tr>
<tr>
<td>PB-g-PPFS-50/5</td>
<td>56.0</td>
<td>71.5</td>
<td>14.9 (1.63)</td>
</tr>
<tr>
<td>PB-g-PPFS-60/5</td>
<td>69.0</td>
<td>71.0</td>
<td>10.4 (1.60)</td>
</tr>
<tr>
<td>PB-g-PPFS-80/5</td>
<td>71.4</td>
<td>54.5</td>
<td>9.15 (1.60)</td>
</tr>
</tbody>
</table>

a Recovered by precipitation of the concentrated extract in methanol.
b Number-average molecular weight ($M_n$), weight-average molecular weight ($M_w$) and polydispersity (pdi = $M_w/M_n$) determined by gel permeation chromatography relative to polystyrene using mean of RI and UV detectors.

tWe also tried Soxhlet extractions to separate the final components of the product mixture. Extraction of this kind with hexanes or acetone extracts both PB or PPFS homopolymer, respectively, and a significant amount of graft copolymer, especially if extracted for longer times, evidently due to the higher temperature of the condensing solvent, and a more continuous flow of fresh solvent onto the sample.
Figure 4.12. $^1$H NMR (300 MHz) spectra in CDCl$_3$ of: (a) Crude poly(butadiene-
graft-pentafluorostyrene) (PB-g-PPFS-60/5), (b) poly(butadiene) (PB) extracted
from PB-g-PPFS-60/5 using hexanes; (c) PPFS Extracted from PB-g-PPFS-60/5
using Acetone; (d) Pure PB-g-PPFS-60/5 Graft Copolymer after Extractions.
* = residual protonated solvent. PB number average molecular weight: $M_n = 3.45$
$x 10^5$ (mean of UV & RI detectors), polydispersity index: $pdi = M_w/M_n = 2.63$,
grafting ratio = 0.268, grafting frequency = 588, 4.41 PPFS grafts of $DP_n = 46.5$
per PB chain.

Figure 4.12 shows the $^1$H NMR spectra of the crude product from the
experiment PB-g-PPFS-60/5, extracted PB, extracted PPFS (recovered by
precipitation in methanol), and the pure graft copolymer obtained after
homopolymer extractions. Figure 4.12.c corresponds to pure (extracted) PPFS.
Figure 4.12.a displays the $^1$H NMR spectrum of the crude product, which is
dominated by the resonances of PPFS homopolymer, the major product of the
copolymerization). Resonances due to the PB backbone are also present in this
spectrum. The resonance due to cis-CH$_2$CH= (2.10 ppm) is overlapped by the
$CH_2CHAr$ resonance of the predominant PPFS centered at 2.00 ppm. Figure 4.12.d shows the extracted graft copolymer, in which the PPFS resonances appear as small shoulders on the PB resonance at 2.10 ppm (due to $cis$-$CH_2CH_\equiv$). $^{19}\text{F}$ NMR spectroscopy also shows that the final extracted copolymer product has PPFS.

4.4 Thermal Behavior of Poly(butadiene-$\text{graft}$-pentafluorostyrene).

The PPFS homopolymers extracted from the graft copolymers range in molecular weight from $M_n = 5.73 \times 10^3$ - $1.49 \times 10^4$ Dalton ($DP_n = 29$-72) as shown in Tables 4.9 and 4.10. Figure 4.12 demonstrates that the glass transition temperatures of these homopolymers vary over this molecular weight range, and increase with increasing chain length to a maximum value of 106 °C, which was higher$^{60}$ and lower$^{45}$ than other values for the maximum $T_g$ of PPFS found in the literature.

Therefore, comparison of the $T_g$s of the extracted PPFS homopolymers and the PB-g-PPFS graft copolymers can be used to test the assumption that the PPFS homopolymers and grafts have equal lengths, provided that the two components of the graft copolymers are microphase separated and therefore exhibit separate phase transitions. Both the starting PB and all of the purified graft copolymers exhibit an exothermic transition at approximately -24 to -10 °C, and an endothermic melting of the same change in enthalpy (1.97 kJ/mol repeat unit for the starting PB homopolymer) at -75 to -58 °C, which is specific to this particular industrial polymer sample. At higher temperature, all of the graft copolymers exhibit a sharp glass transition corresponding to the PPFS grafts.
Table 4.10. Comparison of the glass transition temperatures ($T_g$), of the grafts of poly(butadiene-\textit{graft}-pentfluorostyrene)s (PB-g-PPFS) and the corresponding poly(2,3,4,5,6-pentafluorostyrene) (PPFS) homopolymers extracted with acetone. $T_g$s determined by differential scanning calorimetry; mean of values from second and third heat at 10 °C/min. PB-g-PPFS produced at final conversion (60 h) in the grafting reactions of polybutadiene (PB) with pentfluorostyrene (PFS) in tetrahydrofuran using benzoyl peroxide (BPO) as the initiator.

<table>
<thead>
<tr>
<th>Experiment $^a$</th>
<th>Grafting Ratio $^b$</th>
<th>$DP_n$ of PPFS Homopolymer$^c$</th>
<th>$T_g$ (°C)</th>
<th>PPFS Graft of PB-g-PPFS</th>
<th>Extracted PPFS Homopolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-g-PPFS-60/2.5</td>
<td>0.154 ± 0.009</td>
<td>62.9 ± 6.0</td>
<td>100</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>PB-g-PPFS-60/5</td>
<td>0.268 ± 0.011</td>
<td>46.5 ± 1.0</td>
<td>92</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>PB-g-PPFS-60/10</td>
<td>0.214 ± 0.051</td>
<td>28.7 ± 0.7</td>
<td>92</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>PB-g-PPFS-50/5</td>
<td>0.170 ± 0.021</td>
<td>72.2 ± 2.6</td>
<td>102</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td>PB-g-PPFS-60/5</td>
<td>0.268 ± 0.011</td>
<td>46.5 ± 1.0</td>
<td>92</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>PB-g-PPFS-80/5</td>
<td>0.279 ± 0.015</td>
<td>43.3 ± 2.0</td>
<td>88</td>
<td>96</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ First number in the experiment name corresponds to the copolymerization temperature (°C); second number corresponds to the mol% of BPO initiator used relative to PB repeat units; 2:1 PFS:PB repeat units. First three rows show dependence of increased initiator concentration, last three show effect of increased temperature.

$^b$ Defined by eq 3.3.

$^c$ Number-average degree of polymerization ($DP_n$) determined by gel permeation chromatography relative to polystyrene.

Table 4.10 and Figure 4.13 demonstrate that the glass transition temperatures of the PPFS grafts in the PB-g-PPFS graft copolymers and the corresponding extracted PPFS homopolymers are identical or approximately equal; the only case in which the values differ by more than 4 °C corresponds to a sample in which only 55% of the extracted PPFS was recovered. This supports the assumption that the lengths of the PPFS grafts and the corresponding PPFS homopolymers are equal.
Figure 4.13. Dependence of the glass transition temperatures ($T_g$s) of poly(2,3,4,5,6-pentafluorostyrene) (PPFS) grafts of poly(butadiene- graft-pentafluorostyrene)s (PB-g-PPFS)s and the corresponding PPFS homopolymers extracted from the graft copolymers with acetone as a function of the PPFS degree of polymerization ($DP_n$). PB-g-PPFS graft copolymers produced by copolymerization of 2,3,4,5,6-pentafluorostyrene (PFS) with polybutadiene (PB) in THF in the presence of benzoyl peroxide (BPO); 0.36 M PB, 0.70 M PFS, 2:1 PFS:PB repeat units; 2.5, 5, 10 mol% BPO relative to PB repeat units; 50, 60 or 80 ºC.

4.5 Elemental Analysis of Poly(butadiene- graft-pentafluorostyrene).

The elemental composition of the graft copolymers also supports the assumption that the lengths of the PPFS grafts and the corresponding PPFS homopolymers are approximately equal. Table 4.11 presents the carbon and hydrogen compositions of the purified graft copolymers, and compares them to the values calculated from both the grafting ratios and grafting frequencies. There were no assumptions involved in determining the grafting ratios, although error can be introduced by imperfectly resolved peaks in the GPC. In this case, the calculated compositions differs from the actual compositions by only 0.02 - 2.82% in carbon, and 0.02 - 0.57% in hydrogen. In contrast to the grafting ratios,
calculation of the grafting frequencies assume not only that the lengths of the PPFS grafts and homopolymers are equal, but that the molecular weights of the PPFS homopolymer and the starting PB are accurately determined by GPC relative to linear polystyrene. Nevertheless, the compositions calculated from the grafting frequencies differ from the actual compositions by only 0.65 - 2.42% in carbon, and 0.10 - 0.46% in hydrogen.

Table 4.11. Comparison of the elemental compositions of the poly(butadiene-graft-pentafluorostyrene)s (PB-g-PPFS) with those calculated from the grafting ratios (GR) and grafting frequencies (GF.) PB-g-PPFSs produced at final conversion (60 h) in the grafting reactions of PB with PFS in tetrahydrofuran using benzoyl peroxide as the initiator; performed in triplicate. After purification by extraction with hexanes (12 h) and acetone (36 h.) GR determined from eq. 3.3 and GF determined from eq. 3.4.

<table>
<thead>
<tr>
<th>Experiment a</th>
<th>Elemental Analysis</th>
<th>Composition Calculated From</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Results</td>
<td>Grafting Ratio</td>
</tr>
<tr>
<td></td>
<td>% C</td>
<td>% H</td>
</tr>
<tr>
<td>PB-g-PPFS-60/2.5</td>
<td>84.15</td>
<td>10.26</td>
</tr>
<tr>
<td>PB-g-PPFS-60/5</td>
<td>77.83</td>
<td>8.80</td>
</tr>
<tr>
<td>PB-g-PPFS-60/10</td>
<td>80.52</td>
<td>9.40</td>
</tr>
<tr>
<td>PB-g-PPFS-50/5</td>
<td>83.26</td>
<td>9.64</td>
</tr>
<tr>
<td>PB-g-PPFS-60/5</td>
<td>77.83</td>
<td>8.80</td>
</tr>
<tr>
<td>PB-g-PPFS-80/5</td>
<td>78.59</td>
<td>8.51</td>
</tr>
</tbody>
</table>

a First number in the experiment name corresponds to the copolymerization temperature (°C); second number corresponds to the mol% of BPO initiator used relative to PB repeat units.
5.1 Introduction.

We wanted to attach a perfluorinated aromatic ring to PB to increase the interaction between PB and carbon black fillers. The surface of carbon black is composed of a polyaromatic hydrocarbon structure, which should interact with perfluorinated aromatic molecules by arene π-π interactions developed between the two types of rings. In order to obtain such modification we proposed attaching PFS to PB by either graft copolymerization (Chapter 4) or an ene reaction with PB. PFS is a pentafluorobenzene derivative that has only hydrocarbon and fluorocarbon functional groups. This would eliminate the introduction of any other functional group that could also develop interactions with carbon black fillers, leading to erroneous results. Section 2.1.2 covers the functionalization of PB with maleic anhydride, acrylates, triazoline-diones, and acyclic azocarboxylates following an ene mechanism. There are no literature examples of ene reactions done with PFS, or with any other styrene derivative.
However, based on relative electron affinities of ethyl acrylate (0.25 eV)\textsuperscript{173}, maleic anhydride (0.57 eV)\textsuperscript{173}, and hexafluorobenzene (\(\geq 0.4\) eV)\textsuperscript{174}, PFS should be almost as reactive as maleic anhydride towards PB in an ene reaction.

5.2 Attempted Reaction of 2,3,4,5,6-Pentafluorostyrene with High Molecular Weight Polybutadiene.

We first tried to incorporate PFS into high molecular weight (HMW) PB, as outlined in Scheme 4.3. Although trans isomers are more reactive than cis for the case of 1,2-disubstituted monoolefins, the structure of the PB we used contained 96\% of cis 1,4 vs. only 3.5\% trans. Therefore, if the ene reaction took place, it would be mainly on the cis units. The 1,2-vinyl units are not only less reactive than 1,4 units\textsuperscript{13} but also much less abundant in this particular reactant. The result of the ene reaction on PB is that the structure remains essentially the same, except for migration of the double bond, and incorporation of PFS through a one-carbon spacer (Scheme 4.3).

Due to the high activation energy of the ene reaction, we need to carry it out at very high temperatures to test its viability. The reaction with maleic anhydride and stearyl acrylate is only possible at temperatures above 170 and 180 °C, respectively.\textsuperscript{10,11} The reaction has been performed in bulk\textsuperscript{10,11} and in THF\textsuperscript{12} (bp = 66 °C/760 mm Hg) and toluene\textsuperscript{13,10} (bp = 111 °C/760 mm Hg), but never in 1,3-dichlorobenzene (bp = 173 °C/760 mm Hg) and \(\alpha,\alpha,\alpha\)-trifluorotoluene (bp = 102 °C/760 mm Hg).
Scheme 5.1. Proposed ene reaction between pentafluorostyrene with polybutadiene (PB.) Only 1,4-cis units were considered due to abundance. The two possible products are displayed. High molecular weight PB number average molecular weight: $M_n = 1.25 \times 10^5$, $\text{pdi} = M_w/M_n = 4.6$, 96% 1,4-cis (y), 3.5%, 1,4-trans (x) and 0.5% 1,2-vinyl (z) content according to the supplier: Goodyear; gel permeation chromatography relative to polystyrene standards (GPC$_{PSi}$) $M_n = 3.85 \times 10^5$, $\text{pdi} = 3.51$, mean of UV and RI detectors. Low molecular weight PB $M_n = 3.00 \times 10^3$, 75% 1,4-cis, 24% 1,4-trans and 1.0% 1,2-vinyl content according to the supplier: Aldrich. GPC$_{PSi}$: $M_n = 4.30 \times 10^3$, $\text{pdi} = 2.85$, RI detector. Question mark indicates the results of this reaction are not known.

Since HMW PB was completely soluble in 1,3-dichlorobenzene upon heating at fairly high concentrations we tested the ene reaction in this solvent. We started using a regular 3-neck round bottom flask, equipped with a reflux condenser, at a temperature of 180 °C for up to 12 days. These conditions resulted in both PFS losses and PB oxidation and/or crosslinking, as we deduced from the dark brown color of the final precipitated product, which became a hard solid that was insoluble in any common solvents, and therefore impossible to analyze by any common technique. To prevent PB from oxidation and/or crosslinking, we degassed the PB in 1,3-dichlorobenzene. Also we added 10%
BHT, which is a radical inhibitor, to the reaction mixture and flame-sealed the mixture under vacuum after degassing again in a round bottom glass tube. We also reduced the reaction time to 36 h to minimize PB oxidation and crosslinking and thermal polymerization of PFS, and increased the temperature to 210 °C. Upon cooling, a solid precipitated that we analyzed by both $^1$H and $^{19}$F NMR spectroscopy and GPC. It seems that the product of this reaction is a mixture of grafted PB with PFS, PB (possibly partially oxidized), and/or PPFS homopolymer. However, we do not discard that the PB was modified with PFS by an ene reaction.

Figure 5.1 shows the UV-detected GPC chromatogram of this solid. There are two peaks, similar to the graft copolymerization mixtures of PFS onto PB (Chapter 4.) However, in this case the absorbance is much lower. The first peak may be due to PB that has been partially oxidized, PB in which a small amount of grafting occurred by abstraction of an allylic hydrogen followed by initiation of PFS polymerization, or PB that has been modified by an ene reaction with PFS. The second peak is probably due to PPFS homopolymer formed by thermal initiation of PFS. However, $^1$H NMR spectroscopy analysis of the reaction mixture before and after the reaction did not show any new resonances. Our calculated positions of the new resonances for $-CH_2CH_2Ar$, resulting from the pendant PFS units incorporated onto the PB backbone by an ene reaction, are approx. 1.6 and 3.2 ppm.

The $^1$H NMR spectrum of the reaction mixture showed that PFS was present in the mixture after 36 h, albeit 69% of it had been reacted (converted
into PPFS grafts, homopolymer or PB modified by an ene reaction). A $^1$H NMR spectrum of the purified product showed that PB was present, and possibly PPFS that showed up as shoulders of the $CH_2CH= $ resonance of the PB backbone (centered at 2.00 ppm) between 2.20 and 2.60 ppm. However, these resonances were only visible by expansion of the area, and could therefore also be due simply to noise. However, the $^{19}$F NMR spectrum of the sample taken in $n$-butyl acetate, which is the best solvent for these modified PB with PFS (including the grafted copolymers covered in Chapter 4), showed three resonances at -79.5, -95.0 and -100.7 ppm, which are different from the resonances of PPFS (-162.0, -154.4, and -143.0 ppm, corresponding to C3-F, C4-F, and C2-F, respectively).

We ran the reaction again under the same experimental conditions for $t = 48$ and 72 h. The GPC UV-detected chromatograms of the recovered product shows the same two peaks as displayed in Figure 5.1. However, the second peak is more intense, possibly indicating that a higher amount of PPFS homopolymer was formed.

It seems that our attempted ene reaction with HMW PB and PFS resulted in a mixture of PB, graft copolymer and PPFS homopolymer, as evidenced from the GPC and $^1$H NMR results. However, we cannot exclude the possibility that the ene reaction between PB and PFS worked.

We also carried out the reaction using $\alpha,\alpha,\alpha$-trifluorotoluene as a solvent that might dissolve both PB and PFS, and thereby promote their reaction. However, PB was much less soluble in $\alpha,\alpha,\alpha$-trifluorotoluene than in 1,3-
dichlorobenzene and therefore had to be much more diluted (approx. 20 times more diluted) in \(\alpha,\alpha,\alpha\)-trifluorotoluene. Since the boiling point of \(\alpha,\alpha,\alpha\)-trifluorotoluene is much lower, the reaction was performed at 140 °C for 72 h. The product did not precipitate in this case upon cooling the reaction mixture, and was therefore isolated by precipitation in methanol. There were no changes in the \(^1\)H NMR spectra of the reaction mixture and the recovered product after the reaction.

![Figure 5.1](image_url)

**Figure 5.1.** Gel permeation chromatography (GPC) UV detector (254 nm) responses of samples taken at 0 and 36 h from the reaction of polybutadiene (PB) and pentafluorostyrene (PFS) at 210 °C for 36 h. Number average molecular weight of the reaction product \(M_n = 1.25 \times 10^5\), polydispersity index \(pdi = 4.6\). PB GPC_{PSt} \(M_n = 3.85 \times 10^5\), \(pdi = 3.51\); 96% 1,4-cis, 3.5% 1,4-trans and 0.5% 1,2-vinyl content.

The GPC UV-detected chromatogram showed only one peak, which also appeared in the RI detector, at a number average molecular weight too low to attribute to a product from PB modification, grafting or oxidation. It was probably
therefore due to thermally-initiated homopolymerization of PFS. The homopolymerization may be so dominant that any modification of the PB reagent is difficult to detect on the UV-detected GPC chromatogram.

We also tried the reaction in bulk, in round bottom glass tubes that were flame-sealed under vacuum and with up to 50 mol% BHT. In all cases, the product was a very hard, insoluble and possibly oxidized and/or crosslinked solid. The $^1$H NMR spectra of any products solubilized by CDCl$_3$ show PB resonances at 2.00 and 5.40 ppm, and at 2.40 and 2.75 ppm due to PPFS homopolymer. Therefore, even with very high concentrations of the radical inhibitor, we were not able to avoid the thermal polymerization of PFS in bulk conditions. The oxidation and crosslinking of the PB were not avoided either, probably due to inefficient degassing.

5.3 Attempted Reaction of 2,3,4,5,6-Pentafluorostyrene with Low Molecular Weight Polybutadiene.

We also reacted low molecular weight (LMW) PB with PFS as outlined in Scheme 5.1, using a glass tube that was flame-sealed under vacuum after degassing the mixture and 10 mol% BHT. The reaction was carried out in bulk at a high temperature for 72 h. Under these conditions, the product did not become a hard insoluble solid as with HMW PB, although the initial reaction mixture appeared slightly more viscous. As in the reaction with HMW PB, it seems that PFS either homopolymerized or was grafted onto PB. The conversion/disappearance of PFS was 57.6% according to $^1$H NMR spectroscopy using 1,3-dichlorobenzene as the internal standard. In order to determine what
was consuming PFS, we analyzed the isolated and dried product after workup by NMR spectroscopy and GPC.

The GPC RI-chromatogram of the product has an intense bimodal peak \( (M_n = 6.70 \times 10^3, \text{pdi} = 10.8) \) and the UV-chromatogram had a small intensity peak \( (M_n = 3.00 \times 10^4, \text{pdi} = 3.70) \). Comparison of the RI-GPC chromatogram of the product, shown in Figure 5.2, and unreacted PB, shown in Figure 5.3, which absorbs only in the RI detector \( (M_n = 4.30 \times 10^3, \text{pdi} = 2.6) \) indicates that the product is a mixture of PPFS homopolymer and unreacted PB. The bimodal peak on the RI-detected chromatogram is probably due to two overlapped peaks: one due to PPFS homopolymer at higher molecular weight (which also absorbed on the UV detector) and a lower molecular weight due to PB (not present in the UV-chromatogram).

![Graph](image)

Figure 5.2. Refractive index detected gel permeation chromatography of unreacted low molecular weight polybutadiene (PB). Number average molecular weight PB \( M_n = 4.30 \times 10^3 \), polydispersity index \( \text{pdi} = 2.6 \); 75% 1,4-cis, 24% 1,4-trans and 1.0% 1,2-vinyl content according to the supplier.
Figure 5.3. Refractive index detected gel permeation chromatography of reaction mixture of low molecular weight polybutadiene (PB) and 2,3,4,5,6-pentafluorostyrene at 180 °C for 4 days. Number-average molecular weight PB $M_n = 4.30 \times 10^3$, polydispersity index pdi = 2.6; 75% 1,4-cis, 24% 1,4-trans and 1.0% 1,2-vinyl content according to the supplier. Reaction mixture $M_n 6.70 \times 10^3$, pdi = 10.8.

The $^1$H NMR spectrum of the product shows PB resonances (1.45 ppm due to -CH$_2$CH- of the 1,2-vinyl unit, 1.65 ppm due to to -CH$_2$CH- of the 1,2-vinyl unit, 2.05 and 2.75 ppm due to -CH$_2$CH= of the 1,4 cis and trans respectively, 5.00 ppm due to CH$_2$=CH- of the 1,2-vinyl unit, 5.20 ppm due to CH$_2$=CH- of the 1,2-vinyl unit, and 5.40 ppm due to -CH$_2$=CH- of the 1,4 cis and trans unit.) Traces of PFS monomer were also present in the final product. There is evidence of polymerization of PFS from the broad resonances in the area between 2.20 and 2.80 ppm. The $^{13}$C NMR spectrum of the product also showed resonances attributed to PPFS and to PB.

The final product was extracted with acetone to remove PPFS homopolymer. However, the separation was difficult in this case since LMW PB is a viscous liquid partially soluble in the extraction solvent. The GPC RI-chromatogram,
shown in Figure 5.4, had one monomodal peak \(M_n = 4.95 \times 10^3\), \(\text{pdi} = 4.3\) and the UV-chromatogram, shown in Figure 5.5, had one trimodal peak \(M_n = 9.70 \times 10^3\), \(\text{pdi} = 7.2\).

Figure 5.4. Refractive index (RI) detected gel permeation chromatography of product of the reaction of molecular weight polybutadiene (PB) and 2,3,4,5,6-pentafluorostyrene at 180 °C for 4 days, after extraction with acetone for 24 h. PB number-average molecular weight \(M_n = 4.30 \times 10^3\), polydispersity index \(\text{pdi} = 2.6\); 75% 1,4-cis, 24% 1,4-trans and 1.0% 1,2-vinyl content according to the supplier. Product \(M_n = 4.95 \times 10^3\), \(\text{pdi} = 4.3\); RI detector.

Figure 5.5. UV detected gel permeation chromatography of product of the reaction of molecular weight polybutadiene (PB) and 2,3,4,5,6-pentafluorostyrene at 180 °C for 4 days, after extraction with acetone for 24 h. PB number-average molecular weight \(M_n = 4.30 \times 10^3\), polydispersity index \(\text{pdi} = 2.6\); 75% 1,4-cis, 24% 1,4-trans and 1.0% 1,2-vinyl content according to the supplier. Product \(M_n = 9.70 \times 10^3\), \(\text{pdi} = 7.2\); UV detector.
The $^1$H NMR spectrum showed that the resonances corresponding to the backbone of PPFS homopolymer had disappeared or they were not detectable. The $^{13}$C NMR spectrum had PPFS resonances with very small intensity, and intense resonances due to PB.

NMR spectroscopy and GPC results are consistent with PFS polymerizing either to a homopolymer or grafting PB. PB may also have oxidized and/or crosslinked. However, there is no evidence that supports or discards the successful modification of PB with PFS by an ene reaction.

5.4 Attempted Reaction of 2,3,4,5,6-Pentafluorostyrene with Model Compounds.

We therefore attempted to react PFS with several model compounds by an ene reaction. These reactions should also help us analyze the products due to their lower molecular weight and higher solubility.

We used high molecular weight olefins, with high boiling points to model the ene reaction with PB, in order to use high reaction temperatures. We chose two commercially available terminal alkenes (1-decene and 1-octadecene), and an internal alkene, 9-octadecene, which had to be synthesized.

5.4.1 Synthesis of 9-Octadecene.

Scheme 5.2 outlines the two-step synthesis of 9-octadecene starting with the commercially available oleyl alcohol (9-octadencen-1-ol). In the first step, the alcohol was reacted with $p$-toluensulfonic chloride to create the tosylated alcohol.
Triethyl amine was the optimum base for this reaction. The resulting yield was high and the base was easy to remove. The tosylation provided the alcohol a good leaving group needed for the reduction, the second step of the synthesis. We used sodium tetraborohydride to reduce the tosylated alcohol under mild conditions (temperatures of 55 °C), instead of the more powerful lithium aluminum hydride and higher temperatures, to avoid the possible reduction of the double bond of the olefin.175

5.4.2 Attempted Model Reactions of 2,3,4,5,6-Pentafluorostyrene with 1-Decene, 1-Octadecene and 9-Octadecene.

We reacted the three olefins with PB both in solvent and in bulk. Schemes 5.3 and 5.4 outline the reactions of the terminal (1-decene and 1-octadecene) and the internal (9-octadecene) model compounds, respectively.
We first started with the reaction of 1-octadecene in 1,2-dichlorobenzene, which is a high boiling point solvent (bp = 180 °C/760 mm Hg), in the presence of 10 mol% BHT. We first attempted the reaction in a regular round bottom flask, equipped with a reflux condenser at 100, 150, and 180 °C. There was in all the cases loss of PFS, and of the solvent when the reaction was carried out 180 °C, evidenced from the decrease in the intensity of the PFS and solvent ^1H NMR resonances relative to the BHT resonances.

Scheme 5.3. Attempted ene reaction of pentafluorostyrene (PFS) with model compounds 1-decene (x = 6) and 1-octadecene (x = 14). Question mark indicates the results of this reaction are not known.

Scheme 5.4. Attempted ene reaction of pentafluorostyrene with 9-octadecene. Question mark indicates the results of this reaction are not known.
In order to perform the reaction at even higher temperatures we switched to nitrobenzene (bp = 210 °C/ 760 mm Hg) using the same conditions as explained before at temperatures 200 °C. In this case, no solvent was lost although PFS was again consumed, as evidenced by the decrease in the $^1$H NMR resonances relative to those of BHT. We also tried the reaction with $\alpha,\alpha,\alpha$-trifluorotoluene, which might dissolve both the olefin and PFS, and thereby promote their reaction. We attempted the reaction at 135 °C, at which we observed no change, and at 180 °C, at which there was again loss of both PFS and solvent as determined $^1$H NMR.

We switched to long glass tube sealed to a round bottom glass reactor, which allowed us to degas the mixture before flame-sealing the tubes under vacuum. We attempted the reaction at 180 and 200 °C using 1,2-dichlorobenzene as a solvent. There were no changes in the reactions as evidenced by the $^1$H NMR spectra of the reaction mixture before and after the reaction.

We also attempted the reaction in bulk with 1-octadecene and 1-decene, using 1,3-dichlorobenzene as the internal standard, and 10 mol% BHT. 1,3-Dichlorobenzene has a resonance at 7.40 ppm that does not overlap with the vinyl resonances of PFS (two doublets at 5.70 and 6.10 ppm due to $CH_2$=CHAr and a multiplet at 6.60 ppm due to $CH_2$=CHAr), or with the vinyl resonances of 1-octadecene and 1-decene (quartet at 5.00 ppm due to CH=CH$_2$ and multiplet at 5.80 ppm due to CH=CH$_2$). At 185 °C for 7 days we observed no changes in the $^1$H NMR spectra of the reaction mixture aliquots taken before the reactor was
flame-sealed. We also attempted the same reaction with 9-octadecene, observing no changes in the spectra of the mixture before and after the reaction.

5.4.3 Attempted Model Reactions of 2,3,4,5,6-Pentafluorostyrene with β-Pinene.

β-Pinene is the most reactive ene towards an ene reaction.\textsuperscript{9,131,132} Therefore, we tested its ability to react by an ene reaction with PFS. Scheme 5.5 shows the reaction and its two possible products. However, in all the cases we obtained the copolymer of PFS and β-pinene.

We first attempted the reaction in bulk at 180 °C, with 5 mol% BHT in small vials closed with a screw cap. The reaction mixture had been previously degassed and transferred into these small vials under inert atmosphere conditions. Samples were taken at the beginning and after 4 and 12 h of the reaction. \textsuperscript{1}H NMR spectra of the reaction mixtures showed a new broad singlet at 5.10 ppm after 4 h of reaction, which became more intense after 12 h. This peak could be attributed to the internal CH= resonance in the product of the modification of β-pinene with PFS. There was also a new broad singlet at 2.10 ppm, which could be due to the CH\textsubscript{2}CHAr resonance of PPFS produced by the thermal polymerization of PFS.

\[ \text{Scheme 5.5. Attempted ene reaction of pentafluorostyrene with β-pinene.} \]
We carried out the reaction for 5 days at 185 °C in the presence of 20 mol% BHT and in a round bottom glass reactor flame-sealed under vacuum after degassing the reaction mixture. The conversions (determined by $^1$H NMR spectroscopy using 1,3-dichlorobenzene as the internal standard) of PFS and β-pinene were 80 and 35%, respectively. The same new resonances at 5.10 and 2.10 ppm appeared in the $^1$H NMR spectrum. The GPC UV-chromatogram of the product had an intense peak corresponding to $M_n = 7.4 \times 10^3$ and pdi = 1.87. After 12 days of reaction at 185 °C, the conversions of PFS and β-pinene were 100% and 76.5%, respectively. The GPC UV-detected chromatogram of the product had an intense peak with $M_n = 7.8 \times 10^3$ and pdi = 1.76. We attempted to quantify how much PPFS had the product mixture using the calibration used for the quantification of the grafting copolymerization of PFS onto PB, and by difference determine how much product of the ene reaction was formed. The area of the GPC peak corresponded to an amount of PPFS that was almost five times more than the weight of the sample injected. When the reaction was attempted with 50 mol% BHT, the conversions of PFS and β-pinene were lower (95% and 67%, respectively) and the molecular weight of the product (from UV detector) was $M_n = 4.5 \times 10^3$, pdi = 1.59. With 100% BHT the conversions of PFS and β-pinene were much lower: 69 and 25% respectively, and the new peaks (5.20 and 2.10 ppm) much less intense.
The attempted ene reaction between PFS and β-pinene resulted in their copolymerization, as evidenced from $^1$H NMR and GPC analysis. Chapter 6 covers the study of these copolymers.

5.5 Attempted Synthesis of Arene Complexes.

All the attempts of ene reactions with PFS failed, which could be due to the high temperatures required to activate the reaction that cause thermally initiated homopolymerization of PFS. In order to lower the activation energy of the ene reaction, enophiles are complexed with Lewis acids, which make the double bond more electrophilic.\textsuperscript{9,131,132} In analogy, we proposed to synthesize arene complexes with the π system of the PFS, which will make the double bond more electron poor and therefore more reactive as an enophile. However, we are aware of the difficulties to produce such complexes due to the low electron density of the π system of the PFS. Koelle \textit{et al.}\textsuperscript{176} synthesized a complex with hexafluorobenzene, which was extremely reactive towards nucleophilic aromatic substitution with methanol. We followed their procedure to attempt a similar complex with PFS.

5.5.1 Synthesis of the Ligand.

Scheme 5.6 outlines the multi-step synthesis of the ligand. The first step corresponds to the synthesis of 1,2,3,4,5-pentamethylcyclopentadiene ($C_p^*$) starting with 2-bromo butene and lithium. $C_p^*$ is very sensitive to light and heat, and its purification was always complicated by the oxidation of the product. Our yields of product were very low.
Scheme 5.6. Multi-step synthesis of the ligand [C₆RuOMe]₂ by a) Synthesis of 1,2,3,4,5-pentamethylcyclopentadiene (C₆*), b) reaction of C₆* with RuCl₃·3H₂O to form the ligand intermediate C₆*RuCl₂ and c) reaction of C₆*RuCl₂ with potassium carbonate.

The purified C₆* was reacted with RuCl₃·3H₂O, and the resulting product was reacted with K₂CO₃. We obtained a dark brown crystalline solid that, according to the reported procedure,¹⁷⁷ can be used in the following step/s without removing totally the extracting solvent, diethyl ether.

5.5.2 Attempted Synthesis of the Arene Complex.

Scheme 5.7 outlines the attempted synthesis of the arene complex. With the resulting product from the ligand synthesis in diethyl ether, we added a slight
excess of PFS and a drop of concentrated hydrochloric acid. The mixture was left for a week at room temperature in an inert atmosphere. $^1$H and NMR spectrum of the mixture confirms that no reaction occurred.

Scheme 5.7. Attempted synthesis of a ruthenium arene complex of PFS and 1,2,3,4,5-pentamethylcyclopentadiene.
CHAPTER VI
COPOLYMERIZATION OF 2,3,4,5,6-PENTAFLUOROSTYRENE WITH β-PINENE.

6.1 Introduction.

In an attempt to make the ene reaction work between PFS and the most reactive ene compound found β-pinene,9,131,132 we instead obtained the copolymer between the two monomers. We therefore studied their copolymerization behavior and the properties of the resulting copolymers. This Chapter covers this study.

6.2 Copolymerization of 2,3,4,5,6-Pentafluorostyrene with β-Pinene.

In order to test the ability of PFS to copolymerize with β-pinene, we first copolymerized an equimolar mixture of the two in the presence of 1% mol BPO as the radical initiator, as outlined in Scheme 6.1. We used BPO as the initiator since it is more efficient than AIBN at initiating the polymerization of PFS. We attempted the copolymerization both in THF solution and in bulk at 70 °C, for 20 and 70 h respectively. Table 6.1 shows the results of these two sets of copolymerizations. The maximum yields were achieved after 20 h, as may be concluded from the comparison between these and the yields after 70 h.
Scheme 6.1. Synthesis of poly(pentafluorostyrene-co-β-pinene) by radical copolymerization of pentafluorostyrene (PFS) with β-pinene at 70 °C using benzoyl peroxide (BPO) as the initiator. The copolymerization was carried either in bulk or in tetrahydrofuran (THF) solution.

The yields were very similar for the same times under the different conditions (solution vs. bulk). The number-average molecular weights seem to reach a maximum value after 20 h both in solution and in bulk and the pdi values are higher for the bulk polymerizations. However, these pdi are low, indicating that termination is mainly by combination.\(^{172}\)

Table 6.1. Results of the copolymerizations of equimolar amounts of 2,3,4,5,6-pentafluorostyrene with β-pinene.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Yield (%)</th>
<th>(M_n \times 10^{-3}) (^{a})</th>
<th>pdi (^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>20</td>
<td>10</td>
<td>5.5</td>
<td>1.36</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>70</td>
<td>26</td>
<td>5.9</td>
<td>1.29</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>20</td>
<td>12</td>
<td>4.9</td>
<td>1.51</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>70</td>
<td>24</td>
<td>5.0</td>
<td>1.40</td>
</tr>
</tbody>
</table>

\(^{a}\) Number-average molecular weight (\(M_n\)), weight-average molecular weight (\(M_w\)) and polydispersity (pdi= \(M_w/M_n\)), determined by gel permeation chromatography relative to polystyrene standards.

6.3 Reactivity Ratios in the Copolymerization of 2,3,4,5,6-Pentafluorostyrene with β-Pinene.

Once we determined the ability of these two monomers to copolymerize by a radical mechanism, we studied their reactivity ratios in a radical polymerization.
In order to determine reactivity ratios by the Finemann-Ross$^{178}$ and Kelen-Tüdos$^{179}$ methods, the conversion of the monomers must be kept under 10% to minimize the composition drift, yet the copolymerization time must be long enough to produce enough copolymer to isolate. $^1$H NMR spectroscopy was used to determine the conversion of the monomers, using 1,3-dichlorobenzene as the internal standard. 1,3-Dichlorobenzene is a good internal standard since its resonance at 7.40 ppm is isolated from those of both PFS and β-pinene, and it has a boiling point (173 °C / 760 mm Hg) higher than that of the two monomers (142 and 162 °C / 760 mm Hg, for PFS and β-pinene respectively) and low chain transfer constant (chain transfer of PFS to chlorobenzene $C_s \approx 0$).$^{30}$

We first attempted copolymerizations in a conventional Schlenk tube sealed with a rubber septum, using benzene as the internal standard (isolated $^1$H NMR resonance at 7.00 ppm). However, the monomer conversions determined by $^1$H NMR spectroscopy were too high (especially the PFS conversion) considering the small amount of copolymer that was recovered, and the results were poorly reproducible. This might be due to diffusion of the monomers from the bottom of the reactor to the top areas where they are retained in the joints and cooler areas. We therefore performed each copolymerization in a round bottom reactor attached to a long glass tube, which was flame-sealed under vacuum.

A copolymerization time of 2 h was sufficient to recover enough copolymer to characterize, yet short enough to generally have comonomer conversions of $\leq$ 10 mol%. Copolymerization times of 3.5 h (at 70 °C, 1% mol BPO) were too
long, with monomer conversions of 31 and 26 mol% for PFS and β-pinene, respectively.

Table 6.2 shows the conversions of PFS (M₁) and β-pinene (M₂) determined by ¹H NMR spectroscopy, in which the experiments are labeled PFS-co-PIN-x/y, with x/y the molar ratio of comonomers in the feed. In most cases, neither monomer conversion exceeded 10 mol%, and the conversion of PFS was generally higher. The copolymer yields (equation 3.11) reported in Table 6.2 are similar to the monomer conversions when the amount of PFS in the feed is higher than 20 mol%. The copolymers that resulted from comonomer feeds of less than 30 mol% PFS had lower molecular weights and they had to be isolated from the unreacted monomers by column chromatography rather than by simple precipitation. This isolation method was probably the cause for the lower yield.

Figure 6.1 compares the ¹H NMR spectra of the copolymer products from the experiments PFS-co-PIN-1/9, PFS-co-PIN-5/5 and PFS-co-PIN-9/1 to the spectrum of PPFS homopolymer. The composition of the copolymers was determined by ¹H NMR spectroscopy using the integral of the resonance at 5.15 ppm of the CH= in the β-pinene repeat unit and the contribution of the PFS repeat unit to the alkyl resonances in the range between 0.50 and 2.10 ppm (equations 3.7, 3.8, 3.9 and 3.10).
Table 6.2. Comonomer conversion for the radical copolymerization of pentafluorostyrene (PFS) with β-pinene (PIN) for 2 h in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator and 1,3-dichlorobenzene as an internal standard.

<table>
<thead>
<tr>
<th>Experiment a</th>
<th>Feed Composition (mol%)</th>
<th>Monomer Conversion b (%)</th>
<th>Copolymer Yield c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PFS</td>
<td>β-Pinene</td>
<td>PFS</td>
</tr>
<tr>
<td>PFS-co-PIN-9/1</td>
<td>90</td>
<td>10</td>
<td>12.0</td>
</tr>
<tr>
<td>PFS-co-PIN-8/2</td>
<td>80</td>
<td>20</td>
<td>10.4</td>
</tr>
<tr>
<td>PFS-co-PIN-7/3</td>
<td>70</td>
<td>30</td>
<td>13.0</td>
</tr>
<tr>
<td>PFS-co-PIN-6/4</td>
<td>60</td>
<td>40</td>
<td>13.2</td>
</tr>
<tr>
<td>PFS-co-PIN-5/5</td>
<td>50</td>
<td>50</td>
<td>7.40</td>
</tr>
<tr>
<td>PFS-co-PIN-4/6</td>
<td>40</td>
<td>60</td>
<td>4.20</td>
</tr>
<tr>
<td>PFS-co-PIN-3/7</td>
<td>30</td>
<td>70</td>
<td>8.30</td>
</tr>
<tr>
<td>PFS-co-PIN-2/8</td>
<td>20</td>
<td>80</td>
<td>15.0</td>
</tr>
<tr>
<td>PFS-co-PIN-1/9</td>
<td>10</td>
<td>90</td>
<td>12.5</td>
</tr>
</tbody>
</table>

a Numbers in experiment name correspond to molar ratio of comonomers in feed.
b Determined by 1H NMR spectroscopy using 1,3-dichlorobenzene as internal standard.
c Determined gravimetrically after precipitating the copolymer using equation 3.11.
d Determined gravimetrically after removing unreacted monomers by column chromatography and precipitating the copolymer.
Figure 6.1. $^1$H NMR spectra of: 1) poly(2,3,4,5,6-pentafluorostyrene); 2) poly(pentafluorostyrene-co-β-pinene)-9/1 (poly(PFS-co-PIN)-9-1), with 98% 2,3,4,5,6-pentafluorostyrene (PFS); 3) poly(PFS-co-PIN)-5/5, with 86% PFS; 4) poly(PFS-co-PFS)-1/9 with 58% PFS. Resonances marked with * are due to residual CHCl$_3$.

Table 6.3 presents the compositions of the copolymers. The copolymers are always richer in PFS units, and even when the feed compositions contained an excess of β-pinene, more than half of the resulting copolymer is composed of PFS units. The higher conversion of PFS monomer together with the preferential incorporation of PFS into the copolymers is consistent with the very low probability of β-pinene to homopolymerize by a radical mechanism, and the preference of propagating PPFS radicals to self-propagate with PFS monomer rather than cross-propagating with β-pinene.

We determined the monomer reactivity ratios, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ from the copolymer compositions using the Fineman-Ross and Kelen-Tüdos methods. The monomer reactivity ratios measure the ability of a
propagating species to add its own monomer (homopropagate) over the ability to
cross-propagate or add the other monomer.\textsuperscript{180} The calculated parameters are
listed in Table 6.3. The Fineman-Ross equation is a rearranged form of the
instantaneous copolymerization equation of the terminal model,\textsuperscript{180}
\[ G = r_1 F - r_2 \]  
Eq. 6.1
in which \( G \) and \( F \) are determined from equations 6.2 and 6.3, respectively, and
are expressed as functions of the feed ([M\textsubscript{1}, [M\textsubscript{2}]) and the copolymer (d[M\textsubscript{1}],
d[M\textsubscript{2}]) compositions.
\[ G = \frac{x(y-1)}{y} \quad F = \frac{x^2}{y} \]  
Eq. 6.2, 6.3
\[ x = \frac{[M_1]}{[M_2]} \quad y = \frac{d[M_1]}{d[M_2]} \]  
Eq. 6.4, 6.5

Figure 6.2 shows the Fineman-Ross plot for the copolymerization of PFS
with \( \beta \)-pinene. The data points are adjusted to a straight line whose slope and
intercept correspond to the monomer reactivity ratios \( r_1 = r_{\text{PFS}} = 5.2 \), and \( r_2 = r_{\text{PIN}} = 0.070 \) for PFS and \( \beta \)-pinene, respectively.

The Kelen-Tüdos\textsuperscript{179} equation is a modified form of the Fineman-Ross
equation, in which an arbitrary positive constant, \( \alpha \), is introduced to spread the
data more evenly along the abscissa. We used a typical value of \( \alpha = (F_HF_L)^{1/2} \) in
which \( F_H \) and \( F_L \) are the highest and lowest values of \( F \), respectively,
\[ \eta = \left( r_1 + \frac{r_2}{\alpha} \right) \zeta - \frac{r_2}{\alpha} \]  
Eq. 6.6
and $\eta = G/(\alpha + F)$ (eq. 6.7), and $\zeta = F/(\alpha + F)$ (eq. 6.8). Figure 6.3 shows the Kelen-Túdós plot for the copolymerization of PFS with $\beta$-pinene. The intercepts at $\zeta=1$ and $\zeta=0$ correspond to the reactivity ratios $r_1 = r_{PFS} = 5.0$, and $r_2 = r_{PIN} = 0.017$, for PFS and $\beta$-pinene, respectively.

Table 6.3. Data used to determine the reactivity ratios of pentafluorostyrene (PFS, $M_1$) and $\beta$-pinene (PIN, $M_2$) in their radical copolymerization for 2 h in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>mol% PFS in Copolymer</th>
<th>$F = X^2/Y$</th>
<th>$G = X(Y-1)/Y$</th>
<th>$\zeta = F/(\alpha+F)$</th>
<th>$\eta = G/(\alpha+F)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFS-co-PIN-9/1</td>
<td>98</td>
<td>1.65</td>
<td>8.82</td>
<td>0.931</td>
<td>4.97</td>
</tr>
<tr>
<td>PFS-co-PIN-8/2</td>
<td>95</td>
<td>0.84</td>
<td>3.79</td>
<td>0.874</td>
<td>3.93</td>
</tr>
<tr>
<td>PFS-co-PIN-7/3</td>
<td>92</td>
<td>0.47</td>
<td>2.13</td>
<td>0.796</td>
<td>3.58</td>
</tr>
<tr>
<td>PFS-co-PIN-6/4</td>
<td>90</td>
<td>0.25</td>
<td>1.33</td>
<td>0.673</td>
<td>3.59</td>
</tr>
<tr>
<td>PFS-co-PIN-5/5</td>
<td>86</td>
<td>0.16</td>
<td>0.84</td>
<td>0.572</td>
<td>2.94</td>
</tr>
<tr>
<td>PFS-co-PIN-4/6</td>
<td>80</td>
<td>0.11</td>
<td>0.50</td>
<td>0.478</td>
<td>2.15</td>
</tr>
<tr>
<td>PFS-co-PIN-3/7</td>
<td>73</td>
<td>0.07</td>
<td>0.27</td>
<td>0.358</td>
<td>1.42</td>
</tr>
<tr>
<td>PFS-co-PIN-2/8</td>
<td>69</td>
<td>0.03</td>
<td>0.14</td>
<td>0.187</td>
<td>0.92</td>
</tr>
<tr>
<td>PFS-co-PIN-1/9</td>
<td>58</td>
<td>0.01</td>
<td>0.03</td>
<td>0.068</td>
<td>0.23</td>
</tr>
</tbody>
</table>

* Numbers in experiment name correspond to molar ratio of comonomers in feed.

* Copolymer composition determined by $^1$H NMR analysis of the copolymer after removing unreacted monomers by column chromatography and/or precipitating the copolymer.

* Fineman-Ross parameter determined from eq. 6.2.

* Fineman-Ross parameter determined from eq. 6.3.

* Kelen-Tudós parameter determined from eq. 6.8.

* Kelen-Tudós parameter determined from eq. 6.7.
Figure 6.2. Finemann-Ross plot (equation 6.1) used to determine the reactivity ratios $r_1 = k_{11}/k_{12}$, and $r_2 = k_{22}/k_{21}$ in the radical copolymerization of 2,3,4,5,6-pentafluorostyrene (M₁) and β-pinene (M₂) for 2 h in bulk at 70 °C with benzoyl peroxide (1 mol%) as the initiator.

Figure 6.3. Kelen-Tüdos plot (equation 6.6) used to determine the reactivity ratios $r_1 = k_{11}/k_{12}$, and $r_2 = k_{22}/k_{21}$ in the radical copolymerization of 2,3,4,5,6-pentafluorostyrene (M₁) and β-pinene (M₂) for 2 h in bulk at 70 °C with benzoyl peroxide (1 mol%) as the initiator.
The monomer reactivity ratios determined from both Fineman-Ross and Kelen-Túdos methods demonstrate that PFS prefers to homopropagate rather than cross-propagate with β-pinene, and that β-pinene has a very low probability of homopropagating. Therefore this copolymer is composed of blocks of PFS segments with isolated β-pinene units randomly distributed between them. Scheme 6.2 presents the elementary reactions for this copolymerization. The primary radicals from the dissociation of BPO may initiate the polymerization of either PFS or β-pinene. However, PFS is more reactive toward radical initiation due to its higher resonance stabilization of the radicals formed than those coming from β-pinene. Due to its low reactivity, β-pinene is more likely initiated by the more reactive phenyl radical rather than benzoyl radical. Therefore, the most abundant radicals present will be those from PFS, and although not very probable we have also included the possibility of radical initiation of β-pinene. PPFS propagating radicals would rather add PFS (homopropagate) than cross-propagate with β-pinene, although they did react with β-pinene that generated a radical that underwent isomerization to react almost exclusively with PFS. The most abundant propagating radicals were those based on PFS, which terminates by combination. Therefore, termination mainly occurs by combination of PFS-based radicals. If chain transfer took place, that would be from the less stabilized β-pinene-terminated radicals, which would abstract an allylic hydrogen from either a β-pinene monomer or a β-pinene isolated isomerized unit on the backbone.
Scheme 6.2. Proposed elementary reactions in the radical copolymerization of pentafluorostyrene and $\beta$-pinene for 2 h in bulk at 70 °C using benzoyl peroxide as the initiator.
6.4 Molecular Weight of the Copolymers.

The molecular weights of the copolymers measured in toluene and in some cases in THF are presented in Table 6.4. We first used THF as the eluant for a GPC equipped with columns packed with cross-linked polystyrene. However, the pressure inside the columns increased significantly. We attributed this increase to interactions developed between the aromatic fluorocarbon rings present in the copolymer (electron poor) with the electron-rich aromatic hydrocarbon rings of the polystyrene packing of the columns.$^{2,91}$ We therefore switched to toluene as the eluant, which provided an aromatic structure that could interact with the copolymer, preventing it from interacting with the column. Although it solved the pressure related problem, the copolymers eluted later from the columns, as demonstrated by the lower number-average molecular weight values and lower polydispersities in toluene than in THF. Also the fact that these copolymers are much more soluble in THF than in toluene is inconsistent with the possibility that they are aggregated in THF. We have no explanation for this phenomenon. However, both sets of data in Table 6.4 demonstrate that the molecular weights of the copolymers decreased as the amount of β-pinene in the copolymer increased, consistent with the mechanism proposed for this copolymerization. Figure 6.4 plots the degree of polymerization ($DP_n$) of the copolymers as a function of the amount of PFS in them. The data adjusted very well to a straight line that if extrapolated to 100% PFS, gave a $DP_n$ of 29.3. The number-average molecular weight corresponding to this $DP_n$ is approximately $M_n = 5.7 \times 10^3$. 

175
Table 6.4. Number-average molecular weights ($M_n$) and polydispersities ($\text{pdi}=M_w/M_n$) measured by gel permeation chromatography in tetrahydrofuran (THF) and toluene of the copolymers produced by radical copolymerizations of pentfluorostyrene (PFS) and β-pinene (PIN) for 2 h in bulk at 70 °C with benzoyl peroxide (1 mol%) as the initiator.

<table>
<thead>
<tr>
<th>Experiment $^a$</th>
<th>Mol% PFS in Copolymer $^b$</th>
<th>THF</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_n \times 10^3$</td>
<td>pdi</td>
<td>$M_n \times 10^3$</td>
</tr>
<tr>
<td>PFS-co-PIN-9/1</td>
<td>98</td>
<td>20.2</td>
<td>2.53</td>
</tr>
<tr>
<td>PFS-co-PIN-8/2</td>
<td>95</td>
<td>13.0</td>
<td>1.85</td>
</tr>
<tr>
<td>PFS-co-PIN-7/3</td>
<td>92</td>
<td>13.1</td>
<td>1.83</td>
</tr>
<tr>
<td>PFS-co-PIN-6/4</td>
<td>90</td>
<td>8.80</td>
<td>1.59</td>
</tr>
<tr>
<td>PFS-co-PIN-5/5</td>
<td>86</td>
<td>8.00</td>
<td>1.63</td>
</tr>
<tr>
<td>PFS-co-PIN-4/6</td>
<td>80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFS-co-PIN-3/7</td>
<td>73</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFS-co-PIN-2/8</td>
<td>69</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PFS-co-PIN-1/9</td>
<td>58</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Numbers in experiment name correspond to molar ratio of comonomers in feed.

$^b$Copolymer composition determined by $^1$H NMR analysis of the copolymer after removing unreacted monomers by column chromatography and/or precipitating the copolymer.
Figure 6.4. Dependence of the number-average degree of polymerization \( (DP_n) \) as a function of the composition of the copolymers, synthesized by radical copolymerization of pentafluorostyrene and \( \beta \)-pinene for 2 h in bulk at 70 °C using 1 mol% benzoyl peroxide as the initiator.

6.5 Thermal Behavior of the Copolymers.

Table 6.5 summarizes the \( T_g \)s of these copolymers determined by DSC. The copolymers composed of 27-42 mol% \( \beta \)-pinene did not have a detectable \( T_g \) by DSC. The rest of the copolymers showed a single transition, which is consistent with the proposed mechanism for this copolymerization resulting in blocks of PFS separated by isolated \( \beta \)-pinene units. Table 6.5 demonstrates that the \( T_g \)s increase with increasing molecular weight and PFS content, which corresponds to an increase in the length of the PPFS blocks.
Table 6.5. Dependence of the glass transition temperature \( (T_g) \) of poly(pentafluorostyrene-co-\( \beta \)-pinene)s on their copolymer composition and number-average degree of polymerization \( (DP_n) \).

<table>
<thead>
<tr>
<th>Experiment (^a)</th>
<th>mol% PFS in Copolymer (^b)</th>
<th>( DP_n ) (^c)</th>
<th>( T_g ) (°C) (^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFS-co-PIN-9/1</td>
<td>98</td>
<td>30.1</td>
<td>99.6</td>
</tr>
<tr>
<td>PFS-co-PIN-8/2</td>
<td>95</td>
<td>27.5</td>
<td>87.8</td>
</tr>
<tr>
<td>PFS-co-PIN-7/3</td>
<td>92</td>
<td>24.8</td>
<td>79.8</td>
</tr>
<tr>
<td>PFS-co-PIN-6/4</td>
<td>90</td>
<td>24.3</td>
<td>76.3</td>
</tr>
<tr>
<td>PFS-co-PIN-5/5</td>
<td>86</td>
<td>22.6</td>
<td>63.7</td>
</tr>
<tr>
<td>PFS-co-PIN-4/6</td>
<td>80</td>
<td>20.6</td>
<td>59.6</td>
</tr>
<tr>
<td>PFS-co-PIN-3/7</td>
<td>73</td>
<td>18.4</td>
<td>- (^e)</td>
</tr>
<tr>
<td>PFS-co-PIN-2/8</td>
<td>69</td>
<td>17.1</td>
<td>- (^e)</td>
</tr>
<tr>
<td>PFS-co-PIN-1/9</td>
<td>58</td>
<td>10.9</td>
<td>- (^e)</td>
</tr>
</tbody>
</table>

\(^a\) Numbers in experiment name correspond to molar ratio of comonomers in feed. Copolymers were synthesized by the radical copolymerization of pentafluorostyrene (PFS) and \( \beta \)-pinene (PIN) for 2 h in bulk at 70 °C using 1 mol\% benzoyl peroxide as the initiator.

\(^b\) Copolymer composition determined by \(^1\)H NMR analysis of the copolymer after removing unreacted monomers by column chromatography and/or precipitating the copolymer.

\(^c\) Determined by gel permeation chromatography relative to polystyrene in toluene using and copolymer composition determined by \(^1\)H NMR spectroscopy.

\(^d\) Determined by differential scanning calorimetry (DSC); mean of values from 2\(^{nd}\) and 3\(^{rd}\) heat at 10 °C/min.

\(^e\) Not detectable by DSC.
Figure 6.5. Dependence of the glass transition temperature ($T_g$) of the poly(pentafluorostyrene-co-β-pinene)s as a function of the amount of 2,3,4,5,6-pentafluorostyrene (PFS). The copolymers were synthesized by the radical copolymerization of PFS and β-pinene for 2 h in bulk at 70 °C using 1 mol% of benzoyl peroxide as the initiator.

Figure 6.5 shows the dependence of the $T_g$ of the copolymers on the amount of PFS present in them. As mentioned before, the increase in the PFS content increased the transition temperature. The data points adjusted fairly well to a straight line following the equation $y = 2.2x - 123.5$. Extrapolation to 100% PFS corresponds to a $T_g$ of 99.5 °C. This extrapolated value for 100% PFS is a lower value than the maximum value determined for extracted PPFS ($T_g = 106 °C$ for a $DP_n = 72.2$) but higher than the lowest $T_g$ for extracted PPFS determined for these extracted samples ($T_g = 92 °C$ for a $DP_n = 28.7$). This $DP_n = 28.7$ is in close agreement to that of the extrapolated 100% PFS, which is 29.3.
6.6 Optical Activity and Surface Energy of the Copolymers.

We determined the optical activity of the copolymers. β-Pinene has two chiral centers, C3 and C5, and upon copolymerization with PFS, only one of them, C5, remains chiral, which provides the copolymers with optical activity (Scheme 6.1).

Table 6.6 summarizes the specific rotations of solutions of the copolymers in THF. The specific rotation depends on both the solvent used and the concentration of the sample. While the specific rotation of camphor decreases with increasing dilution with solvents like acetic acid, benzene or ethyl acetate, water increases the specific rotation of ethyl tartrate.181

We determined the rotations of four copolymers with different amounts of β-pinene, to investigate the effect of the amount of the repeat unit that has the chiral center on the specific rotation. We also investigated the dependence of the specific rotation on the concentration of the solution, and measured the specific rotations of different solution concentrations of the copolymers with 86 and 95% PFS. All of the copolymers are optically active. The specific rotations of 0.1% w/v copolymers solutions range from \( [\alpha]^{25}_D = -42.1 \) to \(-4.0\), increasing with increased β-pinene in the copolymer. This is consistent with the structure and the polymerization mechanism proposed on Scheme 6.1 and 6.2, respectively.
Table 6.6. Dependence of the specific Rotations ([α]^{25}_D) of poly(pentafluorostyrene-co-β-pinene)s on their compositions and concentration of the solution.

<table>
<thead>
<tr>
<th>Experiment(^a)</th>
<th>Mol% PFS in copolymer (^b)</th>
<th>Concentration (% w/v) (^c)</th>
<th>Specific rotation ([α]^{25}_D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFS-co-PIN-8/2</td>
<td>95</td>
<td>0.5</td>
<td>-14.2</td>
</tr>
<tr>
<td>PFS-co-PIN-8/2</td>
<td>95</td>
<td>0.2</td>
<td>-9.50</td>
</tr>
<tr>
<td>PFS-co-PIN-8/2</td>
<td>95</td>
<td>0.1</td>
<td>-4.00</td>
</tr>
<tr>
<td>PFS-co-PIN-6/4</td>
<td>90</td>
<td>0.1</td>
<td>-16.7</td>
</tr>
<tr>
<td>PFS-co-PIN-5/5</td>
<td>86</td>
<td>0.1</td>
<td>-21.3</td>
</tr>
<tr>
<td>PFS-co-PIN-5/5</td>
<td>86</td>
<td>0.08</td>
<td>-17.1</td>
</tr>
<tr>
<td>PFS-co-PIN-5/5</td>
<td>86</td>
<td>0.07</td>
<td>-14.3</td>
</tr>
<tr>
<td>PFS-co-PIN-5/5</td>
<td>86</td>
<td>0.06</td>
<td>-12.8</td>
</tr>
<tr>
<td>PFS-co-PIN-2/8</td>
<td>69</td>
<td>0.1</td>
<td>-42.1</td>
</tr>
</tbody>
</table>

\(^a\) Produced by radical copolymerizations of pentafluorostyrene (PFS) and β-pinene (PIN) for 2 h in bulk at 70 °C using 1 mol% benzoyl peroxide as the initiator. Numbers in experiment name correspond to molar ratio of comonomers in feed.

\(^b\) Copolymer composition determined by \(^1\)H NMR analysis of the copolymer after removing unreacted monomers by column chromatography and/or precipitating the copolymer.

\(^c\) In a tetrahydrofuran solution.
The specific rotations of all of the copolymers have the same sign as neat β-pinene ([α]_{25}^D = -17.1) but are different in magnitude. The values of [α]_{25}^D decrease with decreased concentration of the solutions. For a 0.5% (w/v) THF solution of the copolymer having 95% PFS, the value of [α]_{25}^D is –14.2 and decreases to –4.0 when the concentration is 0.1%. A 0.1% solution of the copolymer with 86% PFS has a [α]_{25}^D value of –21.3, and decreases gradually when the solution concentration is decreased. Therefore, the copolymers are optically active as evidenced from their optical rotation measurements. Their activity depends on the amount of β-pinene in the copolymer and on the amount of inactive solvent (THF) in the solution, which lowers this optical activity.

Table 6.7 contains the static contact angles (θ_s) determined for three different copolymers with 69, 86 and 95% PFS, and compares them to that of PPFS homopolymer. These are high contact angles, indicating that they have poor wettability to water, and that they therefore form low surface energies.\(^{55,61,62}\) Since the error of the measurement is ±2°, the surfaces made of the copolymers with 86 and 95% have the same surface energies and wettability within experimental error. The highest value corresponds to the PPFS homopolymer and the lowest value corresponds to the copolymer with the lowest amount of PFS, confirming that an increase in the level of fluorination increases the contact angles and therefore lowers the surface energy of the copolymers.
Table 6.7. Static contact angles ($\theta_s$) of films of poly(2,3,4,5,6-pentafluorostyrene) (PPFS) and poly(pentafluorostyrene-co-β-pinene)s (PFS-co-PIN) films on silicon wafers.

<table>
<thead>
<tr>
<th>Experiment$^a$</th>
<th>mol% PFS in Copolymer $^b$</th>
<th>Contact Angles ($\theta_s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPFS</td>
<td>100</td>
<td>101.1</td>
</tr>
<tr>
<td>PFS-co-PIN-8/2</td>
<td>95</td>
<td>100.4</td>
</tr>
<tr>
<td>PFS-co-PIN-5/5</td>
<td>86</td>
<td>98.1</td>
</tr>
<tr>
<td>PFS-co-PIN-2/8</td>
<td>69</td>
<td>95.2</td>
</tr>
</tbody>
</table>

$^a$ Numbers in experiment name correspond to molar ratio of comonomers in feed. Produced by radical homopolymerization of pentafluorostyrene (PFS) or copolymerization of PFS and β-pinene (PIN) for 2 h in bulk at 70 °C using 1 mol% benzyol peroxide as the initiator.

$^b$ Copolymer composition determined by $^1$H NMR analysis of the copolymer after removing unreacted monomers by column chromatography and/or precipitating the copolymer.
CHAPTER VII
COPOLYMERIZATION OF STYRENE AND VINYL AROMATIC HYDROCARBONS WITH 2,3,4,5,6-PENTAFLUOROSTYRENE

7.1 Introduction.
In the previous chapter, I covered the study of copolymerization of PFS with \( \beta \)-pinene, and the properties of the resulting copolymers. This chapter attempts to correlate the interactions developed between aromatic hydrocarbons and aromatic fluorocarbons with copolymerization reactivity ratios. We studied the radical copolymerization behavior of PFS, which has a perfluorinated ring, with styrene, 2-vinyl naphthalene (2-VN) and 1-vinyl naphthalene (1-VN), which have one or two aromatic rings. This chapter also presents the characterization of the resulting copolymers, in correlation with the interactions developed.

7.2 Copolymerization of Styrene with 2,3,4,5,6-Pentafluorostyrene.

7.2.1 Copolymerization of Styrene with PFS. Determination of Reactivity Ratios.
We first investigated the reactivity ratios from the copolymerization of styrene and PFS using BPO (1 mol%) as the initiator, as outlined in Scheme 7.1, using the same method reported in the previous chapter. We determined the monomer conversions using \(^1\text{H}\) NMR spectroscopy and an internal standard. Our previous choice of internal standard, 1,3-dichlorobenzene, was not useful in
these copolymerizations, since its resonances (at 7.25 and 7.40 ppm) overlap with the resonances of the aromatic protons of styrene (between 7.20 and 7.60 ppm). We chose n-butyl acetate instead, which has a relatively high boiling point (bp = 126 °C / 760 mm Hg), and a resonance at 4.10 ppm (CH₂OCOCH₃, t) that did not overlap with any of the monomers’ resonances. Based on the chain transfer constants determined for PFS polymerization to methyl isobutyl ketone \((C_S = 3.30 \times 10^{-6})^{18}\) and for styrene polymerization to methyl isobutyl ketone \((C_S = 7.67 \times 10^{-5})^{18}\), n-butyl chloride \((C_S = 4.00 \times 10^{-6})^{8}\), and n-butyl bromide \((C_S = 6.00 \times 10^{-6})^{8}\), n-butyl acetate should not promote chain transfer by either of the two propagating monomers.

![Scheme 7.1](image)

Scheme 7.1. Synthesis of poly(styrene-alt-pentafluorostyrene) by radical copolymerization of styrene \((M_1)\) and 2,3,4,5,6-pentafluorostyrene \((M_2)\) at 70 °C for 25 min using 1 mol% benzoyl peroxide as the initiator.

We first carried out the copolymerizations flame-sealed in round bottom reactors at 70 °C for 2 h, which resulted in monomer conversions of 60 % for an equimolar mixture of styrene and PFS. This conversion was too high to apply the methods used previously, the Finemann-Ross\(^{178}\) and Kelen-Tüdos\(^{179}\) methods. We found that 25 min. was enough time to recover enough polymer to characterize and yet limit the comonomer conversions to ≤ 10 %.
Table 7.1 shows the conversions of styrene (M1) and PFS (M2) determined by $^1$H NMR spectroscopy; the experiments are labeled Sty-alt-PFS-x/y, in which x/y is the molar ratio of comonomers in the feed. In all cases neither monomer conversion exceeded 10 mol%, and enough copolymer was recovered to characterize. The composition of the copolymers was determined by $^1$H NMR spectroscopy (Section 3.8.6). These compositions are summarized in Table 7.2. We used the compositions to calculate the parameters required to apply the Fineman-Ross (G and F from equations 6.2 and 6.3), and Kelen-Tüdos ($\zeta$ and $\eta$ determined from equations 6.7 and 6.8) methods. Table 7.2 lists the calculated values.

The plot of G vs. F should be linear, in which $r_1$ and $r_2$ are the slope and the intercept respectively (Fineman-Ross method, equation 6.1). The Kelen-Tüdos method introduces an arbitrary parameter $\alpha$ determined by $\alpha = (F_L F_H)^{1/2}$ in order to weight the data evenly along the abcissa.

Plotting $\eta$ vs. $\zeta$ should result in a straight line intercepting in $r_1$ when $\zeta$ is extrapolated to 1, and $r_2$ when $\zeta$ is extrapolated to 0. Figures 7.1 and 7.2 show the two plots for the copolymerization of styrene (M1) and PFS (M2) at 70 °C using BPO (1 mol%) as the radical initiator. The resulting values for this copolymerization are: $r_1 = r_{sty} = 0.74$, $r_2 = r_{PFS} = 0.16$, and $r_1 r_2 = 0.12$, determined from the Fineman-Ross method (Figure 7.1), and $r_1 = r_{sty} = 0.69$, $r_2 = r_{PFS} = 0.19$ and $r_1 r_2 = 0.13$, determined from the Kelen-Tüdos method (Figure 7.2).
Table 7.1. Comonomer conversions for the radical copolymerization of styrene (Sty) and 2,3,4,5,6-pentafluorostyrene (PFS) in bulk at 70 °C for 25 min. using benzoyl peroxide (1 mol%) as the initiator.

<table>
<thead>
<tr>
<th>Experiment a</th>
<th>Feed Composition (mol%)</th>
<th>Monomer Conversion b (%)</th>
<th>Copolymer Yield c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Styrene</td>
<td>PFS</td>
</tr>
<tr>
<td>Sty-alt-PFS-9/1</td>
<td>90</td>
<td>10</td>
<td>5.3</td>
</tr>
<tr>
<td>Sty-alt-PFS-8/2</td>
<td>80</td>
<td>20</td>
<td>1.0</td>
</tr>
<tr>
<td>Sty-alt-PFS-7/3</td>
<td>70</td>
<td>30</td>
<td>3.4</td>
</tr>
<tr>
<td>Sty-alt-PFS-6/4</td>
<td>60</td>
<td>40</td>
<td>1.9</td>
</tr>
<tr>
<td>Sty-alt-PFS-5/5</td>
<td>50</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>Sty-alt-PFS-4/6</td>
<td>40</td>
<td>60</td>
<td>7.8</td>
</tr>
<tr>
<td>Sty-alt-PFS-3/7</td>
<td>30</td>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>Sty-alt-PFS-2/8</td>
<td>20</td>
<td>80</td>
<td>8.0</td>
</tr>
<tr>
<td>Sty-alt-PFS-1/9</td>
<td>10</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>Sty-alt-PFS-0.5/9.5</td>
<td>5.0</td>
<td>95</td>
<td>10</td>
</tr>
</tbody>
</table>

a Numbers in experiment name correspond to molar ratio of comonomers in feed.
b Determined by 1H NMR spectroscopy using n-butyl acetate as internal standard.
c Determined gravimetrically after precipitating the copolymer, from equation 3.16.
**Table 7.2.** Data used to determine the reactivity ratios of styrene (Sty, \( M_1 \)) and pentafluorostyrene (PFS, \( M_2 \)) in their radical copolymerization for 25 min in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator.

<table>
<thead>
<tr>
<th>Experiment (^a)</th>
<th>mol% Styrene in Copolymer (^b)</th>
<th>( F = X^2/Y ) (^c)</th>
<th>( G = X(Y-1)/Y ) (^d)</th>
<th>( \zeta = F/(\alpha+F) ) (^e)</th>
<th>( \eta = G/(\alpha+F) ) (^f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sty-alt-PFS-9/1</td>
<td>88.0</td>
<td>11.0</td>
<td>7.77</td>
<td>0.96</td>
<td>0.67</td>
</tr>
<tr>
<td>Sty-alt-PFS-8/2</td>
<td>81.6</td>
<td>3.51</td>
<td>3.12</td>
<td>1.00</td>
<td>0.89</td>
</tr>
<tr>
<td>Sty-alt-PFS-7/3</td>
<td>76.0</td>
<td>1.72</td>
<td>1.59</td>
<td>0.77</td>
<td>0.72</td>
</tr>
<tr>
<td>Sty-alt-PFS-6/4</td>
<td>62.0</td>
<td>1.38</td>
<td>0.58</td>
<td>0.59</td>
<td>0.25</td>
</tr>
<tr>
<td>Sty-alt-PFS-5/5</td>
<td>57.0</td>
<td>0.75</td>
<td>0.24</td>
<td>0.43</td>
<td>0.14</td>
</tr>
<tr>
<td>Sty-alt-PFS-4/6</td>
<td>46.5</td>
<td>0.52</td>
<td>-0.10</td>
<td>0.39</td>
<td>-0.08</td>
</tr>
<tr>
<td>Sty-alt-PFS-3/7</td>
<td>43.6</td>
<td>0.23</td>
<td>-0.12</td>
<td>0.28</td>
<td>-0.14</td>
</tr>
<tr>
<td>Sty-alt-PFS-2/8</td>
<td>38.5</td>
<td>0.10</td>
<td>-0.15</td>
<td>0.19</td>
<td>-0.28</td>
</tr>
<tr>
<td>Sty-alt-PFS-1/9</td>
<td>35.0</td>
<td>0.023</td>
<td>-0.095</td>
<td>0.05</td>
<td>-0.23</td>
</tr>
<tr>
<td>Sty-alt-PFS-0.5/9.5</td>
<td>17</td>
<td>0.010</td>
<td>-0.14</td>
<td>0.035</td>
<td>-0.49</td>
</tr>
</tbody>
</table>

\(^a\) Numbers in experiment name correspond to molar ratio of comonomers in feed.

\(^b\) Copolymer composition determined by \(^1\)H NMR analysis of the copolymer after removing unreacted monomers by precipitating the copolymer.

\(^c\) Fineman-Ross parameter determined from eq. 6.2.

\(^d\) Fineman-Ross parameter determined from eq. 6.3.

\(^e\) Kelen-Tudós parameter determined from eq. 6.8.

\(^f\) Kelen-Tudós parameter determined from eq. 6.7.
Figure 7.1. Finemann-Ross plot (equation 6.1) used to determine the reactivity ratios \( k_1 = k_{11} / k_{12} \) and \( k_2 = k_{22} / k_{21} \) in the radical copolymerization of styrene \( (M_1) \) and 2,3,4,5,6-pentafluorostyrene \( (M_2) \) in bulk for 25 min. at 70 °C with benzoyl peroxide (1 mol\%) as the initiator.

Figure 7.2. Kelen-Tüdos plot (equation 6.6) used to determine the reactivity ratios \( k_1 = k_{11} / k_{12} \) and \( k_2 = k_{22} / k_{21} \) in the radical copolymerization of styrene \( (M_1) \) and 2,3,4,5,6-pentafluorostyrene \( (M_2) \) in bulk for 25 min. at 70 °C with benzoyl peroxide (1 mol\%) as the initiator.
Scheme 7.2. Proposed elementary reactions in the radical copolymerization of styrene and 2,3,4,5,6-pentafluorostyrene in bulk for 25 min at 70 °C using benzoyl peroxide (1% mol) as the initiator.
The reactivity values and their products demonstrate that this copolymerization tends to alternation, in which both comonomers have higher tendencies to cross-propagate, or add the other comonomer than homopropagate (add their own monomer). However, the higher reactivity ratio of styrene indicates that it has a higher tendency to homopropagate than PFS, which may be due to steric effects. Scheme 7.2 outlines the elementary reactions corresponding to this type of copolymerization. Although we contemplated all propagation possibilities, according to these reactivity values, crosspropagation (second and fourth reactions on the propagation section of Scheme 7.2) has higher probability than homopropagation (first and third reactions on the propagation. Generally the tendency to alternate increases when the one of the monomers involved in the copolymerization has electron-withdrawing substituent/s and the other monomer has electron-donating substituents.49

Although PFS has an electron-withdrawing substituent and styrene has an electron-donating substituent, we wanted to test whether interactions developed between aromatic hydrocarbon rings (styrene) and aromatic perfluorinated rings (PFS) contribute to the alternation. Patrick and Prosser2 found that benzene and hexafluorobenzene form a 1:1 complex melting at 24 °C. This indicates that complexation between styrene and PFS should be minimal at the 70 °C copolymerization temperature. We therefore performed the copolymerization at 25 °C. Scheme 7.3 outlines the copolymerization of styrene and PFS at 25 °C using t-butyl peroxo pivalate as the radical initiator.
Scheme 7.3. Synthesis of poly(styrene-alt-pentafluorostyrene) by radical copolymerization of styrene (M₁) and 2,3,4,5,6-pentafluorostyrene (M₂) at 25 °C for 2.5 h using benzoyl peroxide (1 mol%) as the initiator.

At 25 °C, the optimum time to recover a sufficient amount of copolymer and yet limit the comonomer conversion to ≤ 10% is 2.5 h. The conversion of the monomers was determined by $^1$H NMR spectroscopy using n-butyl acetate as an internal standard as described for the previous copolymerization. Table 7.3 presents the monomer conversions and the copolymer yield, determined with equation 3.16 using the copolymer compositions determined by $^1$H NMR spectroscopy (equations 3.14 and 3.15). The copolymer yields were quite low, which we attribute to a low efficiency of this radical initiator and incomplete precipitation of lower molecular weight fractions of the copolymers. We could not increase the time to increase the copolymerization yield since the conversions of the monomers would increase above 10%.

We determined the composition of the copolymers by $^1$H NMR spectroscopy (Section 3.8.6). These compositions are summarized in Table 7.4. The calculated values of the parameters required to apply the Fineman-Ross and Kelen-Túdos methods are listed in Table 7.4.
Table 7.3. Comonomer conversions for the radical copolymerization of styrene (Sty) with 2,3,4,5,6-pentafluorostyrene (PFS) for 2.5 h in bulk at 25 °C using t-butyl peroxo pivalate (1 mol%) as the initiator.

<table>
<thead>
<tr>
<th>Experiment a</th>
<th>Feed Composition (mol%)</th>
<th>Monomer Conversion b (%)</th>
<th>Copolymer Yield c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Styrene</td>
<td>PFS</td>
<td>Styrene</td>
</tr>
<tr>
<td>Sty-alt-PFS-9/1</td>
<td>90</td>
<td>10</td>
<td>11</td>
</tr>
<tr>
<td>Sty-alt-PFS-8/2</td>
<td>80</td>
<td>20</td>
<td>4.7</td>
</tr>
<tr>
<td>Sty-alt-PFS-7/3</td>
<td>70</td>
<td>30</td>
<td>5.0</td>
</tr>
<tr>
<td>Sty-alt-PFS-6/4</td>
<td>60</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>Sty-alt-PFS-5/5</td>
<td>50</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>Sty-alt-PFS-4/6</td>
<td>40</td>
<td>60</td>
<td>8.3</td>
</tr>
<tr>
<td>Sty-alt-PFS-3/7</td>
<td>30</td>
<td>70</td>
<td>2.4</td>
</tr>
<tr>
<td>Sty-alt-PFS-2/8</td>
<td>20</td>
<td>80</td>
<td>5.0</td>
</tr>
<tr>
<td>Sty-alt-PFS-1/9</td>
<td>10</td>
<td>90</td>
<td>6.0</td>
</tr>
<tr>
<td>Sty-alt-PFS-0.5/9.5</td>
<td>5.0</td>
<td>95</td>
<td>5.8</td>
</tr>
</tbody>
</table>

a Numbers in experiment name correspond to molar ratio of comonomers in feed.

b Determined by 1H NMR spectroscopy using n-butyl acetate as internal standard.

c Determined gravimetrically after precipitating the copolymer, from equation 3.16.
Table 7.4. Data used to determine the reactivity ratios of styrene (Sty, $M_1$) and pentafluorostyrene (PFS, $M_2$) in their radical copolymerization in bulk for 2.5 h at 25 °C using t-butyl peroxy pivalate (1 mol%) as the initiator.

<table>
<thead>
<tr>
<th>Experiment a</th>
<th>mol% Sty in Copolymer. b</th>
<th>$F = X^2/Y$ c</th>
<th>$G = X(Y-1)/Y^d$</th>
<th>$\zeta = F/(\alpha+F)$ e</th>
<th>$\eta = G/(\alpha+F)$ f</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sty-alt-PFS-9/1</td>
<td>77</td>
<td>24.2</td>
<td>6.31</td>
<td>0.96</td>
<td>0.25</td>
</tr>
<tr>
<td>Sty-alt-PFS-8/2</td>
<td>62</td>
<td>9.81</td>
<td>1.55</td>
<td>0.91</td>
<td>0.14</td>
</tr>
<tr>
<td>Sty-alt-PFS-7/3</td>
<td>57</td>
<td>4.11</td>
<td>0.57</td>
<td>0.80</td>
<td>0.11</td>
</tr>
<tr>
<td>Sty-alt-PFS-6/4</td>
<td>50</td>
<td>2.25</td>
<td>0.00</td>
<td>0.69</td>
<td>0.00</td>
</tr>
<tr>
<td>Sty-alt-PFS-5/5</td>
<td>59</td>
<td>0.69</td>
<td>0.31</td>
<td>0.41</td>
<td>0.18</td>
</tr>
<tr>
<td>Sty-alt-PFS-4/6</td>
<td>45</td>
<td>0.54</td>
<td>-0.15</td>
<td>0.35</td>
<td>-0.096</td>
</tr>
<tr>
<td>Sty-alt-PFS-3/7</td>
<td>40</td>
<td>0.27</td>
<td>-0.21</td>
<td>0.22</td>
<td>-0.168</td>
</tr>
<tr>
<td>Sty-alt-PFS-2/8</td>
<td>34</td>
<td>0.12</td>
<td>-0.23</td>
<td>0.11</td>
<td>-0.21</td>
</tr>
<tr>
<td>Sty-alt-PFS-1/9</td>
<td>23</td>
<td>0.041</td>
<td>-0.26</td>
<td>0.04</td>
<td>-0.25</td>
</tr>
<tr>
<td>Sty-alt-PFS-0.5/9.5</td>
<td>21</td>
<td>0.010</td>
<td>-0.14</td>
<td>0.035</td>
<td>-0.49</td>
</tr>
</tbody>
</table>

$^a$ Numbers in experiment name correspond to molar ratio of comonomers in feed.

$^b$ Copolymer composition determined by $^1$H NMR spectroscopy analysis of the copolymer after removing unreacted monomers by precipitating the copolymer.

$^c$ Fineman-Ross parameter determined from eq. 6.2.

$^d$ Fineman-Ross parameter determined from eq. 6.3.

$^e$ Kelen-Tudós parameter determined from eq. 6.8.

$^f$ Kelen-Tudós parameter determined from eq. 6.7.
Figure 7.3 plots the values of G vs. the values of F (Fineman-Ross), which results in a straight line with slope corresponding to \( r_1 = r_{\text{sty}} = 0.26 \) and an intercept that corresponds to \( r_2 = r_{\text{PFS}} = 0.22 \).

Figure 7.4 plots the Kelen-Tüdos parameters \( \zeta \) and \( \eta \). The reactivity ratio \( r_1 \) is determined from the intercept of the extrapolation of \( \zeta \) to 1, \( r_1 = r_{\text{sty}} = 0.22 \), and \( r_2 \) from the intercept of the extrapolation of \( \zeta \) to 0, \( r_2 = r_{\text{PFS}} = 0.23 \). Both reactivity ratio values and their products \( r_1r_2 = 0.057 \) (Fineman-Ross) and \( r_1r_2 = 0.051 \) (Kelen-Tüdos) are consistent with an alternating copolymerization. In contrast to the relative insensitivity of most monomer reactivity ratios under conventional radical conditions,\(^\text{16} \) the Kelen- Tüdos values of \( r_1r_2 = 0.051 \) at 25 °C and 0.13 at 70 °C, in our system, corresponds to a difference of 61%.

![Figure 7.3. Finemann-Ross plot (equation 6.1) used to determine the reactivity ratios \( (k_1 = k_{11} / k_{12} \) and \( k_2 = k_{22} / k_{21} \) in the radical copolymerization of styrene \( (M_1) \) and 2,3,4,5,6-pentafluorostyrene \( (M_2) \) for 2.5 h in bulk at 25 °C using \( t \)-butyl peroxy pivalate (1 mol%) as the initiator.](image)
Figure 7.4. Kelen-Tüdos plot (equation 6.6) used to determine the reactivity ratios \((k_1 = k_{11} / k_{12}\) and \(k_2 = k_{22} / k_{21}\)) in the radical copolymerization of styrene \((M_1)\) and 2,3,4,5,6-pentafluorostyrene \((M_2)\) for 2.5 h in bulk at 25 °C using \(t\)-butyl peroxy pivalate (1 mol%) as the initiator.

This large difference in the reactivity ratio values determined at 70 °C and 25 °C indicates that \(\pi-\pi\) interactions between the two types of rings contribute to the tendency toward alternation.

7.2.2 NMR Spectroscopy of the Copolymers.

We used \(^1\)H NMR spectroscopy to determine the compositions of the resulting copolymers, which were used to determine the reactivity ratios and their products. Figure 7.5 shows the \(^1\)H NMR spectra of the homopolymers of styrene and PFS (on the bottom) and of three copolymers from the experiments Sty-alt-PFS-7/3, Sty-alt-PFS-5/5, and Sty-alt-PFS-3/7 synthesized at 70 °C. It was fairly simple to determine the copolymer composition from these spectra. The contribution of the styrene unit \((M_1)\) was determined from the integrals of the resonances in the aromatic area, and the contribution of the PFS units was
determined by subtracting the contribution of the styrene units from the total integral of the resonances in the alkyl area.

The aromatic resonances of the copolymers lack the fine structure that the resonances of polystyrene have. We attribute this to a distortion of the aromatic protons on the styrene units of the copolymers due to interactions with neighboring perfluorinated rings. Although the aromatic resonances of the copolymers appear at the same positions as those in the homopolymer, the alkyl resonances are positioned between those positions of the homopolymers; the higher the amount of PFS in the copolymer, the more downfield they appear.

Figure 7.5. $^1$H NMR spectra of 1) polystyrene; 2) poly(2,3,4,5,6-pentafluorostyrene); 3) poly(styrene-alt-pentafluorostyrene)-3/7, 40% styrene; 4) poly(styrene-alt-pentafluorostyrene)-5/5, 54% styrene; 5) poly(styrene-alt-pentafluorostyrene)-7/3, 68% styrene. Peak marked with an asterisk corresponds to residual CHCl$_3$. 

197
The CH₂CHAr units of the copolymers appear as two resonances, in analogy to the spectra of PPFS homopolymer (where there is no overlap between the resonances of the meso and racemo CH₂CHAr units), and in contrast to the polystyrene homopolymer, in which they show up as just one broad singlet. ¹H NMR spectroscopy shows that the backbone of these copolymers is different from that of the homopolymers, presumably due to alternating styrene-PFS units.

Figure 7.6 shows the quantitative ¹³C NMR spectra of the same five samples that were displayed in Figure 7.5. Figure 7.6 covers the range between 0 and 160 ppm. The alkyl area of the spectra of the copolymers is more similar to that of the monomer unit that the copolymers are more abundant in. The methine resonances (CH₂CHAr labeled as f and f*) are broader in the spectra of the copolymers. If Ar is a phenyl ring (styrene units) the resonances of CH₂CHAr are at the same position as in the ¹³C NMR spectrum of the polystyrene homopolymer, and if Ar is a perfluorinated phenyl ring (PFS units) the resonances of CH₂CHAr are at the same position as in the ¹³C NMR spectrum of the PPFS homopolymer. Assignment of the CH₂CHAr resonances (methylene carbons) is more difficult. These resonances are sensitive to tacticity¹⁸²,¹⁸³ and either they are not really distinguishable (spectra of the copolymers poly(styr-alt-PFS)-5/5, and poly(styr-alt-PFS)-7/3 or they appear as a broad resonance overlapped with the methyne resonances (spectrum of the copolymer poly(styr-alt-PFS)-3/7).
Figure 7.6. Quantitative $^{13}$C NMR spectra of 1) polystyrene; 2) poly(2,3,4,5,6-pentafluorostyrene); 3) poly(styrene-alt-pentafluorostyrene)-3/7, 40% styrene; 4) poly(styrene-alt-pentafluorostyrene)-5/5, 54% styrene; 5) poly(styrene-alt-pentafluorostyrene)-7/3, 68% styrene. Resonance at 78.0 ppm due to solvent CHCl$_3$.

Figure 7.7 shows the expanded area between 100 and 160 ppm of the spectra in Figure 7.6. The resonance corresponding to aromatic C1 of the PFS units (labeled a$^\ast$) adopts a different position in the copolymers than in the PPFS homopolymer spectrum. This position is closer to that of the homopolymer as the amount of PFS in the copolymer increases. There are new resonances appearing or the aromatic C1 resonance of the PFS units in the copolymers is splitting.
Figure 7.7. Quantitative $^{13}$C NMR spectra of 1) polystyrene; 2) poly(2,3,4,5,6-pentafluorostyrene); 3) poly(styrene-alt-pentafluorostyrene)-3/7, 40% styrene; 4) poly(styrene-alt-pentafluorostyrene)-5/5, 54% styrene; 5) poly(styrene-alt-pentafluorostyrene)-7/3, 68% styrene. Resonance at 78.0 ppm due to solvent CHCl$_3$. Spectrum shows only area between 100 and 160 ppm.

The aromatic C2 through C6 resonances of the styrene units are in the area between 124 and 130 ppm. Both the shape and the number of resonances vary in the copolymers compared to those in the homopolymer, and vary among the spectra of the three copolymers. The resonances between 134 and 150 ppm also differ from those of the homopolymers with the new resonances shifting the positions. We calculated the composition of the copolymers from those spectra.
finding that they were 66, 54 and 38% of styrene, using the integral of resonance labeled a* for the PFS units and the contribution of the styrene units to the total integral of the resonances between 134 and 150 ppm. There is excellent agreement between these results and the compositions of the copolymers determined by $^1$H NMR spectroscopy (68, 54 and 40% of styrene).

Figure 7.8. $^{19}$F NMR spectra of: 1) poly(2,3,4,5,6-pentafluorostyrene), 2) poly(styrene-alt-pentafluorostyrene)-5/5, 54% styrene; 3) poly(styrene-alt-pentafluorostyrene)-1/9, 35% styrene.

Figure 7.8 shows the $^{19}$F NMR spectra of PPFS homopolymer (bottom) and the spectra of the copolymer products of experiments sty-alt-PFS-5/5, and sty-alt-PFS-1/9 synthesized at 70 °C, with 54 and 35% styrene respectively. The resonances are singlets in the homopolymer. Those same resonances are either a group of resonances or are split in the spectra of the copolymers. Resonances
b and c appear at different positions in the spectrum of the copolymer having 54% of styrene compared to that of the PPFS homopolymer.

Figure 7.9 shows results of the gradient Hetero Nuclear-Single Quantum coherence experiment (HSQC) spectrum for the copolymer product of the experiment sty-alt-PFS-5/5, which has 54% styrene and 46% PFS. HSQC is a 2-dimensional NMR technique that can identify connectivity between carbon atoms and protons. This type of spectroscopy correlates only through bonds, not through space, and only directly attached nuclei show resonance. Therefore, the aromatic area of this spectrum corresponds exclusively to the resonances due to the aromatic carbons of the styrene units attached to their respective aromatic protons, which is not interesting for our analysis. We only need to analyze the resonances of the backbone of the copolymer in order to obtain more information about the sequence of the two different units.

Figure 7.9 displays only this alkyl (backbone) area. The horizontal axis corresponds to the $^{13}$C NMR spectrum and the vertical to the $^1$H NMR spectrum. From the $^{13}$C NMR spectrum of PPFS (Figure 7.6) we know that the resonances of the PPFS units are at 32.0 (CH$_2$CHAR) and 38.0 ppm (CH$_2$CHAR), in long sequences of PFS units. From the $^{13}$C NMR of polystyrene we know that the resonances of the styrene units are at 40.4 (CH$_2$CHAR) and 44.2 ppm (CH$_2$CHAR) in long sequences of styrene units (Figure 7.7). Analogously, the $^1$H NMR spectrum of PPFS shows resonances at 2.00 (CH$_2$CHAR), and 2.40 and 2.75 ppm (CH$_2$CHAR). The polystyrene $^1$H NMR spectrum shows resonances in the alkyl region at 1.50 (CH$_2$CHAR) and 1.80 ppm (CH$_2$CHAR). HSQC of PPFS 202
homopolymer should have resonances at the intersection of 32.0 and 2.40 and 2.75 (corresponding to the CH₂CHAr resonance) and the intersection of 38.0 and 2.00 ppm (for the CH₂CHAr resonance). HSQC spectrum of PS should have resonances at the intersection of 40.4 and 1.80 (corresponding to the CH₂CHAr resonance) and the intersection of 44.2 and 1.50 ppm (for the CH₂CHAr resonance). Excluding the last mentioned and the resonance at the intersection of 32.0 and 2.40 corresponding to PPFS CH₂CHAr, which are present in the spectrum, the rest of the resonances corresponding to the homopolymers do not appear in the HSQC spectrum of the copolymer. Instead, there is a series of resonances at positions that are shifted slightly from those estimated for both homopolymers.

Although it cannot be appreciated in this spectrum in Figure 7.9, since it is a black and white figure, the resonances labeled as a are distinguished to the ones labeled as b and c by their color (only visible in color versions of the figure), which indicates that the former correspond to a different group than the latter. Based on the positions estimated for the PS and PPFS homopolymers we assigned the a group to CH₂CHAr resonances and b and c to CH₂CHAr resonances. Considering this assignment and the estimated positions of the resonances of the PS and PPFS homopolymers, we have interpreted the HSQC spectrum as follows. We assigned the three distinctive resonances at the intersections of 42.4 and 2.10, 44.0 and 2.05, and 43.8 and 1.75, to the CH₂CHAr (labeled b in Figure 7.9) of styrene units in the copolymer, which appear as three different resonances due to the different sequences of units in
the copolymer. The three resonances at the intersections of 33.0 and 2.72, 32.0 and 2.40 and 32.2 and 2.20 are possibly due to CH$_2$CHAr (labeled c in Figure 7.9) of the PFS units in the copolymer. The intersection of 32.0 and 2.40 (same position as estimated for PFS units in PPFS homopolymer) is presumably due to long sequences of PFS units in the copolymer. The resonances due to CH$_2$CHAr (labeled a in Figure 7.9) of the copolymer appear in the region between 36.0 and 46.4 ppm (horizontal axis) and 1.40 and 2.03 ppm (vertical axis). In this region, the following resonances are distinguished. The resonances at the intersections of 36.0 and 1.90, 38.0 and 1.86, 41.7 and 1.70 are assigned to PFS CH$_2$CHAr resonances, which appear as three different resonances due to different sequences in the copolymer. The resonances at the intersections of 44.2 and 1.50 and 46.0 and 1.52 are assigned to styrene CH$_2$CHAr resonances, appearing as two different resonances due to the different sequences of styrene units in the copolymer. The intersection of 44.2 and 1.50 (same position as estimated for styrene units in PS homopolymer) is presumably due to long sequences of styrene units in the copolymer.

We have estimated the position of the resonances of the homopolymers PS and PPFS in the HSCQ spectrum. Groups a and b and c correspond to two different kinds of resonances. Based on the estimated positions of the homopolymers the a area corresponds to CH$_2$CHAr resonances and the b and c areas correspond to CH$_2$CHAr resonances. The appearance of new resonances at positions either upfield or downfield from those estimated for the
homopolymers demonstrates that the copolymer backbone is different from the homopolymers, presumably due to alternating styrene-PFS units.

Figure 7.9. Expanded hetero nuclear single quantum coherence experiment (HSQC) of poly(styrene-alt-pentafluorostyrene-5/5), with 54% mol of styrene. The copolymer was synthesized by the radical copolymerization of styrene and pentafluorostyrene in bulk at 70 °C for 25 min using benzoyl peroxide (1 mol%). The spectrum shows only the area between 21.6 and 52.2 ppm (horizontal axis) and 0.80 and 3.60 ppm (vertical axis), which corresponds to backbone area.

Figures 7.10 and 7.11 show the Nuclear Overhauser Effect Spectroscopy (NOESY) of the same copolymer, product of Sty-alt-PFS-5/5, with 54% mol styrene. Unlike HSQC, NOESY correlates two nuclei of the same kind through space, not through bonds. A pair of protons must be at a distance equal or less than 5 Å to show a resonance in a NOESY spectrum, and the intensity of the resonance is inversely proportional to the sixth power of the distance between
Figure 7.10 shows the full spectrum. The diagonal corresponds to the 1-dimensional spectrum and above and below this diagonal the resonances are symmetrical.

We observed three peaks at the intersections of 1.70 with 2.20 and 2.75 ppm and of 1.60 and 2.40 ppm, corresponding to protons on the backbone that are close enough to interact (labeled a and a’ in Figure 7.10). Based on the assignments of the resonances of the protons of the copolymer (Figure 7.5) we have estimated the assignments of these resonances. We believe that the resonance at the intersection between 1.70 and 2.20 (labeled a) is presumably due to interaction between CH$_2$CHAr protons of the styrene units and CH$_2$CHAr of the PFS units. The interaction of CH$_2$CHAr protons of the PFS units and CH$_2$CHAr of the styrene units presumably appears at the intersections of 1.70 and 2.75 and 1.60 and 2.40 ppm. The interaction of CH$_2$CHAr protons and CH$_2$CHAr of two consecutive units of the same type appear as resonances on both sides but yet attached to the diagonal that defines the 1-dimensional spectrum. There also are two resonances appearing at the intersection of 1.73 and 6.62 and 1.58 and 6.64 ppm (labeled b and b’ in Figure 7.10). This region is expanded in Figure 7.11. We believe that, although at this point and with the information we count on we cannot be completely sure, that these two resonances correspond to the interactions between the CH$_2$CHAr protons on the PFS units of the copolymers (at 1.73 and 6.62 ppm) and the CH$_2$CHAr of the styrene units of the copolymers (at 1.58 and 6.64 ppm) with the aromatic H2 and H6 of the styrene units (labeled b and b’ in Figure 7.11, respectively).
Figure 7.10. Nuclear overhauser effect spectroscopy (NOESY). NOESY full spectrum of poly(styrene-alt-pentafluorostyrene-5/5), with 54% mol of styrene. The copolymer was synthesized by the radical copolymerization of styrene and pentafluorostyrene in bulk at 70 °C for 25 min using benzoyl peroxide (1 mol%).
Provided that our assignment is correct, these interactions indicate that the CH₂ protons of both units of the copolymer (PFS and styrene) are close to the phenyl rings of the styrene units, demonstrating that the structure of this copolymer tends to be alternating. The intensity of the resonance due to the interaction between the styrene CH₂ proton and the aromatic proton (labeled b on spectrum) is slightly higher than the one due to the interaction between the PFS unit proton and the aromatic proton (labeled b'). This can be due to either a higher number of two consecutive styrene dyads than a PFS-styrene dyad, or to a closer distance between the two styrene CH₂ protons the most intense resonance is due to.

![Chemical structure and spectrum](image)

Figure 7.11. Nuclear overhauser effect spectroscopy (NOESY) expanded spectrum of poly(styrene-alt-pentafluorostyrene-5/5), with 54% mol of styrene. The copolymer was synthesized by the radical copolymerization of styrene and pentafluorostyrene in bulk at 70 °C for 25 min using benzoyl peroxide (1 mol%).
7.2.3 Molecular Weight and Thermal Behavior of the Copolymers.

Table 7.5 lists the number-average molecular weight ($M_n$) and the polydispersity index (pdi) values determined by GPC relative to PS standards for all of the copolymers synthesized at 25 and 70 °C. The copolymers synthesized at 25 °C have higher molecular weights and pdi’s than those synthesized at 70 °C; two different initiators were used. The efficiency of the initiator used at 25 °C, t-butyl peroxy pivalate is very low, and the copolymer recovered was not enough for GPC and thermal analysis. We repeated only the experiments whose results are tabulated in higher scales, in order to compare the thermal behavior of the copolymers synthesized at the two different temperatures.

The pdi’s of the copolymers synthesized at 70 °C are all above 2.0, and therefore higher than for polymerizations that terminate by either combination (pdi = 1.5) or disproportionation (pdi = 2.0). This could be due to the bulk conditions of the polymerization, which may lead to uncontrolled acceleration of the polymerization.\(^\text{147}\) The pdi’s of the copolymers synthesized at 25 °C are very high. In fact the GPC chromatograms of these copolymers are in many cases bimodal, with a peak at a lower $M_n$. This bimodal distribution is due to an unequal initiation ability of the two different radicals resulting from the homolytical dissociation of the t-butyl peroxy pivalate (Scheme 7.4).

\[
\begin{align*}
\text{CH}_3\text{C-OO-C-CH}_3 & \quad \text{CH}_3\text{CO}^+ + \cdot\text{O-CClCH}_3 \\
\text{CH}_3 \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

Scheme 7.4. Homolytical cleavage of t-butyl peroxy pivalate at 25 °C.
Table 7.5. Number-average molecular weights ($M_n$) and polydispersities ($pdi=M_w/M_n$) measured by gel permeation chromatography in tetrahydrofuran of the copolymers produced by radical copolymerizations of styrene (Sty) and pentfluorostyrene (PFS) for 25 min in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator and in bulk for 2.5 h at 25 °C using $t$-butyl peroxo pivalate (1 mol%) as the initiator.

<table>
<thead>
<tr>
<th>Experiment&lt;sup&gt;a&lt;/sup&gt;</th>
<th>70 °C Synthesis</th>
<th>25 °C Synthesis</th>
<th>25 °C Synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{Mol% Sty in}$</td>
<td>$M_n \times 10^4$</td>
<td>$M_n \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>Copolymer&lt;sup&gt;b&lt;/sup&gt;</td>
<td>$pdi$</td>
<td></td>
</tr>
<tr>
<td>Sty-Alt-PFS-9/1</td>
<td>88</td>
<td>5.70</td>
<td>2.17</td>
</tr>
<tr>
<td>Sty-Alt-PFS-8/2</td>
<td>82</td>
<td>3.92</td>
<td>2.40</td>
</tr>
<tr>
<td>Sty-Alt-PFS-7/3</td>
<td>76</td>
<td>4.32</td>
<td>2.04</td>
</tr>
<tr>
<td>Sty-Alt-PFS-6/4</td>
<td>62</td>
<td>3.74</td>
<td>2.05</td>
</tr>
<tr>
<td>Sty-Alt-PFS-5/5</td>
<td>57</td>
<td>4.71</td>
<td>2.30</td>
</tr>
<tr>
<td>Sty-Alt-PFS-4/6</td>
<td>46</td>
<td>6.92</td>
<td>2.13</td>
</tr>
<tr>
<td>Sty-Alt-PFS-3/7</td>
<td>44</td>
<td>5.20</td>
<td>2.40</td>
</tr>
<tr>
<td>Sty-Alt-PFS-2/8</td>
<td>38</td>
<td>6.40</td>
<td>2.23</td>
</tr>
<tr>
<td>Sty-Alt-PFS-1/9</td>
<td>35</td>
<td>4.70</td>
<td>2.60</td>
</tr>
<tr>
<td>Sty-Alt-PFS-0.5/9.5</td>
<td>21</td>
<td>4.40</td>
<td>2.61</td>
</tr>
</tbody>
</table>

<sup>a</sup>Numbers in experiment name correspond to molar ratio of comonomers in feed.  
<sup>b</sup>Copolymer composition determined by $^1$H NMR analysis of the copolymer after removing unreacted monomers by column chromatography and/or precipitating the copolymer.  
<sup>c</sup>Bimodal distribution. Lower molecular weight peak more intense.  
<sup>d</sup>Bimodal distribution, two peaks well defined. Lower molecular weight peak more intense.  
<sup>e</sup>Results not available.
Table 7.6. Dependence of the glass transition temperature ($T_g$) of poly(styrene-alt-pentafluorostyrene)s on their copolymer composition and number-average degree of polymerization ($DP_n$). The copolymers were synthesized by radical copolymerization of styrene and pentafluorostyrene (PFS) in bulk at either 70 °C for 25 min using benzyol peroxide (BPO) as the initiator or at 25 °C for 2.5 h using $t$-butyl peroxy pivavlate as the initiator.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>70 °C Synthesis</th>
<th>25 °C Synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mol% Sty in Copolymer</td>
<td>$DP_n$</td>
</tr>
<tr>
<td>Poly(styrene)</td>
<td>100</td>
<td>204</td>
</tr>
<tr>
<td>Sty-alt-PFS-9/1</td>
<td>88</td>
<td>517</td>
</tr>
<tr>
<td>Sty-alt-PFS-8/2</td>
<td>82</td>
<td>345</td>
</tr>
<tr>
<td>Sty-alt-PFS-7/3</td>
<td>76</td>
<td>369</td>
</tr>
<tr>
<td>Sty-alt-PFS-6/4</td>
<td>62</td>
<td>296</td>
</tr>
<tr>
<td>Sty-alt-PFS-5/5</td>
<td>57</td>
<td>362</td>
</tr>
<tr>
<td>Sty-alt-PFS-4/6</td>
<td>46</td>
<td>500</td>
</tr>
<tr>
<td>Sty-alt-PFS-3/7</td>
<td>44</td>
<td>370</td>
</tr>
<tr>
<td>Sty-alt-PFS-2/8</td>
<td>38</td>
<td>440</td>
</tr>
<tr>
<td>Sty-alt-PFS-1/9</td>
<td>35</td>
<td>316</td>
</tr>
<tr>
<td>Sty-alt-PFS-0.5/9.5</td>
<td>21</td>
<td>260</td>
</tr>
<tr>
<td>PPFS</td>
<td>0.0</td>
<td>250</td>
</tr>
</tbody>
</table>

- Numbers in experiment name correspond to molar ratio of comonomers in feed.
- Copolymer composition determined by $^1$H NMR analysis of the copolymer after removing unreacted monomers by column chromatography and/or precipitating the copolymer.
- Determined by gel permeation chromatography relative to polystyrene in tetrahydrofuran using mean of refractive index and UV detectors, and copolymer composition determined by $^1$H NMR spectroscopy.
- Determined by differential scanning calorimetry, mean of values from 2nd and 3rd heat at 10 °C/min.
- Synthesized at 70 °C in bulk for 25 min using BPO as the initiator.
- Bimodal distribution. Lower molecular weight peak more intense.
- Bimodal distribution, two peaks well defined. Lower molecular weight peak more intense.
- Results not available.
Table 7.6 summarizes the $T_g$ values measured by DSC for all of the copolymers synthesized at 70 °C and some of the copolymers synthesized at 25 °C. Those values are compared to the $T_g$s of the homopolymers of styrene and PFS synthesized under the same conditions as the copolymers obtained at 70 °C. All of the copolymers exhibit only one transition, consistent with a non-blocky distribution of the comonomers along the backbone.

Figure 7.12 plots the $T_g$ vs. the amount of PFS present in the copolymer. For those copolymers synthesized at 70 °C there is a slight decrease in the $T_g$ at the lowest amounts of PFS compared to the $T_g$ of PS, which was probably due to a distortion in the structure of PS upon introduction of small amounts of PFS, resulting in a lower $T_g$. The $T_g$ of the copolymers increases with an increased amount of PFS in these copolymers, and becomes higher than the molar-average $T_g$ of the two homopolymers, which corresponds to the straight line joining the homopolymers $T_g$s at the extremes. We attribute this positive deviation of the $T_g$s of the copolymers to stiffening of the backbone of the copolymer due to the interactions developed between the two types of aromatic rings. From the reactivity ratio values obtained for the two temperatures used, we concluded that alternation was more significant in the copolymers synthesized at 25 °C. This should have a more pronounced effect on the $T_g$s of the copolymers, which would make the deviation from the molar average of the $T_g$s of the copolymers even more pronounced. However, this did not occur, and we instead observed the opposite behavior. Although these copolymers show a higher $T_g$ than the molar-average values, the $T_g$s are lower than those of the
copolymers synthesized at 70 °C. The presence of a low molecular weight copolymer fraction is probably causing plasticization of the final product, which results in a depression of the measured T_g.

![Graph](image)

**Figure 7.12.** Plot of the glass transition temperature (T_g) of poly(styrene-alt-pentafluorostyrene) as a function of the 2,3,4,5,6-pentafluorostyrene (PFS) content. T_g's are determined by differential scanning calorimetry, mean of values from 2nd and 3rd heat at 10 °C/min. The trend line does not follow any theoretical or empirical equation, but helps the reader observe the trend followed by the data points.

7.3 Copolymerization of 2-Vinyl Naphthalene with 2,3,4,5,6-Pentafluorostyrene.

Patrick and Prosser\(^2\) studied the phase diagrams of hexafluorobenzene with other aromatic hydrocarbons, in addition to benzene, and found that 2-methyl naphthalene and hexafluorobenzene form an isolatable 1:1 complex that melts at 56 °C. Since the complex between hexafluorobenzene and benzene is transitory, the interactions developed between hexafluorobenzene and 2-methyl
naphthalene are evidently stronger than those between hexafluorobenzene and benzene. We therefore copolymerized 2-VN and PFS to determine if these stronger interactions can be correlated with their copolymerization reactivity ratios and the thermal behavior of their copolymers.

7.3.1 Copolymerization of 2-Vinyl Naphthalene with 2,3,4,5,6-Pentafluorostyrene. Determination of Reactivity Ratios.

Scheme 7.5 outlines the reaction between 2-VN and PFS at 70 °C in bulk using 1 mol% BPO as the radical initiator. The optimum time to limit the monomer conversions to ≤ 10% and still recover sufficient copolymer to characterize was 30 min.

![Scheme 7.5. Copolymerization of 2-vinyl naphthalene (M₁) and 2,3,4,5,6-pentafluorostyrene (M₂) in bulk for 30 min at 70 °C using benzoyl peroxide (BPO, 1 mol%) as the initiator.](image)

Table 7.7 summarizes the conversions of 2-VN (M₁) and PFS (M₂) determined by ¹H NMR spectroscopy, in which the experiments are labeled 2-VN-alt-PFS-x/y, with x/y the molar ratio of comonomers in the feed. In all cases, neither monomer conversion exceeded 10 mol%, as required by the Fineman-Ross and Kelen-Tüdos methods for determining reactivity ratios. In all cases enough copolymer was recovered to characterize. 2-VN is a solid at room
temperature (mp = 63-67 °C) and in many occasions the copolymer product had to be reprecipitated to eliminate 2-VN monomer that was contaminating the copolymer product.

We determined the composition of the copolymers by $^1$H NMR spectroscopy, using the integrals of the resonances in the aromatic region (6.00-8.20 ppm) for the 2-VN units and for the PFS units the integral of the alkyl region.

Table 7.7. Comonomers conversion for the radical copolymerization of 2-vinyl naphthalene (2-VN) with 2,3,4,5,6-pentafluorostyrene (PFS) for 30 min in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator.

<table>
<thead>
<tr>
<th>Experiment $^a$</th>
<th>Feed Composition (mol%)</th>
<th>Monomer Conversion$^b$ (%)</th>
<th>Copolymer Yield$^c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2-VN</td>
<td>PFS</td>
<td>2-VN</td>
</tr>
<tr>
<td>2-VN-alt-PFS-9/1</td>
<td>90</td>
<td>10</td>
<td>3.2</td>
</tr>
<tr>
<td>2-VN-alt-PFS-8/2</td>
<td>80</td>
<td>20</td>
<td>0.5</td>
</tr>
<tr>
<td>2-VN-alt-PFS-7/3</td>
<td>70</td>
<td>30</td>
<td>4.1</td>
</tr>
<tr>
<td>2-VN-alt-PFS-6/4</td>
<td>60</td>
<td>40</td>
<td>3.2</td>
</tr>
<tr>
<td>2-VN-alt-PFS-5/5</td>
<td>50</td>
<td>50</td>
<td>9.3</td>
</tr>
<tr>
<td>2-VN-alt-PFS-4/6</td>
<td>40</td>
<td>60</td>
<td>9.0</td>
</tr>
<tr>
<td>2-VN-alt-PFS-3/7</td>
<td>30</td>
<td>70</td>
<td>9.5</td>
</tr>
<tr>
<td>2-VN-alt-PFS-2/8</td>
<td>20</td>
<td>80</td>
<td>9.3</td>
</tr>
<tr>
<td>2-VN-alt-PFS-1/9</td>
<td>10</td>
<td>90</td>
<td>9.5</td>
</tr>
</tbody>
</table>

$^a$ Numbers in experiment name correspond to molar ratio of comonomers in feed.
$^b$ Determined by $^1$H NMR spectroscopy using $n$-butyl acetate as an internal standard.
$^c$ Determined gravimetrically after precipitating the copolymer, from equation 3.16.
$^d$ Precipitated twice to remove unreacted 2-vinyl naphthalene.
resonances (1.00-3.00 ppm) after subtracting out the 2-VN contribution, followed by application of equations 3.17 and 3.18. The compositions were used to calculate the yields listed in Table 7.7 (equation 3.16).

Table 7.8. Data used to determine the reactivity ratios of 2-vinyl naphthalene (2-VN, \( M_1 \)) and 2,3,4,5,6-pentafluorostyrene (PFS, \( M_2 \)) in their radical copolymerization in bulk for 30 min at 70 °C using benzoyl peroxide (BPO, 1 mol%) as the initiator.

<table>
<thead>
<tr>
<th>Experiment (^a)</th>
<th>mol% 2VN in Copolymer (^b)</th>
<th>F = ( X^2/Y ) (^c)</th>
<th>G = ( X/(Y-1)/Y ) (^d)</th>
<th>( \xi = F/(\alpha + F) ) (^e)</th>
<th>( \eta = G/(\alpha + F) ) (^f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-VN-alt-PFS-9/1</td>
<td>89</td>
<td>10.0</td>
<td>7.89</td>
<td>0.946</td>
<td>0.745</td>
</tr>
<tr>
<td>2-VN-alt-PFS-8/2</td>
<td>74</td>
<td>5.56</td>
<td>2.61</td>
<td>0.906</td>
<td>0.425</td>
</tr>
<tr>
<td>2-VN-alt-PFS-7/3</td>
<td>67</td>
<td>2.68</td>
<td>1.18</td>
<td>0.824</td>
<td>0.364</td>
</tr>
<tr>
<td>2-VN-alt-PFS-6/4</td>
<td>60</td>
<td>1.48</td>
<td>0.51</td>
<td>0.721</td>
<td>0.249</td>
</tr>
<tr>
<td>2-VN-alt-PFS-5/5</td>
<td>58</td>
<td>0.71</td>
<td>0.29</td>
<td>0.552</td>
<td>0.229</td>
</tr>
<tr>
<td>2-VN-alt-PFS-4/6</td>
<td>52</td>
<td>0.41</td>
<td>0.051</td>
<td>0.417</td>
<td>0.052</td>
</tr>
<tr>
<td>2-VN-alt-PFS-3/7</td>
<td>39</td>
<td>0.29</td>
<td>-0.24</td>
<td>0.333</td>
<td>-0.278</td>
</tr>
<tr>
<td>2-VN-alt-PFS-2/8</td>
<td>35</td>
<td>0.12</td>
<td>-0.22</td>
<td>0.170</td>
<td>-0.319</td>
</tr>
<tr>
<td>2-VN-alt-PFS-1/9</td>
<td>27</td>
<td>0.033</td>
<td>-0.18</td>
<td>0.054</td>
<td>-0.304</td>
</tr>
</tbody>
</table>

\(^a\) Numbers in experiment name correspond to molar ratio of comonomers in feed; 30 min reaction time.
\(^b\) Copolymer composition determined by \(^1\)H NMR analysis of the copolymer after removing unreacted monomers by precipitating the copolymer.
\(^c\) Fineman-Ross parameter determined from eq. 4.2.
\(^d\) Fineman-Ross parameter determined from eq. 4.3.
\(^e\) Kelen-Tudös parameter determined from eq. 4.8.
\(^f\) Kelen-Tudös parameter determined from eq. 4.7.
In analogy to the copolymerization of styrene and PFS (Section 7.2) we determined the comonomer reactivity ratios for this copolymerization by the Fineman-Ross (equation 6.1) and Kelen-Tüdos (equation 6.6) methods. The calculated parameters necessary to apply these methods and the composition of the copolymer products that were used to determine these parameters are listed in Table 7.8.

Figure 7.13 plots G vs. F, in which the data are adjusted to a straight line whose slope is \( r_1 = r_{2VN} = 0.76 \), and intercept provides \( r_2 = r_{PFS} = 0.48 \) (Fineman-Ross method, equation 6.1).

Figure 7.13. Finemann-Ross plot (equation 6.1) to determine the reactivity ratios \( (k_1 = k_{11} / k_{12} \) and \( k_2 = k_{22} / k_{21} \) ) in the radical copolymerization of 2-vinyl naphthalene (\( M_1 \)) and 2,3,4,5,6-pentafluorostyrene (\( M_2 \)) for 30 min in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator.
Figure 7.14 shows the plot of $\eta$ vs. $\zeta$, (Kelen-Tüdos method, equation 6.6) in which the data are adjusted to a straight line whose intercept corresponds to as $r_1 = r_{2\text{VN}} = 0.62$ at $\zeta$ equal to 1 and $r_2 = r_{\text{PFS}} = 0.27$ at $\zeta$ equal to 0. The resulting products of the reactivity ratios for this comonomer pair are $r_1 r_2 = 0.37$ and $r_1 r_2 = 0.17$ from the Fineman-Ross and Kelen-Tüdos methods, respectively. These results are consistent with an alternating copolymerization.

Figure 7.14. Kelen-Tüdos plot (equation 6.6) to determine the reactivity ratios ($k_1 = k_{11} / k_{12}$ and $k_2 = k_{22} / k_{21}$) in the radical copolymerization of 2-vinyl naphthalene ($M_1$) and 2,3,4,5,6-pentafluorostyrene ($M_2$) for 30 min in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator.

Figure 7.15 shows the $^1$H NMR spectra of PPFS homopolymer, poly(2-vinyl naphthalene) homopolymer and poly(2-vinyl naphthalene-\textit{alt}-PFS) with 58 mol\% of 2-VN, which is the product of the experiment labeled poly(2-VN-\textit{alt}-PFS)-5/5. The positions of the resonances of the protons on the backbone (alkyl area, between 1.00 and 3.00 ppm) of the poly(2-VN-\textit{alt}-PFS)-5/5 copolymer are
between those of the homopolymers. The CH₂CHAr meso and racemo units of
the copolymer do not overlap in analogy to those of the PPFS spectrum. In
contrast to the spectra of the poly(styrene-alt-PFS), the resonances of the
aromatic protons of the poly(2-VN-alt-PFS)-5/5 copolymer are at different
positions than the aromatic resonances of the poly(2-vinyl naphthalene)
homopolymer. The shapes of the resonances are also different, with the lowest
field resonance not very well defined.

![Chemical structure and NMR spectra](image)

Figure 7.15. ¹H NMR spectra of 1) poly(pentafluorostyrene), 2) poly(2-vinyl
naphthalene); 3) poly(2-vinyl naphthalene-alt-pentafluorostyrene)-5/5, with 58
mol % of 2-vinyl naphthalene. Resonances marked with an asterisk correspond
to residual CHCl₃ from solvent.

Therefore, although the values of the reactivity ratios and their products do not
indicate that there are stronger interactions between the hydrocarbon and
fluorocarbon aromatic rings, the ¹H NMR spectra demonstrate that the aromatic
interactions are in fact stronger, since the aromatic protons of the copolymer are influenced by the interactions with the neighboring PFS rings.

7.3.2 Molecular Weight and Thermal Behavior of the Copolymers.

We also investigated the thermal behavior of the copolymers of 2-VN with PFS as a function of their composition to correlate it with the interactions occurring between the two types of rings, in analogy to the study of the styrene and PFS system. Table 7.9 lists the number-average molecular weights \( M_n \) and the polydispersities for all of the copolymers measured by GPC relative to PS standards, and the number-average degrees of polymerization \( DP_n \) calculated from the \( M_n \) values and the copolymer compositions determined by \(^1\)H NMR spectroscopy. Both the \( M_n \) and \( DP_n \) increase with increasing amount of PFS in the sample. The pdi values are all around 2.00, which corresponded to higher values than expected from termination exclusively by combination, and therefore disproportionation may be occurring in this copolymerization.

The values of the \( T_g \)s determined by DSC are also included in Table 7.9. All of the copolymers show only one transition, consistent with the non-blocky structure of the copolymers. Figure 7.18 plots the \( T_g \) calculated from the average of the second and third heat scans by DSC vs. the amount of PFS in the copolymer (mol\% PFS). To find an appropriate \( T_g \) value for poly(2-vinyl naphthalene) homopolymer that we could include in Figure 7.18, we plotted the \( T_g \)s of several poly(2-vinyl naphthalene)s obtained under different conditions vs. their \( DP_n \) (Table 7.10).
Table 7.9. Number-average molecular weight ($M_n$), polydispersity index (pdi), degree of polymerization ($DP_n$), and glass transition temperature ($T_g$) of poly(2-vinyl naphthalene-alt-pentafluorostyrene)s (poly(2VN-alt-PFS)) as a function of the molar amount (%) of 2-vinyl naphthalene (2-VN) in the copolymer.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>mol% 2-VN in Copolymer b</th>
<th>$M_n \times 10^4$ c</th>
<th>pdi</th>
<th>$DP_n$ d</th>
<th>$T_g$(°C) e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(2-VN)</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>130 g</td>
<td>129.7 g</td>
</tr>
<tr>
<td>2-VN-alt-PFS-9/1</td>
<td>89</td>
<td>2.22</td>
<td>1.87</td>
<td>139</td>
<td>129.0</td>
</tr>
<tr>
<td>2-VN-alt-PFS-8/2</td>
<td>74</td>
<td>2.94</td>
<td>2.57</td>
<td>179</td>
<td>131.6</td>
</tr>
<tr>
<td>2-VN-alt-PFS-7/3</td>
<td>67</td>
<td>3.13</td>
<td>2.16</td>
<td>188</td>
<td>130.7</td>
</tr>
<tr>
<td>2-VN-alt-PFS-6/4</td>
<td>60</td>
<td>3.99</td>
<td>2.13</td>
<td>235</td>
<td>131.3</td>
</tr>
<tr>
<td>2-VN-alt-PFS-5/5</td>
<td>58</td>
<td>4.40</td>
<td>2.05</td>
<td>258</td>
<td>126.6</td>
</tr>
<tr>
<td>2-VN-alt-PFS-4/6</td>
<td>52</td>
<td>4.85</td>
<td>2.02</td>
<td>282</td>
<td>123.8</td>
</tr>
<tr>
<td>2-VN-alt-PFS-3/7</td>
<td>39</td>
<td>5.54</td>
<td>2.04</td>
<td>314</td>
<td>na h</td>
</tr>
<tr>
<td>2-VN-alt-PFS-2/8</td>
<td>35</td>
<td>6.26</td>
<td>2.03</td>
<td>352</td>
<td>120.2</td>
</tr>
<tr>
<td>2-VN-alt-PFS-1/9</td>
<td>27</td>
<td>6.95</td>
<td>2.06</td>
<td>382</td>
<td>113.8</td>
</tr>
<tr>
<td>PPFS</td>
<td>0.0</td>
<td>4.85</td>
<td>1.68</td>
<td>250</td>
<td>106.0</td>
</tr>
</tbody>
</table>

a Numbers in experiment name correspond to molar ratio of comonomers in feed. Poly(2VN-alt-PFS)s were synthesized by the radical copolymerization of 2-VN with 2,3,4,5,6-pentafluorostyrene in bulk at 70 °C for 30 min using benzoyl peroxide (1 mol%) as the initiator.
b Copolymer composition determined by $^1$H NMR analysis of the copolymer after removing unreacted monomers by precipitating the copolymer.
c Determined by gel permeation chromatography relative to polystyrene standards in tetrahydrofuran.
d Determined from $M_n$ data and composition of the copolymer, determined by $^1$H NMR.
e Determined by differential scanning calorimetry, mean of values from 2nd and 3rd heat at 10 °C/min.
f Chosen from the trend followed by copolymers $DP_n$s.
g Extrapolated value from plot on figure 7.16.
h Result not available. $T_g$ not detected.
Table 7.10. Number-average molecular weight ($M_n$), polydispersity index (pdi), degree of polymerization ($DP_n$), and glass transition temperature ($T_g$) of poly(2-vinyl naphthalene)s obtained under different conditions.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>$M_n \times 10^{-3}$ a</th>
<th>pdi</th>
<th>$DP_n$</th>
<th>$T_g(^\circ C)$ b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>48</td>
<td>3.30</td>
<td>2.67</td>
<td>34.4</td>
<td>125.8</td>
</tr>
<tr>
<td>2 c</td>
<td>-</td>
<td>0.50</td>
<td>12.4</td>
<td>2.61</td>
<td>79.5</td>
<td>127.0</td>
</tr>
<tr>
<td>3</td>
<td>tetrahydrofuran</td>
<td>24</td>
<td>27.7</td>
<td>2.93</td>
<td>178</td>
<td>134.9</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>24</td>
<td>53.9</td>
<td>2.30</td>
<td>350</td>
<td>149.2</td>
</tr>
</tbody>
</table>

a Determined by gel permeation chromatography relative to polystyrene standards in tetrahydrofuran.

b Determined by differential scanning calorimetry, mean of values from 2nd and 3rd heat at 10 °C/min.

c Same conditions as used for the copolymerizations. Resulting poly(2-vinyl naphthalene) has a very low $DP_n$ compared to the $DP_n$s of the copolymers.

![Figure 7.16](image)

Figure 7.16. Plot of glass transition temperature ($T_g$) as a function of the degree of polymerization ($DP_n$) for several poly(2-vinyl naphthalene)s. $T_g$s were determined by differential scanning calorimetry; mean of values from 2nd and 3rd heat at 10 °C/min. $DP_n$ values determined by gel permeation chromatography relative to polystyrene standards.
The data points adjusted very well to a straight line (Figure 7.16), and within this 
$DP_n$ range there is still dependence of the $T_g$ on the molecular weight of the 
polymer. The degree of polymerization above which the $T_g$ no longer depends 
on the molecular weight ($T_g^{\infty}$) should be at a $DP_n > 350$.

Figure 7.17. Plot of glass transition temperature ($T_g$) as a function of the degree 
of polymerization ($1/DP_n$) for several poly(2-vinyl naphthalene)s. $T_g$s were 
determined by differential scanning calorimetry; mean of values from 2$^{nd}$ and 3$^{rd}$ 
heat at 10 °C/min. $DP_n$ values determined by gel permeation chromatography 
relative to polystyrene standards.

The plot of $T_g$ vs. $1/ DP_n$ (Figure 7.17) can be adjusted to a straight line that 
intercepts at $T_g^{\infty} = 143.9$ °C. We determined from the equation of the line $T_g$ vs. 
$DP_n$ a $DP_n$ of 130 (slightly lower than that of the copolymer with the lowest molar 
amount of PFS) corresponds to a $T_g$ of 131.9 °C, which was the value we used 
for P-2VN homopolymer in Figure 7.18.

Figure 7.18 shows a positive deviation of the $T_g$s of the copolymers with 
respect to the molar average of the $T_g$s of the homopolymers (which are on the 
straight line joining the two extreme data points of the plot, corresponding to the
$T_g$ of the homopolymers). We attribute this positive deviation to a stiffening effect of the backbone, due to the interactions developed between the two types of aromatic rings. The positive deviation is more pronounced than the one for the thermal behavior of poly(styrene-$alt$-pentfluorostyrene)s. The stronger interaction as proposed by Patrick and Prosser$^2$ of 2-methyl naphthalene and hexafluorobenzene than that of benzene and hexafluorobenzene is reflected in a higher melting point of the 1:1 complex. This stronger interaction is responsible for the higher interactions developed between the two types of rings, reflected on $^1$H NMR spectroscopy results and thermal behavior of the copolymers.

![Figure 7.18](image-url)

Figure 7.18. Plot of the glass transition temperature ($T_g$) of the poly(2-vinyl naphthalene-$alt$-pentfluorostyrene)s as a function of the pentfluorostyrene (PFS) molar amount. $T_g$s were determined by differential scanning calorimetry; mean of values from 2$^{nd}$ and 3$^{rd}$ heat at 10 °C/min. The trend line does not follow any theoretical or empirical equation, but helps the reader observe the trend followed by the data points.
7.4 Copolymerization of 1-Vinyl Naphthalene with 2,3,4,5,6-Pentafluorostyrene.

The phase diagram of hexafluorobenzene and 1-methyl naphthalene reported by Griffith et al.\textsuperscript{79} shows that they form a 1:1 molecular complex with a melting point of around 100 °C (much higher than the melting points of the single components: 5.0 and -22 °C, respectively). 1-Vinyl naphthalene has a similar structure to that of 1-methyl naphthalene. We copolymerized 1-vinyl naphthalene (1-VN) with PFS at 70 °C and at 25 °C. In this case, the melting point of the corresponding non-vinyl complex was above the polymerization temperature of 70 °C, and therefore the reactivity ratio values should not vary much at different copolymerization temperatures.

7.4.1 Synthesis of 1-Vinyl Naphthalene.

Scheme 7.6 outlines the synthesis of 1-VN. We used a Parr reactor to minimize contact with and/or leaks of vinyl bromide, a potential carcinogen.

\[
\text{Br} \quad + \quad \text{Mg} \quad \xrightarrow{\text{ethyl ether, reflux, 6.5 h}} \quad \text{MgBr}
\]

100 % conversion

\[
\text{MgBr} \quad + \quad \text{ethyl ether, toluene} \quad \xrightarrow{\text{Ni(dppp)Cl}_2} \quad \text{Br} \quad \xrightarrow{-95 \ ^\circ\ C \ to \ 25 \ ^\circ\ C, \ 23 \ h} \quad 35-67\%
\]

The solvent system formed by ethyl ether and toluene was optimum to carry out this synthesis. We attempted the reaction with only ethyl ether, obtaining a very low yield due to the insolubility of the Grignard reagent, naphtalyl magnesium bromide, especially after degassing of the reaction mixture. The insolubility of the Grignard reagent makes the transfer to the Parr reactor sleeve less efficient. We also tried the solvent system composed of THF and toluene. The crude yield was very low, and purification of the product was more difficult since the reaction was not as clean.

The purification of the final product was quite challenging. We attempted to distill it under reduced pressure using a short path distillation head several times, which resulted in oxidation and/or polymerization, presumably initiated cationically by traces of acid left in the monomer after work-up. We switched to hot water instead of cold water through the distillation head, since the highly viscous product was clogging the distillation head.

7.4.2 Copolymerization of 1-Vinyl Naphthalene with 2,3,4,5,6-Pentafluorostyrene. Determination of Reactivity Ratios.

Scheme 7.7 outlines the reaction between 1-VN and PFS carried out at 70 °C in bulk using 1 mol% BPO as the radical initiator. The optimum time to limit the monomer conversions to ≤ 10% and still recover a sufficient amount of copolymer to characterize was 2.5 h.
Scheme 7.7. Copolymerization of 1-vinyl naphthalene ($M_1$) and pentafluorostyrene ($M_2$) in bulk for 2.5 h at 70 °C using benzoyl peroxide (BPO, 1 mol%) as the initiator.

Table 7.11 summarizes the conversions of 1-VN ($M_1$) and PFS ($M_2$) determined by $^1$H NMR spectroscopy, in which the experiments are labeled 1-VN-alt-PFS-x/y, with x/y the molar ratio of comonomers in the feed. In all the cases neither monomer conversion exceeded 10 mol%; many times the conversion of the monomer was lower than 1 %, and in some cases it was calculated to be lower than 0 %, due to the experimental error of $^1$H NMR spectroscopy. The yields were very low in most cases, especially when the final product had to be reprecipitated in warm non-solvent to remove unreacted 1-VN.

We determined the composition of the copolymers by $^1$H NMR spectroscopy, using equations 3.19 and 3.20 and the integrals of the resonances in the aromatic region (5.00-8.00 ppm) for the contribution of the 1-VN units and the contribution of the PFS units to the integral of the alkyl region resonances (0.80-3.00 ppm). The composition was used to calculate the yields listed on Table 7.11 (equation 3.16). The yields were very low in all cases and we had to repeat some of the experiments to recover enough copolymer to characterize.
Table 7.11. Comonomer conversions for the radical copolymerization of 1-vinyl naphthalene (1-VN) with 2,3,4,5,6-pentafluorostyrene (PFS) in bulk for 2.5 h at 70 °C using benzoyl peroxide (1 mol%) as the initiator.

<table>
<thead>
<tr>
<th>Experiment a</th>
<th>Feed Composition (mol%)</th>
<th>Monomer Conversion b (%)</th>
<th>Copolymer Yield c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1-VN</td>
<td>PFS</td>
<td>1-VN</td>
</tr>
<tr>
<td>1-VN-alt-PFS-9/1</td>
<td>90</td>
<td>10</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>1-VN-alt-PFS-8/2</td>
<td>80</td>
<td>20</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>1-VN-alt-PFS-7/3</td>
<td>70</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>1-VN-alt-PFS-6/4</td>
<td>60</td>
<td>40</td>
<td>3.0</td>
</tr>
<tr>
<td>1-VN-alt-PFS-5/5</td>
<td>50</td>
<td>50</td>
<td>2.0</td>
</tr>
<tr>
<td>1-VN-alt-PFS-4/6</td>
<td>40</td>
<td>60</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>1-VN-alt-PFS-3/7</td>
<td>30</td>
<td>70</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>1-VN-alt-PFS-2/8</td>
<td>20</td>
<td>80</td>
<td>6.7</td>
</tr>
<tr>
<td>1-VN-alt-PFS-1/9</td>
<td>10</td>
<td>90</td>
<td>&lt; 0</td>
</tr>
</tbody>
</table>

a Numbers in experiment name correspond to molar ratio of comonomers in feed.
b Determined by ¹H NMR spectroscopy using n-butyl acetate as internal standard.
c Determined gravimetrically after precipitating the copolymer, from equation 3.16.

We determined the comonomer reactivity ratios for this copolymerization by the Fineman-Ross\textsuperscript{178} (equation 6.1) and Kelen-Tüdos\textsuperscript{179} (equation 6.6) methods, as in the previous systems. The parameters required to apply these methods
and the composition of the copolymer products used to determine them are listed in Table 7.12.

Table 7.12. Data used to determine the reactivity ratios of 1-vinyl naphthalene (1-VN, M₁) and pentadfluorostyrene (PFS, M₂) in their radical copolymerization in bulk for 2.5 h at 70 °C using benzyol peroxide (1 mol%) as the initiator.

<table>
<thead>
<tr>
<th>Experiment a</th>
<th>mol% 1VN in Copolymer b</th>
<th>F = X²/Y c</th>
<th>G = X(Y-1)/Yd</th>
<th>ζ = F/(α+F)e</th>
<th>η = G/(α+F)f</th>
</tr>
</thead>
<tbody>
<tr>
<td>1VN-alt-PFS-9/1</td>
<td>80.0</td>
<td>20.2</td>
<td>6.7</td>
<td>0.960</td>
<td>0.320</td>
</tr>
<tr>
<td>1VN-alt-PFS-8/2</td>
<td>75.6</td>
<td>5.16</td>
<td>2.71</td>
<td>0.861</td>
<td>0.452</td>
</tr>
<tr>
<td>1VN-alt-PFS-7/3</td>
<td>65.3</td>
<td>2.90</td>
<td>1.09</td>
<td>0.776</td>
<td>0.293</td>
</tr>
<tr>
<td>1VN-alt-PFS-6/4</td>
<td>58.0</td>
<td>1.62</td>
<td>0.414</td>
<td>0.661</td>
<td>0.168</td>
</tr>
<tr>
<td>1VN-alt-PFS-5/5</td>
<td>57.0</td>
<td>0.754</td>
<td>0.246</td>
<td>0.475</td>
<td>0.154</td>
</tr>
<tr>
<td>1VN-alt-PFS-4/6</td>
<td>46.5</td>
<td>0.511</td>
<td>-0.100</td>
<td>0.380</td>
<td>-0.0746</td>
</tr>
<tr>
<td>1VN-alt-PFS-3/7</td>
<td>40.0</td>
<td>0.275</td>
<td>-0.214</td>
<td>0.248</td>
<td>-0.193</td>
</tr>
<tr>
<td>1VN-alt-PFS-2/8</td>
<td>34.7</td>
<td>0.118</td>
<td>-0.220</td>
<td>0.124</td>
<td>-0.232</td>
</tr>
<tr>
<td>1VN-alt-PFS-1/9</td>
<td>26.6</td>
<td>0.0340</td>
<td>-0.195</td>
<td>0.0393</td>
<td>-0.225</td>
</tr>
</tbody>
</table>

a Numbers in experiment name correspond to molar ratio of comonomers in feed.
b Copolymer composition determined by 1H NMR spectroscopy of the copolymer after removing unreacted monomers by precipitating the copolymer.
c Fineman-Ross parameter determined from eq. 6.2.
d Fineman-Ross parameter determined from eq. 6.3.
e Kelen-Tudós parameter determined from eq. 6.8.
f Kelen-Tudós parameter determined from eq. 6.7.

The data in the plot of G vs. F (Figure 7.19, Fineman-Ross) adjusts to a straight line whose slope is r₁ = r₁VN = 0.35; and intercept corresponds to r₂ = rPFS = 0.05 (equation 6.1). Figure 7.20 plots η vs. ζ (Kelen-Tüdös method, equation
which also adjusts to a straight line whose intercept corresponds to $r_1 = r_{1 VN} = 0.44$ at $\zeta = 1$ and $r_2 = r_{PF S} = 0.23$ at $\zeta = 0$. The resulting products of the reactivity ratios for this comonomer pair are $r_{12} = 0.018$ and $r_{11} = 0.10$ from the Fineman-Ross and Kelen-Tüdos methods, respectively. These results correspond to an alternating copolymerization.

Figure 7.19. Finemann-Ross plot (equation 6.1) used to determine the reactivity ratios ($k_1 = k_{11} / k_{12}$ and $k_2 = k_{22} / k_{21}$) in the radical copolymerization of 1-vinyl naphthalene ($M_1$) with 2,3,4,5,6-pentafluorostyrene ($M_2$) for 2.5 h in bulk at 70 °C using benzoyl peroxide (1 mol%) as the initiator.

Figure 7.20. Kelen-Tüdos plot (equation 6.6) used to determine the reactivity ratios ($k_1 = k_{11} / k_{12}$ and $k_2 = k_{22} / k_{21}$) in the radical copolymerization of 1-vinyl naphthalene ($M_1$) and 2,3,4,5,6-pentafluorostyrene ($M_2$) for 2.5 h in bulk at 70 °C using benzoyl peroxide (BPO, 1 mol%) as the initiator.
Figure 7.21 compares the $^1$H NMR spectra of the PPFS homopolymer, poly(1-vinyl naphthalene) homopolymer and poly(1-vinyl naphthalene-alt-PFS) from the 1VN-alt-PFS-5/5 experiment with 57 mol%1-vinyl naphthalene. The area between 1.00 and 3.00 ppm (alkyl area) of the copolymer is very similar to that of the homopolymer of 1-VN, with two very broad resonances with very low resolution. However, the aromatic area of this copolymer spectrum is quite different from that of the poly(1-vinyl naphthalene) homopolymer. The broad resonance at 6.00 ppm present in the spectrum of the homopolymer is absent in the spectrum of the copolymer. The interactions between the naphthalene ring units and perfluorinated rings are apparently distorting the aromatic protons.

Figure 7.21. $^1$H NMR Spectra of 1) poly(2,3,4,5,6-pentafluorostyrene), 2) poly(1-vinyl naphthalene), 3) poly(1- vinyl naphthalene-alt-pentafluorostyrene)-5/5, with 57 mol% of 1-vinyl naphthalene. Resonances marked with an asterisk corresponds to residual CHCl₃.
In order to investigate the effect of the temperature on the interactions developed between these two rings we also copolymerized 1-VN and PFS for 7 h at room temperature, using t-butyl peroxy pivalate as the initiator. Scheme 7.8 outlines this reaction. We determined the monomer conversion by $^1$H NMR spectroscopy using n-butyl acetate as an internal standard. Tables 7.13 contains the monomer conversion data for this copolymerization. In all cases the conversions were under 10 %.

![Scheme 7.8](image)

Scheme 7.8. Copolymerization of 1-vinyl naphthalene ($M_1$) and 2,3,4,5,6-pentafluorostyrene ($M_2$) for 7 h in bulk at 25 °C with t-butyl perxy pivalate (1 mol%) as the initiator.

The copolymer composition was calculated by $^1$H NMR spectroscopy in the same way as in the previous copolymerizations. These values were used to determine the yields of the copolymers, which are fairly low (between around 0.0 and 4.6 %).
Table 7.13. Comonomers conversion for the radical copolymerization of 1-vinyl naphthalene (1-VN) with 2,3,4,5,6-pentafluorostyrene (PFS) in bulk for 7 h at 25 °C using t-butyl peroxo pivalate (1 mol%) as the initiator.

<table>
<thead>
<tr>
<th>Experiment a</th>
<th>Feed Composition (mol%)</th>
<th>Monomer Conversion b (%)</th>
<th>Copolymer Yield c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1-VN</td>
<td>PFS</td>
<td>1-VN</td>
</tr>
<tr>
<td>1-VN-alt-PFS-9/1</td>
<td>90</td>
<td>10</td>
<td>4.5</td>
</tr>
<tr>
<td>1-VN-alt-PFS-8/2</td>
<td>80</td>
<td>20</td>
<td>5.8</td>
</tr>
<tr>
<td>1-VN-alt-PFS-7/3</td>
<td>70</td>
<td>30</td>
<td>1.9</td>
</tr>
<tr>
<td>1-VN-alt-PFS-6/4</td>
<td>60</td>
<td>40</td>
<td>9.5</td>
</tr>
<tr>
<td>1-VN-alt-PFS-5/5</td>
<td>50</td>
<td>50</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>1-VN-alt-PFS-4/6</td>
<td>40</td>
<td>60</td>
<td>3.1</td>
</tr>
<tr>
<td>1-VN-alt-PFS-3/7</td>
<td>30</td>
<td>70</td>
<td>1.2</td>
</tr>
<tr>
<td>1-VN-alt-PFS-2/8</td>
<td>20</td>
<td>80</td>
<td>5.2</td>
</tr>
<tr>
<td>1-VN-alt-PFS-1/9</td>
<td>10</td>
<td>90</td>
<td>2.3</td>
</tr>
</tbody>
</table>

a Numbers in experiment name correspond to molar ratio of comonomers in feed.
b Determined by $^1$H NMR spectroscopy using $n$-butyl acetate as internal standard.
c Determined gravimetrically after precipitating the copolymer, from equation 3.16.
Table 7.14. Data used to determine the reactivity ratios of 1-vinyl naphthalene (1-VN, M$_1$) and pentfluorostyrene (PFS, M$_2$) in their radical copolymerization in bulk for 7 h at 25 °C using t-butyl peroxy pivalate (1 mol%) as the initiator and n-butyl acetate as an internal standard.

<table>
<thead>
<tr>
<th>Experiment  a</th>
<th>mol% 1VN in Copolymer b</th>
<th>$F = X^2/Y$ c</th>
<th>$G = X(Y-1)/Y$ d</th>
<th>$\xi = F/(\alpha+F)$ e</th>
<th>$\eta = G/(\alpha+F)$ f</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-VN-alt-PFS-9/1</td>
<td>82</td>
<td>17.8</td>
<td>7.02</td>
<td>0.958</td>
<td>0.378</td>
</tr>
<tr>
<td>1-VN-alt-PFS-8/2</td>
<td>65</td>
<td>8.61</td>
<td>1.84</td>
<td>0.917</td>
<td>0.196</td>
</tr>
<tr>
<td>1-VN-alt-PFS-7/3</td>
<td>58</td>
<td>3.94</td>
<td>0.644</td>
<td>0.835</td>
<td>0.136</td>
</tr>
<tr>
<td>1-VN-alt-PFS-6/4</td>
<td>55</td>
<td>1.84</td>
<td>0.273</td>
<td>0.703</td>
<td>0.104</td>
</tr>
<tr>
<td>1-VN-alt-PFS-5/5</td>
<td>53</td>
<td>0.887</td>
<td>0.113</td>
<td>0.533</td>
<td>0.0680</td>
</tr>
<tr>
<td>1-VN-alt-PFS-4/6</td>
<td>45</td>
<td>0.543</td>
<td>-0.148</td>
<td>0.411</td>
<td>-0.112</td>
</tr>
<tr>
<td>1-VN-alt-PFS-3/7</td>
<td>39</td>
<td>0.287</td>
<td>-0.242</td>
<td>0.270</td>
<td>-0.227</td>
</tr>
<tr>
<td>1-VN-alt-PFS-2/8</td>
<td>35</td>
<td>0.117</td>
<td>-0.220</td>
<td>0.131</td>
<td>-0.246</td>
</tr>
<tr>
<td>1-VN-alt-PFS-1/9</td>
<td>27</td>
<td>0.0341</td>
<td>-0.195</td>
<td>0.0419</td>
<td>-0.241</td>
</tr>
</tbody>
</table>

a Numbers in experiment name correspond to molar ratio of comonomers in feed.
bCopolymer composition determined by $^1$H NMR analysis of the copolymer after removing unreacted monomers by precipitating the copolymer.
c Fineman-Ross parameter determined from eq. 6.2.
d Fineman-Ross parameter determined from eq. 6.3.
e Kelen-Tudos parameter determined from eq. 6.8.
f Kelen-Tudos parameter determined from eq. 6.7.

Table 7.14 summarizes the data necessary to determine the reactivity ratios by the Fineman-Ross and Kelen-Tudos methods. We applied the Fineman-Ross and Kelen-Tudos methods to determine the reactivity ratios...
(equations 6.1 and 6.6), and the values determined are \( r_1 = r_{1VN} = 0.39 \) and \( r_2 = r_{PFS} = 0.46 \) from the plot of \( G \) vs. \( F \) (Fineman-Ross, Figure 7.22) and of \( r_1 = r_{1VN} = 0.21 \) and \( r_2 = r_{PFS} = 0.41 \) from the plot of \( \zeta \) vs. \( \eta \) (Kelen-Tüdos, Figure 7.23). The products of these values are \( r_1 r_2 = 0.18 \) and 0.095, respectively. The reactivity ratios and their product obtained by the more accurate Kelen-Tüdos method are very similar for the two temperatures, which is a usual tendency in conventional radical polymerizations. There should not be a large difference between the interactions in the corresponding 1:1 non-vinyl complex (1-methyl naphthalene and hexafluorobenzene) at the two temperatures of copolymerization (25 and 70 °C), since it has a melting point of 100 °C. Therefore, the reactivity ratios are similar at both temperatures.

Figure 7.22. Finemann-Ross plot (equation 6.1) used to determine the reactivity ratios \( (k_1 = k_{11} / k_{12} \) and \( k_2 = k_{22} / k_{21} \) in the radical copolymerization of 1-vinyl naphthalene (\( M_1 \)) and 2,3,4,5,6-pentafluorostyrene (\( M_2 \)) for 7 h in bulk at 25 °C using t-butyl peroxy pivalate (1 mol%) as the initiator.
Figure 7.23. Kelen-Tüdos plot (equation 6.6) used to determine the reactivity ratios \( (k_1 = k_{11} / k_{12} \text{ and } k_2 = k_{22} / k_{21}) \) in the radical copolymerization of 1-vinyl naphthalene (\( M_1 \)) and 2,3,4,5,6-pentafluorostyrene (\( M_2 \)) for 7 h in bulk at 25 °C using \( t \)-butyl peroxy pivalate (1 mol%) as the initiator.

7.4.3 Molecular Weight and Thermal Behavior of the Copolymers.

Table 7.15 lists the number-average molecular weight \( (M_n) \) and the pdi of the copolymers of 1-VN and PFS synthesized at 70 °C measured by GPC relative to polystyrene standards, and the \( DP_n \) calculated from the copolymer composition determined by \(^1\)H NMR spectroscopy. The values of \( M_n \), and of \( DP_n \) increase with an increased molar amount of PFS in the sample. The \( T_g \)s of these copolymers determined by DSC are also included in this Table. Only one transition was observed as expected from the non-blocky type of structure of the copolymers.

We homopolymerized 1-VN under the same conditions as the copolymers (in bulk at 70 °C for 2.5 h), which resulted in a homopolymer with a \( DP_n \) that was similar to that of the copolymer with the highest amount of 1-VN. Therefore, we used this poly(1-vinyl naphthalene) to investigate its thermal behavior and compare it with that of the poly(1-vinyl naphthalene-alt-PFS)s.
Table 7.15. Number-average molecular weight ($M_n$), polydispersity index (pdi) and glass transition temperature ($T_g$) of poly(1-vinyl naphthalene-alt-pentafluorostyrene)s synthesized by radical copolymerization of 1-vinyl naphthalene (1-VN) and 2,3,4,5,6-pentafluorostyrene (PFS) in bulk for 2.5 h at 70 °C using benzoyl peroxide (1% mol) as the initiator.

<table>
<thead>
<tr>
<th>Experiment a</th>
<th>mol% 1VN in Copolymer b</th>
<th>$M_n \times 10^3$ c</th>
<th>pdi</th>
<th>$DP_n$ d</th>
<th>$T_g (°C)$ e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(1VN)</td>
<td>100</td>
<td>5.98</td>
<td>1.64</td>
<td>32</td>
<td>126.9</td>
</tr>
<tr>
<td>1-VN-alt-PFS-9/1</td>
<td>80</td>
<td>7.17</td>
<td>1.63</td>
<td>39</td>
<td>141.5</td>
</tr>
<tr>
<td>1-VN-alt-PFS-8/2</td>
<td>76</td>
<td>7.82</td>
<td>1.67</td>
<td>49</td>
<td>135.6</td>
</tr>
<tr>
<td>1-VN-alt-PFS-7/3</td>
<td>65</td>
<td>8.40</td>
<td>1.75</td>
<td>50</td>
<td>138.2</td>
</tr>
<tr>
<td>1-VN-alt-PFS-6/4</td>
<td>58</td>
<td>9.63</td>
<td>1.71</td>
<td>55</td>
<td>126.6</td>
</tr>
<tr>
<td>1-VN-alt-PFS-5/5</td>
<td>57</td>
<td>7.06</td>
<td>1.62</td>
<td>106</td>
<td>116.7</td>
</tr>
<tr>
<td>1-VN-alt-PFS-4/6</td>
<td>46</td>
<td>27.8</td>
<td>1.60</td>
<td>160</td>
<td>122.5</td>
</tr>
<tr>
<td>1-VN-alt-PFS-3/7</td>
<td>40</td>
<td>22.1</td>
<td>1.81</td>
<td>127</td>
<td>118.9</td>
</tr>
<tr>
<td>1-VN-alt-PFS-2/8</td>
<td>35</td>
<td>25.9</td>
<td>1.94</td>
<td>154</td>
<td>112.4</td>
</tr>
<tr>
<td>1-VN-alt-PFS-1/9</td>
<td>27</td>
<td>10.0</td>
<td>1.84</td>
<td>62</td>
<td>98.0</td>
</tr>
<tr>
<td>PPFS</td>
<td>0.0</td>
<td>48.5</td>
<td>1.68</td>
<td>250</td>
<td>106</td>
</tr>
</tbody>
</table>

a Numbers in experiment name correspond to molar ratio of comonomers in feed.
b Copolymer composition determined by $^1$H NMR spectroscopy of the copolymer after removing unreacted monomers by precipitating the copolymer.
c Determined by gel permeation chromatography (GPC) relative to polystyrene standards.
d Calculated from $M_n$ data from GPC and composition of the copolymer determined by $^1$H NMR.
e Determined by differential scanning calorimetry, mean of values from 2nd and 3rd heat at 10 °C/min.

Figure 7.24 plots the $T_g$ of the poly(1-vinyl naphthalene-alt-PFS)s as a function of the molar amount of PFS in the copolymer. The value corresponding
to 1VN-\textit{alt}-PFS-1/9 is not included in this plot, since the \( DP_n \) of this copolymer is lower than the copolymer having the closest composition to it, which causes its \( T_g \) to be much lower than the rest of the copolymers \( T_g \)s.

Figure 7.24. Plot of the glass transition temperature (\( T_g \)) of the poly(1-vinyl naphthalene-\textit{alt}-pentafluorostyrene)s as a function of the molar amount (\%) of pentafluorostyrene (PFS). \( T_g \)s were determined by differential scanning calorimetry (DSC), mean of values from 2\textsuperscript{nd} and 3\textsuperscript{rd} heat at 10 °C/min. The trend line does not follow any theoretical or empirical equation, but helps the reader observe the trend followed by the data points.

Figure 7.24 shows a positive deviation of the \( T_g \)s of the copolymers from their molar average \( T_g \)s of the homopolymers (the straight line joining the two extreme data points of the plot). The \( T_g \) of the copolymer containing 57 mol\% PFS is not included in the curve showing the deviation since it has an anomalous low value, possibly due to experimental error. This is the strongest positive deviation of the three systems investigated. We attribute this to stronger
interactions developed between PFS and 1-vinyl naphthalene than those
developed with PFS and/or 2-vinyl naphthalene and styrene.

7.5 Blends of Polystyrene and Poly(2-Vinyl Naphthalene) with Poly(2,3,4,5,6-pentafluorostyrene).

Table 7.16 shows the $T_g$s of the different blends, made with homopolymers that were synthesized using the same conditions as the copolymers, which resulted in homopolymers with $DP_n$s of 204 (polystyrene), 80 (poly(2-vinyl naphthalene)) and 250 (PPFS). All of the blends exhibited only one transition was observed. The $T_g$s of the blends of PS with PPFS increased with the amount of PPFS present.

Table 7.16. Glass transition temperature ($T_g$) of the blends of polystyrene (PS, $DP_n = 204$), poly(2,3,4,5,6-pentafluorostyrene) (PPFS, $DP_n = 250$) and poly(2-vinyl naphthalene) (P2-VN, $DP_n = 80$) as a function of their composition.

<table>
<thead>
<tr>
<th>Molar Ratio PPFS/PS$^a$</th>
<th>$T_g$ ($°$C)$^b$</th>
<th>Molar Ratio PPFS/P2-VN$^a$</th>
<th>$T_g$ ($°$C)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 /100</td>
<td>100.1</td>
<td>0 /100</td>
<td>127.0</td>
</tr>
<tr>
<td>25 /75</td>
<td>103.1</td>
<td>25 /75</td>
<td>109.1</td>
</tr>
<tr>
<td>50 / 50</td>
<td>103.5</td>
<td>50 / 50</td>
<td>108.5</td>
</tr>
<tr>
<td>75 / 25</td>
<td>104.5</td>
<td>75 / 25</td>
<td>110.0</td>
</tr>
<tr>
<td>100 /0</td>
<td>106.0</td>
<td>100 /0</td>
<td>106.0</td>
</tr>
</tbody>
</table>

$^a$ All the homopolymers were synthesized by radical polymerization at 70 °C in bulk using benzoyl peroxide (BPO, 1% mol) as the initiator. Polymerization times were 25 min for polystyrene and PPFS, and 30 min for poly(2-vinyl naphthalene).

$^b$ Determined by differential scanning calorimetry (DSC); mean of values from 2$^{rd}$ and 3$^{rd}$ heat at 10 °C/min.

Figure 7.25 shows the DSC scans (2$^{nd}$ heat scan) of the blends compared to those of the homopolymers. There is only one transition in all cases, which indicates total miscibility of the two homopolymers, unlike most aliphatic
fluorinated polymers that are inmiscible with regular hydrocarbon polymers. We believe that the interactions developed between the aromatic hydrocarbon and fluorocarbon rings causes this miscibility.

Figure 7.25. Differential scanning calorimetry thermograms of blends of polystyrene (PS, $DP_n = 204$) and poly(2,3,4,5,6-pentafluorostyrene) (PPFS, $DP_n = 250$) prepared by radical polymerization initiated by benzoyl peroxide (1 mol%) at 70 °C. The traces correspond to the second heating scan. Glass transition temperature ($T_g$) values mean of values from 2nd and 3rd heat at 10 °C/min.
Figure 7.26. Plot of the glass transition temperature ($T_g$) of the blends of polystyrene ($DP_n = 204$) and poly(2,3,4,5,6-pentafluorostyrene) (PPFS, $DP_n = 250$) as a function of the molar amount of PPFS in the blend. Glass transition temperature ($T_g$) values mean of values from 2$^{nd}$ and 3$^{rd}$ heat at 10 °C/min.

Figure 7.26 plots the $T_g$s of the blends of PS ($DP_n = 204$) and PPFS ($DP_n = 250$) as a function of the molar amount of PPFS in the blend. The blends exhibit $T_g$s that are intermediate between those of the homopolymers, although there is a slight positive deviation of the $T_g$s from their molar average (the straight line joining the two extreme data points of the plot).

We also investigated the thermal behavior of a blend of PS ($DP_n = 204$) and PPFS ($DP_n = 250$) made by evaporating the solvent from which the polymers were dissolved. In contrast to the two $T_g$s reported by Su of blends of PS and PPFS prepared under the same conditions, this blend had only one transition at 103.7 °C (average of second and third scans). Since the $T_g$s of polystyrene
and PPFS were very close (100 and 106 °C, respectively) we also investigated the thermal behavior of a sample consisting of a regular mixture of the two homopolymers (not blended) to determine if that the blends had two overlapping T\textsubscript{g}s. Figure 7.27 compares the thermograms of the samples made from the film resulting from the blend and the sample made from the two homopolymers mixed directly in the pan. The figure shows that only one transition again appears when the polymers are blended as opposed to when they were not. Although there are two transitions, these are at lower (98.8 vs. 100.1 °C for polystyrene) and higher temperatures (111.0 vs. 106 °C) than the T\textsubscript{g}s of the homopolymers alone. This could be due to error from the partial overlapping of the two transitions.

![Blended vs Non-Blended Thermograms](image.png)

Figure 7.27. Differential scanning calorimetry thermograms of a blended and non-blended sample of polystyrene (\(DP_n = 204\)) and poly(2,3,4,5,6-pentafluorostyrene) (\(DP_n = 250\)) prepared by the radical polymerization initiated by benzoyl peroxide (1 mol%) in bulk at 70 °C for 25 min.
Figure 7.28. Differential scanning calorimetry thermograms of blends of poly(2-vinyl naphthalene) (P2-VN, $DP_n = 80$) and poly(2,3,4,5,6-pentafluorostyrene) (PPFS, $DP_n = 250$) prepared by radical polymerization initiated by benzoyl peroxide (1 mol%) at 70 °C. The traces correspond to second heating scan. Glass transition temperature ($T_g$) values mean of values from 2nd and 3rd heat at 10 °C/min.
For the blends of PPFS \((DP_n = 250)\) and poly(2-vinyl naphthalene) \((DP_n = 80)\) we used homopolymers synthesized under the same conditions as the copolymers (with degree of polymerization for PPFS and P2VN of 204 and 80, respectively). Surprisingly, the \(T_g\) did not increase trend with the amount of poly(2-vinyl naphthalene). The thermograms displayed in Figure 7.28 have only one transition, indicating full miscibility of the blends, caused by interactions between the aromatic fluorinated rings (PPFS) and aromatic hydrocarbon rings (poly(2-vinyl naphthalene)).

![Figure 7.29](image-url)

**Figure 7.29.** Plot of the glass transition temperature \((T_g)\) of the blends of poly(2-vinyl naphthalene) \((DP_n = 80)\) and poly(2,3,4,5,6-pentafluorostyrene) (PPFS, \(DP_n = 250)\) as a function of the molar amount of PPFS in the blend. Glass transition temperature \((T_g)\) values mean of values from 2\(^{nd}\) and 3\(^{rd}\) heat at 10 °C/min.

Figure 7.29 plots the \(T_g\)s of the blends of poly(2-vinyl naphthalene) and PPFS as a function of the molar amount of PPFS in the blend. The blends
exhibit $T_g$s that are intermediate between those of the homopolymers, although much lower than the $T_g$s from their molar average (the straight line joining the two extreme data points of the plot).

7.6 Attempted Synthesis of 1-Vinyl Pyrene.

We attempted to synthesize 1-vinyl pyrene by the same route used to synthesize 1-vinyl naphthalene, starting from pyrene.

Scheme 7.9 outlines the synthesis of 1-bromo pyrene by reaction of a slight excess of pyrene with bromine in carbon tetrachloride. Part of the product was dibrominated, and was contaminated with some unreacted pyrene. We separated the dibromo derivative (insoluble in carbon tetrachloride) by decanting the reaction solution from the precipitate formed, and only the first recrystallization crop was used for the second step, since subsequent crops were primarily unreacted pyrene.

\[
\begin{align*}
\text{Pyrene} + \text{Br}_2 & \xrightarrow{\text{CCl}_4, \text{reflux, 6-15 h}} \text{Br} \\
& \text{58-74%}
\end{align*}
\]

Scheme 7.9. Synthesis of 1-bromo pyrene.

To make the Grignard reagent we first attempted the reaction of 1-bromo pyrene with magnesium in diethyl ether. However, 1-bromo pyrene is insoluble in diethyl ether and we switched to THF. This reaction was not spontaneous,
and we had to activate it by heating of the mixture. Scheme 7.9 outlines this reaction.

![Chemical reaction diagram](image)

Scheme 7.10. Synthesis of pyrenyl magnesium bromide.

We tried the coupling reaction of magnesium pyrenyl bromide with vinyl bromide in the presence of bis(diphenylphosphino)propane nickel (II) chloride (NiCl$_2$(dppp)) as a catalyst. We attempted the reaction with two different amounts of catalyst, and for two different periods of time. We did not get any product either time.

We instead tried the reaction of the Grignard reagent with acetaldehyde, which would lead to the formation of the secondary alcohol, which after dehydration would lead to 1-vinyl pyrene. However, we could not get the reaction between the Grignard and the acetaldehyde to work.

Although we did obtain the Grignard reagent, this is not reactive in either of the two reaction attempted.
CHAPTER VIII
SUMMARY

We have synthesized and characterized several copolymers containing 2,3,4,5,6-pentafluorostyrene (PFS), including graft copolymers of poly(2,3,4,5,6-pentafluorostyrene) (PPFS) onto polybutadiene (PB), and chain copolymers of PFS with β-pinene, styrene, 1-vinyl naphthalene and 2-vinyl naphthalene.

Chapter IV covered the study of graft copolymers of PFS onto PB (PB-g-PPFS). The copolymerization of PFS with PB in tetrahydrofuran using benzoyl peroxide (BPO) as the initiator at 60 °C follows typical radical polymerization kinetics, with the initial rate of polymerization having a linear dependence on $[M][I]^{1/2}$. In addition, the amount of PPFS produced increased with time as expected for a conventional radical polymerization, and the molecular weight decreased as both the amount of initiator used and the polymerization temperature increased. The polydispersities of 1.51 - 1.66 of the isolated PPFS homopolymers are consistent with termination primarily by combination. The UV-detected gel permeation chromatography (GPC) responses of PB-g-PPFS graft copolymer and of the ungrafted PPFS homopolymers (the two main products of the graft copolymerization) were well resolved. Therefore, the monomer
conversion, molecular weight of each component, and the PFS grafting efficiency (relative amount of PFS that is grafted onto PB), grafting ratio (relative amount of the copolymer that is PPFS), and grafting frequency (average number of backbone repeat units between grafts) could be determined by direct injection of the copolymerization mixtures into a GPC without isolating and purifying the graft copolymers. Within experimental error, the grafting efficiency, which was never more than 12%, seems to be independent of monomer conversion, temperature and initiator concentration. The grafting ratio (15-32%) increased with increasing monomer conversion, which is consistent with a system that terminates by combination and generates graft sites by primary initiator radicals; it also increased with increasing temperature and increasing initiator concentration. The number of grafts per PB chain (2-6) increases, and therefore the grafting frequency (454-1424) decreased, with increasing copolymerization temperature and increasing initiator concentration. The graft copolymers were isolated from up to a trace amount (< 5%) of unreacted PB and the large amount (58-81 wt%) of PPFS homopolymer produced by extracting the crude products at room temperature with hexanes and then with acetone, respectively. The glass transition temperatures of the PPFS grafts in the copolymers and the corresponding extracted PPFS homopolymers increase with increasing molecular weight to a maximum of 106 °C, and are approximately equal. The similarity of the glass transitions and elemental compositions of the graft copolymers and PPFS homopolymers confirm that the lengths of the PPFS grafts and corresponding PPFS homopolymers are equal in these copolymerizations.
We also attempted to modify PB with PFS by an ene reaction. The high temperatures necessary to perform an ene reaction, due to their high activation energies, caused the thermally initiated radical homopolymerization of PFS. GPC and $^1$H NMR spectroscopy demonstrated that the products of this attempted reaction were PPFS homopolymer, and PB that was unreacted, oxidized and/or crosslinked. In order to decrease the activation energy of the ene reaction to make it a viable process, the synthesis of an arene complex of PFS is underway.

$\beta$-Pinene is the most reactive ene known for an ene reaction. In order to test the reactivity of PFS as an enophile we reacted it with $\beta$-pinene, which produced their copolymer. The reactivity ratios, determined using the Kelen-Tüdos method$^{179}$ of PFS ($M_1$) and $\beta$-pinene ($M_2$) in their radical copolymerization initiated by BPO at 70 °C are $r_1 = 5.0$ and $r_2 = 0.017$, demonstrate that PFS prefers to homopropagate rather than cross-propagate with $\beta$-pinene, and that $\beta$-pinene has a very low probability of homopropagating. The copolymers are composed of isolated units of $\beta$-pinene randomly distributed between blocks of PFS segments. The compositions of the copolymers determined by $^1$H NMR spectroscopy are between 58 and 98 mol% PFS. Therefore the copolymers are always richer in PFS than $\beta$-pinene units, even when the feed compositions contain excess $\beta$-pinene. Both the higher PFS conversion and the preferential incorporation of PFS into the copolymers are consistent with the very low ability of $\beta$-pinene to homopolymerize by a radical mechanism. In addition, the number-average molecular weight of the copolymers determined by GPC using toluene
as eluant ($M_n$), the number average degree of polymerization ($DP_n$), and their
glass transition temperatures ($T_g$) increase with the amount of PFS present in the
copolymer. The $DP_n$s, determined from the $M_n$ values and the compositions of
the copolymers calculated by $^1$H NMR spectroscopy, vary from 11 (for a
copolymer containing 58 mol% of PFS) to 30 (copolymer with 98 mol% of PFS).
The $T_g$ values range between 60 °C (copolymer with 80 mol%) and 100 °C
(copolymer with 98 mol% PFS), and the transitions are not detectable for
copolymers with less than 80 mol% PFS. The copolymer products have low
surface energies, as demonstrated by the high static water contact angles, which
decrease from 100.4 to 95.2 ° when the PFS amount decreases from 95 to 69
mol % PFS. The copolymers are optically active, due to the presence of a chiral
center in the backbone. The specific rotations of different copolymers measured
for THF solutions of different concentrations are of the same sign but different in
magnitude to that of β-pinene. In addition, they increase with increasing
concentrations amount of β-pinene, which is the unit that contains the chiral
center, in the copolymer.

We copolymerized PFS with a series of vinyl monomers having one
(styrene) or two (1- and 2-vinyl naphthalene) aromatic groups in an attempt to
correlate the interactions developed between aromatic fluorocarbons and
aromatic hydrocarbons with their copolymerization behavior. The reactivity ratios
of styrene ($M_1$) and PFS ($M_2$) in their radical copolymerization initiated by BPO,
determined by the Kelen-Tüdos method$^{179}$ are $r_1 = 0.69$ and $r_2 = 0.19$ ($r_1r_2 = 0.13$), which corresponds to a copolymerization with tendency to alternation.
One-dimensional $^1$H, $^{19}$F, and especially quantitative $^{13}$C NMR spectra of the copolymers show both shifting all of the resonances and appearance of new ones, due to the new structure formed from alternating units in the copolymers. Two-dimensional NMR spectra from gradient heteronuclear multiple bond correlation (HMBC) and nuclear Overhauser effect spectroscopy (NOESY) of the copolymers also show strong evidence for alternation. The $T_g$s of the copolymers, determined by DSC, are between 100 and 109 °C (this last one being higher than PPFS $T_g = 106.0$ °C). We attribute the positive deviation of the copolymer transitions with respect to the molar average $T_g$ values to the interactions developed between the two types of rings, which causes stiffens in the backbone. The tendency of styrene and PFS to alternate at room temperature is higher than at 70 °C, as demonstrated by the reactivity ratios measured for their radical copolymerization at 25 °C initiated by $t$-butyl peroxypivalate and determined using the Kelen-Tüdos method.\textsuperscript{179} $r_1 = 0.22$ and $r_2 = 0.23$ ($r_1r_2 = 0.07$). This is consistent with the higher stability of the complex formed by benzene (aromatic hydrocarbon) and hexafluorobenzene (aromatic fluorocarbon) at room temperature (mp of the 1:1 complex = 24.3 °C\textsuperscript{2}).

The copolymerization of 2-vinyl naphthalene ($M_1$) with PFS ($M_2$) also tends to alternate as demonstrated by the reactivity ratio values determined using the Kelen-Tüdos method,\textsuperscript{179} $r_1 = 0.62$ and $r_2 = 0.27$ ($r_1r_2 = 0.17$), for their BPO-initiated radical copolymerization at 70 °C. $^1$H NMR spectra of the copolymers show shifting of resonances and appearance of new ones compared to those of the homopolymers. The DSC-determined $T_g$ values of the copolymers vary
between 114 and 132 °C, which are higher values than those of the homopolymer T_g s. This increase is attributed to the interactions developed between the two types of rings, which stiffens the backbone.

The reactivity ratios for the BPO-initiated radical copolymerization at 70 °C of 1-vinyl naphthalene (M_1) and PFS (M_2), determined by the Kelen-Tüdos method, are r_1 = 0.44 and r_2 = 0.23 (r_1r_2 = 0.10), which correspond to a copolymerization that tends to alternate. The reactivity ratios for their copolymerization at 25 °C (radically initiated with t-butyl peroxy pivalate) are r_1 = 0.21 and r_2 = 0.41 (r_1r_2 = 0.095). In this case the difference of the r_1r_2 values between the two temperatures is very small, in agreement with the stability of the complex formed between 1-methyl naphthalene and hexafluorobenzene, which melts at 100 °C. The T_g s of the copolymers range from 112 to 142 °C, which is the largest positive deviation from the molar average of the T_g s of the homopolymers of all of the systems studied.

The reactivity ratios determined by the Kelen-Tüdos method, the thermal behavior of the resulting copolymers and the analysis of the structure of the copolymers using NMR spectroscopy support the idea of an alternating copolymer structure. The great difference in the reactivity ratios measured at 70 °C compared to those determined at 25 °C for the styrene-PFS system, but not for the 1-vinyl naphthalene-PFS system is consistent with the complexation of the fluorocarbon and hydrocarbon aromatic rings contributing to the comonomers' tendency to alternate rather than the alternation resulting only from the influence
of the hydrocarbon and fluorocarbon substituents on the frontier molecular orbitals of the vinyl monomers.

The behavior of blends prepared of PS and poly(2-vinyl naphthalene) with PPFS was also investigated. We observed full miscibility of the blends as evidenced by the existence of only one $T_g$ by DSC. In the blends of PS and PPFS, the $T_g$ not only increases with increasing amount of PPFS in the blend, but it has a value that corresponds to the molar average between the $T_g$s of the two components of the blend. The blends of poly(2-vinyl naphthalene) and PPFS show transitions that increase with the amount of poly(2-vinyl naphthalene) (component with the highest $T_g$), but the values are not a direct not a function of the composition. We believe that this unusual behavior for a blend of fluorinated and non-fluorinated polymers is a direct consequence of the strong interactions developed by perfluorinated aromatic rings and regular aromatic hydrocarbons.
REFERENCES AND NOTES


256


257


85 Patrick, C.R. Chemistry and Industry 1959, 28, 940-942.


89 Hahn, B. Goodyear Tire & Co. Private Communication.


91 Swinton, F.L. Molecular Complexes 1974, 2, 63-106.


123 Gesner, B.D. *Rubber Chemistry and Technology* 1965, 655-666.


137 Thomas, C.A. U.S. Patent 1 939 932, 1933.


164 Kuo, S.W.; Chang, F.C. *Polymer* 2003, 3021-3030.


167 If cold water used, the distillation head was clogged due to high viscosity of the 1-VN product, hindering the distillation.


170 270 MHz: Heatley, F.; Bovey, F.A. *Macromolecules* 1968, 1, 301-303.


172 Odian, G. *Principles of Polymerization*, 3rd Ed.; John Wiley & Sons Ltd.: Chichester, 1993; Chapter 3.


180 Odian, G. *Principles of Polymerization*, 3rd Ed.; John Wiley & Sons Ltd.: Chichester, 1993; Chapter 6.

