SYNTHESIS, CHARACTERIZATION, AND RHEOLOGY
OF FUNCTIONAL AND HETEROCYCLIC
LIQUID CRYSTALLINE POLYMERS

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

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

Wenyi Huang
December, 2006
SYNTHESIS, CHARACTERIZATION, AND RHEOLOGY
OF FUNCTIONAL AND HETEROCYCLIC
LIQUID CRYSTALLINE POLYMERS

Wenyi Huang

Dissertation

Approved:
Advisor
Chang Dae Han

Committee Member
Mark D. Soucek

Committee Member
Kyonsuku Min

Committee Member
Stephen Z. D. Cheng

Accepted:
Department Chair
Sadhan C. Jana

Dean of the College
Frank N. Kelley

Dean of the Graduate School
George R. Newkome

Date
ABSTRACT

Three segmented main-chain thermotropic liquid crystalline polymers (TLCPs) functionalized with nitrogen-containing heterocyclic groups were synthesized; namely PyHQ12 having pendent pyridyl group, PABP having side-chain azopyridyl group with flexible spacer, and PTBP containing side-chain terpyridine group with flexible spacer. The principles of specific interactions were applied to prepare supramolecular structures and organoclay or clay nanocomposites based on these functional TLCPs. Three combined main-chain/side-chain liquid-crystalline polymers (MCSCLCPs) were prepared via hydrogen bonding or ionic interactions based on PyHQ12 and PABP. The presence of hydrogen bonds in self-assembled PyHQ12−7CNCOOH and PABP−AA, and the presence of ionic interactions in self-assembled PABP−TSA, which exist above their respective clearing temperatures, were confirmed using Fourier transform infrared (FTIR) spectroscopy, the thermal transitions in each MCSCLCP were determined using differential scanning calorimetry (DSC), and the mesophase structures of each self-assembled MCSCLCP were characterized using polarized optical microscopy (POM) and wide-angle X-ray diffraction (WAXD).

PyHQ12 was observed to be very effective in exfoliating organoclay (Cloisite 30B) aggregates, because of the formation of hydrogen bonds, as determined by in situ FTIR spectroscopy, between the pendent pyridyl group in PyHQ12 and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B. Thus,
functionality in TLCP is necessary to obtain highly dispersed organoclay nanocomposites, but at the same time there is a possibility to lose some degree of liquid crystallinity in the TLCP, due to the proximity of the pendent pyridyl group to the mesogenic main-chain backbone. Thus, another functional TLCP, PABP having side-chain azopyridyl group with flexible spacer, was synthesized. It has been found that the liquid crystallinity of PABP in the organoclay nanocomposites was more or less intact and yet organoclay (Cloisite 30B) aggregates were very well dispersed, which was attributed to the fact that the pyridyl group in the side-chain azopyridine of PABP is located sufficiently far away from the mesogenic main chain. The rheological properties of functional TLCP/organoclay nanocomposites were also investigated.

A unique polymer/ruthenium complex [Ru\textsuperscript{II}(PTBP)(6TPy)](PF\textsubscript{6})\textsubscript{2} based on PTBP was used to prepare natural clay (Montmorillonite, MMT) nanocomposite. X-ray diffraction and transmission electron microscopy indicate that MMT has a high degree of exfoliation in the matrix of PTBP/ruthenium complex. UV-vis spectroscopy and FTIR spectroscopy show that the driving force for exfoliating MMT in PTBP/ruthenium complex is attributable to the Coulombic interactions between the positively charged ruthenium center in the side chain of the polymer and the negatively charged clay surfaces.
ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor, Professor Chang Dae Han, for his advice, patience, and encouragement throughout this study.

I would like to extend my sincere gratitude to the committee members, Professors Mark Soucek, Kyonsuku Min, Stephen Z. D. Cheng, Jun Hu, for their directions during the preliminary stage of this research.

Finally, I would like to dedicate this dissertation to my parents and my wife, Hongyan Chen, for their love, understanding, and support.
TABLE OF CONTENTS

LIST OF TABLES ............................................................................................................ xii
LIST OF FIGURES ......................................................................................................... xiii

CHAPTER

I. INTRODUCTION ......................................................................................................... 1
II. LITERATURE REVIEW ............................................................................................ 8
   2.1 The Role of Specific Interactions in the Formation of Supramolecular Structures Based on Nitrogen-Containing Heterocyclic Polymers ......................... 8
      2.1.1 Supramolecular Liquid Crystalline Polymers Induced by Specific Interactions ........................................................................................................... 9
      2.1.2 Supramolecular Polymers via Metal-Ion Coordination ............................ 19
      2.2 Molecular Design of Heterocyclic Polymers .................................................. 29
         2.2.1 High Performance Heterocyclic Polymers .............................................. 29
         2.2.2 Heterocyclic Conjugated Polymers ....................................................... 29
         2.2.3 Heterocyclic Liquid Crystalline Polymers .............................................. 37
III. EXPERIMENTAL .................................................................................................... 42
   3.1 Synthesis of A Series of Functional Heterocyclic Liquid Crystalline Polymers . 42
      3.1.1 Synthesis of a Segmented Main-Chain Liquid Crystalline Polymer with Pendent Pyridyl Group (PyHQ12) ................................................................. 42
      3.1.2 Synthesis of a Segmented Main-Chain Liquid Crystalline Polymer having Side Chain Azopyridine with Flexible Spacer (PABP) ......................... 46
3.1.3 Synthesis of a Segmented Main-Chain Liquid Crystalline Polymer Having Side-Chain Terpyridine Group (PTBP) ................................................................. 49

3.2 Synthesis of Self-assembled Main-chain/Side-chain Liquid Crystalline Polymers (MCSCLCPs) ........................................................................................................ 53

3.2.1 Synthesis of Self-Assembled PyHQ12−7CNCOOH via Hydrogen Bonding... 53
3.2.2 Synthesis of Self-Assembled PABP−AA via Hydrogen Bonding ..................... 55
3.2.3 Synthesis of Self-Assembled PABP−TSA via Ionic Interactions ...................... 56

3.3 Synthesis of [Ru''(PTBP)(6TPy)](PF₆)₂ (denoted by PTBP-Ru-6TPy) complex ......................................................................................................................... 56

3.4 Preparation of Functional Liquid Crystalline Polymer/Clay (or Organoclay) Nanocomposites ........................................................................................................ 59

3.4.1 Preparation of Organoclay Nanocomposite Based on PyHQ12 or PSHQ12 .... 60
3.4.2 Preparation of Organoclay (or Clay) Nanocomposite Based on PABP .......... 61
3.4.3 Preparation of [Ru''(PTBP)(6TPy)](PF₆)₂/Clay (or Organoclay) Nanocomposites ....................................................................................................................... 61

3.5 Experimental Methods .......................................................................................... 62

3.5.1 Nuclear Magnetic Resonance Spectroscopy (NMR) ......................................... 62
3.5.2 Differential Scanning Calorimetry (DSC) .......................................................... 63
3.5.3 Polarized Optical Microscopy (POM) ................................................................. 63
3.5.4 Fourier Transform Infrared (FTIR) Spectroscopy ............................................. 63
3.5.5 Wide-Angle X-ray Diffraction (WAXD) ............................................................ 64
3.5.6 X-Ray Diffraction (XRD) .................................................................................. 65
3.5.7 Transmission Electron Microscopy (TEM) ........................................................ 65
3.5.8 Ultraviolet-Visible (UV-vis) Spectroscopy ....................................................... 65
3.5.9 Thermogravimetric Analysis (TGA) ................................................................. 66
3.5.10 Rheological Measurements ............................................................................. 66
IV. SYNTHESIS OF COMBINED MAIN-CHAIN/SIDE-CHAIN LIQUID CRYSTALLINE POLYMERS VIA SELF-ASSEMBLE ........................................ 67

4.1 Introduction............................................................................................................ 67

4.2 Self-Assembled PyHQ12–7CNCOOH via Hydrogen Bonding ............................ 69

4.2.1 Thermal Transition and Mesophase Structure of PyHQ12 and Self-Assembled PyHQ12–7CNCOOH ............................................................. 69

4.2.2 WAXD and XRD Patterns of PyHQ12 and Self-Assembled PyHQ12–7CNCOOH ....................................................................................... 76

4.2.3 POM Images of Self-Assembled PyHQ12–7CNCOOH .................................. 76

4.2.4 FTIR Spectra of Self-Assembled PyHQ12–7CNCOOH.................................. 80

4.2.5 Effect of Molar Ratios of 7CNCOOH on the Thermal Transition Temperatures of Self-Assembled PyHQ12-7CNCOOH .............................. 82

4.3 Self-Assembled PABP–AA via Hydrogen Bonding. ........................................ 86

4.3.1 Formation of Hydrogen Bonds Between Monomer PAPM and p-Anisic Acid................................................................................................................... 86

4.3.2 Thermal Transition and Mesophase Structures of PABP and Self-Assembled PABP–AA........................................................... 88

4.3.3 WAXD and XRD Patterns of PABP and Self-Assembled PABP–AA ............ 91

4.3.4 In Situ FTIR Spectra for Self-Assembled PABP–AA...................................... 95

4.4 Self-Assembled PABP–TSA via Ionic Interactions .......................................... 97

4.4.1 Formation of a Mesogenic Phase in a Mixture of Monomer PAPM and p-Toluene Sulfonic Acid via Ionic Interactions ............................................. 97

4.4.2 Thermal Transition and Mesophase Structure of Self-Assembled PABP–TSA................................................................................................. 100

4.4.3 In Situ FTIR Spectra and UV-vis Spectra for Self-Assembled PABP–TSA................................................................................................. 102

4.5 Concluding Remarks............................................................................................ 104
V. DISPERSION CHARACTERISTICS AND RHEOLOGY OF ORGANOCLAY NANOCOMPOSITES BASED ON A SEGMENTED MAIN-CHAIN LIQUID CRYSTALLINE POLYMER HAVING PENDENT PYRIDYL GROUP ............ 107

5.1 Introduction.................................................................................................................. 107

5.2 Characteristics of PyHQ12 and PSHQ12 ................................................................. 110

5.2.1 Thermal Transition and Mesophase Structure of PyHQ12 and PSHQ12 ....... 111

5.2.2 FTIR Spectra of PyHQ12 and PSHQ12............................................................... 114

5.2.3 Temperature Dependence of the Complex Viscosities of PyHQ12 and PSHQ12 .......................................................................................................... 117

5.2.4 Linear Dynamic Viscoelasticity of PyHQ12 and PSHQ12 .............................. 121

5.3 Dispersion Characteristics and Rheology of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12 ........................................................................... 127

5.3.1 XRD Patterns of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12 .......................................................................................................... 127

5.3.2 TEM Images of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12 .......................................................................................................... 129

5.3.3 FTIR Spectra of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12 .......................................................................................................... 129

5.3.4 Thermal Transition and Mesophase Structure of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12........................................... 133

5.3.5 Temperature Dependence of the Complex Viscosity of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12............................................ 140

5.3.6 Linear Dynamic Viscoelasticity of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12....................................................................................... 142

5.4 Concluding Remarks................................................................................................... 150

VI. DISPERSION CHARACTERISTICS AND RHEOLOGY OF ORGANOCLAY NANOCOMPOSITES BASED ON A SEGMENTED MAIN-CHAIN LIQUID CRYSTALLINE POLYMER HAVING SIDE-CHAIN AZOPYRIDINE WITH FLEXIBLE Spacer.............................................................................................. 153

6.1 Introduction............................................................................................................. 153
6.2 Thermal Transition Temperatures and Mesophase Structure of Organoclay Nanocomposites Based on PABP ................................................................. 154

6.3 Dispersion Characteristics of Organoclay Nanocomposites Based on PABP ..... 158
   6.3.1 X-ray Diffraction (XRD) Patterns of Organoclay Nanocomposites Based on PABP .............................................................................................. 158
   6.3.2 Transmission Electron Microscopy (TEM) of Organoclay Nanocomposites Based on PABP ................................................................................. 162
   6.3.3 Fourier Transform Infrared (FTIR) Spectroscopy of Organoclay Nanocomposites Based on PABP ................................................................. 162

6.4 Rheological Behavior of Organoclay Nanocomposites Based on PABP ............ 166

6.5 Rationale for the Design and Synthesis of PABP for the Preparation of Organoclay Nanocomposites .............................................................................. 178

6.6 Concluding Remarks ....................................................................................... 179

VII. RUTHENIUM(II) COMPLEX-INDUCED DISPERSION OF MONTMORILLONITE IN A SEGMENTED MAIN-CHAIN LIQUID CRYSTALLINE POLYMER HAVING SIDE-CHAIN TERPYRIDINE GROUP ................................................................................................................... 184

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

7.2 Thermal Transition Temperatures and Mesophase Structure of PTBP .......... 186

7.3 Characterizations of TPy-RuCl₃ monocomplex and [Ru^{II}(PTBP)(6TPy)](PF₆)₂ complex (PTBP-Ru-6TPy) ........................................................................ 189

7.4 Dispersion Characteristics of Montmorillonite or Organoclay Nanocomposites Based on PTBP-Ru-6TPy Complex ....................................................................... 195
   7.4.1 X-ray Diffraction (XRD) Patterns of Montmorillonite or Organoclay Nanocomposites Based on PTBP-Ru-6TPy Complex ........................................ 195
   7.4.2 Transmission Electron Microscopy (TEM) Images of Montmorillonite or Organoclay Nanocomposites Based on PTBP-Ru-6TPy Complex ........... 198

7.5 Ultraviolet-Visible (UV-vis) Spectroscopy of Montmorillonite or Organoclay Nanocomposites Based on PTBP-Ru-6TPy Complex ............................... 200
7.6 Fourier Transform Infrared (FTIR) Spectroscopy of Montmorillonite or Organoclay Nanocomposites Based on PTBP-Ru-6TPy Complex .................................................. 202

7.7 Concluding Remarks .............................................................................................................. 206

VIII. CONCLUSIONS AND RECOMMENDATIONS ........................................................................... 208

8.1 Conclusions ......................................................................................................................... 208

8.2 Recommendations ............................................................................................................... 212

REFERENCES .................................................................................................................................... 213
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Characteristics of covalent and noncovalent syntheses</td>
<td>2</td>
</tr>
<tr>
<td>2.1 Molecular designs of high-performance heterocyclic polymers</td>
<td>30</td>
</tr>
<tr>
<td>5.1 Enthalpy of N–I Transition, $\Delta H_{NI}$, for PyHQ12, PSHQ12 and Their Organoclay Nanocomposites</td>
<td>136</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Schematic representation of specific interactions of base pairs in DNA</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>Schematic representation of molecular orbital of pyridine</td>
<td>3</td>
</tr>
<tr>
<td>2.1</td>
<td>Schematic illustration of supramolecular polymers: (A) side-chain-type, (B) main-chain-type, (C) combined type, and (D) network type</td>
<td>10</td>
</tr>
<tr>
<td>2.2</td>
<td>The formation of tridirectional proton conduction in the self-assembled side-chain liquid crystalline block copolymer: (a) Side-chain supramolecular complex consisting of PS-b-PVP, TSA, and PDP; (b) Self-organized hierarchical structures of the supramolecular complex</td>
<td>12</td>
</tr>
<tr>
<td>3.1</td>
<td>Synthetic Route for PyHQ12</td>
<td>43</td>
</tr>
<tr>
<td>3.2</td>
<td>Synthetic Route for PABP</td>
<td>47</td>
</tr>
<tr>
<td>3.3</td>
<td>Synthetic route for PTBP</td>
<td>50</td>
</tr>
<tr>
<td>3.4</td>
<td>Synthesis of $\text{<a href="%5Ctext%7BPF%7D_6">Ru}^{II}(\text{PTBP})(6\text{TPy})</a>_2$ complex</td>
<td>57</td>
</tr>
<tr>
<td>4.1</td>
<td>Schemes describing the two methods, (a) method I and (b) method II, employed to prepare combined MCSCLCPs via hydrogen bonding, in which the dark areas represent mesogenic groups</td>
<td>70</td>
</tr>
<tr>
<td>4.2</td>
<td>DSC thermograms for (a) PyHQ12 and (b) 7CNCOOH at a scanning rate of 20 °C/min during (1) heating and (2) cooling cycles, and their POM images at 130 °C during the cooling cycle</td>
<td>72</td>
</tr>
<tr>
<td>4.3</td>
<td>DSC thermograms for self-assembled PyHQ12–7CNCOOH at a scanning rate of 20 °C/min during (1) heating and (2) cooling cycles</td>
<td>73</td>
</tr>
<tr>
<td>4.4</td>
<td>DSC thermograms for self-assembled PyHQ12-7CNCOOH after annealing at 130 °C for various annealed periods at a scanning rate of 20 °C/min</td>
<td>75</td>
</tr>
<tr>
<td>4.5</td>
<td>WAXD patterns of PyHQ12 and self-assembled PyHQ12–7CNCOOH: (a) powder patterns of specimens after annealing at 130 °C for 48 h; (b) fiber patterns of unannealed melt-drawn specimens</td>
<td>77</td>
</tr>
</tbody>
</table>
4.6 XRD patterns of (a) PyHQ12 and (b) self-assembled PyHQ12−7CNCOOH at room temperature.................................................................78

4.7 POM images of self-assembled PyHQ12−7CNCOOH upon heating from 120 to 160 °C (above the $T_{NI}=154.1$ °C) and during cooling from the isotropic state to 25 °C. ........................................................................................................79

4.8 FTIR spectra for (a) 7CNCOOH and (b) PyHQ12 denoted by (*) at room temperature, and in-situ FTIR spectra for self-assembled PyHQ12−7CNCOOH at various temperatures (°C): (1) 25, (2) 100, (3) 120, (4) 140, (5) 150, (6) 160, and (7) 170...............................................................81

4.9 DSC thermograms at a scanning rate of 20 °C/min during the heating cooling cycle for (a) PyHQ12 and self-assembled PyHQ12−7CNCOOH having different [pyridyl group]/[acid group] ratios: (b) 8/1, (c) 4/1, (d) 2/1, and (e) 1/1......................83

4.10 FTIR spectra for (a) PyHQ12 and self-assembled PyHQ12−7CNCOOH having different [pyridyl group]/[acid group] ratios: (b) 8/1, (c) 4/1, (d) 2/1, and (e) 1/1.............................................................................85

4.11 DSC thermograms for (a) PAPM (in which 66.4 °C denotes melting temperature) and (b) self-assembled PAPM−AA at a scanning rate of 20 °C/min during (1) heating and (2) cooling cycles, and POM image taken at 50 °C during the cooling cycle. Here $k$ denotes the crystalline state and $S_{mb}$ denotes smectic B phase. .............................................................................................................87

4.12 FTIR spectra for (1) AA, (2) PAPM, and (3) self-assembled PAPM−AA at room temperature. .........................................................................................................................89

4.13 DSC thermograms for (a) PABP and (b) self-assembled PABP−AA at a scanning rate of 20 °C/min during (1) heating and (2) cooling cycles, and their POM images taken at 130 °C during the cooling cycle.................................................................90

4.14 WAXD powder patterns of (a) PABP and (b) self-assembled PABP−AA at room temperature. .........................................................................................................................92

4.15 Variation of the X-ray diffraction intensity with scattering angle 2θ for an as-cast PABP during the second heating cycle at various temperatures, as indicated on the plot. .........................................................................................94

4.16 FTIR spectrum for PABP denoted by (*) and in-situ FTIR spectra for self-assembled PABP−AA at various temperatures (°C): (1) 25, (2) 100, (3) 120, (4) 140, (5) 150, (6) 160, and (7) 170. The inset shows the absorption peaks at wavenumbers ranging from 1800 cm$^{-1}$ to 1650 cm$^{-1}$. ..................................................96
4.17 DSC thermograms for self-assembled PAPM–TSA at a scanning rate of 20 °C/min during (1) heating and (2) cooling cycles, and POM image taken at 40 °C during the cooling cycle. Here k denotes the crystalline phase and Sm denotes a smectic phase. ................................................................. 98

4.18 FTIR spectra for (1) TSA, (2) self-assembled PAPM–TSA, and (3) PAPM at room temperature................................................................. 99

4.19 Thermal transitions and mesophase of self-assembled PABP–TSA: (a) DSC thermograms at a scanning rate of 20 °C/min for specimens without annealing during (1) heating and (2) cooling cycles, and (b) POM image taken at 130 °C during the cooling cycle................................................................. 101

4.20 FTIR spectrum for PABP denoted by (*) and in-situ FTIR spectra for self-assembled PABP–TSA at various temperatures (°C): (1) 25, (2) 100, (3) 120, (4) 140, and (5) 160. The inset shows the absorption peaks at wavenumbers ranging from 1650 cm⁻¹ to 1550 cm⁻¹. ......................................................... 103

4.21 UV-vis spectra of thin films of (a) PABP and (b) self-assembled PABP–TSA.... 105

5.1 DSC thermograms for (a) PyHQ12 and (b) PSHQ12 at a scanning rate of 20 °C/min, and their POM images at 130 °C. ......................................................... 112

5.2 DSC thermograms for (a) PyHQ12 and (b) PSHQ12 at a scanning rate of 20 °C/min for various annealed periods................................................................. 113

5.3 WAXD (a, b) powder patterns after annealing at 130 °C for (a) 48 h and (b) 144 h, and (c, d) fiber patterns of unannealed melt-drawn specimens for (a, c) PyHQ12 and (b, d) PSHQ12................................................................. 115

5.4 TGA data for (a) PyHQ12 and (b) PSHQ12 at a heating rate of 20 °C/min............. 116

5.5 FTIR spectra for PSHQ12 denoted by (*) and in-situ FTIR spectra for PyHQ12 at various temperatures (°C): (1) 25, (2) 100, (3) 120, (4) 140, (5) 160, and (6) 180................................................................. 118

5.6 Variations of |η*| with temperature during isochronal dynamic temperature sweep experiments at ω = 0.1 rad/s for: (⊙) PyHQ12 and (△) PSHQ12. ......................... 120

5.7 Dynamic frequency sweeps for PyHQ12: (a) Log G' versus log ω plots and (b) log G¨ versus log ω plots at different temperatures (°C): (○) 130, (△) 140, (□) 160, (●) 180, and (▲) 190................................................................. 122
5.8 Dynamic frequency sweeps for PSHQ12: (a) Log $G'$ versus log $\omega$ plots and (b) log $G''$ versus log $\omega$ plots at different temperatures ($^o$C): (○) 130, (△) 140, (□) 165, (●) 180, and (▲) 190. ................................................................. 123

5.9 Log $|\eta^*|$ versus log $\omega$ plots for (a) PyHQ12 and (b) PSHQ12 at various temperatures ($^o$C): (○) 130, (△) 140, (□) 160, (▽) 165, (●) 180, and (▲) 190. ................................................................. 125

5.10 Log $G'$ versus log $\omega$ plots for (a) PyHQ12 and (b) PSHQ12 at various temperatures ($^o$C): (○) 130, (△) 140, (□) 160, (▽) 165, (●) 180, and (▲) 190. ................................................................. 126

5.11 XRD patterns for (a): (1) Cloisite 15A, (2) PyHQ12/Cloisite 15A nanocomposite, (3) PyHQ12/Cloisite 30B nanocomposite, (4) PSHQ12/Cloisite 30B nanocomposite, and (5) Cloisite 30B, and (b): for (1) MMT and (2) PyHQ12/MMT nanocomposite.................................................. 128

5.12 TEM images of PyHQ12/Cloisite 30B nanocomposite, PyHQ12/Cloisite 15A nanocomposite, PyHQ12/MMT, and PSHQ12/Cloisite 30B nanocomposite, in which the dark areas represent the clay and the gray/white areas represent the polymer matrix.................................................................................................................. 130

5.13 FTIR spectra for: (a) PyHQ12, (b) PyHQ12/Cloisite 15A nanocomposite, (c) PyHQ12/MMT nanocomposite, (d) PSHQ12/Cloisite 30B nanocomposite, and in-situ FTIR spectra for PyHQ12/Cloisite 30B nanocomposite at various temperatures ($^o$C): (1) 25, (2) 100, (3) 120, (4) 140, (5) 160, and (6) 180. ........... 132

5.14 DSC thermograms for: (1) PSHQ12/Cloisite 30B nanocomposite, (2) PyHQ12/Cloisite 15A nanocomposite, (3) PyHQ12/Cloisite 30B nanocomposite, and (4) PyHQ12/MMT nanocomposite at a heating rate of 20 $^o$C/min. ............................................................................................................................. 134

5.15 POM images of PyHQ12/Cloisite 30B nanocomposite, PyHQ12/Cloisite 15A nanocomposite, PyHQ12/MMT, and PSHQ12/Cloisite 30B nanocomposite at 140 $^o$C.................................................................................................................. 137

5.16 Scheme describing the distributions of PyHQ12 chains and organoclay Cloisite 30B in the highly dispersed PyHQ12/Cloisite 30B nanocomposite, where the dark sticks represent Cloisite 30B platelets, the thin cylinders (which denote mesogens) plus waved lines (which denote flexible spacers) represent PyHQ12 chains, and the short dashed lines represent hydrogen bonds between the pendent pyridyl group in PyHQ12 and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B.................................................. 138
5.17 Variations of $|\eta^*|$ with temperature during isochronal dynamic temperature sweep experiments at $\omega = 0.1$ rad/s for: (○) PyHQ12/Cloisite 30B nanocomposite, (△) PyHQ12/Cloisite 15A nanocomposite, and (□) PSHQ12/Cloisite 30B nanocomposite................................................................. 141

5.18 Log $|\eta^*|$ versus log $\omega$ plots for (a) PyHQ12/Cloisite 30B nanocomposites, (b) PyHQ12/Cloisite 15A nanocomposites, and (c) PSHQ12/Cloisite 30B nanocomposites at various temperatures (°C): (○) 130, (△) 140, (□) 155, (▽) 160, (●) 180, and (▲) 190................................................................. 143

5.19 Log $G'$ versus log $G''$ plots for (a) PyHQ12/Cloisite 30B nanocomposites, (b) PyHQ12/Cloisite 15A nanocomposites, and (c) PSHQ12/Cloisite 30B nanocomposites at various temperatures (°C): (○) 130, (△) 140, (□) 155, (▽) 160, (●) 180, and (▲) 190................................................................. 146

5.20 Dynamic frequency sweeps for PyHQ12/Cloisite 30B nanocomposites: (a) Log $G'$ versus log $\omega$ plots and (b) log $G''$ versus log $\omega$ plots at different temperatures (°C): (○) 130, (△) 140, (□) 155, (●) 180, and (▲) 190............. 147

5.21 Dynamic frequency sweeps for PyHQ12/Cloisite 15A nanocomposites: (a) Log $G'$ versus log $\omega$ plots and (b) log $G''$ versus log $\omega$ plots at different temperatures (°C): (○) 130, (△) 140, (□) 160, (●) 180, and (▲) 190............. 148

5.22 Dynamic frequency sweeps for PSHQ12/Cloisite 30B nanocomposites: (a) Log $G'$ versus log $\omega$ plots and (b) log $G''$ versus log $\omega$ plots at different temperatures (°C): (○) 130, (△) 140, (□) 160, (●) 180, and (▲) 190............. 149

6.1 DSC thermograms for (a) PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and (d) PABP/Cloisite 30B nanocomposite at a heating rate of 20 °C/min during the heating cycle. .................................................. 155

6.2 POM images for (a) PABP, (b) PABP/MMT nanocomposites (c) PABP/Cloisite 15A nanocomposites, and (d) PABP/Cloisite 30B nanocomposites. ......................... 157

6.3 TGA data for PABP at a heating rate of 20 °C/min................................................. 159

6.4 XRD patterns for: (a) (1) Cloisite 15A, (2) MMT, and (3) Cloisite 30B; (b) (1) PABP, (2) PABP/MMT nanocomposite, (3) PABP/Cloisite 30B nanocomposite, and (4) PABP/Cloisite 15A nanocomposite. .................................................. 160

6.5 TEM images of PABP/Cloisite 30B nanocomposite, PABP/Cloisite 15A nanocomposite, and PABP/MMT nanocomposite, in which the dark areas represent the clay and the gray/white areas represent the polymer matrix. ............ 163
6.6 FTIR spectra for: (a) PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and in-situ FTIR spectra for PABP/Cloisite 30B nanocomposite at various temperatures (°C): (1) 25, (2) 100, (3) 120, (4) 140, (5) 150, and (6) 160. ............................................................................................... 165

6.7 Log $G'$ versus log $\omega$ plots for (a) PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and (d) PABP/Cloisite 30B nanocomposite at different temperatures (°C): (○) 120, (△) 130, (□) 140, (●) 150, and (▲) 160. .................................................................................................................. 167

6.8 Variations of $G'$ with temperature during isochronal dynamic temperature sweep experiments at $\omega = 0.1$ rad/s for (○) PABP, (△) PABP/MMT nanocomposite, (□) PABP/Cloisite 15A nanocomposite, and (▽) PABP/Cloisite 30B nanocomposite. ....................................................................................................... 171

6.9 Log $G''$ versus log $\omega$ plots for (a) PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and (d) PABP/Cloisite 30B nanocomposite at different temperatures (°C): (○) 120, (△) 130, (□) 140, (●) 150, and (▲) 160. ................................................................................................................ 174

6.10 Log $|\eta^*|$ versus log $\omega$ plots for (a) PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and (d) PABP/Cloisite 30B nanocomposite at different temperatures (°C): (○) 120, (△) 130, (□) 140, (●) 150, and (▲) 160. .......................................................... 176

6.11 Scheme describing the distributions of PABP and Cloisite 30B in the highly dispersed PABP/Cloisite 30B nanocomposite, where the dark sticks represent Cloisite 30B platelets, the dark ellipsoids represent the main-chain mesogens, waved lines represent flexible spacers, the empty notched ellipsoids represent the azopyridine in the side chain of PABP, and the empty notched ellipsoids with caps represent hydrogen bonds between the pyridyl group in the side-chain azopyridine of PABP and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B ........................................ 182

7.1 Schematic representation of Coulombic interactions between between the negatively charged surfaces of pristine MMT and the positively charged ruthenium center in the polymer matrix............................................................. 187

7.2 DSC thermograms of PTBP and PMBP during (1) heating and (2) cooling cycles. The inset are the polarized optical microscopy (POM) images taken after annealing at 70 °C for 24 h for PTBP, and taken at 130 °C for PMBP during the cooling cycle. .................................................................................. 188

7.3 FTIR spectra of (a) 6TPy and (b) 6TPy-RuCl$_3$ monocomplex. The Inset gives the absorption band from a wavenumber of 1500 cm$^{-1}$ to 1650 cm$^{-1}$ ...................... 190
7.4 UV-vis spectra of (a) 6TPy in CHCl₃ and (b) 6TPy-RuCl₃ monocomplex in DMF. .......................................................... 192

7.5 FTIR of (a) PTBP and (b) PTBP-Ru-6TPy. The inset gives the absorption band from a wavenumber of 1500 cm⁻¹ to 1700 cm⁻¹. .......................................................... 193

7.6 UV-vis spectra of (a) PTBP in CHCl₃ and (b) PTBP-Ru-6TPy in DMF................. 194

7.7 DSC thermograms of PTBP-Ru-6TPy during (a) heating and (b) cooling cycles... 196

7.8 XRD patterns of (a) (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite, (b) (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, (c) (PTBP-Ru-6TPy)/MMT nanocomposite, and (d) PTBP/MMT nanocomposite. ............................................. 197

7.9 TEM images of (a) (PTBP-Ru-6TPy)//MMT nanocomposite, (b) (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite, (c) (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, and (d) PTBP/MMT nanocomposite. ........................................... 199

7.10 UV-vis spectra of thin films of (a) PTBP-Ru-6TPy, (b) (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, (c) (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite, and (d) (PTBP-Ru-6TPy)/MMT nanocomposite. ........................................ 201

7.11 FTIR spectra of (a) MMT, (b) Cloisite 15A, and (c) Cloisite 30B. ...................... 203

7.12 FTIR spectra of (a) PTBP-Ru-6TPy, (b) (PTBP-Ru-6TPy)/MMT nanocomposite, (c) (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, and (d) (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite. The inset shows the expanded absorption band at wavenumbers ranging from 1800 cm⁻¹ to 1500 cm⁻¹. ........... 204
CHAPTER I
INTRODUCTION

In general, organic molecules can be simply regarded as a collection of atoms connected by strong covalent bonds, which are formed through chemical reactions by the stepwise breaking and formation of covalent bonds. Despite the significant importance of covalent bonding in the construction of polymeric materials, noncovalent (specific) interactions such as van der Waal force, hydrogen bonding, dipole-dipole interactions, ionic interactions, and metal coordination also play an indispensable role in the preparation of new functional polymeric materials, especially in biological processes, such as protein folding or the transfer of genetic information. In the past three decades, noncovalent interactions have been recognized as having an enormous potential for the preparation of polymeric materials exhibiting high degree of structural complexity. This novel synthetic approach, defined as “noncovalent synthesis” or “supramolecular chemistry”,¹ is widely employed in a variety of chemistry subdisciplines. The different characteristics of both covalent and noncovalent syntheses are summarized in Table 1.1.²

Life is encoded in the molecular structure of deoxyribonucleic acid (DNA), which contains all the information for self-replication, development, and survival of the organism. DNA is a polymer with repetitive units made of a sugar molecule, a heterocyclic base, and a phosphate group that links the units together. The heterocyclic bases found in DNA are adenine (A), guanine (G), cytosine (C), and thymine (T), as
Table 1.1. Characteristics of covalent and noncovalent syntheses\textsuperscript{2}

<table>
<thead>
<tr>
<th></th>
<th>Covalent</th>
<th>Noncovalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>building block</td>
<td>atoms</td>
<td>molecules, ions</td>
</tr>
<tr>
<td>target</td>
<td>molecule</td>
<td>assembly</td>
</tr>
<tr>
<td>molecular weight</td>
<td>1-100 Da</td>
<td>1-100 kDa</td>
</tr>
<tr>
<td>bond type</td>
<td>covalent</td>
<td>ionic, hydrophobic</td>
</tr>
<tr>
<td>bond energy</td>
<td>35-135 kcal/mol</td>
<td>2-20 kcal/mol</td>
</tr>
<tr>
<td>kinetic stability</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>(\Delta G) components</td>
<td>(\Delta H \gg T\Delta S)</td>
<td>(\Delta H \approx T\Delta S)</td>
</tr>
<tr>
<td>characteristics</td>
<td>−</td>
<td>cooperativity, reversible</td>
</tr>
</tbody>
</table>

shown in Figure 1.1.\textsuperscript{3} The two strands of DNA are coiled in a double helix through the specific interactions of base pairs, as elucidated by James Watson and Francis Crick in 1953.\textsuperscript{4} A fascinating feature of such specific interactions (molecular recognition) is associated with their high selectivity and directionality.

![Diagram of DNA base pairs](image)

Figure 1.1. Schematic representation of specific interactions of base pairs in DNA.\textsuperscript{3}

Thymine (T) \(\rightleftharpoons\) Adenine (A)

Cytosine (C) \(\rightleftharpoons\) Guanine (G).
Another typical nitrogenous base is pyridine which has six delocalized electrons in its $\pi$ system. The two non-bonding electrons on nitrogen are in a $sp^2$ orbital perpendicular to the plane of the ring, and they do not interact with the $\pi$ electrons of the aromatic system, as indicated in Figure 1.2.\textsuperscript{5} Thus, the lone pair of electrons in $sp^2$ orbital is responsible for basicity and strong permanent dipole of pyridine, which tends to abstract a proton. Consequently, pyridine can act as a strong “proton acceptor”, and it is easy to form strong hydrogen bonds (H-bonds) with “proton donor” molecules. The energy of a H-bond in the gas phase is typically in the range of 2–20 kcal/mol, which is much weaker than that of covalent bonds, but significantly larger than dipolar or London dispersion force energy ($< 2$ kcal/mol). If either the donor or acceptor is charged the electronic attraction will be amplified, and consequently the H-bonds become much stronger (10-45 kcal/mol).\textsuperscript{6,7} This is true when pyridine is quaternarized into pyridium (ionic interactions prevail). Furthermore, the lone pair of electrons in pyridine (Lewis base) paves a way to form complexes with transition metal ions (Lewis acid) via coordination bonds.\textsuperscript{8} It

![Figure 1.2. Schematic representation of molecular orbital of pyridine](image)

1 electron contributed to $\pi$-system by N

Lone electron pair in $sp^2$ orbital

$sp^2$ hybridised N
should be pointed out that 2,2′:6′,2″-terpyridine has recently been recognized as a very powerful chelating ligand for a variety of transition-metal ions in low oxidation state forming very stable octahedral complexes to construct a broad spectrum of metallo-supramolecular polymers.9 These unique features of pyridine can be extrapolated to diazines, triazines, and tetrazines having multiple lone pairs of electrons, although their basicity is reduced as a consequence of destabilisation of the mono-protonated cations due to the inductive withdrawal by the second nitrogen atom.5 Due to the extreme flexibility of heterocyclic molecules, they have been extensively employed in the new fields ranging from supramolecular chemistry10-12 to supramolecular polymers,13,14 and their importance has been widely recognized from experiment to theory.15-17

It is well-known that liquid crystalline polymers (LCPs) have an intermediate morphological state (mesophase) between the solid and liquid state. The unique feature of mesophase lies in that it is described by a positional order parameter because it is geometrically anisotropic in space.18 LCPs have excellent mechanical properties, dimensional stability, thermal stability coupled with the absence of creep and shrinkage; thus they are ideal candidates for high-performance applications.19 The preparation and characterization of supramolecular liquid crystals and liquid crystalline polymers obtained through hydrogen bonding between complementary molecules (particularly pyridyl and carboxylic acid derivatives), has been extensively investigated in recent years.20-23 The liquid crystalline phase in these systems is stabilized by the increased aspect ratio of supramolecular structure compared to the constituent molecules. There is a strong cooperativity between association and the induction of the liquid crystalline
phase, because anisotropy in the liquid crystal strongly enhances the strength of hydrogen bonding.\textsuperscript{17}

To the best of our knowledge, few studies have been focused on the synthesis of main-chain liquid crystalline polymers containing heterocyclic functional groups in the main chain and/or side chain. In view of the flexibility and versatility of nitrogen-containing heterocyclic derivatives, we have synthesized three segmented main-chain thermotropic liquid crystalline polymers functionalized with heterocyclic groups, namely PyHQ12 having pendent pyridyl group, PABP having side-chain azopyridyl group with flexible spacer, and PTBP having side-chain terpyridine group.

In the first part of this dissertation, based on PyHQ12 and PABP, self-assembled combined main-chain/side-chain liquid crystalline polymers (MCSCLCPs) were prepared through specific interactions such as hydrogen bonding or ionic interactions. The role of hydrogen bonding or ionic interactions in the formation of self-assembled supramolecular structures was investigated using in situ Fourier Tranform Infrared (FTIR) spectroscopy, and the phase transitions in these MCSCLCPs were investigated with differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and polarized optical microscopy (POM).

In the second part of this dissertation, we took an effort to answer a fundamental question: Is functionality necessary to achieve a very high degree of dispersion of organoclay in thermotropic liquid crystalline polymers (TLCPs)? For this purpose, we employed two TLCPs, PyHQ12 with pendent pyridyl group and PSHQ12 with pendent phenylsulfonyl group, and chose two organoclays, Cloisite 30B treated with a surfactant having hydroxyl groups and Cloisite 15A treated with a surfactant without hydroxyl groups.
groups. The rationale lies in that we were interested in demonstrating that compatibility, via specific interactions, between the pendent pyridyl group in PyHQ12 and the polar group in a surfactant residing at the surface of an organoclay would facilitate the exfoliation of organoclay in the polymer matrix. The dispersion characteristics of organoclay nanocomposites were characterized with transmission electron microscopy (TEM) and X-ray diffraction (XRD) patterns. The hydrogen bonding between the pendent pyridyl group in PyHQ12 and the hydroxyl group in the surfactant MT2EtOH residing at the surface of organoclay Cloisite 30B was evidenced by in situ FTIR spectroscopy. The rheology and phase transitions in nanocomposites were also investigated.

In the third part of this dissertation, we attempted to attack a question arising from the second part: Is it possible to achieve a very high degree of dispersion of organoclay aggregates in functionalized TLCPs without the loss of liquid crystallinity? PyHQ12 was observed to be very effective in exfoliating organoclay while a significant degree of liquid crystallinity of PyHQ12 in the organoclay nanocomposite was lost due to the proximity of the pendent pyridyl group to the mesogenic main-chain backbone, which formed hydrogen bonds with the the hydroxyl group in the surfactant MT2EtOH residing at the surface of organoclay Cloisite 30B. To overcome this undesirable feature, we employed PABP having side-chain azopyridine group with flexible spacer because the pyridyl group in the side-chain azopyridine of PABP was located sufficiently far away from the mesogenic main chain.

In the fourth part of this dissertation, we tested an idea: Is it possible to exfoliate natural clay (e.g. Montmorillonite) in a functional polymer without the necessity to treat
the clay with a surfactant? Firstly, we incorporated a ruthenium complex into the side-chain terpyridine group of PTBP using the ruthenium(III)/ruthenium(II) chemistry. Then, this polymer/ruthenium complex was employed to prepare nanocomposites with montmorillonite. The dispersion characteristics were determined by TEM and XRD, while the Coulombic interactions between the positively charged ruthenium center of polymer/ruthenium complex and the negatively charged clay surfaces were confirmed by UV-vis spectroscopy and FTIR spectroscopy.
2.1 The Role of Specific Interactions in the Formation of Supramolecular Structures Based on Nitrogen-Containing Heterocyclic Polymers

Specific interactions such as hydrogen bonding, ionic interactions, electrostatic interactions, dipole-dipole interactions, $\pi-\pi$ interactions, and metal-ion coordination have been recognized as being of crucial importance in inducing supramolecular structures in nature.\textsuperscript{1,24} Hydrogen bonding is among the most important intermolecular interactions between macromolecular chains, for example, the crystalline structure of polyamide is mainly controlled by the mode of cooperative hydrogen bonding.\textsuperscript{25,26} Moreover, it has been well accepted to date that hydrogen bonding or ionic interactions between dissimilar polymer pairs would induce the formation of miscible polymer blends, complexes and networks.\textsuperscript{27} These attractive interactions are believed to control the state of aggregation and phase structures of multi-component polymer systems. It should be pointed out that metal-ion coordination is another unique strong bonding that can give rise to very stable supramolecular structures.\textsuperscript{28-30} The principles of supramolecular chemistry learned from the nature have been generalized to supramolecular polymers and other more complexed structures.
2.1.1 Supramolecular Liquid Crystalline Polymers Induced by Specific Interactions

The role of specific interactions in the formation of liquid crystals has not been recognized until the first example of liquid crystal induced by hydrogen bonding between carboxyl and pyridyl moieties was reported by Kato and Fréchet in 1989. Later, a broad spectrum of self-assembled liquid crystalline polymers with well-defined structures, such as side-chain, main-chain, combined, and network structures have been prepared by the self-assembly of polymers and small molecules as shown in Figure 2.1. The introduction of specific interactions as a key for the formation of molecularly assembled structures yields a new type of functional materials.

(a) Side-Chain-Type Supramolecular Liquid Crystalline Polymers

In the molecular design of self-assembled side-chain liquid crystalline polymers (SCLCPs), poly(4-vinylpyridine)(P4VP) is most widely employed primarily due to the easy accessibility of the nitrogen atom in 4-position of the pyridyl ring. In the first case, P4VP-based SCLCPs were achieved through hydrogen bonding between the pyridyl group in P4VP and the hydroxyl or carboxylic groups in phenol, pyrogallol or carboxylic acid derivatives. As an example of pyrogallol group, the as-prepared structure I exhibits smectic mesophase at room temperature and the layer spacing grows with the increase of molar ratio of pyrogallol due to the multifunctionality of the head group. Using 3-pentadecylphenol and 4-nonadecylphenol, the hydrogen bonding between the hydroxyl group of pentadecylphenol or 4-nonadecylphenol and the pyridyl group in P4VP was strong enough to yield mesomorphic lamellar structures and a full complexation is achieved when equimolar amounts of reactants were used. By dynamic
Figure 2.1. Schematic illustration of supramolecular polymers: (A) side-chain-type, (B) main-chain-type, (C) combined type, and (D) network type.\textsuperscript{32}
mechanical spectroscopy, it was demonstrated that these comb-like copolymers exhibited a similar behaviour to that of di- and triblock copolymers. However, it seems impossible for \( p \)-dodecylbenzenesulfonic acid to induce mesophase by ionic interactions with P4VP (Structure 2) in both bulky and solution states.\textsuperscript{36} The introduction of zinc dodecyl 4-benzyl sulfonate salt in a P4VP matrix (Structure 3) has been reported to be sufficient to yield mesomorphic behavior because of the complexation between the cation and pyridine ring.\textsuperscript{37}

Self-assembled side-chain liquid crystalline block copolymers have been employed for the formation of tridirectional proton conduction. The complexes of poly(styrene)-block-poly(4-vinylpyridine) (PS-\( b \)-P4VP), toluene sulfonic acid (TSA), and 3-
Figure 2.2. The formation of tridirectional proton conduction in the self-assembled side-chain liquid crystalline block copolymer: (a) Side-chain supramolecular complex consisting of PS-\textit{b}-PVP, TSA, and PDP; (b) Self-organized hierarchical structures of the supramolecular complex.\textsuperscript{38}
pentadecylphenol (PDP) form nanoscale phase-segregated structures, as shown in Figure 2.2.38 The hierarchical structure can be aligned by shear flow, resulting in monodomains. For the aligned complex, protonic transport is macroscopically tridirectional. The structural changes in two length scales, that is, microphase separation of block copolymer length and nanometer-level complexation as a function of temperatures cause drastic electrical conductivity changes.

A polyamide with 2,6-bis(acylamino)-pyridine moiety in the main chain was synthesized and then self-assembled structures 4 with a variety of benzoic acid derivatives were prepared through double hydrogen bonds.39,40 The polymeric complexes behave as single liquid crystalline polymers and exhibit stable and enantiotropic mesophases. It should be pointed out that these self-assembled complexes possess a very unique structure, because they share the features of side group and main chain polymers.

\[
\text{4}
\]
Very recently, Cui et al.\textsuperscript{41} have synthesized nonmesogenic azopyridine side chain polymers \textbf{5}, which can be transformed into photoactive liquid crystalline polymers through self-assembly. The idea behind the choice of azopyridine lies in that azopyridine has no terminal group, which is generally required for the formation of liquid crystalline phase.\textsuperscript{18} Adding such a terminal group could be accomplished through hydrogen bonding of pyridyl group with carboxylic acid derivatives. As a result, the side-chain azopyridine polymers without photoactivity can be induced into photoactive polymers through self-assembly, and thus smectic A mesophase was observed in most of the self-assembled samples. Using atom transfer radical polymerization, these authors also synthesized diblock copolymers composed of polystyrene (PS) and a polymethacrylate containing an azopyridine group.\textsuperscript{42} While conserving the photoactivity related to the \textit{trans-cis} photoisomerization of azo dyes, the azopyridine moiety made possible the easy use of self-assembly to add new functionalities to the block copolymer, leading to

\[
\begin{align*}
\text{CH}_2 \text{C} & \text{CH}_3 \\
\text{CH}_2 & \\
\text{C} & = \text{O} \\
\text{O} & \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{O} \\
\text{O} & \text{N} \\
\text{N} & \\
\text{HOC} & \text{O} \\
\text{R} & = \text{CN} \\
\text{R} & \text{NO}_2 \\
\text{R} & \text{O(CH}_2\text{)}_n\text{H} \\
n & = 1, 6, 10 \\
\text{(CH}_2\text{)}_n\text{H} & \\
n & = 1, 5, 9
\end{align*}
\]

\textbf{5}
multifunctional diblock copolymers. On one hand, carboxylic acid derivatives can be complexed with azopyridine moieties through hydrogen bonding that transformed the amorphous block copolymers into a liquid crystalline block copolymer. Self-assembly-induced liquid crystalline phases, dependent on the nature of acid used, could enhance the photoinduced orientation of azopyridine moieties. On the other hand, zinc-tetraphenylporphyrin (ZnTPP) has been linked to azopyridine through coordination interaction between the metal and pyridyl group, showing effective loading of metal-porphyrine inside microdomains of the azopyridine block. The complexation with ZnTPP made the azopyridine block become both photoactive and electroactive.

(b) **Main-Chain-Type Supramolecular Liquid Crystalline Polymers**

Specific interactions have been employed to form main-chain supramolecular liquid crystalline polymers between the complementary bifunctional molecules, analogous to the intermolecular reactions of covalent polycondensation. Therefore, when dicarboxylic acid 6 was interacted with the bipyridines 7-9, three main-chain liquid crystalline polymers were achieved through hydrogen bonding. All three polymeric complexes exhibited enantiotropic nematic mesophases, whereas their starting components did not show liquid crystalline behaviour. For complexes 6/7 and 6/9 the nematic-isotropic transition shows only a small hysteresis, while it is quite large (about 25 °C) for the 6/8 complex. In addition, the polymer resulting from 6 and 7 exhibited a smectic A phase as evidenced by the focal conic fan-type texture observed by polarized optical microscopy (POM).
A supramolecular main-chain polymer 10, which exhibits liquid crystallinity over a broad temperature, can be obtained by triple hydrogen bonding between difunctional diaminopyridines and difunctional uracil derivatives.\textsuperscript{44} Due to the presence of the chiral centers in tartaric acid, it was also possible to study the effect of chirality on the material properties. A lyotropic supramolecular liquid crystalline polymer 11 was also prepared through incorporation of a rigid 9,10-dialkoxyanthracene core into the structure of 10.\textsuperscript{45}
(c) Liquid Crystalline Networks Formed by Specific Interactions

The typical polymer networks like epoxy arise from the intermolecular reactions among multiple functional groups of respective monomers. Similarly, the specific interactions can also be utilized to construct a liquid crystalline network, for instance, the hydrogen bonding between a pentaerythritol-based tetrapyridyl derivative 12 with a flexible dicarboxylic acid 13. It can be learned from molecular modelling that the flexibility
about the $-\text{CH}_2\text{O}-$ linkages of the pentaerythritol core is insufficient for the molecule to adopt a tetrahedral conformation. Instead, it exists essentially as a one-dimensional rod with the pyridyl moieties at each of the four ends lying together in pairs. As a result, the texture does not closely resemble any well-known liquid crystalline phase although it may be smectic, being similar to certain liquid crystalline polymers. The polymeric extended chain structure for the complexes can be confirmed by the fact that fibers could be drawn from the mesomorphic melt.

Furthermore, another polymeric network can be also prepared through the hydrogen bonding interactions of a chiral, bifunctional hydrogen-bonding acceptor, 14, with a chiral trifunctional hydrogen-bonding donor 15-18. The chiral stibazole dimer was
complexed with the trifunctional acids in a 1:1 molar ratio. Interestingly, all components used were not mesomorphic, whereas all the complexes, except the one resulting from 14 and 18, exhibited cholesteric phases. These results lead to the conclusion that helical supramolecular networks may be formed from non-mesomorphic molecules. Also, it should be pointed out that the cholesteric texture was preserved in the glassy states of the networks.

2.1.2 Supramolecular Polymers via Metal-Ion Coordination

Metal coordination, besides hydrogen-bonding and ionic interactions, represents another powerful tool for the construction of supramolecular architectures. The incorporation of metal-ligand bonding into organic molecules imparts new and potentially useful physical and chemical properties to the final materials, including optical activity, electrical conductivity, luminescence, and photorefractivity, magnetism, and so on. Usually for the incorporation of metal binding sites into polymers, bidentate and tridentate ligands such as 2,2'-bipyridine (bpy) and 2,2':6',2''-terpyridine (tpy), respectively, are employed, as well as some other nitrogen-containing heterocycles. It should be pointed out that terpyridine has played a significant role as a chelating ligand for a variety of transition-metal ions in low oxidation state, especially Ru(II), Fe(II), Cu(II), Co(II), Os(II), Ir(III), Ni(II), Mn(II), and Zn(II), forming very stable octahedral complexes. Within all these metal ions, ruthenium is one of the most favorable toward the development of coordination polymers because it allows the direct synthesis of both asymmetric complexes and symmetric systems. Didentate ligands, such as bipyridine or phenanthroline, on the other hand, give rise to two different conformations (fac and mer
stereoisomers) around an octahedral metal ion, which are not so easy to selectively control.

Several synthetic strategies for the incorporation of nitrogen-containing heterocyclic ligands into the polymer chains have been reported: end-group modification, copolymerization of terpyridine-modified monomers, functionalized initiators, and end cappers.\textsuperscript{51,52} Moreover, the incorporation of oligopyridine complexing units onto a polymeric backbone has enabled the construction of various architectural systems, such as block copolymers, linear coordination polymers, and star-shaped architectures. Oligopyridine ligands or complexes have been used as initiators for living and controlled polymerizations, leading to well-defined supramolecular polymeric complexes. Another interesting approach is the introduction of pendant nitrogen-containing heterocyclic units as side chains of a polymeric backbone.

(a) **Self-assembled side-chain metallo-supramolecular polymers**

Polymers having pendent or side-chain chelating ligands are of special interest for potential applications such as sequestration agents for a variety of metal ions and for the formation of polymer-metal complexes that may behave as redox polymers and homogeneous or heterogenous catalysts.\textsuperscript{53,54} Polymer-metal complexes containing 2,2'-bipyridinyl pendent ligands have outstanding properties such as redox polymers in chemically modified electrodes and also act as efficient light-harvesting systems in solar energy conversion applications.\textsuperscript{55,56} Poly(vinyl-2,2'-bipyridyls) were found to be effective sequestration agents for transition metals. Homopolymers and styrene copolymers derived from 4'-vinyl-2,2':6',2"-terpyridinyl were prepared in chlorobenzene at 60 °C by using azobis(isobutyronitrile) (AIBN) initiation, and monomer reactivity
ratios were determined for styrene copolymers. These polymeric systems containing terpyridinyl ligands readily formed complexes with Co, Cu, and Zn cations. It should be noted that removal of the metal ions from these polymer-metal complexes occurred readily on washing the complex with acid, indicating the reversibility of these polymer-metal complexes.

A PMMA-based copolymer with terpyridine units in the side chain was synthesized utilizing free-radical polymerization process. Using the the ruthenium(III)/ruthenium(II) chemistry known from supramolecular science, different organic and polymeric moieties were grafted onto the copolymer, yielding a new class of compounds. The materials were characterized by means of NMR and UV-vis spectroscopies as well as GPC and revealed distinct changes in their thermal properties as compared with the starting materials.

Furthermore, well-characterized homopolymers, block copolymers, and statistical polymers containing terpyridine in the side chain with controlled molecular weights,
compositions and relatively narrow polydispersities were synthesized via atom transfer radical polymerization (ATRP) that contain activated esters for the subsequent incorporation of terpyridine under nucleophilic conditions. Here the binding of lanthanide ions including Dy\(^{3+}\), Eu\(^{3+}\), Tb\(^{3+}\), Sm\(^{3+}\) to generate emissive materials with violet, blue, green, and red light has been demonstrated. Another polymer containing side-chain terpyridine ligands was also synthesized using ATRP process. Subsequently, the ruthenium(III)/ruthenium(II) complexation chemistry was employed for the attachment of bis(dodecyloxy)-functionalized terpyridine moieties onto each side-chain 2,2':6',2"-terpyridine unit of the polymeric backbone. Thus, the grafting approach was successfully combined with metal-ligand-coordination chemistry for the preparation of highly soluble polymeric complexes.
(b) Self-assembled metallo-supramolecular block copolymers

Metallo-supramolecular block copolymers were usually obtained through the two-step-organization processes involving mono-complexation of one terpyridine end-functionalized polymer with RuCl₃ followed by bis-complexation of a second, differently substituted terpyridine ligand. For instance, PS-[Ru]-PEO block copolymers 22, where -[Ru]- represents a ruthenium(II)-terpyridine bis-complex, were synthesized by introducing the terpyridine ligand at the chain ends of PEO and PS with various lengths and then combining two blocks using ruthenium(III)/ruthenium(II) chemistry. The melt morphology of the metallo-supramolecular PS-[Ru]-PEO diblock copolymer was studied by small-angle X-ray scattering (SAXS), indicating that the presence of the metal ligand complex (MLC) in the chains leads to a different morphology from that of a conventional counterpart. The electrostatic interaction between the MLC ions and their associated counterions drives them to form aggregates. The PS₃₇₅-[Ru]-PEO₂₂₅ was employed to prepare nanoporous thin films through directly yielding cylindrical microdomains oriented normal to the substrate and then opening the ruthenium(II)-terpyridine bis-complex via redox chemistry and extracting the PEO block to create the nanopores.
A metallo-supramolecular amphiphilic diblock copolymer 23 has been prepared through the self-assembly of a terpyridine functionalized poly(ethylene oxide) (PEO) with an organometallic poly(ferrocenylsilane) (PFS) bearing one terpyridine end-group.65 The exclusive formation of the diblock has been confirmed by a combination of various analytical techniques. Micelles were then prepared in water from this copolymer. Because the bulk sample could not be solubilized directly in water, the transient use of an organic nonselective solvent was required. Crystallization of the short PFS blocks occurred during the micellization process, resulting in the formation of cylindrical micelles.

Another conjugated metallo-supramolecular block copolymers 24 were synthesized through the ruthenium complex between poly(p-phenylenevinylene) (PPV)-donor and PPV-acceptor bearing a terminal terpyridine chelating unit.66 Studies on the incorporation of such ligands and supramolecular building blocks into polymers were performed through photophysical properties. The polymers were found to transfer energy to the complexes as seen through the complexes ability to quench fluorescence. The coordination polymers were applied to photovoltaics, and two types of devices were prepared: polymer solar cells obtained by spin-coating of the coordination polymer.
solution onto indium tin oxide (ITO) substrates and dye-sensitized solar cells obtained by absorption on TiO₂ nanocrystalline films using two different electrolytes. The incorporation of a ruthenium complex into a conjugated polymer has the potential to facilitate the charge carrier generation. Such metal complexes usually exhibit a reversible Ru^{II,III} redox process and some ligand-centered redox processes. In addition, a metal complex incorporated into a polymer will influence the optical and electronic properties of the polymer due to its characteristic metal-to-ligand charge transfer (MLCT) transition at around 500-600 nm, thus extending the absorption range of the material.

![Diagram of a self-assembled end-capped metallo-supramolecular polymer](image)

(c) Self-assembled end-capped metallo-supramolecular polymers

New metal-containing and emissive materials are finding applications in various research fields, such as labeling reagents for biological substrates and display materials.⁶⁷ Although d⁶-transition metals such as ruthenium(II), osmium(II), and rhenium(II) polypyridine complexes have attracted considerable attraction, iridium(III) species are far less investigated, mainly because of synthetic problems in the past. Despite this fact, iridium(III) complexes are highly appealing because of their wide range of emission energies, long lifetimes, and high quantum yields.⁶⁸,⁶⁹ The study of emissive and redox-
active d⁶-transition-metal complexes, such as those of iridium(III) and ruthenium(II), has been extended in recent years to applications in light-emitting devices and in light-emitting electrochemical cells.⁷⁰,⁷¹ For potential applications in devices or in display technology, it is of importance to have phosphorescent emitters that are easily processed, do not decay, and have high quantum yields and lifetimes of several microseconds. These requirements can be fulfilled if the emitted light results from MLCT processes.⁷² In this way, a variation of the ligand set may induce a change in the color of the emitted light. Despite these properties, the ligands of metal-ligand complexes can be used to introduce side chains, which can consist of various functionalities. On the basis of terpyridine functionalized poly(ethylene oxide) (PEO) 25 and polystyrene (PS) 26, a series of light-emitting iridium(III) compounds was effectively synthesized.⁷³,⁷⁴ The described materials have the potential for applications in light-emitting electrochemical cells and molecular electronics. Their optical and electric properties as well as their film forming abilities and processing characteristics have been studied revealing general potential as light-emitting materials.
(d) Self-assembled linear metallo-supramolecular polymers

The synthesis of linear metallo-supramolecular polymers is one of active areas in recent years, which provide new organic-inorganic hybrid materials with potential novel properties, e.g., for application as smart materials, intelligent glues or electro- and photoactive compounds. Ligands containing multiple terpyridine metal-binding domains can be utilized for engineering of linear coordination polymers, as well as metallo-macrocyrcles. Rigid linear building blocks result in rod-like coordination polymers. They have been prepared with different transition metals, such as ruthenium(II), iron(II), zinc(II) and cobalt(II). Building blocks with rigid spacer units that provide a well-defined angle between the metal-binding units lead to cyclic structures. The application of small, rigid spacer units results generally in restricted molecular weights and mostly in poor solubilities. However, well-soluble high-molecular-weight polymers are of special interest and are extensively utilized as functional ingredients in a variety of applications. Reversible systems can serve as intelligent hydrogels and can be applied for drug delivery or as smart materials (e.g. self-healing coatings). Linear ruthenium(II) and iron(II) coordination polymers were synthesized utilizing flexible oligo and poly(ethylene glycol) spacer units: bis(2,2':6',2″-...
terpyridine-4′-yl)-di(ethylene glycol) 27 and the telechelic bis(2,2′:6′,2″-terpyridine-4′-yl)-poly(ethylene glycol)\textsuperscript{180} 28.\textsuperscript{84} The application of higher telechelic concentrations for the synthesis of coordination polymers yielded high solution viscosities.

Most soluble coordination polymers, be they linear or hyperbranched, are held together by kinetically stable metal-ligand interactions and do not show dynamic reversibility that is observed in true supramolecular polymers. Kinetically labile coordination complexes of metal ions such as Cu(I) and Ag(I) are required to form such aggregates.\textsuperscript{85} On the basis of a combination of vapor pressure osmometry and conductivity measurements in methanol, the average degree of polymerization (DP) at 0.14 M concentration was estimated to be approximately 11. The reversibility of association was evident from concentration dependence of the DP; at low concentrations only a monomeric complex was observed. Coordination complexes of Cu(I) (structure 29) and Ag(I) with phenanthroline ligands have been used to prepare the first constitutionally well-defined coordination polymers from kinetically labile complex in 1996.\textsuperscript{86} It was demonstrated that high-molecular-weight polymers can be obtained from rigid bis(phenanthrolinyl)ligand and Cu(I), if the solvent used cannot act as a competitive ligand for the metal.
2.2 Molecular Design of Heterocyclic Polymers

2.2.1 High Performance Heterocyclic Polymers

Heterocyclic polymers were introduced in the 1960s in order to meet the thermal stability requirements for the aerospace industry. Heterocyclic rings offer conjugated rigid structures with high glass transition temperature and strong linkage, allowing good resistance in harsh environments. A large number of heterocyclic polymers are prepared by reactions that lead to intermediate polyamides or related polymers that subsequently undergo cyclization leading to the heterocyclic systems. However, relatively few have seen commercial development, partly due to the high cost of starting materials, but probably because of the difficulty in processing polymers that have very high glass transition temperatures.

Generally, there are four types of reactions that were employed to synthesize heterocyclic polymers: (1) Reaction of di- or polyfunctional monomers that undergo polycondensation reactions; (2) cyclization of precursor polymers, (3) homopolymerization of monomers containing a single functional group capable of undergoing a cyclization reaction; and (4) oxidative polymerization of an existing heterocyclic compound. Up to now, numerous synthetic methods have been explored to obtain heterocyclic polymers for high-performance applications, and they are summarized in Table 2.1.

2.2.2 Heterocyclic Conjugated Polymers

The current interest in heterocyclic conjugated polymers is due to the substantial $\pi$-electron delocalization along their backbones which gives rise to interesting
Table 2.1. Molecular designs of high-performance heterocyclic polymers

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>Molecular Structure</th>
<th>Functional Groups for Reactions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybenzimidazole</td>
<td><img src="image" alt="Structure" /></td>
<td>Phenyl ester + diamine</td>
<td>91-93</td>
</tr>
<tr>
<td>Polyimidazopyrrolone</td>
<td><img src="image" alt="Structure" /></td>
<td>Anhydride + diamine</td>
<td>94</td>
</tr>
<tr>
<td>Polybenzoxazole</td>
<td><img src="image" alt="Structure" /></td>
<td>Phenyl ester + o-aminophenol</td>
<td>95,96</td>
</tr>
<tr>
<td>Polybenzothiazole</td>
<td><img src="image" alt="Structure" /></td>
<td>Phenyl ester + o-aminophenol</td>
<td>97,98</td>
</tr>
<tr>
<td>Polyhydantoin</td>
<td><img src="image" alt="Structure" /></td>
<td>Diisocyanates + bis(α-amino acids)</td>
<td>99,100</td>
</tr>
<tr>
<td>Poly(parabanic acid)</td>
<td><img src="image" alt="Structure" /></td>
<td>Isocyanate + HCN</td>
<td>101,102</td>
</tr>
<tr>
<td>Polyquinoxaline</td>
<td><img src="image" alt="Structure" /></td>
<td>Tetracarbonyl compounds + tetramines</td>
<td>103,104</td>
</tr>
<tr>
<td>Polypyrazine</td>
<td><img src="image" alt="Structure" /></td>
<td>bis(α-haloketones) + ammonia</td>
<td>105</td>
</tr>
<tr>
<td>Polypyrazole</td>
<td><img src="image" alt="Structure" /></td>
<td>1,3-dicarbonyl compounds + hydrazine derivatives</td>
<td>106</td>
</tr>
<tr>
<td>Polyimidazole</td>
<td><img src="image" alt="Structure" /></td>
<td>Tetraketones + dialdehydes + ammonia</td>
<td>107</td>
</tr>
<tr>
<td>Poly(as-triazine)</td>
<td><img src="image" alt="Structure" /></td>
<td>Dihydrazines + bisdicarbonyl compounds</td>
<td>108</td>
</tr>
</tbody>
</table>
Table 2.1. Molecular designs of high-performance heterocyclic polymers (continued)

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>Molecular Structure</th>
<th>Reactant(s)</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polytriazoline</td>
<td><img src="image" alt="Polytriazoline" /></td>
<td>Dihydrazines + dialdehydes</td>
<td>108</td>
</tr>
<tr>
<td>Polyquinoline</td>
<td><img src="image" alt="Polyquinoline" /></td>
<td>Bis(o-aminocarbonyl) compounds + diacetyl compounds</td>
<td>109,110</td>
</tr>
<tr>
<td>Polyanthrazoline</td>
<td><img src="image" alt="Polyanthrazoline" /></td>
<td>Bis(o-aminocarbonyl) compounds + diacetyl compounds</td>
<td>111</td>
</tr>
<tr>
<td>Poly(1,3,4-oxadiazole)</td>
<td>![Poly(1,3,4-oxadiazole)]</td>
<td>Hydrazide</td>
<td>112,113</td>
</tr>
<tr>
<td>Poly(1,2,4-triazole)</td>
<td>![Poly(1,2,4-triazole)]</td>
<td>Hydrazide + amine</td>
<td>114</td>
</tr>
<tr>
<td>Poly(1,3,4-thiadiazole)</td>
<td>![Poly(1,3,4-thiadiazole)]</td>
<td>Thiohydrazide</td>
<td>115</td>
</tr>
<tr>
<td>Polytetraazopyrene</td>
<td><img src="image" alt="Poltetraazopyrene" /></td>
<td>Tetraamine + diphenyl ester</td>
<td>116</td>
</tr>
<tr>
<td>Polybenzoxaninone</td>
<td><img src="image" alt="Polybenzoxaninone" /></td>
<td>Acid chloride + o-aminobenzoic acid</td>
<td>117</td>
</tr>
<tr>
<td>Polyimidine</td>
<td><img src="image" alt="Polyimidine" /></td>
<td>Lacone + amine</td>
<td>118</td>
</tr>
<tr>
<td>polyisoindoloquinazolinedione</td>
<td><img src="image" alt="polyisoindoloquinazolinedione" /></td>
<td>Anhydride + o-aminobenzamide</td>
<td>119</td>
</tr>
<tr>
<td>polyquinazolinedione</td>
<td><img src="image" alt="polyquinazolinedione" /></td>
<td>Isocyanate + o-aminobezamide</td>
<td>120</td>
</tr>
</tbody>
</table>
optical and nonlinear optical properties and allows them to become good electrical conductors, especially when oxidized or reduced. These properties may lead to a variety of practical applications such as information storage and optical signal processing, substitutes for batteries and materials for solar energy conversion.

(a) Polythiophene and Polypyrrole

Polythiophene 30 and polypyrrole 31 are two typical examples of heterocyclic conducting polymers used today. It was not until the early 1980s that any well-defined polythiophene was obtained. After the first reports of a controlled synthesis by Yamamoto and Lin,121,122 using the Grignard-type coupling of 2,5-dibromothiophene, a vast number of articles concerning the synthesis and properties of polythiophenes has been published. This lack of solubility and processability, as well as problems related to the characterization of polythiophenes, has been overcome by the introduction of flexible side chains at the 3- and/or 4-position.123 Appropriate solubility in common organic solvents has been achieved with an alkyl side chain of more than four carbon atoms at every repeating unit. The mechanism of the electrochemical polymerization of polypyrrole is similar to that of thiophene. Oxidized polypyrrole is stable under ambient conditions and up to temperatures exceeding 300 °C. Similar to polythiophene, soluble polypyrroles can also be prepared by the introduction of flexible side chains.124,125
(b) Polypyridine

Polypyridine has been synthesized through the homocoupling of 2,5-dirbromopyridine or 5,5′-dibromo-2,2′-bipyridine with zerovalent nickel catalysts. The polymers (32 and 33) are only soluble in formic acid as is also in the case in methyl substituted polypyridine. However, the introduction of hexyl groups not only increases the molecular weight of the polymer but also induces solubility in other organic solvents. The soluble polymeric platinum or ruthenium complexes can act as photocatalysts for H₂ evolution from aqueous media. The polymeric complexes can also transfer the photoactivated energy to other molecular parts of the systems and thus cause emission of light from other parts of the molecules. Recently, the peculiar properties of these polypyridines have been attributed to self-assembly. Poly(pyrimidine-2,5-diyl) 34 has been prepared utilizing the same method. Other examples of heterocyclic homopolymers are polypyridazine 35, polythiazole 36, poly(quinoline-5,8-diyl) 38, and poly(isoquinoline-1,4-diyl) 39, and poly(quinoxaline-5,8-diyl) 37.
Sassoon first described a two-electrolyte system for energy storage based on tris(bipyridine)ruthenium compounds and a N,N,N,N-tetraalkyl-p-phenylenediamine derivative bound covalently to a poly(3,3-ionene) polyelectrolyte 40. An inhibition of more than five orders of magnitude in the photochemical properties of the system were found relative to the reverse electron-transfer reaction between [Ru(bpy)₃] and the radical cation of N,N,N,N-tetraalkyl- p-phenylenediamine.

\[
\begin{align*}
\text{CH}_3 \quad \text{CH}_3 \\
\text{N} \quad \text{N}
\end{align*}
\]

Wang et al. 136 described a novel approach for preparing metal-ion-sensitive polymers, in which they chose a partially conjugated polymeric system (structure 41 and 42) consisting of different ratios of oligo(p-phenylenevinylene) segments that were covalently connected to bipyridines at their 5,5'-positions by a Wittig type reaction. The corresponding metal complexes formed, and the optical behavior of the uncomplexed polymer and the polymer/ion complex has been compared. The addition of Pd(II) ions to the polymer shifts the absorption maximum of the uncomplexed polymer from 455 to 564 nm. Different absorption maxima were obtained with different metal ions, with the shift ranging from 38 to 112 nm. The effects of conjugation on the photophysics and excitation
dynamics of these polymers were investigated by Chen. Relative to the homopolymers, they demonstrated blue shifts in their absorption and emission spectra, spectral diffusion in stimulated emission, and enhancement in their photoluminescence quantum yields and lifetimes.

\[ \text{41} \]

A conjugated polymer \textbf{43} with a rigid backbone and molecular weights up to 23,000 g/mol was obtained from the reaction of 5,5′-dibromobipyridine and substituted phenyldiacetylenes. Fluorescence quantum yields $\Phi_n$ between 71 and 96% make these new compounds potential candidates for light-emitting diode (LED) or laser dye applications.

\[ \text{43} \]
Bipyridine-containing poly(benzobisoxazole)s and poly(benzobisthiazole)s (structures 44 and 45) were first synthesized by Evers and Moore\textsuperscript{139} when they copolymerized bipyridine-4,4'-dicarboxylic acid chloride with terephthalic acid and 4,6-diamino-1,3-benzenediol dihydrochloride or 2,5-diamino-1,4-benzenedithiol. The polymers were thermally stable up to 316 °C and displayed thermo-oxidative stability for 200 h. Yu et al.\textsuperscript{140,141} later reported the synthesis and physical properties of a series of poly(benzobisoxazole)s and poly(benzobisthiazole)s containing bipyridine derivatives. These polymers were synthesized by polycondensation of bipyridine-4,4'-dicarboxylic acid or bipyridine-5,5'-dicarboxylic acid and diaminobenzenediols in poly(phosphoric acid). The polymers exhibited thermal stability up to 650 °C in a nitrogen atmosphere and up to 590 °C in air. Polymers containing bipyridine-5,5'-dicarboxylic acid demonstrated a lyotropic liquid-crystalline phase in methanesulfonic acid; however, the polymers containing bipyridine-4,4'-dicarboxylic acid did not demonstrate any anisotropy. The formation of polymeric ruthenium complexes increases the mobility of the charge carriers by two orders of magnitude to $10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$.
2.2.3 Heterocyclic Liquid Crystalline Polymers

Introduction of heterocycles into the molecular core of liquid crystals has been extensively investigated in the past 20 years.\textsuperscript{142,143} The mesophases are stabilized by the strong association or dipole-dipole interaction between the heterocyclic rings due to their electronic and geometrical structures. Heterocyclic liquid crystals exhibit particular optical,\textsuperscript{144} ferroelectric or antiferroelectric,\textsuperscript{145,146} photoluminescent, and self-assembled properties.

Hanabusa et al.\textsuperscript{147} first synthesized thermotropic liquid-crystalline polyesters (46 and 47) with the bipyridine unit acting as a mesogene. Polyesters having a flexible spacer were smectic in the absence or at low concentrations of metal ions, while in the case of aromatic polyesters a nematic mesophase was observed. The electron spin resonance (ESR) spectroscopy was used to examine the structural properties of a polyester/Cu(II) complex. Later, Lee et al.\textsuperscript{148} reported the synthesis of a polyester having a chemical structure similar to that synthesized by Hanabusa et al. by employing a modified Schotten-Baumann reaction of 4,4′-bis(hydroxymethyl)bipyridine and dodecanedioyl dichloride in tetrahydrogenfuran (THF). However, they treated bis(hydroxymethyl)bipyridine with [Ru(bpy)\textsubscript{2}Cl\textsubscript{2}] due to the poor solubility of the resulting polymer, and then polymerized the treated ruthenium complex with dodecanedioyl dichloride to obtain a polymer with an average molecular weight of about 5500 g/mol, which became soluble in acetone using PF\textsubscript{6}\textsuperscript{−} counterions. However, in the case of counterions Cl\textsuperscript{−} chosen, the polymer complex was only soluble in polar solvents such as water or methanol. A spin-coating technique or a layer-by-layer self-assembly technique was utilized to prepare light-emitting devices. The spin–coated devices
produced maximum luminance levels of 250-300 cd/m² with an external quantum efficiency of 0.2% photons per electron. Devices based on sequentially adsorbed layers of the polyester and poly(acrylic acid) exhibited a maximum light output of 40-50 cd/m² and external quantum efficiency of 1–3% photons per electron.

![Chemical structure 46]

Recently, Chan et al.\textsuperscript{149,150} described the synthesis of a broad range of bipyridine-based polyamides\textsuperscript{48} that were synthesized by Yamazaki’s method using pyridine and triphenyl phosphite and polyesters\textsuperscript{49} that were synthesized by either alcoholysis of acid chlorides or transesterification. The resulting polymers based on bipyridine-5,5′-dicarboxylic acid demonstrated a higher viscosity and decomposition temperature (300–500 °C) than polymers based on bipyridine-4,4′-dicarboxylic acid. The decomposition temperatures for the polyesters were demonstrated to be in a narrower range, namely 320–440 °C. Static light scattering techniques were applied to determine molecular weight to be 20,000–40,000 g/mol for the polyamides. Some of these polymers exhibit liquid crystallinity, as observed by polarized optical microscope. The polymers were treated with bis(bipyridine)ruthenium complexes to incorporate metal ions.

![Chemical structure 47]
Very recently, Sato et al.\textsuperscript{151-156} synthesized a series of heterocyclic TLCPs (for example, 50–54) containing 1,3,4-thiadiazole in the main chain. 1,3,4-Thiadiazoles are five-membered heterocycles having sulfur and nitrogen atoms, and are analogous to the corresponding 1,3,4-oxadiazoles.\textsuperscript{157} Semi-rigid polyesters containing terphenyl\textsuperscript{153} and quaterphenyl\textsuperscript{154} analogues with 1,3,4-thiadiazole in the main chain can not only form thermotropic nematic and/or smectic mesophases, but also emit photoluminescent (PL) and electroluminescent (EL) light. Polyesters having the distyrylbenzene analogue containing 1,3,4-thiadiazole formed both thermotropic smectic C and lyotropic LC phase.\textsuperscript{155} Quaterphenyl analogues containing 2,2′-bis(1,3,4-thiadiazole) showed EL behavior in addition to LC formation and PL properties with blue and green emission.\textsuperscript{158} Similarly, polyethers 55 containing 1,3,4-oxadiazole was also reported to have nematic mesophase and photoluminescent properties.\textsuperscript{159} The light-emitting properties of these thermotropic liquid crystalline polymers are expected to be candidate materials for organic EL devices.
52

53

54 $m = 8, 10, 12$

55 $m = 5, 8$
3.1 Synthesis of A Series of Functional Heterocyclic Liquid Crystalline Polymers.

Three nitrogen-containing heterocyclic liquid crystalline polymers were synthesized through polycondensation, the detailed synthesis procedures are given as follows.

3.1.1 Synthesis of a Segmented Main-Chain Liquid Crystalline Polymer with Pendent Pyridyl Group (PyHQ12)

PyHQ12 was synthesized using the reaction route shown in Figure 3.1.

*Synthesis of trans-2', 5'-diacetoxy-4-stilbazoale (I).* To a 100 mL three-neck flask was added 2,5-dihydroxybenzaldehyde (2.8 g, 20 mmol), 4-picoline (2.4 g, 25 mmol), and 20 mL acetic anhydride. The reaction mixture was stirred at 120 °C for 24 h. The excessive acetic anhydride and 4-picoline was removed by reduced pressure evaporation. The crude product was then purified over a silica gel column chromatography using chloroform/acetone (10/1, v/v) as eluent to give 1.3 g. Yield = 21%; mp = 131 °C. ^1^H NMR (δ, CDCl_3-d): 2.31 (d, 3H, −CH_3), 2.38 (d, 3H, −CH_3), 6.99 (d, 1H, −CH=CH−), 7.10 (t, 1H, Ar−H), 7.13 (d, 1H, Ar−H), 7.23 (s, 1H, −CH=CH−), 7.34 (d, 2H, Pyridyl−H), 7.42 (d, 1H, Ar−H), 8.59 (d, 2H, Pyridyl−H). FTIR (KBr, cm⁻¹): ν 3060, 3024, 1760, 1594, 1486, 1420, 1368, 1208, 1172, 1094, 1012, 982, 918, 802, 764, 614, 582, 560, 518.
Figure 3.1. Synthetic Route for PyHQ12.
**Synthesis of 4,4′-dicarboxy-1,12-diphenyldodecane (II).** Methylhydroxy benzoate (7.7 g, 50 mmol) and anhydrous K₂CO₃ (11.3 g, 75 mmol) were first dissolved into 50 mL DMF in a 3-neck flask, and at the same time 1,12-dibromodecocane (8.4 g, 25 mmol) was also dissolved into 50 mL DMF (one-neck flask). After both were stirred for 1h at room temperature, the temperature of methyl hydroxyl benzoate/DMF solution was increased to 40-50 °C, and then 1,12-dibromodecocane/DMF solution was added dropwise. The temperature of the mixture was then increased to 135 °C. After refluxing for 4-5 h under atmosphere of argon gas, the reaction system was cooled slowly to room temperature. Then, the reaction mixture was poured into 1 L of cold water. The precipitate was filtered and washed several times by distilled water to remove inorganic salts. The crude product was recrystallized twice in ethanol. The obtained product (9.4 g, 20 mmol) and potassium hydroxide (16.8 g, 300 mmol) were mixed in ethanol. After refluxing for 5 h at 90 °C, hot reaction mixture was immediately poured into 2 L of boiling water, and then the solution became transparent. 3 M Hydrochloric acid (HCl) in water was added until the PH of the solution reached to 2-3. Then, the solution was allowed to cool in the refrigerator for 1 day and filtered. The crude product was dissolved into the mixed solvents of ethanol and DMF and recrystallized twice. It was obtained in white powder. Yield = 65%; mp = 265 °C. ^1H NMR (δ, DMSO): 1.2-1.45 (m, 16H, −CH₂−), 1.69 (m, 4H, −CH₂−), 3.99 (t, 4H, −CH₂O−), 6.96 (d, 4H, Ar−H), 7.87 (d, 4H, Ar−H). FTIR (KBr, cm⁻¹): ν 3064, 2923, 2852, 2670, 2546, 1679, 1604, 1572, 1510, 1470, 1431, 1302, 1250, 1165, 1112, 1032, 997, 930, 842, 767, 727, 691, 638, 545, 501.
Melt polymerization of PyHQ12 via acidolysis. To a three-neck 50 mL flask, equipped with an overhead condenser with argon gas inlet and vacuum line on the adapter, were added monomer I (3.3 g, 10 mmol), monomer II (4.4 g, 10 mmol), and 2 mol% zinc acetate as a catalyst. The reaction mixture was heated to 240 °C in a salt bath while an argon gas passed through. After maintaining the reaction mixture at this temperature for 0.5 h, the temperature was raised to 250 °C and kept there for 3 h, and then a reduced pressure (0.1–0.2 mm Hg) was applied slowly to the system at 260 °C for 0.5 h. A yellowish product was obtained, which was then dissolved in pyridine and precipitated in methanol. The product was filtered and dried in a vacuum oven. Yield = 90%. ¹H NMR (δ, pyridine-d₅): 1.2-1.6 (m, 16H, –CH₂–), 1.82 (m, 4H, –CH₂–), 4.06 (d, 4H, –CH₂O–), 6.99 (d, 1H, –CH=CH–), 7.10 (t, 1H, Ar–H), 7.15 (d, 4H, Ar–H), 7.20 (d, 1H, Ar–H), 7.23 (s, 1H, –CH=CH–), 7.36 (d, 2H, Pyridyl–H), 7.40 (d, 1H, Ar–H), 7.90 (d, 4H, Ar–H), 8.60 (d, 2H, Pyridyl–H).

For comparison, the other LCP having pendent phenylsulfonyl group (PSHQ12) with the chemical structure

![Chemical Structure](attachment:PSHQ12.png)

was synthesized according to the procedures described in the literature.¹⁶⁰,¹⁶¹
3.1.2 Synthesis of a Segmented Main-Chain Liquid Crystalline Polymer having Side Chain Azopyridine with Flexible Spacer (PABP)

PABP was synthesized using the reaction route shown in Figure 3.2.

*Synthesis of 4-(4-hydroxyphenylazo)pyridine (III).* To a 20 mL 10% (w/w) NaOH aqueous solution were added phenol (5.0 g, 53 mmol) and sodium nitrate (4.0 g, 58 mmol), which was added dropwise to a solution of 4-aminopyridine (6.0 g, 64 mmol) dissolved in a HCl solution (25 mL concentrated HCl: 16 mL distilled water) at 0 °C. After stirring for 30 min, the reaction mixture was adjusted to pH = 6-7 by addition of a 10% (w/w) NaOH aqueous solution. An orange precipitate was collected by filtration, washed with water, and dried. Recrystallization from methanol gave 3.5 g of product. Yield = 35%. mp = 265 °C. $^1$H NMR (δ, DMSO): 6.96 (d, 2H, Ar-H), 7.63 (d, 2H, Ar-H), 7.88 (d, 2H, Pyridyl-H), 10.56 (s, 1H, -OH). FTIR (KBr, cm$^{-1}$): ν 3033, 2900, 2794, 2684, 2560, 2471, 1582, 1470, 1395, 1294, 1254, 1130, 1001, 833, 727, 643, 550.

*Synthesis of diethyl 5-[4-(4-pyridylazo)]pentylmalonate (IV),* which was denoted as PAPM hereafter. 4-(4-Hydroxyphenylazo)pyridine (2.0 g, 10 mmol) and anhydrous powdered K$_2$CO$_3$ (4.1 g, 30 mmol) were dissolved in 30 mL butanone and stirred at 50 °C for 1 h. Then, a solution of diethyl (5-bromopentyl)malonate dissolved in 20 mL butanone and a trace of potassium iodide were added to the above mixture and refluxed for 3 days. After filtration and evaporation of the solvent, the crude product was purified over a silica gel column chromatography using chloroform/acetone (5/1, v/v) as eluent, and then recrystallized from hexane/ethyl acetate (2/1, v/v) to give 3.0 g orange product. Yield = 70%; mp = 66 °C. $^1$H NMR (δ, CDCl$_3$): 1.28 (t, 6H, -CH$_3$), 1.30-1.55 (m, 4H, CH$_2$), 1.55-1.60 (m, 2H, CH$_2$), 1.75-1.90 (m, 2H, CH$_2$), 2.64-3.00 (m, 3H, CH$_2$), 3.65-3.90 (m, 2H, CH$_2$), 7.30-7.70 (m, 5H, Ar-H), 8.75-9.00 (m, 2H, Pyridyl-H), 10.50-10.60 (s, 1H, -OH). FTIR (KBr, cm$^{-1}$): ν 3033, 2900, 2794, 2684, 2560, 2471, 1582, 1470, 1395, 1294, 1254, 1130, 1001, 833, 727, 643, 550.
Figure 3.2. Synthetic Route for PABP.
\(-\text{CH}_2\)-), 1.78-2.0 (m, 4H, \(-\text{CH}_2\)-), 3.32 (t, 1H, \(-\text{CH}\)-), 4.06 (t, 2H, \(-\text{CH}_2\text{O}\)-), 4.18 (q, 4H, \(-\text{CH}_2\text{CO}\)-), 7.01 (d, 2H, Ar–H), 7.75 (d, 2H, Ar–H), 7.96 (d, 2H, Pyridyl–H), 8.78 (d, 2H, Pyridyl–H). FTIR (KBr, cm\(^{-1}\)): \(\nu\) 2983, 2943, 2915, 2870, 1727, 1603, 1578, 1497, 1465, 1405, 1373, 1300, 1256, 1216, 1143, 1107, 1059, 1022, 833, 797, 708, 551.

**Synthesis of 4, 4′-bis(6-hydroxy-1-hexyloxy)biphenyl (V).** 4, 4′-bis(6-hydroxy)biphenyl (2.9 g, 15 mmol) was added to a solution of K\(_2\)CO\(_3\) (20.7 g, 150 mmol) in 100 mL of DMF. After the addition of 6-chloro-1-hexanol (6.4 g, 45 mmol) and a trace of potassium iodide, the mixture was refluxed for 12 h and then neutralized with HCl and diluted with 200 mL of distilled water. The precipitate was recrystallized from chloroform to give 2.8 g white solid. Yield = 50%. \(^1\)H NMR (\(\delta\), DMSO): 1.25–1.50 (m, 12H, \(-\text{CH}_2\)-), 1.70 (m, 4H, \(-\text{CH}_2\)-), 3.38 (q, 4H, \(-\text{CH}_2\)-), 3.96 (t, 4H, \(-\text{CH}_2\text{O}\)-), 4.30 (t, 2H, \(-\text{OH}\)), 6.95 (d, 4H, Ar–H), 7.46 (d, 4H, Ar–H). FTIR (KBr, cm\(^{-1}\)): \(\nu\) 3300, 2936, 2870, 1604, 1493, 1470, 1391, 1240, 1170, 1121, 1072, 1037, 992, 917, 815, 665, 585, 510.

**Melt polymerization of PABP via transesterification.** To a 3-neck 50 ml flask, equipped with an overhead condenser with argon gas inlet and vacuum line on the adapter, were added monomer IV (2.14 g, 5 mmol) and monomer V (1.93 g, 5 mmol). The mixture was molten and stirred at 120 °C under Argon gas flow. After the addition of titanium (IV) isoproxide (12.3 mg in 120 \(\mu\)l of diethylene glycol dimethyl ether), bubbles of ethanol became visible. Upon stirring for 15 min, a low vacuum was applied for 15 min. Thereafter, an oil pump was used. The temperature was raised to 160 °C during 10 h. Afterwards, the polymer was purified by dissolution in chloroform and
precipitated in acetone. Yield: 92%. $^1$H NMR (δ, CDCl$_3$): 1.25-1.5 (m, 16 H, −CH$_2$−), 1.55-1.9 (m, 8H, −CH$_2$−), 3.28 (t, 1H, −CH−), 3.88 (t, 4H, −CH$_2$−), 3.95 (t, 2H, −CH$_2$−), 4.06 (t, 4H, −CH$_2$O−), 6.82 (d, 4H, Ar−H), 6.95 (d, 2H, Ar−H), 7.34 (d, 4H, Ar−H), 7.58 (d, 2H, Ar−H), 7.85 (d, 2H, Pyridyl−H), 8.68 (d, 2H, Pyridyl−H).

3.1.3 Synthesis of a Segmented Main-Chain Liquid Crystalline Polymer Having Side-Chain Terpyridine Group (PTBP)

In this study we synthesized a segmented main-chain liquid crystalline polymer (LCP) having side-chain terpyridine group (PTBP), the reaction scheme of which is presented in Figure 3.3.

*Synthesis of 1,5-bis(2′-bipyridyl)pentane-1,3,5-trione (VI).* A solution of acetone (1.8 mL, 25 mmol) and ethyl 2-pyridine-carboxylate (10.1 mL, 75 mmol) in dry THF (50 mL) was added dropwise to a refluxing suspension of sodium hydride (95%, 1.9 g, 75 mmol) in dry THF (50 mL) in a nitrogen atmosphere over 4 h. After an additional reflux for 2 h, the THF was removed under the reduced pressure and the remaining orange paste carefully treated with water (100 mL). The resultant orange solution was filtered through Celite and the pH of the filtrate was adjusted to pH 7 by the dropwise addition of 5% acetic acid. The resultant yellow solid was collected, washed with water and dried, and then recrystallized from ethanol to afford 5.1 g (75%) yellow product. $^1$H NMR (δ, CDCl$_3$): 4.45 (s), 6.94 (s), 6.99 (s), 7.38-7.50 (m), 7.81-7.92 (m), 8.01-8.12 (m), 8.67-8.75 (m). FTIR (KBr, cm$^{-1}$): ν 3140, 1612, 1572, 1442, 1378, 1276, 1146, 1084, 988, 940, 872, 838, 786, 736, 646, 586.

*Synthesis of 2,6-bis(2′-pyridyl)-4-pyridone (VII).* A solution of I (2.0 g, 7.46 mmol) and ammonium acetate (4.0 g, excess) in ethanol (50 mL) was heated to reflux overnight,
Figure 3.3. Synthetic route for PTBP.
after which the dark brown solution was concentrated to half volume. The solution was cooled and the white precipitate was collected by filtration and washed well with diethyl ether. Recrystallization from ethanol yielded 1.35 g (75%) white product. $^1$H NMR ($\delta$, CDCl₃): 7.33 (m), 7.44 (m), 7.90 (m), 7.97 (m), 8.79 (m). FTIR (KBr, cm$^{-1}$): $\nu$ 3276, 3054, 3004, 2240, 1820, 1630, 1578, 1512, 1472, 1432, 1364, 1256, 1204, 1084, 998, 942, 858, 786, 736, 700, 648, 620, 586, 540, 488.

In the synthesis of monomer VIII, monomer VII (2.5 g, 10 mmol) and anhydrous powdered K₂CO₃ (10.4 g, 75 mmol) were dissolved in 100 mL of acetonitrile and the mixture was heated to reflux for 2 h. Then, a solution of diethyl (5-bromopentyl)malonate (3.9 g, 12 mmol) dissolved in 50 mL of acetonitrile and a trace of potassium iodide was added to the above mixture and it was refluxed for 24 h. After filtration and evaporation of the solvent, the crude product was purified using silica gel column chromatography with hexane/ethyl acetate (2/3, v/v) as eluent, and then recrystallized from hexane/ethyl acetate (4/1, v/v) to give 3.1 g white powder. Yield = 65%; mp = 63 °C. $^1$H NMR ($\delta$, CDCl₃): 1.28 (t, 6H, -CH₃), 1.31–1.60 (m, 4H, -CH₂-), 1.78–2.0 (m, 4H, -CH₂-), 3.32 (t, 1H, -CH-), 4.18 (t, 4H, -CH₂CO-), 4.23 (t, 2H, -CH₂O-), 7.38 (t, 2H, Pyridyl-H), 7.90 (t, 2H, Pyridyl-H), 8.06 (s, 2H, Pyridyl-H), 8.65 (d, 2H, Pyridyl-H), 8.72 (d, 2H, Pyridyl-H).

Melt polymerization of PTBP via transesterification. PTBP was obtained via transesterification by melt polymerization using the following procedures. To a 3-neck 50 mL flask, equipped with an overhead condenser with argon gas inlet and vacuum line on the adapter, were added monomer VIII (1.91 g, 4 mmol), 4, 4′-bis(6-hydroxy)biphenyl (V) (1.55 g, 4 mmol), and 0.2 wt% PbO. The mixture was heated to 170 °C
under an Argon flow. After stirring for 3 h, during which methanol was distilled off, the fluid began to become viscous. Then Argon gas inlet was closed and the outlet was connected to the vacuum pump. The reaction mixture was heated for another 4 h at 170 °C under a reduced pressure. Afterwards, the polymer was purified by dissolution in chloroform and precipitated in acetone at least twice. Yield = 90 %. PTBP has a having a number-average molecular weight $M_n = 22,486$ and a weight-average molecular weight $M_w = 26,584$, as determined by gel permeation chromatography (GPC, Waters) using polystyrene as standard and THF as an eluent. $^1$H NMR ($\delta$, CDCl$_3$): 1.25-1.5 (m, 12H, -CH$_2$-), 1.52–1.9 (m, 12H, -CH$_2$-), 3.28 (t, 1H, -CH-), 3.88 (t, 4H, -CH$_2$O-), 4.06 (t, 4H, -CH$_2$O-), 4.22 (t, 2H, -CH$_2$O-), 6.80 (d, 4H, Ar-H), 7.38 (d, 6H, Ar-H and Pyridyl-H), 7.90 (t, 2H, Pyridyl-H), 8.05 (s, 2H, Pyridyl-H), 8.65 (d, 4H, Pyridyl-H).

For comparison, another segmented main-chain liquid crystalline polymer (PMBP) having the same chemical structure as the backbone of PTBP, as shown below

\[
\text{PMBP} = \left[ \begin{array}{c}
O & \text{O} \\
\text{O} & \text{C} & \text{C} & \text{O} & \text{(CH$_2$)$_n$} & \text{O} & \text{O} \\
\text{O} & \text{C} & \text{CH}_2 & \text{C} & \text{O} & \text{(CH$_2$)$_6$} & \text{O} & \text{(CH$_2$)$_6$}
\end{array} \right]
\]

was synthesized through azeotropic solution polycondensation. Specifically, to a three-neck 100 mL flask were dissolved malonic acid (1.04 g, 10 mmol), monomer $V$ (3.86 g, 10 mmol), and p-toluenesulfonic acid (0.11 g, 0.6 mmol) in 50 mL dry 1,2-dichloroethane. The reaction mixture were then refluxed for 3 days, while the water of reaction was removed using a Soxhlet extraction apparatus filled with P$_2$O$_5$. The resulting clear solution was precipitated in acetone to yield the polymer. After filtering, the final
product was dried in vacuum oven at 100 °C for several days. Yield: 90%. \(^1\)H NMR (δ, CDCl\(_3\)): 1.35-1.60 (m, 8H, -CH\(_2\)-), 1.60–1.92 (m, 8H, -CH\(_2\)-), 3.38 (s, 2H, -CH\(_2\)-), 3.98 (t, 4H, -CH\(_2\O\)-), 4.14 (t, 4H, -CH\(_2\O\)-), 6.92 (d, 4H, Ar-H), 7.45 (d, 4H, Ar-H). FTIR (KBr, cm\(^{-1}\)): v 2934, 2866, 1734, 1604, 1498, 1394, 1334, 1270, 1242, 1172, 1032, 816, 732, 688, 632, 596, 518.

### 3.2 Synthesis of Self-assembled Main-chain/Side-chain Liquid Crystalline Polymers (MCSCLCPs)

Three combined main-chain/side-chain liquid-crystalline polymers (MCSCLCPs) were prepared via hydrogen bonding or ionic interactions.

#### 3.2.1 Synthesis of Self-Assembled PyHQ12–7CNCOOH via Hydrogen Bonding

Self-assembled PyHQ12–7CNCOOH was prepared by first synthesizing a liquid crystal having carboxylic moiety \(-7\)-[(4-cyano-4′-biphenyl)oxy]octanoic acid, hereafter referred to as 7CNCOOH. Following the procedures described by Lee and Han,\(^{162}\) 8-bromo-octanoic acid (3.6 g, 15.75 mmol) was dissolved in a single-necked flask with a solvent of acetone, stirring for 1 h at room temperature before use. 4-Cyano-4′-hydroxybiphenyl (3.1 g, 15 mmol) and anhydrous potassium carbonate (6.5 g, 45 mmol) were dissolved into a three-necked flask with a solvent of anhydrous acetone. After stirring for 1 h at room temperature, the temperature was increased to 40-50 °C, and then 8-bromo-octanoic acid/acetone solution and a trace of potassium iodide were added. The reaction temperature was increased to 60-70 °C and remained to reflux for 4 days. After being cooled down to room temperature, 3 M HCl in water was poured into the reaction
mixture, and the reaction product was acidified with HCl solution. When the crude product was precipitated, it was filtered and washed three times with water, followed by recrystallizing twice in methanol. Yield = 60%. \(^1\)H NMR (\(\delta\), DMSO-\(d_6\)): 1.2-1.55 (m, 6H, \(-\text{CH}_2\)), 1.70 (m, 4H, \(-\text{CH}_2\)), 2.19 (t, 2H, \(-\text{CH}_2\)), 3.99 (t, 2H, \(-\text{CH}_2\text{O}\)), 7.04 (d, 2H, Ar\(-\text{H}\)), 7.71 (d, 2H, Ar\(-\text{H}\)), 7.87 (q, 4H, Ar\(-\text{H}\)), 11.93 (s, 1H, \(-\text{COOH}\)). FTIR (KBr, cm\(^{-1}\)): 3047, 2940, 2856, 2223, 1700, 1599, 1524, 1488, 1470, 1431, 1400, 1355, 1311, 1285, 1240, 1196, 1178, 1108, 1059, 1037, 988, 930, 820, 802, 718, 674, 558, 527.

Self-assembled PyHQ\(_{12}\)−7CNCOOH was prepared by dissolving equimolar amounts of pyridyl group in PyHQ\(_{12}\) and acid groups in 7CNCOOH in pyridine, yielding a clear solution. Most of the solvent was first evaporated slowly at 60 °C under atmospheric pressure. The remainder of the solution was then dried in a vacuum oven at

\[
\begin{align*}
\text{PyHQ}_{12} &\quad \text{Hydrogen Bonding} \\
\text{7CNCOOH} &
\end{align*}
\]
100 °C for several days. The mixture formed self-assembled PyHQ12–7CNCOOH via hydrogen bonding between the pyridyl group in PyHQ12 and the carboxylic acid group in 7CNCOOH, as shown below.

3.2.2 Synthesis of Self-Assembled PABP–AA via Hydrogen Bonding

Self-assembled PABP–AA was prepared by dissolving equimolar amounts of azopyridyl group in PABP and carboxylic acid group in p-anisic acid (AA) in chloroform, yielding a clear solution (heated slightly to 50 °C to ensure complete solubilization). Most of the solvent was first evaporated slowly under atmospheric pressure. The remainder of the solution was then dried in vacuum at 100 °C for several days. The mixture formed self-assembled PABP–AA via hydrogen bonding between the pyridyl group in the nonmesogenic azopyridine side chain and the carboxylic acid group in AA, as shown below.
3.2.3 Synthesis of Self-Assembled PABP–TSA via Ionic Interactions

Self-assembled PABP–TSA was prepared by dissolving equimolar amounts of azopyridyl group in PABP and sulfonic acid group in p-toluene sulfonic acid (TSA) in chloroform, yielding a clear solution (heated slightly to 50 °C to ensure complete solubilization). Most of the solvent was first evaporated slowly under atmospheric pressure. The remainder of the solution was then dried under vacuum at 100 °C for several days. The mixture formed self-assembled PABP–TSA via ionic interactions between the pyridyl group in the nonmesogenic azopyridine side chain and the sulfonic acid group in TSA, as shown below.

\[
\text{Self-assembled PABP–TSA}
\]

3.3 Synthesis of [Ru^{II}(PTBP)(6TPy)](PF_6)_2 (denoted by PTBP-Ru-6TPy) complex

In order to prepare PTBP-ruthenium complex as described in Figure 3.4, we first synthesized a small-molecule terpyridine, 1-(2,2′:6′, 2″-terpyridyl-4′-oxy)hexane (hereafter denoted by 6TPy): monomer VII (2.5 g, 10 mmol) and anhydrous powdered
Figure 3.4. Synthesis of $[\text{Ru}^{II}(\text{PTBP})(6\text{TPy})](\text{PF}_6)_2$ complex
K₂CO₃ (6.9 g, 50 mmol) were dissolved in 50 mL of acetonitrile and the mixture was heated to reflux for 2 h. Then, a solution of 1-bromohexane (2.5 g, 15 mmol) dissolved in 50 mL of acetonitrile and a trace of potassium iodide were added to the above mixture and it was refluxed for 24 h. After filtration and evaporation of the solvent, the crude product was purified using silica gel column chromatography with hexane/ethyl acetate (3/2, v/v) as eluent, and then recrystallized from hexane/ethyl acetate (10/1, v/v) to yield 1.65 g of needle-like product. Yield = 50 %. ¹H NMR (δ, CDCl₃): 0.90 (t, 3H, -CH₃), 1.30−1.55 (m, 6H, -CH₂-), 1.78−1.90 (m, 2H, -CH₂-), 4.25 (t, 2H, -CH₂O-), 7.38 (t, 2H, Pyridyl-H), 7.90 (t, 2H, Pyridyl-H), 8.04 (s, 2H, Pyridyl-H), 8.66 (d, 2H, Pyridyl-H), 8.72 (d, 2H, Pyridyl-H). FTIR (KBr, cm⁻¹): ν 3078, 3051, 3011, 2940, 2923, 2852, 1582, 1561, 1465, 1444, 1404, 1359, 1247, 1198, 1093, 1055, 1027, 999, 914, 868, 795, 743, 699, 656, 619, 581.

**Synthesis of 6TPy-RuCl₃ monocomplex.** A solution of 6TPy in methanol (25 mL) was stirred at 60 °C. Then, an equimolar amount of RuCl₃·3H₂O was added. The reaction of the mixture was continued overnight. Subsequently, the reaction mixture was cooled to −20 °C. The resulting dark orange precipitate was collected by filtration and washed twice with ice-cold water, followed by diethyl ether. The product was dried in a vacuum oven at 100 °C for several days. FTIR (KBr, cm⁻¹): ν 3064, 2940, 2865, 1608, 1555, 1462, 1355, 1218, 1161, 1045, 997, 860, 789, 745, 660.

**Synthesis of [Ru¹II(PTBP)(6TPy)](PF₆)₂ complex (PTBP-Ru-6TPy).** PTBP (0.77 g) and 6TPy-RuCl₃ monocomplex (0.54 g, equimolar amount of terpyridine in PTBP) were mixed in 50 mL of a 9:1 mixture of THF/ethanol. Five drops of N-ethylmorpholine were
added and the mixture was heated to reflux for 24 h under argon gas atmosphere. After evaporation of half of the solvent, an excess of ammonium hexafluorophosphate (2.0 g, 13.8 mmol) was added and the mixture cooled to 0 °C. The precipitate was removed by filtration and washed with a 60/40 mixture of ethanol/water (3 × 10 mL), and then dried in a vacuum oven at 100 °C for several days.

3.4 Preparation of Functional Liquid Crystalline Polymer/Clay (or Organoclay) Nanocomposites

To prepare clay (or organoclay) nanocomposites, we employed a natural montmorillonite (MMT, Cloisite Na⁺; cation exchange capacity, CEC = 92 meq/100 g; mean formula unit Na₀.₆₅[Al,Fe]₄Si₈O₂₀(OH)₄), and two commercial organoclays (Southern Clay Products): (i) Cloisite 30B treated with a surfactant (MT2EtOH) having the chemical structure methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride, and (ii) Cloisite 15A treated with a surfactant (2M2HT) having the chemical structure methyl, hydrogenated tallow, quaternary ammonium chloride. The chemical structures of the surfactants, MT2EtOH and 2M2HT, are given below.¹⁶³

\[
\begin{align*}
\text{MT2EtOH} & \quad \text{2M2HT} \\
\text{CH}_3N\text{H}^+\text{T} & \quad \text{CH}_3N\text{H}^+\text{HT} \\
\text{CH}_2\text{CH}_2\text{OH} & \quad \text{HHT} \\
\end{align*}
\]

In the chemical structure of MT2EtOH, N⁺ denotes quaternary ammonium chloride and T denotes tallow consisting of ca. 65 % C18, ca. 30 % C16, and ca. 5 % C14, and in the
chemical structure of 2M2HT, $N^+$ denotes quaternary ammonium chloride and HT denotes hydrogenated tallow consisting of ca. 65 % C18, ca. 30 % C16, and ca. 5 % C14. It should be mentioned that 100 % of Na$^+$ ions in natural clay (montmorillonite) have been exchanged.\textsuperscript{163} Note that Cloisite 30B has hydroxyl groups while Cloisite 15A does not, as confirmed by Fourier transform infrared (FTIR) spectroscopy.\textsuperscript{164} According to the Technical Properties Bulletin\textsuperscript{163} from Southern Clay Products, the amount of surfactant MT2EtOH residing at the surface of Cloisite 30B is 90 meq/100 g and the amount of surfactant 2M2HT residing at the surface of Cloisite 15A is 95 meq/100 g. We have been informed from Southern Clay Products that an extremely small amount of excess surfactant is present at the surface of both Cloisite 30B and Cloisite 15A. Nevertheless, using methanol we washed each of the organoclays to remove any excess surfactant.

3.4.1 Preparation of Organoclay Nanocomposite Based on PyHQ12 or PSHQ12

We prepared organoclay nanocomposites by solution blending; namely, a predetermined amount of PyHQ12 or PSHQ12 was dissolved in pyridine and then an organoclay suspended in pyridine was added slowly, while stirring, into the polymer solution. The solvent in the mixture was evaporated slowly under constant stirring for 2 days. The mixture of PyHQ12 or PSHQ12 with an organoclay was dried completely in a vacuum oven at temperatures well above the boiling point of pyridine and also at ca. 20 °C above the glass transition temperature ($T_g$) of PyHQ12 or PSHQ12 until no weight changes were detected. The amount of organoclay used was 5 wt % in all nanocomposites. Since the amount of surfactant MT2EtOH (or 2M2HT) residing at the
surface of Cloisite 30B (or Cloisite 15A) is 32 wt %, the net amounts of clay are 3.4 wt % in each nanocomposite.

The reason for having chosen these two organoclays lies in that we were interested in demonstrating that miscibility, via specific interactions, between a TLCP and an organoclay is essential to achieve a very high degree of dispersion of organoclay aggregates.

3.4.2 Preparation of Organoclay (or Clay) Nanocomposite Based on PABP

We prepared organoclay nanocomposites by solution blending; namely, a predetermined amount of PABP was dissolved in pyridine upon heating to 80 °C and then an organoclay (or MMT) suspended in pyridine was added slowly, while vigorously stirring, into the polymer solution. The solvent in the mixture was evaporated slowly under constant stirring for 2 days. The mixture of PABP with an organoclay was dried completely in a vacuum oven at temperatures well above the boiling point of pyridine and also at ca. 20 °C above the melting temperature ($T_m$) of PABP until no weight changes were detected. The amount of organoclay (or MMT) used was 5 wt % in all nanocomposites. Since the amount of surfactant MT2EtOH (or 2M2HT) residing at the surface of Cloisite 30B (or Cloisite 15A) is 32 wt %, the net amount of clay was 3.4 wt % in each organoclay nanocomposite.

3.4.3 Preparation of [Ru^{II}(PTBP)(6TPy)](PF$_6$)$_2$/Clay (or Organoclay) Nanocomposites

[Ru^{II}(PTBP)(6TPy)](PF$_6$)$_2$ (denoted by PTBP-Ru-6TPy)/MMT nanocomposite was
prepared by solution blending; namely, a predetermined amount of PTBP-Ru-6TPy was
dissolved in a cosolvent of N,N-dimethylformamide (DMF)/H₂O (10:1,v/v) and then
MMT suspended in a cosolvent of DMF/H₂O (10:1,v/v) was added slowly, while
vigorously stirring, into the polymer solution. The solvent in the mixture was evaporated
slowly under constant stirring for 2 days at ambient temperature. For comparison, the
PTBP/MMT nanocomposite was prepared in the same procedure except that slight heating
was applied to ensure the solubility of PTBP. Nanocomposites were dried completely in a
vacuum oven at 100 °C until no weight change was detected. The amount of MMT used
was 3 wt % in both nanocomposites.

On the other hand, (PTBP-Ru-6TPy)/Organoclay (Cloisite 30B or Cloisite 15A)
nanocomposites were prepared by solution blending in the same procedure as (PTBP-Ru-
6TPy)/MMT nanocomposite. The amount of organoclay used was 5 wt % in both
nanocomposites. Since the amount of surfactant MT2EtOH (or 2M2HT) residing at the
surface of Cloisite 30B (or Cloisite 15A) is 32 wt %, the net amount of clay was 3.4 wt %
in each nanocomposite.

3.5 Experimental Methods

3.5.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectra were obtained with a Varian Gemini 300 MHz NMR spectrometer.
Deuterated dimethyl sulfoxide (DMSO-d₆), chloroform (CDCl₃-d), and pyridine
(pyridine-d₅) were used as solvents.
3.5.2 Differential Scanning Calorimetry (DSC)

The thermal transition temperatures of the monomers and polymers synthesized were determined by differential scanning calorimetry (DSC) (Perkin Elmer 7 Series). All DSC runs were made under a nitrogen atmosphere with heating and cooling rates of 20 °C/min, and the thermal history (namely, annealing temperature and the duration of annealing) of specimens were varied. Indium and zinc were used to calibrate the temperature and heat of fusion.

3.5.3 Polarized Optical Microscopy (POM)

The mesophase structures of the liquid-crystalline phase of liquid crystalline polymers were investigated, via POM, using a Leitz Laborlux 12 Pol S polarized optical microscope equipped with a hot stage (Instec) and a digital camera (Spot insight 2, Diagnostic Instrument Inc.). Specimens were cast from 1 wt % solution of functional and heterocyclic LCPs or their clay nanocomposites on a slide glass to obtain a film of about 2 – 3 µm in thickness, which was then first dried in a fume hood and subsequently in a vacuum oven. The heating and cooling rates employed were 3 °C/min. Images of POM were obtained after keeping a specimen at a preset temperature for at least 10 min.

3.5.4 Fourier Transform Infrared (FTIR) Spectroscopy

Using a Fourier transform infrared spectrometer (16 PC FTIR, Perkin Elmer), in-situ FTIR spectra were obtained at temperatures ranging from 25 to above the clearing temperatures for PyHQ12, PABP, PyHQ12/Cloisite 30B, and PABP/Cloisite 30B nanocomposites as well as for self-assembled PyHQ12-7CNCOOH, PABP-AA and PABP-TSA. The temperature was measured at the sample surface and controlled to
within ± 1.0 °C using a proportional-integral-derivative controller. Specimens were maintained at a preset temperature for 5 min prior to data acquisition. FTIR spectra for other specimens were obtained at room temperature. Spectral resolution was maintained at 4 cm⁻¹. Dry nitrogen gas was used to purge the sample compartment to reduce the interference of water and carbon dioxide in the spectrum. Thin films suitable for FTIR spectroscopy were prepared by casting 2 % (w/v) solution in suitable solvent directly on the KBr salt plate. Film thickness was adjusted, such that the maximum absorbance of any band was less than 1.0, at which the Beer-Lambert law is valid. Film specimens were slowly dried for 24 h in a fume hood until most of the solvent evaporated and then dried at 80 °C for a few days in a vacuum oven, and they were then stored in a vacuum oven until use.

3.5.5 Wide–Angle X–ray Diffraction (WAXD)

WAXD experiments were conducted at room temperature on the as-cast films and melt-drawn fibers of both pure polymers and self-assembled MCSCLCPs, using a General Electric X–ray generator (Model XRD–6) operated at 30 kV and 30 mA (Ni–filtered Cu Kα radiation). The flat–plate diffraction patterns were recorded with a 53.3 mm film–to–specimen distance. The exposure time for each measurement was 4 h.

Also conducted were variable-temperature WAXD experiments on as-cast films of PABP and self-assembled MCSCLCPs during heating and cooling cycles by Professor Jin Kon Kim at Pohang University of Science and Technology in the Republic of Korea. For the experiments, an 18 kW Rigaku rotating-anode X-ray generator operated at 46 kV and 20 mA, mirror optics having point focusing, and one-dimensional position sensitive
detector (M. Braun) were employed. The CuK$_\alpha$ radiation from a 0.1 x 1 mm microfocus cathode was used. The thickness of the sample was 1 mm, and the distance between the sample and the detector was 10.5 cm. Variable-temperature WAXD experiments were conducted at 150, 140, 130, 120, 110, and 100 °C in the first cooling cycle and at 25, 60, 90, 100, 110, 120, 130, 140, 150, and 160 °C in the second heating cycle.

3.5.6 X-Ray Diffraction (XRD)

Using a Rigaku X-ray generator operated at 40 kV and 150 mA, X-ray diffraction patterns were obtained to determine the mean interlayer spacing of the (001) plane (d$_{001}$) for the natural clay or organoclays and their nanocomposites. The X-ray beam was monochromatized to CuK$_\alpha$ with a graphite crystal. The range of 2θ scanning of X-ray intensity employed was 1.5 – 10 degrees. On the other hand, the 2θ range for functional LCPs was 1.5-35 degrees.

3.5.7 Transmission Electron Microscopy (TEM)

TEM images of specimens were taken at room temperature. The ultrathin sectioning (50 – 70 nm) was performed by ultramicrotomy at room temperature for the clay (or organoclay) nanocomposites. A transmission electron microscope (JEM1200EX 11, JEOL) operated at 120 kV was used to obtain images of nanocomposite specimens.

3.5.8 Ultraviolet-Visible (UV-vis) Spectroscopy

UV-visible spectra were obtained at Hewlett-Packard 8435 UV-visible spectrophotometer. Samples were prepared in the form of solution or thin films.
3.5.9 Thermogravometric Analysis (TGA)

The thermal degradation temperature of polymers was determined by a thermogravometric analyzer (TGA 2050, TA Instrument). All TGA data were measured under a nitrogen atmosphere at a heating rate of 20 °C/min, and the thermal degradation temperature was determined at the point of 95 wt% of the original weight.

3.5.10 Rheological Measurements

An Advanced Rheometric Expansion System (ARES, TA Instrument) with a parallel-plate (8 mm diameter plate) fixture was used to conduct oscillatory shear flow experiments, the gap opening being set to 0.8 mm, to measure the dynamic storage modulus (G') and loss modulus (G'') as a function of angular frequencies (ω) in the range from 0.01 to 100 rad/s. The complex viscosity (|η*|) was calculated using the expression, 

$$|\eta^*(\omega)| = \left\{ \frac{G'(\omega)}{\omega} + \frac{G''(\omega)}{\omega} \right\}^{1/2}.$$  

Dynamic temperature sweep experiments under isochronal conditions were conducted, i.e., the dynamic storage modulus (G') and dynamic loss modulus (G'') were measured at an angular frequency (ω) of 0.1 rad/s during heating. Data acquisition was accomplished with the aid of a microcomputer interfaced with the rheometer. The temperature control was satisfactory to within ± 1 °C. All experiments were conducted under a nitrogen atmosphere to preclude oxidative degradation of the samples.
CHAPTER IV
SYNTHESIS OF COMBINED MAIN-CHAIN/SIDE-CHAIN LIQUID CRYSTALLINE POLYMERS VIA SELF-ASSEMBLY

4.1 Introduction

The synthesis of liquid-crystalline polymers (LCPs) has been an active research area for the last three decades. Many of the activities were centered on the syntheses of main-chain liquid-crystalline polymers (MCLCPs)\textsuperscript{160,165-178} and side-chain liquid-crystalline polymers (SCLCPs).\textsuperscript{162,179-190} However, only a relatively small number of research groups\textsuperscript{191-200} reported on the synthesis of combined main-chain/side-chain liquid-crystalline polymers (MCSCLCPs). In the synthesis of MCSCLCPs referred to above, two methods have been employed; one method is to attach mesogenic side group(s) onto the flexible methylene units of a semiflexible main-chain polymer\textsuperscript{191-195} and another method is to attach mesogenic side groups as lateral substituents onto the mesogenic moieties of a semiflexible main-chain polymer.\textsuperscript{196-200} All the synthesis activities cited above utilized condensation polymerization to synthesize combined MCSCLCPs through covalent bonding.

However, there is another, very powerful method to prepare LCPs, namely via self-assembly (e.g., hydrogen bonding). Hydrogen bonding has been discussed extensively in the literature during the last five decades. There are several monographs and hundreds of
papers that dealt with hydrogen bonding. The readers are referred to a relatively recent monograph by Jeffrey, who described the fundamental principles involved with hydrogen bonding in general. During the last two decades, several research groups, notably Kato and Fréchet utilized the concept of hydrogen bonding to obtain LCPs. Specifically, in 1989 Kato and Fréchet demonstrated that an LCP can be prepared via hydrogen bonding between a nonmesogenic polymer containing carboxylic acid group and a mesogenic small molecule containing pyridyl group. In subsequent years, they exploited the concept further to obtain LCPs via hydrogen bonding between a component containing carboxylic acid or acrylic groups and a mesogenic small molecule with pyridyl group. Kato and coworkers, and Cui and Zhao, obtained LCPs via hydrogen bonding between a nonmesogenic polymer containing pyridine moiety and a compound containing carboxylic group. Griffith and coworkers prepared MCLCPs via hydrogen bonding, and Malik et al. obtained an LCP via hydrogen bonding between two nonmesogenic compounds. The readers are referred to comprehensive review articles by Lehn and Paleos and Tsiourvas, who described the role of intermolecular hydrogen-bonding interactions in the formation of liquid crystals and LCPs.

Very recently, we synthesized two MCSCLCPs via hydrogen bonding. For this, we employed two different methods to obtain self-assembled MCSCLCPs. One method employed was to first synthesize an MCLCP with pendent pyridyl group and then to combine, via hydrogen bonding, with a small mesogenic molecule having carboxylic acid group in a common solvent, giving rise to a self-assembled MCSCLCP. That is, the formation of a combined MCSCLCP was realized by hydrogen bonding between two
mesogenic compounds. Another method employed was to first synthesize an MCLCP having nonmesogenic side chain with azopyridyl group and then to combine, via hydrogen bonding, with a small nonmesogenic molecule having carboxylic acid group in a common solvent, giving rise to a self-assembled MCSCLCP. That is, the formation of a combined MCSCLCP was realized by hydrogen bonding between the nonmesogenic azopyridyl group in the side chain of a MCLCP and a small nonmesogenic molecule having carboxylic acid group, giving rise to a self-assembled MCSCLCP. Using Fourier transform infrared (FTIR) spectroscopy we confirmed the formation of hydrogen bonds in both MCSCLCPs prepared in this study. The mechanisms through which the two self-assembled MCSCLCPs were prepared in this study are described in Figure 4.1.

Earlier, Eisenberg and coworkers,211-213 and Chen et al.,214,215 utilized ionic interactions to enhance the miscibility of immiscible polymer blends. More recently, some investigators216-218 demonstrated the formation of supramolecular polymers via ionic self-assembly. Very recently, we have prepared a self-assembled MCSCLCP via ionic interactions between the nonmesogenic azopyridyl group in the side chain of an MCLCP and the sulfonic acid group in a small nonmesogenic molecule.210 We are not aware of any previous study reporting on the formation of self-assembled MCSCLCP via ionic interactions.

4.2 Self-Assembled PyHQ12–7CNCOOH via Hydrogen Bonding

4.2.1 Thermal Transition and Mesophase Structure of PyHQ12 and Self-Assembled PyHQ12–7CNCOOH
Figure 4.1. Schemes describing the two methods, (a) method I and (b) method II, employed to prepare combined MCSCLCPs via hydrogen bonding, in which the dark areas represent mesogenic groups.
Figure 4.2 gives DSC thermograms for (a) PyHQ12 and (b) 7CNCOOH at a scanning rate of 20 °C/min during heating and cooling cycles. The following observations are worth noting in Figure 4.2. (i) PyHQ12 has a $T_g$ of 96 °C and a clearing temperature of 162 °C during heating. The POM image given in the inset of Figure 4.2a indicates that PyHQ12 has Schlieren texture (thus nematic mesophase) at temperatures between 96 and 162 °C, and thus 162 °C represents nematic-to-isotropic (N–I) transition temperature ($T_{NI}$). (ii) Referring to Figure 4.2b, during heating the mesogenic small molecule 7CNCOOH has a $T_{NI}$ of 148 °C, while during cooling it undergoes two thermal transitions: (1) isotropic-to-nematic (I–N) transition at 139 °C, which is 9 °C lower, owing to supercooling, than the $T_{NI}$ determined during heating, and (2) crystallization at 114 °C. The POM image shown in Figure 4.2b indicates that 7CNCOOH has Schlieren texture (thus nematic mesophase) upon cooling.

Figure 4.3 gives DSC thermograms for self-assembled PyHQ12–7CNCOOH during the heating and cooling cycles at a scanning rate of 20 °C/min. It is seen in Figure 4.3 that during heating, PyHQ12–7CNCOOH undergoes glass transition at ca. 54 °C and N–I transition at ca. 154 °C, and both $T_g$ and $T_{NI}$ during cooling are slightly lower, owing to supercooling, than those during heating. Comparison of Figure 4.3 with Figure 4.2a indicates that the $T_g$ of self-assembled PyHQ12–7CNCOOH is ca. 42 °C lower than that of PyHQ12, and the $T_{NI}$ of self-assembled PyHQ12–7CNCOOH is ca. 8 °C lower than that of PyHQ12. Also, there is no evidence of crystallization in PyHQ12–7CNCOOH during cooling. The observed decrease in $T_g$ of self-assembled PyHQ12–7CNCOOH is attributable to the attachment of side-chain mesogenic 7CNCOOH onto the backbone of
Figure 4.2. DSC thermograms for (a) PyHQ12 and (b) 7CNCOOH at a scanning rate of 20 °C/min during (1) heating and (2) cooling cycles, and their POM images at 130 °C during the cooling cycle.
Figure 4.3. DSC thermograms for self-assembled PyHQ12–7CNCOOH at a scanning rate of 20 °C/min during (1) heating and (2) cooling cycles.
PyHQ12 via hydrogen bonding between the pendent pyridyl group in PyHQ12 and the carboxylic acid group in 7CNCOOH.

It is worth pointing out that the observed decrease in $T_g$ and $T_{NI}$ of PyHQ12 in the mixtures of PyHQ12 and 7CNCOOH could not have occurred if 7CNCOOH did not bind to PyHQ12 and instead acted as a nematic solvent. Note that 7CNCOOH melts at 148 °C during heating (see DSC thermograms in Figure 4.2b) and thus it cannot act as a nematic solvent at temperatures below 148 °C. If 7CNCOOH did not bind to PyHQ12 and acted as a nematic solvent, during cooling 7CNCOOH in the mixture with PyHQ12 should have undergone crystallization at 114 °C (see DSC thermograms in Figure 4.2b). However, the DSC thermograms of the mixture of PyHQ12 and 7CNCOOH exhibit only a single exothermic peak at 146 °C during cooling (see Figure 4.3), i.e., there is no evidence that crystallization of 7CNCOOH took place during cooling in the mixture of PyHQ12 and 7CNCOOH. The above observations indicate clearly that 7CNCOOH did not act as a nematic solvent, rather it was bound to PyHQ12 forming self-assembled PyHQ12–7CNCOOH.

Figure 4.4 gives the DSC thermograms for PyHQ12–7CNCOOH specimens after annealing at 130 °C for various annealed periods at a scanning rate of 20 °C/min, indicating that annealing up to 48 h has a relatively small effect on the $T_g$ and $T_{NI}$ of PyHQ12–7CNCOOH. Further, annealing for a long period did not produce a new endothermic peak. These observations indicate that self-assembled PyHQ12–7CNCOOH via hydrogen bonding is thermally stable and little affected by isothermal annealing for an extended period.
Figure 4.4. DSC thermograms for self-assembled PyHQ12-7CNCOOH after annealing at 130 °C for various annealed periods at a scanning rate of 20 °C/min.
4.2.2 WAXD and XRD Patterns of PyHQ12 and Self-Assembled PyHQ12–7CNCOOH

Figure 4.5a gives WAXD powder patterns for PyHQ12 and PyHQ12–7CNCOOH, indicating that even after annealing at 130 °C for 48 h, both PyHQ12 and PyHQ12–7CNCOOH still have very diffuse diffraction in powder patterns and no crystalline structures are discernible. In the WAXD fiber patterns given in Figure 4.5b, both PyHQ12 and PyHQ12–7CNCOOH have only diffuse lateral spacings. Figure 4.6 gives XRD patterns for PyHQ12 and self-assembled PyHQ12–7CNCOOH, showing that they only exhibit strong peaks at 2\(\theta\) of 21° confirming the observations made in Figure 4.5 for WAXD patterns. On the basis of the DSC thermograms (Figure 4.2a and Figure 4.3)) and the WAXD patterns presented in Figure 4.5 we conclude that both PyHQ12 and self-assembled PyHQ12–7CNCOOH are glassy nematic polymers.

4.2.3 POM Images of Self-Assembled PyHQ12–7CNCOOH

Figure 4.7 gives POM images of self-assembled PyHQ12–7CNCOOH during heating from 120 to 160 °C and during cooling from the isotropic state to 25 °C. The significance of Figure 4.7 lies in that interestingly, upon cooling from the isotropic state the nematic structure appears very rapidly in the self-assembled PyHQ12–7CNCOOH. It should be mentioned that phase separation in PyHQ12–7CNCOOH did not occur even when a specimen was raised to a temperature well above its \(T_{NI}\) (ca. 154 °C), suggesting that little breakdown of the hydrogen bonds formed between the pyridyl group and carboxylic acid group appeared to have taken place. What surprised us during our in situ POM experiments was that the reappearance of nematic mesophase, upon cooling from
Figure 4.5. WAXD patterns of PyHQ12 and self-assembled PyHQ12–7CNCOOH: (a) powder patterns of specimens after annealing at 130 °C for 48 h; (b) fiber patterns of unannealed melt-drawn specimens.
Figure 4.6. XRD patterns of (a) PyHQ12 and (b) self-assembled PyHQ12–7CNCOOH at room temperature.
Figure 4.7. POM images of self-assembled PyHQ12–7CNCOOH upon heating from 120 to 160 °C (above the $T_{NI} = 154.1$ °C) and during cooling from the isotropic state to 25 °C.
the isotropic state, was very rapid. Later, we learned the reason for the unexpected experimental observation from conducting in situ FTIR experiments.

4.2.4 FTIR Spectra of Self-Assembled PyHQ12–7CNCOOH

Figure 4.8a gives FTIR spectra for 7CNCOOH and Figure 4.8b gives FTIR spectra for PyHQ12 at room temperature (denoted by *) and in situ FTIR spectra for self-assembled PyHQ12–7CNCOOH, during heating, at various temperatures ranging from 25 to 170 °C. The following observations are worth noting in Figure 4.8. (i) Two absorption peaks appear at wavenumbers of 2500 cm\(^{-1}\) and 1930 cm\(^{-1}\) for self-assembled PyHQ12–7CNCOOH, in contrast to the FTIR spectra for 7CNCOOH and PyHQ12. According to the literature\(^{219}\), hydrogen-bonded and Fermi resonance absorption peaks are expected to appear at those two wavenumbers when hydrogen-bonded complexes are formed between pyridine and carboxylic acid derivatives. (ii) As the temperature is increased, the absorption peaks at wavenumbers of 2500 cm\(^{-1}\) and 1930 cm\(^{-1}\) persist even at 170 °C, which is well above the \(T_{NI}\) (ca. 154 °C) of PyHQ12–7CNCOOH, although the strength of the absorption peak at a wavenumber of 2500 cm\(^{-1}\) is weakened slightly. (iii) The disappearance of a typical absorption peak at a wavenumber of 1704 cm\(^{-1}\) for the carboxylic acid (hydrogen-bonded dimer) in 7CNCOOH is attributable to a shifting to a higher absorption peak due to the formation of hydrogen bonds with the pyridyl groups in PyHQ12, thus overlapping with the absorption peak at a wavenumber of 1732 cm\(^{-1}\) for the carbonyl groups in PyHQ12. According to the literature\(^{27}\), the strength of hydrogen bonds between the phenolic hydroxyl group and the acetate carbonyl group in a polymer blend decreases with increasing temperature. However, in
Figure 4.8. FTIR spectra for (a) 7CNCOOH and (b) PyHQ12 denoted by (*) at room temperature, and in-situ FTIR spectra for self-assembled PyHQ12–7CNCOOH at various temperatures (°C): (1) 25, (2) 100, (3) 120, (4) 140, (5) 150, (6) 160, and (7) 170.
Figure 4.8b we observe that the attractive interactions between the pendent pyridyl group in PyHQ12 and the carboxylic group in 7CNCOOH in self-assembled PyHQ12–7CNCOOH are strong enough to persist over the entire range of temperatures investigated. This seems to suggest that the attractive interactions between the pyridyl group and carboxyl acid group are much stronger than those between the phenolic hydroxyl group and acetate carbonyl group. Notice in Figure 4.7 that we observe a complete disappearance of nematic mesophase in self-assembled PyHQ12–7CNCOOH at 160 °C, which is ca. 6 °C above its $T_{NI}$. Yet, in Figure 4.8b we observe that a significant degree (strength) of hydrogen bonding still persists at 160 and 170 °C. This observation now explains why we observed, during cooling from the isotropic region, a very rapid reappearance of nematic mesophase in PyHQ12–7CNCOOH upon passing the isotropic-to-nematic (I–N) transition temperature ($T_{IN}$).

4.2.5 Effect of Molar Ratios of 7CNCOOH on the Thermal Transition Temperatures of Self-Assembled PyHQ12–7CNCOOH

In order to investigate the effect of molar ratio of 7CNCOOH on the thermal transition temperatures of self-assembled PyHQ12–7CNCOOH, we prepare self-assembled PyHQ12–7CNCOOH with different [pyridyl group]/[acid group] molar ratios: 8/1, 4/1, 2/1, using the same preparation procedures for [pyridyl group]/[acid group] molar ratio of 1/1. Figure 4.9 gives DSC thermograms for PyHQ12 and four samples of self-assembled PyHQ12–7CNCOOH having different [pyridyl group]/[acid group] ratios: 8/1, 4/1, 2/1, and 1/1. It can be seen from Figure 4.9 that the value of $T_g$ decreases considerably from 96.0 °C for PyHQ12 to 90.4 °C, 78.3 °C, 71.8 °C, and 54.1...
Figure 4.9. DSC thermograms at a scanning rate of 20 °C/min during the heating cooling cycle for (a) PyHQ12 and self-assembled PyHQ12–7CNCOOH having different [pyridyl group]/[acid group] ratios: (b) 8/1, (c) 4/1, (d) 2/1, and (e) 1/1.
°C for self-assembled PyHQ12–7CNCOOH having [pyridyl group]/[acid group] ratios of 8/1, 4/1, 2/1, and 1/1, respectively, while the value of $T_{NI}$ decreases moderately and the intensity of endothermal peak at $T_{NI}$ increases greatly, as the [pyridyl group]/[acid group] ratio approaches 1. Such an experimental observation leads to speculation that the attachment of 7CNCOOH onto the backbone of PyHQ12 through hydrogen bonding between the carboxylic acid group of 7CNCOOH and the pyridyl group of PyHQ12 would gradually enlarge the free volume of self-assembled PyHQ12–7CNCOOH, as the amount of 7CNCOOH increases. Consequently, the reduced amount of $T_g$ of self-assembled PyHQ12–7CNCOOH would reach the highest value when [pyridyl group]/[acid group] ratio approaches 1. On the other hand, the $T_{NI}$ of self-assembled PyHQ12–7CNCOOH results from the combined effect of the $T_{NIs}$ of PyHQ12 (162.4 °C) and 7CNCOOH (148 °C).

Figure 4.10 gives FTIR spectra for PyHQ12 and self-assembled PyHQ12–7CNCOOH having different [pyridyl group]/[acid group] ratios: 8/1, 4/1, 2/1, and 1/1. It is seen very clearly from Figure 4.10 that the area under the absorption peak at wavenumbers of ca. 2500 cm$^{-1}$ and 1930 cm$^{-1}$, which represents hydrogen bonding and Fermi resonance between the pyridyl group in PyHQ12 and the acid group in 7CNCOOH respectively, increases as the [pyridyl group]/[acid group] ratio approaches 1. It should be noted that the absorption peak at 2223 cm$^{-1}$ for –CN group in 7CNCOOH also becomes stronger as the amount of 7CNCOOH increases, indicating the presence of 7CNCOOH. This observation is consistent with the DSC thermograms given in Figure 4.9 in that as the amount of 7CNCOOH mixed with PyHQ12 is increased, the larger the
Figure 4.10. FTIR spectra for (a) PyHQ12 and self-assembled PyHQ12−7CNCOOH having different [pyridyl group]/[acid group] ratios: (b) 8/1, (c) 4/1, (d) 2/1, and (e) 1/1.
strength of hydrogen bonding between the two and consequently the lower the $T_g$ of self-assembled PyHQ12–7CNCOOH.

4.3 Self-Assembled PABP–AA via Hydrogen Bonding.

4.3.1 Formation of Hydrogen Bonds Between Monomer PAPM and $p$-Anisic Acid

In this study we had to first confirm that PABP is an MCLCP, i.e., the azopyridyl group in the side chain of PABP is nonmesogenic, and then ascertain that the azopyridyl group in monomer PAPM (monomer IV designated in Figure 3.2), when it is mixed with $p$-anisic acid (AA), forms a mesogenic phase. These two steps were necessary for us to conclude that self-assembled PABP–AA is indeed a combined MCSCLCP. Figure 4.11a gives DSC thermograms for PAPM at a scanning rate of 20 °C/min, showing only a melting temperature of 66.4 °C during heating, while it undergoes crystallization, during cooling, at 19.6 °C. POM image (not presented here) has assured us that no mesophase exists in PAPM and that a crystalline structure forms, during cooling, at temperatures below 20 °C. Thus, we have concluded that PAPM does not exhibit liquid-crystalline characteristics (i.e., PAPM is a nonmesogenic compound and thus PABP having azopyridyl side chain is an MCLCP). Next, we prepared a mixture of PAPM and AA in a common solvent (acetone) and then slowly evaporated the solvent followed by drying in a vacuum oven at 60 °C. Figure 4.11b gives DSC thermograms for a mixture of PAPM and AA at a scanning rate of 20 °C/min. It can be seen that during heating, the mixture undergoes crystal-to-crystal ($k_1$–$k_2$) transition at 40.7 °C, then crystal-to-smectic ($k_2$–S) transition at 58.3 °C, and finally smectic-to-isotropic (S–I) transition at 90.7 °C, while
Figure 4.11. DSC thermograms for (a) PAPM (in which 66.4 °C denotes melting temperature) and (b) self-assembled PAPM–AA at a scanning rate of 20 °C/min during (1) heating and (2) cooling cycles, and POM image taken at 50 °C during the cooling cycle. Here k denotes the crystalline state and $S_{mb}$ denotes smectic B phase.
during cooling the mixture undergoes isotropic-to-smectic (I–S) transition at ca. 60 °C followed by smectic-to-crystal transition (S–k2) at ca. 31 °C. In the inset of Figure 4.11b is given a POM image, taken at 50 °C during cooling, for a mixture of PAPM and AA, confirming the presence of a mosaic mesophase structure (smectic B). Thus we have concluded that a mixture of PAPM and AA has induced a mesogenic phase via hydrogen bonding between the azopyridine group in PAPM and the carboxylic acid group in AA.

Figure 4.12 gives FTIR spectra for (1) p-anisic acid, (2) PAPM, and (3) self-assembled PAPM–AA at room temperature. It can be seen in Figure 4.12 that self-assembled PAPM–AA has two new absorption bands, one absorption peak at a wavenumber of 2500 cm\(^{-1}\) representing hydrogen-bonded carboxylic acid with pyridyl group and another absorption peak at a wavenumber of 1940 cm\(^{-1}\) representing Fermi resonance. The absorption peak at a wavenumber of 1680 cm\(^{-1}\) characteristic of carboxylic acid (stretching of –OH group) is shifted to a higher wavenumber (ca. 1710 cm\(^{-1}\)), close to that of the carbonyl group of PAPM (a shoulder shown in the spectrum (3) in Figure 4.12). Also, the absorption peak for azopyridine at a wavenumber of 1596 cm\(^{-1}\) is shifted to 1604 cm\(^{-1}\), overlapped by the absorption peak of benzene ring of p-anisic acid. The above observations have ensured us that the azopyridyl group in monomer PAPM, when it was mixed with p-anisic acid (AA), indeed formed a mesogenic phase.

4.3.2 Thermal Transition and Mesophase Structures of PABP and Self-Assembled PABP–AA.

Figure 4.13 gives the DSC thermograms for PABP and self-assembled PABP–AA during the heating and cooling cycles at a scanning rate of 20 °C/min. In the insets of
Figure 4.12. FTIR spectra for (1) AA, (2) PAPM, and (3) self-assembled PAPM–AA at room temperature.
Figure 4.13. DSC thermograms for (a) PABP and (b) self-assembled PABP–AA at a scanning rate of 20 °C/min during (1) heating and (2) cooling cycles, and their POM images taken at 130 °C during the cooling cycle.
Figures 4.13a and 4.13b are given POM images, taken at 130 °C, of PABP and self-assembled PABP−AA, showing that both have needle-type (batonnet texture) smectic A mesophase. It can be seen in Figure 4.13a that during heating PABP has a melting temperature \( T_m \) of ca. 113 °C and a smectic-to-isotropic (S–I) transition temperature \( T_{SI} \) of ca. 146 °C, while during cooling its crystallization temperature and isotropic-to-anisotropic (I–S) transition temperature \( T_{IS} \) are slightly lower than the melting and clearing temperatures observed during heating. Notice in Figure 4.13b that self-assembled PABP−AA has a \( T_m \) of ca. 120 °C and a \( T_{SI} \) of ca. 161 °C, which are slightly higher than those of PABP. An increase of \( T_{SI} \) of self-assembled PABP−AA by 15 °C over that of PABP is attributed to the formation of hydrogen bonds between the azopyridyl group in the side chain of PABP and the carboxylic acid group in \( p \)-anisic acid, giving rise to a mesogenic side chain.

### 4.3.3 WAXD and XRD Patterns of PABP and Self-Assembled PABP−AA

Figure 4.14 gives WAXD powder patterns of (a) PABP and (b) self-assembled PABP−AA. It is seen in Figure 4.14 that both PABP and self-assembled PABP−AA exhibit remarkably similar X-ray diffraction patterns, indicating that the attachment of a small nonmesogenic molecule, \( p \)-anisic acid, to PABP has changed little the mesophase structure of PABP. This observation confirms the POM images of PABP and self-assembled PABP−AA, both forming smectic-A mesophase at temperatures between \( T_m \) and \( T_{SI} \), given in the insets of Figures 4.13a and 4.13b.
Figure 4.14. WAXD powder patterns of (a) PABP and (b) self-assembled PABP–AA at room temperature.
Figure 4.15 gives variations of XRD intensity for PABP with scattering angle $2\theta$ for an as-cast PABP specimen during the second heating cycle at various temperatures, as indicated on the plot. The following observations are worth noting in Figure 4.15. (1) Below the melting temperature ($T_m = \text{ca. } 113\ ^\circ\text{C}$) of PABP, there are two reflection peaks, at $2\theta = \text{ca. } 12^\circ\ (d = 7.37\ \text{Å})$ and at $2\theta = \text{ca. } 23.5^\circ\ (d = 3.78\ \text{Å})$, which are assigned to the crystalline structure of PABP because these two peaks disappear as the temperature is increased above $T_m$. (2) Below the clearing temperature ($T_{SI} = \text{ca. } 145\ ^\circ\text{C}$), the strongest peak appears at $2\theta = 21.8^\circ\ (d = 4.08\ \text{Å})$, which corresponds to the very strong bright ring in the WAXD powder patterns given in Figure 4.14a, and is due to the distance between the planes on which the oriented mesogenic groups lies. There are two additional small reflection peaks, at $2\theta = \text{ca. } 3.7^\circ\ (d = 23.85\ \text{Å})$ and at $2\theta = \text{ca. } 7.8^\circ\ (d = 11.32\ \text{Å})$, suggesting the presence of crystalline smectic-A mesophase and they persist until the temperature is raised above $T_{SI}$. Previously, similar XRD patterns were reported on other LCPs forming smectic-A mesophase.\(^{220,221}\) (3) When the temperature is increased to $T_{SI}$, all peaks disappear, except for a broad peak at $2\theta = \text{ca. } 20^\circ$ confirming the presence of an isotropic melt. In the present study, we also obtained variable-temperature XRD intensities of self-assembled PABP-AA, which look virtually identical to those shown in Figure 4.15. This is not surprising in that we already have shown that POM images (Figure 4.13) and WAXD powder patterns (Figure 4.14) of self-assembled PABP-AA are virtually the same as those of PABP. Thus, we have chosen not to present here the variable-temperature XRD intensities of self-assembled PABP-AA. Therefore, we
Figure 4.15. Variation of the X-ray diffraction intensity with scattering angle $2\theta$ for an as-cast PABP during the second heating cycle at various temperatures, as indicated on the plot.
conclude that both PABP and self-assembled PABP–AA are semicrystalline, smectic-forming liquid-crystalline polymers.

4.3.4 In Situ FTIR Spectra for Self-Assembled PABP–AA

Figure 4.16 gives FTIR spectrum for PABP taken at room temperature (denoted by *), and in situ FTIR spectra for self-assembled PABP–AA at various temperatures, during heating, ranging from 25 to 170 °C. The following observations are worth noting in Figure 4.16. (1) Two absorption peaks appear at wavenumbers of 2500 and 1900 cm\(^{-1}\) in self-assembled PABP–AA, in contrast to the spectra for PABP and AA. It is clearly seen in Figure 4.16 that the attractive interactions between the azopyridyl group in the side chain of PABP and the carboxylic acid group in AA are much stronger than the self-association within PABP molecules. (2) As the temperature is increased, the absorption peaks at wavenumbers of 2500 cm\(^{-1}\) and 1900 cm\(^{-1}\) for PABP–AA persist even at 170 °C, which is above its \(T_{\text{SI}}\) (161 °C), although the strength of the absorption peak at a wavenumber of 2500 cm\(^{-1}\) is somewhat weakened. (3) From the inset of Figure 4.16 we observe that the absorption peak at a wavenumber of 1680 cm\(^{-1}\) for the carboxylic acid group in anisic acid (see the spectrum (1) in Figure 4.12) has become a shoulder, getting stronger as the temperature is increased, while the absorption peak at a wavenumber of 1732 cm\(^{-1}\) for carbonyl group of PABP becomes broader and a new stronger peak appears at a wavenumber of 1726 cm\(^{-1}\), which has originated from the formation of hydrogen bonds between the azopyrydyl group in the side chain of PABP and the carboxylic acid group in AA.
Figure 4.16. FTIR spectrum for PABP denoted by (*) and in-situ FTIR spectra for self-assembled PABP–AA at various temperatures (°C): (1) 25, (2) 100, (3) 120, (4) 140, (5) 150, (6) 160, and (7) 170. The inset shows the absorption peaks at wavenumbers ranging from 1800 cm\(^{-1}\) to 1650 cm\(^{-1}\).
4.4 Self-Assembled PABP–TSA via Ionic Interactions

4.4.1 Formation of a Mesogenic Phase in a Mixture of Monomer PAPM and \( p \)-Toluene Sulfonic Acid via Ionic Interactions

In Figure 4.11a we have shown that PAPM does not exhibit mesogenic characteristics. However, in the preparation of a combined MCSCLCP from a mixture of PABP and \( p \)-toluene sulfonic acid (TSA) via ionic interactions, we had to first confirm that monomer PAPM is capable of forming ionic interactions when it is mixed with TSA and the mixture gives rise to a mesogenic phase. For this, we prepared a mixture of PAPM with TSA in a common solvent, ethanol. Figure 4.17 gives DSC thermograms for a mixture of PAPM and TSA at a scanning rate of 20 °C/min. In the inset of Figure 4.17 is given a POM image for a mixture of PAPM and AA obtained at 40 °C during cooling, from which we observe that the mixture forms a smectic A mesophase. From the DSC thermograms in Figure 4.17 we observe that during heating, the mixture undergoes crystal-to-crystal (\( k_1 \rightarrow k_2 \)) transition at ca. 30 °C, then crystal-to-smectic (\( k_2 \rightarrow S \)) transition at ca. 68 °C, and finally S–I transition at ca. 88 °C, while during cooling the mixture undergoes I–S transition at ca. 54 °C followed by smectic-to-crystal transition at ca. 6 °C. Thus we conclude that a mixture of PAPM and TSA has induced a smectic mesophase via ionic interactions between the azopyridine group in PAPM and the sulfonic acid group in TSA.

Figure 4.18 gives FTIR spectra for (1) TSA, (2) a mixture of PAPM and TSA, and (3) PAPM at room temperature. It can be seen in Figure 4.18 that a mixture of PAPM and TSA exhibits a new absorption peak (indicated by an arrow) at a wavenumber of
Figure 4.17. DSC thermograms for self-assembled PAPM–TSA at a scanning rate of 20 °C/min during (1) heating and (2) cooling cycles, and POM image taken at 40 °C during the cooling cycle. Here k denotes the crystalline phase and $S_m$ denotes a smectic phase.
Figure 4.18. FTIR spectra for (1) TSA, (2) self-assembled PAPM–TSA, and (3) PAPM at room temperature.
1632 cm\(^{-1}\), which is characteristic of ionized pyridyl group,\(^{214,215}\) whereas the absorption peak at 1596 cm\(^{-1}\) representing the pyridyl group in the side chain of PAPM disappears. Also, the broad absorption peak from 2500 cm\(^{-1}\) to 3000 cm\(^{-1}\) for the sulfonic acid group in TSA has become weakened, and a new absorption peak at a wavenumber of 2500 cm\(^{-1}\) is formed. The above observations have ensured us that the azopyridyl group in monomer PAPM, when it was mixed with \(p\)-toluene sulfonic acid (TSA), indeed formed ionic interactions, yielding a mesogenic phase.

### 4.4.2 Thermal Transition and Mesophase Structure of Self-Assembled PABP–TSA

Figure 4.19a gives DSC thermograms for self-assembled PABP–TSA during the heating and cooling cycles at a scanning rate of 20 °C/min. It can be seen from Figure 4.19a that, upon heating, self-assembled PABP–TSA has a \(T_g\) of ca. 58 °C, a melting temperature (\(T_{m2}\)) of ca. 110 °C, and a \(T_{SI}\) of ca. 155 °C, while the phase transition temperatures during cooling are slightly decreased. The small endothermic peak appearing at 135 °C in Figure 4.19a is believed to have originated from the presence of high-temperature melting crystals. It has been reported\(^{222-224}\) that some LCPs undergo “dual” melting processes; namely, (1) a fast melting process and (2) a slow melting process. The fast melting process is associated with the melting of usual crystallizable polymers, and the melting temperature associated with this process is usually denoted by \(T_{m2}\). The slow melting process is associated with the melting of crystals that were formed during isothermal annealing and the temperature associated with this process is usually denoted by \(T_{m1}\). Note that \(T_{m2} < T_{m1}\), and the value of \(T_{m2}\) remains more or less
Figure 4.19. Thermal transitions and mesophase of self-assembled PABP−TSA: (a) DSC thermograms at a scanning rate of 20 °C/min for specimens without annealing during (1) heating and (2) cooling cycles, and (b) POM image taken at 130 °C during the cooling cycle.
constant regardless of the duration of annealing while the value of $T_{m1}$ may increase with increasing duration of annealing. POM images in Figure 4.19b also indicate that self-assembled PABP–TSA has smectic mesophase structure. Referring to the DSC thermograms given in Figure 4.13a for PABP, we observe that PABP is a highly crystalline polymer and it does not exhibit a glass transition over the range of temperatures investigated. The appearance of $T_g$ in self-assembled PABP–TSA (Figure 4.19a) indicates that the ionic interactions are much stronger than self-association within PABP molecules, and thus they restrict the mobility of molecular chains or increase the intermolecular interactions (i.e. molecular packing). Comparison of Figure 4.19a with Figure 4.13a indicates that the area under the low-temperature melting peak ($T_{m2}$) appearing at 110 °C for self-assembled PABP–TSA is much smaller than the area under the endothermic peak appearing at 113 °C for PABP, suggesting that the crystallinity of self-assembled PABP–TSA is very much decreased owing to the restricted mobility of molecular chains in self-assembled PABP–TSA.

### 4.4.3 In Situ FTIR Spectra and UV-vis Spectra for Self-Assembled PABP–TSA

Figure 4.20 gives FTIR spectrum for PABP taken at room temperature (denoted by *), and in situ FTIR spectra for self-assembled PABP–TSA at various temperatures, during heating, ranging from 25 °C to 160 °C. The following observations are worth noting in Figure 4.20. (1) In the inset of Figure 4.20, we observe a new absorption peak appearing at a wavenumber of 1632 cm$^{-1}$ for self-assembled PABP–TSA, which is attributed to the ionic interactions between the pyridyl group in the side chain of PABP and the sulfonic acid group in TSA. The absorption peak at a wavenumber of ca. 1594
Figure 4.20. FTIR spectrum for PABP denoted by (*) and in-situ FTIR spectra for self-assembled PABP–TSA at various temperatures (°C): (1) 25, (2) 100, (3) 120, (4) 140, and (5) 160. The inset shows the absorption peaks at wavenumbers ranging from 1650 cm\(^{-1}\) to 1550 cm\(^{-1}\).
cm$^{-1}$ for the pyridyl group has become rather weak. (2) As the temperature is increased, the strength of absorption peaks has not changed much, even at temperatures close to the clearing temperature. (3) The broad absorption peak at wavenumbers ranging from 2500 cm$^{-1}$ to 3000 cm$^{-1}$ for the sulfonic acid group in TSA has been weakened due to the ionic interactions with the pyridyl group in the side chain of PABP, and thus we observe a relatively weaker absorption peak at a wavenumber of 2600 cm$^{-1}$.

The ionic interactions between the pyridyl group in the side chain of PABP and the sulfonic acid group in TSA can be also confirmed by the UV-vis spectroscopy, as shown in Figure 7.21. It can be seen from Figure 7.21 that the absorption wavelength of trans-azopyridine in PABP is ca. 343 nm; whereas after self-assembly of azopyridine in PABP with the sulfonic acid in p-toluenesulfonic acid, the wavelength of trans-azopyridine is shifted to ca. 370 nm. The $\pi-\pi^*$ band of azopyridyl group at a wavelength of ca. 283 nm was weakened due to the ionic interaction of azopyridyl group in the side chain of PABP and the sulfonic acid group in TSA. Thus, self-assembly of azopyridine through hydrogen bonding or ionic interactions not only induces side-chain liquid crystallinity but also provide a unique opportunity to investigate the photoactivity of azopyridine under different situations.

4.5 Concluding Remarks

In this chapter, we synthesized three self-assembled MCSCLCPs, PyHQ12–7CNCOOH, PABP–AA, and PABP–TSA. Self-assembled PyHQ12–7CNCOOH was prepared via hydrogen bonding between the pendent pyridyl group in the MCLCP PyHQ12 and the carboxylic acid group in the mesogenic small
Figure 4.21. UV-vis spectra of thin films of (a) PABP and (b) self-assembled PABP–TSA.
molecule 7CNCOOH. Self-assembled PABP−AA was prepared via hydrogen bonding between the nonmesogenic side-chain azopyridyl group in the MCLCP PABP and the carboxylic acid group in the nonmesogenic small molecule \( p \)-anisic acid (AA). On the other hand, self-assembled PABP−TSA was prepared via ionic interactions between the nonmesogenic side-chain azopyridyl group in the MCLCP PABP and the sulfonic acid group in the nonmesogenic small molecule \( p \)-toluene sulfonic acid (TSA). We confirmed via FTIR spectroscopy that the hydrogen bonds or ionic interactions were formed in the respective MCSCLCPs. We found that self-assembled PyHQ12−7CNCOOH is a glassy LCP having nematic mesophase, while self-assembled PABP-AA and self-assembled PABP−TSA are semicrystalline LCPs having smectic mesophase. Interestingly, we found from in situ FTIR spectroscopy that the intermolecular hydrogen bonding between the pendent pyridyl groups in the MCLCP PyHQ12 and the carboxylic acid groups in the mesogenic small molecule 7CNCOOH and between the side-chain azopyridyl groups in the MCLCP PABP and the carboxylic acid groups in the nonmesogenic small molecule AA, and the ionic interactions between the side-chain azopyridyl groups in the MCLCP PABP and the sulfonic acid group in the nonmesogenic small molecule TSA are sufficiently strong, persisting at temperatures well above the clearing temperature of the respective MCSCLCPs. This observation has enabled us to explain why, upon cooling from the isotropic state, mesophase structure reappeared very quickly in the respective self-assembled MCSCLCPs synthesized in this study. To our knowledge, this is the first study reporting on the synthesis of combined MCSCLCP via hydrogen bonding or ionic interactions, while the previous studies\textsuperscript{191-200} reported on the syntheses of combined MCSCLCPs were based on covalent bonding via condensation polymerization.
CHAPTER V

DISPERSION CHARACTERISTICS AND RHEOLOGY OF ORGANOCLAY
NANCOMPOSITES BASED ON A SEGMENTED MAIN-CHAIN LIQUID
CRYSTALLINE POLYMER HAVING PENDENT PYRIDYL GROUP

5.1 Introduction

Since the publication of a series of papers in the early 1990s by the Toyota scientists\textsuperscript{225-227} who prepared organoclay nanocomposites based on nylon 6, during the last decade well over several hundreds of papers\textsuperscript{228} have been published in the literature dealing with the preparation of organoclay nanocomposites. Such efforts were based on the premise that a very high degree of dispersion of organoclay aggregates will generate very large surface areas, which then would significantly improve the mechanical properties of the nanocomposites. However, the expectation of achieving significantly improved mechanical properties in organoclay nanocomposites has not been realized to a large extent. When some of the improvement in mechanical properties, which was observed early on the organoclay nanocomposites based on nylon 6, is now understood as being not entirely due to the high degree of dispersion of organoclay aggregates, but due to the modification of the morphology of the nylon matrix in the presence of the organoclay.\textsuperscript{229} On the other hand, highly dispersed organoclay nanocomposites have been found to increase heat distortion temperature\textsuperscript{226,230,231} and the gas barrier properties
(i.e., to decrease gas permeability). Therefore, there still are sufficient incentives for preparing highly dispersed organoclay nanocomposites. For such purposes, two fundamental issues must be addressed.

The first issue to be addressed is to achieve compatibility between the thermoplastic polymer matrix and organoclay to obtain highly dispersed nanocomposites. It is well accepted that natural clay, perhaps with some exceptions, is not suitable for preparing highly dispersed nanocomposites. For this reason, during the past decade much effort has been spent on the development of surfactants that can modify the surface of natural clay. But, no general-purpose surfactant exists that can modify the surface of natural clay, which then enables one to prepare highly dispersed nanocomposites based on any thermoplastic polymer. Thus, more often than not, one must also modify the chemical structure of the thermoplastic polymer.

The second issue to be addressed is the preparation methods for nanocomposites. Two methods have widely been employed. One method is in-situ polymerization of monomer in the presence of an organoclay. While this method tends to produce highly dispersed nanocomposites, it is not always possible to adopt this method for the situations where polymers are already synthesized without an organoclay and when the presence of an organoclay interferes with the polymerization of monomer(s) (e.g., in condensation polymerization or anionic polymerization). In such situations, one has no choice but to prepare nanocomposites by mechanical mixing.

In the past, organoclay nanocomposites were prepared by either melt blending or solution blending using different thermoplastic polymers; namely, nylon 6, polypropylene, polystyrene, poly(ethylene oxide), poly(ε-
caprolactone), poly(ethylene-ran-vinyl acetate-ran-vinyl alcohol), poly(vinylpyridine), and elastomeric block copolymers. The majority of the studies referred to above failed to obtain highly dispersed nanocomposites, primarily because there was a lack of sufficient compatibility between the polymer matrix and organoclay employed. Only a few research groups reported on the preparation of organoclay nanocomposites based on thermotropic liquid-crystalline polymers (TLCP), but they observed intercalation of organoclay aggregates owing to the lack of sufficient compatibility between the TLCP and organoclay employed.

The objective of this study was to prepare and characterize highly dispersed organoclay nanocomposites based on a TLCP having pendent functional group. For the study, we synthesized a TLCP having pendent pyridyl group with the chemical structure (which hereafter will be referred to as PyHQ12),

\[
\text{PyHQ12}
\]

The rationale behind the synthesis of PyHQ12 lies in the expectation that the pendent pyridyl group in PyHQ12 may form hydrogen bonds with the polar group in a surfactant residing at the surface of an organoclay, giving rise to highly dispersed nanocomposites. For comparison, we also synthesized a TLCP with the chemical structure (which hereafter will be referred to as PSHQ12,}
Notice that the chemical structure of the backbone of PSHQ12 is exactly the same as that of PyHQ12. Using PyHQ12 and PSHQ12, respectively, we prepared nanocomposites with two different organoclays, one with hydroxyl groups and the other without polar groups. We have investigated (i) dispersion characteristics of the nanocomposites prepared using X-ray diffraction (XRD) and transmission electron microscopy (TEM), (ii) thermal transitions in the nanocomposites using differential scanning calorimetry (DSC), (iii) mesophase structure of the nanocomposites using polarized optical microscopy (POM), (iv) the presence of hydrogen bonds between the pendent pyridyl group in PyHQ12 and the hydroxyl groups in an organoclay using Fourier transform infrared (FTIR) spectroscopy, and (v) the dynamic linear viscoelasticity of the nanocomposites using oscillatory shear rheometry.

5.2 Characteristics of PyHQ12 and PSHQ12

Let us compare the characteristics of PyHQ12 with that of PSHQ12. Such comparison will help us to later interpret the differences in the dispersion characteristics and also in the rheological behavior between the organoclay nanocomposite based on PyHQ12 and the organoclay nanocomposite based on PSHQ12.
5.2.1 Thermal Transition and Mesophase Structure of PyHQ12 and PSHQ12

Figure 5.1 gives the DSC thermograms for (a) PyHQ12 and (b) PSHQ12 at a scanning rate of 20 °C/min during heating and cooling cycles. Keep in mind that PyHQ12 and PSHQ12 are different in the chemical structure of pendent groups. The following observations are worth noting in Figure 5.1. (i) PyHQ12 has a \( T_g \) of 96 °C and a clearing temperature (\( T_{cl} \)) of 162 °C during heating. The POM image given in the inset of Figure 5.1a indicates that PyHQ12 has Schlieren texture at temperatures between 96 and 162 °C, and thus 162 °C represents the nematic-to-isotropic (N–I) transition temperature (\( T_{NI} \)). (ii) PSHQ12 has a \( T_g \) of 80.7 °C and a \( T_{cl} \) of 167 °C during heating. However, PSHQ12 has an additional endothermic peak appearing at 118.1 °C, which represents the melting temperature of the crystalline phase of PSHQ12. The POM image given in the inset of Figure 5.1b indicates that PSHQ12 also has Schlieren texture at temperatures between 118.1 and 167 °C. Thus we conclude that PyHQ12 is a glassy nematic-forming TLCP, while PSHQ12 is a semicrystalline nematic-forming TLCP.

In order to further confirm differences in thermal transition behavior between PyHQ12 and PSHQ12, a series of annealing experiments were conducted. Figure 5.2 describes the annealing effect on the thermal transition in PyHQ12 and PSHQ12. During the annealing experiment the specimens were first heating above the clearing temperature, and then cooled down to a predetermined temperature (130 °C for both PyHQ12 and PSHQ12), and further held there for a certain period. It can be seen that both the \( T_g \) and \( T_{NI} \) of PyHQ12 are little affected by annealing for 6-48 h, whereas an annealing of PSHQ12 for 12 – 72 h gave rise to a new endothermic peak at 163 °C, signifying the presence of high-temperature melting crystal.160,161
Figure 5.1. DSC thermograms for (a) PyHQ12 and (b) PSHQ12 at a scanning rate of 20 °C/min, and their POM images at 130 °C.
Figure 5.2. DSC thermograms for (a) PyHQ12 and (b) PSHQ12 at a scanning rate of 20 °C/min for various annealed periods.
Figure 5.3 gives the WAXD powder patterns for PyHQ12 and PSHQ12 that were annealed at 130 °C for 48 h, and their fiber patterns for unannealed melt-drawn specimens. All WAXD patterns were taken at room temperature. The following observations are worth noting in Figure 5.3: (1) Even after annealing at 130 °C for 48 h, PyHQ12 still has only very diffuse diffraction in powder pattern and no crystal structure is detected, which is almost the same as unannealed specimen (not shown here); in fiber pattern, PyHQ12 has only diffuse lateral spacings. (2) On the other hand, PSHQ12 shows very sharp diffraction rings in the powder pattern of the specimen after annealing at 130 °C for 48 h, indicating the presence of a crystalline phase; in fiber pattern, PSHQ12 has diffuse lateral spacings, several meridional reflections, and off-axis streaks. By comparison of WAXD powder and fiber patterns between PyHQ12 and PSHQ12, we can confirm that PyHQ12 is a glassy TLCP while PSHQ12 is a semicrystalline TLCP.

TGA data given in Figure 5.4 show the degradation temperatures, 345 °C and 350 °C for PyHQ12 and PSHQ12, respectively, which are higher than the clearing temperature of each LCP as determined by DSC and POM. Thus, we can conduct the rheological measurements safely at a very wide temperature window.

5.2.2 FTIR Spectra of PyHQ12 and PSHQ12

Figure 5.5 gives in-situ FTIR spectra for PyHQ12 at various temperatures ranging from 25 to 180 °C, and also, for comparison, the FTIR spectra for PSHQ12 (denoted by *) at room temperature. It can be seen in Figure 5.5 that PyHQ12 has two absorption peaks, a broad peak at a wavenumber of 2580 cm\(^{-1}\) and another at a wavenumber of 1920 cm\(^{-1}\), both persisting over the entire range of temperatures tested. Let us review the
Figure 5.3. WAXD (a, b) powder patterns after annealing at 130 °C for (a) 48 h and (b) 144 h, and (c, d) fiber patterns of unannealed melt-drawn specimens for (a, c) PyHQ12 and (b, d) PSHQ12.
Figure 5.4. TGA data for (a) PyHQ12 and (b) PSHQ12 at a heating rate of 20 °C/min.
polymerization mechanism (acidolysis) for PyHQ12 from trans-2',5'-diacetoxy-4-stilbazole (Monomer I) and 4,4'-dicarboxy-1,12-diphenoxydodecane (Monomer II) (see Figure 3.1). It is well documented\textsuperscript{31,41,266,267} that strong attractive interactions exist between pyridyl and carboxylic acid groups. After polymerization is completed, 50% of the terminal groups in PyHQ12 macromolecular chains could be carboxylic acid group. These terminal acid groups in PyHQ12 can form hydrogen bonds with the pendent styrylpyridyl groups. The absorption peak at a wavenumber of 2580 cm\textsuperscript{-1} is believed to represent hydrogen bonds formed between the terminal carboxylic acid group in the main chain and pendent pyridyl group (i.e., self-association) in PyHQ12, while the absorption peak at a wavenumber of 1920 cm\textsuperscript{-1} represents Fermi resonance. Also, in the inset of Figure 5.5 we observe that the absorption peak for pyridyl group at a wavenumber of 1606 cm\textsuperscript{-1} is shifted to a slightly lower wavenumber (1601 cm\textsuperscript{-1}) as the temperature is increased from 25 to 180 °C. This observation confirms that there actually exist hydrogen bonds between the terminal carboxylic acid group in the main chain and pendent pyridyl group of PyHQ12, the strength of which becoming weaker with increasing temperature. On the other hand, as expected, in Figure 5.5 there is no self-association in PSHQ12. The above observations are very important to interpret the differences in the dispersion characteristics of organoclay aggregates and also the differences in the rheological behavior between the nanocomposites based on PyHQ12 and the nanocomposites based on PSHQ12.

\textbf{5.2.3 Temperature Dependence of the Complex Viscosities of PyHQ12 and PSHQ12}
Figure 5.5. FTIR spectra for PSHQ12 denoted by (*) and in-situ FTIR spectra for PyHQ12 at various temperatures (°C): (1) 25, (2) 100, (3) 120, (4) 140, (5) 160, and (6) 180.
Figure 5.6 describes the temperature dependence of complex viscosity ($|\eta^*|$) for PyHQ12 (○) and PSHQ12 (□), which were obtained from isochronal dynamic temperature sweep experiments at $\omega = 0.1$ rad/s. In Figure 5.6 we observe that values of $|\eta^*|$ for both PyHQ12 and PSHQ12 initially decrease with increasing temperature, going through a minimum, followed by an increase going through a maximum, and then decrease again with a further increase in temperature. Earlier, similar observations have been reported in the literature,\textsuperscript{268} explaining that (i) the initial decrease of $|\eta^*|$ observed in Figure 5.6 is due to the orientation of the nematic mesophase during oscillatory shear, (ii) the increase of $|\eta^*|$ after passing through a minimum is due to the transition from the nematic to the isotropic phase, because the viscosity of the isotropic phase is higher than that of the nematic phase, and (iii) the decrease of $|\eta^*|$, after passing through a maximum, with a further increase of temperature is the characteristic of all homogeneous fluids following the Arrhenius relationship. Indeed we observe in Figure 5.6 that the temperature at which values of $|\eta^*|$ go through a maximum is very close to the $T_{NI}$ of the respective TLCPs, which were determined from the DSC thermograms given in Figure 5.1. However, referring to Figure 5.6 there is a significant difference between PyHQ12 and PSHQ12 in the ways how values of $|\eta^*|$ increase after passing through a minimum and decrease after passing through a maximum. Specifically, the values of $|\eta^*|$ for PyHQ12 increase rather slowly after passing through a minimum and decrease rather slowly after passing through a maximum, as compared to the values of $|\eta^*|$ for PSHQ12. We attribute this observation to a restricted mobility of PyHQ12 chains owing to self-association within the molecule, which arises from the hydrogen bonding between the
Figure 5.6. Variations of \(|\eta^*|\) with temperature during isochronal dynamic temperature sweep experiments at \(\omega = 0.1\) rad/s for: (○) PyHQ12 and (△) PSHQ12.
terminal acid group in the main chain of PyHQ12 and the pendent pyridyl group (see the FTIR spectra given in Figure 5.5). This is in contrast to the situation for PSHQ12 that shows, referring to Figure 5.6, a very rapid increase in $|\eta^*|$ after passing a minimum and also a rapid decrease in $|\eta^*|$ after passing a maximum. After all, no self-association exists in PSHQ12 molecules.

5.2.4 Linear Dynamic Viscoelasticity of PyHQ12 and PSHQ12

Figure 5.7 and 5.8 give plots of log $G'$ versus log $\omega$ and log $G''$ versus log $\omega$ for PyHQ12 and PSHQ12 at various temperatures, respectively. It can be seen in Figure 5.7 that the slope of log $G'$ versus log $\omega$ plots for PyHQ12 over the entire range of $\omega$ tested remains less than 2 at temperatures below the clearing temperature (open symbols) and above the clearing temperature (filled symbols). However, in Figure 5.8 for PSHQ12, the slope of log $G'$ versus log $\omega$ plots for PSHQ12 over the entire range of $\omega$ tested remains less than 2 at temperatures below clearing temperature (open symbols), and then the slope in the terminal region becomes 2 when the temperature is increased to 180 °C (filled symbols). The above observations make sense at temperatures below $T_{NI}$ (162.4 °C for PyHQ12 and 167.1 °C for PSHQ12), because it is in an anisotropic state forming the nematic phase. The difference of log $G'$ versus log $\omega$ at temperatures above $T_{NI}$ for PyHQ12 and PSHQ12 lies in the presence of self-association in PyHQ12.

Figure 5.9 gives log $|\eta^*|$ versus log $\omega$ plots for (a) PyHQ12 and (b) PSHQ12 at various temperatures ranging from 130 to 190 °C. The following observations are worth noting in Figure 5.9: (i) The $|\eta^*|$ of PyHQ12 exhibits shear-thinning behavior with almost the same slope at temperatures below $T_{NI}$ (open symbols) and with a slightly
Figure 5.7. Dynamic frequency sweeps for PyHQ12: (a) Log $G'$ versus log $\omega$ plots and (b) Log $G''$ versus log $\omega$ plots at different temperatures (°C): (○) 130, (△) 140, (□) 160, (●) 180, and (▲) 190.
Figure 5.8. Dynamic frequency sweeps for PSHQ12: (a) Log $G'$ versus log $\omega$ plots and (b) log $G''$ versus log $\omega$ plots at different temperatures (°C): (○) 130, (△) 140, (□) 165, (●) 180, and (▲) 190.
steeper slope at temperatures above T_{NI} (filled symbols) over the entire range of \( \omega \) applied from 10^{-2} to 10^{2} rad/s. (ii) On the other hand, the |\eta^*| of PSHQ12 exhibits shear-thinning behavior with varying slope at temperatures below T_{NI} (open symbols) as \( \omega \) increases from 10^{-2} to 10^{2} rad/s and exhibits Newtonian behavior at low values \( \omega \) at temperatures above T_{NI} (filled symbols). Similar experimental observations, characteristics of all TLCPs without self-association, have also been reported previously. What is significant in the frequency dependence of |\eta^*| for PyHQ12 is that Newtonian behavior is not seen at temperatures above T_{NI}, which is attributable to the presence of self-association in PyHQ12.

Figure 5.10 gives log G' versus log G'' plots for (a) PyHQ12 and (b) PSHQ12 at various temperatures ranging from 130 to 190 °C. Note that Figure 5.10 was prepared using the dynamic frequency sweep data obtained at various temperatures, as shown in Figure 5.7 and 5.8. The following observations are worth noting in Figure 5.10. (i) The log G' versus log G'' plots for PSHQ12 are shifted downward with increasing temperature in the nematic region (open symbols) and then become virtually independent of temperature in the isotropic region at 180 and 190 °C. Similar experimental observations, characteristics of all TLCPs without self-association, have also been reported previously. (ii) However, the temperature dependence of log G' versus log G'' plots for PyHQ12 is quite different from that for PSHQ12; namely, the log G' versus log G'' plots in the nematic region (open symbols) for PyHQ12 show little temperature dependence, and the log G' versus log G'' plots in the isotropic region (filled symbols) lie above those in the nematic region (open symbols). In other words, the storage modulus
Figure 5.9. Log $|\eta^*|$ versus log $\omega$ plots for (a) PyHQ12 and (b) PSHQ12 at various temperatures ($^\circ$C): (○) 130, (△) 140, (□) 160, (▽) 165, (●) 180, and (▲) 190.
Figure 5.10. Log $G'$ versus log $\omega$ plots for (a) PyHQ12 and (b) PSHQ12 at various temperatures ($^\circ$C): (○) 130, (△) 140, (□) 160, (▽) 165, (●) 180, and (▲) 190.
G’ in the isotropic state is greater than that in the nematic state. (iii) The slope of log G’ versus log G” plots in the terminal region is much less than 2 for PyHQ12, while it is close to 2 for PSHQ12. It should be mentioned that the slope of log G’ versus log G” plots in the terminal region (at sufficiently low values of ω) is expected to be close to 2 for flexible homopolymers having no self-association. Thus we conclude that the very unusual temperature dependence of log G’ versus log G” plots observed for PyHQ12 in Figure 5.10a is attributable to the presence of self-association in PyHQ12.

5.3 Dispersion Characteristics and Rheology of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12

5.3.1 XRD Patterns of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12

Figure 5.11 gives XRD patterns for (a) Cloisite 15A, Cloisite 30B, and organoclay nanocomposites based on PyHQ12 or PSHQ12, and (b) MMT and PyHQ12/MMT nanocomposite. Notice in Figure 5.11 that Cloisite 30B has a gallery distance (d₀₀₁ spacing) of 1.9 nm, while Cloisite 15A has a d₀₀₁ spacing of 3.1 nm. The following observations are worth noting in Figure 5.11a. (i) PyHQ12/Cloisite 15A nanocomposite has a d₀₀₁ spacing of 3.4 nm, an increase of 0.3 nm (9.7 % increase) over the d₀₀₁ spacing of Cloisite 15A, suggesting that the nanocomposite might have intercalated Cloisite 15A aggregates. (ii) PyHQ12/ Cloisite 30B nanocomposite shows featureless XRD patterns. We hasten to point out that the disappearance of XRD peak does not necessarily signify that organoclay aggregates are highly dispersed. (iii) PSHQ12/Cloisite 30B nanocomposite has a d₀₀₁ spacing of 2.1 nm, an increase of 0.2 nm (10.5% increase) over
Figure 5.11  XRD patterns for (a): (1) Cloisite 15A, (2) PyHQ12/Cloisite 15A nanocomposite, (3) PyHQ12/Cloisite 30B nanocomposite, (4) PSHQ12/Cloisite 30B nanocomposite, and (5) Cloisite 30B, and (b): for (1) MMT and (2) PyHQ12/MMT nanocomposite
the $d_{001}$ spacing of Cloisite 30B, suggesting that the nanocomposites might have intercalated Cloisite 30B aggregates. It is very clear from the above observations that PyHQ12/Cloisite 30B nanocomposite has XRD patterns, which are distinctly different from the XRD patterns of the two other organoclay nanocomposites, the origin of which will be elaborated on below. As expected, the XRD patterns for PyHQ12/MMT nanocomposite, showing little difference from the XRD patterns of MMT, as indicated in Figure 5.11b.

5.3.2 TEM Images of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12

Figure 5.12 gives TEM images of PyHQ12/Cloisite 30B, PyHQ12/Cloisite 15A, PyHQ12/MMT, and PSHQ12/Cloisite 30B nanocomposites, in which the dark areas represent the organoclay and the gray/white areas represent the polymer matrix. It is clearly seen in Figure 5.12 that PyHQ12/Cloisite 30B nanocomposite has a very high degree of dispersion of Cloisite 30B aggregates in the matrix (PyHQ12), whereas PyHQ12/Cloisite 15A and PSHQ12/Cloisite 30B nanocomposites have large aggregates of organoclay, indicating poor dispersion of organoclay aggregates. We observe a correlation between the XRD patterns (see Figure 5.11) and the TEM images (see Figure 5.12). A TEM image of PyHQ12/MMT nanocomposite, showing very poor dispersion of MMT aggregates in the matrix PyHQ12, is also given in Figure 5.12. Such a poor dispersion of MMT aggregates in the matrix PyHQ12 can easily be understood from the point of view of the structure of MMT.273,274

5.3.3 FTIR Spectra of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12

Figure 5.13 gives FTIR spectra for (a) PyHQ12, (b) PyHQ12/Cloisite 15A
Figure 5.12  TEM images of PyHQ12/Cloisite 30B nanocomposite, PyHQ12/Cloisite 15A nanocomposite, PyHQ12/MMT, and PSHQ12/Cloisite 30B nanocomposite, in which the dark areas represent the clay and the gray/white areas represent the polymer matrix.
nanocomposite, (c) PyHQ12/MMT nanocomposite, and (d) PSHQ12/ Cloisite 30B nanocomposite at room temperature, showing slight evidence (spectrum b) of attractive interactions between PyHQ12 and Cloisite 15A, and no evidence (spectrum c and d) of attractive interactions between PyHQ12 and MMT as well as between PSHQ12 and Cloisite 30B. This observation is not surprising, because organoclay Cloisite 15A does not have functional groups that can have attractive interactions with the pendent pyridyl group in PyHQ12, and PSHQ12 does not have functionality that can have attractive interactions with the hydroxyl group in the surfactant MT2EtOH residing at the surface of organoclay Cloisite 30B, although the hydroxyl group in MT2EtOH may have attractive interactions with the carbonyl group in PSHQ12, which might have contributed to a slight increase in d_{001} spacing of Cloisite 30B in the PSHQ12/Cloisite 30B nanocomposite (Figure 5.11a). Similarly, there is no evidence of attractive interactions existing between the pendent pyridyl group in PyHQ12 and MMT, which can be attributed to the fact that the terminal hydroxylated edge of the MMT apparently is not effective to form hydrogen bonds with the pendent pyridyl group in PyHQ12, as compared to the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B platelets. In other words, the hydroxyl groups in the surfactant MT2EtOH are distributed on the entire surface of the organoclay Cloisite 30B.

Also given in Figure 5.13, for comparison, are in situ FTIR spectra for PyHQ12/Cloisite 30B nanocomposite at various temperatures ranging from 25 to 180 °C. Notice in Figure 5.13 that the size of the absorption peak at a wavenumber of 2570 cm\(^{-1}\) for PyHQ12/Cloisite 30B nanocomposite is larger than that for PyHQ12 although it tends to decrease, while the size of the absorption peak at a wavenumber of 3460 cm\(^{-1}\) for the
Figure 5.13  FTIR spectra for: (a) PyHQ12, (b) PyHQ12/Cloisite 15A nanocomposite, (c) PyHQ12/MMT nanocomposite, (d) PSHQ12/Cloisite 30B nanocomposite, and in-situ FTIR spectra for PyHQ12/Cloisite 30B nanocomposite at various temperatures (°C): (1) 25, (2) 100, (3) 120, (4) 140, (5) 160, and (6) 180.
hydroxyl group tends to increase, as the temperature is increased to 180 °C. What is remarkable in the FTIR spectra for the PyHQ12/Cloisite 30B nanocomposite displayed in Figure 5.13 is that the rather strong absorption peak at a wavenumber of 2570 cm\(^{-1}\) persists even at a temperature as high as 180 °C. Thus, we can conclude that the attractive interactions exist (i.e., hydrogen bonds are formed) between the pendent pyridyl group in PyHQ12 and the hydroxyl group in the surfactant MT2EtOH residing at the surface of organoclay Cloisite 30B, which then helped achieve a very high degree of dispersion of Cloisite 30B aggregates in the matrix PyHQ12 (see the TEM image given in Figure 5.12). We hasten to point out that we cannot rule out the possibility of ionic interactions between the pendent pyridyl groups in PyHQ12 and N\(^+\) ion in the surfactant 2M2HT residing at the surface of Cloisite 15A, contributing to a slight increase in \(d_{001}\) spacing of the PyHQ12/Cloisite 15A nanocomposite (see Figure 5.11a).

**5.3.4 Thermal Transition and Mesophase Structure of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12**

Figure 5.14 gives the DSC thermograms for PSHQ12/Cloisite 30B, PyHQ12/Cloisite 15A, PyHQ12/Cloisite 30B, and PyHQ12/MMT nanocomposites at a heating rate of 20 °C/min. Comparison of Figure 5.14 with Figure 5.1 indicates that the \(T_{NI}\) of PyHQ12/Cloisite 30B nanocomposite is decreased by 8.7 °C, the \(T_{NI}\) of PyHQ12/Cloisite 15A nanocomposite is only slightly decreased (1.3 °C), and the \(T_{NI}\) of PSHQ12/Cloisite 30B nanocomposite is decreased by 3.7 °C, while the \(T_{NI}\) of PyHQ12/MMT nanocomposite does not change much. As shown in Table 5.1, the
Figure 5.14. DSC thermograms for: (1) PSHQ12/Cloisite 30B nanocomposite, (2) PyHQ12/Cloisite 15A nanocomposite, (3) PyHQ12/Cloisite 30B nanocomposite, and (4) PyHQ12/MMT nanocomposite at a heating rate of 20 °C/min.
enthalpy of N–I transition, $\Delta H_{NI}$, for the PyHQ12/Cloisite 30B nanocomposite is much smaller than that for neat PyHQ12, suggesting that the strength of liquid crystallinity of PyHQ12 in the PyHQ12/Cloisite 30B nanocomposite is decreased considerably in the presence of Cloisite 30B. On the other hand, the $\Delta H_{NI}$ for the PSHQ12/Cloisite 30B nanocomposite is only slightly smaller than that for neat PSHQ12, indicating that the strength of liquid crystallinity of PSHQ12 in the PSHQ12/Cloisite 30B nanocomposite is little affected by the presence of organoclay Cloisite 30B. Also, the $\Delta H_{NI}$ for the PyHQ12/MMT nanocomposite is only slightly smaller than that for neat PyHQ12, indicating that the strength of liquid crystallinity of PyHQ12 in the PyHQ12/MMT nanocomposite is little affected by the presence of MMT. Notice in Table 5.1 that the difference in $\Delta H_{NI}$ between the PyHQ12/Cloisite 30B and PSHQ12/Cloisite 30B nanocomposites is very large, while the difference in $\Delta H_{NI}$ between PyHQ12 and PSHQ12 is rather small. In Figure 5.13 we already have observed the presence of strong attractive interactions (i.e., the formation of hydrogen bonds) between the pendent pyridyl group in PyHQ12 and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B, while little or no attractive interaction is present between the pendent phenylsulfonyl group in PSHQ12 and the surfactant MT2EtOH. Thus we can conclude that the much smaller value of $\Delta H_{NI}$ for the PyHQ12/Cloisite 30B nanocomposite, as compared to the $\Delta H_{NI}$ for neat PyHQ12, is attributable to the presence of hydrogen bonds between the pendent pyridyl group in PyHQ12 and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B.
Table 5.1. Enthalpy of N–I Transition, $\Delta H_{NI}$, for PyHQ12, PSHQ12 and Their Organoclay Nanocomposites

<table>
<thead>
<tr>
<th>sample code</th>
<th>$\Delta H_{NI}$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PyHQ12</td>
<td>3.80</td>
</tr>
<tr>
<td>PSHQ12</td>
<td>4.05</td>
</tr>
<tr>
<td>PyHQ12/Cloisite 30B</td>
<td>2.83</td>
</tr>
<tr>
<td>PyHQ12/Cloisite 15A</td>
<td>3.37</td>
</tr>
<tr>
<td>PyHQ12/MMT</td>
<td>3.62</td>
</tr>
<tr>
<td>PSHQ12/Cloisite 30B</td>
<td>3.94</td>
</tr>
</tbody>
</table>

Figure 5.15 gives POM images of PyHQ12/Cloisite 30B, PyHQ12/Cloisite 15A, PyHQ12/MMT, and PSHQ12/Cloisite 30B nanocomposite. In Figure 5.15 we observe that a considerable degree of liquid crystallinity of PyHQ12 is lost in the PyHQ12/Cloisite 30B nanocomposite, which is attributable to the formation of hydrogen bonds between the pendent pyridyl group in PyHQ12 and the hydroxyl group in the surfactant MT2EtOH residing at the surface of Cloisite 30B.

Figure 5.16 gives a scheme describing the state of dispersion of Cloisite 30B aggregates in the PyHQ12/Cloisite 30B nanocomposite, where the dark sticks represent Cloisite 30B platelets, the thin cylinders (which denote mesogens) plus waved lines (which denote flexible spacers) represent the segmented PyHQ12 chains, and the short dashed lines represent hydrogen bonds between the pendent pyridyl group in PyHQ12 and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B. Referring to Figure 5.16, the formation of hydrogen bonds between the pendent
Figure 5.15. POM images of PyHQ12/Cloisite 30B nanocomposite, PyHQ12/Cloisite 15A nanocomposite, PyHQ12/MMT, and PSHQ12/Cloisite 30B nanocomposite at 140 °C.
Figure 5.16. Scheme describing the distributions of PyHQ12 chains and organoclay Cloisite 30B in the highly dispersed PyHQ12/Cloisite 30B nanocomposite, where the dark sticks represent Cloisite 30B platelets, the thin cylinders (which denote mesogens) plus waved lines (which denote flexible spacers) represent PyHQ12 chains, and the short dashed lines represent hydrogen bonds between the pendent pyridyl group in PyHQ12 and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B.
pyridyl group in PyHQ12 and the hydroxyl groups in the surfactant MT2EtOH might have restricted the mobility of PyHQ12 chains in the nanocomposite. As a result, the orientation of PyHQ12 chains in PyHQ12/Cloisite 30B nanocomposite is severely restricted and thus the formation of nematic mesophase having long-range order of PyHQ12 would have become very difficult. Consequently, the domain size of PyHQ12 mesophase in PyHQ12/Cloisite 30B nanocomposite might have become very small, as shown in the POM image given in Figure 5.15.

On the other hand, the nematic mesophase of PyHQ12 in the PyHQ12/MMT nanocomposite (see Figure 5.15) is virtually identical to that of neat PyHQ12 (see Figure 5.1). Similarly, the nematic mesophase of PSHQ12 in the PSHQ12/Cloisite 30B nanocomposite (see Figure 5.15) is virtually identical to that of neat PSHQ12 (see Figure 5.1). This observation is not surprising, because little or no attractive interactions exist between PyHQ12 and MMT as well as between PSHQ12 and Cloisite 30B in the nanocomposite (see FTIR spectrum c and d in Figure 5.13). Notice in Figure 5.13 that in the presence of Cloisite 15A, the nematic mesophase of PyHQ12 in the PyHQ12/Cloisite 15A nanocomposite has been modified only slightly when compared with the nematic mesophase of neat PyHQ12 given in Figure 5.1. This observation may be attributable to the possibility of having had very weak interactions between the pendent pyridyl group in PyHQ12 and the positively charged N⁺ ion in the surfactant 2M2HT residing at the surface of organoclay Cloisite 15A.
5.3.5 Temperature Dependence of the Complex Viscosity of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12

Figure 5.17 describes the temperature dependence of $|\eta^*|$ for PyHQ12/Cloisite 30B, PyHQ12/Cloisite 15A, and PSHQ12/Cloisite 30B nanocomposites, which were obtained from isochronal dynamic temperature sweep experiments at $\omega = 0.1$ rad/s. It is instructive to compare Figure 5.17 with Figure 5.6. Namely, in Figure 5.17 we observe that values of $|\eta^*|$ for PyHQ12/Cloisite 30B nanocomposite decrease steadily with increasing temperature, and only a very narrow transition region can be discerned near its $T_{NI}$ (ca. 154 °C as shown in Figure 5.14). On the other hand, in Figure 5.6 we observe that the $|\eta^*|$ for PyHQ12 first decreases, going through a minimum, followed by an increase going through a maximum at $T_{NI}$, and then decreases again with a further increase in temperature. In other words, the liquid crystallinity of PyHQ12 in the PyHQ12/Cloisite 30B nanocomposite is partially lost, which is consistent with the observation made from the POM image given in Figure 5.15. That is, the formation of hydrogen bonds in the PyHQ12/Cloisite 30B nanocomposite has disrupted the orientation characteristics of PyHQ12, while giving rise to a very high degree of dispersion of Cloisite 30B aggregates in the nanocomposite.

Comparison of Figure 5.17 with Figure 5.6 indicates that the temperature dependence of $|\eta^*|$ for PSHQ12/Cloisite 30B nanocomposite is virtually identical to that for neat PSHQ12. This makes sense, because the mesophase structure of PSHQ12 in the PSHQ12/Cloisite 30B nanocomposite is little different from that of neat PSHQ12 (compare Figure 5.15 with Figure 5.1) and little attractive interaction exists between
Figure 5.17. Variations of $|\eta^*|$ with temperature during isochronal dynamic temperature sweep experiments at $\omega = 0.1$ rad/s for: (○) PyHQ12/Cloisite 30B nanocomposite, (△) PyHQ12/Cloisite 15A nanocomposite, and (□) PSHQ12/Cloisite 30B nanocomposite.
PSHQ12 and the surfactant MT2EtOH residing at the surface of Cloisite 30B (see Figure 5.13 for FTIR spectrum). Notice in Figure 5.17 that the $|\eta^*|$ for PyHQ12/Cloisite 15A nanocomposite initially decreases rapidly with increasing temperature to ca. 145 °C, remains more or less constant as the temperature is increased to ca. 160 °C, and then decreases again with a further increase of temperature. The absence of an increasing trend of $|\eta^*|$ at temperatures between 145 and 165 °C in the PyHQ12/Cloisite 15A nanocomposite suggests that liquid crystallinity of PyHQ12 in the PyHQ12/Cloisite 15A nanocomposite is disrupted somewhat, although not as much as that in the PyHQ12/Cloisite 30B nanocomposite.

5.3.6 Linear Dynamic Viscoelasticity of Organoclay Nanocomposites Based on PyHQ12 or PSHQ12

Figure 5.18 gives log $|\eta^*|$ versus log $\omega$ plots for PyHQ12/Cloisite 30B, PyHQ12/Cloisite 15A, and PSHQ12/Cloisite 30B nanocomposites at various temperatures ranging from 130 to 190 °C. PyHQ12/Cloisite 30B nanocomposite shows shear-thinning behavior over the entire range of $\omega$ ($10^{-2}$ – $10^2$ rad/s) applied at all temperatures investigated. Comparison of Figure 5.18a with Figure 5.9a indicates that values of $|\eta^*|$ at low angular frequencies are much greater for PyHQ12/Cloisite 30B nanocomposite than for neat PyHQ12. The driving force giving rise to such a strong shear-thinning behavior of PyHQ12/Cloisite 30B nanocomposite is the attractive interactions between PyHQ12 and organoclay Cloisite 30B, while the driving force giving rise to shear-thinning behavior of neat PyHQ12 is self-association within the molecules. Comparison of Figure 5.18c with Figure 5.9b indicates that values of $|\eta^*|$ for
Figure 5.18. Log |$\eta^*$| versus log $\omega$ plots for (a) PyHQ12/Cloisite 30B nanocomposites, (b) PyHQ12/Cloisite 15A nanocomposites, and (c) PSHQ12/Cloisite 30B nanocomposites at various temperatures (°C): (○) 130, (△) 140, (□) 155, (▽) 160, (●) 180, and (▲) 190.
PSHQ12/Cloisite 30B nanocomposite are virtually the same as those for neat PSHQ12. This observation is not surprising, because little or no attractive interactions exist between PSHQ12 and Cloisite 30B in the nanocomposite (see FTIR spectra given in Figure 5.13). The absence of attractive interactions in the PSHQ12/Cloisite 30B nanocomposite is further evidenced by the fact that at low values of \( \omega \) Newtonian behavior is observed in Figure 5.18c. Had there been attractive interactions in the PSHQ12/Cloisite 30B nanocomposite, values of \( |\eta^*| \) would have been much greater than those seen in Figure 5.18c.

In Figure 5.18b we observe that the temperature dependence of log \( |\eta^*| \) versus log \( \omega \) plots for PyHQ12/Cloisite 15A nanocomposite also show shear-thinning behavior over the entire range of \( \omega \) applied, very similar to that for PyHQ12/Cloisite 30B nanocomposite, except for that values of \( |\eta^*| \) for PyHQ12/Cloisite 15A nanocomposite are lower than those for PyHQ12/Cloisite 30B nanocomposite. However, the temperature dependence of log \( |\eta^*| \) versus log \( \omega \) plots for PyHQ12/Cloisite 15A nanocomposite appears to be similar to that for PSHQ12/Cloisite 30B nanocomposite, in spite of the fact that little or no hydrogen bonds exist between PyHQ12 and organoclay Cloisite 15A, as evidenced from the FTIR spectra given in Figure 5.13. Since in the PyHQ12/Cloisite 15A nanocomposite little or very weak attractive interactions exist between PyHQ12 and the surfactant 2MT2HT residing at the surface of Cloisite 15A (see the FTIR spectra given in Figure 5.13), the frequency dependence of \( |\eta^*| \) for the PyHQ12/Cloisite 15A nanocomposite, observed in Figure 5.18b, is primarily due to the frequency dependence of \( |\eta^*| \) for neat PyHQ12 (see Figure 5.9a).
Figure 5.19 gives the log $G'$ versus log $G''$ plots for PyHQ12/Cloisite 30B, PyHQ12/Cloisite 15A, and PSHQ12/Cloisite 30B nanocomposites at various temperatures ranging from 130 to 190 °C. Figure 5.19 was prepared from the results of dynamic frequency sweep experiments at various temperatures. Figure 20, 21 and 22 give plots of log $G'$ versus log $\omega$ and log $G''$ versus log $\omega$ for PyHQ12/Cloisite 30B, PyHQ12/Cloisite 15A, and PSHQ12/Cloisite 30B nanocomposites. The following observations are worth noting in Figure 5.19. We observe a distinct difference in temperature dependence of log $G'$ versus log $G''$ plots between PyHQ12/Cloisite 30B and PSHQ12/Cloisite 30B nanocomposites, while PyHQ12/Cloisite 30B and PyHQ12/Cloisite 15A nanocomposites have similar temperature dependence of log $G'$ versus log $G''$ plots. Specifically, the log $G'$ versus log $G''$ plots for the PyHQ12/Cloisite 30B nanocomposite tend to move upwards as the temperature is increased from 130 °C in the nematic region to 190 °C in the isotropic region (see Figure 5.14 for DSC traces), whereas the log $G'$ versus log $G''$ plots for the PSHQ12/Cloisite 30B nanocomposite moves downwards as the temperature is increased from 130 °C in the nematic region to 190 °C in the isotropic region (see Figure 5.14 for DSC traces). In other words, for a fixed value of loss modulus $G''$ the storage modulus $G'$ is higher in the isotropic region than in the nematic region for the PyHQ12/Cloisite 30B nanocomposite, which is quite opposite to the trend for the PSHQ12/Cloisite 30B nanocomposite. Had there been no attractive interactions in the PyHQ12/Cloisite 30B nanocomposite, an upward shift of log $G'$ versus log $G''$ plot with increasing temperature could not be observed. Earlier, similar observations were observed in organoclay nanocomposites based on a functionalized
Figure 5.19. Log $G'$ versus log $G''$ plots for (a) PyHQ12/Cloisite 30B nanocomposites, (b) PyHQ12/Cloisite 15A nanocomposites, and (c) PSHQ12/Cloisite 30B nanocomposites at various temperatures (°C): (○) 130, (△) 140, (□) 155, (▽) 160, (●) 180, and (▲) 190.
Figure 5.20. Dynamic frequency sweeps for PyHQ12/Cloisite 30B nanocomposites: (a) Log $G'$ versus log $\omega$ plots and (b) log $G''$ versus log $\omega$ plots at different temperatures (°C):

(○) 130, (△) 140, (□) 155, (●) 180, and (▲) 190.
Figure 5.21. Dynamic frequency sweeps for PyHQ12/Cloisite 15A nanocomposites: (a) Log $G'$ versus log $\omega$ plots and (b) log $G''$ versus log $\omega$ plots at different temperatures (°C): (○) 130, (△) 140, (□) 160, (●) 180, and (▲) 190.
Figure 5.22. Dynamic frequency sweeps for PSHQ12/Cloisite 30B nanocomposites: (a) Log $G'$ versus log $\omega$ plots and (b) log $G''$ versus log $\omega$ plots at different temperatures (°C): (○) 130, (△) 140, (□) 160, (●) 180, and (▲) 190.
polystyrene-block-polyisoprene (SIOH diblock) copolymer, in which the hydroxyl
groups in the SIOH diblock copolymer had hydrogen bonding with the hydroxyl groups
in the surfactant MT2EtOH residing at the surface of organoclay Cloisite 30B.

One may then raise a question as to why the PyHQ12/Cloisite 15A nanocomposite,
which shows no evidence of having formed hydrogen bonds between PyHQ12 and
organoclay Cloisite 15A (see FTIR spectra given in Figure 5.13), also shows the same
trend of temperature dependence of log G’ versus log G” plot as the PyHQ12/Cloisite
30B nanocomposite does. As described above, it is quite possible to have very weak
ionic interactions between the pendent vinilenepyridyl group in PyHQ12 and the
positively charged N⁺ ion in the surfactant 2M2HT residing at the surface of organoclay
Cloisite 15A.

5.4 Concluding Remarks

Previously, two research groups reported intercalation of organoclay
aggregates in nanocomposites based on main-chain TLCPs. Such experimental
observations are not surprising in that the TLCPs employed in both studies did not have
any functionality. To demonstrate whether functionality is necessary to obtain highly
dispersed nanocomposites based on TLCP, in this study we synthesized two main-chain
TLCPs, one having pendent pyridyl group (PyHQ12) and the other having pendent
phenylsulfonyl group (PSHQ12). Then, each TLCP was mixed with two different
organoclays, one with hydroxyl groups (Cloisite 30B) and another without polar groups
(Cloisite 15A). We have found that the PyHQ12/Cloisite 30B nanocomposite yielded a
very high degree of dispersion of organoclay aggregates, while the PyHQ12/Cloisite 15A
and PSHQ12/Cloisite 30B nanocomposites yielded a very low degree of dispersion of organoclay aggregates. The origin of the differences in the dispersion characteristics between PyHQ12/Cloisite 30B and PSHQ12/Cloisite 30B nanocomposites, and between PyHQ12/Cloisite 30B and PyHQ12/Cloisite 15A nanocomposites is explained in terms of the attractive interactions, as determined by FTIR spectroscopy, between the pendent pyridyl group in PyHQ12 and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of organoclay Cloisite 30B. We observed little or no attractive interactions between PSHQ12 and Cloisite 30B, and between PyHQ12 and Cloisite 15A. These observations explain why the previous investigators\textsuperscript{263,264} only observed intercalation of organoclay nanocomposites based on a TLCP without functionality.

We have observed a considerable loss in the degree of liquid crystallinity of PyHQ12 in the PyHQ12/Cloisite 30B nanocomposite, while the nanocomposite has a very high degree of dispersion of organoclay aggregates. We have explained this observation based on the argument that attractive interactions, via hydrogen bonding, between the pendent pyridyl group in PyHQ12 and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B might have restricted the mobility of PyHQ12 chains in the nanocomposite, and consequently the orientation of the nematic mesophase might have been severely restricted. Note that the formation of hydrogen bonds between PyHQ12 and Cloisite 30B in the PyHQ12/Cloisite 30B nanocomposite is random in space (see Figure 5.16), making the orientation of PyHQ12 chains very difficult. Thus we conclude that functionality in TLCP is necessary to obtain highly dispersed nanocomposites, but at the same time there is a possibility to lose some degree of liquid crystallinity in the TLCP. A challenge ahead us is to design and synthesize
TLCP that would give rise to a very high degree of dispersion of organoclay aggregates without a loss in the degree of liquid crystallinity of the TLCP in organoclay nanocomposites prepared.

In this chapter we have presented dramatic differences in linear dynamic viscoelasticity between PyHQ12/Cloisite 30B and PSHQ12/Cloisite 30B nanocomposites. The presence of hydrogen bonding in PyHQ12/Cloisite 30B nanocomposite is clearly demonstrated by the temperature dependence of complex viscosity (see Figure 5.17) and also by the temperature dependence of log $G'$ versus log $G''$ plots (see Figure 5.19). We conclude that an investigation of linear dynamic viscoelasticity of organoclay nanocomposites based on TLCP is very useful to determine whether the TLCP employed is effective to achieve a high degree of dispersion of organoclay aggregates.
CHAPTER VI

DISPERSION CHARACTERISTICS AND RHEOLOGY OF ORGANOCLAY NANOCOMPOSITES BASED ON A SEGMENTED MAIN-CHAIN LIQUID CRYSTALLINE POLYMER HAVING SIDE-CHAIN AZOPYRIDINE WITH FLEXIBLE SPACER

6.1 Introduction

In the previous chapter, we synthesized a segmented main-chain TLCP having pendent pyridyl group (referred to as PyHQ12), which was then used to prepare organoclay nanocomposites. We found that PyHQ12 was very effective to achieve a very high degree of dispersion of the organoclay aggregates having hydroxyl groups. Using Fourier transform infrared (FTIR) spectroscopy we have confirmed the formation of hydrogen bonds between the pendent pyridyl group in PyHQ12 and the hydroxyl group in the surfactant residing at the surface of the organoclay. But, a significant degree of liquid crystallinity of PyHQ12 in the organoclay nanocomposite was lost due to the formation of hydrogen bonds. We then realized that this was due to the proximity of the pendent pyridyl group to the mesogenic main-chain backbone. In other words, the pendent pyridyl group was located so close to the mesogenic main-chain backbone of PyHQ12, that hydrogen bonding between the pendent pyridyl group in PyHQ12 and the
hydroxyl group in the surfactant residing at the surface of organoclay greatly restricted the mobility (thus orientation) of the mesogenic main chain of PyHQ12.

To overcome the undesirable feature described above, subsequently we synthesized a new segmented main-chain TLCP (referred to as PABP) having side-chain azopyridyine with flexible spacer, the chemical structure of which is shown below,

\[
\begin{array}{c}
\text{O} \quad \text{O} \\
\text{O} \quad \text{CH}_2 \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{C}_5 \\
\text{N} \\
\text{N} \\
\end{array}
\]

In this study we have found that the liquid crystallinity of PABP in the organoclay nanocomposites was more or less intact and yet organoclay aggregates were very well dispersed. Thus, our goal to obtain a highly dispersed organoclay nanocomposite based on a segmented main-chain TLCP has been accomplished. In this chapter we summarize the highlights of our findings.

### 6.2 Thermal Transition Temperatures and Mesophase Structure of Organoclay Nanocomposites Based on PABP

Figure 6.1 gives the DSC thermograms at a heating rate of 20 °C/min for (a) neat PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and (d) PABP/Cloisite 30B nanocomposite. The following observations are worth noting in
Figure 6.1. DSC thermograms for (a) PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and (d) PABP/Cloisite 30B nanocomposite at a heating rate of 20 °C/min during the heating cycle.
Figure 6.1. (i) Neat PABP is a semicrystalline TLCP having a melting temperature ($T_m$) of ca. 114 °C (the lower endothermic peak) and a clearing (isotropization) temperature ($T_{cl}$) of ca. 146 °C (the upper endothermic peak). From POM image (see Figure 4.13a) and WAXD patterns (see Figure 4.14a and 4.15), we conclude that at temperatures between ca. 114 and ca. 146 °C PABP has only a smectic mesophase and thus the upper endothermic peak in the DSC thermogram given in Figure 6.1 represents a smectic–to–isotropic (S–I) transition temperature ($T_{SI}$). (ii) The DSC thermogram for PABP/MMT nanocomposite is virtually identical to that for neat PABP, suggesting that the presence of MMT has not affected the thermal transition temperatures of PABP and thus no attractive interaction exists between MMT and PABP. (iii) The DSC thermogram for PABP/Cloisite 15A nanocomposite shows that both $T_m$ and $T_{cl}$ are increased only by ca. 0.5 °C over those of neat PABP, the increase being practically insignificant. (iv) The DSC thermogram for PABP/Cloisite 30B nanocomposite shows that $T_m$ is increased by ca. 2 °C and $T_{cl}$ is increased only by ca. 0.7 °C. In view of the fact that the $T_{cl}$ of PABP in the PABP/Cloisite 15A and PABP/Cloisite 30B nanocomposites increased only slightly (0.5–0.7 °C) over that of neat PABP, we can tentatively conclude that the mesophase structure of PABP in both nanocomposites might be very little different from that of neat PABP. It is worth noting in Figure 6.1 that the area under the upper endothermic peak is virtually identical for all three nanocomposites, suggesting further that the mesophase structure of neat PABP might have changed very little.

Figure 6.2 gives POM images of (a) PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and (d) PABP/Cloisite 30B nanocomposite. Notice
Figure 6.2. POM images for (a) PABP, (b) PABP/MMT nanocomposites (c) PABP/Cloisite 15A nanocomposites, and (d) PABP/Cloisite 30B nanocomposites.
Figure 6.2 that PABP has a smectic phase, and the mesophase structure of PABP/MMT nanocomposite is virtually identical to that of PABP, while the mesophase structure of PABP in the PABP/Cloisite 15A and PABP/Cloisite 30B nanocomposites is only slightly different from that of neat PABP. This observation is consistent with that made above from the DSC thermograms given in Figure 6.2. Thus we can conclude that the presence of organoclay in both PABP/Cloisite 15A and PABP/Cloisite 30B nanocomposites has affected little the mesophase structure of PABP in the respective nanocomposites. What remains to be seen is whether the degree of dispersion of organoclay aggregates in the respective nanocomposites might be the same or not.

TGA data given in Figure 6.3 show the degradation temperatures, 285 °C for PABP, which is higher than its clearing temperature (ca. 145 °C) as determined by DSC and POM. Thus, we can conduct the rheological measurements safely at a very wide temperature window.

6.3 Dispersion Characteristics of Organoclay Nanocomposites Based on PABP

6.3.1 X-ray Diffraction (XRD) Patterns of Organoclay Nanocomposites Based on PABP

Figure 6.4a gives XRD patterns for MMT having a gallery distance \( d_{001} \) spacing of 1.1 nm, Cloisite 30B having a \( d \) spacing of 1.9 nm, and Cloisite 15A having a \( d \) spacing of 3.1 nm. It is seen that chemical treatment of MMT with a surfactant has increased the gallery distance of the respective organoclays. Figure 6.4b gives XRD patterns for (1) neat PABP, (2) PABP/MMT nanocomposite, (3) PABP/Cloisite 30B nanocomposite, and
Figure 6.3. TGA data for PABP at a heating rate of 20 °C/min.
Figure 6.4. XRD patterns for: (a) (1) Cloisite 15A, (2) MMT, and (3) Cloisite 30B; (b) (1) PABP, (2) PABP/MMT nanocomposite, (3) PABP/Cloisite 30B nanocomposite, and (4) PABP/Cloisite 15A nanocomposite.
(4) PABP/Cloisite 15A nanocomposite. Since PABP is a semicrystalline TLCP as evidenced by the DSC thermogram given in Figure 6.1 and by the WAXD powder patterns given in Figure 4.14a, the two XRD peaks at $2\theta$ of ca. 3.75° and 7.40° are attributable to smectic layered mesophase structure of PABP, as evidenced by the variation of the X-ray diffraction intensity during the second heating cycle (see Figure 4.15). Notice in Figure 6.4b that the XRD peak at $2\theta = 7.40$° appears in all three nanocomposites and the XRD peak at $2\theta = 3.75$° also appears in the PABP/MMT nanocomposite. This observation suggests that the mesophase structure of PABP in the PABP/MMT nanocomposite might have been little affected although the $d$ spacing of MMT has increased by 0.5 nm. Indeed, from the POM image given in Figure 6.2b we already have observed little change in the mesophase structure of PABP in the PABP/MMT nanocomposite.

However, the XRD peak at $2\theta = 3.75$° due to the mesophase structure of PABP is not very discernible in Figure 6.4b for the PABP/Cloisite 15A and PABP/Cloisite 30B nanocomposites. This observation suggests that some type of interaction between the organoclay and PABP might have occurred, supporting the slight change in the mesophase structure of PABP observed in the respective nanocomposites (see the POM images given in Figures 6.2c and 6.2d). Notice in Figure 6.4 that the $d$ spacing of Cloisite 15A in PABP/Cloisite 15A nanocomposite has increased only slightly from 3.1 nm to 3.5 nm, but interestingly the PABP/Cloisite 30B nanocomposite shows virtually featureless XRD patterns. This observation seems to suggest the presence of strong attractive interactions between PABP and Cloisite 30B in the PABP/Cloisite 30B
nanocomposite. We hasten to point out that the disappearance of the XRD peak does not necessarily signify that organoclay aggregates are highly dispersed.

6.3.2 Transmission Electron Microscopy (TEM) of Organoclay Nanocomposites

Based on PABP

Figure 6.5 gives TEM images of PABP/MMT, PABP/Cloisite 15A, and PABP/Cloisite 30B nanocomposites. In Figure 6.5 we observe (i) very poor dispersion of MMT aggregates in PABP/MMT nanocomposite, (ii) intercalation of Cloisite 15A aggregates in PABP/Cloisite 15A nanocomposite, and (iii) very high degree of dispersion of Cloisite 30B aggregates in PABP/Cloisite 30B nanocomposite. These observations are consistent with those made above from the XRD patterns given in Figure 6.4b. What is significant here is that a very high degree of dispersion of Cloisite 30B aggregates has affected little the mesophase structure (liquid crystallinity) of PABP in the PABP/Cloisite 30B nanocomposite (see Figure 6.2). This was not the case for the PyHQ12/Cloisite 30B nanocomposite described in the previous chapter, in which much of the liquid crystallinity of a segmented main-chain TLCP, PyHQ12, was lost while Cloisite 30B aggregates were dispersed very well in the matrix of PyHQ12, as discussed in Chapter V. The origin of the difference between the two situations, PABP/Cloisite 30B nanocomposite and PyHQ12/Cloisite 30B nanocomposite, will be elaborated on later in this chapter.

6.3.3 Fourier Transform Infrared (FTIR) Spectroscopy of Organoclay Nanocomposites Based on PABP

Figure 6.6 gives FTIR spectra for (a) neat PABP at room temperature, (b)
Figure 6.5. TEM images of PABP/Cloisite 30B nanocomposite, PABP/Cloisite 15A nanocomposite, and PABP/MMT nanocomposite, in which the dark areas represent the clay and the gray/white areas represent the polymer matrix.
PABP/MMT nanocomposite at room temperature, (c) PABP/Cloisite 15A nanocomposite at room temperature, and (d) in-situ FTIR spectra for PABP/Cloisite 30B nanocomposite at various temperatures ranging from 25 to 160 °C. It can be seen in Figure 6.6 that neat PABP has two absorption peaks (spectrum a), a broad peak at a wavenumber of 2560 cm$^{-1}$ and another at a wavenumber of 1890 cm$^{-1}$. These two absorption peaks indicate the presence of attractive interactions, though very weak, between the pyridyl group in the side-chain azopyridine and hydroxyl groups at the end of the main chain of PABP (see the chemical structure of PABP given above). It should be mentioned that after polymerization is completed, 50% of the terminal groups in PABP macromolecular chains could be hydroxyl groups. Thus the absorption peak at a wavenumber of 2560 cm$^{-1}$ is believed to represent hydrogen bonds formed between the terminal hydroxyl group at the end of the main chain of PABP and the pyridyl group in the side-chain azopyridine (i.e., self-association in PABP), while the absorption peak at a wavenumber of 1890 cm$^{-1}$ represents Fermi resonance.

Referring to Figure 6.6, little evidence can be seen of the presence of hydrogen bonds in the PABP/MMT nanocomposite (spectrum b) and a very weak interaction in PABP/Cloisite 15A nanocomposite (spectrum c), while the in-situ spectra (1–6) for PABP/Cloisite 30B nanocomposite indicate the presence of strong attractive interactions. Notice in Figure 6.6 that the size (or area) of the absorption peak at 2570 cm$^{-1}$ for the PABP/Cloisite 30B nanocomposite is larger than that for neat PABP although it tends to decrease, while the size of the absorption peak at 3460 cm$^{-1}$ for the hydroxyl group tends to increase, as the temperature is increased to 160 °C. Of particular note in the FTIR spectra for the PABP/Cloisite 30B nanocomposite displayed in Figure 6.6 is that the
Figure 6.6. FTIR spectra for: (a) PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and in-situ FTIR spectra for PABP/Cloisite 30B nanocomposite at various temperatures (°C): (1) 25, (2) 100, (3) 120, (4) 140, (5) 150, and (6) 160.
relatively strong absorption peak at 2570 cm\(^{-1}\) persists even at a temperature as high as 160 °C, which is above the clearing temperature of PABP (see Figure 6.1). This observation will be important later to explain the rheological behavior of PABP/Cloisite 30B nanocomposite. Thus, we conclude that attractive interactions exist (i.e., hydrogen bonds are formed) between the pyridyl group in the side-chain azopyridine in PABP and the hydroxyl group in the surfactant MT2EtOH residing at the surface of organoclay Cloisite 30B. We conclude further that the presence of hydrogen bonding in the PABP/Cloisite 30B nanocomposite helped achieve a very high degree of dispersion of Cloisite 30B aggregates in the PABP matrix (see the TEM image given in Figure 6.5). Earlier, Sato et al.\textsuperscript{219} reported on hydrogen bonding between a polymer containing pyridine group and another polymer with hydroxyl group. Some investigators\textsuperscript{276-278} reported on an improvement in miscibility between two polymers via hydrogen bonding.

The above observations can now explain the reasons for the very poor dispersion of MMT aggregates in PABP/MMT nanocomposite, some intercalation of Cloisite 15A aggregates in PABP/Cloisite 15A nanocomposite, and a very high degree of dispersion of Cloisite 30B aggregates in PABP/Cloisite 30B nanocomposite (see Figure 6.5).

### 6.4 Rheological Behavior of Organoclay Nanocomposites Based on PABP

Figure 6.7 describes the frequency dependence of the dynamic storage modulus (G') for (a) PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and (d) PABP/Cloisite 30B nanocomposite at various temperatures below and above the isotropization temperature of PABP as determined by the upper endothermic peak in the DSC thermograms (see Figure 6.1). Below we will refer to the isotropization
Figure 6.7. Log $G'$ versus log $\omega$ plots for (a) PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and (d) PABP/Cloisite 30B nanocomposite at different temperatures (°C): (○) 120, (△) 130, (□) 140, (●) 150, and (▲) 160.
temperature of each material as smectic–to–isotropic transition temperature ($T_{SI}$) since we have confirmed that all four materials have smectic mesophase at temperatures between the melting temperature (the lower endothermic peak in the DSC thermogram) and the isotropization temperature (the upper endothermic peak in the DSC thermogram). The following observations are worth noting in Figure 6.7.

Referring to Figure 6.7a, in the isotropic state at 160 °C that is ca. 14 °C above the $T_{SI}$ (ca. 146 °C) of PABP, the slope of log $G'$ versus log $\omega$ plot in the terminal region for neat PABP is much less than 2. Such unusual rheological characteristics have never been observed for typical TLCPs and flexible homopolymers. We attribute this observation to the self-association taking place within the PABP molecules having pyridyl groups in the side-chain azopridine as well as the hydroxyl group at the end of the main chain of PABP, as pointed out above in reference to the FTIR spectra given in Figure 6.6. A similar observation can be made in Figure 6.7b for the PABP/MMT nanocomposite, suggesting that the presence of MMT has not influenced the frequency dependence of PABP in the nanocomposite. This can be explained by the fact that there are little or no attractive interactions between MMT and PABP, as evidenced by XRD patterns (see Figure 6.4) and by TEM image (see Figure 6.5).

However, the situation becomes quite different for the PABP/Cloisite 15A nanocomposite given in Figure 6.7c and for the PABP/Cloisite 30B nanocomposite given in Figure 6.7d. Namely, referring to Figure 6.7c, the slope of log $G'$ versus log $\omega$ plot in the terminal region for the PABP/Cloisite 15A nanocomposite in the isotropic state is extremely small with a downward trend at angular frequencies below about 0.1 rad/s.
Such rheological characteristics seem to indicate the presence of some interactions between the organoclay Cloisite 15A and PABP, different from the rheological characteristics observed in Figure 6.7b for the PABP/MMT nanocomposite. Indeed we already have observed the presence of a weak interaction in the PABP/Cloisite 15A nanocomposite from the FTIR spectrum given in Figure 6.6. However, although we observe a similar trend in Figure 6.7d for the PABP/Cloisite 30B nanocomposite, there is a subtle difference between the PABP/Cloisite 30B and PABP/Cloisite 15A nanocomposites in that no downward trend in the terminal region of log G’ versus log ω plot is discernible for the PABP/Cloisite 30B nanocomposite. Most importantly, values of G’ in the terminal region of log G’ versus log ω plot for the PABP/Cloisite 30B nanocomposite are an order of magnitude larger than those for the PABP/Cloisite 15A nanocomposite. Such a significant difference between the two nanocomposites is attributable to the presence of strong attractive interactions, via hydrogen bonding, between the pyridyl group in the side-chain azopyridine of PABP and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B. What is remarkable here is the observation, which can be made from Figure 6.6d, that apparently the strength of hydrogen bonding in the isotropic state of PABP/Cloisite 30B nanocomposite is very high at 160 °C, which is above the T_{SI} (ca. 147 °C) of PABP in the nanocomposite. We hasten to point out that PABP begins to undergo thermal degradation at ca. 285 °C as determined from thermal gravimetric analysis given in Figure 6.3. Thus, there is no chance whatsoever for thermal degradation/crosslinking to have caused the very unusual rheological behavior displayed in Figure 6.7.
It is fair to state that the greater the strength of hydrogen bonding, the better the compatibility between the organoclay Cloisite 30B and the matrix PABP in the PABP/Cloisite 30B nanocomposite, giving rise to an improved dispersion of organoclay aggregates in the nanocomposite owing to the larger surface areas available. In turn, the larger the surface areas available, the greater will be the values of $G'$ in the nanocomposites. This is precisely the reason why in Figure 6.7d we observe such large values of $G'$ in the terminal region of log $G'$ versus log $\omega$ plot for the PABP/Cloisite 30B nanocomposite, as compared to the PABP/MMT and PABP/Cloisite 15A nanocomposites. Referring to Figure 6.7d, it should be pointed out further that the solidlike rheological behavior at temperatures below the $T_{SI}$ (ca. 147 °C) of PABP arises in large part from the mesophase structure (see Figure 6.2) of PABP. However, the solidlike rheological behavior of the PABP/Cloisite 30B nanocomposite at temperatures above the $T_{SI}$ (ca. 147 °C) of PABP is solely due to the strong attractive interactions in the nanocomposites. Hence, we can conclude that the results of rheological measurements displayed in Figure 6.7 shed an additional light on the mechanism that explains why the PABP/Cloisite 30B nanocomposite has a very high degree of dispersion of Cloisite 30B aggregates in the matrix PABP.

Figure 6.8 describes the temperature dependence of $G'$ during isochronal temperature sweep experiments at an angular frequency of 0.1 rad/s for PABP (○), PABP/MMT nanocomposite (△), PABP/Cloisite 15A nanocomposite (□), and PABP/Cloisite 30B nanocomposite (▽). In Figure 6.8 we observe that values of $G'$ for PABP initially decrease very slowly with increasing temperature up to ca. 130 °C.
Figure 6.8. Variations of $G'$ with temperature during isochronal dynamic temperature sweep experiments at $\omega = 0.1$ rad/s for (○) PABP, (△) PABP/MMT nanocomposite, (□) PABP/Cloisite 15A nanocomposite, and (▽) PABP/Cloisite 30B nanocomposite.
followed by a rapid decrease with a further increase of temperature up to ca. 140 °C, and then decrease at a very slow rate as the temperature is increased further to 155 °C. Note that the $T_{SI}$ of PABP is ca. 146 °C (see Figure 6.1). What is unusual in the temperature dependence of $G'$ observed in Figure 6.8 for PABP is that values of $G'$ do not decrease steadily when the temperature is increased above its $T_{SI}$. Such a temperature dependence of $G'$ has never been observed for typical TLCPs without self-association and flexible homopolymers. Therefore, we ascribe the unusual temperature dependence of $G'$ of PABP at elevated temperatures to the presence of self-association within the molecules.

Above, referring to Figure 6.6 we have pointed out that a weak attractive interaction exists between the pyridyl group in the side-chain azopyridine and hydroxyl groups at the end of the main chain of PABP.

In Figure 6.8 we observe further that the temperature dependence of $G'$ for the PABP/MMT nanocomposite is very similar to that of neat PABP, which can be understood from the point of view that little or no attractive interaction exists between PABP and MMT (see Figure 6.6). However, in Figure 6.8 we observe that the temperature dependence of $G'$ for the PABP/Cloisite 15A and PABP/Cloisite 30B nanocomposites is quite different from that for the PABP/MMT nanocomposite. Specifically, values of $G'$ for the PABP/Cloisite 30B nanocomposite at temperatures above the $T_{SI}$ of PABP are exceedingly large (more than two orders of magnitude) compared to those for the PABP/MMT nanocomposite, and about one order of magnitude larger than those for the PABP/Cloisite 15A nanocomposite. In turn, values of $G'$ for the PABP/Cloisite 15A nanocomposite at temperatures above the $T_{SI}$ of PABP are about an
order of magnitude larger than those for the PABP/MMT nanocomposite. These observations can be explained from the point of view that strong attractive interactions exist, via hydrogen bonding, between the pyridyl group in the side-chain azopyridine and the hydroxyl group in the surfactant MT2EtOH residing at the surface of organoclay Cloisite 30B. Notice in Figure 6.6 that the extent of hydrogen bonding in the PABP/Cloisite 30B nanocomposite is still strong even at temperatures above the T_{SI} (ca. 146 °C) of PABP.

Figure 6.9 describes the frequency dependence of the dynamic loss modulus (G'') for (a) PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and (d) PABP/Cloisite 30B nanocomposite at various temperatures below and above the T_{SI} of PABP. It is interesting to observe in Figure 6.9 that the slope of log G'' versus log ω plots in the terminal region is close to 1 for both neat PABP and PABP/MMT nanocomposite at 160 °C in the isotropic state, usually observed for TLCPs without self-association and flexible homopolymers. However, this observation is at variance with the observation made from the log G' versus log ω plots given in Figure 6.7 in that the slope of the log G' versus log ω plots in the terminal region are much less than 2, which is not expected from typical TLCPs without self-association in the isotropic state and flexible homopolymers. This difference between the two situations indicates that the elastic property (G') is much more sensitive to the state of self-association of PABP molecules than the viscous property (G'') with G'' being related to dynamic viscosity (η') by η' = G''/ω. On the other hand, in Figure 6.9d we observe clear evidence of the presence of strong attractive interactions in the PABP/Cloisite 30B nanocomposite in that the slope of
Figure 6.9. Log $G''$ versus log $\omega$ plots for (a) PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and (d) PABP/Cloisite 30B nanocomposite at different temperatures (°C): (○) 120, (△) 130, (□) 140, (●) 150, and (▲) 160.
log G'' versus log ω plots in the terminal region is much less than 1 in the isotropic state of PABP. Again, in Figure 6.9c we observe a similar rheological characteristic from the log G'' versus log ω plots in the terminal region for the PABP/Cloisite 15A nanocomposite in the isotropic state. This can be explained by the presence of a very weak interaction in the PABP/Cloisite 15A nanocomposite as evidenced from the FTIR spectrum given in Figure 6.6. Notice, however, the difference in the values of G'' between the PABP/Cloisite 30B and PABP/Cloisite 15A nanocomposites in the isotropic state; namely, values of G'' for the PABP/Cloisite 30B nanocomposite are an order of magnitude larger than those for the PABP/Cloisite 15A nanocomposite. As pointed out above, this difference between the two nanocomposites is attributable to the presence of strong attractive interactions in the PABP/Cloisite 30B nanocomposite.

Figure 6.10 gives log |η*| versus log ω plots for (a) neat PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and (d) PABP/Cloisite 30B nanocomposite at various temperatures below and above the T_SI of PABP. The following observations are worth noting in Figure 6.10. Referring to Figure 6.10a, neat PABP exhibits a strong frequency dependence of |η*| over the entire range of ω (10^{-2}–10^{2} rad/s) applied at temperatures below the T_SI of PABP. It is well established that such a frequency dependence of |η*| is characteristic of TLCP in an anisotropic state, although there is no plateau region (so-called region I) at intermediate angular frequencies. However, PABP exhibits Newtonian behavior in the terminal region at temperatures well above its T_SI. Notice in Figure 6.10a that log |η*| versus log ω plots for
Figure 6.10. Log $|\eta^*|$ versus log $\omega$ plots for (a) PABP, (b) PABP/MMT nanocomposite, (c) PABP/Cloisite 15A nanocomposite, and (d) PABP/Cloisite 30B nanocomposite at different temperatures ($^\circ$C): ($\bigcirc$) 120, ($\triangle$) 130, ($\square$) 140, ($\bullet$) 150, and ($\Delta$) 160.
neat PABP at 150 °C, which is only ca. 4 °C above its \( T_{SI} \), still exhibits frequency
dependence. This is attributable to the fact that PABP is a polydisperse polymer and thus
it cannot have a very sharp, single value of \( T_{SI} \). Therefore the upper endothermic peak in
the DSC thermogram (see Figure 6.1) should be regarded as an average value of \( T_{SI} \) for
the polydisperse PABP.

In Figure 6.10b we observe that the frequency dependence of \( |\eta^*| \) for PABP/MMT
nanocomposite persists over the entire range of temperatures tested up to 160 °C, which
is ca. 14 °C above the \( T_{SI} \) of PABP. It should be remembered that values of \( |\eta^*| \) come
from the contributions of both \( G' \) and \( G'' \): \( |\eta^*(\omega)| = \left\{ \left[ \frac{G'(\omega)}{\omega} \right]^2 + \left[ \frac{G''(\omega)}{\omega} \right]^2 \right\}^{1/2} \). Thus,
the frequency dependence of \( |\eta^*| \) depends on the relative magnitude of \( G' \) and \( G'' \).
Apparently, the contribution of \( G' \) is stronger than that of \( G'' \) (compare Figure 6.7b with
Figure 6.9b), giving rise to the frequency dependence of \( |\eta^*| \) given in Figure 6.10b.

From the frequency dependence of \( |\eta^*| \) given in Figures 6.10c and 6.10d we observe
that values of \( |\eta^*| \) for the PABP/Cloisite 30B nanocomposite are much larger than those
for the PABP/Cloisite 15A nanocomposite. This can be explained by the fact that values
of both \( G' \) and \( G'' \) for the PABP/Cloisite 30B nanocomposite are much larger than those
for the PABP/Cloisite 15A nanocomposite (compare Figures 6.7c and 6.7d with Figures
6.9c and 6.9d). Once again, such large values of \( |\eta^*| \) for the PABP/Cloisite 30B
nanocomposite are attributed to the hydrogen bonding between the pyridyl group in the
side-chain azopyridine of PABP and the hydroxyl groups in the surfactant MT2EtOH
residing at the surface of Cloisite 30B.
6.5 Rationale for the Design and Synthesis of PABP for the Preparation of Organoclay Nanocomposites

In the past, a few research groups\textsuperscript{263,264} reported on the preparation of organoclay nanocomposites by melt blending based on TLCPs having the following chemical structures,

![Chemical structure image]

In the preparation of nanocomposites, the authors employed organoclays very similar to Cloisite 30B and Cloisite 15A employed in the present study. They observed large XRD peaks in $2\theta$ scanning, suggestive of poor dispersion (or intercalation at best) of organoclay aggregates, and indeed intercalated structure as determined by TEM.\textsuperscript{264} The above observations were to be expected from the point of view of the absence of specific interaction between the TLCPs and organoclays employed in those studies.

One should keep in mind that in the preparation of organoclay nanocomposites by melt blending, the most important requirement is the presence of specific interactions between the polymer matrix (e.g., TLCP) and organoclay, which can promote compatibility between the two. A close look at the chemical structures of TLCPs shown above and the chemical structure of the surfactant residing at the surface of Cloisite 30B

178
and Cloisite 25A, respectively, reveals that one cannot expect any specific interactions between the TLCPs and organoclays employed.\textsuperscript{263,264}

On the other hand, the present study has demonstrated unambiguously the presence of specific interactions, via hydrogen bonding, between PABP and Cloisite 30B (see Figure 6.6), which then gave rise to highly dispersed aggregates of Cloisite 30B (see Figure 6.5). Most importantly, the liquid crystallinity of PABP in the PABP/Cloisite 30B nanocomposites is more or less intact with a very high degree of dispersion of Cloisite 30B aggregates (see Figure 6.2d). Thus, the rationale for the present study is to demonstrate the fundamental concept for the design and synthesis of TLCP that can give rise to highly dispersed organoclay aggregates in nanocomposites without sacrificing the inherent characteristics (liquid crystallinity) of TLCP. To our knowledge, such a study has never been reported in the literature.

\section*{6.6 Concluding Remarks}

In this study we synthesized a segmented main-chain TLCP, PABP, having side-chain azopyridine with flexible spacer to prepare nanocomposites. We have found that PABP is a semicrystalline, smectic-forming TLCP having a $T_m$ of 114 $^\circ$C and a $T_{SI}$ of 146 $^\circ$C. In the preparation of nanocomposites we employed natural clay (MMT), an organoclay (Cloisite 15A) treated with a surfactant without polar group, and another organoclay (Cloisite 30B) treated with a surfactant having hydroxyl group. We have found that PABP/Cloisite 30B nanocomposite has a very high degree of dispersion of Cloisite 30B aggregates, while PABP/Cloisite 15A nanocomposite has intercalation of Cloisite 15A aggregates, and PABP/MMT nanocomposite has very poor dispersion of
MMT aggregates. Using in-situ FTIR spectroscopy we obtained evidence that hydrogen bonds were formed between the pyridyl group in the side-chain azopyridine of PABP and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B in the PABP/Cloisite 30B nanocomposite, while very weak interaction in the PABP/Cloisite 15A nanocomposite and no interaction in the PABP/MMT nanocomposite. The present study has demonstrated that successful preparation of organoclay nanocomposites having a very high degree of dispersion of organoclay aggregates depends very much on the extent of compatibility between an organoclay and a thermoplastic polymer. That is, a mismatch or lack of compatibility between an organoclay and a thermoplastic polymer would not produce nanocomposites having a very high degree of dispersion of organoclay aggregates. This has been illustrated in the PABP/Cloisite 15A nanocomposite in that PABP and the surfactant 2M2HT residing at the surface of Cloisite 15A do not have sufficient attractive interactions and thus the nanocomposite gives rise to only intercalation of Cloisite 15A aggregates.

Further, we have found that the mesophase structure (liquid crystallinity) of PABP in the PABP/Cloisite 30B nanocomposite is little affected by the hydrogen bonding between PABP and Cloisite 30B. This is attributed to the fact that the pyridyl group in the side-chain azopyridine of PABP is located sufficiently far away from the mesogenic main chain, and thus the hydrogen bonds formed between the pyridyl group at the end of the side-chain azopyridine with five methylene units, which lie in the middle of flexible spacers having twelve methylene units, and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B apparently have not interfered with the mobility (thus the orientation) of the mesogenic main chain of PABP. This observation is
depicted schematically in Figure 6.11, in which the dark ellipsoidal areas represent the mesogens of the main chain interconnected by the flexible spacers (shown by thin waved lines), and the dark sticks represent Cloisite 30B platelets that form hydrogen bonds with the pyridyl group located at the end of side-chain azopyridyl group. Notice in Figure 6.11 that the side-chain azopyridine is connected to the main chain through five methylene units (shown by thin waved lines). The situation depicted in Figure 6.11 is quite different from that depicted in Figure 5.16, in which the pendent pyridyl group was connected to the mesogenic main chain (PyHQ12, the chemical structure of which is given in the Figure 3.1) only through an vinylene unit and thus the hydrogen bonds formed between the pendent pyridyl group and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B might have interfered with the orientation of the mesogenic main chain, consequently disrupting the mesogenic structure of PyHQ12.

In this chapter we have compared the dynamic viscoelastic properties of PABP with those of three nanocomposites prepared. Specifically, we have shown how the dynamic viscoelastic properties of PABP, which has self-association within the molecules, are different from those of typical TLCPs without self-association, and how the hydrogen bonds formed between the pyridyl group in PABP and the surfactant residing at the surface of Cloisite 30B affected the dynamic viscoelastic properties of PABP/Cloisite 30B nanocomposite. The present study has demonstrated that rheological measurements, when properly interpreted, can be used as a powerful tool for a better understanding of the dispersion characteristics of organoclay nanocomposites.
Figure 6.11. Scheme describing the distributions of PABP and Cloisite 30B in the highly dispersed PABP/Cloisite 30B nanocomposite, where the dark sticks represent Cloisite 30B platelets, the dark ellipsoids represent the main-chain mesogens, waved lines represent flexible spacers, the empty notched ellipsoids represent the azopyridine in the side chain of PABP, and the empty notched ellipsoids with caps represent hydrogen bonds between the pyridyl group in the side-chain azopyridine of PABP and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B.
Above all, the present study has demonstrated the fundamental concept for the design and synthesis of TLCP that can give rise to a highly dispersed organoclay aggregates in nanocomposites without sacrificing the inherent characteristics (liquid crystallinity) of TLCP. To our knowledge, such a study has never been reported in the literature.
CHAPTER VII

RUTHENIUM(II) COMPLEX-INDUCED DISPERSION OF MONTMORILLONITE IN A SEGMENTED MAIN-CHAIN LIQUID CRYSTALLINE POLYMER HAVING SIDE-CHAIN TERPYRIDINE GROUP

7.1 Introduction

Compatibility represents one of the most important issues when one designates to achieve a very high degree of dispersion of clay aggregates in the polymer matrix. Montmorillonite, which is referred to as MMT hereafter and widely employed to prepare polymer nanocomposites, is a type of smectic natural clay that tends to swell when exposed to water.\textsuperscript{279} Thus, in its pristine state MMT is only miscible with hydrophilic polymers, such as poly(ethylene oxide) (PEO)\textsuperscript{249} or poly(vinyl alcohol) (PVA).\textsuperscript{280} To render the miscibility between MMT and hydrophobic polymers, in most cases MMT was treated with a surfactant through ion-exchange reactions to convert the hydrophilic silicate surface into an organophilic one, and thus formed the so-called organoclay.\textsuperscript{225,281,282} Unfortunately, very high degree of dispersion seldom happens in conventional polymer/organoclay nanocomposites, primarily due to the lack of attractive interactions between the surfactant and polymers. Therefore, one must design and synthesize a polymer that can have strong specific interactions with the selected
organoclay, such that the chemically modified clay can have strong attractive interactions with the selected polymer.265,275

Recently, Fournaris et al.257 prepared nanocomposites of sodium montmorillonite with poly(4-vinylpyridium) salts (1,2-form), the quaternized ionene polymer (1,6-form) and poly(4-vinylpyridine) (neutral form). Basically, they prepared polyvinylpyridine/clay nanocomposites using intercalative polymerization, namely by polymerizing 4-vinylpyridium monomer in the clay galleries. The rationale behind this approach lied in that 4-vinylpyridine monomer in the protonated form would easily intercalate into the layers of clay having negatively charged surfaces by an ion exchange process and then the monomer would undergo polymerization within the spatially constrained interlamellar space of the clay. In most cases, only intercalation of clay aggregates was observed. Besides cationic ions, metal ions were also employed to prepare clay nanocomposites through in-situ intercalative polymerization process. Tudor et al.283 have demonstrated the ability of soluble metalloocene catalysts to intercalate inside silicate layers and to promote the coordination polymerization of propylene.

Intercalated/exfoliated nanocomposites based on high density polyethylene matrixes have been synthesized by the polymerization-filling technique.284 Specifically, a Ziegler-Natta type catalyst or any other coordination catalysts, which include activated metalloccenes, was first anchored onto a filler surface, and then ethylene was in-situ polymerized directly from the surface treated fillers. The use of ruthenium(II) complex for the preparation of a clay-metal complex hybrid film285 or selective absorption onto clay surfaces has extensively been studied,286-289 usually in connection with harnessing the specific interactions between metal-ion center and negatively charged clay surface.
In this chapter, we first synthesized a segmented main-chain liquid-crystalline polymer having side-chain terpyridine group (PTBP) and prepared a ruthenium metal complex \([\text{Ru}^{II}(\text{PTBP})(6\text{TPy})](\text{PF}_6)_2\) (referred to as PTBP-Ru-6TPy) by mixing PTBP with a monocomplex (6TPy-RuCl\(_3\)), which was formed between a terpyridine (6-(2,2′:6′,2″-terpyridyl-4′-oxy)hexane (6TPy) and ruthenium chloride (RuCl\(_3\·3\text{H}_2\text{O}\)). Subsequently, we prepared a (PTBP-Ru-6TPy)/MMT nanocomposite by solution blending. We found that the MMT aggregates in the nanocomposite to be very well dispersed in the matrix of PTBP-Ru-6TPy. We attribute the very high degree of exfoliation of MMT aggregates observed to the Coulombic interactions between the negatively charged surfaces of pristine MMT and the positively charged ruthenium center in the polymer matrix, as schematically shown in Figure 7.1. We are not aware of any previous study, which has reported on the formation of very high degree of exfoliation of pristine MMT aggregates in a polymer matrix having a metal complex.

7.2 Thermal Transition Temperatures and Mesophase Structure of PTBP

Figure 7.2 gives the DSC thermograms for PTBP and PMBP at a scanning rate of 20 °C/min during the heating and cooling cycles. It should be mentioned that PMBP is a segmented main-chain liquid crystalline polymer, while PTBP has the same backbone as PMBP but a side-chain terpyridine group in the middle of flexible spacer, and the chemical structure of PABP discussed in Chapters IV and VI differs from PTBP only in the side-chain azopyridine group. It can be seen from Figure 7.2b that PMBP has a glass transition temperature \(T_g\) of 86.2 °C, a melting temperature \(T_m\) of 125.4 °C, and a clearing temperature \(T_{cl}\) of 149.7 °C during the heating cycle. The POM image given in
Figure 7.1. Schematic representation of Coulombic interactions between between the negatively charged surfaces of pristine MMT and the positively charged ruthenium center in the polymer matrix.
Figure 7.2. DSC thermograms of PTBP and PMBP during (1) heating and (2) cooling cycles. The inset are the polarized optical microscopy (POM) images taken after annealing at 70 °C for 24 h for PTBP, and taken at 130 °C for PMBP during the cooling cycle.
the inset of Figure 7.2b suggests that PMBP has smectic mesophase at temperatures between 125.4 °C and 149.7 °C, and thus 149.7 °C represents smectic-to-isotropic (S-I) transition temperature (T_{SI}). Similarly, it can be seen in Figure 4.13a that during heating PABP has a melting temperature (T_m) of ca. 113 °C and a smectic-to-isotropic (S–I) transition temperature (T_{SI}) of ca. 146 °C, but has no appearance of T_g, due to the effect of side-chain azopyridine group. In contrast, it can be seen from Figure 7.2a that PTBP only exhibits a T_g of 49.9 °C and a clearing temperature (T_{cl}) of 80.7 °C during heating. The POM image given in the inset of Figure 7.2a indicates that PTBP has smectic mesophase at temperatures between 49.9 and 80.7 °C, and thus 80.7 °C represents smectic-to-isotropic (S-I) transition temperature (T_{SI}). Surprisingly, there does not exhibit crystallinity for PTBP, due to the bulky side-chain terpyridine groups. Thus, we can conclude that the side chain and the bulky size of functional groups have significantly affected the thermal transition temperatures and mesophase of liquid crystalline polymers.

7.3 Characterizations of TPy-RuCl₃ monocomplex and [Ru^{II}(PTBP)(6TPy)](PF₆)₂ complex (PTBP-Ru-6TPy)

A monocomplex (6TPy-RuCl₃), which would be used for preparing PTBP-Ru-6TPy, was reacted between a terpyridine (6-(2,2′:6′,2″-terpyridyl-4′-oxy)hexane (6TPy) and ruthenium chloride (RuCl₃·3H₂O). Figure 7.3 gives FTIR spectra for (a) 6TPy and (b) 6TPy-RuCl₃ monocomplex. It can be seen in Figure 7.3 that the interaction of RuCl₃ with the terpyridine in 6TPy makes a shift of C-N stretching at wavenumbers of 1560 cm⁻¹ and 1577 cm⁻¹ to 1604 cm⁻¹, also indicated in the inset for details. It should be mentioned that the appearance of a strong new absorption peak at a wavenumber of 3055 cm⁻¹
Figure 7.3. FTIR spectra of (a) 6TPy and (b) 6TPy-RuCl$_3$ monocomplex. The Inset gives the absorption band from a wavenumber of 1500 cm$^{-1}$ to 1650 cm$^{-1}$. 
(assigned to –CH- stretching in the pyridyl ring in 6TPy due to the influence of RuCl₃) for 6TPy-RuCl₃ monocomplex is another evidence for confirming the successful coordination between 6TPy and RuCl₃. Figure 7.4 gives the UV-vis spectra for (a) 6TPy in CHCl₃ and (b) 6TPy-RuCl₃ monocomplex in DMF. The characteristic metal-to-ligand charge-transfer (MLCT) band for the mono(terpyridine) ruthenium (III) complex at around 405 nm can be observed in Figure 7.4. In addition, it can be seen that the characteristic bathochromic shift of the π–π* absorption bands of the ligand occur approximately at 279 and 310 nm. From the results of FTIR and UV-vis spectroscopy, we can conclude that 6TPy has successfully coordinated with RuCl₃ and formed 6TPy-RuCl₃ monocomplex.

The polymer-ruthenium complex [RuII(PTBP)(6TPy)](PF₆)₂ (referred to as PTBP-Ru-6TPy) was synthesized by reacting PTBP with a monocomplex (6TPy-RuCl₃) using the ruthenium(III)/ruthenium(II) chemistry. Figure 7.5 gives FTIR spectra for PTBP and PTBP-Ru-6TPy. It can be clearly seen from the inset of Figure 7.5 that the two absorption peaks at wavenumbers of 1562 cm⁻¹ and 1573 cm⁻¹ of C-N stretching for PTBP weaken in PTBP-Ru-6TPy. Instead, there are one strong new peak exhibiting at a wavenumber of 1610 cm⁻¹ for C-N stretching, which gives evidence of the successful formation of ruthenium complex between 6TPy and PTBP. Figure 7.6 gives the UV-vis spectra for PTBP and PTBP-Ru-6TPy in DMF. The characteristic metal-to-ligand charge-transfer (MLCT) band for the terpyridine ruthenium(II) complex at around 493 nm can be observed in Figure 7.6. In addition, it can be seen that the characteristic bathochromic shift of the π–π* absorption bands of the ligand occurs approximately at 270 and 309 nm.
Figure 7.4. UV-vis spectra of (a) 6TPy in CHCl$_3$ and (b) 6TPy-RuCl$_3$ monocomplex in DMF.
Figure 7.5. FTIR of (a) PTBP and (b) PTBP-Ru-6TPy. The inset gives the absorption band from a wavenumber of 1500 cm$^{-1}$ to 1700 cm$^{-1}$.
Figure 7.6. UV-vis spectra of (a) PTBP in CHCl$_3$ and (b) PTBP-Ru-6TPy in DMF.
Figure 7.7 shows the DSC thermograms of PTBP-Ru-6TPy at a scanning rate of 20 °C/min during the heating and cooling cycles. It can be seen that PTBP-Ru-6TPy only exhibits a T_g of 123.4 °C during the heating cycle, which has 73.5 °C higher than that of PTBP. POM images (not shown here) indicate that do not have any liquid crystallinity, due to the increased bulky size of the side chain in PTBP and the strong interactions between ruthenium metal ion centers.

7.4 Dispersion Characteristics of Montmorillonite or Organoclay Nanocomposites Based on PTBP-Ru-6TPy Complex

7.4.1 X-ray Diffraction (XRD) Patterns of Montmorillonite or Organoclay Nanocomposites Based on PTBP-Ru-6TPy Complex

Figure 7.8 shows the XRD patterns of (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite, (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, (PTBP-Ru-6TPy)/MMT nanocomposite, and PTBP/MMT nanocomposite. From XRD patterns given in Figure 6.4a, we learned that MMT has a gallery distance (d_{001} spacing) of 1.1 nm, Cloisite 30B has a d-spacing of 1.9 nm, and Cloisite 15A has a d-spacing of 3.1 nm. The following observations can be made from Figure 7.8: (i) The d-spacing of MMT in PTBP/MMT nanocomposite has increased only slightly from 1.1 nm to 1.3 nm, indicating that there would be little chance to obtain a highly dispersed MMT in PTBP; (ii) The d-spacing of organoclay aggregates in (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite has only increased from 1.9 nm to 4.4 nm, and that of (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite has slightly increased from 3.1 nm to 3.5 nm; (iii) Interestingly, (PTBP-
Figure 7.7. DSC thermograms of PTBP-Ru-6TPy during (a) heating and (b) cooling cycles.
Figure 7.8. XRD patterns of (a) (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite, (b) (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, (c) (PTBP-Ru-6TPy)/MMT nanocomposite, and (d) PTBP/MMT nanocomposite.
Ru-6TPy)/MMT nanocomposite has a featureless XRD pattern, the origin of which can be attributed to the incorporation of ruthenium complex into PTBP that largely improves the miscibility between the MMT and the polymer. Therefore, the treatment of MMT with surfactant is not necessary for the high degree of exfoliation of MMT aggregates in PTBP-Ru-6TPy matrix, whereas the surfactants (e.g. in Cloisite 30B and Cloisite 15A) may have adverse effects for the exfoliation of MMT in PTBP-Ru-6TPy.

7.4.2 Transmission Electron Microscopy (TEM) Images of Montmorillonite or Organoclay Nanocomposites Based on PTBP-Ru-6TPy Complex

Figure 7.9 gives TEM images of (PTBP-Ru-6TPy)/MMT, (PTBP-Ru-6TPy)/(Cloisite 30B), (PTBP-Ru-6TPy)/(Cloisite 15A), and PTBP/MMT nanocomposites. In Figure 7.9 we observe (i) very poor dispersion of MMT aggregates in PTBP/MMT nanocomposite, (ii) intercalation of Cloisite 15A aggregates in (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, (iii) flocculated dispersion of Cloisite 30B aggregates in (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite, and (iv) a very high degree of exfoliation of MMT in (PTBP-Ru-6TPy)/MMT nanocomposite. The poor dispersion of Cloisite 15A or 30B in PTBP-Ru-6TPy means that the chance of direct interactions between the positively charged ruthenium center in PTBP-Ru-6TPy and the negatively charged clay surface has been largely diminished, because of the shielding effect of positively charged surfactants. That is, the Coulombic interactions between the positively charged ruthenium center in PTBP-Ru-6TPy and the negatively charged clay surfaces, which exist in the (PTBP-Ru-6TPy)/MMT nanocomposite, are absent in the (PTBP-Ru-6TPy)/(Cloisite 30B) and (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposites.
Figure 7.9. TEM images of (a) (PTBP-Ru-6TPy)//MMT nanocomposite, (b) (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite, (c) (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, and (d) PTBP/MMT nanocomposite.
7.5 Ultraviolet-Visible (UV-vis) Spectroscopy of Montmorillonite or Organoclay Nanocomposites Based on PTBP-Ru-6TPy Complex

Tris(2,2′-bipyridine)ruthenium(II) complex was reported to very selectively adsorb into the gallery of clay.\textsuperscript{286,287} The evidence of strong interactions between ruthenium center and the negatively charged clay surface is related to the red-shift of the positions of the metal-to-ligand charge-transfer band (MLCT) of tris(2,2′-bipyridine)ruthenium(II) complex and the decrease of the $\pi-\pi^*$ band. In this study, the excellent ion-exchange property of ruthenium(II) complex was employed to exfoliate MMT aggregates in the polymer matrix. Figure 7.10 gives the UV-vis spectra of thin films of PTBP-Ru-6TPy, (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite, and (PTBP-Ru-6TPy)/MMT nanocomposite. It can be seen from Figure 7.10 that the position of the MLCT band at a wavelength of about 493 nm for PTBP-Ru-6TPy has only slightly red-shifted to a wavelength of 508 nm for (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, and to a wavelength of 516 nm for (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite, and notably to a wavelength of 520 nm for (PTBP-Ru-6TPy)/MMT nanocomposite. The $\pi-\pi^*$ band at a wavelength of 272 nm for PTBP-Ru-6TPy has decreased to a wavelength of 269 nm for both (PTBP-Ru-6TPy)/(Cloisite 15A) and (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposites, but to a wavelength of 265 nm for (PTBP-Ru-6TPy)/MMT nanocomposite. Both red-shifted amount of MLCT band and the reduced amount of $\pi-\pi^*$ band of (PTBP-Ru-6TPy)/MMT nanocomposite have been largely increased giving rise to a very high degree of exfoliation of MMT aggregates in the matrix of PTBP-Ru-6TPy. We have attributed such experimental observations to the presence of the Coulombic interactions between the positively
Figure 7.10. UV-vis spectra of thin films of (a) PTBP-Ru-6TPy, (b) (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, (c) (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite, and (d) (PTBP-Ru-6TPy)/MMT nancomposite.
charged ruthenium center and the negatively charged MMT surfaces. If this kind of Coulombic interactions were absent or very small due to the shielding effect of a surfactant (MT2EtOH or 2M2HT) residing at the surface of Cloisite 30B or Cloisite 15A, a high degree of exfoliation of organoclay aggregates in (PTBP-Ru-6TPy)/(Cloisite 30B) and (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposites would not be possible. This is the reason why exfoliation does not occur in both (PTBP-Ru-6TPy)/(Cloisite 30B) and (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposites.

7.6 Fourier Transform Infrared (FTIR) Spectroscopy of Montmorillonite or Organoclay Nanocomposites Based on PTBP-Ru-6TPy Complex

Figure 7.11 shows FTIR spectra of MMT, Cloisite 15A, and Cloisite 30B. It can be seen from Figure 7.11 that these three clays all have an absorption peak at a wavenumber of 3625 cm\(^{-1}\) for O–H stretching of structural hydroxyl group, which are assigned to hydroxyl groups coordinated to octahedral cations.\(^{290}\) The absorption peak at 3433 cm\(^{-1}\) indicated in Figure 11a has originated from H–OH hydrogen bonded water. Notice in Figure 11c that the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B has an absorption peak at a wavenumber of 3410 cm\(^{-1}\).

Figure 7.12 shows the FTIR spectra of PTBP-Ru-6TPy, (PTBP-Ru-6TPy)/MMT nanocomposite, (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, and (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite. Figure 7.12 further confirm the presence of specific interactions between the positively charged ruthenium center and negatively charged MMT surface, as evidenced by the increased intensity at a wavenumber of about 1680 cm\(^{-1}\) (see the inset of Figure 7.12) and the new broad absorption peak appearing at a
Figure 7.11. FTIR spectra of (a) MMT, (b) Cloisite 15A, and (c) Cloisite 30B.
Figure 7.12. FTIR spectra of (a) PTBP-Ru-6TPy, (b) (PTBP-Ru-6TPy)/MMT nanocomposite, (c) (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite, and (d) (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite. The inset shows the expanded absorption band at wavenumbers ranging from 1800 cm\(^{-1}\) to 1500 cm\(^{-1}\).
wavenumber of about 3420 cm$^{-1}$ for (PTBP-Ru-6TPy)/MMT nanocomposite. When MMT was dispersed in PTBP-Ru-6TPy complex, the hydroxyl groups on the surface of MMT would form hydrogen bonds with the terpyridine groups in PTBP-Ru-6TPy complex. Thus, the absorption peak at 3625 cm$^{-1}$ for pristine MMT has been shifted to 3420 cm$^{-1}$ for (PTBP-Ru-6TPy)/MMT nanocomposite (see Figure 12b). The absorption peak at 1680 cm$^{-1}$ (see the inset of Figure 12) is attributed to the ionization of terpyridine group and its strength is expected to increase in (PTBP-Ru-6TPy)/MMT nanocomposite due to the Coulombic interactions between the positively charged ruthenium center and the negatively charged MMT surface. In contrast, we observe from the inset of Figure 7.12 that similar to PTBP-Ru-6TPy, both (PTBP-Ru-6TPy)/(Cloisite 15A) and (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposites exhibit a very small absorption peak at a wavenumber of 1680 cm$^{-1}$, suggesting that little or no Coulombic interactions took place between the positively charged ruthenium center and the surface of organoclay (Cloisite 30B or Cloisite 15A) aggregates in the respective organoclay nanocomposites. This observation is in consonance with the conclusion drawn above from the UV-vis spectra (see Figure 7.10) of the (PTBP-Ru-6TPy)/(Cloisite 15A) and (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposites. Referring to Figure 7.12, (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite shows a broad absorption peak at a wavenumber of about 3560 cm$^{-1}$, which is very close to the absorption peak at about 3625 cm$^{-1}$ (assigned to structural hydroxyl group) for Cloisite 15A (see Figure 7.11b). Also, we observe in Figure 7.12 that (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite shows an absorption peak at a wavenumber of 3415 cm$^{-1}$, which is very close to the absorption peak at about 3410 cm$^{-1}$ for the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite
30B (see Figure 7.11c). The above observations seem to reinforce our conclusion drawn above that little interactions took place between the positively charged ruthenium center and the surface of Cloisite 15A (or Cloisite 30B) aggregates in the respective nanocomposites, owing to the shielding effect of a surfactant (MT2EtOH or 2M2HT) residing at the surface of Cloisite 30B or Cloisite 15A aggregates. In contrast to PTBP, there has not any change in the FTIR spectrum of PTBP/MMT nancomposite (though not presented here), because little attractive interactions occur between PTBP and MMT. As expected, MMT has a poor dispersion in PTBP, and similar observations have been made for PyHQ12/MMT (see Chapter V) and PABP/MMT nancomposites (see Chapter VI).

7.7 Concluding Remarks

In this study we synthesized a segmented main-chain thermotropic liquid crystalline polymer (TLCP), PTBP, bearing side-chain terpyrdine group, which was further employed to form ruthenium complex, PTBP-Ru-6TPy, with a small molecular terpyrdine, 6TPy, utilizing ruthenium(III)/ruthenium(II) chemistry. We have found that PTBP is a glassy, smectic-forming TLCP with a T_g of 49.9 °C and a T_SI of 80.7 °C during heating, while PTBP-Ru-6TPy only have a T_g of 123.4 °C. Here we have presented for the first time an experimental observation, in which ruthenium(II) complex in a functional liquid-crystalline polymer has exfoliated the pristine MMT aggregates as confirmed by XRD and TEM. UV-vis spectroscopy and FTIR spectroscopy give evidence of the Coulombic interactions between the positively charged ruthenium center in PTBP-Ru-6TPy and the negatively charged MMT surfaces giving rise to the high degree of exfoliation of MMT aggregates in PTBP-Ru-6TPy.
However, we have only observed intercalation of Cloisite 15A aggregates in (PTBP-Ru-6TPy)/(Cloisite 15A) nanocomposite and flocculated dispersion of Cloisite 30B aggregates in (PTBP-Ru-6TPy)/(Cloisite 30B) nanocomposite, when MMT is treated with surfactants (e.g. Cloisite 30B or Cloisite 15A). This is because the Coulombic interactions between the positively charged ruthenium center and the negatively charged MMT surfaces that are the driving force to exfoliate MMT in PTBP-Ru-6TPy matrix were absent or very small due to the shielding effect of a surfactant (MT2EtOH or 2M2HT) residing at the surface of Cloisite 30B or Cloisite 15A.

These observations provide a new concept for molecular design to achieve a very high degree of dispersion of the aggregates of natural clay in the polymer matrix without the need to treat the natural clay with surfactant, and may pave a new way for preparing nanocomposites based on natural clay.
CHAPTER VIII
CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

In this dissertation, we have designed and synthesized three segmented main-chain thermotropic liquid crystalline polymers (TLCPs) functionalized with nitrogen-containing heterocyclic groups, namely PyHQ12 having pendent pyridyl group, PABP having side-chain azopyridyl group with flexible spacer, and PTBP having side-chain terpyridine group with flexible spacer.

Further, we have demonstrated the synthesis of self-assembled combined main-chain/side-chain liquid crystalline polymers (MCSCLCPs), including PyHQ12−7CNCOOH, PABP−AA, and PABP−TSA, through specific interactions such as hydrogen bonding and ionic interactions. Self-assembled PyHQ12−7CNCOOH was prepared via hydrogen bonding between the pendent pyridyl group in the main-chain liquid-crystalline polymer (MCLCP) PyHQ12 and the carboxylic acid group in the mesogenic small molecule 7CNCOOH. Self-assembled PABP−AA was prepared via hydrogen bonding between the nonmesogenic side-chain azopyridyl group in the MCLCP PABP and the carboxylic acid group in the nonmesogenic small molecule p-anisic acid (AA). On the other hand, self-assembled PABP−TSA was prepared via ionic interactions
between the nonmesogenic side-chain azopyridyl group in the MCLCP PABP and the
sulfonic acid group in the nonmesogenic small molecule p-toluene sulfonic acid (TSA).
We found that self-assembled PyHQ12−7CNCOOH is a glassy LCP having nematic
mesophase, while self-assembled PABP-AA and self-assembled PABP−TSA are
semicrystalline LCPs having smectic mesophase. Interestingly, we observed from in situ
FTIR spectroscopy that the intermolecular hydrogen bonding between the pendent
pyridyl groups in the MCLCP PyHQ12 and the carboxylic acid groups in the mesogenic
small molecule 7CNCOOH and between the side-chain azopyridyl groups in the MCLCP
PABP and the carboxylic acid groups in the nonmesogenic small molecule AA, as well as
the ionic interactions between the side-chain azopyridyl groups in the MCLCP PABP and
the sulfonic acid group in the nonmesogenic small molecule TSA are sufficiently strong,
persisting at temperatures well above the clearing temperature of the respective
MCSCLCPs. This observation has enabled us to explain why, upon cooling from the
isotropic state, mesophase structure reappeared very quickly in the respective self-
assembled MCSCLCPs synthesized in this study.

To demonstrate whether functionality is necessary to obtain highly dispersed
nanocomposites based on TLCP, in this dissertation we have chosen two main-chain
TLCPs, one having pendent pyridyl group (PyHQ12) and the other having pendent
phenylsulfonyl group (PSHQ12). Then, each TLCP was mixed with two different
organoclays, one with hydroxyl groups (Cloisite 30B) and another without polar groups
(Cloisite 15A). We have found that the PyHQ12/Cloisite 30B nanocomposite yielded a
very high degree of dispersion of organoclays aggregates, while the PyHQ12/Cloisite 15A
and PSHQ12/Cloisite 30B nanocomposites yielded a very low degree of dispersion of
organoclay aggregates. The origin of the differences in the dispersion characteristics between PyHQ12/Cloisite 30B and PSHQ12/ Cloisite 30B nanocomposites, and between PyHQ12/Cloisite 30B and PyHQ12/Cloisite 15A nanocomposites is explained in terms of the attractive interactions, as determined by FTIR spectroscopy, between the pendent pyridyl group in PyHQ12 and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of organoclay Cloisite 30B. We observed little or no attractive interactions between PSHQ12 and Cloisite 30B, and between PyHQ12 and Cloisite 15A.

However, we have observed a considerable loss in the degree of liquid crystallinity of PyHQ12 in the PyHQ12/Cloisite 30B nanocomposite, which is attributable to the fact that the pendent pyridyl group was located so close to the mesogenic main-chain backbone of PyHQ12, that hydrogen bonding between the pendent pyridyl group in PyHQ12 and the hydroxyl group in the surfactant residing at the surface of organoclay greatly restricted the mobility (thus orientation) of the mesogenic main chain of PyHQ12. Thus we synthesized another segmented main-chain TLCP, PABP, having side-chain azopyridine with flexible spacer to prepare organoclay nanocomposites. We have found that PABP/Cloisite 30B nanocomposite has a very high degree of dispersion of Cloisite 30B aggregates, while PABP/Cloisite 15A nanocomposite has intercalated Cloisite 15A aggregates, and PABP/MMT nanocomposite has very poor dispersion of MMT aggregates. Using in situ FTIR spectroscopy we obtained evidence that hydrogen bonds were formed between the pyridyl group in the side-chain azopyridine of PABP and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B in the PABP/Cloisite 30B nanocomposite. Further, we found that the mesophase structure (liquid crystallinity) of PABP in the PABP/Cloisite 30B nanocomposite is little affected
by the hydrogen bonding between PABP and Cloisite 30B. This is attributed to the fact that the pyridyl group in the side-chain azopyridine of PABP is located sufficiently far away from the mesogenic main chain, and thus the hydrogen bonds formed between the pyridyl group at the end of the side-chain azopyridine with five methylene units, and the hydroxyl groups in the surfactant MT2EtOH residing at the surface of Cloisite 30B apparently did not interfere with the mobility (thus the orientation) of the mesogenic main chain of PABP.

In this dissertation, we have compared the dynamic viscoelastic properties of PyHQ12, PABP, and their organoclay nanocomposites. Specifically, we have shown how the dynamic viscoelastic properties of PyHQ12 and PABP, having self-association within the molecules, are different from those of typical TLCPs without self-association, and how the hydrogen bonds formed between the pyridyl group in PyHQ12 or PABP and the surfactant residing at the surface of Cloisite 30B affected the dynamic viscoelastic properties of their nanocomposites. In this dissertation, we have demonstrated that rheological measurements, when properly interpreted, can be used as a powerful tool for a better understanding of the dispersion characteristics of organoclay nanocomposites.

In this dissertation, we have successfully synthesized a ruthenium metal complex [RuII(PTBP)(6TPy)](PF6)2 (referred to as PTBP-Ru-6TPy) based on PTBP. Subsequently, we prepared a (PTBP-Ru-6TPy)/MMT nanocomposite by solution blending. We found the MMT aggregates in the nanocomposite to be very well dispersed in the matrix of PTBP-Ru-6TPy. We attribute the very high degree of exfoliation of MMT aggregates observed to the Coulombic interactions between the negatively charged surfaces of pristine MMT and the positively charged ruthenium center in the polymer matrix. We
are not aware of any previous study, which has reported on the formation of very high
degree of exfoliation of pristine MMT aggregates in a polymer matrix having a metal
complex. This observation provides a new concept for molecular design to achieve a
very high degree of dispersion of the aggregates of natural clay in the polymer matrix
without the need to treat the natural clay with surfactant, and may pave a new way for
preparing nanocomposites based on natural clay.

8.2 Recommendations

We recommend the following investigations for future study:

(1) We recommend that theoretical study be conducted to predict the role and strength of
specific interactions (e.g. hydrogen bonding, ionic interactions, and metal
 coordinations) in supramolecular systems.

(2) We recommend that the principles of exfoliating organoclay in functional
heterocyclic liquid crystalline polymers (LCPs) as well as natural clay in
LCP/ruthenium complex be generalized to other polymer systems, and used to pursue
industrial applications.

(3) We recommend that heterocyclic functional groups (such as terpyridine and
tetrazine) be incorporated into the polymer backbone or side chain. Such polymers
may have potential applications in magnetic or luminescent materials.

(4) Besides nitrogen-containing heterocyclic functional groups, we also
recommend that other functional groups containing sulfur or phosphorus elements be
incorporated into the macromolecular chains. Such polymers have potential for
applications in novel bioactive or bioinspired materials.
REFERENCES


175. Percec, V.; Yourd, R. “Liquid Crystalline Polyethers and Copolyethers Based on Conformational Isomerism. 3. The Influence of Thermal History on the Phase Transitions of the Thermotropic Polyethers and Copolyethers Based on 1-(4-Hydroxyphenyl)-2-(2-methyl-4-hydroxyphenyl)ethane and Flexible Spacers Containing an Odd Number of Methylene Units.” *Macromolecules* **1989**, *22*, 3229.


228. Over several hundreds of references are listed under the title of “Clay Nanocomposites” in the Science Finder available on the Internet.


Montmorillonite Nanocomposites Prepared by Compounding Nylon 6 with Na+-

Polylactide/Layered Silicate Nanocomposites. 3. High-Performance Biodegradable

235. Hoffmann, B.; Kressler, J.; Stoppelmann, G.; Friedrich, C.; Kim, G.-M. “Rheology
of Nanocomposites Based on Layered Silicates and Polyamide-12.” *Colloid Polym.

236. Reynaud, E.; Jouen, T.; Gauthier, C.; Vigier, G.; Varlet, J. “Nanofillers in


6333.

239. Liu, X.; Wu, Q. “PP/Clay Nanocomposites Prepared by Grafting-melt

Hierarchical Structure and Properties of Intercalated Polypropylene/Clay

241. Sikka, M.; Cerini, L. N.; Ghosh, S. S.; Winey, K. I. “Melt Intercalation of

3359.

and Rheology of Polystyrene Nanocomposites Based upon Organoclay.”

244. Ogata, N.; Kawakage, S.; Ogihara, T. “Structure and Thermal/Mechanical

Kanatzidis, M. G. “Synthesis, Structure, and Reactions of Poly(ethylene


