SYNTHESIS, CHARACTERIZATION, AND SURFACE FUNCTIONALIZATION OF
POLYISOBUTYLENE BASED BIOMATERIALS

A Dissertation

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

Elizabeth A. Orlowski

August, 2009
SYNTHESIS, CHARACTERIZATION, AND SURFACE FUNCTIONALIZATION OF POLYISOBUTYLENE BASED BIOMATERIALS

Elizabeth A. Orlowski
Dissertation

Approved: Advisor
Dr. Judit E. Puskas

Accepted: Department Chair
Dr. Ali Dhinojwala

Committee Member
Dr. Joseph P. Kennedy

Dean of the College
Dr. Stephen Cheng

Committee Member
Dr. Roderic Quirk

Dean of the Graduate School
Dr. George Newkome

Committee Member
Dr. Alexi Sokolov

Date

Committee Member
Dr. Claire Tessier
ABSTRACT

Synthesis of the *inimer* (initiator-monomer) 4-(1,2-oxirane-isopropyl)styrene (EPOIM) and copolymerization of this inimer with isobutylene (IB) to form arborescent polyisobutylene (*arb_PIB*) was carried out using TiCl$_4$ coinitiator. The effect of reaction conditions was investigated. Size exclusion chromatography (SEC) was used to show incorporation of EPOIM across the molecular weight distribution. The average number of branches was measured by selective link destruction. Polymer architecture analysis was carried out using branching parameters based on the radii of gyration ($R_g$) and hydrodynamic radii ($R_h$) determined by multidetector SEC. *In situ* FTIR was utilized to monitor the polymerization of EPOIM. Block copolymers were synthesized by the blocking of *arb_PIB* with *p*-methylstyrene to form novel 4th generation SIBS materials, *arb_poly*[isobutylene(OH)-b-(isobutylene-co-*p*-methylstyrene)] [*arb_IB(OH)-MS*]. Proof of the presence of hydroxyl groups in the polymer was obtained using $^1$H-NMR spectroscopy and by silylation with chlorotrimethylsilylamine.

The reinforcement and surface functionalization of thermoplastic elastomers (TPEs) for soft tissue replacement was investigated. The materials investigated were soft TPE based PIBs, with surfaces more hydrophilic than poly(styrene-[*b*-isobutylene-*b*-styrene]) (SIBS) and silicone rubber. The material reinforced with carbon black (CB) [*arb_IB(OH)-MS_CB*] had an interpenetrating network structure, in which the $T_g$ of the
dispersed phase increased to 126 °C, making the material steam-sterilizable. It also had the lowest water contact angle at 82°, and superior mechanical properties in comparison with silicone rubber. After 180 days implantation into rabbits \(arb\text{\_IB(OH)-MS\_CB}\) displayed the thinnest capsule around the implant in comparison to \(arb\text{\_IB(OH)-MS}\) and silicone.

A new method of surface functionalization to increase the hydrophilicity of \(arb\text{\_IB(OH)-MS}\) was developed. Using a low molecular weight thymine-functionalized polyisobutylene (PIB-T), a layer of PIB-T was spin coated on top of a layer of \(arb\text{\_IB(OH)-MS}\). This resulted in the “gluing” of the low molecular weight PIB-T onto the surface of the \(arb\text{\_IB(OH)-MS}\), and showed a 15° decrease in contact angle indicating an increase in hydrophilicity. Evidence of nitrogen and oxygen near the surface of the polymers containing thymine was obtained by XPS. These low molecular weight PIB-Ts will be electrosprayed onto the surface of the \(arb\text{\_IB(OH)-MS}\); the products are expected to show properties similar to those obtained by spin coating. Surfaces with PIB-T will allow for hydrogen bonding of various proteins to allow the surface to be modified.
DEDICATION

This dissertation is dedicated to my husband James and my parents for all of their love and support.
ACKNOWLEDGEMENTS

I would like to thank Dr. Judit E. Puskas for all of her help and encouragement over the past five years. Her advice and assistance have been extremely beneficial to me. I would also like to thank my committee members Dr. Joseph Kennedy, Dr. Roderic Quirk, Dr. Alexi Sokolov, and Dr. Claire Tessier (Chemistry). I would also like to thank the following individuals for their help and guidance: Dr. Miroslawa El Fray (University of Szczecin, Poland) for all of her help and assistance with the implantation studies of our polymers, as well as Dr. Marta Piatek, Dr. Wayne Jennings (Case Western Reserve) for all his help with XPS, Krystal Lovejoy (Polyinsight) for help with AFM, Dr. Goy Teck Lim for all of his assistance with compression molding as well as TEM, and Mustafa Sen for his help and synthesis of PIB-T. Most importantly I would like to thank Dr. Paul Foreman (my father) as well as Marika Foreman (my mother) for their research advice throughout my graduate studies.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>xv</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I.  INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. HISTORICAL REVIEW</td>
<td>5</td>
</tr>
<tr>
<td>2.1 History of silicone breast implants</td>
<td>5</td>
</tr>
<tr>
<td>2.2 Types of silicone breast implants</td>
<td>7</td>
</tr>
<tr>
<td>2.3 Chemistry of silicone breast implants</td>
<td>8</td>
</tr>
<tr>
<td>2.4 Complications with silicone breast implants</td>
<td>13</td>
</tr>
<tr>
<td>2.5 Surface modification of silicone gel-filled breast implants</td>
<td>23</td>
</tr>
<tr>
<td>2.6 Methods of surface modification</td>
<td>27</td>
</tr>
<tr>
<td>2.6.1 Modification by plasma-induced polymerization</td>
<td>27</td>
</tr>
<tr>
<td>2.6.2 Adsorption and covalent attachment of proteins to polymer surface</td>
<td>29</td>
</tr>
<tr>
<td>2.6.3 Surface modification with carbon black</td>
<td>33</td>
</tr>
<tr>
<td>2.7 PIB-PS block copolymers</td>
<td>35</td>
</tr>
<tr>
<td>2.7.1 Generations of poly(styrene-\textit{b}-isobutylene-\textit{b}-styrene) (SIBS) based biomaterials</td>
<td>36</td>
</tr>
<tr>
<td>2.7.2 Properties of SIBS</td>
<td>37</td>
</tr>
</tbody>
</table>
2.7.3 Phase separation of SIBS

2.8 Synthesis and characterization of arb_IB

2.8.1 Synthesis of arb_IB

2.8.2 Branching analysis of arb_IB

2.8.3 Architecture analysis of arb_IBs

2.9 Synthesis of arb_SIBS

2.10 Biomedical applications of SIBS

2.11 The use of α-methylstyrene epoxide (MSE) for living carbocationic isobutylene polymerization

2.12 Thymine-functionalized polystyrene

III. EXPERIMENTAL

3.1 Materials

3.2 Instrumentation/Characterization

3.2.1 NMR spectroscopy

3.2.2 Size Exclusion Chromatography (SEC)

3.2.3 In situ FTIR spectroscopy

3.2.4 Differential Scanning Calorimetry (DSC)

3.2.5 TGA (thermogravimetric analysis)

3.2.6 Tensile testing

3.2.7 Contact angle measurement

3.2.8 X-ray Photoelectron Spectroscopy (XPS)

3.2.9 Atomic Force Microscopy (AFM)

3.2.10 Transmission Electron Microscopy (TEM)
3.2.11 Shore hardness..............................................................................................66
3.2.12 Electrical resistance (Kent State University).................................................66
3.3 Synthesis of 4-(1,2-oxirane-isopropyl)styrene inimer (EPOIM).........................66
3.4 Polymerization of \textit{arb}_{IB(OH)}........................................................................68
  3.4.1 EPOIM: Small scale screening polymerizations .............................................68
  3.4.2 Polymerization of \textit{arb}_{IB(OH)} (LANXESS using UA EPOIM)....................69
  3.4.3 Selective Link Destruction ..........................................................................70
3.5 Synthesis of \textit{arborescent} poly[isobutylene(OH)-b-(isobutylene-co paramethylstyrene): \textit{arb}_{IB(OH)}-MS (LANXESS using UA EPOIM)........................................70
  3.5.1 Procedure for the synthesis of \textit{arb}_{IB(OH)}-MS(16).....................................70
  3.5.2 Procedure for the synthesis of \textit{arb}_{IB(OH)}-MS(3.5).......................................71
3.6 \textit{In situ} FTIR monitoring..................................................................................72
  3.6.1 Procedure for self condensing vinyl polymerization (SCVP) of EPOIM with \textit{in-situ} FTIR monitoring.........................................................72
  3.6.2 Self condensing vinyl copolymerization (SCVCP) of EPOIM and IB in a 1:3 M ratio .................................................................73
3.7 Silylation of \textit{arb}_{IB(OH)}-MS(3.5)..................................................................74
3.8 Spin coating of polymers.....................................................................................74
3.9 Soxhlet extraction of \textit{arb}_{IB(OH)}-MS(16).........................................................75
3.10 Compounding.....................................................................................................75
3.11 Preparation of test specimens for implantation...............................................75
3.12 Buffer uptake study..........................................................................................76
3.13 \textit{In vitro} cytocompatibility (ISO 10 993-5).......................................................76
3.14 \textit{In vivo} implantation test...............................................................................77
IV. RESULTS AND DISCUSSION .................................................................78

4.1 IB Polymerizations with 4-(1,2-oxirane-isopropyl)styrene (EPOIM) ........78

4.1.1 Synthesis of 4-(1,2-oxirane-isopropyl)styrene inimer (EPOIM) ......79

4.1.2 Small scale polymerizations ..........................................................81

4.1.3 Large scale IB polymerizations with EPOIM (UA inimer, LANXESS polymerization) ...............................................................96

4.1.3.1 SEC analysis of IB polymerizations with EPOIM ..........96

4.1.3.2 Architecture analysis of large scale polymerizations .........102

4.1.4 In situ FTIR studies .................................................................106

4.1.4.1 Self condensing vinyl polymerization (SCVP) .................106

4.1.4.2 Self condensing vinyl copolymerization (SCVCp).............118

4.2 Block copolymerizations: \textit{arb}_IB(OH)-MS(3.5 and 16) (LANXESS Inc) .................................................................126

4.2.1 Block synthesis using UA inimer and recipe at LANXESS ..........127

4.2.2 Composition analysis .............................................................128

4.2.2.1 Copolymer composition ..........................................................128

4.2.2.1.1 Composition analysis by NMR spectroscopy ......................128

4.2.2.1.2 SEC analysis of \textit{arb}_IB(OH)-MS(16) and \textit{arb}_IB(OH)MS(3.5) ..........................................................134

4.2.2.2 OH content of \textit{arb}_IB(OH)-MS: Proof from NMR and silylation of \textit{arb}_IB(OH)-MS ..................................................138

4.2.2.2.1 Calculation of weight % of hydroxyl groups .......................138

4.2.2.2.2 Silylation of \textit{arb}_IB(OH)-MS(3.5) .........................140

4.3 Block copolymer and carbon nanocomposite characterization ..........143
4.3.1 Physical properties of arb_IB(OH)-MS(16) and 
arb_IB(OH)-MS_CB(16) .................................................................143

4.3.1.1 DSC measurements .........................................................143

4.3.1.2 TGA measurements of arb_IB(OH)-MS(16) 
and arb_IB(OH)-MS_CB(16) ......................................................145

4.3.2 Phase morphology of arb_IB(OH)-MS and 
arb_IB(OH)-MS_CB ..................................................................147

4.3.2.1 TEM of arb_IB(OH)-MS and 
arb_IB(OH)-MS_CB ..........................................................147

4.3.2.2 AFM of arb_IB(OH)-MS and arb_IB(OH)-MS_CB ....151

4.3.3 Electrical conductivity measurements (Kent State University)......154

4.3.4 Mechanical properties of arb_IB(OH)-MS(16) and 
arb_IB(OH)-MS_CB(16) (LANXESS) ..............................................154

4.3.5 Surface analysis of arb_IB(OH)-MS(16) and 
arb_IB(OH)-MS_CB(16) ................................................................156

4.3.5.1 Contact angles of arb_IB(OH)-MS(16) 
and arb_IB(OH)-MS_CB(16) ..............................................156

4.3.5.2 XPS results of arb_IB(OH)-MS(16) and 
arb_IB(OH)-MS_CB(16) ..................................................158

4.4 Bicompatibility studies .................................................................................160

4.4.1 Purification of arb_IB(OH)-MS(16) for biomedical use 
using UA inimer and recipe (LANXESS) – in-kind 
contribution to NSF project .........................................................161

4.4.2 In vitro studies ..................................................................................162

4.4.2.1 In vitro cytocompatibility test of arb_SIBS .....................162

4.4.2.2 Buffer uptake study of arb_IB(OH)-MS(16) and 
arb_IB(OH)-MS_CB(16) ..........................................................163

4.4.3 In vivo implantation studies of arb_IB(OH)-MS(16) and 
arb_IB(OH)-MS_CB(16) .................................................................164
4.4.3.1  *In vivo* implantation in muscle ..........................................................164

4.4.3.2  *In vivo* implantation in bone .............................................................169

4.5  Modular surface modification of *arb* _IB(OH)-MS(3.5)_
- proof of concept ..............................................................................................172

4.5.1  Ellipsometry results for spin coated films ................................................176

4.5.2  Contact angle results from surface functionalization ............................176

4.5.3  XPS results from modular surface functionalization
     of *arb* _IB(OH)-MS(3.5)_ .............................................................................177

     4.5.3.1  Determination of necessary conditions for
             XPS sample preparation ....................................................................178

     4.5.3.2  XPS results from modular surface functionalization
             with PIB-T .........................................................................................181

V. CONCLUSIONS ..................................................................................................187

REFERENCES ........................................................................................................191
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Physical properties of silicone SiO₂ reinforced rubber for breast implants...........13</td>
</tr>
<tr>
<td>2.2</td>
<td>Baker grading of capsular contracture severity .....................................................16</td>
</tr>
<tr>
<td>2.3</td>
<td>Asplund study: comparison of capsular contracture in saline vs. silicone gel-filled implants..............................................17</td>
</tr>
<tr>
<td>2.4</td>
<td>Cairns study: capsular contracture in saline vs. silicone gel-filled implants ...........18</td>
</tr>
<tr>
<td>2.5</td>
<td>Gylbert study: comparison capsular contracture in saline-filled vs. silicone gel-filled implant ..............................................19</td>
</tr>
<tr>
<td>2.6</td>
<td>Properties of SIBS in comparison to silicone ........................................................38</td>
</tr>
<tr>
<td>2.7</td>
<td>Mechanical properties of SIBS materials ..............................................................38</td>
</tr>
<tr>
<td>4.1</td>
<td>Conditions for the synthesis of (arb_{IB}(OH)) using EPOIM ..................................81</td>
</tr>
<tr>
<td>4.2</td>
<td>Peak molecular weights from SEC ........................................................................84</td>
</tr>
<tr>
<td>4.3</td>
<td>SEC analysis of (arb_{IB}(OH)s) from EPOIM .........................................................86</td>
</tr>
<tr>
<td>4.4</td>
<td>Analysis of architecture by SEC ........................................................................92</td>
</tr>
<tr>
<td>4.5</td>
<td>Large scale polymerizations .................................................................................97</td>
</tr>
<tr>
<td>4.6</td>
<td>Branching analysis of large scale polymerizations .................................................101</td>
</tr>
<tr>
<td>4.7</td>
<td>Architecture analysis of large scale polymerizations............................................102</td>
</tr>
<tr>
<td>4.8</td>
<td>SCVP of EPOIM: conditions for FTIR monitoring.....................................................107</td>
</tr>
<tr>
<td>4.9</td>
<td>SEC results for the SCVP of EPOIM .......................................................................113</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Crosslinked PDMS</td>
<td>5</td>
</tr>
<tr>
<td>2.2</td>
<td>Formation of heat cured rubber (high temperature vulcanization)</td>
<td>8</td>
</tr>
<tr>
<td>2.3</td>
<td>Formation of a silicone gel by platinum cure (hydrosilation)</td>
<td>9</td>
</tr>
<tr>
<td>2.4</td>
<td>Room temperature vulcanization</td>
<td>10</td>
</tr>
<tr>
<td>2.5</td>
<td>Tin catalyzed RTV</td>
<td>10</td>
</tr>
<tr>
<td>2.6</td>
<td>Formation of a crosslinked network</td>
<td>11</td>
</tr>
<tr>
<td>2.7</td>
<td>Deactivation of tin catalyst</td>
<td>12</td>
</tr>
<tr>
<td>2.8</td>
<td>Handel study: comparison of saline and silicone implants</td>
<td>20</td>
</tr>
<tr>
<td>2.9</td>
<td>Handel study: comparison of types of surgery vs. capsular contracture</td>
<td>21</td>
</tr>
<tr>
<td>2.10</td>
<td>Argon plasma induced grafting</td>
<td>28</td>
</tr>
<tr>
<td>2.11</td>
<td>Advancing and receding contact angles of water on untreated and surface modified silicone</td>
<td>29</td>
</tr>
<tr>
<td>2.12</td>
<td>Covalent attachment of GRGDS to the surface of PAAc</td>
<td>30</td>
</tr>
<tr>
<td>2.13</td>
<td>Binding capacity of fibronectin onto surface modified silicones in percent relative to untreated silicone</td>
<td>31</td>
</tr>
<tr>
<td>2.14</td>
<td>Cell growth of L929 cells on modified silicone materials</td>
<td>32</td>
</tr>
<tr>
<td>2.15</td>
<td>Growth curves for human synovial fibroblasts on plain and DLC coated polystyrene</td>
<td>33</td>
</tr>
<tr>
<td>2.16</td>
<td>Sheet resistance ($R_s$) as a function of CB concentration in PE + CB mixture</td>
<td>34</td>
</tr>
</tbody>
</table>
2.17 Dependency of density of vascular smooth muscle cells on the CB concentration in PE + CB mixtures measured after (■) 18 h and (▲) 96 h incubation time ..........................................................35

2.18 Generations of SIBS based biomaterials ...........................................................................36

2.19 Synthesis of arb_SIBS from MeOIM ..............................................................................37

2.20 C1s XPS of SIBS and PS ..................................................................................................39

2.21 Morphology of SIBS-based materials: (a) AFM image of an arb_SIBS (1 μm scale) (b) schematic of SIBS morphology based from AFM and XPS results ......................................................................................................40

2.22 Carbocations generated from the 4-(2-methoxyisopropyl)styrene inimer/TiCl4/IB system ........................................................................................................................................42

2.23 Selective link destruction of arb_IBs ..................................................................................44

2.24 Dependence of Mn and BR on the [IM]0/[M]0 ratios in inimer IB polymerizations from MeOIM: [IB]0 = 2 mol/L; [TiCl4]0 = 10[IM]0; [DibBP] = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v; T= -80 °C ..........................................................44

2.25 Dependence of Mn and BR on the [TiCl4]0/[IM]0 ratios in inimer IB polymerizations from MeOIM: [IM]0 = 0.008 mol/L; [IB]0 = 2.0 mol/L; [DibBP] = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v; T= -80 °C ..........45

2.26 Blocking of PST from arb_IB by reactivating the chain ends ........................................48

2.27 Possible reactions between α-methylstyrene epoxide and TiCl4 ..................................51

2.28 1H-NMR spectrum of a primary hydroxyl-functionalized PIB (Mn = 4,300 g/mol) (400 MHz), CD2Cl2 ..............................................................................................................52

2.29 1H-NMR spectrum of a silylated PIB (Mn = 4,300 g/mol) (400 MHz, CDCl3) ..........................................................52

2.30 Versatility of 1-VBT .........................................................................................................54

2.31 Structure of PS-VBT copolymers ......................................................................................54

2.32 XPS high-resolution spectra (4.85 wt% VBT): (a) XPS high-resolution C 1s; (b) XPS high-resolution O 1s; (c) XPS high-resolution N 1s ..........................................................55
2.33 Effect of pH on the adsorption of BSA and BHb on PS and PS-VBT4-20. C0 = 0.25 g/L, T = 25 °C ............................................................56
3.1 Reaction scheme for synthesis of 4-(1, 2-oxirane-isopropyl)styrene ................67
3.2 Staining agents: (a) hematoxylin (b) eosin .................................................77
4.1 Inimer type copolymerization of EPOIM with IB ........................................78
4.2 1H-NMR spectrum of 4-(1,2-oxirane-isopropyl)styrene inimer ..................79
4.3 13C-NMR spectrum of 4-(1,2-oxirane-isopropyl)styrene inimer ..................80
4.4 SEC traces of arb_IB(OH) shown in Table 4.1: (a) EF141205-2 (b) EF141205-1 (c) EF141205-5 (d) EF141205-6..................................................82
4.4 SEC traces of arb_IB(OH) shown in Table 4.1 (continued): (e) EF141205-4 (f) EF141205-3 (g) EF141205-7 ..................................................83
4.5 RI trace before and after LD: (a) EF141205-2 (b) EF141205-3 .......................85
4.6 Dependence of M_n and B on [IM]_0/[M]_0: (a) MeOIM 137 (b) EPOIM ........88
4.7 Structure of propagating carbocations of MeOIM and EPOIM .....................89
4.8 Plots of: (a) Log R_g (b) Log R_h and (c) Log η, vs Log M_w (g/mol) .............91
4.9 Dependence of the branching parameters g, h, and ρ on the number of chain ends (f) of arb_IB(OH)s listed in Table 4.4 .........................93
4.10 Conformation plots: (a) EF141205-2 (b) EF142305-3 .................................94
4.11 Branching distribution in small scale polymerizations for samples (a) EF141205-2 (b) EF141205-3 .........................................................95
4.12 In[M]_0/[M] versus time in large scale polymerizations. Data in Table 4.5 164 .............98
4.13 M_n versus conversion in large scale polymerizations. Data in Table 4.5 164 ............98
4.14 SEC traces of polymers from polymerization 1: arb_IB(OH)-1,2,5, and 6 .......99
4.15 SEC traces of polymers from polymerization 2: arb_IB(OH)-2, 3, 4, and 5 ......100
4.16 Branching distribution in large scale polymerizations for samples (a) Polymerization 2: arb_IB(OH)-5 (b) Polymerization 1: arb_IB(OH)-6.......104
4.17 \( \rho \) distribution in EPOIM-initiated \( arb\_IB(OH) \): (a) Polymerization 2: \( arb\_IB(OH)-5 \) (b) Polymerization 1: \( arb\_IB(OH)-6 \) .........................................................104

4.18 Star-like architecture with an \( arb\_IB(OH) \) core .................................................................105

4.19 FTIR spectrum of EPOIM ........................................................................................................107

4.20 FTIR monitoring of EPOIM SCVP: 1650-1580 cm\(^{-1}\) (see Table 4.8) ..................108

4.21 FTIR from SCVP of EPOIM: 1100-1050 cm\(^{-1}\) (see Table 4.8) ..........................109

4.22 Possible reaction mechanisms of the ring opening polymerization of EPOIM...110

4.23 Possible propagation reactions of the SCVP of the EPOIM.................................111

4.24 SEC trace from EPOIM SCVP ................................................................................113

4.25 \(^1\)H NMR spectrum and resonance assignments (500 MHz, solvent CDCl\(_3\)) of the soluble fraction from EPOIM SCVP .................................................................115

4.26 DEPT \(^{13}\)C NMR spectrum of SCVP ........................................................................116

4.27 HSQC spectra of SCVP (Yellow and red regions: methine and methyl protons; blue regions: methylene protons) .................................................................117

4.28 FT-IR spectrum of EPOIM/IB SCVCP: 1700-1560 cm\(^{-1}\) (see Table 4.10) ......119

4.29 FT-IR spectrum of EPOIM/IB SCVCP: 1280-1230 cm\(^{-1}\) (see Table 4.10) ......120

4.30 FT-IR spectrum of EPOIM/IB SCVCP: 1150-1050 cm\(^{-1}\) (see Table 4.10) ......121

4.31 SEC trace of SCVCP of EPOIM ...............................................................................121

4.32 Proposed initiation pathway of the EPOIM (SCVCP) ..................................................123

4.33 Possible propagation reactions in SCVCP ..................................................................124

4.34 \(^1\)H-NMR spectrum and resonance assignments of SCVCP ...................................125

4.35 \( arb\_IB(OH)-MS(16)\): (a) \(^1\)H NMR spectrum and resonance assignments; solvent CDCl\(_3\) (b) synthesis ..................................................................................................129

4.36 \(^{13}\)C NMR spectrum and resonance assignments of \( arb\_IB(OH)-MS(16) \) ........133
4.37 SEC traces of polymers from (a) Polymerization 1: \textit{arb}\_IB(OH)-6 (b) \textit{arb}\_IB(OH)-MS(3.5) (c) Polymerization 2: \textit{arb}\_IB(OH)-5 (d) \textit{arb}\_IB(OH)-MS(16) ......................................................................................135

4.38 Mechanism of the silylation of primary alcohols .............................................140

4.39 Silylation of primary alcohols from \textit{arb}\_IB(OH)-MS(3.5) (chloroform solvent).................................................................................................................141

4.40 Silylation of primary alcohols from \textit{arb}\_IB(OH)-MS(3.5) (CCl\textsubscript{4} solvent).................................................................................................................142

4.41 DSC scan of \textit{arb}\_IB(OH)-MS(16) and \textit{arb}\_IB(OH)-MS\_CB(16)........144

4.42 TGA plots of: (a) \textit{arb}\_IB(OH)-MS(16) (b) \textit{arb}\_IB(OH)-MS\_CB(16) ..........146

4.43 TEM images of: (a) \textit{arb}\_IB(OH)-MS(3.5) unstained and (b) \textit{arb}\_IB(OH)-MS(3.5) stained with osmium tetroxide for 15 min: dark regions are PMS, light regions are PIB .................................................148

4.44 TEM images of \textit{arb}\_IB(OH)-MS(3.5) stained with ruthenium tetroxide: (a) for 30 min and (b) for 60 min ......................................................................................148

4.45 TEM images of (a & b) \textit{arb}\_IB(OH)-MS(3.5) (c & d) \textit{arb}\_IB(OH)-MS(16) stained with ruthenium tetroxide for 1 hour ........................................................................149

4.46 TEM images of cryomicrotomed (a & b) \textit{arb}\_IB(OH)-MS(16) and (c & d) \textit{arb}\_IB(OH)-MS\_CB(16) stained with osmium tetroxide (carried out at the University of Bayreuth in Germany) .............................................150

4.47 AFM images of: \textit{arb}\_IB(OH)-MS (3.5) at (a) 2 \textmu m and (b) 1 \textmu m, and \textit{arb}\_IB(OH)-MS\_CB (3.5) at (c) 2 \textmu m and (d) 1 \textmu m ......................................................................................152

4.48 AFM images of \textit{arb}\_IB(OH)-MS (16) at (a) 2 \textmu m and (b) 1 \textmu m and \textit{arb}\_IB(OH)-MS\_CB (16.0) at (c) 2 \textmu m and (d) 1 \textmu m ........................................................................153

4.49 Stress-strain plots of \textit{arb}\_IB(OH)-MS(16) and \textit{arb}\_IB(OH)-MS\_CB(16).......155

4.50 XPS of \textit{arb}\_IB(OH)-MS(16), 45\degree grazing angle .................................................159

4.51 RI trace: \textit{arb}\_IB(OH)-MS(16) (D) before extraction and (E) after extraction .................................................................................................................161

4.52 Cell apoptosis \textit{in vitro} ..........................................................................................163
4.53 Buffer uptake study of \textit{arb}_{IB(OH)}-MS(16) and \textit{arb}_{IB(OH)}-MS\_CB(16) ...................................................................................164

4.54 \textit{arb}_{IB(OH)}-MS(16): (a) Cross section of the muscle with the connective tissue capsule (b) the connective tissue capsule around the polymer: placement of polymer indicated by arrows ........................................166

4.55 \textit{arb}_{IB(OH)}-MS\_CB(16): (a) Cross section of the muscle with the connective tissue capsule around the polymer (b) connective tissue capsule around carbon black filled polymer showing compactly adhered cells ..............167

4.56 Capsule thickness around \textit{arb}\_IB(OH)-MS(16) (E – polymer after extraction, D- polymer before extraction), \textit{arb}_{IB(OH)}-MS\_CB(16) and SIL after 180 days implantation ........................................................................168

4.57 \textit{arb}_{IB(OH)}-MS(16): (a) bone, connective tissue capsule (b) callus formed in the middle after implantation into periosteum (c) newly formed callus after the removal of the periosteum from the surface of the bone and implantation of the polymer in this site ........................................170

4.58 Carbon black filled polymer, callus\(^{45}\) (arrow) under the periosteum .............171

4.59 Number of Havers channels: (E) \textit{arb}_{IB(OH)}-MS(16) after extraction (D) \textit{arb}_{IB(OH)}-MS(16) before extraction (D+C) \textit{arb}_{IB(OH)}-MS\_CB(16) (S) silicone (P) periosteum (B) bone ........................................................................171

4.60 Rabbit internal organs after implantation of \textit{arb}_{IB(OH)}-MS(16) and \textit{arb}_{IB(OH)}-MS\_CB(16): (a) liver morphology (b & c) kidneys (d) heart ........................................................................................................172

4.61 Modular surface functionalization: Silicon wafer with (a) \textit{arb}_{IB(OH)}-MS(3.5) film (b) PIB-T deposition and (c) \textit{arb}_{IB(OH)}-MS(3.5) film with PIB-T film (T represents thymine) entangled into outer PIB block of \textit{arb}_{IB(OH)}-MS(3.5) ........................................................................174

4.62 Synthetic strategy for the synthesis of PIB-T (M\(_n\)= 5500 g/mol and M\(_w/M_n\) = 1.07) .........................................................................................................................175

4.63 XPS results (low resolution- 93.9 eV): (a) PIB-T 2 wt\% and (b) \textit{arb}_{IB(OH)}-MS(3.5)/PIB-T 3/2 wt\%, taken at a 45° X-ray angle ..........................................................................................179

4.64 Survey scan of \textit{arb}_{IB(OH)}-MS(3.5) ........................................................................................................179

4.65 High resolution XPS traces (45° angle), C1s of: (a) PIB(OH) and (b) \textit{arb}_{IB(OH)}-MS(3.5) ........................................................................................................184

xx
4.66 High resolution XPS traces (45° angle), C1s of: (a) PIB-T and (b) \textit{arb\_IB(OH)-MS(3.5)/PIB-T}
CHAPTER I
INTRODUCTION

The objective of this work was to increase the hydrophilicity of the surface of polyisobutylene-based biomaterials and to correlate this with the biocompatibility of the material.

SIB was developed by the Kennedy group at The University of Akron. SIBS block copolymers are among the most important biomaterials developed by this group. Since the polyisobutylene (PIB) and polystyrene (PS) blocks are covalently bonded, microphase separation occurs, leading to thermoplastic elastomeric (TPE) behavior. SIBS was shown to be biocompatible and biostable in vivo and in vitro and is FDA approved as a coating on drug eluting cardiovascular stents. Various medical devices (e.g., ophthalmic implants, heart valves) are currently being developed using SIBS, because of minimal platelet activation and polymorphonuclear leukocyte formation, and clinically insignificant scarring and encapsulation around the implant in the eye. To date, degradation of SIBS has not been observed in any living systems. These SIBS-based biomaterials are known to be more chemically stable in vivo, to have lower permeability, higher tensile strength and higher elongation at break than silicone biomaterials. The microphase separated morphology gives physical strength to the material without the need of chemical crosslinking. All of these characteristics led us to consider the use of
SIBS as an alternative material for breast implants where permeability of the shell is a concern.

Although biocompatible, SIBS is known to suffer from creep which could be a problem in applications such as breast implants where the implant must be able to withstand much stress and deformation both during and after implantation. Recently, dendritic SIBS based materials have been developed by the Puskas group and have been shown to have less deformation under stress due to their branched PIB core which leads to chain entanglement. As a result, it was decided that dendritic SIBS-based materials would be a better choice for use in breast implants.

Two of the main complications that occur with breast implants are capsular contracture and gel bleed. Capsular contracture is the tightening of a fibrous capsule, which forms around breast implants, and any foreign material that is implanted into the body. Although silicone rubber, polytetrafluoroethylene and SIBS are amongst the most biocompatible materials, it is believed that the human body recognizes such hydrophobic materials as foreign and isolates them by forming a fibrous capsule around the material. To help reduce capsular contracture it was thought that surface modification of the implant would be beneficial. A remarkable decrease of capsular contracture was reported with polyurethane foam (PU) covered implants. Unfortunately, the PU coatings suffered hydrolytic degradation in vivo. Hydrophilization of the implant surface is believed to improve tissue interaction, but contradictions exist: for instance, a poly(acrylic acid) grafted surface showed poorer cell binding capability than silicone itself, while GRGDS (Gly-Arg-Gly-Asp-Ser) improved cell-material interactions.
recent study claimed that poly(2-hydroxyethyl methacrylate) hydrogel was useful as a capsule-resistant material \textit{in vivo} in rats.\textsuperscript{17}

Another approach to reduce capsule formation was texturing the surface of breast implants. It was proposed that texturing the shell would cause tissue to grow into the interstices of projections or pores thereby disorienting collagen fibrils and weakening their contractile forces.\textsuperscript{18,19} However, micron-scale texturing of implants did not seem to lead to improved tissue interaction.\textsuperscript{16,20} Unfortunately, no clinical solution exists today to prevent capsule formation around breast implants.

An interesting approach to surface modification is the use of carbon coating, but again there is contradictory information in the literature. The improved hemocompatibility is thought to come from chemical inertness of the carbon as well as the adsorption of a layer of blood proteins on its surface.\textsuperscript{21,22} Pyrolytic carbon black (PCB) has been established as the choice material in heart valves and has also been successfully used in other applications such as pacemaker electrodes, subperiosteal dental implant frames, percutaneous electrical connectors, and hand joints.\textsuperscript{23} Svorcik et al.\textsuperscript{24} found that polyethylene mixed with carbon black (CB) showed markedly improved cell adhesion and proliferation, reaching their maximum at the percolation limit of \(\sim 6\) wt% CB.

One of the other problems with SIBS is that it is non-polar and hydrophobic; it is, however, this property that makes SIBS biostable \textit{in vivo}.\textsuperscript{1} These studies show the need for an increase in the hydrophilicity of hydrophobic biomaterials. This dissertation discusses a novel method for the surface functionalization of polyisobutylene-based biomaterials by the living carbocationic polymerization of the 4-(1,2-oxirane-
isopropyl)styrene (EPOIM). An arborescent polyisobutylene core with hydroxyl functionality and poly(isobutylene-co-p-methylstyrene) end blocks was synthesized (arb_IB(OH)-MS). In a physiological environment, arbo_IB(OH)-MS was expected to have hydroxyl groups segregated to the surface increasing the hydrophilicity, with the reinforcing hard PS phases embedded in the continuous PIB matrix. The arbo_IB(OH)-MS was compounded with carbon black to increase the mechanical strength by forming a novel nanocomposite, arbo_IB(OH)-MS_CB. arbo_IB(OH)-MS_CB led to the formation of new biocompatible materials which showed a significant increase in hydrophilicity (~15° drop in water contact angle) and the ability to be steam sterilized!

Dr. Puskas developed a new method of modular surface functionalization using a low molecular weight functionalized PIB which was “glued” to the surface of a high molecular weight SIBS-based polymer, to allow the tailoring of the surface chemistry of the material. Preliminary work was carried out using a low molecular weight thymine-functionalized polyisobutylene with multiple hydrogen bonding sites to allow for further surface modification. In a physiological environment we expect thymine to migrate to the surface of the polymer thereby increasing surface hydrophilicity. XPS showed that even in air, nitrogen was present close to the surface of the materials. This new method of surface modification also showed a significant increase in hydrophilicity (~15° decrease in water contact angle).
2.1 History of silicone breast implants

Silicone breast implants were introduced in 1962\textsuperscript{25} and were clinically introduced in 1963 based on work done by Cronin and Gerow\textsuperscript{26} on the implantation of silicone shells into dogs. Silicone breast implants consist of a rubbery shell, and filler, either silicone gel or saline solution. The silicone gel consists of a low molecular weight uncrosslinked silicone fluid, polydimethylsiloxane (PDMS), and a higher molecular weight gel of crosslinked PDMS (Figure 2.1). The formation of the silicone gel by platinum cure will be discussed in Section 2.3.

![Figure 2.1 Crosslinked PDMS. (Reprinted with permission from Bondurant, S.; Ernster, V.; Herdman, R., “Safety of Silicone Breast Implants” Institute of Medicine. National Academy Press: 2000\textsuperscript{25}.)](image)

The shell provides strength and barrier properties, whereas the filling supplies bulk and consistency. In 1997 there were more than 240 different types...
of breast implants made in the U.S.\textsuperscript{27} Between 1962 and 1996 over 2 million women in
the U.S. and Canada received silicone breast implants; about 20-30\% of these were for
reconstruction and the remaining were for cosmetic breast augmentation.\textsuperscript{13} It wasn’t until
1976 that breast implants came under FDA regulation. In 1991 silicone gel-filled
implants were removed from the US market except for use in clinical trials. In 1993 it
was ruled that even saline filled implants must be submitted with proof of product
safety.\textsuperscript{13}

Breast implants are typically categorized into three generations. The first
generation silicone gel implants (1960s-1970s) had shells made from high molecular
weight silicone filled with amorphous silica and a process aid. They were mixed with
2,4-dichlorobenzoyl peroxide and cured in a mold. Two sides of the shell were made and
glued together. Uncured gel mixture was then injected through a hole in the shell and
cured in place. The hole was then sealed with a patch. These implants had the thickest
shells ( > 0.254 mm)\textsuperscript{3} and the most viscous gel. These implants felt too firm compared
with natural breast tissue, so the shell thickness and gel viscosity were reduced in the
second generation implants which were introduced in the 1970’s. Using platinum-cured,
liquid silicone rubber and a dip-coating process which gave more uniform thickness of
the shell enabled the shell of the implants to be made thinner.\textsuperscript{25} This resulted, however,
in shell rupture and gel bleed. The third generation of silicone breast implants consisted
of shells of intermediate thickness filled with gels of medium viscosity.\textsuperscript{9} Barrier layers
and textured shells were introduced in both saline and gel filled implants.\textsuperscript{25} Cohesive gel
implants, approved recently, are considerably firmer, and perceived to be harder than
natural breast tissue.
2.2 Types of silicone breast implants

Breast implants come in a large range of sizes, from 80 to 800 cubic centimeters (cc) even 1000 cc implants have been used on occasion. Their diameter ranges from 7.5 to 16.8 cm with a projection of 1.5 to 7.5 cm. Various shapes are available such as round, oval, teardrop, or contoured. There are several different construction types of implants. Single lumen implants consist of a single silicone elastomer shell filled with silicone gel or saline. The silicone gel has different chemical composition and molecular weight depending on the manufacturer. The gel consists of crosslinked silicone and silicone fluid; the amount of silicone fluid affects the feel of the implant.\textsuperscript{25} Sometimes expanders are used to inflate the implants after surgery. This is typically used in reconstructive surgery. Since the early 1980s implants with detachable reservoirs have been available to allow the expander to remain in place permanently.\textsuperscript{28,29} The single lumen gel filled implant was the most commonly used implant in the U.S. comprising 60-80\% of all implants. After the 1992 FDA moratorium on gel-filled implants, single lumen saline implants replaced the gel filled implants.\textsuperscript{27,30,31}

There are also standard double-lumen implants. Standard double-lumen implants have two shells which are either connected, patched together, or has one shell freely floating within the other. Usually the inner lumen is gel filled and the outer is saline filled, although this can be reversed. The gel provides the cosmetic advantages of gel while the saline part allows for inflation or an expander and reservoir. The outer saline lumen was also supposed to provide an additional barrier from the silicone gel.\textsuperscript{32,33} This feature was found to be ineffective.\textsuperscript{34} It was found that measured amounts of gel fluid diffusion from the double lumen implant were about twice as much as that explanted
from a single lumen gel implant in the same patient.\textsuperscript{35} Triple lumen implants, which are very rarely used, have the inner and middle shells filled with silicone gel and the outer with saline.\textsuperscript{25}

The shells of breast implants are made from silicone rubber with reinforcing filler. The characteristics of the elastomers vary greatly in composition. Amorphous silica is generally used as the filler. The thickness of the shells also varies greatly from 0.13 to 0.75 mm, with some shells having been made even thicker.\textsuperscript{25} The implant shells can also be made smooth or textured.

2.3 Chemistry of silicone breast implants

The chemistry involved in breast implants can vary greatly depending on the type of implant and the manufacturer and the details on the synthesis are often hard to find. However, there are three types of silicones used in implant manufacture: RTV (room temperature vulcanized), gum based peroxide cured (heat cured) rubber, and platinum cured (gel or LSR [liquid silicone rubber]).\textsuperscript{25} The formation of heat cured rubber is shown in Figure 2.2.

![Figure 2.2  Formation of heat cured rubber (high temperature vulcanization).\textsuperscript{25}](image)

The Cronin implants developed by Dow Corning Co. utilized the simplest of the gels, a platinum cured gel. A slightly vinyl substituted PDMS fluid was crosslinked with a
hydrogen-containing PDMS fluid by a platinum catalyzed reaction. This vinyl group is susceptible to hydrosilation reactions with a hydride group on a neighboring siloxane polymer chain forming crosslinks (Figure 2.3).

\[
\text{PMVS (excess vinyl)} + \text{Hydrogen-stopped PDMS} \rightarrow \text{Silicone gel}
\]

Figure 2.3  Formation of a silicone gel by platinum cure (hydrosilation). (Reprinted with permission from Bondurant, S.; Ernster, V.; Herdman, R., “Safety of Silicone Breast Implants” Institute of Medicine. National Academy Press: 2000.)

RTV implants are mainly used for the shells of saline-filled implants. They use acetate endcapped polysiloxanes obtained from the reaction of silanol terminated PDMS with triacetoxyssilane to build a crosslinked network (Figure 2.4).\textsuperscript{36} Commercially, fillers are added for reinforcement. This process uses a tin catalyst in the place of the platinum catalyst.\textsuperscript{36} This usually involves silicone fluids that are chain stopped with alkyltriacetoxyssilane and thickened with amorphous silica filler; these cure to RTV silicone rubbers when exposed to moist air. The tin catalyst catalyzes the end capping and crosslinking through the formation of stannosiloxanes. During end capping of the
polysiloxane with alkyltriacetoxysilane, a catalytic amount of water is used to initiate the hydrolysis of the tin catalyst forming a tin hydroxide compound.

Figure 2.4 Room temperature vulcanization. (Reprinted from Pujol, J.M.; Frances, J.M.; and M. Letoffe, Condensation vulcanizing silicone elastomers- an overview of research and development, in Progress in Organosilicon Chemistry with permission 36)

Figure 2.5 Tin catalyzed RTV. (Reprinted with permission from Pujol, J. M.; Frances, J. M.; Letoffe, M., Condensation vulcanizing silicone elastomers- an overview of research and development. In Progress in Organosilicon Chemistry, Marciniec, B.; Chojnowski, J., Eds. Gordon and Breach Publishers: Postfach, Switzerland, 1995; pp 503-522.)
The tin hydroxide reacts with the alkyltriacetoxysilane crosslinker to produce a stannosiloxane compound. The stannosiloxane then undergoes silanolysis with the silanol terminated PDMS resulting in the triacetoxy end-capped polymer (Figure 2.5). 36

![Reaction Scheme](image)

Figure 2.6 Formation of a crosslinked network. (Reprinted with permission from Pujol, J. M.; Frances, J. M.; Letoffe, M., Condensation vulcanizing silicone elastomers- an overview of research and development. In Progress in Organosilicon Chemistry, Marciniec, B.; Chojnowski, J., Eds. Gordon and Breach Publishers: Postfach, Switzerland, 1995; pp 503-522.36)

Upon exposure of the end capped polymer to moisture from the air the reaction will continue to proceed as before, the tin carboxylate is hydrolyzed and the hydrolyzed tin carboxylate reacts with the end capped polysiloxane. The stannosiloxane is then hydrolyzed by moisture in the air giving a silanol which can condense with another...
stannosiloxane to start building a crosslinked three-dimensional network as shown in Figure 2.6.

It is also possible for silica to react with the tin catalyst by the reaction of surface silanols. This deactivates the catalyst until it is hydrolyzed (Figure 2.7).36

\[
\text{Si-OH} + \text{R'COO-Sn-OCOR'} \rightarrow \text{Si-O-Sn-OCOR'} + \text{R'COOH}
\]

\[
\text{Si-O-Sn-OCOR'} + \text{H}_2\text{O} \rightarrow \text{Si-OH} + \text{HO-Sn-OCOR'}
\]

Figure 2.7  Deactivation of tin catalyst. (Reprinted with permission from Pujol, J. M.; Frances, J. M.; Letoffe, M., Condensation vulcanizing silicone elastomers—an overview of research and development. In Progress in Organosilicon Chemistry, Marciniec, B.; Chojnowski, J., Eds. Gordon and Breach Publishers: Postfach, Switzerland, 1995; pp 503-522.36).}

The physical properties of the crosslinked silicone rubber used for the shells of breast implants are shown in Table 2.1. Silicone rubber has low tensile strength, high elongation at break and is highly permeable to gases and liquids. It has been said that the material used for breast implants must have mechanical properties close to that of the human breast.37,38 This is fairly vague, but the material does need to be soft and deformable while being able to maintain its shape.9 This makes silicone rubber a good choice for use as the shell of breast implants, although the material needs to be chemically crosslinked and reinforcing filler must be added.
Table 2.1  Physical properties of silicone SiO$_2$ reinforced rubber for breast implants.\(^9\)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>5-9</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>300-1000</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>20-70</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>13498</td>
</tr>
<tr>
<td>O$_2$</td>
<td>2250</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1975</td>
</tr>
<tr>
<td>H$_2$O vapor transmission Rate</td>
<td>4.9-9.0</td>
</tr>
<tr>
<td>Permeability (x10$^{18}$ m$^2$/s Pa)</td>
<td></td>
</tr>
</tbody>
</table>

2.4 Complications with silicone breast implants

Since breast implants have been introduced several complications have been reported in the literature. One of the biggest concerns in the history of breast implants was the possibility of a relationship between breast implants and connective-tissue diseases, first proposed in 1982.\(^{39}\) These claims resulted in the removal of silicone-gel filled breast implants from the U.S. market after the FDA moratorium on silicone breast implants in 1992.\(^{13}\) Several reports were published confirming the diagnoses of disorders such as systemic sclerosis, rheumatoid arthritis, and systemic lupus erythematosus in patients following implantation of silicone gel-filled breast implants.\(^{40-43}\) “Human adjuvant disease”, a term that was coined by Miyoshi et al.\(^{44}\) in 1969 was used to describe a connective-tissue illness in two patients with breast implants that had been injected with paraffin for augmentation. This term was discredited for lacking precise and reproducible criteria and is not used anymore.\(^{45,46}\) Silicone has been shown to cause a fibrotic and granulomatous response in tissues surrounding silicone implants in animals and humans.\(^{31,46-50}\) Several studies using cohort, case-control, and cross-sectional designs...
have shown that there is no risk of developing rheumatic diseases or disorders following implantation of silicone breast implants. As a result of the lack of evidence connecting silicone breast implants with autoimmune disorders, the American College of Rheumatology issued a statement: ‘There is no convincing evidence that these implants cause any generalized disease’. 

Platinum has also been considered a problem with silicone breast implants. There have been several reviews examining the amount of platinum that bleeds from silicone breast implants \textit{in vitro} or \textit{in vivo} during implantation, which concluded that there are no clinical consequences of platinum in silicone breast implants.

Carcinogenicity of breast implants has also been a concern. Several studies have suggested a potential link between silicone breast implants and breast cancer. Other studies have shown there is no increase in breast cancer amongst women with breast implants as compared to those without. Interference with breast cancer detection is a bigger concern. Breast implants can impede the interpretation of mammograms, mainly because of the compression of breast tissue more-so than the opacity of the implant; however, the American College of Radiology has stated that adequate examination can be achieved with current mammography techniques.

The two most significant problems with breast implants are gel bleed and capsular contracture. All silicone gel implants have bleeding of gel fluid (low molecular weight linear and cyclic silicones) through the shell. These components can range in molecular weight from 5,200 to 400,000 g/mol; however, these are generally less than 25,000 or 10,000 g/mol in implants with and without barrier shells. The higher molecular weight compounds might be from non-crosslinked silicone from the shell. The high molecular
weight, highly crosslinked PDMS from the gel cannot diffuse through the shell. The gel does not appear outside of the implant unless there is actual physical damage to the implant shell.\textsuperscript{25} The silicone fluid is found regularly on the outside of the shells of gel filled implants. Pressure on the implant, such as squeezing, can help accelerate gel bleed. With no pressure the diffusion of silicone fluid across the membrane will decrease as silicone builds up on the outside surface of the implant.\textsuperscript{35} Silicone is hydrophobic, so microdroplets of silicone do not migrate easily throughout the body; macrodroplets injected into the body are able to migrate throughout the body driven by gravitational force. The only way for silicone microdroplets to travel in the body is by macrophages (giant cells that engulf and digest debris).\textsuperscript{80}

Capsular contracture is possibly the largest problem with breast implants, as well as the most commonly reported one.\textsuperscript{51,81,82} Part of the body’s normal response to silicone breast implants is the formation of a fibrous capsule with varying thicknesses which can range from 0.3mm to 7mm.\textsuperscript{83-85} This capsule helps keep the implant properly in place. The histological composition of this capsule has been studied previously.\textsuperscript{85-88} Calcification of these fibrous capsules around the implant has also been reported.\textsuperscript{89-91} Calcification was present over the entire inner aspect of the capsules.\textsuperscript{91} According to histological studies by Wolfram and coworkers,\textsuperscript{83} the fibrous capsules showed a three layer composition. The internal layer closest to the implant appeared to be single/or multilayered and was previously thought to contain only macrophages; it was now found to contain significant amounts of fibroblasts. Fibroblasts are present when there is a wound in the body; they work to form the extracellular matrix (ECM) which is comprised of collagen (the main protein in the ECM) and fibronectin (an adhesive binding protein).
The second layer contains loosely arranged connective tissue, including the internal vascular supply. The outermost layer was dense connective tissue and contained the external vascular supply.

Capsular contracture is the tightening of the fibrous capsule surrounding the implant. Capsular contracture results in a moderate to extreme hardening of the breast, tightness, deformation, and mild to severe pain. The reasons for the differences in capsule formation from one patient to another are not known. There is a scale used to determine the severity of capsular contracture in patients with breast implants (Table 2.2). The incidence of contracture varies greatly from study to study from 0.6% to 100%, this is largely due to a lack of detail on the duration of follow-up and diagnostic criteria. Capsular contracture occurs in both silicone gel-filled and saline-filled breast implants.

<table>
<thead>
<tr>
<th>Grade</th>
<th>None</th>
<th>Normal breast</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade I</td>
<td>Minimal</td>
<td>Palpable, slightly firm</td>
</tr>
<tr>
<td>Grade II</td>
<td>Moderate</td>
<td>Firm, obviously palpable, slight distortion</td>
</tr>
<tr>
<td>Grade IV</td>
<td>Severe</td>
<td>Hard, cold breasts with severe distortion, tender</td>
</tr>
</tbody>
</table>

In several studies they found capsular contracture to be more common in silicone-gel implants. Asplund did a study examining 72 breast implants in 65 women; silicone and saline implants were randomly selected. The women in the study were
referred by oncologists or general surgeons for breast reconstruction following mastectomy, which in seven women was bilateral. Pre- or post-mastectomy irradiation had been given to twenty of the breasts, 5 breasts had cancer *in situ*, $T_{1-3}N_0M_0$ cancer was found in 54 women, $T_{1-2}N_0M_0$ cancer was found in 7, and benign disease in 7 women prior to reconstruction. In 35 of the operations they used the McGhan silicone-gel style 80 or 81. In 37 operations the Heyer-Schulte inflatable 350 saline-filled type was used. The size of the implant ranged from 100 to 600 mL with the median being 240 mL. The implants were placed submuscularly in all except one case in which a musculocutaneous from the latissimus dorsi was added. The observation time ranged from ½ to 2½ years with the average observation time being 16 months. The results from the implantation were calculated using Fisher’s exact test (Table 2.3). Table 2.3 showed the silicone gel filled implants had a much higher occurrence of capsular contracture compared to the saline-filled implants. Similar results were found by Cairns.  

<table>
<thead>
<tr>
<th></th>
<th>No. of implants</th>
<th>Grade I (%)</th>
<th>Grade II (%)</th>
<th>Grade III (%)</th>
<th>Grade IV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel-filled</td>
<td>35</td>
<td>14.0</td>
<td>31.0</td>
<td>49.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Saline-filled</td>
<td>35</td>
<td>46.0</td>
<td>34.0</td>
<td>20.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Cairns\textsuperscript{93} examined 64 patients who underwent breast augmentation between 1974 and 1978, of which 21 patients did not follow up leaving 43 patients for the study. All implants were placed in the same manner; using an inframammary incision, a retromammary pocket was dissected above the pectoral fascia. After obtaining haemostasis the washed prosthesis was inserted and the wound was sewn shut; no drains were used and no steroids were injected near the prosthesis. Forty-three, gel-filled prostheses were used in the study as well as thirty-six, saline-filled implants. The follow up period for this study was 7-19 months with the majority of capsular contracture occurring within 3 to 4 months following implantation (Table 2.4). Once again, the silicone gel-filled prostheses exhibited a much higher incidence of capsular contracture.

Table 2.4 Cairns study: capsular contracture in saline vs. silicone gel-filled implants. (Adapted from Cairns, T. S.; deVilliers, W. \textit{African Med J} \textbf{1980}, \textit{57}, 951-953.\textsuperscript{93} with permission).

<table>
<thead>
<tr>
<th>No. of breasts</th>
<th>Grade I (%)</th>
<th>Grade II (%)</th>
<th>Grade III (%)</th>
<th>Grade IV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel-filled – 43</td>
<td>9.3</td>
<td>9.3</td>
<td>74.4</td>
<td>7.0</td>
</tr>
<tr>
<td>Saline-filled- 36</td>
<td>77.8</td>
<td>13.9</td>
<td>8.3</td>
<td>0.0</td>
</tr>
</tbody>
</table>

In a study by Gylbert and coworkers,\textsuperscript{94} a longer follow up period of six years was used. This was the same case study shown earlier by Asplund and coworkers\textsuperscript{92} with a 16 month follow up time. The results at six years can be seen in Table 2.5.
Six years later, the patients with the silicone gel-filled implants still had the highest rates of capsular contracture when compared to the saline-filled implants. They speculated silicone gel-filled implants may result in more capsular contracture than saline-filled implants because migration of silicone particles from the gel implants into the surrounding tissue might initiate fibrosis.\textsuperscript{92-94}

Another study by Handel and coworkers\textsuperscript{82} in 1995 showed much different results. They decided to use the Kaplan-Meier method of analyses which allows for staggered entry of cases into the trial and irregular loss due to follow-up. The implants were entered into the study on the date of operation and follow up time was defined as the date of entry until the time that a patient developed significant capsular contracture (grade III or IV) or until the date of last examination. Data relating to the implant was not taken into consideration, so results were based on observations. The probability of capsular contracture was calculated as the number of failures (grade III or IV contracture) divided by the total number of active cases at the time of failure. Over the course of the study 1655 implants were examined. They did not take into account whether the implants were

### Table 2.5  Gylbert study: comparison capsular contracture in saline filled vs. silicone gel-filled implant. (Adapted from Gylbert, L.; Asplund, O.; Jurell, G. \textit{Plastic and Reconstructive Surgery} \textbf{1990}, \textit{85}, (3), 373-377. with permission \textsuperscript{94}).

<table>
<thead>
<tr>
<th>No. Implants</th>
<th>Grade I (%)</th>
<th>Grade II (%)</th>
<th>Grade III (%)</th>
<th>Grade IV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel-filled</td>
<td>34</td>
<td>9.0</td>
<td>41.0</td>
<td>47.0</td>
</tr>
<tr>
<td>Saline filled</td>
<td>26</td>
<td>46.0</td>
<td>38.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>
smooth or textured when comparing saline and silicone implants. The results from this study can be seen in Figure 2.8.

Figure 2.8  Handel study: comparison of saline and silicone implants. (Reprinted with permission from Handel, N.; Jensen, J. A.; Black, Q.; Waisman, J. R.; Silverstein, M. J. Plastic and Reconstructive Surgery 1995, 336, 677-682).

Figure 2.8 shows that both the saline and silicone-gel filled implants have similar rates of contracture. There are several other variables that need to be taken into account such as whether there is a higher risk for contracture in patients who underwent augmentation versus those that underwent reconstruction, or even implant replacement, and factors such as the size of the implant.
Figure 2.9 clearly shows that patients who undergo reconstruction are much more likely than patients who undergo augmentation or implant replacement to develop capsular contracture. In the earlier studies, Asplund\textsuperscript{92} examined solely patients who underwent reconstruction, and Cairns\textsuperscript{93} examined those who underwent augmentation. They also did not consider the size of the implant in the development of capsular contracture. In this study it was determined that contracture occurred sooner with implants larger than 350 cc than with medium or small sized implants. These studies show that capsular contracture is a progressive phenomenon which will occur regardless of the type of implant used and that the risk of contracture increases steadily with time, occurring more frequently following reconstruction.\textsuperscript{82}
Another problem with breast implants is rupture. The rupture of an implant or loss of integrity is usually only diagnosed when the silicone gel is found outside of the implant. Ruptures can result from small flaws in the shell caused by accidental needle sticks or from injection or biopsy of hematomas. Other factors which have been linked to rupture include implant age, trauma or injury to the breast, and mammography. Wrinkles or folds are found in 15-67% of gel or saline filled implants and are found by methods such as palpation (feeling with the hands during a physical exam), mammography, or on explantation. Tears can result from wrinkles in the shell abrading on the chest wall from the motion of the breast or from muscular contraction in the case of submuscular implants. The abraded areas can be observed by scanning electron microscopy (SEM). A mammogram can reveal the rupture of a capsule, but not necessarily the failure of the implant shell. ‘silent rupture’ can occur which refers to a failed implant within a fibrous capsule that is intact. This means that the patient does not have any symptoms and the mammogram is normal. When rupture is confirmed the replacement of the implant is required. Silicone gel implant rupture is reported between 5% and 71% of the time, an extremely wide range, based on several clinical studies. Evidence has also been found showing ‘gel bleed’ following the rupture of an implant. Several studies have shown that one reason why the occurrence of rupture might be so high is because the mechanical properties of implants significantly decrease over time. It has even been shown that exposure to the \textit{in vivo} environment weakens silicone gel breast implant shells over time and that the force required to break the shell of the implant is dependent on implant type, shell thickness, and implantation time.
Out of all of the problems with silicone breast implants, the two real concerns are capsular contracture and gel bleed. With the aim of reducing gel bleed, barrier shells were developed to lessen the diffusion of silicone fluid from the gel into the tissues. These shells can be made by adding one or two layers of polydiphenylsiloxane or other modified polysiloxanes. A fluorosilicone layer can also be used between the shell and the gel. The fluorosilicone layer is about 10 μm thick and is a coating on the interior surface of the implant shell. The fluorosilicone layer reduces gel bleed by slowing Diffusion because it has a solubility parameter that is substantially different from that of the gel fluid. This renders diffusion of higher molecular weight silicones unfavorable thereby limiting diffusion to relatively low molecular weight silicone compounds.

2.5 Surface modification of silicone gel-filled breast implants

With the idea of helping to minimize capsular contracture, textured implant shells were developed. Texturing the shell results in modification of the breast implant surface. The form of this texturing can vary greatly according to the manufacturer. The first form of texturing used was a polyurethane foam coating.

Polyurethane foam covered implants were first introduced in 1970. These implants had a 1 or 2 mm thick coating of poly(ester)urethane textured foam. This foam was produced by the polymerization of poly(diethylene glycol adipate) with a 4:1 mixture of 2,4- and 2,6-toluene-diisocyanate. This foam was secured to the implant using an RTV silicone adhesive. It was reported that these polyurethane foam-covered implants resulted in a reduced risk of capsular contracture. More recently it was found that eight years following implantation, 80% of polyurethane foam-covered
implants remained contracture free compared to 65% of textured implants and 50% of smooth implants.\textsuperscript{114} Polyester polyurethanes undergo enzymatic hydrolysis by chain cleavage at the ester groups leading to the degradation of the foam.\textsuperscript{13} In the late 1980s it was reported that \textit{in vitro} degradation of polyurethane could lead to the formation of substances that are known carcinogens in animals.\textsuperscript{110} There was concern about the formation of highly toxic toluene-diamine (TDA) from the degradation of these implants; however, a study done by Szycher et al.\textsuperscript{115} found that TDA was formed over a 4 day period forming a maximum of 8.3 ppm (parts per million) TDA. Based on studies like these, the FDA concluded that the risk of polyurethane induced cancer in women with a foam–covered implant is about 1 in 1,000,000.\textsuperscript{116} Since the risk was deemed to be low, the FDA did not recommend the explantation of these implants; despite this, Bristol-Meyers Squibb, the manufacturer of polyurethane foam-covered implants in the US, withdrew its product in 1991. These polyurethane implants are still manufactured and widely used throughout Europe. Despite the reduction of capsular contracture, there are still some problems that can occur with polyurethane foam-covered implants, particularly skin rash.\textsuperscript{114,117} A distinctive skin rash was connected to the use of polyurethane covered implants in 4 out of 70 implants in 54 patients, 5.7\textsuperscript{\%},\textsuperscript{22} and in 15\% of patients, as found by Essen.\textsuperscript{118} Gasperoni et al.\textsuperscript{119} noted that this rash occurs in only 1\% of cases and disappears after 2 to 4 weeks.

As a result of the reduction in capsular contracture by polyurethane foam coatings, texturing of the implant shell began. How the texturing is done can vary greatly from one manufacturer to another. For example, Dow Corning\textsuperscript{25} used regular pillars which were 750 μm high and 250 μm in diameter spaced 500 μm apart, McGhan Biocell
used an open pore network with 3.1 pores/μm² with a variable pore size of 300-600 μm and a height of 500-800 μm. Meanwhile, Mentor used surface irregularities which were 65-150 μm high and 60-275 μm wide. By the mid 1980s most of the major smooth shelled implants were textured with the goal of minimizing capsular contracture. It was assumed that texturing the shell would have a similar effect on capsular contracture as the polyurethane foam coating did. It was also assumed that the tissue would grow into the interstices of projections or pores prolonging chronic inflammation and disorienting collagen fibrils thereby weakening their contractile forces. According to a study by Hammerstad et al. smooth implants gave either no capsule or severe capsular contracture, while textured implants had more of a tendency to result in less severe capsular contracture according to the Baker’s scale. Similar results were found in studies by Coleman et al. and Burkhardt et al.

Since the body recognizes hydrophobic materials such as silicone rubber as foreign, which initiates fibrosis and the formation of a fibrous capsule, efforts have been made to modify the surface of silicone rubber with (PEG) in an attempt to reduce the formation of the fibrous capsule. According to Kinoshita et al. collagen and hydrogel coatings can reduce fibrosis in biomaterials. Vladkova used poly(ethylene glycol) hydrogel coatings to modify the surface of silicone rubber. PEG is used quite frequently to improve the biocompatibility of polymers. Vladkova and coworkers prepared polymers by photopolymerization of a monoacrylated methoxy PEG with OE (oxyethylene) chains of different lengths on the surface of PDMS. The silicone rubber samples were prepared by injection molding after the vulcanization of PDMS, and then sonicated the samples for 30 minutes in a 1:1 mixture of ethanol and water and allowed
the samples to dry in an air flow. Mixtures of monomethoxy PEG monoacrylate, hexanediol diacrylate (HDDA), and 2,2-hydroxy-2-propiophenone (HPP) were prepared using 1/1/1 (w/w/w) toluene/ethanol/ethyl acetate as the solvent. Films were made with PEG 500, PEG 1900, and PEG 5000 with varying ratios of HDDA and TMP(OE)₂. They diluted the mixtures to a final dry content of 1 wt% and a 1% solution was applied to the surface of the silicone rubber using a spiral-rod applicator. The films were allowed to dry and then UV cured in a two-step cure procedure. The films were then rinsed with de-ionized water twice. Time-dependent contact angles showed that swelling occurred in all the coatings attached to silicone rubber. The PDMS contact angle remained constant at ~90°. These contact angles varied with both PEG molecular weight and PEG/HDDA ratio. The lowest water contact angles were observed in films containing PEG 5000 mixed with HDDA in varying ratios. This shows that these materials are hydrophilic. These materials showed fibroblasts adhering to bare silicone rubber and PEG 5000 coated surfaces. On both surfaces, cells were intact and were not growing. PEG-coated surfaces had lower cell adhesion than the bare silicone rubber.¹⁴ This study showed that PEG 5000 (Mₙ = 5000 g/mol) with HDDA in a 1:1 ratio greatly improved the hydrophilicity of silicone rubber and reduced the amount of cell adhesion. This shows that increasing hydrophilicity of the surface of breast implants could help reduce fibrous capsule formation.

In conclusion, the two main problems with silicone breast implants are capsular contracture and gel-bleed. It is clear that some form of surface modification needs to be done to minimize the formation of the fibrous capsule. It is not yet clear what will make the surface more biocompatible; but it has been shown that either texturing the surface of
the implant, or modifying the surface to make it more hydrophilic could help minimize fibrous capsule formation.

Since one of the goals of this dissertation is to increase the hydrophilicity of the biomaterials and correlate this to the biocompatibility of the material, it is necessary to discuss some commonly used methods of surface modification. Only a few methods relevant to this research will be discussed because the number of methods to modify a surface is very large.

2.6 Methods of surface modification

There are a large variety of methods used to modify the surfaces of biomaterials. The modifying of biomaterial surfaces can be complex, although typically modification involves functionalization of the surface by either wet chemical or by physical methods. Deposition of thin films can be done using plasma polymerization of functional monomers. This can be accomplished using electron-beam or UV-radiation-induced coupling of molecules, radical induced coupling of molecules to the surface, or just physical adsorption of molecules to the surface. More recently surface modification has been achieved using carbon black. These methods of surface modification will be discussed in this section.

2.6.1 Modification by plasma-induced polymerization

The argon plasma-induced grafting of different monomers such as poly(acrylic acid) (pAA) has been carried out by Sigelkow and Volcker and their coworkers. Silicone elastomers were exposed to argon plasma causing the formation of radicals on
the surface. The samples were then exposed to air forming hydroperoxides on the surface. These hydroperoxide groups were used in the subsequent thermally initiated polymerization of monomers such as acrylic acid (AAc), methacrylic acid (MAAc), and glycidyl methacrylate (GMA), as seen in Figure 2.10.

![Diagram of the process](image)

**Figure 2.10** Argon plasma induced grafting. (Adapted from Volcker, N.; Klee, D.; Hocker, H.; Langefeld, S. J. Mater. Sci.: Materials in Medicine 2001, 12, 111-119129).

Contact angle measurements by Volcker and coworkers129 showed the hydrophobic nature of silicone; after argon plasma treatment of the surface there was an approximately 17° decrease in contact angle showing an increase in hydrophilicity of the surface (Figure 2.11). The advancing (θₐ) and receding (θᵣ) water contact angles were measured. Contact angle hysteresis (θₐ – θᵣ) enables an understanding of the surface homogeneity of the polymer films.129 From these results, a decrease in the hysteresis of the argon plasma-treated silicone can be seen (Figure 2.11). From Figure 2.11 it is clear that both grafted poly(methacrylic acid) (PMAAc) and PAAc are more hydrophilic than silicone; grafted PAAc (poly(acrylic acid)) was the most hydrophilic with a water contact angle of around
87°. Interestingly, vapor-phase grafted PAAc [PAAc(v)] showed an increase in surface homogeneity when compared to the thermally-initiated radical polymerization of PAAc. This shows that the method of polymerization can have a very large effect on the surface.

Figure 2.11 Advancing and receding contact angles of water on untreated and surface modified silicone. (Reprinted with permission from Volcker, N.; Klee, D.; Hocker, H.; Langefeld, S. J. Maters. Sci.: Materials in Medicine 2001, 12, 111-119129).

The very large hysteresis of the PGMA was said to be attributed to large amounts of heterogeneity as well as dynamic swelling affects and molecular rearrangements. These results show that by using plasma induced polymerization of silicone, the hydrophilicity as well as homogeneity of the surface can be significantly altered.

2.6.2 Adsorption and covalent attachment of proteins to polymer surface

Sigelkow and coworkers16 studied the effects of adsorptively and covalently attached fibronectin, as well as covalently attached GRGDS on the surface of silicone-\textit{graft}-PAAc. Volcker and coworkers129 studied fibronectin which was both adsorptively
and covalently attached to the surface of PAAc, PMAc, and PGMA. Fibronectin is a disulfide-linked glycoprotein synthesized by a variety of cells; it is found on the surface of cells, in the extracellular matrix, plasma, as well as other body fluids. It is known that fibronectin plays an important role in platelet function and is secreted upon platelet activation. It was found that in the cell-binding domain of fibronectin is a peptide sequence known as GRGDS (gly-arg-gly-asp-ser). The adsorption of fibronectin to the surface of the grafted PAAc yielded materials with a much lower concentration of

![Diagram of covalent attachment of GRGDS to the surface of PAAc.]

Figure 2.12 Covalent attachment of GRGDS to the surface of PAAc.
Fibronectin bound to the surface than covalently attached fibronectin. Because adsorption is known to result in weakly physisorbed attachment of proteins to the surface, the long term effect on the surface is negligible. Grafting of fibronectin or GRGDS to the surface of PAAc was carried out using EDC (1-ethyl-3-[3-DIaminomethylpropyl] carbodiimide) (Figure 2.12).

Volcker found that immobilization of fibronectin on polymer surfaces was larger when covalently attached using EDC as compared to plain adsorption. Interestingly, immobilization of fibronectin was greatest on PGMA (Figure 2.13). This is thought to be a result of higher surface area in silicone-graft-PGMA found by AFM and shown by the hysteresis from contact angle. This shows that the increase in binding is caused by both covalent bonding as well as adsorptive binding.

The groups of Sigelkow\textsuperscript{16} and Volcker\textsuperscript{129} showed that adsorption of fibronectin does not improve cell growth (of L929 cells: fibroblasts). Sigelkow and coworkers\textsuperscript{16} showed that unmodified PAAc actually exhibits less cell growth than plain silicone, even with covalently or adsorptively attached fibronectin, although cell adhesion was higher with the covalently than the adsorptively-attached fibronectin. Interestingly the GRGDS used showed a larger amount of cell growth than any other material, except for the positive control. This can be seen in Figure 2.14. This could be because of the synthetic protein GRGDS’s ability to reduce the binding of blood platelets to itself. These results also show that having too hydrophilic a surface (such as PAAc) can actually decrease biocompatibility. This further demonstrates that biocompatibility of a polymer is extremely complex.

![Figure 2.14 Cell growth of L929 cells on modified silicone materials. (Reprinted with permission from Sigelkow, W.; Gescher, D. M.; Sigelkow, A.; Klee, D.; Malik, E.; Rath, W.; Faridi, A. \textit{Int. J. Artif. Organs} \textbf{2004}, 27, 1100-1108\textsuperscript{16}).](image-url)
2.6.3 Surface modification with carbon black

Carbon black is known to be thromboresistant and hemocompatible.\textsuperscript{21,23} Diamond-like carbon black (DLC) is composed solely of carbon, hydrogen, and nitrogen which are all biocompatible. DLC is known to have high hardness, chemical inertness, a low coefficient of friction, as well as high electrical conductivity.\textsuperscript{21} Studies comparing cell growth of fibroblasts on plain polystyrene culture dishes to carbon-coated polystyrene dishes have shown that fibroblasts grow well on the carbon-coated dishes, and that cell damage didn’t occur \textit{in vitro} (Figure 2.15).\textsuperscript{21}

![Growth curves for human synovial fibroblasts on plain and DLC coated polystyrene. (Copied with permission from Cui, F. Z.; Li, D. J. \textit{Surf. Coat. Technol.} 2000, \textbf{131}, 481-487\textsuperscript{21}).](image)

Recently, it was discovered that biocompatibility of carbon-based nanomaterials depends on several factors such as mass, purity, aspect ratio, and surface functional groups.\textsuperscript{132} Svorcik and coworkers\textsuperscript{24} showed that a polymer’s conductivity plays an important role in
its biocompatibility, contributing to the biocompatibility of carbon black- filled biomaterials. They examined carbon black-filled polyethylene. The weight percent of carbon black was varied, and cell adhesion after 18 and 96 hours of incubation was examined. The resistivity of the polyethylene- carbon black blends was measured and can be seen in Figure 2.16. Figure 2.16 shows that there is a percolation threshold (critical loading) at around 5.5-6 wt% carbon black, below which the material remains non-conductive. The results from incubation with vascular smooth muscle cells show an increase in adhesion of muscle cells to the polymer with an increase in the wt% carbon black. Figure 2.17 shows that this increase in smooth muscle cell adhesion occurs up to about 10 wt% carbon black, and then reaches a plateau.

![Figure 2.16 Sheet resistants (R_s) as a function of CB concentration in PE + CB mixture. (Svorcik, V.; Rybka, V.; Hnatowicz, V.; Bacakova, L. J. Mater. Sci: Lett. 1995, 14, 1723-1724).](image-url)
2.7 PIB-PS block copolymers

One of the main complications mentioned with silicone breast implants was gel bleed of the low molecular weight silicone fluid from the implants. Gel bleed occurs because of the permeability of the silicone elastomer’s shell; therefore, a material with low permeability and known biocompatibility would be a suitable material for investigation as an alternative material for breast implants. Poly(styrene-\(b\)-isobutylene-\(b\)-styrene) (SIBS) is known to have extremely low permeability\(^9\) so we decided to investigate it for use in breast implants.
2.7.1 Generations of poly(styrene-\textit{b}-isobutylene-\textit{b}-styrene) (SIBS) based biomaterials

The first generation of this class of materials, SIBS, is FDA-approved as a coating in drug eluting cardiovascular stents.\textsuperscript{8,133} These block copolymers have been shown to be biocompatible and biostable \textit{in vivo} and \textit{in vitro}.\textsuperscript{4-8,11,133-136} The second generation materials are star-branched polyisobutylene with a PIB core and styrene end blocks.\textsuperscript{4}

![Diagram of generations of SIBS based biomaterials](image)

Figure 2.18 Generations of SIBS based biomaterials.\textsuperscript{135}

High molecular weight (MW) arborescent (randomly branched, tree-like) polyisobutylene (\textit{arb}\_IB) have been produced by inimer-type living carbocationic
polymerization of 4-(2-methoxyisopropyl)styrene inimer (initiator-monomer, MeOIM) with IB and TiCl₄ coinitiator. Subsequently polyisobutylene-polystyrene block copolymers, \textit{arb} SIBS, were produced by blocking of styrene or \textit{p}-methylstyrene from the living \textit{arb} IB chain ends.

\textit{arb} SIBS polymers are in the third generation of polyisobutylene-based thermoplastic elastomers, as seen in Figure 2.18. The synthesis of these third generation \textit{arb} SIBS is shown in Figure 2.19. The polymerization was carried out using 4-(2-methoxyisopropyl)styrene inimer with TiCl₄ coinitiator in methylcyclohexane (MeCHx)/MeCl in a 60/40 v/v ratio using 2,6-di-tert-butylpyridine (D\textit{t}BP) proton trap at -80°C. The synthesis of these polymers will be discussed in more detail in Section 2.8.1.

![Figure 2.19 Synthesis of \textit{arb} SIBS from MeOIM. (Reprinted with permission from Paulo, C.; Puskas, J. E. Macromolecules 2001, 34, 734-729\textsuperscript{137}).](image)

2.7.2 Properties of SIBS

As can be seen from Table 2.6, SIBS polymers have similar hardness as silicone, with a higher tensile strength and elongation at break. SIBS also have much lower permeability and higher hydrophilicity, as can be seen from contact angle data.\textsuperscript{1,9,10}
Table 2.6 Properties of SIBS in comparison to silicone.\textsuperscript{1,9,10}

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness (Shore A)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at Break (%)</th>
<th>Gas Transmission Rate 25 °C, 10 cm(^2)/sec/atm</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIBS</td>
<td>20-90</td>
<td>3-24</td>
<td>250-1800</td>
<td>1.0</td>
<td>3.9</td>
</tr>
<tr>
<td>SILICONE</td>
<td>20-90</td>
<td>3-10</td>
<td>300-1000</td>
<td>7.0</td>
<td>36.8</td>
</tr>
</tbody>
</table>

arb_SIBS have improved fatigue and creep compared to SIBS, because the branched arb_IB core gives rise to a “double network” with a branched core embedded into a self-assembled, thermolabile network,\textsuperscript{4,138,140,141} as seen in Figure 2.19. The mechanical properties of the linear SIBS (L_SIBS), star branched SIBS (S_SIBS) and arborescent SIBS (arb_SIBS) can be seen in Table 2.7. From Table 2.7 it is clear that there is a slight improvement of the mechanical properties of the S_SIBS and arb_SIBS materials.

Table 2.7 Mechanical Properties of SIBS materials.\textsuperscript{142,143}

<table>
<thead>
<tr>
<th>Sample ID*</th>
<th>M(_n) (g/mol)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L_SIBS (34)</td>
<td>78,000</td>
<td>9.9</td>
<td>340</td>
</tr>
<tr>
<td>S_SIBS (34)</td>
<td>108,000</td>
<td>18.7</td>
<td>430</td>
</tr>
<tr>
<td>arb_SIBS (34)</td>
<td>585,000</td>
<td>8.7</td>
<td>950</td>
</tr>
</tbody>
</table>

*number in parentheses is weight percent polystyrene
2.7.3 Phase separation of SIBS

It is known that block copolymers with an elastomeric segment having a low $T_g$ and a hard thermoplastic segment with a high $T_g$ behave as TPEs (thermoplastic elastomers).\(^{144}\) The hard segments result in the formation of physical crosslinks which dissociate when heated above a certain temperature ($T_g$ or $T_m$) and form on cooling. Phase separation occurs because the hard and soft blocks are incompatible, which causes them to phase separate on a microscopic scale. XPS was carried out on SIBS and PS to determine the surface composition of SIBS-based materials; similar results were obtained with \textit{arb}\_SIBS. Figure 2.20 shows the XPS of SIBS and PS taken at a 2.5 nm, $15^\circ$ angle. The peaks at 285 eV in both SIBS and PS are from the main carbon peaks (C-C, C-H, C=C). The peak at 292.6 eV in PS is from the $\pi \rightarrow \pi^*$ transition from the aromatic ring of PS. In the case of SIBS at the 15 and 30$^\circ$ angle, the peak at 292.6 eV from the $\pi \rightarrow \pi^*$ transition is absent which indicates that to a depth of 5 nm there is no PS on the surface. At the 90$^\circ$ angle, the peak at 292.6 eV can be seen in SIBS.

![Figure 2.20 C1s XPS of SIBS and PS. (Reprinted with permission from Puskas, J. E.; Kwon, Y.; Antony, P.; Bhowmick, A. K. \textit{J. Polym. Sci., Part A} 2005, 43 (9), 1811-1826\(^{12}\).)]](image)
These results coupled with AFM phase images, which show the phase separation in SIBS (Figure 2.21), show SIBS based materials have a spherical to cylindrical morphology depending on the amount of PS content.

The AFM image (Figure 2.21a) shows the spherical morphology of an *arb_SIBS* (dark regions from styrene domains). Figure 2.20 shows that PIB, due to its low surface energy phase separates to the surface of the material, PS forms spherical physically crosslinked, amorphous glassy regions which are at least 10 nm from the surface of the polymer as seen in Figure 2.21 (b).\(^\text{12}\)

![Figure 2.21 Morphology of SIBS based materials: (a) AFM image of an *arb_SIBS* (1 \(\mu\)m scale) (b) schematic of SIBS morphology based from AFM and XPS results. (a) was (Reprinted with permission from Puskas, J. E.; Chen, Y.; Antony, P.; Kwon, Y.; Kovar, M.; Harbottle, R.; de Jong, K.; Norton, P.; Cadieux, P.; Burton, J.; Reid, G.; Beiko, D.; Watterson, J.; Denstedt, J. *Polym. Adv. Technol.* 2003, 14, 763\(^\text{135}\)); (b) was (Reprinted with permission from El Fray, M.; Prowans, P.; Alstät, V. *Biomacromolecules* 2006, 7, (3), 844-850\(^\text{11}\)).](image-url)
2.8 Synthesis and characterization of \textit{arb}_IB

Since this work includes a new method of inimer type polymerization to make a novel \textit{arb}_SIBS, a detailed explanation on the synthesis and characterization of these materials will be given.

2.8.1 Synthesis of \textit{arb}_IB

The first PIB based inimer-type polymerization was carried out by Paulo and Puskas\textsuperscript{137} using the 4-(2-methoxyisopropyl)styrene inimer, shown in Figure 2.11. They stated that the degree of branching in an inimer (IM) type polymerization is influenced not only by the \([IM]_0/[M]_0\) ratio, but also by the amount of \(\text{TiCl}_4\), as studied previously by Puskas and coworkers.\textsuperscript{145} In this study they used both \([\text{TiCl}_4]_0 \leq [I]_0\) and \([\text{TiCl}_4]_0 > [I]_0\) and showed that when \([\text{TiCl}_4]_0 \leq [I]_0\) both initiation and propagation were first order in \([\text{TiCl}_4]\). With \([\text{TiCl}_4]_0 > [I]_0\) they observed instantaneous initiation. The rate of propagation was second order in \([\text{TiCl}_4]\). The same results for dependence on \(\text{TiCl}_4\) were observed by Paulo and Puskas;\textsuperscript{137} the rate of polymerization was shown to increase with increasing \([IM]\) and \([\text{TiCl}_4]\). In order to obtain a truly arborescent (randomly branched) polymer the propagating cumyl carbocation and the \textit{para}-substituted secondary benzylic carbocation need to have similar reactivities (Figure 2.22).\textsuperscript{12}

2.8.2 Branching analysis of \textit{arb}_IB

Key to the synthesis of high MW randomly branched \textit{arb}_IB are living conditions (i.e., the absence of irreversible chain termination and chain transfer), and similar reactivities of the initiating and propagating carbocations.
Figure 2.22 Carbocations generated from the 4-(2-methoxyisopropyl)styrene inimer/TiCl₄/IB system. (Reprinted with permission from Puskas, J. E.; Kwon, Y.; Antony, P.; Bhowmick, A. K. J. Polym. Sci., Part A 2005, 43(9), 1811-1826).
In the case of MeOIM, the initiating carbocation is a cumyl-type tertiary carbocation stabilized by resonance, while the propagating active species are tertiary alkyl and secondary benzylic carbocations. In this case the MeOIM is expected to be incorporated randomly into the polymer chain, and the average number of branching points (B) in the \textit{arb}_IB core can be predicted from kinetics as shown in eq. (1)\textsuperscript{146}:

$$B_{\text{kr}} = \left( \frac{M_{\text{n, total}}}{M_{\text{n, theo}}} \right) - 1$$ \hspace{1cm} (1)

where \(M_{n,\text{theo}}\) stands for the MW that would arise if the IM would act only as initiator.

Since the branching sites of \textit{arb}_IB can be cleaved selectively without affecting the PIB, the predicted \(B_{\text{kin}}\) values can be expressed by:

$$B_{\text{ld}} = \frac{M_{n,\text{total}}}{M_{n,\text{segment}}}$$ \hspace{1cm} (2)

where \(B_{\text{ld}}\) is obtained by “disassembling” the branched structure by selective link destruction, as shown in Figure 2.23.\textsuperscript{137} Indeed, in the case of \textit{arb}_IBs synthesized with MeOIM (\(M_{n,\text{total}}\sim 40,000\) to 1,000,000 g/mol), good agreement was found between \(B_{\text{kin}}\) and \(B_{\text{ld}}\) (B ~2-60).\textsuperscript{137,139} Branching with the MeOIM was also found to increase with increasing molecular weight across the molecular weight distribution of the polymer.\textsuperscript{146}

Using selective link destruction (LD) Paulo and Puskas\textsuperscript{137} were able to show a trend with the \([\text{IM}]_0/[\text{M}]_0\) ratio and the resulting molecular weight and degree of branching (Figure 2.24) as well as a trend with the \([\text{TiCl}_4]_0/[\text{IM}]_0\) ratio and the resulting molecular weight and degree of branching (Figure 2.25).
Figure 2.23  Selective link destruction of *arb* _IBs._

Figure 2.24  Dependence of M<sub>n</sub> and BR on the [IM]<sub>0</sub>/[M]<sub>0</sub> ratios in inimer IB polymerizations from MeOIM: [IB]<sub>0</sub> = 2 mol/L; [TiCl<sub>4</sub>]<sub>0</sub> = 10[IM]<sub>0</sub>; [D&lt;sub&gt;r&lt;/sub&gt;BP] = 0.008 mol/L; MeCHx/MeCl = 60/40 v/v; T= -80 °C. (Reprinted with permission from Paulo, C.; Puskas, J. E. *Macromolecules* **2001**, *34*, 734-729).
In Figure 2.24, $M_n$ was seen to decrease with $[\text{IM}]_0/[\text{M}]_0$ ratio and then increase as expected because the IM is mostly initiating and as branching occurs, the increase in $M_n$ is observed along with an increase in branching. From Figure 2.25, it is clear that with the MeOIM, both $M_n$ and BR decrease with increasing $[\text{TiCl}_4]_0/[\text{IM}]_0$.

While link destruction provides the amount of branching, it does not give insight into polymer architecture. Therefore, we have analyzed our polymers by the use of branching parameters of Burchard, Schmidt and Stockmayer to gain insight into the architecture of our polymers.

2.8.3 Architecture analysis of $arb_{-}\text{IBs}$

Burchard, Schmidt and Stockmayer discussed the analysis of various polymer architectures based on integrated and quasielastic light scattering (LS and QELS). They
considered mono- and polydisperse linear and star-branched polymers with \( f \) number of arms (“rays”), and “random polycondensates” of \( A_f \) or ABC type (identical or DIfferent functional groups, respectively). Dendrimers and other dendritic (hyperbranched, arborescent, etc.) structures had not been considered at that time. The authors identified parameters which give insight into polymer architectures:

\[
\begin{align*}
g &= \left( \frac{<R_g^2>_{br}}{<R_g^2>_{lin}} \right) \\
h &= \left( \frac{R_{h,br}}{R_{h,lin}} \right) \\
\rho &= \left( \frac{<R_g^2>_{z}^{1/2}}{<R_h^2>_{z}} \right)
\end{align*}
\]

\( lin \) refers to linear monodisperse polymers. \( g \) and \( h \) are computed by comparison with a linear polymer at the same weight average molecular weight. \( \rho \) is a function of branching, polydispersity, and branch flexibility, but independent of bond angles and degree of polymerization; it is considered the most accurate and reliable parameter of polymer architecture.\(^6,7,134\)

Burchard et al.\(^{147}\) wrote that “It is commonly presumed that \( g \) and \( h \) are continuously decreasing functions of the branching density and always smaller than unity.” This statement is correct for monodisperse samples as well as regular (monodisperse) stars. In other cases, however, \( g \) and \( h \) are larger than unity for low branching densities, and in the case of randomly branched polycondensates or randomly crosslinked molecules they even increase with the number of functional groups, in contrast to the decrease for star molecules. The reason for this behavior is that polydispersity causes a larger increase of the \( z \)-average mean-square radius of gyration than the corresponding increase of the weight-average molecular weight. Thus \( g \) and \( h \) embody two effects with converse behavior: polydispersity, which causes increase, and branching, which causes the familiar decrease. The equations led to identical solutions.
for stars and ABC polycondensates with $B = (f-1)/2$, where $f$ is the number of branches or “rays”. For example, the $g = 0.77$, $h = 0.94$, $\rho = 1.4$, i.e., parameters assumed by Burchard et al.\textsuperscript{147} for a polymer sample, were most consistent with a 3-arm star monodisperse polymer; a polydisperse 3-arm star would exhibit $g = 1.12$, $h = 1.05$, $\rho = 1.6$. The second example cited was poly(vinyl acetate) (PVAc) prepared by emulsion polymerization. Since no data for a linear equivalent was available, $g$ and $h$ were not calculated. At lower conversion/molecular weight $\rho = 1.84$ was found, only slightly higher than the theoretically expected $\rho = 1.73$ for a randomly branched architecture. $\rho$ slightly decreased with increasing $M_w$, indicating that branching was not completely random. Above $M_w \sim 15 \times 10^6$ g/mol, $\rho$ dropped sharply to 0.55, consistent with a more compact spherical shape. The authors also pointed out that $g > 2$ and $h > 1$ measured for a polymer would clearly indicate random branching. If our polymers are truly arborescent (randomly branched), which is also an indication of the reactivity of propagating carbocations (a randomly branched system would have propagating carbocations of equal reactivity), values of $g > 2$ and $h > 1$ should be observed along with a $\rho$ value of approximately 1.73. With the core of the polymer fully analyzed, the synthesis of block copolymers can be carried out with full understanding of the branching and architecture of the resulting polymer.

2.9 Synthesis of \textit{arb\_SIBS}

\textit{arb\_SIBS} were synthesized by blocking styrene from \textit{arb\_IB} macroinitiators. Synthesis was carried out in methylcyclohexane (MeCHx) and methyl chloride (MeCl) in a 60/40 v/v ratio. The \textit{arb\_IB} was dissolved in the solvent mixture along with DtBP
(proton trap to prevent protic initiation), dimethyl acetamide (DMA) (used as an electron donor), and TiCl₄. Styrene monomer (St) was added to initiate blocking (Figure 2.26).

![Chemical structure diagram](image)

**Figure 2.26** Blocking of PSt from *arb* IB by reactivating the chain ends. (Reprinted with permission from Puskas, J. E.; Kwon, Y.; Antony, P.; Bhowmick, A. K. *J. Polym. Sci., Part A* 2005, 43(9), 1811-1826).

DMA is used as a strong electron donor (ED) to prevent nucleophilic substitution of the styrene (St) rings and allow for the controlled polymerization St; it does, however, slow down the rate of polymerization.¹⁴⁸ These conditions result in the controlled polymerization of *arb*_SIBS. The synthesis of *arb*_SIBS has also been carried out by a one pot method,¹³⁸ as shown in Figure 2.19. In this method, after the polymerization of *arb*_IB for 1-2 hours, DMA was added and after 5 minutes stirring a pre-chilled mixture of styrene with 50% MeCHₓ was added; blocking was allowed to proceed for 25 to 30 minutes. This method also resulted in the controlled polymerization of *arb*_SIBS.
2.10 Biomedical applications of SIBS

Currently, the Taxus™ drug eluting stent (Boston Scientific) is the largest biomedical application of SIBS. Many factors were considered in the design and development of the Taxus™ stent. According to Kamath and coworkers\textsuperscript{149} of Boston Scientific “The polymer carrier, as a drug delivery coating on the stent, needs to meet several criteria, which include compatibility with the drug, ability to withstand processing, sterilization and storage, adjustable formulation and drug release properties, good mechanical integrity during handling and throughout the clinical deployment procedure in the tortuous vessel anatomy, as well as through its residence in the mechanically and biologically demanding coronary artery. Last, but not least, it needs to demonstrate vascular compatibility, i.e. have no adverse biological response beyond that of the non-coated-bare-metal coronary stent (BMS).” They found SIBS to meet all of these qualifications, having good mechanical strength, and most importantly being biostable. Kamath and coworkers\textsuperscript{149} examined the biostability of SIBS after implantation in the coronary artery of a pig up to a year and saw no evidence of molecular degradation.

The biocompatibility of SIBS is thought to be due to the fact that PIB is saturated, non-polar, and contains no groups prone to chemical or oxidative attack.\textsuperscript{1} This, along with the success of the Taxus™ stent, has started to attract a great deal of attention to SIBS for use in biomedical applications. Currently SIBS is being examined for use in ophthalmic applications such as in the MIDI-Tube glaucoma shunt, as well as for an intraocular lens (IOL).\textsuperscript{1} So far both the MIDI-Tube and IOL appear to be biocompatible in ophthalmic applications, showing even more biocompatibility than silicone.\textsuperscript{1}
The biocompatibility of SIBS as well as the mechanical integrity of SIBS demonstrated by the Taxus™ stent has attracted the attention of the Puskas group for use as an alternative material for breast implants. As mentioned earlier, it is hypothesized that an increase in hydrophilicity of the surface of SIBS will help improve its biocompatibility. Therefore, the Puskas group has developed a novel initiator 4-(1,2-oxirane-isopropyl) styrene (EPOIM) which will be discussed in this dissertation. It was hypothesized that this inimer will allow for the introduction of hydroxyl groups to the surface of the polymer. EPOIM is an epoxide similar in structure to α-Methylstyrene epoxide (MSE); therefore, it is necessary to discuss the ring opening and synthesis of polymers using MSE.

2.11 The use of α-methylstyrene epoxide (MSE) for living carbocationic isobutylene polymerization

α-Methylstyrene epoxide (MSE) has been used as an initiator for the living carbocationic polymerization of isobutylene. The ring opening of epoxides by carbocationic polymerization can occur following both an Sn1 and an Sn2 mechanism (Figure 2.27). In Figure 2.27 shows that when ring opening proceeds by an Sn1 mechanism a tertiary carbocation is formed which can initiate polymerization, whereas ring opening by the Sn2 mechanism results in the formation of polyethers. In situ FT-IR monitoring was carried out for the IB polymerization with α-methylstyrene epoxide. In the absence of IB, when [TiCl4]0 = [I]0, polyethers were formed (Sn2 mechanism). The formation of a peak at 1615 cm⁻¹ from the stretching vibration of the O-TiCl3 group (product from Sn1 mechanism in Figure 2.27) was observed. Upon the addition of IB, no
polymerization occurred until the addition of an excess of TiCl₄. This shows that to initiate polymerization of isobutylene \([\text{TiCl}_4]_0 > [\text{I}]_0\)\(^{151}\).

![Possible reactions between α-methylstyrene epoxide and TiCl₄](image)

Figure 2.27 Possible reactions between α-methylstyrene epoxide and TiCl₄. (Reprinted with permission from Puskas, J. E.; Michel, A. *Macromol. Symp.* **2000**, *161*, 141-148).

Using MSE to initiate IB polymerization results in the formation of a linear PIB with a primary hydroxyl group at the methylstyrene chain end (Figure 2.28)\(^{152}\). This primary hydroxyl group can be chemically modified. The \(^1\)H-NMR spectrum of the resulting polymer (Figure 2.28) shows that the methylene protons \(\alpha\) to the primary hydroxyl group appear as two sets of doublets at 3.4 and 3.6 ppm.
Figure 2.28 $^1$H-NMR spectrum of a primary hydroxyl-functionalized PIB ($M_n = 4,300$ g/mol) (400 MHz), CD$_2$Cl$_2$. (Reprinted with permission from Song, J.; Bodis, J.; Puskas, J. E. J. Polym. Sci. Part A 2002, 40, 1005).

Figure 2.29 $^1$H-NMR spectrum of a silylated PIB ($M_n = 4,300$ g/mol) (400 MHz, CDCl$_3$). (Reprinted with permission from Song, J.; Bodis, J.; Puskas, J. E. J. Polym. Sci. Part A 2002, 40, 1005).
This is because these protons are diastereomeric protons which are adjacent to a chiral center.

To further confirm that the resulting polymer had a primary hydroxyl head group, silylation of the polymer was carried out in the presence of CCl₄ using chlorotrimethylsilane and pyridine as a catalyst. The presence of a new peak at 0.08 ppm (from the methyl protons of trimethylsilane) was taken as confirmation of silylation and the presence of hydroxyl groups in the polymer (Figure 2.29).¹⁵²

As mentioned earlier, Dr. Puskas developed a novel method of surface modification using a low molecular weight thymine-functionalized PIB which will be discussed in this dissertation. Therefore, a brief discussion of work done in the Puskas group to make thymine-functionalized polystyrene will now be discussed.

2.12 Thymine-functionalized polystyrene

Dahman and coworkers¹⁵³ functionalized polystyrene with thymine because of thymine’s ability to hydrogen bond (Figure 2.30). Thymine functionalized polystyrene was made by copolymerizing styrene with 1-(vinylbenzyl) thymine (1-VBT) by free radical emulsion copolymerization. The benzene ring spacer between the polymer backbone and the thymine was expected to give flexibility to the functional groups. The structure of poly-[styrene-co-(vinylbenzyl)thymine] is shown in Figure 2.31.¹⁵⁴

To determine how much thymine might be on the surface, high resolution XPS was performed on a sample containing 4.85 wt% VBT (Figure 2.32). Results from high resolution XPS showed five different type of carbon atoms, including C=O and C-N both of which are found in thymine.
Figure 2.30 Versatility of 1-VBT. (Reprinted with permission from Dahman, Y.; Puskas, J. E.; Margaritis, A. *Macromolecules* 2003, 36, 2198-2205).

Figure 2.31 Structure of PS-VBT copolymers. (Reprinted with permission from Puskas, J. E.; Dahman, Y.; Margaritis, A. *Biomacromolecules* 2004, 5 (4), 1412-1421).
Figure 2.32. XPS high-resolution spectra (4.85 wt% VBT) (a) XPS high-resolution C 1s. (b) XPS high-resolution O 1s. (c) XPS high-resolution N 1s. (Reprinted with permission from Dahman, Y.; Puskas, J. E.; Margaritis, A. *Macromolecules* **2003**, *36*, 2198-2205).
The high resolution O 1s showed one peak from C=O and the high resolution N 1s showed a peak from the N-C and N-H atoms in thymine confirming the presence of thymine on the surface. With these results coupled with quantitative XPS they determined that the sample had 22.8 wt% VBT on the surface.

![Figure 2.33. Effect of pH on the adsorption of BSA and BHb on PS and PS-VBT4-20. C₀ = 0.25 g/L, T = 25 °C. (Reprinted with permission from Puskas, J. E.; Dahman, Y.; Margaritis, A. Biomacromolecules 2004, 5(4), 1412-1421).](image)

PS-VBT microsphere latexes were then freeze dried to preserve the thymine and ground to give an average particle size of 2.07 μm. The hydrogen bonding of bovine serum albumin (BSA) and bovine hemoglobin (BHb) to the surface of these polymers was then studied. Protein adsorption studies were carried out by adding PS-VBT to vials containing protein solutions (made of protein and buffer solution). They found that
protein adsorption of both BSA and BHb onto the PS-VBT was greater than on plain PS with maximum adsorption occurring in a buffer with a pH of 4.5 for BSA and 7.0 for BHb (Figure 2.33). From FT-IR they observed a shift in the amide I band from the thymine in PS-VBT when BSA was adsorbed to the surface. This result indicated that BSA was hydrogen bonded to thymine. These results led to the idea of making thymine-functionalized polyisobutylene (PIB-T), and more recently to the idea of using this low molecular weight PIB-T to modify the surfaces of other polymers.
CHAPTER III
EXPERIMENTAL

3.1 Materials

N,N-Dimethylacetamide (Aldrich Chemical Co.) was used as received and stored in a dry box under a dry nitrogen atmosphere.

p-Methylstyrene (Aldrich Chemical Co.) was purified by column chromatography with silica to remove the p-tert-butylcatechol inhibitor present at 100 ppm.

pH 7.4 monophosphate buffer (Hydrion).

2,6-di-tert-butylpyridine (Aldrich Chemical Co.) was used as received and stored in a dry box under a dry nitrogen atmosphere.

4-Bromostyrene (Aldrich Chemical Co.) was used as received.

4-(dimethylamino)pyridine (Aldrich Chemical Co.) was used as received.

Acetone (Aldrich Chemical Co.) was used as received.

Ammonium chloride (Fisher Scientific Co.) was used as received.

Benzophenone (Fisher Scientific Co.) was used as received.

Calcium hydride (Aldrich Chemical Co.) was used as received.

Carbon black N234, CTAB absorption specific surface area 121m²/g (Cabot) was used as received.

Carbon tetrachloride (Aldrich Chemical Co.) was used as received.
Chloroacetone (Aldrich Chemical Co.) was used as received.

Chloroform (Aldrich Chemical Co.) was used as received.

Chloroform-d 100%, 99.6 atom %D (Aldrich Chemical Co.) was dried over molecular sieves.

Chlorotrimethylsilane ≥ 97% (Aldrich Chemical Co.) was used as received.

De-ionized water.

Dichloromethane (Aldrich Chemical Co.) was used as received.

Diethyl ether, reagent grade > 99% (Pharmco Co.) was used as received.

Eosin Y certified by the biological stain commission, dye content 90% (Aldrich Chemical Co.) was used as received.

Ethyl alcohol, absolute-200 proof (Aaper alcohol and Chemical Co.) was used as received.

Hematoxylin certified by the biological stain commission (Aldrich Chemical Co.) was used as received.

Hexane (Aldrich Chemical Co.) was used as received.

Hexanes (EM Scientific Co.) was refluxed over and distilled from sodium and benzophenone.

Hydrofluoric acid, 48% (Aldrich Chemical Co.) was used as received.

Hydrogen peroxide (30% solution) (EM Scientific Co.) was used as received.

Iodine crystals (Aldrich Chemical Co.) was used as received.

Isobutylene (Linde Division, Union Carbide Corp.) was purified by passing the gas through a column packed with calcium chloride and barium oxide and was condensed from the gas phase at the polymerization temperature (-72 °C or -95°C) before use.
Isopropanol (Aldrich Chemical Co.) was used as received.

Kaneka 103T was obtained from Kaneka and compression molded.

Magnesium sulfate, anhydrous (Fisher Scientific Co.) was used as received.

Magnesium turnings (Aldrich Chemical Co.) were used as received.

MED-4050 (NuSil) silicone elastomers sheeting was used as received.

Methanol (Aldrich Chemical Co.) was used as received.

Methyl chloride (Linde Division, Union Carbide Corp.) was purified by passing the gas through a column packed with calcium chloride and barium oxide was condensed from the gas phase at the polymerization temperature (-72 °C or -95°C) before use.

Methyl cyclohexane (Aldrich Chemical Co.) was refluxed over and distilled from sodium and benzophenone.

Methyl ethyl ketone (Aldrich Chemical Co.).

Nagosil - NA 500-5 (SIL) (Nagor Ltd, UK) was used as received.

Osmium tetroxide, 2% Aqueous solution (Aldrich Chemical Co.) was used as received.

Polyisobutylene: PIB 135K, (American Polymer Standards) was used as received.

Ruthenium tetroxide, 0.5% Aqueous solution (Electron Microscopy Sciences) was used as received.

Silicon wafers (Wafer world) were etched with hydrofluoric acid prior to use.

Sodium (Aldrich Chemical Co.) was used as received.

Sodium chloride (Fisher Scientific Co.) was used as received.

Sodium hydride (Aldrich Chemical Co.) was used as received.

Sodium hydroxide (Fisher Scientific Co.) was used as received.

TEM grids, carbon coated were used as received.
Tetrahydrofuran, reagent grade (for GPC) (EM Scientific Co.) was refluxed over and distilled from calcium hydride.

Tetrahydrofuran, reagent grade (EM Scientific Co.) was refluxed over and distilled from sodium and benzophenone.

Titanium tetrachloride (Aldrich Chemical Co.) was used as received and stored in a dry box under a dry nitrogen atmosphere.

Toluene (Aldrich Chemical Co.) was refluxed over and distilled from sodium and benzophenone.

Triethylamine 99.5% (Aldrich Chemical Co.) was used as received.

Trifluoroacetic acid (Aldrich Chemical Co.) was used as received.

3.2 Instrumentation/Characterization

Polymers were characterized by several techniques such as NMR, SEC, TGA, DSC, AFM, and XPS which will be described below.

3.2.1 NMR spectroscopy

The PpMS content of the blocks was measured by $^1$H NMR spectroscopy using a Varian Gemini 300 MHz system in deuterated chloroform ($d$-CDCl$_3$) with concentrations of 40-50 mg/0.75 mL. A relaxation delay ($d_1$) of 10 was used and 128 FIDs (nt) were collected. For proof of hydroxyl groups in the polymers, $^1$H NMR spectra were obtained using a Varian INOVA 750 MHz system. Samples were prepared in deuterated chloroform ($d$-CDCl$_3$) with concentrations of 50 mg/0.75 mL, with $d_1 = 5$ and nt = 600. $^1$H NMR spectra used for proof of silylation were run on a Varian NMRS 500 at
concentrations of 50 mg/0.75 mL, with \( d_1 = 5 \) and \( nt = 64 \). \(^{13}\text{C}\) NMR spectra for polymers were run on a Varian NMRS 500 using 10 mm NMR tubes at concentrations of 150 mg/mL using \( d_1 = 5 \) for 18 h.

HSQC (Heteronuclear Single Quantum Coherence), which correlates \(^1\text{H}\) and \(^{13}\text{C}\) spectra, was carried out for the SCVP (self condensing vinyl polymerization) of the EPOIM on the 750 MHz NMR. The sample was dissolved in CDCl\(_3\) and filtered. Frequencies of 750 MHz for \(^1\text{H}\) and 200 MHz for \(^{13}\text{C}\) were used, 32 transients were collected, \( d_1 = 1 \), with a total run time of 1 h.

DEPT (distortionless enhancement by polarization transfer) was done on the SCVP of the EPOIM using CDCl\(_3\) as the solvent. The sample was dissolved in CDCl\(_3\) and filtered. Using parameters of \( lb = 1 \), \( d_1 = 2 \), power of 37 db was on during acquisition and off during delay, WALTZ-16 decoupling was used. \(^{13}\text{C}\) NMR resonance was observed using 100 MHz, and the \(^1\text{H}\) nuclei were decoupled using 400 MHz. The total run time was 9 hours.

3.2.2 Size Exclusion Chromatography (SEC)

The molecular weight (MW) and molecular weight distribution (MWD) of \( arb\_\text{SIBS} \) were determined using a system equipped with six Waters Styragel\textsuperscript{®} columns (HR0.5, HR1, HR3, HR4, HR5 and HR6), thermostated at 35°C, a Waters 515 HPLC pump, a Waters 2487 Dual Absorbance UV Detector, a Wyatt Optilab DSP Interferometric Refractometer, a Wyatt DAWN EOS multi-angle laser light scattering detector, a Wyatt Viscostar viscometer, a Wyatt QELS quasi-elastic light scattering detector and a Waters 717plus autosampler. THF was used as mobile phase at 1 mL/min.
and was continuously distilled from CaH$_2$ and recirculated. The ASTRA® software (version 5.3.2.14) controlled the data acquisition from the detectors and processed the data to obtain MWs. The MW of the new materials was determined by both 100 % mass recovery and known $dn/dc$ methods (copolymer $dn/dc$ was calculated based on the weight fraction and $dn/dc$ of the individual components). Since no data was available for PpMS, the $dn/dc$ of PS was used (PIB = 0.108, PS = 0.183).$^{155}$ This method gave good agreement with MW data obtained by assuming 100% mass recovery on the columns.$^{155}$ Radii of gyration and hydrodynamic radii and viscosity were also determined from Astra.

3.2.3 In situ FTIR spectroscopy

A liquid transmission probe (TR) (Remspec, Inc), coupled to a MID-IR detector module through fiber optic cables and attached to a FTIR unit (Varian 3100 FT-IR Excalibur Series), was used. Spectra were recorded every 7.8 seconds until the polymerization reactions were terminated.

3.2.4 Differential Scanning Calorimetry (DSC).

DSC was performed with a TA Instruments Q2000 Differential scanning calorimeter. The process was carried out in a triple cycle: first heating, subsequent cooling and second heating, in the temperature range from -100 to +200 °C. The rate of heating and cooling was 10 °C/min. The glass transition temperature was determined from the midpoint of the curve of the second heating.
3.2.5 TGA (thermogravimetric analysis)

TGA was carried out on a TA Instruments TGA Q500 V20.7. Samples were heated to 600 °C using a heating rate of 10 °C per minute. Plots showed weight % vs. temperature in °C. The degradation temperature was then calculated by drawing lines tangent to the curve, the point where the lines cross was taken as the degradation temperature.

3.2.6 Tensile testing

A testing rig (Instron 5567) with a 1000-N load cell was used for testing, and the testing cross-head speed adopted was 500 mm/min according to ASTM D 412-06a. The tensile strain of the micro-dumbbell was measured by a long-travel extensometer attached to its mid-section with a gauge length of 10mm. Load and extensometer calibration were performed prior to the testing. The accuracy of the extensometer was checked with an Instron standard gauge to fall within an error of 2 % in the range of the measured strain for this study. To prevent slippage of the specimen off the fixture, hydraulic clamps or normal clamps with sand-papers were employed to secure the specimen during testing. Ultimate tensile strength, elongation at break, and tensile strength at 100% strain were determined.

3.2.7 Contact angle measurement

Drops of 5 μL in size of ultra pure DI water were pipetted onto polymer-coated Si wafers, film side up in the contact angle goniometer from Rame-Hart Inc., Model # 100-07-00. Twenty static contact angle measurements were taken for each material.
3.2.8 X-ray Photoelectron Spectroscopy (XPS)

Samples were analyzed using a PHI VersaProbe XPS microprobe X-ray photoelectron spectrometer. C1s, N1s, and O1s analyses were carried out on an area 300 microns in diameter using pass energies of 93.9 eV for low resolution and 20 eV for high resolution. The X-ray beam was set to a 15°, 45°, or 90° grazing angle in order to view the surface of the films at different depths.

3.2.9 Atomic Force Microscopy (AFM)

AFM imaging of cryo-microtomed slices of compression-molded samples was carried out by PolyInsight Inc., Akron. Each sample was mounted in a cross-section holder such that a section approximately 2.5 mm x 0.5 mm was exposed for cryo-facing. A Leica cryomicrotome was used, with sample and diamond knife held at -150 °C. The cryo-faced surface of each sample was analyzed with a Veeco Instruments Multimode SPM with a Nanoscope IV controller. The microscope was operated with an “E” scanner in tapping-mode, with height and phase images collected simultaneously. Silicon cantilevers with a nominal resonance frequency of 170 kHz, with medium-light tapping forces characterized by 0.75–0.85 set point reduction ratios, were used. Size measurements were performed with the Nanoscope software (version 5.30) provided by Veeco Instruments (PolyInsight).

3.2.10 Transmission Electron Microscopy (TEM)

Polymers were dissolved in THF at 0.5 wt%. Carbon-coated grids were floated on hot water and polymer solution was dropped onto the carbon-coated grid. Samples were
then allowed to dry in a vacuum oven for 12 hours at room temperature before annealing at 140 °C for 24 h. Staining was carried out using osmium tetroxide, 2% aqueous solution, or ruthenium tetroxide. The staining agent was placed in a beaker with the glass slide and samples on top; a larger water dish was placed upside down on top. Staining was carried out over a 30 min or 1 h period. The instrument used was a JEM 1200XII transmission electron microscope.

3.2.11 Shore hardness

The indentation hardness of \textit{arb}_IB(OH)-MS(16) with and without carbon black was evaluated using an Instron Shore A Durometer. In accordance with ASTM D2240-05, the thickness of the materials used for the hardness measurement was recorded and the Shore A hardness values were noted after the indenter was applied into the material for 3 seconds. For each material, at least three hardness and thickness measurements were taken at different locations and averaged values were reported together with the standard deviations.

3.2.12 Electrical resistance (Kent State University)

Resistance measurements were carried out on 2 cm x 2 cm square specimens coated with silver conducting paint, using a Hewlett Packard HP3441A multimeter.

3.3 Synthesis of 4-(1,2-oxirane-isopropyl)styrene inimer (EPOIM)

The procedure for the synthesis of 4-(1,2-oxirane-isopropyl)styrene (EPOIM) was adapted from the work of Tanimoto and Oda.\textsuperscript{157} The reaction is shown in Figure 3.1.
Figure 3.1. Reaction scheme for synthesis of 4-(1,2-oxirane-isopropyl)-styrene.

A 500 mL, three-neck flask equipped with nitrogen inlet, addition funnel and thermometer was placed in an ice bath and charged with magnesium turnings (3.8 g, 0.156 mol), an iodine crystal and dry THF (150 mL). A solution of para-bromostyrene (pBrSt) (25 g, 0.137 mol) in THF (120 mL) was added dropwise to maintain the temperature of the reaction mixture below 10 °C. The reaction mixture was stirred in an ice bath for 2 h. After that time, a solution of α-chloroacetone (12.64 g, 0.137 mol) in THF (100 mL) was added dropwise to the mixture over 2 h. The reaction mixture was stirred for another 2 h, and decanted into a clean round-bottom flask thereby removing the unreacted magnesium. The reaction mixture was neutralized with ammonium chloride solution to pH =7-8. The aqueous phase was extracted with diethyl ether twice, and the combined organic phases were washed with de-ionized water, brine, dried over anhydrous magnesium sulfate and concentrated down to 120 mL in THF. The crude product was a pale yellow liquid. Without further purification, the crude product (I) was directly used in next step.

To a 500 mL, three-neck flask equipped with nitrogen inlet, addition funnel and thermometer in an ice bath was charged with sodium hydride (5.70 g, 0.143 mol) and THF (200 mL), a solution of (I) in THF (120 mL) was added dropwise over 2 h in an ice bath. The resulting reaction mixture was stirred for 2 h. Then water and diethyl ether
were added, and the phases were separated. The aqueous phase was extracted with diethyl ether twice, and the combined organic phases were washed with DI water, brine, dried over anhydrous magnesium sulfate, and concentrated. The product was purified by vacuum distillation (55-58 °C, 0.2 mmHg) to give a pale yellow liquid (12 g, 48% yield).

3.4 Polymerization of \textit{arb\_IB(OH)}

\textit{arb\_IB(OH)} was polymerized utilizing the EPOI by living carbocationic polymerization in a dry box under a dry nitrogen atmosphere. The polymerization conditions will be described below.

3.4.1 EPOIM: Small scale screening polymerizations

IB polymerizations were carried out under a dry nitrogen atmosphere (H\textsubscript{2}O < 1 ppm and O\textsubscript{2} < 3 ppm) in an MBraun LabMaster 130 glovebox at -72 °C using a FTS Flexi Cool Immersion Cooler. A series of reactions were carried out in 10 mL screw-cap vials using a vortex stirrer, with 2.0 M of IB, 0.008 M of D\textsubscript{t}BP as a proton trap, and MeCH\textsubscript{x}/MeCl (60/40 v/v). Stock solutions were made for TiCl\textsubscript{4}, inimer, and D\textsubscript{t}BP in MeCH\textsubscript{x}/MeCl 60/40 v/v (D\textsubscript{t}BP: 1.67 x 10\textsuperscript{-2} g/mL, TiCl\textsubscript{4}: 3.86 x10\textsuperscript{-1} g/mL and EPOIM: 3.83 x10\textsuperscript{-1} g/mL). The solvent mixture was added to each test tube in varying amounts depending on the amount of inimer and TiCl\textsubscript{4} stock solutions needed to make a total volume of 10 mL. IB (1.6 mL), 1 mL of D\textsubscript{t}BP stock solutions, and the desired amount of EPOIM stock solution were added. Polymerizations were started by the addition of TiCl\textsubscript{4} stock solution. Specific concentrations are given in the text as well as in figure and table captions. Polymerizations were terminated by addition of methanol after 45 min.
Polymers were allowed to stand in a fume hood overnight for evaporation of MeCl before re-dissolving them in hexane. The hexane solutions were washed three times with water, and the hexane was allowed to evaporate. The polymers were dried in a vacuum oven at room temperature until reaching constant weight. Polymer yield was determined gravimetrically.

3.4.2 Polymerization of \textit{arb}_{IB(OH)} (LANXESS using UA EPOIM)

Two large scale polymerizations (Polymerization 1 and 2) were carried out at -95 °C in round-bottom flasks equipped with an overhead stirrer and a thermocouple. Polymerization 1 and 2 were synthesized as follows: to a 3 L, round-shape, baffled glass reactor, 0.7 grams of EPOIM, 900 mL of hexane (measured at room temperature), 600 mL of methyl chloride (measured at -95 °C), 2 mL of di-\textit{tert}-butylpyridine (DrBP, measured at room temperature) and 240 mL of isobutylene (measured at -95 °C) were added. Polymerization was started at -93 °C by the addition of a pre-chilled mixture of 6 mL of TiCl\textsubscript{4} and 30 mL of hexane (both measured at room temperature). The total volume was 1500 mL. Samples were taken at specified times during the reactions for analysis by NMR spectroscopy and SEC. The reactions were terminated with a solution of NaOH in methanol. The reactor was removed from the dry box and placed into a fume hood to allow for the evaporation of MeCl. The polymer was re-dissolved in hexane and washed with water three times before coagulating it into methanol. The polymer was dried and conversion was determined gravimetrically.
3.4.3 Selective Link Destruction

Link destruction was carried out as reported by Paulo and Puskas.\textsuperscript{137} A solution of 1% PIB in 75 mL of CCl\textsubscript{4} was added to a 2 neck, round-bottom flask fitted with a reflux condenser and glass stopper. A solution of 36 mL of aqueous 30% H\textsubscript{2}O\textsubscript{2} and trifluoroacetic acid was added under agitation. The mixture was heated to reflux over a 72 hour period. Samples were taken every 24 hours and analyzed by SEC.

3.5 Synthesis of \textit{arborescent} poly(isobutylene(OH)-\textit{b}-(isobutylene-\textit{co} paramethylstyrene): \textit{arb}_\text{IB(OH)}-MS (LANXESS using UA EPOIM)

\textit{arb}_\text{IB(OH)}-MS was synthesized by LANXESS using the EPOIM made at the University of Akron as described below.

3.5.1 Procedure for the synthesis of \textit{arb}_\text{IB(OH)}-MS(16)

\textit{arb}_\text{IB(OH)}-MS(16) was synthesized as follows: to a 3 L, round-shape, baffled glass reactor, equipped with a glass stirrer rod (mounted with a crescent shaped Teflon\textsuperscript{®} impeller) and a thermocouple, 0.7 grams of EPOIM, 900 mL of hexane (measured at room temperature), 600 mL of methyl chloride (measured at –95 °C), 2 mL of di-\textit{tert}-butylpyridine (DtBP, measured at room temperature) and 240 mL of isobutylene (measured at –95 °C) were added. Polymerization was started at –93 °C by the addition of a pre-chilled mixture of 6 mL of TiCl\textsubscript{4} and 30 mL of hexane (both measured at room temperature). After 37.5 min of polymerization time, a pre-chilled mixture of 250 mL of hexane, 70 mL of pMeSt, 1.0 mL of DtBP, 0.9 mL of dimethyl acetamide (all measured at room temperature) and 150 mL of methyl chloride were added. After 151 min of total
polymerization time, the reaction was terminated by the addition of a solution of 11 grams of NaOH dissolved in 125 mL of methanol. After evaporation of the methyl chloride, hexane was added to the polymer solution and washed with water until neutral. The resulting polymer was isolated with steam coagulation and dried on a hot mill followed by molding the polymer in a press at 180 °C. The dried weight of the polymer was 152.43 g (65.2% conversion). The polymer was further purified by precipitation of a 5 wt% polymer solution in THF into acetone as reported. Aliquots were taken throughout the course of the polymerization for analyses by NMR spectroscopy and SEC. Polymerization 1: arb(IB(OH)) is the arborescent core of arb(IB(OH))_MS(16) prior to blocking with MS.

3.5.2 Procedure for the synthesis of arb(IB(OH)-MS(3.5))

arb(IB(OH))-MS(3.5), was synthesized as follows: to a 3 L, round-shape, baffled glass reactor, equipped with a glass stirrer rod (mounted with a crescent shaped Teflon impeller) and a thermocouple, 0.7 grams of EPOIM, 900 mL of hexane (measured at room temperature), 600 mL of methyl chloride (measured at –95 °C), 2 mL of di-tert-butylpyridine (DtBP, measured at room temperature) and 240 mL of isobutylene (measured at –95 °C) were added. Polymerization was started at –93 °C by the addition of a pre-chilled mixture of 6 mL of TiCl₄ and 30 mL of hexane (both measured at room temperature). After 65 min of polymerization time, a pre-chilled mixture of 250 mL of hexane, 70 mL of pMeSt, 1.0 mL of DtBP, 0.9 mL of dimethylacetamide (all measured at room temperature), 120 mL of IB and 150 mL of methyl chloride were added (measured at -95 °C). After 160 min of total polymerization time, the reaction was terminated by
the addition of 8.8 grams of NaOH dissolved in 100 mL of methanol. After evaporation of the methyl chloride, hexane was added to the polymer solution and washed with water until neutral. The resulting polymer was isolated with steam coagulation and dried on a hot mill followed by molding the polymer in a press at 180°C. The dried weight of the polymer was 156 grams (48.9% conversion). The polymer was further purified by precipitation of a 5 wt% polymer solution in THF into acetone as reported. Aliquots were taken throughout the course of the polymerization for analyses by NMR spectroscopy and SEC. Polymerization 2: arb_IB(OH) is the arborescent core of arb_IB(OH)_MS(3.5) prior to blocking with MS.

3.6 In situ FTIR monitoring

To gain insight into the possible mechanisms of polymerization with the EPOIM, polymerizations were carried out using in situ FTIR monitoring as described below.

3.6.1 Procedure for self condensing vinyl polymerization (SCVP) of EPOIM with in-situ FTIR monitoring

Polymerization was carried out using 0.1 M inimer to 0.05 M TiCl₄ and 0.007 M DtBP. The reaction was carried out in a 250 mL three neck round-bottom flask equipped with an overhead stirrer. The total volume was 100 mL, and was carried out in the presence of methycyclohexane (MeCHx) and MeCl with a 60/40, v/v, ratio. First the solvent was collected and allowed to chill for 15 minutes until it reached -72 °C. Then 62 mL of MeCHx, 44 mL of MeCl, and 0.140 mL of DtBP were added to the round-bottom flask. The FTIR probe was placed in the flask containing the solvent and DtBP
and was allowed to reach -72 °C over a 20 minute period. Then a baseline spectrum was collected. EPOIM (1.5 g) was added, followed by three separate additions of 0.6 mL of TiCl₄ over a 1h period. The reaction was monitored over a 98 minute period (when the vinyl adsorption from IB disappeared) and terminated with 0.39 g of methanol and 0.16 g of NaOH. The polymer was left in a fume hood for MeCl to evaporate off overnight. The polymers were rinsed with DI water and hexane until a pH of 7-8 was obtained. As expected, the molecular weight of the polymer was too low to precipitate in methanol so the solvent was removed by rotary evaporation and the polymer was dried in the vacuum oven (under 35 psi).

3.6.2 Self condensing vinyl copolymerization (SCVCP) of EPOIM and IB in a 1:3 M ratio

Polymerization was carried out using 0.1 M inimer to 0.3 M IB to 0.05 M TiCl₄ and 0.007 M DtBP. The reaction was carried out in a 250 mL, three-neck, round-bottom flask equipped with an overhead stirrer. The total polymerization volume was 100 mL, and the solvent was MeCHx and MeCl with a 60/40, v/v, ratio. First the solvent and IB were collected and allowed to chill for 15 minutes. Then 60 mL of MeCHx, 38 mL of MeCl, and 0.20 mL of DtBP were added to the round-bottom flask. The FTIR probe was placed in the flask containing the solvent and the DtBP and was allowed to come to temperature over a 20 minute period. A baseline was collected. The EPOIM (1.8 g) was added to the flask, followed by 2.2 mL of IB. TiCl₄ (0.64 mL) was added three times over 1 h. The reaction was monitored over a 100 min 45 sec period. When the vinyl group absorption from IB disappeared from the FTIR, the reaction was terminated with 0.38 g
of methanol and 0.16 g of NaOH. Polymer solutions were then left in the fume hood for MeCl to evaporate off and were rinsed with water and hexane until the polymer had a pH of 7.0. The low molecular weight of the polymer did not allow for precipitation in methanol; therefore, the solvent was removed by rotary evaporation and the polymer placed in a vacuum oven to dry.

3.7 Silylation of \textit{arb\_IB(OH)-MS} (3.5)

The procedure for the silylation of the polymer was adapted from work done by the Kennedy group.\textsuperscript{159} Solutions of 0.5 g of polymer in 10 mL of carbon tetrachloride were prepared. Because a 1:1.5 molar ratio of OH groups to chlorotrimethylsilane is not accurately measurable with a syringe, a large measurable excess of silane was used. A 1:1 molar ratio of chlorotrimethylsilane to DMAP (catalyst) was used. The polymer was dissolved in the solvent and 0.39 g (0.386 moles) of DMAP was then added. Two freeze, pump, thaw cycles were carried out to remove any residual moisture. The reactions were placed under nitrogen and 0.4 mL of chlorotrimethylsilane was added. The reactions were allowed to stir under nitrogen at room temperature for 24 h. The CCl\textsubscript{4} was boiled off at 70 °C. The polymer was dissolved in THF, filtered, precipitated in acetone and isopropyl alcohol (IPA) and dried in a vacuum oven.

3.8 Spin coating of polymers

The Si wafers were etched in HF, and rinsed and dried with nitrogen gas. Films were spin-coated onto the surface from a 3 wt\% solution in filtered toluene and allowed
to anneal for 24 h at 137 °C [above the T_g of poly(p-methylstyrene)] and were left in the vacuum oven for another 24 h at room temperature.

3.9 Soxhlet extraction of $arb_{-}IB(OH)-MS(16)$

Exhaustive extraction of $arb_{-}IB(OH)-MS(16)$ was carried out in the presence of methyl ethyl ketone (MEK), ethanol, and hexane in that order, (10 to 15 passes at reflux temperature). MEK was used for the removal of residual polystyrene homopolymer, hexane for polyisobutylene homopolymer, and ethanol for the removal of polar materials. The polymer was dried in a vacuum oven, and SEC and NMR spectroscopic analyses were performed.

3.10 Compounding

$arb_{-}IB(OH)-MS(16)$ was mixed with 37.5 wt% N234 carbon black (CB) in a Brabender mixer using a 78.8 fill factor in order to prepare $arb_{-}IB(OH)-MS_CB(16)$.

3.11 Preparation of test specimens for implantation.

Sheets 1 mm thick were compression molded from the neat and carbon composites. Microdumbbells (1mm thick with a 12 mm² cross sectional area) were stamped out of the sheets. The neat $arb_{-}IB(OH)-MS(16)$ was compression molded at 120 °C and the $arb_{-}IB(OH)-MS_CB$ at 145 °C for 3 min at 0.304 MPa. Microdumbbells were also stamped out from 0.5 mm thick sheets of Nagosil - NA 500-5 (SIL).
3.12 Buffer uptake study

A pH 7.4 buffer packet from hydrion was prepared using 500 mL of de-ionized water as directed. A hydrion color key buffer preservative was added to show freshness of the buffer (when the color disappears the buffer should not be used). Sterile 12-well polystyrene culture dishes were used. Twenty-four, 12 mm discs, cut from compression-molded films of \textit{arb\_IB(OH)-MS(16)} with and without carbon black (12 of each), were placed into wells and 2 mL of buffer was added to each well. The tray was placed in an incubator (Selutec TECO 20 – made in Germany) set at 36 °C on a shaker (CAT 520) at motor level 2. For 20 days, every 2 days the buffer was changed and the mass of the polymer buttons was recorded and checked for swelling and mass loss. The buttons were then allowed to dry and analyzed by SEC.

3.13 \textit{In vitro} cytocompatibility (ISO 10 993-5).

05DNX121 (\textit{arb\_SIBS}) with $M_n = 220,300$, $M_w/M_n = 1.87$ and 32.6 wt% PS (synthesized from the 4-(2-methoxy-isopropyl)styrene inimer and characterized as reported\textsuperscript{12}), Kaneka 103T (SIBS), and medical grade silicone (Nagosil) were stamped into round disks of 15 mm diameter, sterilized by ethylene oxide and placed in 24-well plates (Greiner). Polystyrene of the 24-well culture plates served as positive control. 3T3 mouse fibroblasts (DSMZ, Braunschweig) were seeded at 1.0 x 10\textsuperscript{5} cells/mL for 5 days in 90\% RPMI 1640 medium (GIBCO) supplemented with 10\% fetal bovine serum (GIBCO) and 1\% Penstrep (GIBCO). Cells were cultured at 37 °C in a humidified atmosphere (RH = 95\%) and 5\% CO\textsubscript{2}. Propidium iodide [3,8-diamino-5-[3-(diethylmethylammonio)propyl]-6-phenylphenanthridinium diiodide] was used as
staining agent to estimate the number of apoptic cells. Three measurements on each material were performed with the use of a flow citometer. The test results were evaluated as increase in the cell population assuming, $1.0 \times 10^5$ cells/mL as the initial value.

3.14 In vivo implantation test

Microdumbbell specimens of extracted and non extracted $arb_{IB}$(OH)-MS(16), and $arb_{IB}$(OH)-MS_CB(16) were sterilized with ethylene oxide and implanted into the soft tissue of the abdominal wall, the bone, and muscle tissue of rabbits ($n=10$) using medical grade silicone rubber as control. Samples of polymers retrieved from rabbits sacrificed at 180 days were fixed in 10% buffered formaldehyde and embedded in paraffin. Semi-thin (4–6 μm) sections were stained with hematoxylin (Figure 3.2 a) and eosin (Figure 3.2 b) for cellular detail and morphology, and examined by light microscopy. These tests were performed at the Pomeranian Medical Academy in Szczecin by Dr. Piotr Prowans (in collaboration with Dr. El Fray at the Technical University of Szczecin in Szczecin, Poland) based on the permission from the Ethical Commission dated 10.01.2005.

![Staining agents: (a) hematoxylin (b) eosin.](image-url)
4.1 IB Polymerizations with 4-(1,2-oxirane-isopropyl) styrene (EPOIM)

We decided to use EPOIM because the epoxide functionality introduces a primary hydroxyl group into the polymer at every branch point upon termination, as shown in Figure 4.1.

Figure 4.1  Inimer-type copolymerization of EPOIM with IB.
By this strategy one can prepare \(arb_{\text{IB}}(\text{OH})\), having a dendritic PIB core with primary hydroxyl groups at the branch points to make \(arb_{\text{IB}}(\text{OH})\).

4.1.1 Synthesis of 4-(1,2-oxirane-isopropyl)styrene inimer (EPOIM)

This molecule was previously synthesized by Tanimoto and Oda,\textsuperscript{157} although characterization data were not given. The original experimental procedure\textsuperscript{157} was carried out to determine the repeatability of previous results (Figure 3.1. page 66). Repeating this experiment with \(\text{C}_2\text{H}_3\text{ONa}\) in the last step yielded a pale yellow liquid (3.181 g, 0.0199 moles) with 14.5% yield, which is slightly higher than the reported 12% yield. Using \(\text{NaH}\) in THF in the last step instead of \(\text{C}_2\text{H}_3\text{ONa}\) increased the yield to 48%. The product was characterized by \(^1\text{H}-\text{NMR}\) (300 MHz) and \(^{13}\text{C}-\text{NMR}\) (500 MHz) spectroscopy.

![1H-NMR spectrum of the 4-(1,2-oxirane-isopropyl)styrene inimer.](image)

Figure 4.2 \(^1\text{H}-\text{NMR}\) spectrum of the 4-(1,2-oxirane-isopropyl)styrene inimer.
Figure 4.3 $^{13}\text{C}$-NMR spectrum of the 4-(1,2-oxirane-isopropyl)styrene inimer.

The solvent used was CDCl$_3$. The NMR spectra can be seen in Figures 4.2 and 4.3. From the $^1\text{H}$ and $^{13}\text{C}$ NMR spectra it can be seen that the expected structure was obtained. The $^1\text{H}$ NMR spectrum shows that the aromatic protons and vinyl protons were obtained in the appropriate 4:1:1 ratio with the two CH$_2$ protons integrating to a total value of two, and methyl protons to three. This structure is further confirmed by the $^{13}\text{C}$ NMR spectrum in Figure 4.3. Polymerizations were carried out on a small scale to determine the optimum conditions for polymerization using the new EPOIM.
4.1.2 Small scale polymerizations

Several small scale polymerizations (10 mL total polymerization volume) were carried out. In the first six polymerizations the \([IM]_0/[M]_0\) ratio was increased while keeping the \([TiCl_4]/[IM]_0\) ratio constant at 10. One polymerization was also carried out with \([TiCl_4]/[IM]_0 = 2\) (Table 4.1). Polymerizations were carried out at -72 °C using DrtBP to prevent protic initiation.


<table>
<thead>
<tr>
<th>Sample ID</th>
<th>[IM]_0 (M)</th>
<th>[TiCl_4]_0</th>
<th>[IM]_0/[M]_0</th>
<th>Conv. %</th>
<th>M_n g/mol</th>
<th>M_w/M_n</th>
</tr>
</thead>
<tbody>
<tr>
<td>EF141205-2</td>
<td>0.002</td>
<td>0.02</td>
<td>0.0001</td>
<td>66</td>
<td>65,300</td>
<td>1.5</td>
</tr>
<tr>
<td>EF141205-1</td>
<td>0.005</td>
<td>0.04</td>
<td>0.00025</td>
<td>73</td>
<td>94,600</td>
<td>2.2</td>
</tr>
<tr>
<td>EF141205-5</td>
<td>0.007</td>
<td>0.06</td>
<td>0.0035</td>
<td>60</td>
<td>72,700</td>
<td>2.1</td>
</tr>
<tr>
<td>EF141205-6</td>
<td>0.010</td>
<td>0.08</td>
<td>0.005</td>
<td>70</td>
<td>105,200</td>
<td>3.2</td>
</tr>
<tr>
<td>EF141205-4</td>
<td>0.011</td>
<td>0.10</td>
<td>0.0055</td>
<td>77</td>
<td>96,700</td>
<td>2.5</td>
</tr>
<tr>
<td>EF141205-3</td>
<td>0.024</td>
<td>0.20</td>
<td>0.012</td>
<td>76</td>
<td>116,700</td>
<td>5.3</td>
</tr>
<tr>
<td>EF141205-7</td>
<td>0.010</td>
<td>0.016</td>
<td>0.005</td>
<td>73</td>
<td>92,400</td>
<td>1.8</td>
</tr>
<tr>
<td>PS30K</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30,000</td>
<td>1.0</td>
</tr>
</tbody>
</table>

\([IB] = 2.0 \text{ M}, [DrtBP] = 0.008 \text{ M}, \text{MeCHx/MeCl (60/40 v/v); 45 mins; -72 °C}\)

The polymerizations were terminated with methanol after 45 minutes (Figure 4.1). Table 4.1 shows the various polymerization conditions and resulting conversions and molecular weights. Table 4.1 shows that as the \([IM]_0/[M]_0\) ratio is increased the molecular weight increases. When the \([TiCl_4]/[IM]_0\) ratio was reduced from 10 in EF141205-6 to 2 in
EF141205-7 a decrease in the molecular weight and $M_n/M_0$ was observed indicating that a more controlled polymerization and less branching was obtained with less TiCl$_4$.

Figure 4.4 SEC traces of \textit{arb} IB(OH) shown in Table 4.1: (a) EF141205-2 (b) EF141205-1 (c) EF141205-5 (d) EF141205-6.
Figure 4.4  SEC traces of \textit{arb} IB(OH) shown in Table 4.1 (continued): (e) EF141205-4 (f) EF141205-3 (g) EF141205-7.
All SEC traces were multimodal, and showed evidence of EPOIM incorporation as shown in Figure 4.4. These depict the polymerizations in order of increasing inimer concentration. PIB is transparent to UV, thus the presence of UV absorption demonstrates EPOIM incorporation. From the UV trace it appears that the inimer is incorporated throughout the entire molecular weight distribution. Due to the high MW of the polymers, and the less than 1% EPOIM, the presence of OH groups could not be detected by elemental analysis, which has a detection limit of 0.5 At%.

Table 4.2 lists the peak molecular weights and the average chain length between branch points measured by selective link destruction (LD) where the aromatic \textit{inimer} links of the polymer were destroyed leaving behind the linear PIB chains, as discussed in the historical background (Figure 2.15).


<table>
<thead>
<tr>
<th>Sample ID</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>Branch Length (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EF141205-2</td>
<td>50,000</td>
<td>100,000</td>
<td>150,000</td>
<td></td>
<td>34,700</td>
</tr>
<tr>
<td>EF141205-1</td>
<td>50,000</td>
<td>100,000</td>
<td>150,000</td>
<td></td>
<td>39,300</td>
</tr>
<tr>
<td>EF141205-5</td>
<td>30,000</td>
<td>60,000</td>
<td>120,000</td>
<td></td>
<td>13,100</td>
</tr>
<tr>
<td>EF141205-6</td>
<td>35,000</td>
<td>70,000</td>
<td>150,000</td>
<td></td>
<td>18,500</td>
</tr>
<tr>
<td>EF141205-4</td>
<td>35,000</td>
<td>70,000</td>
<td>150,000</td>
<td></td>
<td>21,300</td>
</tr>
<tr>
<td>EF141205-3</td>
<td>35,000</td>
<td>70,000</td>
<td>150,000</td>
<td>1,500,000</td>
<td>22,400</td>
</tr>
<tr>
<td>EF141205-7</td>
<td>50,000</td>
<td>100,000</td>
<td>150,000</td>
<td></td>
<td>27,800</td>
</tr>
</tbody>
</table>
An example of this is shown in Figure 4.5 which shows that the RI trace after LD becomes monomodal and shifts toward lower MW. In the case of EF141205-2 the MW decreases and the shoulder disappears, but $M_w/M_n$ remains equal to 1.5 before and after LD. EF141205-3 shows a decrease in the MWD from 6.0 to 1.4. Comparison of Table 4.1 and 4.2 showed that in all cases the individual peak molecular weights were higher than the MW between branches. This indicates that branching occurred in each fraction of the polymer and that the EPOIM is present in all fractions.

![Figure 4.5 RI trace before and after LD: (a) EF141205-2 (b) EF141205-3.](image)

Table 4.3 shows SEC and branching data. The average number of branches per chain from LD is defined as:

$$B_{ld} = \left( \frac{M_{n,\text{total}}}{M_{n,\text{segments}}} \right)$$
Table 4.3  SEC analysis of \textit{arb}\_IB(OH)s from EPOIM.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$M_{n,\text{theo}}^a$</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>$M_z$ (g/mol)</th>
<th>$\eta$ (mL/g)</th>
<th>$R_h$ (nm)</th>
<th>$R_g$ (nm)</th>
<th>$B$</th>
<th>LD $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EF141205-2</td>
<td>36,900</td>
<td>65,300</td>
<td>97,000</td>
<td>163,100</td>
<td>39.4</td>
<td>10.3</td>
<td>12.8</td>
<td>11.3</td>
<td>0.8</td>
</tr>
<tr>
<td>EF141205-1</td>
<td>17,000</td>
<td>94,600</td>
<td>203,400</td>
<td>406,400</td>
<td>53.5</td>
<td>16.2</td>
<td>16.8</td>
<td>21.4</td>
<td>4.6</td>
</tr>
<tr>
<td>EF141205-5</td>
<td>9,300</td>
<td>72,700</td>
<td>153,000</td>
<td>344,500</td>
<td>42.2</td>
<td>13.9</td>
<td>13.6</td>
<td>16.7</td>
<td>6.8</td>
</tr>
<tr>
<td>EF141205-6</td>
<td>8,100</td>
<td>105,200</td>
<td>325,600</td>
<td>866,700</td>
<td>59.3</td>
<td>23.1</td>
<td>20.5</td>
<td>29.5</td>
<td>11.9</td>
</tr>
<tr>
<td>EF141205-4</td>
<td>8,000</td>
<td>96,700</td>
<td>233,400</td>
<td>571,100</td>
<td>55.1</td>
<td>18.7</td>
<td>17.6</td>
<td>22.5</td>
<td>11.2</td>
</tr>
<tr>
<td>EF141205-3</td>
<td>3,500</td>
<td>116,700</td>
<td>612,400</td>
<td>2,511,000</td>
<td>63.7</td>
<td>38.0</td>
<td>32.1</td>
<td>48.5</td>
<td>32.0</td>
</tr>
<tr>
<td>EF141205-7</td>
<td>8,500</td>
<td>92,400</td>
<td>165,100</td>
<td>303,600</td>
<td>49.3</td>
<td>15.3</td>
<td>14.0</td>
<td>19.1</td>
<td>9.9</td>
</tr>
<tr>
<td>PS30K</td>
<td>-</td>
<td>30,000</td>
<td>30,100</td>
<td>30,300</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) $M_{n,\text{theo}} = \text{IB (g)/EPOIM (moles)}, \(^b\) LD: selective link destruction
In case of equal reactivity of the initiating and propagating sites, the average number of branching points (B) in the arborescent polyisobutylene core (arb\_IB) can be predicted from:

\[
B_{\text{kin}} = \left( \frac{M_{n,\text{total}}}{M_{n,\text{theo}}} \right) - 1
\]

where \( M_{n,\text{theo}} \) stands for the MW that would arise if the IM would act only as initiator and is defined as:

\[
M_{n,\text{theo}} = \frac{\text{IB} \text{ (g)}}{\text{IM} \text{ (moles)}}
\]

Figure 4.6 shows that for the EPOIM B increased with increasing \([\text{IM}]_0/\text{[M]}_0\), but the measured B was well below the predicted value (B_{\text{kin}}) at higher \([\text{IM}]_0/\text{[M]}_0\) ratios (Table 4.3). In the case of the MeOIM\(^{137}\) the values of B_{\text{kin}} and B measured by LD were in fairly good agreement; this is because in the case of the MeOIM the propagating cumyl and benzyl carbocations (Figure 4.7) have almost equal reactivity creating a truly randomly branched polymer as seen in Lucas Dos Santos’ dissertation.\(^{160}\)
Figure 4.6  Dependence of $M_n$ and $B$ on $[\text{IM}]_0/[\text{M}]_0$: (a) MeOIM$^{137}$ (b) EPOIM. (Copied with permission from Foreman, E. A.; Puskas, J. E.; Kaszas, G. J. Polym. Sci., Part A 2007, 45(24), 5847 - 5856).
Comparison of EF141205-6 and EF141205-7 reveals that lower [TiCl$_4$]$_0$ at the same [IM]$_0$ led to lower MW and MWD, and also to less branching. This shows that with only a two-fold excess of TiCl$_4$ we can obtain a better controlled polymerization. We established that $R_h$ measured for linear PS and PIB standards by VIS and QELS agreed, with VIS being more precise and reproducible. The initiating carbocation arising from EPOIM (Figure 4.7) is stabilized by the $-I$ effect of the electron donating OTiCl$_4$ and/or -OTiCl$_3$ groups. The electron pairs of the oxygen may interact with the electron-deficient p orbital of the carbocation, leading to stabilization. Thus direct comparison with the initiating cumyl-type resonance-stabilized carbocation forming from MeOIM is not straightforward.

![Figure 4.7 Structure of propagating carbocations of MeOIM and EPOIM.](image)

Plotting log $R_g$, $R_h$, and $\eta$ versus log $M_w$ obtained from the values in Table 4.3 showed that all these values increase linearly with increasing molecular weight (Figure 4.8).

Branching was characterized by branching parameters of Stockmayer and coworkers.
where \( g \) is the ratio of the \( R_g \) of a branched polymer over the \( R_g \) of a linear polymer at the same \( M_w \); \( h \) is the ratio of the \( R_h \) of a branched polymer over the \( R_h \) of a linear polymer at the same \( M_w \); and \( \rho \) is the ratio of the \( R_g \) of a branched polymer over the \( R_h \) of the same branched polymer. The branching parameters were calculated using \( R_g \) and \( R_h \) data generated with narrow MWD linear PIB standards, normalized by MWD. Log-Log plots from the linear PIB standards were used to calculate \( R_{g,\text{lin}} \) and \( R_{h,\text{lin}} \) at the same \( M_w \) as the branched polymer:

\[
R_{g,\text{lin}} = 10e^{[(0.5342)\times\text{Log}(M_w,\text{br})-1.61083]}
\]

\[
R_{h,\text{lin}} = 0.0149\times(M_w,\text{br})e^{0.5574}
\]

Table 4.4 lists \( g \), \( h \), and \( \rho \) values. In our arborescent polymers, \( f \) (the average number of chain ends) = \( B+2 \); these values are also listed in Table 4.4, together with the MWD of the starting polymer and the fragments after link destruction and \( g' \) (one of the most commonly used branching parameters) defined as:

\[
g' = \frac{\eta_{w,\text{br}}}{\eta_{w,\text{lin}}}
\]
Figure 4.8  Plots of: (a) Log $R_g$  (b) Log $R_h$ and  (c) Log $\eta$ vs. Log $M_w$ (g/mol).
The \( \eta_{w,\text{lin}} \) was calculated from the Mark-Houwink-Sakurada equation with \( K = 0.2 \) and \( \alpha = 0.67 \) obtained with linear PIB standards from SEC.\(^{155} \) Similar results for linear PIB standards were found by Jackson and coworkers.\(^{161} \) The branched polymer has \( \alpha = 0.88 \) which shows that the polymer is less compact compared to linear PIB.

Figure 4.9 shows the correlation between \( f \) and the branching parameters. \( g \) values are consistently higher than 1 and increase with increasing \( f \). EF141205-3, with \( g = 2.57 \) and \( h = 1.53 \) is consistent with random branching. The \( \rho = 1.28 \) measured for this sample is less than the \( \rho = 3^{1/2} \) predicted for \( A_f \) polycondensates, and more in line with ABC polycondensates.\(^{147,150} \) \( \rho \sim 1.2 \) for all samples) seems to be independent of \( f \), as predicted for randomly branched structures.\(^{147} \) LD of the multimodal samples yielded

Table 4.4 Analysis of architecture by SEC.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>( M_w/M_n )</th>
<th>( f )</th>
<th>( g )</th>
<th>( h )</th>
<th>( \rho )</th>
<th>( g' )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EF141205-2</td>
<td>1.5</td>
<td>1.5</td>
<td>4.9</td>
<td>1.00</td>
<td>1.14</td>
<td>1.10</td>
</tr>
<tr>
<td>EF141205-1</td>
<td>2.2</td>
<td>1.2</td>
<td>4.8</td>
<td>1.63</td>
<td>1.21</td>
<td>1.32</td>
</tr>
<tr>
<td>EF141205-5</td>
<td>2.1</td>
<td>1.5</td>
<td>7.6</td>
<td>1.35</td>
<td>1.22</td>
<td>1.20</td>
</tr>
<tr>
<td>EF141205-6</td>
<td>3.4</td>
<td>1.3</td>
<td>7.7</td>
<td>1.85</td>
<td>1.31</td>
<td>1.28</td>
</tr>
<tr>
<td>EF141205-4</td>
<td>2.6</td>
<td>1.5</td>
<td>6.5</td>
<td>1.48</td>
<td>1.26</td>
<td>1.20</td>
</tr>
<tr>
<td>EF141205-3</td>
<td>6.0</td>
<td>1.4</td>
<td>11.5</td>
<td>2.57</td>
<td>1.53</td>
<td>1.28</td>
</tr>
<tr>
<td>EF141205-7</td>
<td>1.9</td>
<td>1.3</td>
<td>5.3</td>
<td>1.58</td>
<td>1.27</td>
<td>1.25</td>
</tr>
</tbody>
</table>

monomodal SEC traces with narrower MWD (Figure 4.5). This seems to indicate that the segments between branch points are more uniform than in the case of MeOIM which yielded fragments with the most probable distribution of 2.
EF141205-2 had the narrowest MWD at 1.5 which did not change numerically after LD indicating a polydisperse star. The $g'$ values show a decrease with an increase in branching and molecular weight. EF141205-7 has a larger $g'$ value than EF141205-6.
which indicates that with less TiCl₄ less branching occurred. Figure 4.10 shows conformation plots for EF141204-2 and EF141205-3. The plots show R₉ vs. Mᵢ (molar mass of a single slice); R₉ values are obtained for each individual molar mass slice across the molecular weight distribution. Conformation plots for EF141205-2 and EF141205-3 (Figure 4.10) revealed that EF141205-2 had a slope of 0.54 indicating that the polymer is closer to a random coil.¹⁵⁵,¹⁶²

\[
y = 0.5446x - 1.7685 \\
R^2 = 0.9987
\]

\[
y = 0.4761x - 1.3923 \\
R^2 = 0.9974
\]

Figure 4.10  Conformation plots: (a) EF141205-2  (b) EF142305-3.

EF141205-3 had a slope of 0.48 which is somewhere between a sphere (0.3) and a random coil (0.56) as found for arb_PIB.¹⁶² All of the other polymer samples had slopes similar to EF141205-3 ranging from 0.42 – 0.46 (somewhere between a sphere and random coil). The slope of EF141205-3 is another indication, along with the fact that this sample had the smallest g’ value of 0.42, that the degree of branching in this sample is very large. It appears that polymers from the EPOIM have more uniform chain lengths
between branching points. This is because the unequal reactivity of the propagating carbocations does not produce a truly random system; the MeOIM produces carbocations with equal reactivity resulting in a random system.\textsuperscript{160} Branching can also be calculated with ASTRA® V software by using:

\[
g = \frac{6}{B} \left\{ \frac{1}{2} \left( \frac{2 + B}{B} \right)^{1/2} \ln \left[ \frac{(2 + B)^{1/2} + B^{1/2}}{(2 + B)^{1/2} - B^{1/2}} \right] - 1 \right\}
\]

which compares \(R_g\) data generated with linear PIB standards, taking the actual \(R_g\) measured for the nearly monodisperse slice at the same MW as that of the branched polymer. In the case of EF141205-2, branching increased from 2 to 50 across the MWD; the more randomly branched samples such as EF141205-3 showed branching increase from 2 to 15 across the MWD (Figure 4.11).

![Figure 4.11 Branching distribution in small scale polymerizations for samples (a) EF141205-2 (b) EF141205-3.](image-url)
4.1.3 Large scale IB polymerizations with EPOIM (UA inimer, LANXESS polymerizations)

We were interested in further exploring the reaction conditions used in the synthesis of EF141205-2 because of its architecture. Thus two large scale polymerizations were carried out by LANXESS at the R&D facilities of LANXESS Inc. Canada.

4.1.3.1 SEC analysis of IB polymerizations with EPOIM

Table 4.5 summarizes the results of two large scale polymerizations. LANXESS, using EPOIM synthesized at UA, kept the \([\text{IM}]_0/\text{[M]}_0\) ratio the same as in EF141205-2, but reduced the \([\text{TiCl}_4]_0\) and lowered the temperature to -90 °C for a more controlled living polymerization. The samples were analyzed at UA. Figure 4.12 shows a \(\ln([\text{M}]_0/\text{[M]}) – \)time plot and Figure 4.13 shows an \(M_n – \)conversion plot. Both plots are linear, with the latter showing a slight upturn at high conversions. This upturn in conversion is the result of branching which is typical in branched polymers\(^{137,163}\) from self condensing vinyl polymerizations (SCVP). The data demonstrate excellent reproducibility of the repeat experiments.

Figure 4.14 shows the SEC traces of the polymer from polymerization 1: \(arb\text{-IB(OH)}-1, 2, 5 \) and 6. The first trace is monomodal with a small shoulder from high MW polymer. The peak shifts to higher MW and a shoulder from low MW polymer develops. The SEC traces of the polymer from polymerization 2, \(arb\text{-IB(OH)}\)-2,3,4, and 5, are very similar and can be seen in Figure 4.15.
Table 4.5. Large scale polymerizations.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Time (min)</th>
<th>Conv (%)</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>$M_z$ (g/mol)</th>
<th>$\eta$ (mL/\text{g})</th>
<th>$R_g$ (nm)</th>
<th>$R_h$ (nm)</th>
<th>$B_{\text{kin}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pzn 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$arb_{-}IB(OH)-1$</td>
<td>5</td>
<td>19</td>
<td>39,000</td>
<td>52,600</td>
<td>82,800</td>
<td>22.1</td>
<td>26.1</td>
<td>7.1</td>
<td>4.4</td>
</tr>
<tr>
<td>$arb_{-}IB(OH)-2$</td>
<td>10</td>
<td>29</td>
<td>52,500</td>
<td>68,700</td>
<td>120,300</td>
<td>28.5</td>
<td>22.3</td>
<td>8.0</td>
<td>3.6</td>
</tr>
<tr>
<td>$arb_{-}IB(OH)-3$</td>
<td>20</td>
<td>48</td>
<td>80,700</td>
<td>107,600</td>
<td>180,200</td>
<td>40.5</td>
<td>19.3</td>
<td>10.7</td>
<td>3.3</td>
</tr>
<tr>
<td>$arb_{-}IB(OH)-4$</td>
<td>30</td>
<td>66</td>
<td>114,400</td>
<td>159,100</td>
<td>267,800</td>
<td>50.2</td>
<td>21.8</td>
<td>13.3</td>
<td>3.4</td>
</tr>
<tr>
<td>$arb_{-}IB(OH)-5$</td>
<td>50</td>
<td>87</td>
<td>167,200</td>
<td>258,200</td>
<td>440,400</td>
<td>64.3</td>
<td>24.3</td>
<td>17.2</td>
<td>3.9</td>
</tr>
<tr>
<td>$arb_{-}IB(OH)-6$</td>
<td>64</td>
<td>92</td>
<td>197,900</td>
<td>318,900</td>
<td>576,800</td>
<td>74.2</td>
<td>26.3</td>
<td>19.9</td>
<td>4.5</td>
</tr>
<tr>
<td>Pzn 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$arb_{-}IB(OH)-1$</td>
<td>5</td>
<td>16</td>
<td>34,400</td>
<td>41,900</td>
<td>60,500</td>
<td>20.9</td>
<td>20.0</td>
<td>5.8</td>
<td>4.4</td>
</tr>
<tr>
<td>$arb_{-}IB(OH)-2$</td>
<td>10</td>
<td>27</td>
<td>43,400</td>
<td>58,900</td>
<td>83,500</td>
<td>25.7</td>
<td>16.6</td>
<td>7.6</td>
<td>3.1</td>
</tr>
<tr>
<td>$arb_{-}IB(OH)-3$</td>
<td>20</td>
<td>44</td>
<td>71,700</td>
<td>95,500</td>
<td>184,500</td>
<td>37.4</td>
<td>20.4</td>
<td>10.2</td>
<td>3.2</td>
</tr>
<tr>
<td>$arb_{-}IB(OH)-4$</td>
<td>30</td>
<td>62</td>
<td>101,200</td>
<td>139,100</td>
<td>232,000</td>
<td>48.0</td>
<td>18.1</td>
<td>12.3</td>
<td>3.2</td>
</tr>
<tr>
<td>$arb_{-}IB(OH)-5$</td>
<td>34</td>
<td>70</td>
<td>115,700</td>
<td>162,000</td>
<td>259,400</td>
<td>50.8</td>
<td>18.8</td>
<td>12.9</td>
<td>3.3</td>
</tr>
<tr>
<td>PS30K</td>
<td></td>
<td></td>
<td>30,200</td>
<td>20,200</td>
<td>30,200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 4.12 $\ln[M_0]/[M]$ versus time in large scale polymerizations. Data in Table 4.5 \(^{164}\)

Figure 4.13 $M_n$ versus conversion in large scale polymerizations. Data in Table 4.5 \(^{164}\)
Figure 4.14  SEC traces of polymers from Polymerization 1: \textit{arb}_{IB(OH)}-1, 2, 5, and 6.
Table 4.6. Branching analysis of large scale polymerizations.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>M&lt;sub&gt;n, theo&lt;/sub&gt; (g/mol)</th>
<th>Peak MW(g/mol)</th>
<th>Branch MW (g/mol)</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt;</th>
<th>B&lt;sub&gt;LD&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>#1</td>
<td>#2</td>
<td>Before LD</td>
<td>After LD</td>
</tr>
<tr>
<td>Pzn 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>arb_IB(OH)-1</td>
<td>7,300</td>
<td>34,400</td>
<td>17,600</td>
<td>1.29</td>
<td>2.2</td>
</tr>
<tr>
<td>arb_IB(OH)-2</td>
<td>11,400</td>
<td>49,900</td>
<td>30,500</td>
<td>1.29</td>
<td>1.7</td>
</tr>
<tr>
<td>arb_IB(OH)-3</td>
<td>18,900</td>
<td>68,400</td>
<td>70,000</td>
<td>1.33</td>
<td>1.2</td>
</tr>
<tr>
<td>Pzn 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>arb_IB(OH)-1</td>
<td>6,100</td>
<td>30,000</td>
<td>-</td>
<td>1.27</td>
<td>-</td>
</tr>
<tr>
<td>arb_IB(OH)-2</td>
<td>10,500</td>
<td>38,400</td>
<td>-</td>
<td>1.28</td>
<td>1.03</td>
</tr>
<tr>
<td>arb_IB(OH)-3</td>
<td>17,000</td>
<td>58,800</td>
<td>143,600</td>
<td>1.33</td>
<td>1.07</td>
</tr>
<tr>
<td>arb_IB(OH)-5</td>
<td>27,200</td>
<td>88,800</td>
<td>167,000</td>
<td>-</td>
<td>1.3</td>
</tr>
</tbody>
</table>
The relative intensity of the UV signal decreases with increasing MW, but indicates that EPOIM is present in all fractions. Since PIB is transparent to UV, the decreasing intensity of the UV signal with increasing MW can be attributed to the incorporation of IB. The large difference between $M_n$ and $M_n$ theot (defined in section 4.1.2) shows that EPOIM behaves not only as an initiator but also incorporates into the polymer as a monomer (Table 4.6). LD of the large scale polymerizations resulted in a decrease in molecular weight followed by an increase. This was not experienced with the MeOIM or in the small scale polymerizations with EPOIM (4.1.2) and is most likely because a phenolic antioxidant Irganox was added to the polymers by LANXESS Researchers.

4.1.3.2 Architecture analysis of large scale polymerizations

As in the case of the small scale polymerizations branching and architecture analysis was performed by using the parameters of Stockmayer and coworkers\(^{147}\) (see Section 4.1.2, Table 4.4).

Table 4.7 Architecture analysis of large scale polymerizations.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>g</th>
<th>h</th>
<th>$\rho$</th>
<th>$g'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>arb_IB(OH)-1</td>
<td>10.26</td>
<td>1.11</td>
<td>3.68</td>
<td>0.76</td>
</tr>
<tr>
<td>arb_IB(OH)-2</td>
<td>5.63</td>
<td>1.09</td>
<td>2.75</td>
<td>0.81</td>
</tr>
<tr>
<td>arb_IB(OH)-3</td>
<td>2.61</td>
<td>1.13</td>
<td>1.80</td>
<td>0.83</td>
</tr>
<tr>
<td>arb_IB(OH)-4</td>
<td>2.19</td>
<td>1.13</td>
<td>1.64</td>
<td>0.78</td>
</tr>
<tr>
<td>arb_IB(OH)-5</td>
<td>1.63</td>
<td>1.11</td>
<td>1.41</td>
<td>0.71</td>
</tr>
<tr>
<td>arb_IB(OH)-6</td>
<td>1.52</td>
<td>1.14</td>
<td>1.32</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Polymerization 2

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>g</th>
<th>h</th>
<th>$\rho$</th>
<th>$g'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>arb_IB(OH)-1</td>
<td>9.81</td>
<td>1.03</td>
<td>3.90</td>
<td>0.82</td>
</tr>
<tr>
<td>arb_IB(OH)-2</td>
<td>2.91</td>
<td>1.05</td>
<td>2.07</td>
<td>0.84</td>
</tr>
<tr>
<td>arb_IB(OH)-3</td>
<td>3.31</td>
<td>1.15</td>
<td>2.00</td>
<td>0.84</td>
</tr>
<tr>
<td>arb_IB(OH)-4</td>
<td>1.75</td>
<td>1.12</td>
<td>1.47</td>
<td>0.82</td>
</tr>
<tr>
<td>arb_IB(OH)-5</td>
<td>1.60</td>
<td>1.08</td>
<td>1.46</td>
<td>0.78</td>
</tr>
</tbody>
</table>
The viscosity and $R_h$ (Table 4.5) steadily increase, while $B_{\text{kin}}$ is steady around 4 in each sample. $g' = [\eta]_{w,br}/[\eta]_{w,\text{lin}}$ values (Table 4.7) are all less than 1, showing first an increase followed by a decrease with increasing molecular weight. $g'$ values less than 1 are an indication of branching. In both polymerization 1 and 2, $g'$ increased and then decreased. In the large scale polymerizations $R_g$ (z average) (see Table 4.5) remains fairly constant at $\sim 20$ nm even in the lowest MW samples and barely changes with increasing MW.

In the first three samples $g > 2$, $h > 1$ and $\rho > 1.73$ are all indicative of random branching. Towards the end of the reaction, $g$ decreases but remains larger than 1, and $\rho$ drops to about 1.4. The decrease in $g$ is caused by the fact that the degree of branching remains fairly steady because most of the EPOIM is incorporated but addition of IB and increase in the molecular weight of the polymers is still occurring. Interestingly, $h$ remains constant at slightly above 1. $1 < g < 2$, $h > 1$, and $\rho < 1.73$ indicates that branching is not completely random.

$B$ shown in Figure 4.16 was calculated by the use of ASTRA® V software using the equation given in section 4.1.2. In all arborescent samples, $B$ increased with MW across the molecular weight distribution up to about 16-20 (see Figure 4.16). Figure 4.17 shows the $\rho$ distribution for EPOIM-initiated polymerizations; $R_g$ and $R_h$ given for each SEC fraction by ASTRA were used for these calculations and $\rho$ was calculated across the entire molecular weight distribution at each molar mass point ($M_i$). In the case of self-similar dendritic architectures, a constant $R_g/R_h$ ratio ($\rho$) is expected.
Figure 4.16  Branching distribution in large scale polymerizations for samples
(a) Polymerization 2: \textit{arb\_IB(OH)-5}  (b) Polymerization 1: \textit{arb\_IB(OH)-6}.

Figure 4.17  $\rho$ distribution in EPOIM initiated \textit{arb\_IB(OH)s}: (a) Polymerization 2: \textit{arb\_IB(OH)-5}  (b) Polymerization 1: \textit{arb\_IB(OH)-6}.
In the case of EPOIM $\rho$ decreased across the molecular weight distribution with increasing molar mass (Figure 4.17). The decrease in $\rho$ throughout the polymerization, as seen by Stockmayer and coworkers$^{147}$, indicates a polydisperse star. The decrease in $\rho$ across the molecular weight range agrees with the results shown in Table 4.7. The first three samples were randomly branched; in subsequent samples $\rho$ decreased to less than randomly branched. This might result in a randomly branched dendritic PIB core with continued addition of PIB resulting in a star-like architecture as shown in Figure 4.18.

Figure 4.18 Star-like architecture with an $arb\_IB(OH)$ core.
Since the critical entanglement molecular weight of PIB is ~10,000 g/mol the first samples with ~3 branch points and relatively similar branch lengths close to this critical length may not be entangled. As propagation proceeds, some branches may entangle but the architecture remains restrictive to gyration. The branching parameters listed in Table 4.7 are consistent with this picture. The results from Polymerization 1 and 2 are nearly identical. The recipes for the two polymerizations are identical, the only difference is the extent of conversion. The repeatability of the results helps to confirm the SEC results. The EPOIM gives polymers with architectures that are not truly randomly branched.

4.1.4 *In situ* FTIR studies

To better understand the mechanism of polymerization using EPOIM, the reaction between IB and EPOIM was monitored using *in situ* FTIR.

4.1.4.1 Self-condensing vinyl polymerization (SCVP)

The *in situ* FTIR setup included a liquid transmission probe (TR) (Remspec Inc) coupled with a MID-IR monitor using fiber optic cables, as described in Chapter 3. The TR probe was chosen because of its ability to monitor reactions in very dilute solutions (0.001-0.5 mol/L for IB). High sensitivity is necessary to observe the weak epoxide ring stretching. Before starting the polymerization the FTIR spectrum of EPOIM was analyzed (Figure 4.19). The high noise level was a result of the dilute concentration of EPOIM in solution. The peak at 1630 cm\(^{-1}\) is due to the C=C double bond stretching from the inimer as seen with the MeOIM. The peak from the epoxide ring appears at
1276 cm$^{-1}$ and is due to ring stretching and breathing modes of the epoxide.$^{151,166}$ Using this information the polymerizations can be monitored in situ.

![FTIR spectrum of EPOIM.](image)

Figure 4.19 FTIR spectrum of EPOIM.

Table 4.8 shows the reaction conditions used in the SCVP of EPOIM. This reaction was monitored using the TR probe which can monitor concentrations up to 0.5 mol/L.

<table>
<thead>
<tr>
<th>Addition Time</th>
<th>Chemical</th>
<th>M (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 min 20 s</td>
<td>Inimer</td>
<td>0.086</td>
</tr>
<tr>
<td>10 min</td>
<td>TiCl$_4$-1</td>
<td>0.051</td>
</tr>
<tr>
<td>37 min</td>
<td>TiCl$_4$-2</td>
<td>0.051</td>
</tr>
<tr>
<td>65 min 30 s</td>
<td>TiCl$_4$-3</td>
<td>0.051</td>
</tr>
</tbody>
</table>
Upon the addition of EPOIM at 7 min 20 sec, a peak for the C=C stretch appeared at 1633 cm\(^{-1}\) (peak I). Upon the addition of TiCl\(_4\) at 10 min a new absorbance appeared at 1614 cm\(^{-1}\) (II). This absorbance was assigned to the oxonium ion forming in the reaction between the epoxide ring of the EPOIM with TiCl\(_4\) (Figure 4.20).\(^{151}\) At the same time, a sharp drop in peak I (C=C double bond stretching from vinyl group of EPOIM) occurs, indicating that the vinyl groups of the EPOIM are reacting. Upon further additions of TiCl\(_4\) to the system, a further decrease in peak I was observed. Unfortunately, the epoxide ring stretching was unobservable due to a weak signal and could not be monitored. However, the appearance of a new peak at 1069 cm\(^{-1}\) (III) at the time of TiCl\(_4\) addition (Figure 4.21) indicated the formation of ether bonds, possibly oligoethers.\(^{151,166}\) This means that the epoxide rings from the EPOIM reacted at least
partially. Peak III (polyether peak) initially gains in intensity and then levels off around the time of the second addition of TiCl$_4$ which results in a slight molar excess of TiCl$_4$ compared to EPOIM.

![FTIR spectrum](image)

**Figure 4.21** FTIR from SCVP of EPOIM: 1100-1050 cm$^{-1}$ (see Table 4.8).

The FTIR spectrum indicates the disappearance of vinyl groups of EPOIM as well as the formation of polyether. As discussed in the historical background, the ring opening of epoxides can occur by both an S$_N$1 and S$_N$2 mechanism (Figure 4.22). Figure 4.22 shows that the first event, is the formation of the oxonium ion. The reaction pathway depends on relative rates. If $k_1 - k_2$ ([TiCl$_4$] $\geq$ [I]) then initiation and propagation likely proceed via the S$_N$1 mechanism. If $k_1 < k_2$ ([TiCl$_4$]<[I]) then propagation likely proceeds via the S$_N$2 mechanism.$^{150}$ Because no kinetic data are available the mechanism of polymerization cannot be fully determined.
Figure 4.22 Possible reaction mechanisms of the ring opening polymerization of EPOIM.
If the S_N1 mechanism does occur, the oxonium ion opens to form a tertiary carbocation, which is less stable than the cumyl carbocation formed by the MeOIM as discussed in section 4.1.2 (Figure 4.7). Some propagation can occur before rearrangement to the dormant (tertiary C-Cl) chain end occurs (product II in Figure 4.22) as seen by the immediate decrease in the vinyl groups of the EPOIM (Figure 4.20).
From the FTIR results we can determine that two major reactions are occurring: ether formation and vinyl polymerization. Typically with the ring opening of epoxides, two methods of forming polyethers are possible: the activated monomer mechanism, and the activated polymer mechanism. For the activated monomer mechanism to occur, which proceeds by alcoholysis, a source of alcohol is necessary. In these polymerizations alcohol is not present since a proton trap was used to prevent protic initiation; therefore, polyether formation should occur by the activated chain mechanism. The possible propagation reactions (from products I* and II* in Figure 4.22) are shown in Figure 4.23. It is also possible for the vinyl groups in the polyether to undergo vinyl polymerization as shown in reaction 2 in Figure 4.23. Figure 4.23 shows propagation via the SN2 mechanism to form polyether. In this case the oxygen from the epoxide ring of another EPOIM will attack the CH2 proton in the epoxide ring of the oxonium ion. Due to steric hindrance the attack will most likely occur solely at the less hindered carbon of the ring. This results in ring opening of the epoxide and the formation of a dimer with a partial positive charge on the epoxide ring and negative charge on the TiCl4. Reaction 2 in Figure 4.23 shows unreacted epoxide rings present in the polymer. It is possible for these epoxides to be opened by excess TiCl4 or for an unreacted vinyl group in a polymer chain to incorporate with another polymer chain. The formation of multiple epoxides in the polymer can result in crosslinking in the polymer after polymerization in the presence of acids or bases.
Table 4.9  SEC results for the SCVP of EPOIM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M_n ) (g/mol)</th>
<th>( M_w ) (g/mol)</th>
<th>MW (g/mol)</th>
<th>Peak MW (g/mol)</th>
<th>( D )</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCVP</td>
<td>34,000</td>
<td>129,200</td>
<td>241,200</td>
<td>50,200</td>
<td>26,700</td>
<td>25,200</td>
<td>22,100</td>
<td>16,800</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS30K</td>
<td>31,100</td>
<td>31,200</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.24  SEC trace from EPOIM SCVP.
We noticed that the polymer was not fully soluble in THF i.e., it had crosslinked. The SEC results for the soluble fraction (83%) of the polymer can be seen in Table 4.9. The SEC trace (Figure 4.24) shows a multimodal distribution with a low concentration of high molecular weight fraction.

From proton NMR spectroscopy (Figure 4.25) of the soluble fraction, the presence of a small amount of polyether can be seen by the presence of the CH$_2$-O-C protons at about 4 ppm (peak 1 in Figure 4.25). The peaks around 3 ppm (peak 2) are from the CH$_2$-O-C protons of intact epoxide rings. The presence of protons from vinyl groups can be seen at 6.6, 5.8 and 5.2 ppm (peaks 3, 4, and 5 respectively). The aromatic protons from the resulting polymer can be seen at 6.8 to 7.5 ppm (peaks 6-8). From the normalization of these peaks to the aromatic peaks it can be seen that the ratio is no longer 4:1:1:1:1, and that 35.7 % of the vinyl groups remain unreacted; however, since this is only the soluble fraction of the polymer no clear conclusion can be made as to the amount of vinyl groups that remain unreacted or the amount of unopened epoxide rings. Insufficient structural information was available from the proton NMR spectrum in Figure 4.25 to assign resonances for the CH and CH$_2$ protons from the styrenic backbone of the polymer. In order to assign these peaks DEPT (distortionless enhancement by polarization transfer) and HSQC (heteronuclear single quantum coherence) were carried out. The DEPT helps to identify carbon atoms with one, two, and three hydrogen atoms covalently attached. This allows for the distinction of methine, methylene, and methyl groups.
Figure 4.25 $^1$H NMR spectrum and resonance assignments (500 MHz, solvent CDCl$_3$) of the soluble fraction from EPOIM SCVP (SEC results in Table 4.9).
The HSQC is two dimensional NMR analysis which correlates a $^1$H-NMR spectrum on one axis with a $^{13}$C-NMR spectrum on the other axis. This allows for the determination of which proton is bonded to which carbon. This knowledge combined with DEPT should allow for the determination of which peaks in the proton NMR spectrum (Figure 4.25) are due to the backbone of the polymer.

DEPT (Figure 4.26) was able to clarify which carbons were methine and methylene and with this knowledge by looking at the $^{13}$C axis of the HSQC (Figure 4.28) we were able to determine which peaks were from the backbone of the polymer.
In the HSQC the blue regions correlate to methylene protons, the yellow and red regions correlate to methine and methyl protons. The large red region in the HSQC is from the aromatic protons in the polymer.

Figure 4.27 HSQC spectrum of SCVP (Yellow and red regions: methine and methyl protons; blue regions: methylene protons).
Therefore the three peaks at 2.23, 2.07, and 1.88 ppm (Figure 4.25) are the three methine peaks (peak 9 in Figure 4.25) which come from the backbone of the substituted polystyrene. The methylene proton from the backbone appears at 1.47 ppm (peak 10). The methyl group appears at 1.56 ppm (peak 11). The peak at 1.69 ppm (peak 12) is from methyl protons of intact epoxides in the polymer. The peaks at 1.3 and 1.25 ppm are from methylene protons in the polymer (determined from DEPT and HSQC) although no definitive assignment can be made.

With these results we can conclude that some epoxy groups remained intact in the polymer, and that there was some ether formation confirming the polymer structure shown in Figure 4.25.

4.1.4.2 Self condensing vinyl copolymerization (SCVCP)

The self condensing vinyl copolymerization studied the reaction between EPOIM and IB. The reaction conditions used can be seen in Table 4.10. These are not typical polymerization conditions, the high concentration of EPOIM was used so that the reaction could be monitored by in situ FTIR spectroscopy.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Chemical</th>
<th>Chemical M (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 min</td>
<td>EPOIM</td>
<td>0.105</td>
</tr>
<tr>
<td>7 min 30 s</td>
<td>IB</td>
<td>0.267</td>
</tr>
<tr>
<td>16 min 20 s</td>
<td>TiCl₄ - 1</td>
<td>0.056</td>
</tr>
<tr>
<td>25 min 40 s</td>
<td>TiCl₄ – 2</td>
<td>0.075</td>
</tr>
<tr>
<td>55 min 10 s</td>
<td>TiCl₄ – 3</td>
<td>0.0065</td>
</tr>
</tbody>
</table>
As with the SCVP, 0.05 mol/L of TiCl₄, which is half the amount of EPOIM, was added over time (Table 4.10). Figure 4.28 shows that when the inimer was added, a new peak appeared at 1633 cm⁻¹ (I) from the C=C stretch of the EPOIM. When IB was added a second peak appeared at 1655 cm⁻¹ (II) for the C=C stretching of IB. No decrease in the intensity of the peaks was observed, indicating the absence of protic initiation. When TiCl₄ was added a new peak appeared at 1612 cm⁻¹ (II) corresponding to TiCl₄ forming an oxonium ion with the oxygen from the epoxide ring of the inimer. Peak II (from the oxonium ion) gained in intensity around 25 min 40 sec upon the second addition of TiCl₄.

Figure 4.28  FT-IR spectrum of EPOIM/IB SCVCP: 1700-1560 cm⁻¹ (see Table 4.10).

The second addition of TiCl₄ resulted in the decrease in peaks I and III (from the vinyl stretching of the EPOIM and IB), indicating vinyl polymerization. This is a good
indication of IB and EPOIM consumption, most likely by copolymerization. From the FTIR spectrum (Figure 4.28) it appears that the inimer and IB were completely consumed. There are also two peaks at 1248 cm\(^{-1}\) (IV) and 1260 cm\(^{-1}\) from the distorted carbon tetrahedron \(-\text{C-(CH}_3\text{)}_2\) upon forming PIB (IV) and C-C stretching in the polymer, respectively (Figure 4.29). Both peaks appear after the addition of TiCl\(_4\) and increase in intensity due to polymer formation. Once again, due to a weak intensity, the epoxide ring stretching could not be monitored. Two peaks at 1104 cm\(^{-1}\) (VI) and 1090 cm\(^{-1}\) (VII) from C-O-C stretching (Figure 4.30) appeared after the addition of TiCl\(_4\) and increased in intensity during the polymerization before leveling off. These peaks are most likely due to the formation of ethers in the polymer. From the FTIR spectrum we can conclude that vinyl polymerization of the EPOIM and IB occurred, as well as the formation of ether.

![FTIR spectrum of EPOIM/IB SCVCP: 1280-1230 cm\(^{-1}\) (see Table 4.10).](image_url)

Figure 4.29 FTIR spectrum of EPOIM/IB SCVCP: 1280-1230 cm\(^{-1}\) (see Table 4.10).
Figure 4.30 FT-IR spectrum of EPOIM/IB SCVCP: 1150-1050 cm⁻¹ (see Table 4.10).

Figure 4.31 SEC trace of SCVCP of EPOIM.
As in the case of SCVP, crosslinking occurred, but to a lesser degree. The SEC results from the soluble fraction (93%) show a multimodal molecular weight distribution as well as incorporation of the EPOIM throughout the polymer as seen from the UV trace (Figure 4.31). The results from SEC for SCVCP are shown in Table 4.11. The polymer obtained has a very broad molecular weight distribution, which shows branching.

Table 4.11  SEC results from the SCVCP of the EPOIM.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>$M_w/M_n$</th>
<th>Peak MW (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCVCP</td>
<td>16,200</td>
<td>201,200</td>
<td>12.4</td>
<td>1,713,000</td>
</tr>
<tr>
<td>PS30K</td>
<td>31,100</td>
<td>31,200</td>
<td>1.0</td>
<td>-</td>
</tr>
</tbody>
</table>

The possible reactions in this polymerization mechanism are shown in Figure 4.32 and 4.33. As discussed in connection with SCVP, initiation in SCVCP occurs in the same manner. If $[I] < [TiCl_4]$ the reaction should proceed as shown in Figure 4.32. The initiating carbocation arising from EPOIM is stabilized by the –I effect of the electron donating OTiCl$_4^-$ and/or –OTiCl$_3$ groups. Furthermore, the electron pairs of the oxygen may interact with the electron-deficient p orbital of the carbocation, leading to further stabilization and decreased reactivity of the carbocation. We propose that with one mole of TiCl$_4$ a tertiary carbocation will form, which may lead to polymerization before rearrangement to the dormant state (Cl end group). This dormant chain end can be activated by an additional mole of TiCl$_4$ to result in the reversible equilibrium between active species (Figure 4.32). It is also possible for polyethers to
form in the same manner as in SCVP. The possible propagation reactions are shown in Figure 4.33. Figure 4.33 shows that the tertiary carbocation formed by EPOIM (I) can react with either IB or EPOIM. These products can than each react with IB or EPOIM and copolymerization should proceed.

![Proposed initiation pathway of the EPOIM (SCVCP)](image)

Figure 4.32 Proposed initiation pathway of the EPOIM (SCVCP).

From the $^1$H-NMR spectrum (Figure 4.34) of the soluble polymer fraction, the aromatic peaks due to EPOIM can be seen from 6.8-7.5 ppm (peaks 1-3 in Figure 4.34), as well as vinyl groups indicated by the vinyl protons at 6.6, 5.8, and 5.2 ppm (peaks 4-6 respectively). The presence of a small amount of ether can be seen by the presence of CH$_2$-O-C protons at about 4 ppm (peak 7). The peaks around 3 ppm are due to the CH$_2$-O-C protons of the intact epoxide rings (peak 8). The aliphatic protons from both IB and EPOIM can clearly be seen with the CH$_3$ protons from IB at 1.13 ppm and the CH$_2$ protons at around 1.36 ppm (peaks 9 and 10, respectively).
Figure 4.33 Possible propagation reactions in SCVCP.

G: Geigon Ion
Figure 4.34 $^1$H-NMR spectrum and resonance assignments of SCVCP.
In the expanded scale inset in Figure 4.34, the peaks corresponding to the backbone of the styrenic material from EPOIM are clearly visible; the three methine peaks appear at 1.97, 2.16, and 2.99 ppm (peak 11) and the methylene groups at 1.43 ppm (peak 12). A peak from the methyl protons of a tertiary Cl end group (PIB chain ends) appears at 1.67 ppm (peak 13). The methyl groups from the ring-opened EPOIM units of the polymer appear at 1.55 ppm (peak 14), and the methyl groups from the intact epoxides appear at 1.7 ppm (peak 15). The integration values from the $^1$H NMR spectrum (Figure 4.34) show a 1: 2.76 ratio of EPOIM:IB, which is fairly close to the initial calculated ratio of EPOIM:IB of 1:2.54 from Table 4.10. These results indicate that unlike MeOIM$^{160}$ which shows random IB and MeOIM incorporation, in the case of EPOIM blocking of IB and EPOIM occurs. This is an indication of unequal reactivity of the propagating carbocations. The results from NMR spectroscopy corroborate the final structure of the polymer as shown in Figure 4.34.

In summary, *in situ* FTIR monitoring of SCVP and SCVCP by the use of EPOIM showed that, due to the unequal reactivity of EPOIM’s propagating carbocations, the vinyl groups of EPOIM react leaving some epoxide rings unopened. The use of a half molar equivalent of TiCl$_4$ relative to EPOIM resulted in ether formation as seen by FTIR and $^1$H NMR spectroscopy.

### 4.2 Block copolymerizations: *arb_IB(OH)-MS*(3.5 and 16) (LANXESS Inc)

Two large scale block copolymerizations were carried out at LANXESS Inc. In these experiments $p$-methylstyrene (MS) was copolymerized with IB because MS and IB have similar reactivities leading to improved block formation$^{168}$; MS was added before
100% conversion of IB to avoid proton expulsion in the absence of monomer. This method led to block copolymers with a high MW dendritic PIB core and short copolymer end sequences that exhibit TPE properties. The polymers were purified by precipitation of a 5 wt% solution of the polymer in THF into acetone and isopropyl alcohol (IPA) as described in Chapter 3.

MS exhibits phase inversion when precipitated in acetone (plastic) or methanol (rubber) allowing for the removal of residual poly(p-methylstyrene) homopolymer to < 5ppm (as determined by GC head space analysis). The removal of residual monomers and solvents is extremely important in biomedical applications.

4.2.1 Block synthesis using UA inimer and recipe at LANXESS

Polymers from polymerizations 1 and 2 (see Section 4.1.3) were copolymerized with MS to form block copolymers arb_IB(OH)-MS(3.5) and arb_IB(OH)-MS(16), respectively. The numbers in parentheses indicate wt% MS.

Table 4.12 Conditions for polymerization of arb_IB(OH)-MS (3.5 and 16).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>[EPOIM]₀ mol/L</th>
<th>[IB]₀ mol/L</th>
<th>1st Addition</th>
<th>2nd Addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>arb_IB(OH)MS(3.5)</td>
<td>0.0025</td>
<td>1.74</td>
<td>92.0</td>
<td>61.22</td>
</tr>
<tr>
<td>arb_IB(OH)MS(16)</td>
<td>0.0025</td>
<td>1.74</td>
<td>70.0</td>
<td>44.95</td>
</tr>
</tbody>
</table>

The conditions for blocking are shown in Table 4.12. The initial volume of the charge at the time of the 1st monomer addition was 1.5 liters. After the 2nd monomer addition the
The volume of \( \text{arb}_{\text{IB(OH)-MS}}(3.5) \) was 2.3 L and \( \text{arb}_{\text{IB(OH)-MS}}(16) \) was 2.2 L. The wt% of IB and MS in the feed after the 2\(^{\text{nd}}\) addition is shown in Table 4.12. Table 4.12 shows that MS was added before 100% conversion of the \( \text{arb}_{\text{IB}} \) core; this results in the formation of copolymer end blocks poly(isobutylene-\text{-co-p-methylstyrrene}).

4.2.2 Composition analysis

The composition of \( \text{arb}_{\text{IB(OH)-MS}}(16) \) and \( \text{arb}_{\text{IB(OH)-MS}}(3.5) \) was analyzed by NMR and SEC to determine the molecular weight of the polymer and the weight percent of \( p \)-methylstyrrene. NMR was also used to show proof of hydroxyl groups in the polymer.

4.2.2.1 Copolymer composition

The composition of the copolymers was analyzed using NMR spectroscopy to show proof of hydroxyl groups in the polymer and calculate the wt% poly(\( p \)-methylstyrrene) (PMS) in the polymer. The wt% PMS allowed for calculation of the \( dn/dc \) of the polymers for SEC. The polymers were also analyzed by SEC.

4.2.2.1.1 Composition analysis by NMR spectroscopy

\(^1\text{H} \) and \(^{13}\text{C} \) NMR spectra were obtained for each polymer. \(^1\text{H} \) NMR spectra were obtained by 750 MHz NMR spectroscopy with a relaxation delay of 5 secs with \( nt = 600 \) for proof of hydroxyl groups in the polymer. \(^1\text{H} \) NMR spectra for composition analyses were obtained on a 300 MHz NMR with a relaxation delay of 10 secs with \( nt = 600 \). The
$^{13}$C NMR spectra were obtained using 10 mm NMR tubes at 150 mg/mL concentration on the 500 MHz VNMRJ instrument from Varian.

![NMR spectrum](image)

Figure 4.35 *arb* IB(OH)-MS(16); (a) $^1$H NMR spectrum and resonance assignments; solvent CDCl$_3$ (b) synthesis.
A relaxation delay of 5 seconds was used with a collection time of 18 hours. The $^1$H NMR spectrum of $arb$-IB(OH)-MS(16) (the number in parenthesis is the wt% PMS) can be seen in Figure 4.36(a). $arb$-IB(OH)-MS(16) was synthesized as shown in Figure 4.35 (b). The aromatic protons of PMS appear around 7 ppm (peak 4 in Figure 4.35) with the methyl protons appearing at 2.6 ppm (peak 3). The methyl protons from PIB appear around 1 ppm (peak 1) with the methylene protons appearing at about 1.5 ppm (peak 2). The inset expanded spectrum shows the CH$_2$ protons alpha to the hydroxyl groups, which result from the ring opening of the inimer. They appear as two sets of doublets, which result from the two protons splitting each other, at 3.38 and 3.61 ppm (peaks 5a and 5b).\textsuperscript{152} The presence of two sets of doublets at 3.4 and 3.6 ppm (peaks 6a and 6b) can be explained by the possibility of the epoxide ring opening and terminating (i.e. without addition of IB) forming a primary hydroxyl end group and a tertiary C-Cl chain end. These peaks show proof of the presence of hydroxyl groups in the polymer. Unfortunately, since the content of hydroxyl groups within the polymer are so low, proof by elemental analysis (which has a detection limit of 0.5 wt %) could not be obtained. The $^1$H NMR spectrum of $arb$-IB(OH)-MS(3.5) is similar, except for the amount of PMS in the polymer.

The weight percent PMS was calculated from $^1$H NMR spectroscopy using the integration of the aromatic protons to the aliphatic protons of PIB, or the integration of the methyl protons of $p$-methylstyrene to the aliphatic protons of PIB using the following equations:

Aromatic: $4*\text{PMS} = \text{(integration)}$; Aliphatic: $3*(\text{PMS}) + 8*(\text{PIB}) = \text{integration}$ \hspace{1cm} (1)
PMS, CH₃ protons: 3*PMS = (integration);  Aliphatic = 3*(PMS) + 8* (PIB)

= integration

Equations 1 and 2 use peaks with known integration values to calculate mol% PMS and PIB. Since it is known that the aromatic protons from PMS should equal 4, equation 1 calculates mol % of PMS as 4P*MS = integration. The methyl protons from PMS appear at 2.6 ppm (separate from PIB) as seen in Figure 4.25. Equation 2 calculates mol % of PMS as 3*PMS = integration. The mol % of PMS is entered into the equations for the main aliphatic protons to give mol % of PIB. Using these numbers, the weight percent of PMS in the polymers can be calculated. The results from both methods should be essentially the same; however, equation 1 gives slightly higher weight percentages which is most probably due to the fact that the residual proton signal from CDCl₃ (solvent) overlaps with the PMS proton signals in the aromatic region and is integrated into the aromatic region with PMS (Table 4.13). This is why the integration ratios of the aromatic protons of PMS and the CH₃ protons of PMS are not in a ratio of 4:3. The wt% PMS used are those calculated using equation 2 (Table 4.13). Since aliquots were taken during the course of the polymerization, NMR spectra were obtained of each sample to follow the incorporation of MS throughout the polymerization. These numbers are shown in Table 4.13. These weight percentages, allowed us to calculate dn/dc (change in refractive index with change in concentration) for the polymers using the known dn/dc for PIB and PMS in THF weighted by the composition as shown:

\[
\text{dn/dc} = 0.108(\text{weight % PIB}) + 0.183(\text{weight % PMS})
\]
The known dn/dc for PIB is 0.108 and for PMS is 0.183. Results calculated from equation 3 can also be seen in Table 4.13. If the calculated dn/dc agrees with the measured data from 100% mass recovery, then the method is valid. The discrepancy between the dn/dc for 100% mass recovery (obtained from SEC, assumes that the 100% of the injected mass was recovered for analysis) is most likely from human error in weighing of the polymers, as well as error from $^1$H NMR spectroscopy.

Table 4.13 Calculations of weight percent PMS and dn/dc.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ar. (MS)</th>
<th>CH$_3$ (MS)</th>
<th>Aliphatic PMS</th>
<th>Weight %</th>
<th>dn/dc</th>
<th>dn/dc 100% mass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Integration Eq 1 Eq 2 Eq 2</td>
</tr>
<tr>
<td>arb_IB(OH)-MS(16)-6</td>
<td>4</td>
<td>2.2</td>
<td>989.2</td>
<td>1.68</td>
<td>1.24</td>
<td>0.109 0.080</td>
</tr>
<tr>
<td>arb_IB(OH)-MS(16)-7</td>
<td>4</td>
<td>1.8</td>
<td>328.2</td>
<td>4.93</td>
<td>3.00</td>
<td>0.110 0.117</td>
</tr>
<tr>
<td>arb_IB(OH)-MS(16)-8</td>
<td>4</td>
<td>2.8</td>
<td>287.6</td>
<td>5.59</td>
<td>5.30</td>
<td>0.112 0.098</td>
</tr>
<tr>
<td>arb_IB(OH)-MS(16)-9</td>
<td>4</td>
<td>3.0</td>
<td>187.5</td>
<td>8.37</td>
<td>8.26</td>
<td>0.114 0.080</td>
</tr>
<tr>
<td>arb_IB(OH)-MS(16)-</td>
<td>4</td>
<td>2.8</td>
<td>87.2</td>
<td>16.67</td>
<td>15.85</td>
<td>0.120 0.122</td>
</tr>
<tr>
<td>arb_IB(OH)-MS(3.5)-</td>
<td>4</td>
<td>1.7</td>
<td>1551.6</td>
<td>1.08</td>
<td>0.62</td>
<td>0.108 0.101</td>
</tr>
<tr>
<td>arb_IB(OH)-MS(3.5)-</td>
<td>4</td>
<td>2.6</td>
<td>457.3</td>
<td>3.58</td>
<td>3.11</td>
<td>0.110 0.097</td>
</tr>
<tr>
<td>arb_IB(OH)-MS(3.5)-</td>
<td>4</td>
<td>3.1</td>
<td>481.3</td>
<td>3.40</td>
<td>3.50</td>
<td>0.111 0.080</td>
</tr>
</tbody>
</table>

The $^{13}$C NMR spectrum for arb_IB(OH)-MS(16) is shown in Figure 4.36. All of the main carbon peaks were observed from the $^{13}$C NMR spectrum.
Figure 4.36 13C NMR spectrum and resonance assignments of $arb_{IB(OH)}$-MS(16).
The peak at 31.0 ppm (peak 1 in Figure 4.36) is from the methyl group of PIB. The carbons from the methylene groups of PIB appear at 38.1 ppm (peak 2), and the quaternary carbon from PIB appears at 59.5 ppm (peak 3). The carbon from the methyl group of PMS appears at 22 ppm (peak 4). The aromatic carbons from PMS and the inimer appear at 127.5 ppm and 128.6 ppm (peaks 5 and 6). The aromatic carbons from the incorporated EPOIM appear at 126 and 127 ppm (peaks 7 and 8). The aromatic C from PMS α to the methyl group in the para position appears at 134.6 ppm (peak 9) and the carbon from the inimer para to the ring opened epoxide appears at 138 ppm (peak 10). The aromatic C from the inimer α to the quaternary carbon of the ring opened epoxide, due to the proximity to the alcohol, appears at 142 ppm (peak 11). Carbons from intact vinyl groups appear at 144 ppm (peak 12).

4.2.2.1.2 SEC analysis of arb_IB(OH)-MS(16) and arb_IB(OH)-MS(3.5)

The polymers were analyzed by SEC. The resulting information is in Table 4.14. The polymers obtained had multimodal molecular weight distributions which can be seen from the SEC traces of the final polymers (Figure 4.37). The UV traces give proof of PMS blocking, as can be seen by the increase in the UV signal after MS incorporation, as well as confirming the small amount of PMS incorporation in arb_IB(OH)-MS(3.5). Peak molecular weight data is shown in Table 4.15 (peaks were chosen using the RI trace). The SEC results in Table 4.14 show that polymers with high molecular weights ($M_n = 150,000 – 200,000$ g/mol) were obtained. From these results it can be seen that the molecular weight of the polymers increased with increasing conversion, as did the MWD, R_g, R_h, and viscosity of the polymer.
Figure 4.37 SEC traces of polymers from (a) Polymerization 1: \textit{arb}_IB(OH)-6  
(b) \textit{arb}_IB(OH)-MS(3.5)  (c) Polymerization 2: \textit{arb}_IB(OH)-5 
(d) \textit{arb}_IB(OH)-MS(16).
Table 4.14  SEC results of *arb_IB(OH)-MS*(16) and *arb_IB(OH)-MS*(3.5).

<table>
<thead>
<tr>
<th>ID</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>$M_w/M_n$</th>
<th>$R_{g,z}$ (nm)</th>
<th>$R_{h,z}$ (nm)</th>
<th>$\eta_w$ (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>arb_IB(OH)-MS</em>(16)-6</td>
<td>125,200</td>
<td>182,300</td>
<td>1.46</td>
<td>21.5</td>
<td>14.4</td>
<td>54.9</td>
</tr>
<tr>
<td><em>arb_IB(OH)-MS</em>(16)-7</td>
<td>124,800</td>
<td>179,900</td>
<td>1.44</td>
<td>20.2</td>
<td>14.2</td>
<td>56.7</td>
</tr>
<tr>
<td><em>arb_IB(OH)-MS</em>(16)-8</td>
<td>131,900</td>
<td>190,200</td>
<td>1.44</td>
<td>22.2</td>
<td>14.4</td>
<td>57.4</td>
</tr>
<tr>
<td><em>arb_IB(OH)-MS</em>(16)-9</td>
<td>141,800</td>
<td>201,400</td>
<td>1.42</td>
<td>22.3</td>
<td>15.0</td>
<td>59.8</td>
</tr>
<tr>
<td><em>arb_IB(OH)-MS</em>(16)-10</td>
<td>146,600</td>
<td>214,700</td>
<td>1.46</td>
<td>26.0</td>
<td>17.2</td>
<td>64.4</td>
</tr>
<tr>
<td><em>arb_IB(OH)-MS</em>(3.5)-7</td>
<td>207,300</td>
<td>348,100</td>
<td>1.68</td>
<td>28.3</td>
<td>21.4</td>
<td>78.7</td>
</tr>
<tr>
<td><em>arb_IB(OH)-MS</em>(3.5)-8</td>
<td>205,900</td>
<td>330,700</td>
<td>1.61</td>
<td>26.7</td>
<td>21.0</td>
<td>78.6</td>
</tr>
<tr>
<td><em>arb_IB(OH)-MS</em>(3.5)-9</td>
<td>208,700</td>
<td>353,800</td>
<td>1.7</td>
<td>29.3</td>
<td>21.3</td>
<td>79.3</td>
</tr>
<tr>
<td>PS30K</td>
<td>30,200</td>
<td>30,200</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
As determined from $^1$H NMR spectroscopy (Table 4.13) coupled with SEC (Table 4.5) $arb$ _IB(OH)-MS(16) had (8.27 mol%) 16 wt% PMS and $arb$ _IB(OH)-MS(3.5) had (1.69 mol %) 3.5 wt% PMS. This information coupled with SEC data (Table 4.14) allows the determination of the end block composition. $arb$ _IB(OH)-MS(16) before blocking had an $M_n = 115,700$ g/mol, after blocking $M_n = 146,600$ g/mol; therefore, the molecular weight of the end block is:

$$146,600 \text{ g/mol} - 115,700 \text{ g/mol} = 30,900 \text{ g/mol}.$$ 

Since it is known that the polymer has 16 wt% PMS the molecular weight of the polymer from PMS can be calculated as:

$$146,600 \text{ g/mol} * 0.16 = 23,500 \text{ g/mol from PMS}$$

The composition of the copolymer end blocks can be calculated as:

$$\frac{23,500 \text{ g/mol PMS}}{30,900 \text{ g/mol (end block)}} = 75.9 \text{ wt % PMS (24.1 wt% PIB)}$$

The end block composition of $arb$ _IB(OH)-MS(3.5), which prior to blocking had an $M_n = 197,900$ (Table 4.5) and after blocking had an $M_n = 208,700$ (Table 4.14) was calculated in the same manner to give 67.6 wt% PMS and 32.4 wt% PIB. For both the $arb$ _IB(OH)-MS(16) and the $arb$ _IB(OH)-MS(3.5) the wt% PMS in the end block was significantly different from the wt% MS in the feed (Table 4.12) showing a higher wt% of PMS in the end block of the polymer than in the feed Unlike polymers obtained with the MeOIM where the wt% PMS in the end block and the feed were similar.168 This shows that the copolymerization is less than ideal and that MS is preferentially incorporated. The $arb$ _IB(OH)-MS(16) had 38.8% conversion of MS and the
arb_IB(OH)-MS(3.5) had 8.7% conversion of MS, unlike the polymerizations done by Puskas and coworkers\textsuperscript{168} where close to 100% conversion of MS was obtained. The peak molecular weights for both polymers showed an increase in molecular weight after blocking; the peak molecular weights prior to blocking are shown in Table 4.15. This shows that blocking occurred across the entire molecular weight distribution.

Table 4.15  Peak molecular weight of \textit{arb}_IB(OH)-MS(3.5 and 16).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Peak MW (g/mol)</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{arb}_IB(OH)-MS(3.5)</td>
<td></td>
<td>117,900</td>
<td>276,400</td>
<td>-</td>
</tr>
<tr>
<td>\textit{arb}_IB(OH)-MS(16)</td>
<td></td>
<td>107,200</td>
<td>233,700</td>
<td>4,700,000</td>
</tr>
</tbody>
</table>

4.2.2.2 OH content of \textit{arb}_IB(OH)-MS: Proof from NMR and silylation of \textit{arb}_IB(OH)-MS

Evidence for the presence of hydroxyl groups was obtained by \textsuperscript{1}H NMR spectroscopy (Figure 4.35). The wt% of hydroxyl groups in the polymer was calculated. Silylation of the hydroxyl groups in the polymer was carried out to prove the presence of hydroxyl groups in the polymer.

4.2.2.2.1 Calculation of weight% of hydroxyl groups

The weight % of OH groups in \textit{arb}_IB(OH)-MS(16) was calculated based on the total dry weight of the polymer, assuming that 100% of EPOIM and all monomers were incorporated into the polymer. The starting amounts of the monomers used in the polymerization are shown in Table 4.16.
Table 4.16 Calculation of mol % \(arb\text{-}IB(OH)-MS(16 \text{ and } 3.5)\).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Monomer</th>
<th>Grams</th>
<th>FW (g/mol)</th>
<th>Moles</th>
<th>Mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(arb\text{-}IB(OH)-MS(16)) (152.4g polymer)</td>
<td>Inimer</td>
<td>0.7</td>
<td>160</td>
<td>0.004</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>IB</td>
<td>127.43</td>
<td>56</td>
<td>2.276</td>
<td>91.55</td>
</tr>
<tr>
<td></td>
<td>MS</td>
<td>24.27</td>
<td>118</td>
<td>0.206</td>
<td>8.27</td>
</tr>
<tr>
<td>(arb\text{-}IB(OH)-MS(3.5)) (156g polymer)</td>
<td>Inimer</td>
<td>0.7</td>
<td>160</td>
<td>0.004</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>IB</td>
<td>149.86</td>
<td>56</td>
<td>2.676</td>
<td>98.15</td>
</tr>
<tr>
<td></td>
<td>MS</td>
<td>5.44</td>
<td>118</td>
<td>0.046</td>
<td>1.69</td>
</tr>
</tbody>
</table>

Assuming the inimer was incorporated into the polymer, and knowing that the final mass of the dry polymer was 152.4 g, the moles of inimer was calculated based on the wt % PMS seen from the NMR spectrum (Table 4.13) as shown in Table 4.16. Since the weight of the polymer was 152.4 g and the assumption was that 100% of EPOIM was incorporated, using wt% PMS obtained from \(^1\)H NMR spectroscopy (Table 4.13), the grams of PMS and the moles of each monomer can be calculated as follows:

Subtracting 0.7 g of the inimer gives 151.7 g of polymer

\[
\begin{align*}
151.7 \text{ g} \times \frac{16.0}{100} &= 24.27 \text{ g MS} \\
151.7 \text{ g} \times \frac{84.0}{100} &= 127.43 \text{ g IB}
\end{align*}
\]

Since each molecule of inimer contributes one hydroxyl group, one mole of inimer is equivalent to one mole of hydroxyl group. Since the polymer contains 0.18 mol% of inimer, it also contains 0.18 mol% of hydroxyl groups. Thus the weight percentage of hydroxyl groups can be calculated:

\[
\begin{align*}
\text{Wt} \% \text{ OH} &= 0.004375 \text{ moles inimer} \times \frac{17 \text{ g/mol}}{1 \text{ mol}} = 0.074375 \text{ g OH} \\
0.074375 \text{ g} / 152.4 \text{ g polymer} \times 100 &= 0.049 \text{ wt} \% \text{ OH}
\end{align*}
\]
The mole and weight percent OH in \(arb\_IB(OH)-MS(3.5)\) were calculated in the same way and gave 0.16 mol% and 0.048 wt% OH.

### 4.2.2.2 Silylation of \(arb\_IB(OH)-MS(3.5)\)

Silylation of \(arb\_IB(OH)-MS(3.5)\) was carried out to get additional proof for the presence of primary hydroxyl groups in the polymer. The polymer \(arb\_IB(OH)-MS(3.5)\) was used for the silylation because of a shortage of \(arb\_IB(OH)-MS(16)\). Figure 4.38 shows the mechanism of silylation of a primary alcohol.\(^{172}\)

![Figure 4.38 Mechanism of the silylation of primary alcohols.\(^{172}\)](image)

Silylation is a base-catalyzed \(S_N2\) reaction. In this case the DMAP [4-(dimethylamino) pyridine] serves as the catalyst. Since our polymer has an extremely high molecular weight and very few sterically hindered hydroxyl groups, silylations were carried out for 24 hours at room temperature using an excess (2734 x moles of OH) of chlorotrimethylsilane (0.4 mL) and catalyst in a 1:1 molar ratio. DMAP was used instead of pyridine because it is a stronger base.
Initially this reaction was carried out in the presence of dichloromethane, a common solvent for silylations. The polymer appeared to be fully soluble; however, at high molecular weights PIB is not fully soluble in dichloromethane so this attempt was unsuccessful. For the second attempt, silylation was carried out following the procedure of Ivan and coworkers with chloroform as the solvent instead of CCl₄. In this case silylation was complete (Figure 4.39). The CH₂ protons alpha to the hydroxyl group shifted from 3.38 and 3.61 to 3.31 and 3.47 ppm with the presence of new peaks near 0 ppm characteristic of the methyl protons from the trimethyl group of chlorotrimethylsilane.

![Figure 4.39 Silylation of primary alcohols from *arb_IB(OH)-MS(3.5)* (chloroform solvent).](image-url)
This experiment was also repeated using CCl₄ as a non-polar solvent. Figure 4.40 shows that this reaction is also successful when carried out in the presence of CCl₄ in the same manner as Ivan and coworkers.¹⁵⁹ Once again the CH₂ protons alpha to the hydroxyl groups shift to about 3.32 and 3.47 ppm with a new peak appearing at around 0.01 ppm. The appearance of this new peak at 0.01 ppm along with the shifting of the CH₂ protons gives further proof that the primary hydroxyl groups in the polymer were silylated.

Figure 4.40  Silylation of primary alcohols from \textit{arb}_IB(OH)-MS(3.5) (CCl₄ solvent).
4.3 Block copolymer and carbon nanocomposite characterization

Carbon black (CB) was added to \textit{arb\_IB(OH)-MS(16)} and \textit{arb\_IB(OH)-MS(3.5)} as a reinforcing filler to improve the mechanical properties of the polymers. N234 CB was purchased from Cabot and has a CTAB Absorption Specific Surface Area of 121 m\(^2\)/g, with a small particle size (120 Iodine Adsorption No.) and high structure (DBP No. 125). Sixty phr (parts per hundred parts rubber) CB (37.5 wt\%), which is a standard butyl-type recipe, was added by LANXESS to form carbon black-filled composites: \textit{arb\_IB(OH)-MS_CB(16)} and \textit{arb\_IB(OH)-MS_CB(3.5)}. It will be shown that these were nanocomposites with well-dispersed nano-size filler clusters. The physical and mechanical properties were characterized by LANXESS; the surface of the \textit{arb\_IB(OH)-MS(16)} and its composite were analyzed at UA. Characterization of the phase morphologies of \textit{arb\_IB(OH)-MS(16)} and \textit{arb\_IB(OH)-MS(3.5)} were carried out at UA.

4.3.1 Physical properties of \textit{arb\_IB(OH)-MS(16)} and \textit{arb\_IB(OH)-MS_CB(16)}

The physical properties of \textit{arb\_IB(OH)-MS(16)} and \textit{arb\_IB(OH)-MS_CB(16)} were analyzed by DSC and TGA.

4.3.1.1 DSC measurements.

DSC was carried out on the materials (Figure 4.41). Since \textit{arb\_IB(OH)-MS(16)} is a thermoplastic elastomer (TPE), phase separation should be observable. Phase separated copolymers typically exhibit two \(T_g\)'s, characteristic of each of the blocks in the material. Puskas and coworkers\textsuperscript{168} performed DSC studies on dendritic isobutylenes made from the
MeOIM with IB-co-pMS end blocks. A $T_g$ of 116 °C was observed for homo-poly($p$-methylstyrene).

![DSC scan of arb_IB(OH)-MS(16) and arb_IB(OH)-MS_CB(16).](image)

In block copolymers having (IB-co-pMS) end blocks, the $T_g$ from the end blocks could not be observed below 20 mol % (35 wt %) of PMS. A $T_g$ for the end blocks was observed for block copolymers with 20-60 mol%, (35-75 wt%), PMS which ranged from 40 to 80 °C, depending on the wt% PMS. Polymers having PMS content of the end blocks in the 40-60 wt% range had $T_g$’s above room temperature; however the high $T_g$’s could not be detected because of the low overall PMS content.
*arb_IB(OH)-MS(16)*, made from EPOIM, has (IB-co-pMS) end blocks containing 75.9 wt% PMS, as shown in Section 4.2. Figure 4.41 also shows very weak but observable transitions for the high T<sub>g</sub> block. The block copolymer had a T<sub>g</sub> of 105 °C. In the case of *arb_IB(OH)-MS_CB(16)*, the high T<sub>g</sub> increased to 126 °C while the low T<sub>g</sub> was at -67 °C (Figure 4.39). This is significant because the novel composite could be steam-sterilized.

4.3.1.2 TGA measurements of *arb_IB(OH)-MS(16)* and *arb_IB(OH)-MS_CB(16)*

TGA (theromogravimetric analysis) measurements were carried out to determine the thermal degradation behavior of block copolymers (Figure 4.42). The neat *arb_IB(OH)-MS(16)* showed an onset of degradation (point at which there is a sudden large decrease in wt%) at around 332 °C. Close to 100 % weight loss of the polymer occurred by 375 °C. The neat *arb_IB(OH)-MS_CB(16)* showed an onset of degradation at around 397°C. Close to 100% mass loss of the polymer occurred at around 400°C and 37.5 wt% (Figure 4.42 b). The remaining 37.5 wt% is from the CB. The second step in the TGA plot of *arb_IB(OH)-MS_CB(16)* is from the degradation of the CB. The *arb_IB(OH)-MS_CB(16)* showed an increase in heat stability compared to the *arb_IB(OH)-MS(16)*; the degradation temperature increased from 332 °C to 397 °C. This is a result of the CB which is known to improve thermal resistance in polymers and acts as a radical scavenger. This is a 65 °C increase in the degradation temperature! This TGA shows that the carbon black has a profound effect on the heat stability of the *arb_IB(OH)-MS(16)*. An increase of the degradation temperature to 397 °C was also observed in the *arb_IB(OH)-MS_CB(3.5)*
Figure 4.42 TGA plots of: (a) *arb* IB(OH)-MS(16) (b) *arb* IB(OH)-MS_CB(16).
4.3.2 Phase Morphology of \textit{arb\textsubscript{IB}}(OH)-MS and \textit{arb\textsubscript{IB}}(OH)-MS\textsubscript{CB}

The phase morphology of \textit{arb\textsubscript{IB}}(OH)-MS(16) and \textit{arb\textsubscript{IB}}(OH)-MS\textsubscript{CB}(16) was analyzed by TEM and AFM.

4.3.2.1 TEM of \textit{arb\textsubscript{IB}}(OH)-MS and \textit{arb\textsubscript{IB}}(OH)-MS\textsubscript{CB}

Initially samples were prepared for TEM using carbon-coated grids. Polymer solutions of about 0.5 wt\% in THF were dropped onto the grids. After annealing for 24 hours at 140 °C (above the \(T_g\) of PMS as discussed in Chapter 3), the samples were stained using a 2\% aqueous solution of osmium tetroxide (stains PMS domains). Osmium tetroxide was chosen because it is known to stain double bonds as seen with styrene-butadiene-styrene (SBS).\textsuperscript{175,176} Osmium tetroxide stains the aromatic regions in polymers, and results in enhancement of contrast in the PS domains of SBS for TEM. The amount of time necessary for staining was initially unknown. According to the literature the amount of time necessary to stain a sample can range from 5 – 30 minutes depending on the composition of the polymer (the wt\% of each phase).\textsuperscript{177} The initial samples had films with uneven thicknesses; so the films were then prepared by floating the TEM grids in hot water and then dropping the polymer solution onto the grids. Annealing and staining were carried out in the same manner as before. In the TEM images the dark regions represent the PMS domains and the light regions represent the PIB continuous phase. Figure 4.43 shows TEM images of unstained \textit{arb\textsubscript{IB}}(OH)-MS(3.5). [Figure 4.43 (a) and \textit{arb\textsubscript{IB}}(OH)- MS(3.5) stained for 15 minutes (Figure 4.43 (b)]. Only one picture of unstained \textit{arb\textsubscript{IB}}(OH)-MS(3.5) was obtained, so the scales of
the two images in Figure 4.43 are different. The staining can be seen in Figure 4.43 b by the improved contrast in the image.

Figure 4.43  TEM image of: (a) \textit{arb} \_IB(OH)-MS(3.5) unstained and (b) \textit{arb} \_IB(OH)-
MS(3.5) stained with osmium tetroxide for 15 min: dark regions are PMS, light regions are PIB.

Figure 4.44  TEM images of \textit{arb} _IB(OH)-MS(3.5) stained with ruthenium tetroxide: (a) for 30 min and (b) for 60 min.

The PMS domain size was \(~20 \text{ nm}\) before staining, after staining an increase in domain size to \(~40 \text{ nm}\) was observed which may be a result of improved contrast from staining. \textsuperscript{176}
It was decided to try staining with another known staining agent for polystyrene, ruthenium tetroxide, a stronger oxidizing agent. Sample preparation was carried out as before. This time samples were stained for 30 minutes and 1 hour to determine the optimum staining time in an effort to improve contrast. Figure 4.44 shows that after 30 minutes of staining, the PMS domain sizes were ~40-50 nm (Figure 4.44 a) and after 1 hour of staining, the PMS domain sizes were ~40-50 nm (Figure 4.44 b). The domain sizes were fairly consistent between the samples stained for 30 minutes and 1 hour. This indicates that 1 hour of staining should be sufficient to obtain an image with good contrast.

![Figure 4.45 TEM images of (a & b) arb_IB(OH)-MS(3.5) (c & d) arb_IB(OH)-MS(16) stained with ruthenium tetroxide for 1 hour.](image-url)
Figure 4.45 shows TEM images of \textit{arb\_IB(OH)-MS(3.5)} and \textit{arb\_IB(OH)-MS(16)}. These TEM images show that there may be PIB trapped within the discrete PMS domains; this means that the discrete domains are PMS rich. This entrapped PIB and the irregularly dispersed domains are due to the copolymer end blocks and the dendritic structure of the polymer.\textsuperscript{168,178} These TEM images also show that the size of the discrete PMS domains is \textasciitilde40-50 nm.

![Figure 4.45 TEM images of arb\_IB(OH)-MS(3.5) and arb\_IB(OH)-MS(16).]

Figure 4.46 TEM images of cryomicrotomed (a & b) \textit{arb\_IB(OH)-MS(16)} and (c & d) \textit{arb\_IB(OH)-MS\_CB(16)} stained with osmium tetroxide (carried out at the University of Bayreuth in Germany).
TEM images were also obtained from cryomicrotomed samples (carried out at the University of Bayreuth in Germany) of \textit{arb}_{IB(OH)}-\text{MS(16)} with and without carbon black (Figure 4.46). The TEM images of neat \textit{arb}_{IB(OH)}-\text{MS(16)} (Figure 4.46 a & b) and \textit{arb}_{IB(OH)}-\text{MS\_CB} (Figure 4.46 c & d) show irregular phase morphology. The images (Figure 4.46) showed an increase in the size of the discrete domains from 40-50 nm to 70-80 nm for the CB composites. The domain sizes of neat \textit{arb}_{IB(OH)}-\text{MS(16)} are in agreement with those obtained from films spin coated from solution. This increase in domain size shows that carbon black is incorporated into the PMS rich domains of the polymer.\textsuperscript{168} The TEM images also show that there is no agglomeration of carbon black particles indicating that the carbon black particles (N234: particle size 20-30 nm\textsuperscript{179}) are well distributed in the PMS domains of \textit{arb}_{IB(OH)}-\text{MS} forming a true nano-composite, \textit{arb}_{IB(OH)}-\text{MS\_CB}.

4.3.2.2 AFM of \textit{arb}_{IB(OH)}-\text{MS} and \textit{arb}_{IB(OH)}-\text{MS\_CB}

AFM also showed nanoscale phase separation of the rubbery PIB and plastic PMS rich phases in neat and carbon-filled nanocomposites (Figures 4.47 and 4.48); this phase separation imparts mechanical strength. The largest observed plastic domain size (light regions of AFM) in both neat \textit{arb}_{IB(OH)}-\text{MS} block copolymers was < 50 nm, which grew to around 70 nm in carbon black filled nanocomposites. The growth of the plastic domains from the neat to the carbon black filled material indicates CB incorporation into PMS domains. The incorporation of CB into the plastic PMS rich domains is observed in both \textit{arb}_{IB(OH)}-\text{MS (3.5)} and \textit{arb}_{IB(OH)}-\text{MS (16.)} indicated by TEM (Figure 4.46).
It is also evident by looking at the AFM images of the two polymer samples that the amount of PMS in \textit{arb\_IB(OH)-MS (3.5)} is definitely less than in \textit{arb\_IB(OH)-MS (16)}.

![AFM images of \textit{arb\_IB(OH)-MS (3.5)} and \textit{arb\_IB(OH)-MS\_CB (3.5)}](image)

**Figure 4.47** AFM images of \textit{arb\_IB(OH)-MS (3.5)} at (a) 2 \(\mu\)m and (b) 1 \(\mu\)m and \textit{arb\_IB(OH)-MS\_CB (3.5)} at (c) 2 \(\mu\)m and (d) 1 \(\mu\)m.
Figure 4.48  AFM images of $arb$ _IB(OH)-MS (16) at (a) 2 $\mu$m and (b) 1 $\mu$m and $arb$ _IB(OH)-MS CB (16.0) at (c) 2 $\mu$m and (d) 1 $\mu$m.
Both AFM and TEM showed spherical or cylindrical phase morphology of the nanocomposites. The incorporation of CB into the PMS domains explains the increase in the T_g of the PIB-PMS end blocks seen by DSC, this increase in T_g was also observed by Puskas and coworkers.\textsuperscript{168}

4.3.3 Electrical conductivity measurements (Kent State University)

CB-filled materials, depending on the weight percent carbon black, exhibit conductivity, as was discussed in the historical background. Svorcik and coworkers\textsuperscript{24} showed that the percolation limit in polyethylene (PE) is reached at ~6 wt%. Roland and coworkers\textsuperscript{180} showed that the volume resistance of a dendritic PIB containing 9 wt% N234 CB was \textasciitilde10\textsuperscript{12} Ohm cm, dropping to \textasciitilde10\textsuperscript{3} Ohm cm at 37.5% CB. Percolation in PIB was observed at 20 phr CB and in dendritic PIB the percolation threshold was 30 phr CB indicating more agglomeration in the dendritic PIB.\textsuperscript{180} Surprisingly, with 37.5 wt% CB the novel nanocomposite \textit{arb}_IB(OH)-MS_CB(16) had \textit{3}\times10\textsuperscript{11} Ohm cm resistance demonstrating excellent filler dispersion. Based on TEM, AFM, conductivity and thermal properties, we conclude that the CB filler preferentially segregates in the PMS-containing phases, forming a true nanocomposite.

4.3.4 Mechanical properties of \textit{arb}_IB(OH)-MS(16) and \textit{arb}_IB(OH)-MS_CB(16) (LANXESS)

At a rate of 500 mm/min according to ASTM D 412-06a, neat \textit{arb}_IB(OH)-MS(16) had a tensile strength at break of 6.8 MPa with 660% elongation, while the CB filled \textit{arb}_IB(OH)-MS_CB(16) showed 13.8 MPa tensile strength at break with 400%
elongation, demonstrating reinforcement of the material by the CB (Figure 4.49). The modulus at 100% strain shows an increase in the stress from 0.5 MPa in neat \textit{arb\_IB(OH)-MS(16)} to 2.2 MPa in \textit{arb\_IB(OH)-MS\_CB(16)}. This indicates that the CB particles stiffen the material.

![Stress-strain plots](image)

**Figure 4.49** Stress-strain plots of \textit{arb\_IB(OH)-MS(16)} and \textit{arb\_IB(OH)-MS\_CB(16)}.

The doubling in the tensile strength from the neat \textit{arb\_IB(OH)-MS(16)} to the \textit{arb\_IB(OH)-MS\_CB(16)} shows the increase in the strength of the polymer from CB. Reinforcement by CB also results in a more rigid material, as shown by the lower elongation at break in \textit{arb\_IB(OH)-MS\_CB(16)}. Comparison of the softness (Shore A) and the tensile properties of the new materials to a commercial SIBS with 18 wt% PS is given in Table 4.17.\textsuperscript{144}
Table 4.17 Mechanical properties of biomaterials.

<table>
<thead>
<tr>
<th>ID</th>
<th>Shore A</th>
<th>Modulus at 100% (MPa)</th>
<th>UTS&lt;sup&gt;a&lt;/sup&gt; (MPa)</th>
<th>Elongation at Break (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>arb_IB(OH)-MS(16)</td>
<td>52</td>
<td>0.54</td>
<td>7.6</td>
<td>660</td>
</tr>
<tr>
<td>arb_IB(OH)-MS_CB(16)</td>
<td>56</td>
<td>2.26</td>
<td>13.8</td>
<td>400</td>
</tr>
<tr>
<td>SIBS&lt;sup&gt;144&lt;/sup&gt;</td>
<td>-</td>
<td>0.5</td>
<td>7.3</td>
<td>640</td>
</tr>
<tr>
<td>Silicone&lt;sup&gt;c&lt;/sup&gt;</td>
<td>50</td>
<td>1.5</td>
<td>10.2</td>
<td>850</td>
</tr>
</tbody>
</table>

<sup>a</sup>UTS- ultimate tensile strength; <sup>b</sup> rate of 500 mm/min; <sup>c</sup>MED-4050 silicone elastomer sheeting from NuSil

Despite *arb_IB(OH)-MS(16)* having copolymer end blocks (PIB-PMS) it has very similar mechanical properties to SIBS. In comparison with *arb_IB(OH)-MS(16)*, the tensile strength of *arb_IB(OH)-MS_CB(16)* increases, and there is a reduction in elongation, and increase in hardness, but very slight.

4.3.5 Surface analysis of *arb_IB(OH)-MS(16)* and *arb_IB(OH)-MS_CB(16)*

The surface of *arb_IB(OH)-MS(16)* and *arb_IB(OH)-MS_CB(16)* was analyzed using contact angle goniometry and XPS. For comparison, a non-hydroxyl functionalized *arb_SIBS* and medical grade silicone from NuSil (MED-4050) were used.

4.3.5.1 Contact angles of *arb_IB(OH)-MS(16)* and *arb_IB(OH)-MS_CB(16)*

The surfaces of spin coated *arb_IB(OH)-MS(16)* and compression molded *arb_IB(OH)-MS_CB(16)* were analyzed using static water contact angles and XPS to determine the hydrophilicity of the surface. Compression molded sheets of *arb_IB(OH)*-
MS_CB(16) were used since it could not be spin-coated. Contact angle measurements of the block copolymers were taken along with that of a linear PIB standard (PIB 135K: $M_n = 135,000$ g/mol), a $arb$-SIBS made with MeOIM so it did not contain OH groups (06LD002, $M_n = 224,300$ g/mol, $M_w/M_n = 2.39$, 19 wt% PS), and a medical grade silicone (Table 4.18). $arb$-IB(OH)-MS, with hydroxyl groups in its dendritic PIB core, had a lower water contact angle than both PIB 135K and $arb$-SIBS (Table 4.18).

Table 4.18  Comparison of contact angles of PIB-based polymers to silicone.

<table>
<thead>
<tr>
<th></th>
<th>PIB 135K</th>
<th>$arb$-IB(OH)-MS(16)</th>
<th>$arb$-IB(OH)-MS_CB(16)</th>
<th>$arb$-SIBS$^a$</th>
<th>Silicone$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>96.7 (2.5)</td>
<td>91.9 (1.7)</td>
<td>81.2 (7.5)</td>
<td>95.1 (1.1)</td>
<td>117.7 (0.43)</td>
</tr>
</tbody>
</table>

$^*$stdev in parenthesis, $^a$ (06LD002, $M_n = 224,300$ g/mol, $M_w/M_n = 2.39$, 19 wt% PS) $^b$MED-4050 silicone elastomer sheeting from NuSil

This supports our hypothesis$^{181}$ that under water some -OH groups attached to the PIB core might migrate to the surface. It has been reported earlier that polar groups in non-polar rubbers, with $T_g$ below room temperature, can migrate to the surface in a polar environment because of the mobility of the elastomeric chains.$^{182}$ All PIB-containing materials had significantly lower water contact angle than the control silicone rubber, indicating higher hydrophilicity in the former. Interestingly, the $arb$-IB(OH)-MS_CB(16) had the lowest contact angle. This lower contact angle indicates an increase in the hydrophilicity of the material.
4.3.5.2 XPS results of \textit{arb}_IB(OH)-MS(16) and \textit{arb}_IB(OH)-MS_CB(16)

XPS at a 90° grazing angle (~10 nm depth) revealed only C, H, and O in the surface layer of \textit{arb}_IB(OH)-MS(16) and \textit{arb}_IB(OH)-MS_CB(16); no \(\pi-\pi^*\) transition was observed.

Table 4.19 XPS results for \textit{arb}_IB(OH)-MS(16) and \textit{arb}_IB(OH)-MS_CB(16)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>XPS Survey Scan (Atomic %)</th>
<th>High Resolution C1s Analysis (Atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>\textit{arb}_IB(OH)-MS(16)</td>
<td>94.2</td>
<td>3.7</td>
</tr>
<tr>
<td>\textit{arb}_IB(OH)-MS_CB(16)</td>
<td>98.4</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The \(\pi-\pi^*\) transition is an indication of the presence of PS on the surface. Since this transition was not observed, it means that the surface is purely PIB. High resolution XPS results are shown in Table 4.19. First a survey scan was taken to determine the composition of the surface of the polymers. Then high resolution C1s analysis was run on just the C1s peaks which were de-convoluted to determine the different types of carbon present on the surface (shown in the last two columns in Table 4.19). The results in Table 4.19 show that the amount of oxygen found in the survey scan of \textit{arb}_IB(OH)-MS(16) was higher than the atomic % (At %) of carbon bonded to oxygen from the high resolution C1s analysis. This shows that there is oxygen on the surface which is not from the polymer. The silicon present on the surface and the high atomic percent (At %) of oxygen indicates that there is silicon dioxide on the surface of \textit{arb}_IB(OH)-MS(16) from the silicon wafer. The silicon on the surface of \textit{arb}_IB(OH)-MS_CB(16) is most likely
from silicone grease. Both \textit{arb\_IB(OH)-MS16} and \textit{arb\_IB(OH)-MS\_CB(16)} have similar amounts of carbon bonded to oxygen on the surface. Figure 4.50 shows a typical survey scan of \textit{arb\_IB(OH)-MS(16)} over all binding energies in XPS which shows all of the elements in the polymer. This shows that only carbon and oxygen are present on the surface of the polymer, with a small amount of silicon. The carbon bound to oxygen from either C-OH or C-O-C in the polymers could be at least partially from hydroxyl groups in the polymer (from the primary hydroxyl groups in the PIB core).

![XPS Scan](image)

Figure 4.50 XPS of \textit{arb\_IB(OH)-MS(16)}, 45° grazing angle.

If the carbon from either C-OH or C-O-C was from hydroxyl groups, this means that at least some of the primary hydroxyl groups in the polymer migrated to the surface; however, this is not sufficient evidence to draw that conclusion. The surface composition measured in air does not explain the significantly lower water contact angle of the CB which suggests that in water hydroxyl groups may be drawn to the surface of the polymer resulting in the decrease in the water contact angle.
In summary, composites of \textit{arb\_IB(OH)-MS\_CB(3.5)} and \textit{arb\_IB(OH)-MS\_CB(16)} were made with 37.5 wt% CB. DSC of \textit{arb\_IB(OH)-MS\_CB(16)} showed an increase in the \(T_g\) of the copolymer end block from 105 °C in the neat material to 126 °C in the composite resulting in a material that can be steam sterilized. TGA showed that CB incorporation resulted in a 65 °C increase in the heat resistance of \textit{arb\_IB(OH)-MS(16)} and \textit{arb\_IB(OH)-MS(3.5)}. TEM images of \textit{arb\_IB(OH)-MS(3.5)} and \textit{arb\_IB(OH)-MS(16)} showed irregularly dispersed, discrete PMS-rich domains of the order of 40-50 nm. TEM images of cryomicrotomed \textit{arb\_IB(OH)-MS(16)} and \textit{arb\_IB(OH)-MS\_CB(16)} showed an increase from 40-50 nm domain size in the neat material to 70-80 nm domain size in \textit{arb\_IB(OH)-MS\_CB(16)}. This shows CB incorporation into the PMS-rich domains. These results were confirmed by AFM. The absence of CB agglomeration in \textit{arb\_IB(OH)-MS\_CB(16)} and 3 \times 10^{11} \text{ Ohm cm} resistivity demonstrated excellent filler dispersion within the PMS rich domains and showed true nanocomposite formation. The \textit{arb\_IB(OH)-MS\_CB(16)} had twice the tensile strength of \textit{arb\_IB(OH)-MS(16)} showing reinforcement by CB. \textit{arb\_IB(OH)-MS(16)} exhibited a contact angle 5° lower than PIB. \textit{arb\_IB(OH)-MS\_CB(16)} exhibited a 15° decrease in contact angle compared to \textit{arb\_IB(OH)-MS(16)}. XPS showed the presence of oxygen as well as C-O at the surface of both \textit{arb\_IB(OH)-MS(16)} and \textit{arb\_IB(OH)-MS\_CB(16)}.

4.4 Biocompatibility studies

To assess biocompatibility of the nanocomposites, materials were checked for extractables and \textit{in vivo} and \textit{in vitro} tests were carried out according to ISO 10 933-5 in
collaboration with Dr. El Fray and Dr. Piotr Prowans at the Szczecin University of Technology, Szczecin, Poland.

4.4.1 Purification of \textit{arb\_IB(OH)-MS(16)} for biomedical use using UA inimer and recipe (LANXESS) – in-kind contribution to NSF project

The purity of \textit{arb\_IB(OH)-MS(16)} was checked according to the specifications set forth in the ISO standard method (discussed in Chapter three). The presence of residual polar contaminants or homo-poly\textit{(p-methylstyrene)} may affect the biocompatibility of biomaterials. After exhaustive Soxhlet extraction by three different solvents [to remove homo-poly\textit{(p-methylstyrene)}, homo-polyisobutylene, and polar contaminants] there was no decrease in mass, indicating that \textit{arb\_IB(OH)-MS(16)} purified with our new process was free of contaminants.\textsuperscript{158}

![RI trace: \textit{arb\_IB(OH)-MS(16)} (D) before extraction and (E) after extraction.](image)

This new process for purification involves re-precipitation from a 5 wt\% solution in THF into acetone and isopropyl alcohol as discussed in Chapter 3. Polymers purified by this
process were found to contain less than 5 ppm residual MS and no detectable nonpolar contaminants. SEC analysis supported this conclusion (Figure 4.51). The RI trace of \textit{arb}_{IB(OH)}-MS(16) before and after extraction shows no measurable mass loss. This demonstrates that there is no need of further purification.

4.4.2 \textit{In vitro} studies

Two \textit{in vitro} studies were carried out according to the ISO standard 10 993-5. A buffer uptake study was performed to check if swelling of \textit{arb}_{IB(OH)}-MS(16) and \textit{arb}_{IB(OH)}-MS\_CB(16) will occur in a physiological environment. A cell apoptosis (cell death) study (carried out on a non-hydroxyl functionalized \textit{arb}\_SIBS with $M_n=220,300$, $M_w/M_n=1.87$ and 32.6 wt% PS) was performed to see if the material will allow for cell growth. \textit{arb}\_SIBS was chosen because hydroxyl-functionalized material was unavailable at the time.

4.4.2.1 \textit{In vitro} cytocompatibility test of \textit{arb}\_SIBS

The \textit{in vitro} cytocompatibility test was carried out with \textit{arb}\_SIBS, a commercially available SIBS (Kaneka 103T), and a medical grade silicone to determine the percent of apoptotic cells. Apoptosis is programmed cell death\textsuperscript{183} (cell suicide) necessary to maintain a healthy organism. Apoptosis occurs when a cell becomes ‘diseased’, infected by toxic chemicals, or malfunctioning. This test is a good indicator of the materials ‘toxicity’ or biocompatibility.

\textit{In vitro} studies with 3T3 mouse fibroblasts revealed much less apoptosis with \textit{arb}\_SIBS than with silicone (5 vs. 25\%) or SIBS (7.5\%) (Figure 4.52). These results
show that \textit{arb\_SIBS} is the most biocompatible of these materials in terms of cytocompatibility. This might be a result of the purification procedure we used with our \textit{arb\_SIBS} as compared to purification of commercially available SIBS.

![Cell apoptosis](image)

**Figure 4.52** Cell apoptosis \textit{in vitro}.

### 4.4.2.2 Buffer uptake study of \textit{arb\_IB(OH)-MS}(16) and \textit{arb\_IB(OH)-MS\_CB}(16)

Polymers were compression molded, cut into buttons, and placed in a pH 7.4 buffer at 36 °C as described in Chapter 3. These buttons were checked for mass loss by gravimetry over a 20 day period. The \textit{in vitro} degradation study showed that \textit{arb\_IB(OH)-MS}(16) and \textit{arb\_IB(OH)-MS\_CB}(16) are quite stable in pH 7.4 monophosphate buffer. Figure 4.53 shows buffer uptake data. Less than 1% uptake was observed with \textit{arb\_IB(OH)-MS}, while \textit{arb\_IB(OH)-MS\_CB} showed a 2% uptake. This would seem to indicate that the film with carbon black is more hydrophilic than the neat polymer film. This finding is in line with contact angle data shown in Table 4.18.
4.4.3 In vivo implantation studies of $arb_{\text{IB(OH)}}$-MS(16) and $arb_{\text{IB(OH)}}$-MS_CB(16)

Since $arb_{\text{IB(OH)}}$-MS(16) and $arb_{\text{IB(OH)}}$-MS_CB(16) did not show degradation in vitro, preliminary in vivo biocompatibility studies were performed. The polymers were studied for biocompatibility both in muscles and in bones of rabbits for six months.

4.4.3.1 In vivo implantation in muscle

The results from in vivo muscle implantation show that after implantation of $arb_{\text{IB(OH)}}$-MS(16) for 180 days there was no inflammation of the surrounding muscle.
tissue as can be seen in Figure 4.54. \textit{arb}_IB(OH)-MS_CB(16) (Figure 4.55) also had cells compactly adhered to the surface, indicating that the tissue had very good adhesion to the nanocomposite. The capsule thickness around the implanted nanocomposites was measured and the comparison can be seen in Figure 4.56. It can be seen that the samples after Soxhlet extraction had slightly thinner capsules than before; both samples had slightly thicker capsules than medical grade silicone rubber. Interestingly, \textit{arb}_IB(OH)-MS_CB(16) had the thinnest capsules. The tissue changes observed with \textit{arb}_IB(OH)-MS(16) and \textit{arb}_IB(OH)-MS_CB(16) were similar to those obtained with silicone, with no evidence of contact necrosis being observed. From these results it is apparent that the small increase in hydrophilicity of \textit{arb}_IB(OH)-MS(16) is not enough to significantly reducing the fibrous capsule thickness as presented in Figure 4.56.

What could be the major factors contributing to the decreased immune response of \textit{arb}_IB(OH)-MS_CB(16)? In general, the CB network greatly reinforces “gum” rubber, leading to an almost ten-fold increase in tensile strength, and renders the compound electrically conductive \cite{173,184}. When deformed, the carbon network breaks reversibly which gives the compounds excellent dynamic properties. For good network properties, the elastomer needs to be well entangled which requires high molecular weight of the elastomer phase. The surface of these “filled” CB compounds, however, is pure elastomer and the carbon is not exposed. \cite{173} The volume resistance of a dendritic PIB containing 9 wt\% N234 CB was shown to be \( \sim 10^{12} \) Ohm cm, dropping to \( \sim 10^3 \) Ohm cm at 37.5\% CB.\cite{160} Surprisingly with 37.5 wt\% CB the novel nanocomposite had \( 3 \times 10^{11} \) Ohm cm resistivity, demonstrating excellent filler dispersion. This resulted in substantial reinforcement and T\textsubscript{g} increase.
Figure 4.54  *arb_IB(OH)-MS(16):* (a) Cross section of the muscle with the connective tissue capsule  (b)the connective tissue capsule around the polymer: placement of polymer indicated by arrows.
Figure 4.55 *arb_IB(OH)-MS_CB(16)*: (a) Cross section of the muscle with the connective tissue capsule around the polymer 
(b) connective tissue capsule around carbon black filled polymer showing compactly adhered cells.
While all implanted samples had tissue reaction similar to the control silicone rubber, in soft tissues \( \text{arb}_1 \text{B(OH)-MS(16)} \) had the thinnest capsules around the implants after 180 days in the rabbits. Both the more hydrophilic and nano-textured surface may have contributed to this finding. The CB nanocomposite is also expected to have greatly reduced creep and improved dynamic properties, similar to those found in all CB-rubber composites.\(^{173,185,186}\) Degradation assessment in phosphate buffer solution demonstrated that both \( \text{arb}_1 \text{B(OH)-MS(16)} \) and \( \text{arb}_1 \text{B(OH)-MS(CB(16))} \) are stable and showed buffer uptake lower than 1-2%. 

Figure 4.56 Capsule thickness around \( \text{arb}_1 \text{B(OH)-MS(16)} \) (E – polymer after extraction, D- polymer before extraction), \( \text{arb}_1 \text{B(OH)-MS(CB(16))} \) and SIL after 180 days implantation.
4.4.3.2 *In vivo* implantation in bone

Since breast implants are placed in the area surrounding the ribs, hard tissue response was also investigated. The polymers implanted subperiostially (under the lining of the bone) against the femoral (thigh) bone showed good integration and biocompatibility. In Figure 4.57(a) the connective tissue capsule around *arb_IB*(OH)-MS(16) can be seen and the callus (toughened or thickened tissues) formed after 180 days of implantation is visible in Figure 4.57(b). Moreover, after the removal of the periosteum from the surface of the bone and implantation of the polymer against the femur, a newly formed callus can be seen in Figure 4.57(c). New bone tissue formed without any pathological changes. This shows good integration of the polymer into the hard tissue. The *arb_IB*(OH)-MS_CB(16) also showed good integration with the bone (Figure 4.58). The connective tissue produced a callus (indicated by the arrow in Figure 4.58) and there was no defect in the bone. A capsule formed under the periosteum was covered with a callus showing good integration with the bone tissue. Figure 4.59 shows the number of Havers channels (channels in the bone present for vascular and nerve infiltration) in the capsules surrounding the implanted polymers compared to normal bone and periosteum. The presence of Havers channels is an indication that the material is being integrated into the bone. These results show that our polymers behaved comparably to the control sample (silicone) when implanted into soft and hard tissues. The pathology of internal organs, including rabbit liver, kidney, and heart after implantation was also investigated. The presence of dead or damaged tissue in the organs of the rabbit would be an indication that the implanted materials were toxic to the rabbits.
Figure 4.57 arb IB(OH)-MS(16): (a) bone, connective tissue capsule (b) callus formed in the middle after implantation into periosteum (c) newly formed callus after the removal of the periosteum from the surface of the bone and implantation of the polymer in this site.

The unchanged morphology of rabbit liver hepatocytes (liver cells), seen in Figure 4.60(a) as well as of the kidneys [Figure 4.60 (b) and (c)], and heart [Figure 4.60 (d)] and the lack of parenchymal necrosis (death of the functional cells of the organ) also indicated that exposure to the materials did not cause cytotoxic reactions.
Figure 4.58  Carbon black filled polymer, callus$^4$ (arrow) under the periosteum.

Figure 4.59  Number of Havers channels: (E) \textit{arb IB(OH)-MS(16)} after extraction  (D) \textit{arb IB(OH)-MS(16)} before extraction  (D+C) \textit{arb IB(OH)-MS CB(16)}  (S) silicone  (P) periosteum (B) bone.
Figure 4.60  Rabbit internal organs after implantation of \textit{arb IB(OH)-MS(16)} and \textit{arb IB(OH)-MS_CB(16)}: (a) liver morphology  (b & c) kidneys  (d) heart.

4.5  Modular surface modification of \textit{arb IB(OH)-MS(3.5)} – proof of concept

As discussed in section 4.3.5.1, although a small decrease in water contact angle was observed in \textit{arb IB(OH)-MS(16)} compared to \textit{arb SIBS}, the amount of hydroxyl groups that can be introduced by the inimer into the \textit{arb IB} core is low (0.049 wt%). Thus we concluded that this level of hydroxyl content is too low to have a profound effect on the surface. For these experiments \textit{arb IB(OH)-MS(3.5)} was used because of a shortage of \textit{arb IB(OH)-MS(16)}. The amount of hydroxyl groups in \textit{arb IB(OH)-MS(3.5)} is low (0.048 wt% OH). As with \textit{arb IB(OH)-MS(16)}, \textit{arb IB(OH)-MS(3.5)} showed a slight decrease in contact angle compared to \textit{arb SIBS} (Table 4.18). Therefore,
another method was needed to modify the surface. Professor Puskas developed the concept of “modular” surface functionalization, “gluing” low molecular weight functionalized polyisobutylenes to the surface of our TPE’s. When “gluing” the functionalized polymer, which has been dissolved in solvent, onto the surface of the block copolymers, the outer layer of PIB will soften allowing the PIB block of the functionalized polymer to penetrate and entangle into the PIB surface layer (Figure 4.61). This will allow the chemistry of the surface to be changed depending on the need. Thymine-functionalized polyisobutylene (PIB-T) was decided upon because of thymine’s ability to hydrogen bond, which would allow for the attachment of drugs or other molecules to the surface of the polymer as previously reported with thymine functionalized polystyrene by the Puskas group.\textsuperscript{9,153} It was expected that in a physiological environment thymine groups will migrate closer to the surface allowing for hydrogen bonding of proteins to the surface. Earlier reports have shown that polar groups in non-polar rubbers, with $T_g$ below room temperature, can migrate to the surface in a polar environment due to chain mobility (Figure 4.61).\textsuperscript{182} PIB-T was made by Mustafa Sen.\textsuperscript{187} Acrylate-functionalized poly(isobutylene) (PIB-Ac) was synthesized by the reaction of PIB-OH (made as reported by Song and coworkers\textsuperscript{152}) with acryloyl chloride in the presence of triethylamine as a weak base. Thymine was added to the acrylated PIB by Michael addition in DMSO/THF using $t$-BuOK as a weak base to make the thymine more nucleophilic (Figure 4.62). The spin coated films are shown in Table 4.21. \textit{arb}_IB(OH)-MS(3.5) has a high contact angle, the same as the PIB standard. In contrast, the PIB-T and the modular surface functionalized \textit{arb}_IB(OH)-MS/PIB-T had very similar contact angles of around 80°.
Figure 4.61 Modular surface functionalization: Silicon wafer with (a) arb_IB(OH)-MS(3.5) film (b) PIB-T deposition and (c) arb_IB(OH)-MS(3.5) film with PIB-T film (T represents thymine) entangled into outer PIB block of arb_IB(OH)-MS(3.5).
Figure 4.62  Synthetic strategy for the synthesis of PIB-T (Mₙ= 5500 g/mol and Mₘ/Mₙ = 1.07).

For preliminary studies the PIB-T was spin coated onto a layer of *arb_IB(OH)-MS(3.5)* (which was spin coated onto a silicon wafer). This was expected to result in the PIB block of PIB-T entangling into the outer PIB layer of the *arb_IB(OH)-MS(3.5).*
4.5.1 Ellipsometry results for spin coated films.

Film thickness measurements were obtained by ellipsometry for \textit{arb}\_IB(OH)-MS(3.5), PIB-T and \textit{arb}\_IB(OH)-MS(3.5)/PIB-T (Table 4.20). The results from ellipsometry show that the blended film, \textit{arb}\_IB(OH)-MS(3.5)/PIB-T is thicker than the \textit{arb}\_IB(OH)-MS(3.5) film. This is an indication that a layer of PIB-T was successfully added to \textit{arb}\_IB(OH)-MS(3.5). When only PIB-T was coated onto the silicon wafer, a thinner layer was obtained than with \textit{arb}\_IB(OH)-MS(3.5) because of the higher MW (higher viscosity) of the latter. Evidence of surface modification was obtained using contact angle measurements to determine if the hydrophilicity of the surface increased with PIB-T.

<table>
<thead>
<tr>
<th></th>
<th>\textit{arb}_IB(OH)-MS(3.5)</th>
<th>PIB-T</th>
<th>\textit{arb}_IB(OH)-MS(3.5)/PIB-T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film thickness (nm)</td>
<td>190.9</td>
<td>118.2</td>
<td>228.7</td>
</tr>
</tbody>
</table>

4.5.2 Contact angle results from surface functionalization

Contact angle measurements were taken for \textit{arb}\_IB(OH)-MS(3.5), PIB-T, \textit{arb}\_IB(OH)-MS/PIB-T, and a PIB standard (PIB135K). Contact angle results for all of the spin coated films are shown in Table 4.21. \textit{arb}\_IB(OH)-MS(3.5) has a high contact angle, the same as the PIB standard. In contrast, the PIB-T and the modular surface functionalized \textit{arb}\_IB(OH)-MS/PIB-T had very similar contact angles of around 80°.
Table 4.21 Contact angle results from “gluing” of PIB-T.

<table>
<thead>
<tr>
<th></th>
<th>PIB135K</th>
<th>\textit{arb_IB(OH)-MS(3.5)}</th>
<th>PIB-T</th>
<th>\textit{arb_IB(OH)-MS(3.5)/ PIB-T}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Angles</td>
<td>96.7(2.5)</td>
<td>96.7 (3.5)</td>
<td>81.4 (2.3)</td>
<td>80.2 (1.7)</td>
</tr>
</tbody>
</table>

| standard deviation in parenthesis

These results show that both samples with PIB-T exhibit an increase in hydrophilicity. Soaking of \textit{arb\_IB(OH)-MS(3.5)} and PIB-T films in de-ionized water for 24 hours prior to taking contact angles showed a further decrease in the contact angle of \textit{arb\_IB(OH)-MS(3.5)} by 4° and of the PIB-T by 3.5° (Table 4.22). This is a strong indication that in an aqueous environment, hydrophilic groups are drawn to the surface of the material, which results in a decrease in contact angle (increase in hydrophilicity).

Table 4.22 Contact angle results of films soaked in water for 24 hours.

<table>
<thead>
<tr>
<th></th>
<th>\textit{arb_IB(OH)-MS(3.5)}</th>
<th>PIB-T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Angles</td>
<td>92.8 (1.7)</td>
<td>77.9 (1.3)</td>
</tr>
</tbody>
</table>

4.5.3 XPS results from modular surface functionalization of \textit{arb\_IB(OH)-MS(3.5)}

To detect the presence of thymine at or near the surface of the films, XPS was carried out. Three different grazing angles were used to penetrate the surface of the films to different depths: 15° (~2.5 nm), 45° (5 nm), and 90° (10 nm). For this study four different materials were used. One fresh film of PIB-OH was tested to see the surface
composition of the films prior to functionalization with thymine. PIB-T, \(arb\text{-}IB(OH)\)-MS(3.5), and \(arb\text{-}IB(OH)\)-MS(3.5)/PIB-T were also studied.

4.5.3.1 Determination of necessary conditions for XPS sample preparation

To determine the necessary conditions of sample preparation to obtain repeatable results, preliminary experiments were carried out. Preliminary results were obtained using a 45° grazing angle which penetrates ~5 nm into the surface of the film. Figure 4.63 shows that within ~5 nm of the surface nitrogen is present at 0.4 and 0.3 At % in PIB-T and \(arb\text{-}IB(OH)\)-MS(3.5)/PIB–T films respectively. Oxygen is also present in both PIB-T and \(arb\text{-}IB(OH)\)-MS(3.5)/PIB-T. The amount of oxygen present in \(arb\text{-}IB(OH)\)-MS(3.5)/PIB-T was nearly double the amount found in PIB-T. These results lead to the conclusion that there is moisture or adsorbed CO\(_2\) on the film. XPS was then obtained on \(arb\text{-}IB(OH)\)-MS(3.5) as well as PIB-T and \(arb\text{-}IB(OH)\)-MS(3.5)/PIB-T. Measurements were taken at 15°, 45°, and 90° X-ray angles to see if a gradient in the amount of nitrogen and oxygen content could be seen approaching the surface of the film. The results obtained are in Table 4.23. \(arb\text{-}IB(OH)\)-MS(3.5) showed that no nitrogen was present in the film; however, the oxygen level was quite noticeably higher at the 15° angle. The amount of oxygen was also quite high in the PIB-T. Results from PIB-T and \(arb\text{-}IB(OH)\)-MS(3.5)/PIB-T show that as you approach the surface of the films the nitrogen content decreases (Table 4.23). In the table “ND” means not detectable, indicating that the At% is below 0.1 ppm which is the detection limit of the instrument.\(^{188}\) The oxygen content in the \(arb\text{-}IB(OH)\)-MS/PIB-T remains low at all angles.
Figure 4.63  XPS results (low resolution- 93.9 eV): (a) PIB-T 2 wt% and (b) \textit{arb\_IB(OH)-MS(3.5)/PIB-T 3/2 wt%}, taken at a 45° X-ray angle.

Figure 4.64  Survey scan of \textit{arb\_IB(OH)-MS(3.5)}. 

179
The survey scan of \textit{arb IB(OH)-MS(3.5)} (Figure 4.64) also showed the presence of silicon in the sample which is most likely from the wafer. This is a result of the wafers with the films being cut to obtain a small piece to fit on the sample mount of the instrument. The large amount of oxygen on the surface at 15° in \textit{arb IB(OH)-MS(3.5)} and the presence of silicon raised the question of whether or not the films would give reproducible results no matter where the beam was focused on the sample.

Table 4.23  Summary of XPS data.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>15° (At %)</th>
<th>45° (At %)</th>
<th>90° (At %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N1s  O1s</td>
<td>N1s  O1s</td>
<td>N1s  O1s</td>
</tr>
<tr>
<td>\textit{arb IB(OH)-MS}</td>
<td>ND  2.5</td>
<td>ND  0.5</td>
<td>ND  0.2</td>
</tr>
<tr>
<td>PIB-T</td>
<td>-  -</td>
<td>0.2  1.5</td>
<td>0.3  3.8</td>
</tr>
<tr>
<td>\textit{arb IB(OH)-MS/PIB-T}</td>
<td>ND  0.2</td>
<td>0.2  1.2</td>
<td>0.1  0.1</td>
</tr>
</tbody>
</table>

* At% = atomic %

Table 4.24 shows that with old films, the amount of oxygen in the samples had increased and varies greatly from spot to spot. One fresh film of PIB-OH \((M_\text{w}= 5500 \text{ g/mol and } M_\text{w}/M_\text{n} = 1.07)\) as well as an old film of PIB-OH were tested to see how much oxygen is on the surface of the films when the films are fresh, as well as to see how much should be in the precursor of PIB-T. The fresh PIB-OH film shows that as long as the samples are fresh, the repeatability of XPS is very good. These results showed two other things: the films must be made fresh and transported for XPS under vacuum, and smaller pieces must be spin-coated to avoid the presence of silicon in the samples. Once a reliable method of sample preparation had been determined, XPS was carried out on the PIB-OH, \textit{arb IB(OH)-MS(3.5)}, PIB-T, and \textit{arb IB(OH)-MS(3.5)/PIB-T} films.
Table 4.24 XPS for proof of repeatability of results.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Run 1 (At%)</th>
<th>Run 2 (At%)</th>
<th>Run 3 (At%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N1s  O1s</td>
<td>N1s  O1s</td>
<td>N1s  O1s</td>
</tr>
<tr>
<td>PIB-OH (fresh)</td>
<td>ND  1.1</td>
<td>ND  0.5</td>
<td>ND  1.0</td>
</tr>
<tr>
<td>PIB-OH (old)</td>
<td>ND  7.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>arb_IB(OH)-MS (old)</td>
<td>ND  6.0</td>
<td>ND  4.2</td>
<td>ND  5.4</td>
</tr>
<tr>
<td>PIB-T (old)</td>
<td>0.3  8.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>arb_IB(OH)-MS/PIB-T (old)</td>
<td>0.3  4.6</td>
<td>0.4  4.8</td>
<td>-</td>
</tr>
</tbody>
</table>

4.5.3.2 XPS results from modular surface functionalization with PIB-T

XPS results were obtained for all four samples at 93.9 eV (low resolution) at 15°, 45° and 90° angles (Table 4.25). When silicon (from silicon dioxide) is found in the samples, the oxygen 1s peaks can be de-convoluted to determine the amount of oxygen from silicon in the samples. When there was silicon present, two bands were seen in the oxygen peak, one at 532 eV from oxygen bound to carbon, and another peak at 534 eV from oxygen in silicone. Using the percentages of each of these peaks gives a better idea how much of the oxygen present is from the sample.

Table 4.25 XPS results for modular surface functionalization: proof of concept.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>15 degrees (At %)</th>
<th>45 degrees (At %)</th>
<th>90 degrees (At %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N1s   O1s</td>
<td>N1s   O1s</td>
<td>N1s   O1s</td>
</tr>
<tr>
<td>PIB-OH</td>
<td>ND 3.9(1.1)</td>
<td>ND 1.0</td>
<td>ND 4.7(.7)</td>
</tr>
<tr>
<td>arb_IB(OH)-MS</td>
<td>ND     ND</td>
<td>ND 0.4(0.1)</td>
<td>ND 0.3</td>
</tr>
<tr>
<td>PIB-T</td>
<td>0.2 1.32(.18)</td>
<td>0.2 6.4(.1)</td>
<td>0.3 2.8</td>
</tr>
<tr>
<td>arb_IB(OH)-MS/PIB-T</td>
<td>0.1 0.3</td>
<td>0.1 0.5</td>
<td>0.3 0.44(.06)</td>
</tr>
</tbody>
</table>

* numbers in parenthesis are the amount of oxygen from silicon (silicon dioxide)
Table 4.25 shows the XPS results of the fresh polymer samples at 15°, 45°, and 90° after subtracting silicon.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>C-C, C-H (284.6 eV)</th>
<th>C-OH, C-O-C, C-N (285.5 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIB-OH</td>
<td>91.2</td>
<td>8.8</td>
</tr>
<tr>
<td>arb_IB(OH)-MS</td>
<td>96.3</td>
<td>3.7</td>
</tr>
<tr>
<td>PIB-T</td>
<td>95.0</td>
<td>5.0</td>
</tr>
<tr>
<td>arb_IB(OH)-MS/PIB-T</td>
<td>94.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 4.26 Carbon 1s analyses: high resolution XPS at 45° X-ray angle.

High resolution XPS (20 eV) was carried out in the carbon region in order to determine the amount of different types of carbon atoms in the polymer. These results can be seen in Figures 4.66 and 4.67 and Table 4.26. Low resolution XPS for PIB-OH (Table 4.25) showed no detectable nitrogen present at any of the X-ray angles. The amount of oxygen in this sample was fairly high at the 15° and 90° angles (3.9 At% and 4.7 At% respectively); however, the numbers in parenthesis showed that this sample had a large amount of oxygen present from silicon dioxide. The high resolution C1s analysis (Figure 4.65) shows that there are two carbon peaks. The main carbon peak appears at 284.6 eV and is from C-C and C-H, the second peak appears at 285.5 eV and is from C-OH, C-O-C, or C-N (Table 4.26). In the PIB-OH approximately 8.8 At% was from the peak at 285.5 eV. The low resolution results for arb_IB(OH)-MS(3.5) (Table 4.25) showed that no detectable nitrogen was present in the film at any angle. Oxygen in this sample was in very low amounts (~0.3 At%) and was only observed at the 45° and 90° X-ray angles. High resolution C1s analysis (Figure 4.65) showed two peaks at 285.5 eV.
and 284.6 eV. This sample had only 3.7 At % from the peak at 285.5 eV (Table 4.26). The PIB-T (Table 4.25) had small amounts of nitrogen present in the sample. The amount of nitrogen in the sample increased from 0.2 At % at 15° to 0.3 At % at the 90° X-ray angle. High resolution C1s analysis (Figure 4.66) showed the same two peaks from carbon at 284.6 eV and 285.5 eV. This sample had 5 At % carbon from the second peak at 285.5 eV, which is higher than the amount found in the $arb_{IB(OH)}$-MS(3.5) (Table 4.26). The $arb_{IB(OH)}$-MS93.5)/PIB-T (Table 4.25) also had small amounts of nitrogen. The amount of nitrogen present increased from 0.1 At % at 15° to 0.3 At % at the 90° X-ray angle. As with the other samples, high resolution C1s analysis (Figure 4.66) showed two peaks from carbon at 284.6 eV and 285.5 eV. This sample had 5.5 At% carbon from the peak at 285.5 eV (Table 4.26).

The results in Table 4.25 show that the only materials in which nitrogen was detected by XPS, are the samples with PIB-T. In both pure PIB-T and the blend the amount of nitrogen observed increased as the X-ray angle increased. No clear trend was observed with oxygen, and it was noted that the amount of oxygen present is not reliable as it was seen from high resolution XPS that there is oxygen from silicon dioxide and the air present.

The results from high resolution C1s analysis (Table 4.26) show that samples with thymine have a larger percentage of carbon from the second peak at 285.5 which could be from the C-N bond in thymine as well as C-O bond from carboxylic groups in the PIB-T. This is another good indication that the nitrogen observed is from the sample.

These results from XPS coupled with the water contact angle data show that the PIB-T polymer did indeed increase the hydrophilicity of the $arb_{IB(OH)}$-MS(3.5).
Figure 4.65  High resolution XPS traces (45° angle), C1s of: (a) PIB(OH) and (b) arb_IB(OH)-MS(3.5).
Figure 4.66 High resolution XPS traces (45° angle), C1s of: (a) PIB-T and (b) \( \text{arb}_{\text{IB(OH)-MS(3.5)}}/ \text{PIB-T} \).
This was seen from the decreased contact angle of the surface functionalized film, and that nitrogen was observed by XPS in air near the surface, with more nitrogen being present at around a 10 nm depth. \textit{arb\_IB(OH)-MS(3.5)} had no detectable amounts of O at the 15° grazing angle in air, yet had lower water contact angle than a block copolymer without O groups. These findings indicate that the modular surface modification of PIB-based block copolymers produces stimuli responsive surfaces, with the polar groups migrating to the interface. More experimentation is needed to verify these results.
CHAPTER V
CONCLUSIONS

A novel inimer, 4-(1,2-oxirane-isopropyl)-styrene (EPOIM) was synthesized with 48% yield and its structure was verified by $^1$H NMR spectroscopy. The EPOIM produced high MW $arb$-IB(OH)s. SEC analysis proved EPOIM incorporation. Selective link destruction yielded lower $B$ (average number of branches per chain) values than predicted by kinetics, indicating a reactivity difference of the initiating and propagating carbocations. SEC analysis of branching (by parameters based on $R_g$ and $R_h$ values) corroborated the proposed architecture. This method, coupled with selective link destruction, is useful for branching analysis and is of general applicability.

Large scale polymerizations of EPOIM with IB resulted in controlled living polymerizations of IB, producing a hydroxyl functionalized arborescent polyisobutylene: $arb$-IB(OH). Branching and architecture analysis of these polymers showed that the unequal reactivity of propagating carbocations produces a not truly randomly branched $arb$-IB(OH).

In situ FTIR monitoring of the SCVP and SCVCP with EPOIM showed that due to the unequal reactivity of EPOIM’s propagating carbocations, the vinyl groups of EPOIM react leaving some epoxide rings unopened. Use of a half molar equivalent of TiCl$_4$ relative to EPOIM yielded polyether, as seen by FTIR and $^1$H NMR spectroscopy. The unequal reactivity was also seen by the blocking of EPOIM and IB by SCVCP.
Novel 4\textsuperscript{th} generation PIB-based TPE’s were synthesized by the blocking of \textit{arb}_IB(OH) with MS. The products were block copolymers having an \textit{arborescent} polyisobutylene core (with primary hydroxyl groups at each branching point) and PIB-
\textit{co}-PMS copolymer end blocks producing \textit{arb}_IB(OH)-MS. Proof of hydroxyl groups in the polymer was obtained by NMR spectroscopy and silylation of the \textit{arb}_IB(OH)-MS. Two TPE’s were synthesized and the MS content was calculated by NMR spectroscopy: \textit{arb}_IB(OH)-MS(3.5) and \textit{arb}_IB(OH)-MS\_CB(16),

A novel PIB-based TPE and its CB nanocomposite were made and characterized to prepare new implantable biomaterials. The essential aspects of the materials, i.e., water contact angle, mechanical properties and \textit{in vivo} biocompatibility, were investigated. Composites of \textit{arb}_IB(OH)-MS(3.5) and \textit{arb}_IB(OH)-MS\_CB(16) were made with 37.5 wt\% CB. DSC of \textit{arb}_IB(OH)-MS\_CB(16) showed an increase in the \(T_g\) of the copolymer end block from 105°C in the neat material to 126°C resulting in a material, which can be steam sterilized. TGA showed that the incorporation of CB gave a 65°C increase in the heat resistance of \textit{arb}_IB(OH)-MS(16) and \textit{arb}_IB(OH)-MS(3.5). TEM images of \textit{arb}_IB(OH)-MS(3.5) and \textit{arb}_IB(OH)-MS(16) showed irregularly dispersed discrete PMS rich domains on the order of 40-50 nm. TEM images of cryomicrotomed \textit{arb}_IB(OH)-MS(16) and \textit{arb}_IB(OH)-MS\_CB(16) showed an increase in the domain size of the neat materials to 70-80 nm in \textit{arb}_IB(OH)-MS\_CB(16). This shows the incorporation of CB into the PMS rich domains; these results were confirmed by AFM. The lack of agglomeration of CB in \textit{arb}_IB(OH)-MS\_CB(16) and the \(3 \times 10^{11}\) Ohm cm resistivity demonstrates excellent filler dispersion and shows that a true nanocomposite was formed. The \textit{arb}_IB(OH)-MS\_CB(16) exhibited a doubling of tensile strength.
relative to \textit{arb}\_IB(OH)-MS(16), demonstrating excellent mechanical properties covering the stiffness range of soft tissues. In contrast to silicone rubber, the new CB nanocomposite can be shaped by melt-processing and can be steam-sterilized. \textit{arb}\_IB(OH)-MS(16) showed a small decrease in water contact angle compared to \textit{arb}\_SIBS. \textit{arb}\_IB(OH)-MS\_CB(16) had a 15° decrease in contact angle compared to \textit{arb}\_IB(OH)-MS(16). XPS showed the presence of oxygen as well as C-O on the surface of both \textit{arb}\_IB(OH)-MS(16) and \textit{arb}\_IB(OH)-MS\_CB(16).

\textit{In vitro} and \textit{in vivo} implantation studies of \textit{arb}\_IB(OH)-MS and \textit{arb}\_IB(OH)-MS\_CB, in comparison to silicone, showed all implanted samples had tissue reaction similar to the control silicone rubber. In soft tissues \textit{arb}\_IB(OH)-MS\_CB had the thinnest capsules around the implants after 180 days in the rabbits, the more hydrophilic surface may have contributed to this finding. Degradation assessment in phosphate buffer solution demonstrated that both \textit{arb}\_IB(OH)-MS and \textit{arb}\_IB(OH)-MS\_CB are stable and showed buffer uptake less than 1-2%. Results from \textit{in vivo} and \textit{in vitro} biocompatibility studies demonstrated that the novel PIB-based CB nanocomposite represents a new concept in biomaterials, and shows great promise for soft tissue replacement.

A small decrease in the water contact angle was observed in \textit{arb}\_IB(OH)-MS(16) compared to \textit{arb}\_SIBS; however, the amount of hydroxyl groups that can be introduced by the inimer into the \textit{arb}\_IB core is low (0.049 wt% OH). Since this level of hydroxyl content is too low to have a profound effect on the surface, another method was needed to modify the surface. Professor Puskas developed the concept of “modular” surface
functionalization, “gluing” low molecular weight functionalized polyisobutylenes to the surface of our TPE’s. For preliminary studies a low molecular weight PIB-T was used.

Results from XPS coupled with water contact angle data show that the PIB-T polymer increases the hydrophilicity at the surface of \textit{arb\_IB(OH)-MS(3.5)}. This was seen from the decreased contact angle of the surface functionalized film, and that nitrogen was observed by XPS in air near the surface, with more nitrogen being present at around a 10 nm depth. \textit{arb\_IB(OH)-MS(3.5)} did not show detectable amounts of oxygen at the 15° grazing angle in air, yet had lower water contact angle than a block copolymer without oxygen containing groups. These findings indicate that the modular surface modification of PIB-based block copolymers produces stimuli responsive surfaces, with the polar groups migrating to the interface. More experimentation is needed to verify these results.
REFERENCES


196


