RHEOLOGY OF MISCIBLE POLYMER BLENDS
WITH HYDROGEN BONDING

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ABSTRACT

Poly(4-vinylphenol) (PVPh) was blended with four different polymers: poly(vinyl methyl ether) (PVME), poly(vinyl acetate) (PVAc), poly(2-vinylpyridine) (P2VP), and poly(4-vinylpyridine) (P4VP) by solvent casting. The miscibility of these four PVPh-based blend systems was investigated using differential scanning calorimetry (DSC) and the composition-dependent glass transition temperature (\(T_g\)) was predicted by a thermodynamic theory. The hydrogen bonds between phenolic group in PVPh and ether group, carbonyl group or pyridine group was confirmed by Fourier transform infrared (FTIR) spectroscopy. The fraction of hydrogen bonds was calculated by the Coleman-Graf-Painter association model. Linear dynamic viscoelasticity of four PVPh-based miscible polymer blends with hydrogen bonding was investigated. Emphasis was placed on investigating how the linear dynamic viscoelasticity of miscible polymer blends with specific interaction might be different from that of miscible polymer blends without specific interaction. We have found that an application of time-temperature superposition (TTS) to the PVPh-based miscible blends with intermolecular hydrogen bonding is warranted even when the difference in the component glass transition temperatures is as large as about 200 °C, while TTS fails for miscible polymer blends without specific interactions. On the basis of such an observation, we have concluded that hydrogen bonding suppressed concentration fluctuations in PVPh-based miscible blends. It has been found that both the intra-association (self-association) of the phenoxy hydroxyl...
groups in PVPh and inter-association (intermolecular interactions) between the constituent components have a profound influence on the frequency dependence of dynamic moduli in the terminal region of the PVPh-based miscible blend systems investigated.

Hydrogenated functional polynorbornenes (HFPNBs) were synthesized and they were used to investigate the miscibility and rheology of HFPNB-based miscible blends with hydrogen bonding. Specifically, functional norbornenes with carboxylic (−COOH) group or hydroxyl (−OH) group were first synthesized and then they were polymerized, via ring-opening metathesis polymerization followed by hydrogenation, to obtain HFPNBs, HPNBCOOH and HPNBOH. Subsequently, the miscibility of binary blends consisting of (1) HPBNCOOH and polycarbonate (PC), (2) HPBNCOOH and poly(2-vinylpyridine) (P2VP), and (3) HPBNOH and PC was investigated using DSC and FTIR spectroscopy. It has been found that both PC/HPBNCOOH and P2VP/HPBNCOOH blend systems exhibit a broad, single glass transition over the entire blend compositions as determined by DSC, indicating that the respective blend systems are miscible, and they form hydrogen bonds as determined by FTIR spectroscopy. On the other hand, PC/HPBNOH blends were found to exhibit two glass transition temperatures, indicating that the blends are not miscible. The dynamic oscillatory shear rheometry has shown that reduced log $G'$ versus log $a_\tau\omega$ and log $G''$ versus log $a_\tau\omega$ plots, and also log $G'$ versus log $G''$ plots of PC/HPBNCOOH and P2VP/HPBNCOOH blend systems are independent of temperature. We have concluded that an application of TTS to the miscible polymer blends with hydrogen bonding is warranted although the difference in component glass transition temperatures is as large as 91 °C for the PC/HPNBCOOH blend system.
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Finally, I would like to dedicate this dissertation to my parents, my wife, Jiao, and my daughter, Nadia for their love, understanding, and patience.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>List</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xii</td>
</tr>
</tbody>
</table>

## CHAPTER

### I. INTRODUCTION

### II. LITERATURE REVIEW

- 2.1 Miscible Polymer Blends
  - 2.1.1 The Glass Transition in Polymer Blends
  - 2.1.2 Time-Temperature Superposition
  - 2.1.3 Effect of Specific Interactions on Rheological Properties
- 2.2 Functionalized Polynorbornenes

### III. EXPERIMENTAL

- 3.1 Polymer Synthesis
  - 3.1.1 Synthesis of Poly(styrene-ran-vinyl phenol) copolymer (STVPh)
  - 3.1.2 Synthesis of Hydrogenated Polynorbornene with Carboxylic Acid Group
  - 3.1.3 Synthesis of Hydrogenated Polynorbornene with Hydroxyl Group
  - 3.1.4 Synthesis of Hydrogenated Polynorbornene with Amine Group
  - 3.1.5 Synthesis of Poly(2-vinyl pyridine) (P2VP)
- 3.2 Sample Preparation


3.3 Experimental Methods Employed .................................................................39

3.3.1 Differential Scanning Calorimetry (DSC) .................................................39

3.3.2 Thermo Gravimetric Analysis (TGA) ..........................................................39

3.3.3 Nuclear Magnetic Resonance Spectroscopy (NMR) .......................................40

3.3.4 Fourier Transform Infrared Spectroscopy (FTIR) .......................................40

3.3.5 Gel Permeation Chromatography (GPC) ....................................................40

3.3.6 Rheological Measurements ......................................................................40

IV. SPECIFIC INTERACTIONS AND RHEOLOGY OF FIVE NEAT HOMOPOLYMERS AND COPOLYMERS INVESTIGATED .............................. 42

4.1 Self-association and Rheological Behavior of Five Neat Homopolymers Investigated .............................................................................................................42

4.2 Characterization of STVPh Copolymers ............................................................50

4.3 Rheological Behavior of STVPh Copolymers ....................................................57

4.3.1 Time-Temperature Superposition and Log $G'$ versus Log $G''$ Plots ............57

4.3.2 Plateau Modulus .........................................................................................60

4.3.3 Zero-Shear Viscosity ..................................................................................61

4.4 Concluding Remarks ......................................................................................65

V. CHARACTERIZATION AND RHEOLOGY OF MISCIBLE BLENDS ............. 67

5.1 The Strength of Specific Interaction, as Determined by FTIR Spectroscopy, in Four PVPh-Based Miscible Polymer Blend Systems .........................67

5.1.1 Qualitative Analysis of Experimental Observations .....................................67

5.1.2 Effect of Temperature on Hydrogen Bonding ..........................................70

5.1.3 Quantitative Analysis of Experimental Results via the Coleman-Graf-Painter (CGP) Association Model .................................................................72

5.1.4 Curve Fitting of FTIR Spectra of PVPh/P2VP and PVPh/P4VP Blends ......76
5.2  The Strength of Hydrogen Bonds, as Determined by DSC, in Four PVPh- 
Based Miscible Polymer Blend Systems .................................................................82

5.2.1  Composition Dependence of $T_g$ for PS/PVME and PSAN/PEMA Blends ....88

5.2.2  Prediction of $T_g$ of Four PVPh-Based Miscible Polymer Blend Systems by 
the Kim Theory ........................................................................................................90

5.2.3  Prediction of $T_g$ of Four PVPh-Based Miscible Polymer Blend Systems by 
the Lu-Weiss Theory .............................................................................................92

5.2.4  Prediction $T_g$ of Four PVPh-Based Miscible Polymer Blend Systems by 
the Painter Theory ...............................................................................................94

5.3  Linear Dynamic Viscoelasticity of Two Miscible Polymer Blends without 
Specific Interactions Investigated ........................................................................101

5.3.1  Log $G'$ versus Log $G''$ Plots and Time-Temperature Superposition ........101

5.3.2  Plateau Modulus ..........................................................................................107

5.3.3  Zero–Shear Viscosity ..................................................................................111

5.4  Linear Dynamic Viscoelasticity of Four PVPh-Based Miscible Polymer Blend 
Systems Investigated .............................................................................................116

5.4.1  Construction of Reduced Plots of Dynamic Moduli, Composition 
Fluctuations, and Time-Temperature Superposition .....................................116

5.4.2  Log $G'$ versus Log $G''$ Plots, Composition Fluctuations, and Time-
Temperature Superposition ................................................................................128

5.4.3  Plateau Modulus ........................................................................................135

5.4.4  Zero–Shear Viscosity ................................................................................137

5.5  Concluding Remarks .........................................................................................144

VI. MISCIBILITY AND RHEOLOGY OF FUNCTIONALIZED 
POLYNOBORBONENE-BASED BLENDS ............................................................ 148

6.1  Synthesis of Functionalized Polynorbornenes ..............................................148

6.1.1  Synthesis of HPNBOOH ............................................................................148
6.1.2 Synthesis of HPNBOH ..........................................................152
6.1.3 Synthesis of HPNBNH₂ ..........................................................156
6.1.4 Molecular Characteristics of PNB ...........................................159

6.2 Miscibility of Functionalized Polynorbornene-Based Blends ............160
6.2.1 Miscibility of PC/HPNBCOOH Blends .....................................160
6.2.2 Miscibility of P2VP/HPNBCOOH Blends ...................................163
6.2.3 Miscibility of PC/HPNBOH Blends ..........................................166
6.2.4 Miscibility of PA66/HPNBNH₂ Blends .....................................168
6.2.4 Miscibility of PVPh/HPNBCOOH Blends .................................168

6.3 Rheological Behavior of HPNBCOOH-Based Blends .......................170
6.3.1 Rheology of PC/HPNBCOOH Blends ......................................170
6.3.2 Rheology of P2VP/HPNBCOOH Blends ....................................173

6.4 Concluding Remarks ..................................................................177

VII. CONCLUSIONS AND RECOMMENDATIONS ..................................179
7.1 Conclusions ............................................................................179
7.2 Recommendations ....................................................................184

REFERENCES ..................................................................................185

APPENDICES ..................................................................................205
APPENDIX A. THE COLEMAN GRAF PAINTER (CGP) ASSOCIATION MODEL ..................................................206
APPENDIX B. THE THERMODYNAMIC THEORY OF PAINTER .............212
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 1</td>
<td>Bond Energy and Relative Strength of Different Intermolecular Forces</td>
<td>2</td>
</tr>
<tr>
<td>3. 1</td>
<td>Molecular Characteristics of Seven Homopolymers Employed in This Study</td>
<td>38</td>
</tr>
<tr>
<td>4. 1</td>
<td>Solubility of PVP in THF after Annealing at Various Temperatures for Different Periods</td>
<td>49</td>
</tr>
<tr>
<td>4. 2</td>
<td>Content of VPh in STVPh Copolymers</td>
<td>51</td>
</tr>
<tr>
<td>4. 3</td>
<td>Molecular Weights and Polydispersity of STVPh Copolymers</td>
<td>54</td>
</tr>
<tr>
<td>4. 4</td>
<td>Summary of $T_g$ for SAS and SVTPh Copolymers</td>
<td>55</td>
</tr>
<tr>
<td>4. 5</td>
<td>Characteristics of Poly(styrene-\textit{ran}-vinyl phenol) Copolymers</td>
<td>64</td>
</tr>
<tr>
<td>5. 1</td>
<td>Values of the Parameters Used for the Calculation of the Fraction of Hydrogen Bonding in Four PVP-Base Blend Systems Investigated in This Study</td>
<td>75</td>
</tr>
<tr>
<td>5. 2</td>
<td>Calculated Fractions of Free Hydrogen Group B and Hydrogen-Bonded Group A for Four PVP-Base Blend Systems Investigated in This Study</td>
<td>75</td>
</tr>
<tr>
<td>5. 3</td>
<td>Parameters Used for Curve Fitting of FTIR Spectra of PVP/P2VP and PVP/P4VP Blends at 100 °C to the Coleman-Graf-Painter Association Model and Predicted Fraction of Hydrogen Bonding</td>
<td>81</td>
</tr>
<tr>
<td>5. 4</td>
<td>Summary of the Thermal Properties of Four PVP-Base Blend Systems Investigated in This Study</td>
<td>84</td>
</tr>
<tr>
<td>5. 5</td>
<td>Summary of the Thermal Properties of PS/PVME Blends and PSAN/PEMA Blends Investigated in This Study</td>
<td>85</td>
</tr>
<tr>
<td>5. 6</td>
<td>Parameters Used to Predict the Composition Dependence of $T_{gm}$ for Four PVP-Base Blend Systems Investigated in This Study</td>
<td>96</td>
</tr>
</tbody>
</table>
5. 7. Values of Three Terms on the Right-Hand Side of Eq 5.13 for Four PVPh-Based Blend Systems Investigated in This Study ................................................................. 97

5. 8. Values of q Calculated from Eq 5.13 for Four PVPh-Based Blend Systems Investigated in This Study .................................................................................... 99

5. 9. Entanglement Characteristics for Various Polymers Investigated...................... 108

5. 10. WLF Constants for Four PVPh-Based Blend Systems Investigated ............... 125

6. 1. GPC Characterization of PNBs........................................................................... 159

6. 2. Summary of T_g for PC/HPNB COOH Blends.................................................... 161

6. 3. Summary of T_g for P2VP/HPNB COOH Blends ............................................. 164
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>FTIR spectra for neat P2VP at room temperature.</td>
<td>37</td>
</tr>
<tr>
<td>4.1</td>
<td>FTIR spectra for five neat polymers: (a) PVAc, (b) PVME, (c) P2VP, (d) P4VP, and (e) PVPh.</td>
<td>43</td>
</tr>
<tr>
<td>4.2</td>
<td>TGA data for (a) PVAc; (b) PVME; (c) P2VP; (d) P4VP; (e) PVPh.</td>
<td>44</td>
</tr>
<tr>
<td>4.3</td>
<td>FTIR spectra for neat P4VP at room temperature: (a) before annealing; (b) held at 100 °C for 20 min followed by cooling down to room temperature under a nitrogen atmosphere.</td>
<td>45</td>
</tr>
<tr>
<td>4.4</td>
<td>Rheology for four neat homopolymer: (a) PVAc at various temperatures (°C): (⊙) 78, (△) 88, (□) 98, and (▽) 108; (b) PVME at various temperatures (°C): (⊙) 11, (△) 21, (□) 31, (▽) 41, (◇) 51, and (⊙) 61; (c) P2VP at various temperatures (°C): (⊙) 107, (△) 117, (□) 127, (▽) 137, (◇) 147, and (⊙) 157; (d) P4VP at various temperatures (°C): (⊙) 183, (△) 193, (□) 203, (▽) 213, (◇) 223, and (⊙) 233.</td>
<td>46</td>
</tr>
<tr>
<td>4.5</td>
<td>Rheology of neat PVPh at various temperatures (°C): (⊙) 200, (△) 210, (□) 220, and (▽) 230.</td>
<td>47</td>
</tr>
<tr>
<td>4.6</td>
<td>$^1$H NMR spectra for SAS5.</td>
<td>50</td>
</tr>
<tr>
<td>4.7</td>
<td>FTIR spectra before and after hydrolysis reaction.</td>
<td>51</td>
</tr>
<tr>
<td>4.8</td>
<td>FTIR spectra recorded in the hydroxyl stretching region for STVPh copolymer containing different weight fractions of vinyl phenol: (1) PVPh, (2) STVPh50, (3) STVPh40, (4) STVPh20, (5) STVPh5.</td>
<td>53</td>
</tr>
<tr>
<td>4.9</td>
<td>Correlation of infrared intensity with STVPh copolymer composition.</td>
<td>53</td>
</tr>
<tr>
<td>4.10</td>
<td>DSC thermograms for SAS and SVTPh copolymers: (a) before and after hydrolysis of SVTPh40; (b) different contents of VPh groups.</td>
<td>55</td>
</tr>
</tbody>
</table>
4.11. Correlation of $T_g$ with STVPh copolymer composition ........................................ 56

4.12. TGA of (a) STVPh5 and (b) STVPh40 .................................................................. 56

4.13. Plots of $\log G'$ versus $\log \omega$ (a) and $\log G''$ versus $\log \omega$ (b) for STVPh5 at various temperatures: 133 $^\circ$C (○), 143 $^\circ$C (△), 153 $^\circ$C (□), 163 $^\circ$C (▽), 173 $^\circ$C (◇). ................................................................................................................ 58

4.14. Plots of $\log G'$ versus log $a_T\omega$ (a) and $\log G''$ versus log $a_T\omega$ (b) for STVPh5 at various temperatures with $T_r = T_g + 50 ^\circ$C (153$^\circ$C) as the reference temperature: 133 $^\circ$C (○), 143 $^\circ$C (△), 153 $^\circ$C (□), 163 $^\circ$C (▽), 173 $^\circ$C (◇) .... 58

4.15. Plots of $\log G'$ versus $\log G''$ for (a) STVPh5 at 133 $^\circ$C (○), 143 $^\circ$C (△), 153 $^\circ$C (□), 163 $^\circ$C (▽), 173 $^\circ$C (◇); (b) STVPh20 at 156 $^\circ$C (○), 166 $^\circ$C (△), 176 $^\circ$C (□), 186 $^\circ$C (▽), 196 $^\circ$C (◇); (c) STVPh40 at 169 $^\circ$C (○), 179 $^\circ$C (△), 189 $^\circ$C (□), 199 $^\circ$C (▽); (d) PVPh at 200 $^\circ$C (○), 210 $^\circ$C (△), 220 $^\circ$C (□), 230 $^\circ$C (▽). ................................................................................................................ 59

4.16. Plots of $\log G'$ versus log $a_T\omega$ and log tan $\delta$ versus log $a_T\omega$ at $T_r = T_g + 50 ^\circ$C for (a) PS, (b) STVPh5, (c) STVPh20, (d) STVPh40, (e) PVPh. ...................... 62

4.17. Plots of $\log \eta'$ versus log $a_T\omega$ at $T_r = T_g + 50 ^\circ$C for (a) PS, (b) STVPh5, (c) STVPh20, (d) STVPh40, (e) PVPh. ................................................ 63

4.18. Plots of $\log \eta$ versus log $\gamma$ (filled symbols) and plots of $\log \eta'$ versus log $\omega$ (open symbols) for (a) STVPh5 at 153 $^\circ$C, (b) STVPh20 at 176 $^\circ$C, (c) STVPh40 at 189 $^\circ$C, and (d) PVPh at 230 $^\circ$C. ............................................................... 64

5.1. FTIR spectra at room temperature for (a) PVPh/PVME blends, (b) PVPh/PVAc blends, (c) PVPh/P2VP blends, and (d) PVPh/P4VP blends............. 68

5.2. FTIR spectra for (a) 40/60 PVPh/PVME blend, (b) 60/40 PVPh/PVAc blend, (c) 80/20 PVPh/P2VP blend, (d) 80/20 PVPh/P4VP blend at various temperatures ($^\circ$C): (1) 25, (2) 50, (3) 100, (4) 150, and (5) 200. ...................... 71

5.3. Illustration of the parameters in eq 5.6 and bandshapes predicted by Gaussian function (solid line) and Lorentzian function (dash line), respectively. .......... 78

5.4. FTIR spectra at wavenumbers of 1030 and 970 cm$^{-1}$ for (a) PVPh/P2VP blends and (b) PVPh/P4VP blends. ........................................................... 78

5.5. FTIR spectra for (a) 20/80 and (b) 60/40 PVPh/P4VP blend. The upper curve is the second derivative, the open symbols denote experimental data, and the solid lines are the calculated spectra obtained from the sum of Gaussian-Lorentzian bandshapes (dash lines). .................................................. 81
5. 6. DSC thermograms for (a) PS/PVME blends, (b) PSAN/PEMA blends, (c) PVPh/PVAc blends, (d) PVPh/PVME blends, (e) PVPh/P2VP blends, and (f) PVPh/P4VP blends. ................................................................. 83

5. 7. Composition-dependent glass transition temperature ($T_g$) for (a) PS/PVME, (b) PSAN/PEMA, (c) PVPh/PVAc, (d) PVPh/PVME, (e) PVPh/P2VP, and (f) PVPh/P4VP blends, in which the dashed line represents a linear behavior and the dotted line denotes experimental data. ................................................................. 87

5. 8. Composition-dependent glass transition temperatures ($T_g$) for (a) PS/PVME and (b) PSAN/PEMA blends, in which the dashed line represents a linear behavior, the open symbols (○) denote experimental data, and the filled symbols (●) denoted predicted values from eq 2.1. ................................................................. 89

5. 9. Composition-dependent glass transition temperatures ($T_g$) for (a) PVPh/PVAc blends, (b) PVPh/PVME blends, (c) PVPh/P2VP blends, and (d) PVPh/P4VP blends, in which the dashed line represents a linear behavior, the open symbols (○) denote experimental data, and the filled symbols (●) denoted predicted values from eq 5.8. ....................................................................................... 91

5. 10. Composition-dependent glass transition temperatures ($T_g$) for (a) PVPh/PVAc blends, (b) PVPh/PVME blends, (c) PVPh/P2VP blends, and (d) PVPh/P4VP blends, in which the dashed line represents a linear behavior, the open symbols (○) denote experimental data, and the filled symbols (●) denoted predicted values from eq 5.10. ....................................................................................... 93

5. 11. Composition-dependent glass transition temperatures ($T_g$) for (a) PVPh/PVAc blends, (b) PVPh/PVME blends, (c) PVPh/P2VP blends, and (d) PVPh/P4VP blends, in which the dashed line represents a linear behavior, the open symbols (○) denote experimental data, and the filled symbols (●) denoted predicted values from eq 5.12. ....................................................................................... 100

5. 12. Log $G'$ versus log $G''$ plots for: (a) 70/30 PS/PVME blend at different temperatures (°C): (○) 75, (△) 85, (□) 95, (◇) 105, (◇) 110, (●) 115, (▲) 120; (b) 20/80 PS/PVME blend at different temperatures (°C): (○) 20, (△) 30, (□) 40, (◇) 50, (◇) 60, (○) 70. ....................................................................................... 102

5. 13. Plots of log $G'$ versus log $\alpha_{\gamma\omega}$ (open symbols), log $G''$ versus log $\alpha_{\gamma\omega}$ (filled symbols), and log tan $\delta$ versus log $\alpha_{\gamma\omega}$ at various temperatures with $T_r = T_g + 50$ °C as the reference temperature for PS/PVME blends: (a) 20/80: (○) 20 °C, (△) 30 °C, (□) 40 °C, (◇) 50 °C, (◇) 60 °C, (○) 70 °C; (b) 50/50: (○) 52 °C, (△) 62 °C, (□) 72 °C, (◇) 82 °C, (◇) 92 °C; (c) 70/30: (○) 75, (△) 85, (□) 95, (◇) 105, (◇) 110. ....................................................................................... 103
5.14. Plots of log $G'$ versus log $G''$ at various temperatures for PSAN/PEMA blend (a) 20/80: (○) 100 °C (△) 110 °C (□) 120 °C (▽) 130 °C (◇) 140 °C (◇) 150 °C (◇) 160 °C; (b) 40/60: (○) 113 °C (△) 123 °C (□) 133 °C (▽) 143 °C (◇) 153 °C (□) 163 °C; (c) 60/40: (○) 125 °C (△) 135 °C (□) 145 °C (▽) 155 °C (◇) 165 °C (□) 175 °C; (d) 80/20: (○) 132 °C (△) 142 °C (□) 152 °C (▽) 162 °C (◇) 172 °C (□) 182 °C ........................................................................... 104

5.15. Plots of log $G'$ versus log $a_T\omega$ (open symbols), log $G''$ versus log $a_T\omega$ (filled symbols), and log tan $\delta$ versus log $a_T\omega$ at various temperatures for PSAN/PEMA blend (a) 20/80: (○) 100 °C (△) 110 °C (□) 120 °C (▽) 130 °C (◇) 140 °C (○) 150 °C (◇) 160 °C; (b) 40/60: (○) 113 °C (△) 123 °C (□) 133 °C (▽) 143 °C (◇) 153 °C (□) 163 °C; (c) 60/40: (○) 125 °C (△) 135 °C (□) 145 °C (▽) 155 °C (◇) 165 °C (□) 175 °C; (d) 80/20: (○) 132 °C (△) 142 °C (□) 152 °C (▽) 162 °C (◇) 172 °C (□) 182 °C. .................................... 106

5.16. Plots of $a_T$ versus $T - T_r$ for (a) PS/PVME and (b) PSAN/PEMA blends with $T_r = T_{gm} + 50$ °C as the reference temperature: (○) 0/100, (△) 20/80, (□) 40/60, (▽) 60/40, (◇) 80/20, and (○) 100/0. Full line is the fit to WLF equation............................................................................................................... 107

5.17. Comparison of experimental results (filled symbols) with theoretical predictions for the dependence of $G_N^0$ on composition for (a) PS/PVME blends, (b) PSAN/PEMA blends. Curve (1)–(3) represents the predictions made with eqs 5.15–5.17, respectively. Curve (4) represents the prediction made with eq 5.22. ............................................................................................... 108

5.18. Plots of log $\eta'_b$ versus log $a_T\omega$ for the PS/PVME blend system at $T_g + 50$ °C: (a) PVME; (b) 20/80; (c) 50/50; (d) 70/30; (e) PS........................................................................................................... 112

5.19. Plots of log $\eta'_b$ versus log $a_T\omega$ for the PSAN/PEMA blend system at $T_g + 50$ °C: (a) PEMA; (b) 20/80; (c) 40/60; (d) 60/40; (e) 80/20; (f) PSAN ..................... 113

5.20. Plots of log $\eta_b$ versus log $\gamma$ (open symbols) and plots of log $\eta'_b$ versus log $\omega$ (filled symbols) for (a) PEMA at two different temperatures; (b) PSAN/PEMA bends at $T_r = T_g + 50$ °C; (c) PVPh/PEMA blends at $T_r = T_g + 50$ °C.................................................................................................................... 114

5.21. Composition dependence of $\eta_0$ at $T_g + 50$ °C for: (a) PS/PVME blends, (b) PSAN/PEMA blends. The straight line represents linear behavior ..................... 114

5.22. (a) Log $G'$ versus log $\omega$ plots and (b) log $G''$ versus log $\omega$ plots for 20/80 PVPh/PVME blend at different temperatures (°C): (○) 29, (△) 39, (□) 49, (▽) 59, (◇) 69, (○) 79. ........................................................................................................... 117
5. 23. Plots of log $G'$ versus log $a_T\omega$ (open symbols), log $G''$ versus log $a_T\omega$ (filled symbols), and log tan $\delta$ versus log $a_T\omega$ at various temperatures for PVPh/PVME blends: (a) 20/80: (○) 29 °C, (△) 39 °C, (□) 49 °C, (▽) 59 °C, (◇) 69 °C, (◇) 79 °C; (b) 40/60: (○) 54 °C, (△) 64 °C, (□) 74 °C, (▽) 84 °C, (◇) 94 °C, (◇) 104 °C; (c) 60/40: (○) 102 °C, (△) 112 °C, (□) 122 °C, (▽) 132 °C, (◇) 142 °C, (◇) 152 °C; (d) 80/20: (○) 136 °C, (△) 146 °C, (□) 156 °C, (▽) 166 °C, (◇) 176 °C ......................................................... 118

5. 24. Plots of log $G'$ versus log $a_T\omega$ (open symbols), log $G''$ versus log $a_T\omega$ (filled symbols), and log tan $\delta$ versus log $a_T\omega$ at various temperatures for PVPh/PVAc blends: (a) 20/80: (○) 74 °C, (△) 84 °C, (□) 94 °C, (▽) 104 °C, (◇) 114 °C, (◇) 124 °C; (b) 40/60: (○) 100 °C, (△) 110 °C, (□) 120 °C, (▽) 130 °C, (◇) 140 °C, (◇) 150 °C; (c) 60/40: (○) 131 °C, (△) 141 °C, (□) 151 °C, (▽) 161 °C, (◇) 171 °C; (d) 80/20: (○) 162 °C, (△) 172 °C, (□) 182 °C, (▽) 192 °C, (◇) 202 °C .......................................................... 120

5. 25. Plots of log $G'$ versus log $a_T\omega$ (open symbols), log $G''$ versus log $a_T\omega$ (filled symbols), and log tan $\delta$ versus log $a_T\omega$ at various temperatures for PVPh/P2VP blends: (a) 20/80: (○) 151 °C, (△) 161 °C, (□) 171 °C, (▽) 181 °C, (◇) 191 °C, (◇) 201 °C; (b) 40/60: (○) 176 °C, (△) 186 °C, (□) 196 °C, (▽) 206 °C, (◇) 216 °C, (◇) 226 °C; (c): (○) 191 °C, (△) 201 °C, (□) 211 °C, (▽) 221 °C, (◇) 231 °C; (d) 80/20: (○) 201 °C, (△) 211 °C, (□) 221 °C, (▽) 231 °C, (◇) 241 °C ............................................................... 121

5. 26. Plots of log $G'$ versus log $a_T\omega$ (open symbols), log $G''$ versus log $a_T\omega$ (filled symbols), and log tan $\delta$ versus log $a_T\omega$ at various temperatures for PVPh/P4VP blends: (a) 20/80: (○) 209 °C, (△) 219 °C, (□) 229 °C, (▽) 239 °C; (b) 40/60: (○) 216 °C, (△) 226 °C, (□) 236 °C, (▽) 246 °C; (c) 60/40: (○) 222 °C, (△) 232 °C, (□) 242 °C, (▽) 252 °C; (d) 80/20: (○) 216 °C, (△) 226 °C, (□) 236 °C, (▽) 246 °C ................................................................. 122

5. 27. Plots of $a_T$ versus $T - T_r$ with $T_r = T_{gm} + 50$ °C as the reference temperature for (a) PVPh/PVAc blends, (b) PVPh/PVME blends, (c) PVPh/P2VP blends, and (d) PVPh/P4VP blends at various blend compositions: (○) 0/100, (△) 20/80, (□) 40/60, (▽) 60/40, (◇) 80/20, and (○) 100/0. The solid line represents a fit to the WLF expression ................................................................. 124

5. 28. Reference temperature dependence of shift factor $a_T$ for PVPh/PVME 60/40 blend at different reference temperature: (○) $T_g + 30$ °C, (△) $T_g + 40$ °C, (□) $T_g + 50$ °C, (▽) $T_g + 60$ °C, (◇) $T_g + 70$ °C, and (○) $T_g + 80$ °C ................................................................. 125
5. 29. Log $G'$ versus log $G''$ plots for PVPh/PVAc blend at different temperatures:
(a) 20/80: (○) 74 °C, (△) 84 °C, (□) 94 °C, (▽) 104 °C, (◇) 114 °C, (◇) 124 °C;
(b) 40/60: (○) 100 °C, (△) 110 °C, (□) 120 °C, (▽) 130 °C, (◇) 140 °C,
(◇) 150 °C; (c) 60/40: (○) 131 °C, (△) 141 °C, (□) 151 °C, (▽) 161 °C, (◇)
171 °C; (d) 80/20: (○) 162 °C, (△) 172 °C, (□) 182 °C, (▽) 192 °C, (◇) 202 °C.

5. 30. Log $G'$ versus log $G''$ plots for PVPh/PVME blends at different temperatures:
(a) 20/80: (○) 29 °C, (△) 39 °C, (□) 49 °C, (▽) 59 °C, (◇) 69 °C, (◇) 79 °C;
(b) 40/60: (○) 54 °C, (△) 64 °C, (□) 74 °C, (▽) 84 °C, (◇) 94 °C, (◇) 104 °C;
(c) 60/40: (○) 102 °C, (△) 112 °C, (□) 122 °C, (▽) 132 °C, (◇) 142 °C, (◇)
152 °C; (d) 80/20: (○) 136 °C, (△) 146 °C, (□) 156 °C, (▽) 166 °C, (◇) 176 °C.

5. 31. Plots of log $G'$ versus log $G''$ for PVPh/P2VP blends at different temperatures:
(a) 20/80: (○) 151 °C, (△) 161 °C, (□) 171 °C, (▽) 181 °C, (◇) 191 °C, (◇)
201 °C; (b) 40/60: (○) 176 °C, (△) 186 °C, (□) 196 °C, (▽) 206 °C, (◇)
216 °C, (◇) 226 °C; (c): (○) 191 °C, (△) 201 °C, (□) 211 °C, (▽) 221 °C, (◇)
231 °C; (d) 80/20: (○) 201 °C, (△) 211 °C, (□) 221 °C, (▽) 231 °C, (◇)
241 °C.

5. 32. Plots of log $G'$ versus log $G''$ for PVPh/P4VP blends annealed at 200 °C for 3 h:
(a) 20/80: (○) 209 °C, (△) 219 °C, (□) 229 °C, (▽) 239 °C; (b) 40/60: (○)
216 °C, (△) 226 °C, (□) 236 °C, (▽) 246 °C; (c) 60/40: (○) 222 °C, (△)
232 °C, (□) 242 °C, (▽) 252 °C; (d) 80/20: (○) 216 °C, (△) 226 °C, (□)
236 °C, (▽) 246 °C.

5. 33. Comparison of experimental results (symbol ) with theoretical predictions for
the dependence of $G_N^0$ on composition for (a) PVPh/PVAc blends, (b)
PVPh/PVME blends, (c) PVPh/P2VP blends, (d) PVPh/P4VP blends. Curve
(1)–(3) represents the predictions made with eq 5.15–5.17, respectively.
Curve (4) represents the prediction made with eq 5.22.

5. 34. Plots of log $\eta'$ versus log $a_T\omega$ for (a) PVAc, (b) PVME, (c) P2VP, (d) P4VP,
and (e) PVPh.

5. 35. Plots of log $\eta'_b$ versus log $a_T\omega$ for PVPh/PVAc blends: (a) 20/80, (b) 40/60,
(c) 60/40, (d) 80/20.

5. 36. Plots of log $\eta'_b$ versus log $a_T\omega$ for PVPh/PVME blends: (a) 20/80, (b) 40/60,
(c) 60/40, (d) 80/20.

5. 37. Plots of log $\eta'_b$ versus log $a_T\omega$ for PVPh/P2VP blends: (a) 20/80, (b) 40/60,
(c) 60/40, (d) 80/20.
5. 38. Plots of log $\eta'_b$ versus log $aT_{fo}$ for PVPh/P4VP blends: (a) 20/80, (b) 40/60, (c) 60/40, (d) 80/20. ................................................................. 142

5. 39. Composition dependence of zero-shear viscosity of four PVPh-based miscible blend systems investigated: (a) PVPh/PVAc blends, (b) PVPh/PVME blends, (c) PVPh/P2VP blends, and (d) PVPh/P4VP blends. ................................................. 143

6. 1. FTIR spectra of (a) NB-COOH and (b) NBCOOSiMe$_3$. The numbers in lower part are the wave numbers corresponding to the indicated bonds. .......... 149

6. 2. $^1$H-NMR spectrum of (a) NB-COOH and (b) NBCOOSiMe$_3$ in DMSO. .... 150

6. 3. FTIR spectra of (a) PNBCOOSiMe$_3$ and (b) HPNBCOOH. .................... 151

6. 4. $^1$H-NMR spectrum of HPNBCOOH in DMSO. ........................................ 151

6. 5. FTIR spectra of (1) NB-OH and (2) NB-CH$_2$OSiMe$_3$. The numbers in lower part are the wave numbers corresponding to the indicated bonds. .......... 153

6. 6. $^1$H-NMR spectra of NB-CH$_2$OH and NB-CH$_2$OSiMe$_3$ in DMSO. Starred peak is due to solvent. ......................................................... 154

6. 7. FTIR spectra of (1) PNB-OSiMe$_3$, (2) PNB-OH, and (3) HPNB-OBH. .......... 156

6. 8. FTIR spectra of (a) NBNH$_2$ and (b) NB-MP. The numbers in lower part are the wave numbers corresponding to the indicated bonds. .......... 157

6. 9. FTIR spectra for (a) PNB-MP, (b) HPNB-MP, and (c) HPNB-NH$_2$. .......... 158

6. 10. DSC thermograms for PC/HPNBCOOH blends during heating at a rate of 20 $^\circ$C/min: (1) HPNB; (2) 20/80; (3) 40/60; (4) 60/40; (5) 80/20; (6) PC. .......... 160

6. 11. Composition-dependent glass transition temperature $T_{gm}$ for PC/HPNBCOOH blends, in which the solid line represents linear behavior and the dash line is obtained from experimental data. ......................................................... 162

6. 12. FTIR spectra for PC/HPNBCOOH blends in the carbonyl stretching region at room temperature: (a) PC, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80, and (f) HPNBCOOH. ......................................................... 162

6. 13. DSC Thermograms for P2VP/HPNBCOOH blends: (1) HPNBCOOH, (2) 20/80, (3) 40/60, (4) 60/40, (5) 80/20, (6) P2VP. ......................................................... 163

6. 14. Composition dependence of $T_{gm}$ for P2VP/HPNBCOOH blends. .......... 164
6. 15. FTIR spectra in the range of 1500–1800 cm\(^{-1}\) for P2VP/HPNBOOH blends at room temperature: (a) HPNBOOH, (b) 20/80, (c) 40/60, (d) 60/40, (e) 80/20, and (f) P2VP. .......................................................... 165

6. 16. DSC thermograms for PC/HPNBOOH blends during heating at a rate of 20 °C/min: (1) 10/90; (2) 50/50; (3) 70/30.................................................................................. 166

6. 17. DSC thermograms for PC/PNBOOH blends during heating at a rate of 20 °C/min: (a) 10/90; (b) 20/80................................................................................ 167

6. 18. FTIR spectra for (a) HPNBOOH, (b) 25/75 PC/HPNBOOH, (c) 90/10 PC/HPNBOOH, and (d) PC........................................................................... 167

6. 19. DSC thermogram for 80/20 PA66/HPNBNH\(_2\) blends during heating at a rate of 20 °C/min........................................................................................................ 168

6. 20. DSC thermogram of 60/40 PVPh/HPNBOOH blend ........................................ 169

6. 21. FTIR spectra in the range of (a) 4000 to 2400 (hydroxyl stretching region) and (b) 2000 to 1600 (carbonyl stretching region) cm\(^{-1}\) for (1) PVPh, (2) 60/40 PC/HPNBOOH blend, (3) HPNBOOH................................. 170

6. 22. Plots of log G' versus log a\(_T\omega\) and log G'' versus log a\(_T\omega\) for PC/HPNBOOH blends at various temperatures with T\(_r\) = T\(_{gm}\) + 50 °C as the reference temperature: (a) and (b) 20/80: (○) 102 °C (△) 112 °C (□) 122 °C (▽) 132 °C; (c) and (d) 40/60: (○) 122 °C (△) 132 °C (□) 142 °C.................................. 172

6. 23. Plots of log G' versus log G'' for PC/HPNBOOH blends at various temperatures: (a) 20/80: (○) 102 °C (△) 112 °C (□) 122 °C (▽) 132 °C; (b) 40/60: (○) 122 °C (△) 132 °C (□) 142 °C. ........................................................ 173

6. 24. Plots of log G' versus log a\(_T\omega\) and log G'' versus log a\(_T\omega\) for P2VP/HPNBOOH blends at various temperatures with T\(_r\) = T\(_{gm}\) + 50 °C as the reference temperature: (a) and (b) 20/80: (○) 98 °C (△) 108 °C (□) 118 °C (▽) 128 °C; (c) and (d) 40/60: (○) 104 °C (△) 114 °C (□) 124 °C (▽) 134 °C; (e) and (f) 60/40: (○) 110 °C (△) 120 °C (□) 130 °C; (g) and (h) 80/20: (○) 119 °C (△) 129 °C (□) 139 °C................................................................. 175

6. 25. Plots of log G' versus log G'' for P2VP/HPNBOOH blends at various temperatures: (a) 20/80: (○) 98 °C (△) 108 °C (□) 118 °C (▽) 128 °C; (b) 40/60: (○) 104 °C (△) 114 °C (□) 124 °C (▽) 134 °C; (c) 60/40: (○) 110 °C (△) 120 °C (□) 130 °C; (d) 80/20: (○) 119 °C (△) 129 °C (□) 139 °C............. 176
Polymer blends have received much attention since blending is a simple, effective approach to develop new materials exhibiting combinations of properties that cannot be obtained by individual polymers. However, most polymer blends are immiscible (or incompatible) because both the enthalpy and the entropy of mixing, generally, are unfavorable. Therefore, it is very important to study the miscibility or phase behavior of polymer blends. There are many different experimental methods that can be used to investigate the miscibility of polymer blends, such as differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), dielectric measurement, cloud point measurement, small-angle neutron scattering (SANS), nuclear magnetic resonance spectroscopy (NMR), etc. Each of the methods can only probe the homogeneity at a certain range of sizes. For instance, cloud point measurement can only determine the presence of microheterogeneity having domain sizes larger than the wavelength of the laser light source (ca. 450 nm). Generally, polymer blends are considered as miscible if a single, reasonably sharp glass transition appears. The appearance of multiple glass transition temperatures ($T_g$) reflects macrophase separation or partial miscibility of the constituent components.1-4
There are two types of miscible polymer blends: (i) miscible polymer blends having weak or little interactions and (ii) miscible polymer blends having strong specific interactions. However, in the literature there is confusion about the definitions of “weak interactions” and “strong interactions.” Since it is well established from a thermodynamic point of view that miscible polymer blends have “negative” values of Flory-Huggins interaction parameter ($\chi$), some investigators regard miscible polymer blends with $|\chi| \leq 0.001$ as having “weak interactions” and miscible polymer blends with $|\chi| \geq 0.01$ as having “strong interaction.” However, such a definition is somewhat arbitrary. Further, $\chi$ may not be an appropriate parameter that can define whether a miscible polymer blend has weak or strong interactions. It seems more appropriate to describe whether a miscible polymer blend has weak or strong interactions in terms of intermolecular forces. Intermolecular forces are discussed in the literature.\textsuperscript{5, 6} Table 1.1 gives a summary of bond energy and relative strength of different intermolecular forces. In this dissertation, on the basis of Table 1.1 we regard miscible polymer blends with van der Waals interaction as having weak interactions and miscible polymer blends with other types of interactions as having strong interactions.

<table>
<thead>
<tr>
<th>type of interaction</th>
<th>bond energy (kJ/mol)</th>
<th>relative strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>ionic attraction</td>
<td>850–1700</td>
<td>1000</td>
</tr>
<tr>
<td>hydrogen bonding</td>
<td>50–170</td>
<td>100</td>
</tr>
<tr>
<td>dipole-dipole interaction</td>
<td>2–8</td>
<td>10</td>
</tr>
<tr>
<td>van der Waals interaction</td>
<td>$\sim$1</td>
<td>1</td>
</tr>
</tbody>
</table>
For miscible polymer blends without specific interactions, generally a phase transition can be observed. In many polymer blends, two different types of phase behavior are primarily observed: upper critical solution temperature (UCST) phase behavior and lower critical solution temperature (LCST) phase behavior. Although not observed very often, some polymer blend systems exhibit combined UCST and LCST phase behaviors, as schematically shown below.

![Schematic representation of the phase behavior of polymer blends](image)

Schematic representation of the phase behavior of (a) UCST blend system, (b) LCST blend system, (c) combined UCST and LCST blend system, (d) combined UCST and LCST blend system with hourglass.

The viscoelastic properties of polymer blends exhibit different characteristics in different phase regions. As a result, rheological measurement is used to study the miscibility of polymer blends. Han and coworkers\textsuperscript{7-14} have shown experimentally that the logarithmic plots of storage modulus ($G'$) versus loss modulus ($G''$) show temperature independence and have a slope of 2 in the terminal region for monodisperse homopolymers or a homogeneous blend of two monodisperse polymers. On the other hand, the plots of log $G'$ versus log $G''$ for heterogeneous systems show temperature
dependence. It is believed that log $G'$ versus log $G''$ plot is very sensitive to the morphological state of a polymer blend.$^{15}$

During the past three decades, numerous investigators reported on the rheological behavior of miscible polymer blends having little or very weak interactions. The polymer blend systems investigated include (1) blends of polystyrene (PS) and poly(2,6-dimethylphenylene ether) (PPE),$^{16-18}$ (2) blends of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA),$^{19}$ (3) blends of PMMA and poly(styrene-co-acrylonitrile) (PSAN),$^{20-27}$ (4) blends of PMMA and poly(vinylidene fluoride) (PVDF),$^{22-24,28}$ (5) blends of PS and poly(vinyl methyl ether) (PVME),$^{29-41}$ (6) blends of PS and poly(a-methylstyrene) (PaMS),$^{36}$ and (7) blends of poly isoprene (PI) and poly(vinyl ethylene) (PVE).$^{42-47}$

It has been observed that some polymer blend systems having little or very weak interactions exhibit very broad, single glass transition$^{18,32,43-46}$ and thus such polymer blends are also referred to as ‘thermodynamically’ miscible polymer blends. As one might expect, very broad, single glass transition is observed when the difference in glass transition temperature ($T_g$) between the constituent components, $\Delta T_g$, is large. Thus, it is not surprising to find that the width of a single glass transition is rather narrow for polymer blends when $\Delta T_g$ is below a certain critical value.$^{26,48,49}$ While there is no theoretical guideline on the choice of a critical value of $\Delta T_g$, $\Delta T_g \approx 20 \, ^\circ C$ has been suggested on an empirical basis.$^{26,49}$ The origin of very broad, single glass transition in miscible polymer blends having little or very weak interaction has been discussed extensively in the past. Today, it is a general consensus among researchers$^{31,35,42,43,46,50-57}$ that very broad, single glass transition in miscible polymer blends having little or weak
interaction is caused by the presence of concentration fluctuations that broaden the
distribution of segmental relaxation times, which depend not only on blend composition
but also on temperature.

Another interesting experimental observation made for some miscible polymer
blends having little or very weak interactions is a failure of time-temperature
superposition (TTS),\textsuperscript{19,30,31,34-37,42-44,46,47,58} and such polymer miscible blends are referred
to as being thermorheologically complex. On the other hand, it has also been found that
an application of TTS to some other miscible polymer blends having little or very weak
interactions is warranted\textsuperscript{26,48,49} and such polymer blends are then referred to as being
thermorheologically simple. An important question is the origin of a failure of TTS in
some miscible polymer blends having little or very weak interactions. It has been
observed empirically that the miscible polymer blends with large $\Delta T_g$ invariably give rise
to a failure of TTS. It is then natural to relate the failure of TTS to the presence of
concentration fluctuations. In turn, the concentration fluctuations present in
thermodynamically miscible polymer blends having little or very weak interactions have
been related to dynamic heterogeneity.\textsuperscript{34,37,43,44} In other words, although those polymer
blends are thermodynamically miscible, the component dynamics are heterogeneous;
namely, in such dynamically heterogeneous blends, the components have measurably
different segmental mobilities and relaxation times within the same composition. It then
seems natural that a failure of TTS in thermodynamically miscible polymer blends having
little or very weak interactions may be attributed to the presence of dynamic
heterogeneity. Thus, efforts have been put on a better understanding of segmental
dynamics in thermodynamically miscible polymer blends having little or very weak
interactions. Dynamic heterogeneity has been investigated by a number of investigators using dielectric relaxation spectroscopy,\textsuperscript{34,37} electron spin resonance spectroscopy,\textsuperscript{54,59} solid-state nuclear magnetic resonance spectroscopy,\textsuperscript{43,44,60-63} and thermally stimulated depolarization current method.\textsuperscript{61} It can then be concluded that concentration fluctuations, dynamic heterogeneity, failure of TTS, and the broadness of glass transition in miscible polymer blends having weak interactions are interrelated, as shown pictorially below.

Today, it is well established that hydrogen bonding enhances miscibility of a polymer blend\textsuperscript{64-85} and a number of research groups investigated the miscibility of polymer blends having strong intermolecular hydrogen bonding.\textsuperscript{64} The polymer blend systems investigated include (i) blends of poly(vinyl phenol) (PVPh) and PVME;\textsuperscript{65-67} (ii) blends of PVPh and poly(vinyl acetate) (PVAc);\textsuperscript{68,69} (iii) blends of PVPh and poly(2-vinylpyridine) (P2VP);\textsuperscript{80} and (iv) blends of PVPh and poly(4-vinylpyridine) (P4VP).\textsuperscript{81,82} However, to date only a few research groups\textsuperscript{86,87} reported on the rheological behavior of miscible polymer blends with specific interactions. Despite the efforts made, at present the effect of specific interactions between the constituent components of miscible polymer blends on rheological behavior is not clear. This subject is of fundamental importance to have a better understanding of the role(s) strong attractive interaction
between the constituent components plays in determining the rheological behavior of miscible polymer blends.

In this dissertation, linear dynamic viscoelasticity of miscible polymer blend systems with specific interactions was investigated. For comparison, rheological properties of polymer blends without specific interactions were studied as well. The investigation was motivated to answer the following fundamental question: How would the linear dynamic viscoelasticity of miscible polymer blends with specific interactions be different from that of miscible polymer blends without specific interaction? To answer the question posed above, we have attempted to answer the following specific questions. (1) How would one know a priori whether an application of TTS to thermodynamically miscible polymer blends with specific interactions is warranted? (2) Will dynamic heterogeneity be present in miscible polymer blends with specific interactions? (3) Will relatively small differences in $T_g$ (say less than 25 °C) between the constituent components of a miscible polymer blend with specific interactions be necessary to suppress dynamic heterogeneity?
CHAPTER II

LITERATURE REVIEW

2.1 Miscible Polymer Blends

2.1.1 The Glass Transition in Polymer Blends

The glass transition temperature ($T_g$) reflects the molecular rearrangement rate in supercooled liquid and thus is one of the most important factors among the many transitions and relaxations in polymers. The glass transition behavior of polymer blends has long been used as a measure of component miscibility (single $T_g$ or not). Also, it is believed that a very broad, single glass transition in miscible polymer blends having little or very weak interactions is caused by the presence of concentration fluctuations that broaden the distribution of segmental relaxation times, which depend not only on blend composition but also on temperature. Further, it has been observed empirically that the miscible polymer blends with large difference in $T_g$ between the constituent components ($\Delta T_g$) will give rise to a failure of TTS. In addition, some polymer blends show a negative deviation from linearity, while other blend systems exhibit a positive deviation from linearity. It is believed that a positive deviation from linearity is caused by strong intermolecular attractions between the constituent components. Therefore, it is very
important to investigate the glass transition behavior and the composition dependence of
T_g of miscible polymer blends.

Several theoretical and empirical equations have been proposed to describe the
composition dependence of T_g of miscible polymer blends. The earliest expressions were
developed by Gordon and Taylor to predict the T_g in random copolymers and then was
used to miscible polymer blends, which is based on the consideration of volume
additivity (“free-volume models”)^{89}:

\[
T_g = \frac{w_1 T_{g1} + K w_2 T_{g2}}{w_1 + K w_2}
\]

(2.1)

where w_1 and w_2 are the weight fractions, and T_{g1} and T_{g2} are and glass transition
temperatures of components 1 and 2, respectively. The parameter K appearing in eq 2.1
is equal to \frac{\rho_1 \Delta \alpha_2}{\rho_2 \Delta \alpha_1} with \rho_i representing the density of component i and \Delta \alpha_i

\[\Delta \alpha_i = \alpha_i^L - \alpha_i^G.\]

DiMarzio and Gibbs^{90} also obtained an identical
expression but differ in the physical significance of the coefficient K.

Assuming that \frac{\rho_1}{\rho_2} = 1 and \Delta \alpha_i T_{gi} is constant^{91}, then K = T_{g1}/T_{g2}, from eq 2.1 we
have:

\[
\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}
\]

(2.2)

This simple expression is known as Fox equation^{92} and the prediction of T_g leads to a
negative deviation from the linear rule of mixtures (i.e., linear variation in T_g with
composition). This equation is expected to apply to blend systems with little of very weak interactions.

Couchman\textsuperscript{93} derived an expression for $T_g$ in miscible blends based upon the continuity of the extensive thermodynamic properties at the glass transition. He proposed the following expression:

\[
\ln T_g = \frac{w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \tag{2.3}
\]

in which $\Delta C_{pi}$ is the magnitude of the incremental increase in heat capacity at $T_g$. Application of $\Delta C_{pi} T_{gi} = \text{constant}\textsuperscript{94}$ to eq 2.3 leads to the form\textsuperscript{95}

\[
\frac{\ln T_g}{T_g} = \frac{w_1 \ln T_{g1}}{T_{g1}} + \frac{w_2 \ln T_{g2}}{T_{g2}} \tag{2.4}
\]

Alternatively, if the ratio $T_{g1}/T_{g2}$ is close to unity, then the logarithmic terms in eq 2.3 can be approximated such that an expression identical to that originally derived by Wood\textsuperscript{96} is obtained:

\[
T_g = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \tag{2.5}
\]

Equation 2.5 has the same form as the Gordon–Taylor equation (eq 2.1), where $K = \Delta C_{p2}/\Delta C_{p1}$. Application of $\Delta C_{pi} T_{gi} = \text{constant}\textsuperscript{94}$ into this expression leads to the Fox equation.

The Gordon–Taylor equation has been extended by Kwei to account for the effects of polymer-polymer interactions, such that
\[ T_g = \frac{w_1T_{g1} + Kw_2T_{g2}}{w_1 + Kw_2} + qw_1w_2 \]  

(2.6)

where \( q \) reflects the nature and magnitude of those specific interactions.\(^{97,98} \) When \( K = 1 \), eq 2.6 reduces to the form originally proposed by Jenckel and Heusch.\(^{99} \)

Kim et al.\(^{100} \) proposed a molecular thermodynamic model based on the configurational entropy model and Flory–Huggins theory and they obtained:

\[
\ln \left( \frac{T_{gm}}{T_{gl}} \right) = \frac{zR}{M_1\Delta C_{pl}} \left[ 1 - \gamma_{spe} \ln \left( \frac{z - 1}{e} \right) \right] + \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \phi_2 \ln \left( \frac{T_{g2}}{T_{g1}} \right) \]  

(2.7)

where \( z \) is the lattice coordination number, \( \gamma_{spe} \) is a proportionally constant representing the specific interaction between two polymers, \( \phi_i \) is the volume fraction, \( r_1 = V_1/V_0 \), and \( r_2 = V_2/V_0 \), with \( V_i \) being the molar volumes of components 1 and 2, respectively, and \( V_0 \) being the unit lattice volume.

Lu and Weiss\(^{101} \) reported a comprehensive thermodynamic expression for the prediction of \( T_g \) in miscible binary polymer blends that accounts for the strength of polymer-polymer interaction via inclusion of the Flory–Huggins interaction parameter, \( \chi \). They also obtained an expression that is very similar to that (eq 2.6) given earlier by Kwei but the physical significance of the coefficient \( K \) and \( q \) in both expression are different, namely in the expression suggested by Lu and Weiss, \( q \) is defined by

\[
q = \frac{-\chi R(T_{g1} - T_{g2})(\rho_1 / \rho_2)}{M_1\Delta C_{pl}(w_1 + Kw_2)(w_1 + (M_2 / M_1)w_2)(w_1 + (\rho_1 / \rho_2)w_2)^2} 
\]  

(2.8)
where \( K = \frac{\Delta C_{p2} - w_1 \delta C_p}{\Delta C_{p1} - w_2 \delta C_p} \) with \( \delta C_p \) being the specific heat change due to mixing, \( \rho_i \) is the density of polymer \( i \), and \( M_i \) is the molar mass per chain segment of component \( i \).

Note that when the relationship between \( T_g \) and composition is known, the \( \chi \) value can be calculated from eq 2.8.

Painter et al.\(^{102}\) studied the composition dependence of the glass transition temperature for miscible polymer blends with strong specific interactions, such as hydrogen bonding, by using a classical thermodynamic theory and they obtained:

\[
T_g = \frac{X_1 \Delta C_{p1} T_{g1} + X_2 \Delta C_{p2} T_{g2} - \frac{X_2}{X_1 \Delta C_{p1} + X_2 \Delta C_{p2}} \left[(H_B^{H,i})_{T_{gm}} - (H_B^{H,i})_{T_{gb}}\right] + \Delta H_{m}^{H,i}}{X_1 \Delta C_{p1} + X_2 \Delta C_{p2}} \tag{2.9}
\]

where \( X_i \) is the mole fraction, \( [(H_B^{H,i})_{T_{gm}} - (H_B^{H,i})_{T_{gb}}] \) represents the contribution of the enthalpy from the temperature dependence of the specific heat of the self-associating component and \( \Delta H_{m}^{H,i} \) is the heat of mixing that depends on the balance of interactions between self-associations and association between unlike polymers. The prediction of \( T_g \) has been found to be in good agreement with experiment using parameters reported in the literatures. Equation 2.9 can be reduced to the form given by Kwei (eq 2.6) if \( q \) and \( K \) are defined as follows:

\[
q = \frac{X_2 \left\{ [H_B^{H,i}]_{T_{gm}} - [H_B^{H,i}]_{T_{gb}} \right\} + \Delta H_{m}^{H,i}}{X_1 X_2 (X_1 + K X_2) \Delta C_{p1}}; \quad K = \frac{\Delta C_{p2}}{\Delta C_{p1}}.
\]

For blends without specific interactions, the most frequently cited equations are those proposed by Gordon and Taylor, Fox, and Couchman et al. Generally, these
equations are able to predict $T_g$-composition curves that exhibit negative deviation from linearity. However, those equations cannot predict the positive deviation from linearity with blend composition. The failure of the predictions is due to the fact that they do not take into account interchain interactions.\(^8\)

The Kwei equation can predict both negative and positive deviations from the linear mixing rule. The value of $q$ is used to estimate the strength of the interchain interactions. For example, when the interactions are very weak, that is, $\chi \approx 0$, then $q = 0$ and thus the equation is identical in form to the Gordon–Taylor equation (eq 2.1), which describe a negative deviation from linear rule of mixtures. Binary blends with strong specific interactions typically display positive deviations in $T_g$, which give a positive value of $q$. However, since $K$ and $q$ are adjustable empirical parameters, it is difficult to obtain fundamental information by this approach. As a result, the theories proposed by Kim et al., Lu and Weiss, and Painter et al. do really consider the effect of the strength of specific interactions.

### 2.1.2 Time–Temperature Superposition

For homogenous system, $\log G'$ versus $\log \omega$ and $\log G''$ versus $\log \omega$ plots at different temperatures can be reduced to a master plots, $\log G'$ versus $\log a_T \omega$ and $\log G''$ versus $\log a_T \omega$ plots, where $a_T$ is a temperature-dependent shift factor.

One complication in miscible polymer blends having little of very weak interactions is that whether the TTS is applicable to all miscible blends. Several research groups reported that TTS breaks down in some blend systems\(^{19,42-44,46,47,52,53,103,104}\) and such polymer miscible blends are referred to as being thermorheologically complex. On the
other hand, it has also been found that an application of TTS to some other miscible polymer blends\textsuperscript{26,48,49} is warranted and such polymer blends are referred to as being thermorheologically simple.

Colby\textsuperscript{19} was the first who reported that TTS failed for miscible 20/80 PMMA/PEO blend in the terminal region. He suggested that the failure of TTS is caused by the presence of concentration fluctuations. Subsequently, Ngai and Plazek\textsuperscript{58} explained Colby’s results using an argument of “coupling.” They attributed the breakdown of TTS to the different segmental relaxation times of the constituent components.

Failure of TTS is observed in the miscible blends of 1,4-polyisoprene (PI) and poly(vinyl ethylene) (PVE) as well.\textsuperscript{44,105} A series of PI/PVE blends with different molecular weights of PI were examined over a range of compositions and temperatures by Arendt et al.\textsuperscript{44} They found that TTS appears to hold for the blends with components having equal entanglement number but fail for any of the others. Haley and Lodge\textsuperscript{105} studied the dynamic viscosity for miscible blends of PI and PVE at the extremes of composition (1 \% tracer in 99 \% matrix) and found that TTS failed in these tracer blends. Miller et al.\textsuperscript{51} and Chung et al.\textsuperscript{43,53} investigated thermodynamic miscibility of PI/PVE blends using NMR spectroscopy. They attributed a single, broad glass transition to the presence of dynamical heterogeneity. Roland and Ngai\textsuperscript{42} suggested that the deviation from TTS for PI/PVE miscible blends is a consequence of the dynamical heterogeneity.

On the other hand, it has been reported that TTS works in some miscible blends.\textsuperscript{48,49} For example, Pathak et al.\textsuperscript{37} reported that the miscible PMMA/PSAN blends are thermorheologically simple, and these results are anticipated by a theory of concentration-fluctuation-induced dynamic heterogeneity\textsuperscript{57} in miscible polymer blends.
The PMMA/poly(vinylidene fluoride) (PVDF) blends are constituted by an amorphous polymer with a semicrystalline polymer, which is similar to the PMMA/PEO blends. Note that PVDF and PEO are semicrystalline polymer having a melting point of about 170 °C and 70 °C, respectively. However, Wu\(^2\) reported that PMMA and PVDF are truly molecularly compatible and a single WLF shift factor \(a_T\) was found applicable to all PMMA/PVDF blends.

Aoki and coworkers\(^{106}\) studied the dynamic viscoelastic properties of poly(\(\varepsilon\)-caprolatone) (PCL)/PSAN miscible blends. They found that TTS was applicable over the entire temperature range studied for the blends.

Similarly, the dynamic viscoelastic properties for miscible polymer blends of poly[styrene-\(co\)-(N-phenylmaleimide)] (SMI) and three kinds of PSAN with the same composition but different molecular weights were investigated by Aoki.\(^ {107}\) It was found that TTS was applicable over the entire range of temperatures for the blends. The zero-shear viscosities of the blends at constant temperatures increase concavely with the SMI content. However, when compared at the same free volume fractions, the zero-shear viscosities decrease convexly with SMI content. It is emphasized that the viscoelastic functions of miscible blends should be compared at the iso-free volume condition.

For some miscible blend systems, the validity of TTS is still under discussion. For instance, the applicability of TTS to the viscoelastic response of PS/PVME blends has been debated in the literature. Stadler et al.\(^ {38}\) constructed master curves of tan \(\delta\) for PS/PVME blends and arrived at the conclusion that the blend shows departures from TTS above the phase-separation temperature (\(T_c\)). On the other hand, below the phase-separation temperature, TTS can be applied. Ferry\(^ {108}\) suggests that a necessary condition
for TTS to be applicable is that the internal structure of the system does not change with
temperature. Obviously, an application of TTS above the phase-separation temperature is
incorrect. However, Kapnistos et al.35 found that a failure of TTS is observed in the
pretransitional region, which is still in the single phase region according to the phase
diagram. This observation is very similar to that reported by Kim et al.36 and Ajji et al.31.
Moreover, dielectric relaxation studies indicate that a failure of TTS for PS/PVME blends
is observed.26,34 Pathak et al.26 used both dielectric relaxation spectroscopy and
oscillatory shear flow to study the temperature dependence of relaxation of PS/PVME
blends. They found from rheological measurements that TTS appears to be valid when
shifting $G'$ and $G''$ along the frequency ($\omega$) axis, and the master curves of tan $\delta$ work
approximately. From dielectric relaxation measurement they observed that TTS fails for
PS/PVME blends. Concentration fluctuations are believed to be responsible for the
failure of TTS in PS/PVME blends.34

Kloffer et al.109 studied the viscoelastic properties polybutadiene/polyisoprene
(PB/PI) blends for temperature between about $T_g + 30^\circ C$ and $T_g + 110^\circ C$, and found that
TTS holds for PB/PI blends. Jeon et al.110 also investigated the viscoelastic properties of
PB/PI blends above and below the lower critical solution temperature (LCST). They
found that a single master curve in the loss modulus was obtained above and below the
LCST. On the contrary, Zawada et al.47 and Roovers and Toporowski46, 52 measured the
viscoelastic properties of PB/PI blends using a Rheometrics mechanical spectrometer and
found that TTS failed, because the relaxation time of the polymer with the higher $T_g$ has
a stronger temperature dependence than the relaxation time of the blend component with the lower $T_g$. 

16
From the above discussion we can conclude that miscible polymer blends having little or very weak interactions generally exhibit LCST or UCST behavior, which means that the miscibility of the blend depends on temperature significantly. That is, at certain temperatures, they are homogeneous but at other temperatures they are heterogeneous. However, some miscible polymer blend systems show a failure of TTS in the homogenous region based on cloud point measurement. Since different experimental methods used to determine the miscibility can only probe the homogeneity at a certain scale range, the prevailing view of the origin of the failure of TTS in miscible polymer blends having little or very weak interactions is the presence of dynamical heterogeneity or concentration fluctuation.\textsuperscript{51,55-57} Kumar et al.\textsuperscript{57} suggested that dynamic heterogeneity is induced by concentration fluctuation and they predicted an application of TTS to miscible polymer blends having closely matched $T_g$ or having strong interactions between two constituent components.

It is reported that miscible polymer blends with strong specific interactions are miscible over a wide range of temperatures. Therefore, we can expect that TTS is applicable to the blend systems with strong specific interactions. For example, Zhang et. al.\textsuperscript{74} investigated the properties of PVPh/PVEE blends using dielectric relaxation measurements and found that TTS holds for PVPh/PVEE blends. Luengo et. al.\textsuperscript{111} reported that a single $\alpha$ relaxation was also observed using dynamic mechanical spectroscopy (DMTA) and a master curves of loss modulus $E''$ could be constructed, indicating TTS is valid for 20/80 PVPh/PVAc blend. Similarly, TTS also has been found to be applicable for PVPh/PEO\textsuperscript{86} and PVPh/PVME\textsuperscript{87} blends. It is believed that the application of TTS is due to the presence of hydrogen bonding.
2.1.3 Effect of Specific Interactions on Rheological Properties

As mentioned above, for blends without specific interactions, the Flory–Huggins interaction parameter $\chi$ has been used to determine whether a polymer blend has favorable forces for miscible or not, that is, a large negative value of $\chi$ indicates strong attraction interactions between the constituent components. For example, the value of $\chi$ for PS/PVME blends is reported to about $-1.4 \times 10^{-4}$, which suggests that the interactions responsible for miscibility in the PS/PVME blend system are very weak.\textsuperscript{36} On the other hand, it is reported that the $\chi$ value for PSAN/PMMA blends is about $-0.01$.\textsuperscript{25,112} Therefore, it is regarded that the intermolecular interaction between PMMA and PSAN is stronger than that between PS and PVME. Actually, based on the $^{13}$C NMR experimental results of Feng et al.\textsuperscript{113}, it is found that there are attractive interactions between the phenyl groups in PSAN and the carbonyl groups in PMMA. Some research groups thought that the viscoelastic properties of polymer blends are related to $\chi$, but others\textsuperscript{27,114} suggested that $\chi$ (or interchain interactions) have no influence on the viscoelastic properties of miscible polymer blends.

For instance, Han and Kim\textsuperscript{22,23} developed a molecular theory to predict the linear viscoelastic properties of binary mixtures of miscible blends, using the concept of the tube model of Doi and Edwards.\textsuperscript{115} They assumed that each primitive chain reptates in a respective tube but that molecular interactions between the two chemically dissimilar primitive chains take place under the influence of an external potential, dependent upon the interaction parameter of the constituent components. They found that the predicted behavior of $\log \eta_{0b}$ versus blend composition is in agreement with experimental data for PMMA/PSAN blends of the nearly zero value of $\chi$. However, because of the use of a
3.4-power blending law or a linear blending law for the relaxation modulus, it is not so perfect to predict the relationship between the plateau modulus of the blend and the blend composition. Therefore, further study is needed to develop a blending law that will give satisfactory predictions of viscoelastic properties for miscible polymer blends. Wu\textsuperscript{21,28,116} studied viscoelastic properties of several miscible blends and found that dissimilar chains are less likely to entangle than similar chains due to interchain interactions. He discussed the entanglement, friction, and free volume between dissimilar chains in miscible polymer blends in connection with the Flory–Huggins interaction parameter $\chi$ and suggested that the entanglement probability between dissimilar chains becomes smaller as the interchain interaction becomes stronger.

In contrast, Haley and Lodge\textsuperscript{114} proposed a model to predict the viscosity of miscible polymer blends, which suggests that $\chi$ plays at most a modest role in affecting the viscosity of miscible blends. It combines a mixing rule for chain relaxation with a calculation of the concentration dependence of the monomeric friction factors, which are based on the double reptation concept as adopted by Tsenoglou\textsuperscript{117} and the assumption of self-concentration by Lodge and McLeigh.\textsuperscript{118} This approach model was successful in favorably predicting the experimental observations of the composition dependence of zero-shear viscosity for some blend systems but not for other blend systems.

Aoki et al.\textsuperscript{27} studied viscoelastic properties of three kinds of PSAN/PMMA blends with different molecular weights. They found that the interchain interactions responsible for the miscibility did not influence the rheological properties on the large time scale such as the plateau modulus and zero-shear viscosity of miscible blends. They suggested the weak interactions in blends can be regarded as a kind of nematic interaction, an
interaction between the segments of the chain and the matrix. Furthermore, they explained their experiments observations using the theory proposed by Watanabe et al. and Doi and Watanabe, which formulated the dynamics of Rouse chains that interact with each other by nematic potential. The theory predicted that the rheological properties on the large time scale are very insensitive to the nematic interaction. Actually, nematic interaction is a specific interaction in polymer melts, which tends to orient the neighboring polymer segments in melts toward the same direction. It is clear that this so-called nematic interaction is quite different from those specific interactions, for example, hydrogen bonding, which can improve the miscibility of polymer blends.

To date only a few research groups reported on the rheological behavior of miscible polymer blends with specific interactions.

Akiba and Akiyama studied the viscoelastic properties of blends of PVME with PVPh or PS having relatively low molecular weight. They found that the composition dependence and magnitude of zero-shear viscosity of PVPh/PVME blends were almost the same as those of PS/PVME blends without specific interaction under iso-free volume condition. In addition, they found that there are no differences in viscoelastic properties in terminal region between PS/PVME and PVPh/PVME blends. They concluded that the effect of the differences in chemical structure or specific interactions on flow behavior is very small. It should be pointed out that the molecular weight of the PVPh and PS used was very low (ca. 5000). The rheological behavior of oligomer would be quite different with that of high-molecular-weight polymers.

Cai et al. investigated the rheological behavior of PVPh/PEO and PS/PPO blends. It was also found that the rheological behavior of PVPh/poly(ethylene oxide) (PEO)
blends with specific interaction differed significantly from that of PS/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blends without specific interaction. It is attributed to the formation of strong hydrogen bonds in PVPh/PEO mixtures. For PVPh/PEO blends, Zhang et al.\textsuperscript{121} found that the miscibility and the phase structure of the blends show a significant compositional dependence. Since PEO is semicrystalline polymer, when PEO is rich, the blends appear to be partially miscible. Therefore, PVPh/PEO blend system is not a good blend system to investigate the rheological behavior of polymer blends with specific interaction over an entire range of composition.

From the above discussion we can conclude that the effect of specific interactions between the constituent components of miscible polymer blends on rheological behavior is still not clear. As we can observe in Table 1.1, however, the relative strength of specific interactions is much stronger than that of Van der Waals forces. As a result, the rheological properties of blends with specific interactions should be different with that of blends without specific interactions.

### 2.2 Functionalized Polynorbornenes

Polynorbornene (PNB) has received much attention since it can be easily functionalized. Functionalized norbornene monomers are prepared by Diels–Alder-reactions. For example, 5-norbornene-2,3-dicarboxylic anhydride can be produced via the Diels–Alder reaction between dicyclopentadiene and maleic anhydride, as shown below.\textsuperscript{122}
Norbornene and its derivatives can be polymerized via different routes. Basically, there are three different ways to polymerize norbornene, namely (i) ring opening metathesis polymerization (ROMP), (ii) addition polymerization, and (iii) radical or cationic polymerization, as schematically shown below.

The structure and properties of the polynorbornene obtained are dependent upon the catalyst used. By free radical or cationic polymerization, 2,7-connected polynorbornene is obtained.\textsuperscript{123-125} Initiators for the free radical polymerization are, for example, azoisobutyronitrile (AIBN), \textit{tert}-butyl peracetate, or \textit{tert}-butyl perpivalate. The cationic polymerization of norbornene can be conducted using EtAlCl\textsubscript{2} as initiator. The polymers synthesized by cationic polymerization yield low molecular weights. In 1967 the vinylic polymerization of norbornene with palladium (II) catalysts was patented.\textsuperscript{126} The vinylic polymerization is conducted by opening only the double bond of the $\pi$-component and leaving the bicyclic structural unit intact. The PNBs synthesized by vinylic
polymerization are saturated 2,3-inserted rotationally constrained polymers, exhibiting a high density, high chemical resistance, high refractive index, low birefringence, etc.\textsuperscript{127-129}

During the past decade, numerous research groups investigated the ROMP of norbornene.\textsuperscript{130} ROMP is an efficient method for synthesizing model polymers with a rather narrow molecular weight distribution owing to the living nature of ROMP. PNB synthesized via ROMP was first developed by CdF Chemie/Nippon Zeon in the late 1970s using a tungsten-carbene complex as catalyst. This polymer is commercially known as Norsorex, which is a linear, amorphous polymer that were used as rubber or elastomer.\textsuperscript{131,132} The PNB obtained contains 70 – 80 mol % trans-linked norbornene units, the molecular weight which is about $3 \times 10^6$ and has a glass transition temperature between 35 and 45 °C.\textsuperscript{133-135}

PNBs with functional groups usually are produced via ROMP of the corresponding norbornene derivatives.\textsuperscript{136-142} However, some functional groups such as hydroxyl and carboxylic group will do harm to the reactivity of ROMP catalyst.\textsuperscript{143} As a result, PNB with these groups should be obtained via alternative ways. For example, it is well known that Schrock or Grubbs’s catalysts have high tolerance of various functional groups such as ethers, esters, amides, amines, and sulfides. But it is difficult to polymerize 5-norbornene-2-carboxylic acid directly using Schrock or Grubbs’s catalysts. Therefore, a suitable protection group must be used to protect the carboxylic acid functionality. Such a protection group should not interfere with the ROMP and should be stable enough to allow proper purification of the monomers and polymers. Also it should offer an easy and clean deprotection from the precursor.
Depending on the characteristics of substitution groups, the resultant polymers vary over a wide range from a rubberlike polymer to a highly rigid plastic. For example, the introduction of bulky trimethylsilyl group into the main chain leads to an increase in the glass transition temperature ($T_g = 113 \, ^\circ\text{C}$), whereas the introduction of the even bulkier side group $\text{Si}(\text{Me}_2)\text{CH}_2\text{SiMe}_3$ with Si-C-Si flexible linkage results in a decrease in $T_g$ to a value (24 °C) lower than the $T_g$ (35 °C) of neat PNB.\textsuperscript{144} Therefore, PNB can be regarded as an intermediate between elastomers and thermoplastics.\textsuperscript{145}

Most of the investigations of PNB in the past focused on the PNB rubber. Because of the compatibility of PNB rubber with naphthenic or aromatic oils that act as a plasticizer, the glass transition temperature of the PNB/oil mixture can be lowered to – 60 °C. The amount of plasticizer included in a compound determines the softness of the vulcanizate. Very low hardness values down to 10 Shore A can be reached with amazingly good mechanical properties. The type of plasticizer used affects the cold resistance and rebound properties of the final compound. The presence of double bonds in the polymeric chain allows vulcanization with common peroxides or sulfur cure systems.\textsuperscript{146}

While much of the studies reported in the literature focused on the catalyst systems for ROMP,\textsuperscript{147-156} some efforts have been spent on applications of PNB, such as for gas permeation and sorption membranes\textsuperscript{157} and shape memory materials.\textsuperscript{145} Galperin et al.\textsuperscript{158} found that the tensile strength and extensibility of PNB increased, while Young’s modulus decreased with increasing molecular weight and with increasing content of trans relative to cis unsaturation. Matsumoto et al.\textsuperscript{159} investigated the physical/mechanical properties of poly(5-norbornene-2-nitrile) (PNB-CN) and found that PNB-CN has good
tensile and flexural properties, high creep resistance, and high abrasion resistance that are comparable with those of engineering plastics.

ROMP also has been used to synthesize a wide range of copolymers including graft copolymers and block copolymers. Feast et al.\textsuperscript{160-162} reported on a synthesis of 5-norbornene-2,3-\textit{trans}-bis(polystyryl carboxylate) macromonomers and its ROMP using the Schrock molybdenum initiators and obtained PNB-g-polystyrene copolymers. Lecomte et al.\textsuperscript{163, 164} synthesized PNB-g-poly(\varepsilon\text{-}caprolactone) (PCL) copolymers by sequential ROMP. These graft copolymers can be used to compatibilize PNB with polymers miscible with PCL, such as poly(vinyl chloride), nitrocellulose, and poly(epichlorohydrin). Block copolymers can be synthesized using the following living polymerizations: ROMP, atom-transfer radical polymerization, group transfer polymerization, or sequential anionic polymerization.\textsuperscript{165-167} For example, Notestein et al.\textsuperscript{168} synthesized a PNB-\textit{block}-polystyrene copolymer via living ROMP. Liaw et al.\textsuperscript{169,170} synthesized a series of novel diblock copolymers of 5-(N-carbazolyl methyl) bicyclo [2.2.1]hept-2-ene. Sundararajan et al.\textsuperscript{171} used a macro-difunctional initiator for metathesis polymerization to obtain triblock copolymers. Slugovc et al.\textsuperscript{172} used the third generation Grubbs initiator to synthesize ABC-type triblock copolymer. Because of this initiator’s outstanding tolerance of functional groups and living property of ROMP, three kinds of norbornene derivatives were reacted sequentially and then an ABC-type triblock copolymer was obtained.

Schrock and coworkers\textsuperscript{173-180} synthesized, via ROMP of norbornene derivatives, norbornene-containing side-chain liquid-crystalline polymers (SCLCP) with one pendant mesogenic group per repeating unit. They investigated the effects of molecular weight,
polydispersity, and the number of methylene flexible spacers \((n = 2–12)\) on thermotropic behavior. They found that the SCLCPs having short spacer lengths \((n = 2–10)\) formed a nematic mesophase while the SCLCPs having longer flexible spacer \((n = 11–12)\) formed a smectic phase. Wewerka et al.\(^{181}\) also synthesized norbornene-containing SCLCPs having varying flexible spacer lengths and made an observation similar to that made earlier by Schrock et al. The purpose of their study was to investigate the rheological behavior of the SCLCPs synthesized. They observed that upon cessation of shear flow, the structural recovery of the SCLCP with \(n = 5\) was found to be much shorter than the SCLCP with \(n = 9\). The influence of backbone rigidity on SCLCP was another feature of interest.\(^{182}\) Maughon et al.\(^{183}\) investigated the effect of backbone flexibility on the thermotropic behavior. To examine the role of the backbone rigidity on the liquid crystallinity of SCLCPs, a comparison was made between the fairly rigid PNB backbone and a more flexible polybutadiene backbone. The synthesis of substituted norbornenes and cyclobutenes having a \(p\)-nitrostilbene moiety as the mesogenic unit was accomplished. The ROMP of these monomers with the highly functional group tolerant initiator \((PCy_3)_2Cl_2Ru=CHPh\)\(^{184,185}\) produced SCLCPs with PNB and poly(cyclobutene) backbones, respectively.

To date only a few research groups reported on PNB-based thermoplastic blends. Kokuryo\(^{186}\) reported on blends of PNB with poly(vinyl chloride) (PVC), polystyrene (PS), acrylonitrile-butadiene-styrene (ABS) copolymers, and polycarbonate (PC). It is very doubtful that PNB/PVC, PNB/PS, PNB/ABS, and PNB/PC pairs can form miscible blends because PNB does not have any functional group that may have attractive interactions with PVC, PS, ABS, or PC.
On the other hand, because of highly unsaturated character of the main chain, PNB is very sensitive to oxidation, which requires a large amount of stabilizer. Therefore, hydrogenation of PNB is necessary. A commercial material Zeonex has been developed in Japan (Nippon Zeon). The functional groups in this product are unknown, but the chemical structure of Zeonex is shown below:

\[ \text{R}_1 \text{R}_2 \begin{array}{c} \text{n} \\ \text{R}_1 \text{R}_2 \end{array} \]

where \( \text{R}_1 \) and \( \text{R}_2 \) are hydrocarbon substituents.

Zeonex is an amorphous, colorless and transparent polymer with a high \( T_g \) (ca. 140 °C). It can be used as macromolecular material for optical purpose. Moreover, another product, Zeonor, is also accepted for use in optical, electronics and automobile applications. Zeonor is an amorphous hydrogenated copolymer and has been commercialized since 1998.

\[ \text{R}_1 \text{R}_2 \begin{array}{c} \text{n} \\ \text{R}_3 \text{R}_4 \end{array} \]

in which \( \text{R}_i \) are hydrocarbon substituents.

Up to now, polycarbonate (PC) is the most widely used optical material. Zeonex is reported to have lower birefringence, lower water absorption, and better optical characteristics, but Zeonex is more expensive than PC. Therefore, mixing PC with Zeonex will be a good idea to obtain optical material with good properties and low cost.

Moreover, the mechanical properties of Zeonex are also very good. Polyamide (PA) has good processability, impact strength, but with poor water absorption, heat deflection
temperature (HDT). When hydrogenated PNB is mixed with polyamide, it can improve the water absorption and HDT of polyamide.

However, it is reported in literature that hydrogenated polynorbornene without functional (HPNB) groups is similar to polyethylene (PE). Both of them have a low $T_g$ and a melting point at about 136 °C. Since PE is not miscible with most of the polymers, it can be predicted that HPNB is also hard to blend with PC or PA. Functionalization of polynorbornene, which provides attractive interactions between the constituent components, is a possible method to achieve miscible polymer blends. To the best of our knowledge, there is no miscibility study reported on blends based on hydrogenated functionalized PNBs.
CHAPTER III

EXPERIMENTAL

3.1 Polymer Synthesis

3.1.1 Synthesis of Poly(styrene-ran-vinyl phenol) copolymer (STVPh)

It is difficult to synthesize poly(vinylphenol) by direct polymerization of vinylphenol due to the occurrence of side reactions involving the hydroxyl group during polymerization. As a result, poly(styrene-ran-vinylphenol) (STVPh) random copolymers with different contents of vinylphenol (VPh) were prepared by free radical polymerization of styrene and 4-acetoxy styrene using azobis (isobutyronitrile) AIBN as the initiator, followed by the hydrolysis of the acetoxy groups using hydrazine hydrate according to the procedure of Green and Khatri, as shown in Scheme 3.1. Hereinafter, STVPh(n) denotes a STVPh copolymer with n mol % VPh.

As an example, the procedure for the synthesis of STVPh10 is shown below. Styrene and 4-acetoxy styrene were purchased from the Aldrich Chemical. Both monomers were purified by distillation under vacuum (82–86 °C/2 Torr). AIBN was recrystallized from acetone. 20 mL of styrene, 2.96 mL of 4-acetoxy styrene, and 0.079 g of AIBN (0.4 wt%) were transferred into a 250 mL flask along with 100 mL of dry toluene (or 1,4-dioxane). The flask was heated at 65 °C for 18 h, after which the reaction
mixture was slowly poured into methanol to obtain poly(styrene-
ran-4-acetoxystyrene) (SAS). Then the polymer was dried in a vacuum oven for one day. The copolymer formed is random since the monomer reactivity ratios are \( r_1 = 0.80 \) and \( r_2 = 1.02 \).\(^{190}\)

The hydrolysis reaction was carried out by following Ledwith et al.\(^{191}\). Typically, 2 g of poly(styrene-co-acetoxystyrene), 6 mL of hydrazine hydrate, and 40 mL of dioxane were stirred in a 250 mL flask for 40 h at room temperature. The resulting solution was slowly poured into methanol and then dried under vacuum in an oven at 70 °C for 3 days. The completion of deprotection of the acetoxy group was verified by the disappearance of the carbonyl group absorption at 1764 cm\(^{-1}\) in the FTIR spectrum. The VPh content of STVPh random copolymers was determined by \(^1\)H NMR from the precursor – SAS.

On standing for several months, this copolymer fails to dissolve in solvents which dissolve freshly prepared material, indicating a slow cross-linking reaction.\(^{189}\)

\[
\begin{align*}
\text{CH}_2\text{CH} + \text{CH}_2\text{CH} & \xrightarrow{\text{a,a'-azobisisobutyronitrile (AIBN)}} \text{CH}_2\text{CH} - \text{CH}_2\text{CH} - x \xrightarrow{\text{1,4-dioxane (60 °C)}} \\
\text{styrene} & \quad \text{4-acetoxystyrene} & \text{Poly(styrene-ran-4-acetoxystyrene) (SAS)}
\end{align*}
\]

\[
\begin{align*}
\text{hydrazine hydrate (N}_2\text{H}_4\text{H}_2\text{O}) & \xrightarrow{\text{1,4-dioxane (25 °C)}} \text{CH}_2\text{CH} - \text{CH}_2\text{CH} - x \\
\text{Poly(styrene-ran-4-vinylphenol) (STVPh)}
\end{align*}
\]

Scheme 3.1 Scheme of the synthesis of STVPh copolymer.\(^{189}\)
3.1.2 Synthesis of Hydrogenated Polynorbornene with Carboxylic Acid Group (HPNBCOOH)

The reaction scheme for the HPNBCOOH is shown in Scheme 3.2. (a) Synthesis of 5-norbornene-2-carboxylic acid. This functionalized norbornene monomer was prepared by the Diels–Alder reaction of acrylic acid and cyclopentadiene (CPD) in cyclohexane. Firstly, a flask containing dicyclopentadiene was heated until it refluxes briskly. Heat was applied continuously to promote rapid distillation without exceeding the boiling point of 42 °C. Fresh cracked cyclopentadiene in an ice-cooled receiver was obtained via this fractional distillation.

The reaction mixture of cyclopentadiene and acrylic acid in cyclohexane was stirred at 90 °C for 12 h. The acids produced were separated from cyclohexane (and the slight excess of cyclopentadiene) by extraction with aqueous NaOH (10% sodium hydroxide), followed by acidification (20% hydrochloric acid, HCl), extraction with chloroform, drying with magnesium sulfate, and distillation under vacuum (b.p. 134 °C/16mm Hg). The product was crystallized in the receiver as colorless needles, m.p. 44–45°C.

(b) Synthesis of 2-[(trimethylsilyl)carboxylate]-5-norbornene (NBCOOSiMe3). It is reported that carboxylic acid group will reduce the reactivity of ROMP catalyst.143 As a result, PNB with carboxylic acid group cannot be obtained directly from ROMP of 5-norbornene-2-carboxylic acid. A suitable protection group was needed to protect the carboxylic acid group. In this study we used trimethylsiloxy as a protection group.169 NBCOOSiMe3 was prepared from the reaction of 5-norbornene-2-carboxylic acid with trimethylchlorosilane and triethylamine in diethyl ether at room temperature. The product was distillated under vacuum (44–46 °C/2 mm Hg) to obtain colorless oil.
Scheme 3.2. Synthesis of HPNBCOOH.
(c) Ring-Opening Metathesis Polymerization. To control the content of hydroxyl groups, copolymer of norbornene and 5-norbornene-2-trimethylsilyl ester was synthesized. The polymerization via Ring-opening metathesis polymerization (ROMP) was carried out using Grubbs metathesis catalyst ($\text{Cl}_2\text{Ru(CHPh)}[\text{P(C}_6\text{H}_{11})_3])_2$) under oxygen-free condition in anhydrous methylene chloride. The reaction was carried out at 25 °C for 2 h and was terminated by the addition of a small amount of ethyl vinyl ether. The copolymer was then precipitated in excess methanol. The copolymer was further purified by dissolving it in tetrahydrofuran (THF) and re-precipitating it with methanol, and then dried overnight in a vacuum oven at room temperature.

(d) Hydrogenation. To improve the thermal stability and anti-ozone ability of functionalized polynorbornenes, the C=C double bonds in PNBs were hydrogenated. Poly(5-norbornene-2-(trimethylsiloxy) methylene) and ($p$-toluenesulfonylhydrazide (TSH) were mixed in anhydrous $p$-xylene and heated for 1 h at 120 °C under a nitrogen atmosphere. A complete solution was generally achieved by the time the temperature reached 100 °C. The onset of the reaction was marked by the vigorous evolution of gas. After the reaction was finished, the mixture was allowed to cool and was poured into methanol. The hydrogenated polymer was collected on a Teflon filter, washed with methanol several times, and then dried under vacuum.

(e) Deprotection. A copolymer was hydrolyzed by adding THF and 1N HCl to copolymer and allowing the mixture to stand at room temperature for 3 h. The copolymer was then precipitated in excess methanol and dried overnight in a vacuum oven at room temperature.
3.1.3 Synthesis of Hydrogenated Polynorbornene with Hydroxyl Group (HPNBOH)

Similar to the synthesis of PNB with carboxylic acid group described above, we used trimethylsiloxy as a protection group as well. Copolymer of norbornene and 5-[(trimethylsiloxy)methylene]-2-norbornene was synthesized using the Grubbs catalyst. After hydrogenation, this copolymer was hydrolyzed to produce HPNBOH, as shown in Scheme 3.3.

\[
\begin{align*}
\text{COOH} \quad &\xrightarrow{\text{LiAlH}_4/\text{Et}_2\text{O}} \quad \text{Water} \quad &\xrightarrow{20\% \text{HCl}} \quad \text{Water/ether} \\
\text{CH}_2\text{OH} \quad &\xrightarrow{10\% \text{NaOH}} \quad \text{Water} \quad &\xrightarrow{\text{Saturated brine (NaCl)}} \quad \text{Distillation} \\
\text{yield 60\%} \quad &\xrightarrow{\text{ether layer}} \quad \text{yield 60\%} \\
\text{FW 124.18, d 1.027} \quad &\text{bp 97 °C/20mmHg} \\
\text{bp 44-46 °C/2mmHg} \quad &\text{yield 70\%} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{OSiMe}_3 + \text{Cl}_2\text{Ru(CHPh)}[\text{P(C}_6\text{H}_{11})_3]_2 & \xrightarrow{\text{methylene chloride, 25 °C, 2h}} \text{CH}_2\text{OSiMe}_3 \\
p\text{-Toluenesulfonylhydrazide, TSH} & \xrightarrow{\text{p-xylene, 120 °C, 1h}} \text{CH}_2\text{OSiMe}_3 \\
\text{cyclohexane:THF (4:1)} & \xrightarrow{1\text{N HCl (1:15 THF)}} \text{CH}_2\text{OSiMe}_3 \\
\text{yield 80\%} \quad &\xrightarrow{\text{yield 80\%}} \\
\end{align*}
\]

Scheme 3.3. Synthesis of HPNBOH.
It should be pointed out here that the synthesis of 5-norbornene-2-methanol was not accomplished via the Diels–Alder condensation of fresh cracked cyclopentadiene and allyl alcohol. Since this method had a very low conversion, we used the following alternative method. A solution of 5-norbornene-2-carboxylic acid in ether was slowly added to a mixture of lithium aluminum hydride in ether for 4 h. After an additional 9 h at room temperature and 45 min at reflux, the mixture was cooled and treated successively with water and 20% hydrochloric acid. The ether layer was separated, combined with the ether layer from extraction of the aqueous layer, washed with 10% sodium hydroxide, water, and saturated brine, and finally dried over calcium sulfate. Evaporation and distillation yielded the 5-norbornene-2-methanol.

3.1.4 Synthesis of Hydrogenated Polynorbornene with Amine Group (HPNBNH₂)

Similarly, the synthesis of 5-norbornene-2-methyl amine was accomplished via the Diels-Alder reaction (Scheme 3.4). A mixture of freshly cracked cyclopentadiene and allyl amine was placed in a sealed pressure tube and kept at 175 °C for 8h. Phthalic anhydride was used as a protective agent. 5-norbornene-2-methylphthalimide was prepared by refluxing an equimolar solution of NB-NH₂ and phthalic anhydride in xylene with Soxhlet extractor to remove water. After removing the solvent, the residue was recrystallized from n-hexane, m.p. = 99–100°C. After polymerization and hydrogenation, the copolymer of norbornene and 5-norbornene-2-methylphthalimide was suspended in ethanol in a Schlenk tube. To the above mixture were added hydrazine hydrate and a trace of 2,6-di-tert-butyl-4-methylphenol. The mixture was degassed thrice via a freeze-pump-thaw cycle, and then the tube was heated to 100 °C. Hydrazinolysis was continued
for 6 h and then the solution was cooled to room temperature. The solution was precipitated in methanol and dried in vacuum oven over night.

Scheme 3.4. Synthesis of HPNBNH$_2$.\textsuperscript{194}
3.1.5 Synthesis of Poly(2-vinyl pyridine) (P2VP)

2-Vinylpyridine (2-VP) dried with potassium hydroxide and distilled in vacuum was sealed in ampoules with calcium hydride. Before polymerization it was vacuum-distilled. Radical polymerization of 2-VP was carried out with azobisisobutyronitrile (AIBN) as an initiator in toluene at 65 °C for 24 h. The polymerization was stopped by pouring the solution into ether. The crude polymer was then dissolved in methanol and precipitated into ether. The polymer thus obtained was dried in vacuum oven at 50 °C. Figure 3.1 gives the FTIR spectroscopy of P2VP. FTIR (KBr, cm\(^{-1}\)): 3061 (CH, in pyridine ring), 2930 (CH\(_2\)-CH, backbone), 1590, 1568, 1435 (C=C in pyridine), 1474 (C=N).

![FTIR spectra for neat P2VP at room temperature.](image-url)
3.2 Sample Preparation

(a) Materials. Poly(4-vinyl phenol) (PVPh) and poly(4-vinyl pyridine) (P4VP) were purchased from Aldrich Chemical. Poly(vinyl acetate) (PVAc) and poly(vinyl methyl ether) (PVME) in aqueous solution (50 wt %) were purchased from Scientific Polymer Products. After completely removing the water, PVME was dissolved into toluene (5 wt % of solid) and precipitated using hexane. Poly(styrene-co-acrylonitrile) (PSAN) with 20% acrylonitrile was purchased from Dow Chemical Company. Polystyrene (PS) was synthesized via anionic polymerization. A random copolymer of styrene and vinylphenol (STVPh) and P2VP was synthesized by free radical polymerization. The molecular weights and polydispersities of selected polymers were determined by gel permeation chromatography (GPC) (Waters), as listed in Table 3.1.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVPh</td>
<td>$2.16 \times 10^4$</td>
<td>1.62</td>
</tr>
<tr>
<td>PVAc</td>
<td>$1.42 \times 10^5$</td>
<td>1.71</td>
</tr>
<tr>
<td>PVME</td>
<td>$1.64 \times 10^5$</td>
<td>1.33</td>
</tr>
<tr>
<td>PSAN</td>
<td>$7.07 \times 10^4$</td>
<td>1.44</td>
</tr>
<tr>
<td>PS</td>
<td>$1.32 \times 10^5$</td>
<td>1.15</td>
</tr>
<tr>
<td>P2VP</td>
<td>$4.11 \times 10^4$</td>
<td>1.37</td>
</tr>
<tr>
<td>P4VP</td>
<td>$6.00 \times 10^4$</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*P4VP was not soluble in common solvent and thus it was not possible to determine $M_w/M_n$ using solution GPC.*
(b) Preparation of Miscible Polymer Blends. Samples for rheological measurements and DSC experiments were prepared by solvent casting. PVPh-based blends of different compositions were prepared by dissolving a predetermined amount of the constituent components in methyl ethyl ketone (5% solids in solution) in the presence of 0.1 wt % antioxidant (Irganox 1010, Ciba-Geigy Group). The solution was kept at room temperature for 24 h in a fume hood to allow for evaporation of most of the solvent. Following this, they were freeze-dried at room temperature for 3 days under vacuum and further dried at a temperature near T_g for 2 days under vacuum. The dried sample was compression molded at T_g + 50 °C and annealed at T_g + 20 °C in a vacuum oven. PS/PVME blends were prepared benzene as a solvent, and PSAN/PEMA blends were prepared using THF as a solvent.

3.3 Experimental Methods Employed

3.3.1 Differential Scanning Calorimetry (DSC)

The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC) (TA instrument or Perkin-Elmer DSC-7). DSC thermograms were recorded at a heating rate of 20 °C/min and T_g is taken as the midpoint of the transition in the second scan.

3.3.2 Thermo Gravimetric Analysis (TGA)

The thermal decomposition temperature was determined by TGA (TA instrument) to ensure that materials would not degrade over the range of temperatures employed for rheological measurements.
3.3.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

$^1$H NMR spectra were obtained using 200 MHz Varian Gemini-200 spectrometer.

3.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were recorded on a Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer 16PC) and 16 scans were collected with a spectral resolution of 4 cm$^{-1}$. The solution (2 % w/v) containing the blend was cast onto potassium bromide (KBr) disk. 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. It was slowly dried for 24 h in a fume hood until most of the solvent evaporated and then dried at 50 °C for a few days in a vacuum oven. Samples were then stored in a desiccator until use.

3.3.5 Gel Permeation Chromatography (GPC)

GPC measurements were performed using a Waters GPC equipped with Ultrastyragel columns using THF as an elution solvent at a rate of 1 mL/min. Monodisperse polystyrenes were used as calibration standards.

3.3.6 Rheological Measurements

Dynamic storage and loss moduli ($G'$ and $G''$) were measured as functions of angular frequency ($\omega$) ranging from 0.04 to 100 rad/s (lower frequency of 0.005 rad/s was used for some samples), at various temperatures during heating, using an advanced rheometrics expanded system (ARES) in the oscillatory mode with parallel-plate fixtures (8 mm diameter). The measurement temperature was varied depending on the $T_g$ of the specimen (from $T_g + 30 ^\circ C$ to $T_g + 80 ^\circ C$). All of the measurements were conducted
under a nitrogen atmosphere in order to avoid oxidative degradation of the samples. Only one sample was used for the entire rheological measurement (≤ 3 h) for various temperatures below 200 °C, while at temperatures above 200 °C a fresh specimen was used for each temperature. Cone-and-plate fixture was used to investigate steady-state flow behavior of some blend samples to obtain their zero-shear viscosity when η₀ could not be determined using oscillatory shear rheometry.
CHAPTER IV

SPECIFIC INTERACTIONS AND RHEOLOGY OF FIVE NEAT HOMOPOLYMERS AND COPOLYMERS INVESTIGATED

4.1 Self-association and Rheological Behavior of Five Neat Homopolymers Investigated

FTIR spectroscopy has proven to be a very powerful technique to detect the presence of self-association (intra-association) within a given molecule (or polymer) or inter-association (intermolecular attractive interactions) between two chemically dissimilar molecules. For instance, the infrared (IR) hydroxyl stretching range of phenolic hydroxyl (–OH) group is sensitive to the formation of hydrogen bonds. Figure 4.1 gives FTIR spectra of the hydroxyl stretching vibration region for the five neat homopolymers employed in this study. In Figure 4.1 we observe two vibration bands in PVPh: one centered at 3530 cm\(^{-1}\) which is related to “free” hydroxyl group, and another centered at 3380 cm\(^{-1}\) which is related to intra-associated hydrogen bonding of phenolic –OH group (i.e. self-association).\(^{72}\) On the other hand, in Figure 4.1 we do not observe evidence of the presence of self-association in four other homopolymers, PVAc, PVME, P2VP, and P4VP. This observation is very important to interpret the rheological behavior of the four PVPh-based polymer blend systems investigated in this study, which is presented below. TGA measurements of all five homopolymers indicate that thermal
degradation temperature is higher than 320 °C, which is above the highest rheological measurements employed in this study, as shown in Figure 4.2.

It is known that P2VP and P4VP absorb moisture very easily from air. Figure 4.3 gives FTIR spectra of P4VP before and after removing the moisture in the specimens, showing that the presence of an absorption band centered at 3300 cm\(^{-1}\) (the spectrum in Figure 4.2a) is due to the presence of moisture in the specimen. The FTIR spectrum of P4VP given in Figure 4.3b was obtained using a specimen that had been annealed at 100 °C under a nitrogen atmosphere for 20 minutes and then cooling down to room temperature. As a result, the absorption band for moisture has disappeared completely in Figure 4.3b. We took the same precaution for all rheological experiments conducted in the present study. We mention this rather important observation made from this study for the reason that the rheological responses of P2VP and P4VP were found to be quite different after removal of moisture from the specimens.

![FTIR spectra for five neat polymers: (a) PVAc, (b) PVME, (c) P2VP, (d) P4VP, and (e) PVPh.](image)

Figure 4.1. FTIR spectra for five neat polymers: (a) PVAc, (b) PVME, (c) P2VP, (d) P4VP, and (e) PVPh.
Figure 4.2. TGA data for (a) PVAc; (b) PVME; (c) P2VP; (d) P4VP; (e) PVPh.
Figure 4.3. FTIR spectra for neat P4VP at room temperature: (a) before annealing; (b) held at 100 °C for 20 min followed by cooling down to room temperature under a nitrogen atmosphere.

Figure 4.4 gives plots of log $G'$ versus log $\omega$, log $G''$ versus log $\omega$, and log $G'$ versus log $G''$ at various temperatures for each of the four homopolymers, PVAc, PVME, P2VP and P4VP. Notice in Figure 4.4 that the slope of log $G'$ versus log $G''$ plots in the terminal region is very close to 2 and the plots are independent of temperature for all four homopolymers. Such an observation is a very clear rheological manifestation that all four homopolymers are homogeneous and free from self-association! It should be mentioned that we observed the slope of log $G'$ versus log $G''$ plots in the terminal region for P2VP and P4VP to be smaller than 2 before moisture was removed from the specimens.
Figure 4.4. Rheology for four neat homopolymer: (a) PVAc at various temperatures (°C): (○) 78, (△) 88, (□) 98, and (▽) 108; (b) PVME at various temperatures (°C): (○) 11, (△) 21, (□) 31, (▽) 41, (◇) 51, and (○) 61; (c) P2VP at various temperatures (°C): (○) 107, (△) 117, (□) 127, (▽) 137, (◇) 147, and (○) 157; (d) P4VP at various temperatures (°C): (○) 183, (△) 193, (□) 203, (▽) 213, (◇) 223, and (○) 233.
Figure 4.5 gives plots of log $G'$ versus log $\omega$, log $G''$ versus log $\omega$, and log $G'$ versus log $G''$ at various temperatures for PVPh after annealing at 200 °C for 1h. It is of great interest to observe in Figure 4.5 that the slope of log $G'$ versus log $\omega$ plots in the terminal region is much smaller than 2 at all four measurement temperatures, while the slope of log $G''$ versus log $\omega$ plots in the terminal region is very close to 1 at all four measurement temperatures. As a result, the slope of log $G'$ versus log $G''$ plots in the terminal region for PVPh is much smaller than 2, which is quite different from the observation we have made above from Figure 4.4 for PVAc, PVME, P2VP, and P4VP. We wish to point out that the curvature of log $G'$ versus log $G''$ plots in the terminal region for the PVPh has little to do with the sensitivity of transducer of ARES for the reason that the lowest value of $G'$ (100 Pa) for PVPh given in Figure 4.5 is the same as that for PVAc, PVME, P2VP, and P4VP given in Figure 4.4, in which the slope of log $G'$ versus log $G''$ plots in the terminal region is very close 2.

Figure 4.5. Rheology of neat PVPh at various temperatures (°C): (○) 200, (△) 210, (□) 220, and (▽) 230.
Earlier, Still and Whitehead\textsuperscript{196} noted that a cross-linking reaction might occur for PVPh at elevated temperatures, as illustrated below. It is a result of combination of radicals, which could be obtained from PVPh by scission of the oxygen-hydrogen bond of the phenol groups.

![Crosslinking reaction of PVPh](image)

Therefore, in obtaining the rheological data summarized in Figure 4.5, we investigated the extent of possible cross-linking reaction in PVPh at elevated temperatures by conducting solubility test of annealed PVPh specimens that had been subjected to various temperatures and durations in a vacuum oven, the results of which are summarized in Table 4.1. It can be seen in Table 4.1 that a PVPh specimen was soluble in THF after annealing at 200 °C for 3 h but partially soluble after annealing at 200 °C for 24 h, and a PVPh specimen was soluble in THF after annealing at 220, 230, 240 °C for 40 min but partially soluble after annealing at 250 °C for 2 h. It should be mentioned that in all rheological measurements conducted in this study including those summarized in Figures 4.4 and 4.5, all specimens had 0.1 wt % antioxidant (Irganox 1010, Ciba-Geigy Group). In the rheological measurements for PVPh, a single specimen was used at and below 200 °C under a nitrogen atmosphere. However, a fresh specimen was used at each temperature and each frequency sweep experiment that lasted less than 25
Therefore, we believed that the precaution taken in our rheological measurements preclude any possibility of cross-linking reaction in PVPh specimen.

Table 4.1. Solubility of PVPh in THF after Annealing at Various Temperatures for Different Periods

<table>
<thead>
<tr>
<th>annealing temperature (°C)</th>
<th>duration of annealing</th>
<th>solubility in THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>10 h</td>
<td>soluble</td>
</tr>
<tr>
<td>150</td>
<td>16 h</td>
<td>soluble</td>
</tr>
<tr>
<td>200</td>
<td>3 h</td>
<td>soluble</td>
</tr>
<tr>
<td>200</td>
<td>24 h</td>
<td>partially soluble</td>
</tr>
<tr>
<td>220</td>
<td>1 h</td>
<td>soluble</td>
</tr>
<tr>
<td>230</td>
<td>50 min</td>
<td>soluble</td>
</tr>
<tr>
<td>240</td>
<td>40 min</td>
<td>soluble</td>
</tr>
<tr>
<td>250</td>
<td>2 h</td>
<td>partially soluble</td>
</tr>
</tbody>
</table>

Zhang et al. suggested that hydrogen bonding is a dynamic process, and hydrogen bonds are in equilibrium between breaking and reassociating. If the lifetime of a hydrogen bond is long enough, it is reasonable to speculate that PVPh might behave like a physically cross-linked network. Therefore, we attribute the curvature of log $G'$ versus log $G''$ plots in the terminal region of PVPh, observed in Figure 4.5, to the presence of self-association in PVPh.

To further confirm this, a random copolymer of styrene and vinylphenol, Poly(styrene-\textit{ran}-4-vinylphenol) (STVPh), was synthesized. Because of the incorporation of styrene, the glass transition temperature of the STVPh copolymer is
lower than that of neat PVPh. Therefore, STVPh copolymer is an ideal model polymer to investigate the effect of specific interactions on the rheological behavior.

4.2 Characterization of STVPh Copolymers

1H-NMR Measurement. The chemical structure of the copolymers was confirmed by 1H-NMR and FTIR. The VPh content of STVPh copolymers was determined by 1H NMR from the precursor – poly(styrene-co-acetoxy styrene) (SAS). For example, the 1H NMR spectra of the copolymer containing 5 mol % acetoxy styrene (SAS5) is shown in Figure 4.6. The broad resonances between 6.4 ppm and 6.9 ppm correspond to the aromatic protons. Resonance near 1.4 (2H, CH₂), 1.7 (1H, CH), and 2.3 (3H, -OCOCH₃) ppm correspond to the aliphatic backbone and methyl group, respectively.¹⁹⁰,¹⁹⁷

For example, the content of acetoxy styrene in STVPh5 can be calculated as following and the results was listed in Table 4.2.

\[ \delta_1.4/\delta_1.7 = 2 \text{ and } \delta_2.2 / (\delta_1.4 + \delta_1.7) = 2.5 / (11.27 + 25.76) = 6.37\% \]

![Figure 4.6. 1H NMR spectra for SAS5.](image-url)
Table 4. 2. Content of VPh in STVPh Copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Content of VPh (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STVPh5</td>
<td>6.37</td>
</tr>
<tr>
<td>STVPh20</td>
<td>25.8</td>
</tr>
<tr>
<td>STVPh40</td>
<td>46.0</td>
</tr>
</tbody>
</table>

**FTIR Measurement.** Polymer samples for infrared analyses were prepared by casting films on KBr windows from 5% solution in tetrahydrofuran (THF). After most of the solvent had evaporated the samples were carefully dried under vacuum at 70 °C for 24 h to completely remove residual solvent. Infrared measurements were recorded on a FTIR spectrometer (Perkin–Elmer 16PC model) at a resolution of 4 cm\(^{-1}\) for 16 scans.

FTIR spectra of the STVPh containing 20 mol % VPh before and after deprotection are shown in Figure 4.7.

![FTIR Spectra](image)

Figure 4.7. FTIR spectra before and after hydrolysis reaction of SAS20.
Note in Figure 4.7 that the carbonyl group absorption is at 1764 cm$^{-1}$ and the absorptions at 1600, 1500, 1450 cm$^{-1}$ are related to the C=C stretching vibrations of the benzene ring. After hydrolysis, the carbonyl group absorption at 1764 cm$^{-1}$ disappears completely and a strong broadband can be observed at 3320–3600 cm$^{-1}$, which are the stretching frequencies of free and self-associated phenolic hydroxyl groups.

As we mentioned before, phenolic hydroxyl groups can form strong self-association through intramolecular hydrogen bonding. Figure 4.8 gives FTIR spectra for STVPh copolymers with different content of vinyl phenol. The infrared band at 3530 cm$^{-1}$ is assigned to "free" phenolic hydroxyls, while the broad band centered at 3310 cm$^{-1}$ reflects a broad distribution of hydrogen bonded structures. As the content of styrene increases, the relative intensity of the "free" hydroxyl band increases, while the relative intensity of self-association absorption band decreases. This may be simply interpreted in terms of dilution effect. The incorporation of styrene into the PVPh chain via copolymerization to form random STVPh copolymers effectively dilutes the system. As a result, the probability of contact between hydroxyl groups is reduced.

Several characteristic infrared bands can be used to identify and measure the amount of styrene or 4-vinyl phenol chemical repeat units in the copolymers. The most convenient infrared bands for quantitative analysis are those present at 1512 and 1492 cm$^{-1}$ which are assigned to the localized ring modes associated with the phenolic and phenyl groups, respectively. It should be pointed out that these two bands have very different absorption coefficients. A calibration curve of STVPh copolymer composition versus the intensity ratio, $R = \frac{I_{1492}}{I_{1492} + I_{1512}}$, can be obtained (Figure 4.9), which is similar with that proposed by Xu$^{198}$. With this calibration curve, a simple compositional
analysis of an unknown STVPh copolymer, which is not feasible by $^1$H NMR method without labeling the VPh component, can be readily performed by infrared spectroscopy.

Figure 4.8. FTIR spectra recorded in the hydroxyl stretching region for STVPh copolymer containing different weight fractions of vinyl phenol: (1) PVPh, (2) STVPh50, (3) STVPh40, (4) STVPh20, (5) STVPh5.

Figure 4.9. Correlation of infrared intensity with STVPh copolymer composition.
**Molecular Weight Characteristics.** The molecular weights of the copolymers were analyzed by gel permeation chromatograph (GPC) and results were listed in Table 4.3. It can be seen that the polydispersity of all STVPh copolymers is not very broad.

Table 4.3. Molecular Weights and Polydispersity of STVPh Copolymers

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>Polydispersity $M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>STVPh5</td>
<td>27100</td>
<td>37000</td>
<td>1.37</td>
</tr>
<tr>
<td>STVPh10</td>
<td>22000</td>
<td>30200</td>
<td>1.36</td>
</tr>
<tr>
<td>STVPh20</td>
<td>43800</td>
<td>63300</td>
<td>1.44</td>
</tr>
<tr>
<td>STVPh40</td>
<td>37300</td>
<td>52700</td>
<td>1.41</td>
</tr>
<tr>
<td>STVPh50</td>
<td>24000</td>
<td>29200</td>
<td>1.21</td>
</tr>
</tbody>
</table>

**DSC measurement.** The DSC thermograms of SAS and STVPh copolymers are given in Figure 4.10. The arrow upward denotes the onset point ($T_{gi}$), the symbol + denotes the midpoint ($T_{gm}$), and the arrow downward denotes the end point ($T_{ge}$) of the glass transition. It is worth noting that the width of glass transition of the copolymers, $\Delta w_{T_g} = T_{gi} - T_{ge}$, is relatively narrow. After hydrolysis, the $T_{gm}$ of copolymer becomes higher (Figure 4.10a). It is due to the presence of hydrogen bonded OH. Also, as the content of VPh increases, the $T_{gm}$ of the STVPh copolymer increases. Table 4.4 gives a summary of the values of $T_{gi}$, $T_{gm}$, and $T_{ge}$, determined from DSC at a heating rate of 20 $^\circ$C/min.
Figure 4.10. DSC thermograms for SAS and SVTPh copolymers: (a) before and after hydrolysis of SVTPh40; (b) different contents of VPh groups.

Table 4.4. Summary of the Glass Transition Temperature for SAS and SVTPh Copolymers

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$T_{gi}$ ($^\circ$C)</th>
<th>$T_{gm}$ ($^\circ$C)</th>
<th>$T_{gf}$ ($^\circ$C)</th>
<th>$\Delta w_{Tg}$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SVTPh5</td>
<td>97</td>
<td>103</td>
<td>107</td>
<td>10</td>
</tr>
<tr>
<td>SVTPh20</td>
<td>119</td>
<td>126</td>
<td>130</td>
<td>11</td>
</tr>
<tr>
<td>SAS40</td>
<td>98</td>
<td>107</td>
<td>111</td>
<td>13</td>
</tr>
<tr>
<td>SVTPh40</td>
<td>131</td>
<td>139</td>
<td>142</td>
<td>11</td>
</tr>
<tr>
<td>SVTPh50</td>
<td>136</td>
<td>144</td>
<td>148</td>
<td>12</td>
</tr>
</tbody>
</table>

It is found that the glass transition temperature of STVPh copolymer shows a linear relationship with content of phenolic groups, as shown in Figure 4.11. This observation is consistent with that reported by Gonzalez et al.\textsuperscript{109}. Therefore, we can use Figure 4.11 to estimate the content of VPh in the copolymer by DSC measurement.
Figure 4.11. Correlation of $T_g$ with STVPh copolymer composition.

**TGA Measurement.** The thermal Stability of the copolymer was evaluated by thermal gravimetric analysis (TGA) in nitrogen atmosphere. Figure 4.12 gives the TGA curves for STVPh5 and STVPh40. The decomposition temperature for both of them is about 350 °C, which ensure that the copolymer is thermo-stable in the range of temperatures for rheological measurement.
4.3 Rheological Behavior of STVPh Copolymers

4.3.1 Time-Temperature Superposition and Log G’ versus Log G” Plots

Figure 4.13 gives plots of log $G'$ versus log $\omega$ and log $G''$ versus log $\omega$ at various temperatures for STVPh5. It can be seen in Figure 4.13 that both $G'$ and $G''$ decrease with increasing temperature. By shifting the log $G'$ versus log $\omega$ and log $G''$ versus log $\omega$ plots given in Figure 4.13 along the $\omega$ axis to the data at $T_r = T_{gm} + 50^\circ$C as reference temperature, the master curve of $G'$ and $G''$ reduced to $T_r$ for STVPh5 was obtained, as given in Figure 4.14. It is seen from Figure 4.14 that the log $G''$ versus log $a_T\omega$ plots have a slope 1 and the log $G'$ versus log $a_T\omega$ plots have a slope 2 in the terminal region.

Figure 4.15 gives plots of log $G'$ versus log $G''$ at various temperatures for STVPh5, STVPh20, and STVPh40. It is worth noting that the slope of log $G'$ versus log $G''$ plots for STVPh5 (Figure 4.15a) in the terminal region is very close to 2 and the plots are independent of temperature. This observation is consistent with that made from Figure 4.14. Such an observation suggests that STVPh5 is homogeneous and the effect of self-association, if any, is very small. As the content of VPh increase, the slope in the terminal region of log $G'$ versus log $G''$ plots becomes less than 2. From FTIR spectra analysis we knew that self-association of hydroxyl groups increases as the content of VPh increases. Therefore, it is very clear that the curvature of log $G'$ versus log $G''$ plots in the terminal region of STVPh copolymer is due to the presence of self-association. In addition, since the glass transition temperature for STVPh copolymers is lower than that of neat PVPh and the temperatures investigated in rheological measurement are below 200 °C, the possibility of crosslinking can be precluded.
Figure 4.13. Plots of log $G'$ versus log $\omega$ (a) and log $G''$ versus log $\omega$ (b) for STVPh5 at various temperatures: 133 °C (○), 143 °C (△), 153 °C (□), 163 °C (▽), 173 °C (◇).

Figure 4.14. Plots of log $G'$ versus log $a_T\omega$ (a) and log $G''$ versus log $a_T\omega$ (b) for STVPh5 at various temperatures with $T_r = T_g + 50$ °C (153°C) as the reference temperature: 133 °C (○), 143 °C (△), 153 °C (□), 163 °C (▽), 173 °C (◇).
Figure 4.15. Plots of log $G'$ versus log $G''$ for (a) STVPh5 at 133 °C ($\bigcirc$), 143 °C ($\triangle$), 153 °C ($\blacksquare$), 163 °C ($\triangledown$), 173 °C ($\Diamond$); (b) STVPh20 at 156 °C ($\bigcirc$), 166 °C ($\triangle$), 176 °C ($\blacksquare$), 186 °C ($\triangledown$), 196 °C ($\Diamond$); (c) STVPh40 at 169 °C ($\bigcirc$), 179 °C ($\triangle$), 189 °C ($\blacksquare$), 199 °C ($\triangledown$); (d) PVPh at 200 °C ($\bigcirc$), 210 °C ($\triangle$), 220 °C ($\blacksquare$), 230 °C ($\triangledown$).
4.3.2 Plateau Modulus

Figure 4.16 gives the master curves of $G'$ and tan $\delta$ for STVPh copolymers reduced to $T_r = T_{gm} + 50 \, ^\circ\text{C}$ as reference temperature, from which the plateau modulus was obtained.

Generally, if the molecular weight of polymer is high enough, the plateau modulus $G_N^0$ was determined as the storage modulus $G'$ in the plateau zone. However, for polymers with lower molecular weight, it is found empirically that the storage modulus $G'$ at the frequency where tan $\delta$ is at a minimum is close to the plateau modulus $G_N^0$. It can be observed from Figure 4.16 that there is no plateau zone in the storage modulus curves. Therefore, the values of $G_N^0$ were obtained from the master curves of $G'$ where tan $\delta$ is minimum. Note that the plateau modulus is insensitive to molecular parameters and depends only on polymer species and concentration.\textsuperscript{108,200} Therefore, even when the molecular weight is not high enough, the plateau modulus $G_N^0$ and the entanglement molecular weight $M_e$ (using the relationship $M_e = \rho RT/G_N^0$) for these copolymers still can be estimated. The number of entanglement $N = M_w/M_e$ is also calculated and the results are listed in Table 4.5.

From Table 4.5 we can see that the rheological properties of PS and STVPh5 are very close to each other. As the content of VPh is increased, the values of the plateau modulus $G_N^0$ decrease while the entanglement molecular weight $M_e$ increase, which means the copolymer become less entangled. Aharoni\textsuperscript{201} reported that entanglement is largely controlled by chain convolution. Based on this opinion, Wu\textsuperscript{21,28,116} suggested that
specific interactions tend locally to align the chain segments for association and thus stiffen the chains and reduce their convolution, resulting in reduced chains entanglement. Accordingly, the stronger interchain interactions, the smaller entanglement probability between chains, which can be seen clearly from the number of entanglement in Table 4.5. For example, N of STVPh40 and PVPh is 0.80 and 0.50, respectively, indicating they are unentangled chains.

4.3.3 Zero-Shear Viscosity

Zero-shear viscosities ($\eta_0$) for blends were obtained by using the following equation:\textsuperscript{108}

$$\eta_0 = \lim_{\omega \to 0} (\eta' = G''/\omega) \quad (4.1)$$

Figure 4.17 gives plots of log $\eta'$ versus log $\omega$ for STVPh copolymers at iso-free volume state ($T_g + 50^\circ$C). The values of $\eta_0$ are also given in Table 4.5. It should be pointed out that curves are not perfectly flat at the low frequency region for STVPh40 and neat PVPh (Figure 4.17d and 4.17e). Therefore, using the cone-and-plate fixture the measurement of steady-state shear flow was taken to obtain the viscosity at lower shear rates. Figure 4.18 gives plots of log $\eta$ versus log $\dot{\gamma}$ (filled symbols) in steady-state shear flow and plots of log $\eta'$ versus log $\omega$ (open symbols) in oscillatory shear flow for STVPh copolymers. It can be seen that the Cox-Merz rule is applicable to STVPh5 and STVPh 20 while not valid for STVPh 40 and neat PVPh. We contribute this to the presence of a high degree of self-association.
Figure 4.16. Plots of log $G'$ versus log $a_1\omega$ and log tan $\delta$ versus log $a_1\omega$ at $T_r = T_g + 50^\circ C$ for (a) PS, (b) STVPh5, (c) STVPh20, (d) STVPh40, (e) PVPh.
Figure 4.17. Plots of log $\eta'$ versus log $a_T\omega$ at $T_r = T_g + 50$ °C for (a) PS, (b) STVPh5, (c) STVPh20, (d) STVPh40, (e) PVPh.
Figure 4.18. Plots of log $\eta$ versus log $\dot{\gamma}$ (filled symbols) and plots of log $\eta'$ versus log $\omega$ (open symbols) for (a) STVPh5 at 153 °C, (b) STVPh20 at 176 °C, (c) STVPh40 at 189 °C, and (d) PVPh at 230 °C.

Table 4.5. Characteristics of Poly(styrene-ran-vinyl phenol) Copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
<th>$\eta_0$</th>
<th>$G_N^0$</th>
<th>$M_c$</th>
<th>$M_w/M_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>$2.13 \times 10^4$</td>
<td>1.04</td>
<td>$2.2 \times 10^3$</td>
<td>$2.5 \times 10^5$</td>
<td>$1.4 \times 10^4$</td>
<td>1.51</td>
</tr>
<tr>
<td>STVPh5</td>
<td>$3.70 \times 10^4$</td>
<td>1.37</td>
<td>$3.4 \times 10^3$</td>
<td>$2.7 \times 10^5$</td>
<td>$1.3 \times 10^4$</td>
<td>2.82</td>
</tr>
<tr>
<td>STVPh20</td>
<td>$6.33 \times 10^4$</td>
<td>1.44</td>
<td>$3.5 \times 10^4$</td>
<td>$1.4 \times 10^5$</td>
<td>$2.7 \times 10^4$</td>
<td>2.37</td>
</tr>
<tr>
<td>STVPh40</td>
<td>$5.27 \times 10^4$</td>
<td>1.41</td>
<td>$1.6 \times 10^4$</td>
<td>$5.8 \times 10^4$</td>
<td>$6.6 \times 10^4$</td>
<td>0.80</td>
</tr>
<tr>
<td>PVPh</td>
<td>$2.16 \times 10^4$</td>
<td>1.62</td>
<td>$3.5 \times 10^3$</td>
<td>$9.0 \times 10^4$</td>
<td>$4.3 \times 10^4$</td>
<td>0.50</td>
</tr>
</tbody>
</table>
The \( \eta_0 \) is affected by molecular weight, chain entanglement, interchain friction and free volume. For these copolymers, they are in an iso-free volume state \( (T_r = T_{gm} + 50 ^\circ C) \) but have different molecular weight. The \( \eta_0 \) increases with the increase of molecular weight, as shown in Table 4.5. For neat PS and PVPh, they have similar molecular weight. If only the effect of entanglement was considered, the \( \eta_0 \) of PVPh is expected to be reduced because of the decrease in entanglement. But from Table 4.5 we can see that the \( \eta_0 \) of PVPh is larger than that of PS. Therefore, the effect of interchain friction on \( \eta_0 \) is significant. Wu\(^{116} \) found that specific interactions tend to increase the interchain friction, which will give a net increase of \( \eta_0 \).

### 4.4 Concluding Remarks

In this chapter, we have shown that intramolecular hydrogen bonding between phenolic \(-\)OH groups (self-association) can be formed in neat PVPh and STVPh copolymers via FTIR spectroscopy. Both the self-association and the glass transition temperature \( (T_g) \) of the STVPh copolymers are proportional to the content of VPh. The rheological properties of STVPh copolymers were studied. It was found that with small content of VPh, the viscoelastic behavior of STVPh copolymer is similar to that of neat polymers without self-association. However, as the content of VPh is increased, plots of log \( G' \) versus log \( G'' \) show temperature independent but have a slope much smaller than 2 in the terminal region, which is different from the behavior of homogeneous polymers without intramolecular interactions. In addiction, TTS can be applicable to the STVPh copolymers. The master curves of log \( G' \) versus log \( a_T \omega \) has a slope less than 2 but log \( G'' \) versus log \( a_T \omega \) plots have a slope close to 1 in the terminal region. We attribute the
curvature in the terminal region to the self-association, not cross-linking. Moreover, the
STVPh copolymers with higher content of VPh have a smaller value of plateau modulus
but with higher $\eta_0$, suggesting that self-association will reduce the possibility of
entanglement but increase the friction between the chains. The above observations lead
us to conclude that the self-association has significant effect on the viscoelastic properties
of STVPh copolymers and neat PVPh.
CHAPTER V

CHARACTERIZATION AND RHEOLOGY OF MISCIBLE BLENDS

5.1 The Strength of Specific Interaction, as Determined by FTIR Spectroscopy, in Four PVPh-Based Miscible Polymer Blend Systems

5.1.1 Qualitative Analysis of Experimental Observations

Figure 5.1 gives FTIR spectra of the hydroxyl stretching vibration region for four PVPh-based blends investigated. When the FTIR spectra of PVPh/PVME blend (see Figure 5.1a) are compared with the FTIR spectrum of neat PVPh, we observe that the absorption band of the hydrogen bonds between the phenolic –OH group in PVPh and the ether oxygen in PVME is shifted to a lower wavenumber, which is centered at about 3320 cm\(^{-1}\). Zhang et al.\(^{65}\) pointed out that the difference in wavenumber (\(\Delta \nu_H\)) between the absorption bands of hydrogen-bonded and free hydroxyl groups could be used as a measure of the relative strength of hydrogen bonding. According to them, the large value of \(\Delta \nu_H\) (\(\approx 210\) cm\(^{-1}\)) in PVPh/PVME blends indicates that hydrogen bonding between PVME and PVPh is stronger than the self-association (\(\Delta \nu_S = 150\) cm\(^{-1}\)) among PVPh repeat units.

Referring to the FTIR spectra of PVPh/PVAc blends (see Figure 5.1b), the shoulder of the free hydroxyl group (3530 cm\(^{-1}\)) becomes undetectable, while the absorption band...
Figure 5.1. FTIR spectra at room temperature for (a) PVPh/PVME blends, (b) PVPh/PVAc blends, (c) PVPh/P2VP blends, and (d) PVPh/P4VP blends.
centered at 3380 cm$^{-1}$ is shifted to a higher wavenumber (3458 cm$^{-1}$). This shift in wavenumber is attributable to the inter-association between PVPh and PVAc through hydrogen bonding. The difference in wavenumber between the inter-association due to hydrogen bonding in PVPh/PVAc blends and the free hydroxyl group is about $\Delta \nu_H = 72$ cm$^{-1}$ (a shift from 3530 to 3458 cm$^{-1}$), which is smaller than the shift in wavenumber ($\Delta \nu_S = 150$ cm$^{-1}$) due to the self-association in PVPh. Therefore, the hydrogen bonding in PVPh/PVAc blends is weaker than that in neat PVPh.

Referring to the FTIR spectra of PVPh/P2VP blends (see Figure 5.1c), as the P2VP content in the blends increases, the intensity of the free hydroxyl band at a wavenumber of 3530 cm$^{-1}$ decreases, indicating that more free hydroxyl groups in PVPh are hydrogen bonded with the pyridine groups in P2VP. Furthermore, the center of absorption band for the broad hydrogen bonding is shifted from 3380 to 3135 cm$^{-1}$ when the content of P2VP increases to 60 wt %, yielding $\Delta \nu_H = 395$ cm$^{-1}$. The large shift in wavenumber signifies a strong intermolecular hydrogen bonding between PVPh and P2VP.

The FTIR spectra of PVPh/P4VP blends (see Figure 5.1d) also exhibit the same trend as those of PVPh/P2VP blends. Since $\Delta \nu_H = 410$ cm$^{-1}$ in PVPh/P4VP blends, we can conclude that the strength of hydrogen bonds in PVPh/P4VP blends is slightly greater than that in PVPh/P2VP blends.$^{202}$

From the above observations we conclude that the strength of the hydrogen bonds (SH) in the four PVPh-based miscible blends can be ranked as follows: $SH_{PVPh/P4VP}$ ($\Delta \nu_H = 410$ cm$^{-1}$) > $SH_{PVPh/P2VP}$ ($\Delta \nu_H = 395$ cm$^{-1}$) > $SH_{PVPh/PVME}$ ($\Delta \nu_H = 210$ cm$^{-1}$) > $SH_{PVPh/PVAc}$ ($\Delta \nu_H = 72$ cm$^{-1}$).
5.1.2 Effect of Temperature on Hydrogen Bonding

Figure 5.2a gives IR spectra of 40/60 PVPh/PVME blend at various temperatures. It can be seen from Figure 5.2a that the areas under the absorption band at 3320 cm\(^{-1}\) (i.e., hydrogen bonds between PVPh and PVME) decrease steadily and the peaks shift to higher wavenumber with increasing temperature. On the other hand, the absorption band at 3550 cm\(^{-1}\) (i.e., free hydroxyl group) increases as the temperature is increased. Therefore, we can conclude that the number of the hydrogen bonds decreases with increases in the temperature. However, hydrogen bonds still exist even at temperatures as high as 200 °C. The same tendency can be observed for other compositions. As a result, PVPh/PVME blends are miscible over a wide range of temperatures.

For PVPh/PVAc blend system, a similar tendency can be observed. For example, IR spectra of 80/20 PVPh/PVAc blend at various temperatures is given in Figure 5.2b. The absorption band of hydrogen bonds between PVPh and PVAc at 3350 cm\(^{-1}\) decreases and shift to higher wavenumber, while that of free hydroxyl group (3530 cm\(^{-1}\)) increases with increases in temperature. But the absorption band of hydrogen bonds did not disappear at temperatures as high as 200 °C.

Figure 5.2c gives IR spectra of 80/20 PVPh/P2VP blend at various temperatures. It can be seen from Figure 5.2c that the absorption band at 3135 cm\(^{-1}\) do not shift at all, indicating the hydrogen bonds between PVPh and P2VP are very stable in increasing temperature. On the other hand, the absorption band centered at 3380 cm\(^{-1}\) (i.e., self-association in PVPh) shifts to higher wavenumber with increasing temperature and the absorption band at 3550 cm\(^{-1}\) (i.e., free hydroxyl group) increases as the temperature is increased. It can be seen that the number of self-association of PVPh decreases with
Figure 5.2. FTIR spectra for (a) 40/60 PVPh/PVME blend, (b) 60/40 PVPh/PVAc blend, (c) 80/20 PVPh/P2VP blend, (d) 80/20 PVPh/P4VP blend at various temperatures (°C): (1) 25, (2) 50, (3) 100, (4) 150, and (5) 200.
increases in temperature. However, hydrogen bonds between PVPh and P2VP are still strong even at high temperatures. The same tendency can be observed for other compositions. It also suggests that the relative strength of hydrogen bonds in PVPh/P2VP blends is stronger than that in PVPh/PVME and PVPh/PVAc blends.

Similarly, for PVPh/P4VP blends, it can be seen from Figure 5.2d that the absorption band of hydrogen bonds between PVPh and P4VP (3120 cm\(^{-1}\)) do not shift as the temperature is increased. Also, On the other hand, the absorption band of self-association in PVPh (3380 cm\(^{-1}\)) shifts to a higher wavenumber and the absorption band of free hydroxyl group (3350 cm\(^{-1}\)) increases as the temperature increases. All of these indicate that the hydrogen bonds in PVPh/P4VP blends are very strong.

5.1.3 Quantitative Analysis of Experimental Results via the Coleman-Graf-Painter (CGP) Association Model

The CGP association model\(^{64}\) can be used to describe the thermodynamics of polymer blends with hydrogen bonding, which can be written using the following scheme:

\[
\begin{align*}
B_1 + B_1 & \rightleftharpoons B_2 \\
B_h + B_1 & \rightleftharpoons B_{h+1} \quad (h \geq 2) \\
B_h + A_1 & \rightleftharpoons B_h A_1
\end{align*}
\]

where B and A denote the self-associating and non-self-associating species, respectively. In this study, B represents phenolic –OH group and A represents proton acceptors, such as ether, carbonyl, and pyridine group. \(B_2\) is the hydrogen-bonded dimer formed between
two phenolic −OH groups, $B_h$ is the hydrogen-bonded multimer, and $B_hA$ is the inter-
molecular hydrogen bonding. The equilibrium constant for the first reaction is $K_2$, for the
second reaction is $K_B$, and for the third reaction is $K_A$, respectively, and the definitions of
which are given in the Appendix A, corresponding to association, which can be
determined from FTIR spectroscopic measurements of a dilute solution of low-
molecular-weight analogue compounds (model compounds). For example, $K_2$ and $K_B$
for PVPh was determined from the equilibrium constants for dilute solutions of phenol in
cyclohexane.203

The CGP association model for miscible polymer blends with hydrogen bonding
can be summarized as follows.64

\[
\Phi_B = \Phi_{B_1} \left[ \left( 1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \frac{1}{(1 - K_B \Phi_{B_1})^2} \right] \left[ 1 + \frac{K_A \Phi_{A_1}}{r} \right] \quad \text{(5.1)}
\]

\[
\Phi_A = \Phi_{A_1} + K_A \Phi_{A_1} \Phi_{B_1} \left[ \left( 1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \frac{1}{(1 - K_B \Phi_{B_1})} \right] \quad \text{(5.2)}
\]

where $\Phi_B$ and $\Phi_A$ are the volume fractions of components B and A, respectively, in the
blend, $\Phi_{B_1}$ and $\Phi_{A_1}$ are the volume fractions of free B and A groups, respectively, and $r$
$= V_A/V_B$ with $V_A$ and $V_B$, respectively, being the molar volumes of components A and B.
Equations 5.1 and 5.2 give relationships between the composition ($\Phi_A$ and $\Phi_B$) of a blend
and the distribution of species present ($\Phi_{B_1}$ and $\Phi_{A_1}$). The fraction of free B molecule
($f_{FB}$) can be determined from:64
\[ f_{FB} = \left[ \frac{1 - \frac{K_2}{K_B}}{1 - \frac{K_2}{K_B}} + \frac{K_2}{K_B} \left( \frac{1}{(1 - K_B \Phi_{B_1})} \right) \right] \left[ \frac{1}{1 + \frac{K_A \Phi_{A_1}}{r}} \right] \]  

(5.3)

and the fraction of hydrogen-bonded A groups \( f_{BA} \) can be determined from:

\[ f_{BA} = 1 - f_{FA} = \left( 1 - \frac{\Phi_{A_1}}{\Phi_A} \right) \]  

(5.4)

The derivations of eqs 5.1–5.3 are given in the Appendix A. The temperature dependence of equilibrium constants \( K_i \) can be expressed by

\[ K_i = K_i^\circ \exp \left[ \frac{-\Delta h_i}{R \left( \frac{1}{T} - \frac{1}{T^\circ} \right)} \right] \]  

(5.5)

where \( K_i^\circ (i = 2, B, A) \) are the equilibrium constants at the absolute temperature \( T^\circ \) (usually taken as 298 K), \( R \) is the universal gas constant, and \( \Delta h_i \) is the molar enthalpy of the formation of individual hydrogen bonds. Using eq 5.5 we can calculate the equilibrium constants \( (K_2, K_B, \text{ and } K_A) \) at different temperatures. For example, for 20/80 PVPh/P4VP blend at 100 °C, we have \( r = 0.849, \Phi_A = 0.8, \text{ and } \Phi_B = 0.2 \). From eq 5.5 we obtain \( K_2 = 3.14, K_B = 11.65, \text{ and } K_A = 78.10 \).

For given blend compositions \( (\Phi_B \text{ and } \Phi_A) \) and values of equilibrium constants \( (K_2, K_B, \text{ and } K_A) \), we can calculate \( \Phi_{B_1} \text{ and } \Phi_{A_1} \) from eqs 5.1 and 5.2. Then, substituting the calculated values of \( \Phi_{B_1} \text{ and } \Phi_{A_1} \) into eqs 5.3 and 5.4, the quantities \( f_{FB} \) and \( f_{BA} \) can be calculated. The numerical values of the parameters necessary for the
Table 5.1. Values of the Parameters Used for the Calculation of the Fraction of Hydrogen Bonding in Four PVPh-Based Blend Systems Investigated in This Study

<table>
<thead>
<tr>
<th>polymer</th>
<th>PVAc</th>
<th>PVME</th>
<th>P2VP</th>
<th>P4VP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_A$ (mL/mol)</td>
<td>70.0</td>
<td>55.3</td>
<td>84.9</td>
<td>84.9</td>
</tr>
<tr>
<td>$\Delta h_{BA}$ (cal/mol)</td>
<td>$-4000$ $-5400$ $-5900$ $-6000$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_A^o$</td>
<td>57.5</td>
<td>88.3</td>
<td>500</td>
<td>598</td>
</tr>
</tbody>
</table>

PVPh

<table>
<thead>
<tr>
<th></th>
<th>Hydrogen-bonded dimer</th>
<th>Hydrogen-bonded multimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_B = 100.2$ (mL/mol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta h_2 = -5600$ (cal/mol)</td>
<td>$\Delta h_B = -5200$ (cal/mol)</td>
<td></td>
</tr>
</tbody>
</table>

$K_2^o = 21.0$ $K_B^o = 68.0$

Table 5.2. Calculated Fractions of Free Hydrogen Group B and Hydrogen-Bonded Group A for Four PVPh-Based Blend Systems Investigated in This Study

<table>
<thead>
<tr>
<th>composition (wt %)</th>
<th>20/80</th>
<th>40/60</th>
<th>60/40</th>
<th>80/20</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVPh/ PVAc blends</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f_{FB}$</td>
<td>0.062</td>
<td>0.089</td>
<td>0.116</td>
<td>0.143</td>
</tr>
<tr>
<td>$f_{BA}$</td>
<td>0.156</td>
<td>0.345</td>
<td>0.507</td>
<td>0.628</td>
</tr>
<tr>
<td>PVPh/PVME blends</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f_{FB}$</td>
<td>0.051</td>
<td>0.073</td>
<td>0.101</td>
<td>0.132</td>
</tr>
<tr>
<td>$f_{BA}$</td>
<td>0.126</td>
<td>0.293</td>
<td>0.462</td>
<td>0.599</td>
</tr>
<tr>
<td>PVPh/P2VP blends</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f_{FB}$</td>
<td>0.019</td>
<td>0.039</td>
<td>0.090</td>
<td>0.134</td>
</tr>
<tr>
<td>$f_{BA}$</td>
<td>0.202</td>
<td>0.506</td>
<td>0.785</td>
<td>0.879</td>
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<tr>
<td>PVPh/P4VP blends</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$f_{FB}$</td>
<td>0.016</td>
<td>0.034</td>
<td>0.087</td>
<td>0.134</td>
</tr>
<tr>
<td>$f_{BA}$</td>
<td>0.207</td>
<td>0.517</td>
<td>0.803</td>
<td>0.893</td>
</tr>
</tbody>
</table>
calculations of various quantities described above are summarized in Table 5.1, which are taken from the literature.\textsuperscript{72,102,204} The values of the equilibrium constants and the molar enthalpy of the formation of hydrogen bonds in PVPh/P4VP blends reported in the literature are different depending on the sources.\textsuperscript{205-208} In the present study we used the average values: $\Delta h_{BA} = -6000$ cal/mol and $K_A = 598$ for PVPh/P4VP blends, and we used $K_A = 500$ for PVPh/P2VP blends.\textsuperscript{209} We estimated the value of the molar enthalpy of the formation of hydrogen bonds in PVPh/P2VP blends to be $\Delta h_{BA} = -5900$ cal/mol (because the specific interaction in PVPh/P2VP blends is slightly weaker than that in PVPh/P4VP blends). The calculated values of the fraction of free B groups and hydrogen-bonded A groups are summarized in Table 5.2. It can be seen from Table 5.2 that both $f_{FB}$ and $f_{BA}$ increase as the amount of PVPh in the respective blend systems increases. A close examination of the values of $f_{BA}$ given in Table 5.2 reveals that the stronger the specific interactions, the larger the values of $f_{BA}$, i.e., the more intermolecular hydrogen bonds have been formed. For example, at the same composition, $f_{BA}$ of PVPh/P4VP blends are much larger than $f_{BA}$ of PVPh/PVAc blends. The procedures used to calculate the fraction of the hydrogen bonds formed for the four PVPh-based miscible polymer blends are described in the Appendix A.

5.1.4 Curve Fitting of FTIR Spectra of PVPh/P2VP and PVPh/P4VP Blends

Compared with quantitative analysis of liquid samples, a quantitative analysis of polymer samples is more susceptible to errors. Therefore, not all polymer blend systems are suitable for quantitative analysis. First of all, the equilibrium constants need to be determined from FTIR spectroscopic measurements of a dilute solution of low-
molecular-weight analogue compounds (model compounds). For example, for PVPh/PVME blend system, the ether (C-O-C) stretching vibration is not a localized mode and is conformationally sensitive, which precludes quantitative analysis of the fraction of hydrogen-bonded ether groups in the blend. Therefore, inter-association equilibrium constant $K_A$ of PVPh/PVME blends can be estimated from the inter-association parameters of phenol–diethyl ether mixtures in carbon tetrachloride solution. Some may doubt the reliability of using equilibrium constants of low molecules to polymer. For pyridine group, there are some absorption bands that are suitable for quantitative analysis. Therefore, PVPh/P2VP or PVPh/P4VP blend systems can be used to check whether the CGP association model is reliable.

In this study, the following procedures were used for curve-fitting FTIR spectra of PVPh/P4VP blends. The following Gaussian-Lorentzian function

$$I_j(v) = g I_j^0 \exp \left[ -\ln 2 \left( \frac{2(v - \nu_j^0)}{\Delta \sigma_j} \right)^2 \right] + \frac{(1 - g)I_j^0}{1 + [2(v - \nu_j^0)/\Delta \sigma_j]^2} \quad (5.6)$$

was applied to fit the bandshape. $I_j$ is the absorbance, $v$ is the wavenumber coordinate of $I_j$, and $j$ is the number of component bands. Figure 5.3 gives the bandshape predicted by the Gaussian function (appearing in the first term on the right-hand side of eq 5.6) and the Lorentzian function (appearing in the second term on the right-hand side of eq 5.6). Note that eq 5.6 has three parameters: band position ($\nu_j^0$), band height ($I_j^0$), and bandwidth at half height ($\Delta \sigma_j$), as illustrated in Figure 5.3. The number of component bands and the center-band wavenumber $\nu_j^0$ were determined by the minima in the second derivatives of a FTIR spectrum.
Figure 5.3. Illustration of the parameters in eq 5.6 and bandshapes predicted by Gaussian function (solid line) and Lorentzian function (dash line), respectively.

Figure 5.4. FTIR spectra at wavenumbers of 1030 and 970 cm$^{-1}$ for (a) PVPh/P2VP blends and (b) PVPh/P4VP blends.
Figure 5.4 gives the FTIR spectra at wavenumbers ranging from 970 to 1030 cm\(^{-1}\) for PVPh/P2VP blends and PVPh/P4VP blends obtained at 100 °C. The absorption band at a wavenumber of 992 cm\(^{-1}\) corresponds to the pyridine ring stretching in neat P2VP or P4VP and the absorption band at a wavenumber of 1012 cm\(^{-1}\) corresponds to the phenolic \(-\text{OH}\) group in neat PVPh. The two bands are well separated and no overlap is observed. When PVPh was mixed with P2VP or P4VP, an absorption band at a wavenumber of 1003 cm\(^{-1}\) can be observed, which is due to the hydrogen bonds formed between the pyridine groups and the phenolic \(-\text{OH}\) groups in PVPh. The fraction of the hydrogen-bonded pyridine group (\(f_H\)) can be calculated from the expression\(^8\)

\[
f_H = \frac{A_H}{A_H + A_F(\alpha_{992}/\alpha_{1003})}
\]

where \(A_F\) and \(A_H\) are the peak areas corresponding to the absorptions from the free pyridine ring (at 992 cm\(^{-1}\)) and the hydrogen-bonded pyridine ring (at 1003 cm\(^{-1}\)), respectively. \(\alpha_{992}/\alpha_{1003}\) is the ratio of absorption band coefficients of free pyridine ring (\(\alpha_{992}\)) and hydrogen-bonded pyridine ring (\(\alpha_{1003}\)). It is assumed that \(\alpha_{992}/\alpha_{1003} = 1\).\(^8\)

Following we take PVPh/P4VP blends as example to show the procedures employed for curve fitting FTIR spectra. In determining the fraction of hydrogen bonds formed in PVPh/P4VP blends, first we had to obtain the bandwidth at half height (\(\Delta\sigma_j\)) for absorption bands at wavenumbers of 992 cm\(^{-1}\) and 1012 cm\(^{-1}\), which were determined from the FTIR spectra of neat PVPh and P4VP, respectively. From Figure 5.4b we obtain \(\Delta\sigma_{992} = 9.5\) and \(\nu_{992}^0 = 992\) cm\(^{-1}\) for the absorption band of pyridine groups, and \(\Delta\sigma_{1013} = 8.5\) and \(\nu_{1013}^0 = 1012\) cm\(^{-1}\) for the absorption band of phenolic \(-\text{OH}\) groups.
groups. Note that for a single absorption band, the only adjustable parameter is $g$ appearing in eq 5.6. In this study, we used $g = 0.5$ for an absorption band at a wavenumber of 992 cm$^{-1}$ and $g = 0.9$ for an absorption band at a wavenumber of 1012 cm$^{-1}$. Next, from the second derivative of the FTIR spectrum of, for example, 20/80 PVPh/P4VP blend (the solid line in Figure 5.5a) we observe two minima. Therefore, two Gaussian–Lorentzian bands were used to curve-fit the FTIR spectrum: one corresponding to the absorption band of free pyridine ring in P4VP (at 992 cm$^{-1}$), at which $\Delta \sigma_{992} = 9.5$ and $\nu_{992}^0 = 992$ cm$^{-1}$, and another corresponding to the absorption band of hydrogen bond formed between the pyridine ring in P4VP and the phenolic –OH group in PVPh, at which we have $\Delta \sigma_{1005} = 10.5$ and $\nu_{1013}^0 = 1005$ cm$^{-1}$, for which we assumed the absorption band to be symmetric. Then, we adjusted the values of $I_j^0$ ($j = 1, 2$) to obtain the best curve-fit to the FTIR spectrum. The results of curve-fitting were evaluated visually by overlapping the reconstituted overall curve on the original spectrum using a regression analysis. We calculated the areas of component absorption bands using the trapezoidal rule. For blends having higher content of PVPh, for example, in 60/40 PVPh/P4VP blend, three minima from the second derivative of FTIR spectrum (the solid line in Figure 5.5b) were observed. Therefore, three Gaussian–Lorentzian absorption bands were used to curve-fit the FTIR spectrum. $I_j^0$ ($j = 1, 2, 3$) were adjustable parameters. Table 5.3 gives a summary of the curve-fitting results for PVPh/P4VP and PVPh/P2VP blends with four different blend compositions. Note that the fraction of hydrogen-bonded pyridine group ($f_{H}$) in Table 5.3 is obtained from curve-fitting of
Figure 5. FTIR spectra for (a) 20/80 and (b) 60/40 PVPh/P4VP blend. The upper curve is the second derivative, the open symbols denote experimental data, and the solid lines are the calculated spectra obtained from the sum of Gaussian-Lorentzian bandshapes (dash lines).

Table 5.3. Parameters Used for Curve Fitting of FTIR Spectra of PVPh/P2VP and PVPh/P4VP Blends at 100 °C to the Coleman-Graf-Painter Association Model and Predicted Fraction of Hydrogen Bonding

<table>
<thead>
<tr>
<th>Blend (wt %)</th>
<th>Free pyridine group</th>
<th>H-bonded pyridine group</th>
<th>$f_H$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu_{992}^0$</td>
<td>$\Delta \sigma_{992}$</td>
<td>Area $A_F$</td>
</tr>
<tr>
<td>PVPh/P2VP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20/80</td>
<td>992</td>
<td>9.5</td>
<td>0.482</td>
</tr>
<tr>
<td>40/60</td>
<td>992</td>
<td>9.5</td>
<td>0.378</td>
</tr>
<tr>
<td>60/40</td>
<td>992</td>
<td>9.5</td>
<td>0.247</td>
</tr>
<tr>
<td>80/20</td>
<td>992</td>
<td>9.5</td>
<td>0.118</td>
</tr>
<tr>
<td>PVPh/P4VP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20/80</td>
<td>992</td>
<td>9.5</td>
<td>0.649</td>
</tr>
<tr>
<td>40/60</td>
<td>992</td>
<td>9.5</td>
<td>0.273</td>
</tr>
<tr>
<td>60/40</td>
<td>992</td>
<td>9.5</td>
<td>0.208</td>
</tr>
<tr>
<td>80/20</td>
<td>992</td>
<td>9.5</td>
<td>0.167</td>
</tr>
</tbody>
</table>
experimental data. Note that values of $f_{BA}$ given in Table 5.2 are calculated from the CGP association model. The agreement between $f_H$ and $f_{BA}$ is good, indicating that the equilibrium constants we used for the CGP association model are reliable.

### 5.2 The Strength of Hydrogen Bonds, as Determined by DSC, in Four PVPh-Based Miscible Polymer Blend Systems

The glass transition of all four PVPh-based blend systems has been studied using DSC. Figure 5.6 gives DSC thermograms of four different blend compositions for each blend system investigated. A broad, single glass transition for each blend composition is observed in Figure 5.6, in which the arrow upward denotes the onset point ($T_{gi}$), the symbol + denotes the midpoint ($T_{gm}$), and the arrow downward denotes the end point ($T_{gf}$) of the glass transition. A single $T_g$, though broad, indicates that each blend is miscible within the size scale which DSC can detect and each of the four blend systems investigated is miscible over the entire blend composition. Tables 5.4 gives a summary of the glass transition temperature ($T_g$) in terms of $T_{gm}$ and the breadth of glass transition denoted by $\Delta w_{T_g} = T_{gf} - T_{gi}$ for each blend composition of all four PVPh-based blend systems investigated in this study. It is seen in Table 5.4 that the $\Delta w_{T_g}$ for a certain blend composition is as large as 28 °C, while the $\Delta w_{T_g}$ for neat components is about 10 °C. Notice in Table 5.4 that the difference in $T_{gm}$ between the constituent components, $\Delta T_{gm}$, is 152 °C for PVPh/PVAc blends, 199 °C for PVPh/PVME blends, 83 °C for PVPh/P2VP, and 27 °C for PVPh/P4VP blends.
Figure 5.6. DSC thermograms for (a) PS/PVME blends, (b) PSAN/PEMA blends, (c) PVPh/PVAc blends, (d) PVPh/PVME blends, (e) PVPh/P2VP blends, and (f) PVPh/P4VP blends.
Table 5.4 Summary of the Thermal Properties of Four PVPh-Based Blend Systems Investigated in This Study

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$T_{gi}$ ($^\circ$C)</th>
<th>$T_{gm}$ ($^\circ$C)</th>
<th>$T_{gf}$ ($^\circ$C)</th>
<th>$\Delta w_{Tg}$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PVPh/PVAc blends</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAc</td>
<td>23</td>
<td>28</td>
<td>33</td>
<td>10</td>
</tr>
<tr>
<td>20/80 PVPh/PVAc</td>
<td>33</td>
<td>44</td>
<td>52</td>
<td>19</td>
</tr>
<tr>
<td>40/60 PVPh/PVAc</td>
<td>55</td>
<td>65</td>
<td>75</td>
<td>20</td>
</tr>
<tr>
<td>60/40 PVPh/PVAc</td>
<td>89</td>
<td>101</td>
<td>117</td>
<td>28</td>
</tr>
<tr>
<td>80/20 PVPh/PVAc</td>
<td>129</td>
<td>140</td>
<td>146</td>
<td>17</td>
</tr>
<tr>
<td><strong>PVPh/PVME blends</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVME</td>
<td>-23</td>
<td>-19</td>
<td>-14</td>
<td>9</td>
</tr>
<tr>
<td>20/80 PVPh/PVME</td>
<td>-16</td>
<td>-1</td>
<td>12</td>
<td>28</td>
</tr>
<tr>
<td>40/60 PVPh/PVME</td>
<td>12</td>
<td>24</td>
<td>36</td>
<td>24</td>
</tr>
<tr>
<td>60/40 PVPh/PVME</td>
<td>60</td>
<td>72</td>
<td>81</td>
<td>21</td>
</tr>
<tr>
<td>80/20 PVPh/PVME</td>
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<td>106</td>
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<tr>
<td><strong>PVPh/P2VP blends</strong></td>
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<td>101</td>
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<td>20/80 PVPh/P2VP</td>
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<td>121</td>
<td>129</td>
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</tr>
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<td>40/60 PVPh/P2VP</td>
<td>138</td>
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<td>60/40 PVPh/P2VP</td>
<td>152</td>
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<td>177</td>
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<td><strong>PVPh/P4VP blends</strong></td>
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<td>156</td>
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<td>20/80 PVPh/P4VP</td>
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<td>185</td>
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<td>186</td>
<td>191</td>
<td>21</td>
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<tr>
<td>60/40 PVPh/P4VP</td>
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<td>197</td>
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</tr>
<tr>
<td>80/20 PVPh/P4VP</td>
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<td>186</td>
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<tr>
<td>PVPh</td>
<td>174</td>
<td>180</td>
<td>184</td>
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</table>
Table 5.5. Summary of the Thermal Properties of PS/PVME Blends and PSAN/PEMA Blends Investigated in This Study

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$T_{gi}$ (°C)</th>
<th>$T_{gm}$ (°C)</th>
<th>$T_{gf}$ (°C)</th>
<th>$\Delta w_{Tg}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PS/PVME blends</strong></td>
<td></td>
<td></td>
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<td>-10</td>
<td>5</td>
<td>25</td>
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<td>42</td>
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<tr>
<td>PEMA</td>
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<tr>
<td>PSAN</td>
<td>102</td>
<td>109</td>
<td>114</td>
<td>12</td>
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</tbody>
</table>
On the other hand, the thermal transition behavior of miscible PS/PVME and PSAN/PEMA blend systems that have no specific interactions is also investigated. DSC thermograms were given in Figure 5.6e and f and the values of $T_{gm}$ and $\Delta w_{T_g}$ for each blend composition of these two blend systems are summarized in Table 5.5. It can be seen from Table 5.5 that $\Delta w_{T_g}$ was as large as 42 °C for a certain blend composition of PS/PVME blends, and as large as 29 °C for a certain blend composition of PSAN/PEMA blends, while $\Delta T_{gm}$ between the constituent components was about 120 °C for PS/PVME blends and about 49 °C for PSAN/PEMA blends.

It is of great interest to note from the above observations that values of $\Delta w_{T_g}$ for PVPh/PVAc and PVPh/PPVME blends are much smaller than those of PS/PVME and PSAN/PEMA blends, in spite of the fact that values of $\Delta T_{gm}$ for PVPh/PVAc and PVPh/PPVME blends are much larger than those for PS/PVME and PSAN/PEMA blends. In other words, the magnitude of $\Delta T_{gm}$ between the constituent components in the PVPh-based blend systems with hydrogen bonding does not seem to be correlated to the magnitude of $\Delta w_{T_g}$. The above observations lead us to conclude that the PVPh-based blend systems with hydrogen bonding have smaller values of $\Delta w_{T_g}$ than the PS/PVME and PSAN/PEMA blend systems without specific interaction. As summarized in the Introduction section, the current consensus, though strictly empirical, among researchers is that the broadness of glass transition is related to the extent of composition fluctuations and dynamic heterogeneity in miscible polymer blends without specific interaction, and a failure of TTS in such blend systems is associated with the presence of concentration
Figure 5.7. Composition-dependent glass transition temperature ($T_{gm}$) for (a) PS/PVME, (b) PSAN/PEMA, (c) PVPh/PVAc, (d) PVPh/PVME, (e) PVPh/P2VP, and (f) PVPh/P4VP blends, in which the dashed line represents a linear behavior and the dotted line denotes experimental data.
fluctuations and dynamic heterogeneity. What remains to be seen here is whether such a consensus would also be applicable to the PVPh-based blend systems with hydrogen bonding. If it does, we will be able to conclude that TTS would work for the PVPh-based blend systems owing to a lesser degree of, if not negligible, concentration fluctuations and dynamic heterogeneity.

Plots of experimentally determined T\(_g\) (accurately stated, T\(_{gm}\)) versus blend composition (open symbols) for PS/PVME blends, PSAN/PEMA blends, and four PVPh-based blend systems are given in Figure 5.7, in which the dashed lines represent a linear relationship. It is seen in Figure 5.7 that some blend systems show positive deviation from a linear relationship, while other blend systems show negative deviation from a linear relationship.

In the past, several research groups\(^{89,92,93,97,98,100-102,210,211}\) suggested expressions for relationships between T\(_g\) and blend compositions in miscible polymer blend systems; some expressions are for miscible polymer blend systems without specific interaction\(^{89,92,93,210,211}\) and others are for miscible polymer blend systems with specific interactions.\(^{97,98,100-102}\) Following, we used different expressions to predict the composition dependence of T\(_g\) for miscible polymer blends investigated.

5.2.1 Composition Dependence of T\(_g\) for PS/PVME and PSAN/PEMA Blends

For PS/PVME and PSAN/PEMA blends without specific interactions, the Gordon–Taylor expression is the most commonly employed equation, in which K is treated as an arbitrary fitting parameter:
However, the Gordon–Taylor expression can be also derived from the thermodynamic theory of Couchman–Karasz,\textsuperscript{93,210,211} in which K is no longer an adjustable parameter and \( K = \frac{\Delta C_p_2}{\Delta C_p_1} \). The predictions of the Gordon–Taylor equation for PS/PVME and PSAN/PEMA blends are given in Figure 5.8. As can be seen, the predictions are in good agreement with the experimental data. It should be pointed out that we didn’t use any fitting parameter here and the values of K can be obtained from experiment.

\[
T_g = \frac{w_1 T_{g1} + w_2 K T_{g2}}{w_1 + Kw_2}
\]  

(2.1)

Figure 5. 8. Composition-dependent glass transition temperatures (\( T_{gm} \)) for (a) PS/PVME and (b) PSAN/PEMA blends, in which the dashed line represents a linear behavior, the open symbols (\( \bigcirc \)) denote experimental data, and the filled symbols (\( \bullet \)) denoted predicted values from eq 2.1.
5.2.2 Prediction of $T_g$ of Four PVPh-Based Miscible Polymer Blend Systems by the Kim Theory

Kim et al.\textsuperscript{100} derived a new mathematical model to predict the glass transition temperature of miscible blends, which is based on configurational entropy and Flory–Huggins theory, as shown in following equation:

$$T_{gm} = \text{EXP} \left( \frac{zR}{M_1\Delta C_p} \left( 1 - \gamma_{spe} \ln \left( \frac{z-1}{e} \right) \right) \left( \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 \right) + \left( \phi_1 \ln T_{g1} + \phi_2 \ln T_{g2} \right) \right)$$

(5.8)

where $z$ is the lattice coordination number, $\gamma_{spe}$ is a proportionally constant representing the specific interaction between two polymers, $\phi$ is the volume fraction. $r_1 = V_1/V_0$ and $r_2 = V_2/V_0$, where $V_1$ are the molar volumes of components 1 and 2, respectively, and $V_0$ is the unit lattice volume (normally set $V_0 = 1$ for convenience).

This model includes only one adjustable parameter $\gamma_{spe}$, which represents the strength of specific interaction, i.e., the higher value of $\gamma_{spe}$ represents the stronger specific interactions. Therefore, this model can only predict composition-dependence of $T_{gm}$ with positive deviation or simple linear additivity. The theoretical prediction of $T_{gm}$ calculated from eq 5.8 was shown in Figure 5.9. As seen in the Figure 5.9, for PVPh/PVAc blends and PVPh/PVME blends, a negative value of $\gamma_{spe}$ is needed to fit the data.
Figure 5. Composition-dependent glass transition temperatures ($T_{gm}$) for (a) PVPh/PVAc blends, (b) PVPh/PVME blends, (c) PVPh/P2VP blends, and (d) PVPh/P4VP blends, in which the dashed line represents a linear behavior, the open symbols (○) denote experimental data, and the filled symbols (●) denoted predicted values from eq 5.8.
5.2.3 Prediction of $T_g$ of Four PVPh-Based Miscible Polymer Blend Systems by the Lu-Weiss Theory

Lu and Weiss\textsuperscript{101} assume that the enthalpy of mixing can be represented by a van Laar relationship

\begin{equation}
\Delta H_m(T) = \chi RT \phi_1 \phi_2
\end{equation}

where $\chi$ is the Flory–Huggins interaction parameter. Then they obtain

\begin{equation}
T_{gm} = \frac{w_1 T_{g1} + kw_2 T_{g2}}{w_1 + kw_2} + \frac{Aw_1 w_2}{(w_1 + kw_2)(b w_1 + bw_2)(w_1 + bw_2)^2}
\end{equation}

\begin{equation}
A = -\frac{\chi R(T_{g1} - T_{g2})c}{M_1 \Delta C_p^l} \quad \text{and} \quad k = \frac{\Delta C_{p2} - w_1 \delta C_p^1}{\Delta C_{p1} - w_2 \delta C_p^g}
\end{equation}

where $c = \rho_1/\rho_2 \approx 1$, $b = M_2/M_1$, $M_i$ is the molar mass per chain segment of component $i$. $\delta C_p$ is the specific heat change due to mixing, which is usually negative for a miscible blend but their value is unknown. As a result, $k$ is slightly dependent on blend composition and actually is used as an adjustable parameter. Also, it is not easy to obtain the value of $\chi$ for blends with strong specific interactions from experimental measurement. Therefore, $A$ is used as an adjustable parameter as well.

This model can predict very well for blends with weak or no specific interactions, which generally exhibit negative deviation of the $T_g$-composition relationship. It can be simplified to the form of Couchman’s equation or Gordon–Taylor equation. However, for blends with strong specific interactions, which generally exhibit positive deviation in $T_g$ from linear additivity, a positive value of $A$ is obtained. Note that by definition, polymer 1 is the lower $T_g$ component, and, therefore, $\chi$ will have the same sign as $A$. 

92
Thus, a large positive deviation of composition-dependence of $T_g$ will give a large positive value of $\chi$, as shown in Figure 5.10c and d.

![Figure 5.10. Composition-dependent glass transition temperatures ($T_{gm}$) for (a) PVPh/PVAc blends, (b) PVPh/PVME blends, (c) PVPh/P2VP blends, and (d) PVPh/P4VP blends, in which the dashed line represents a linear behavior, the open symbols (○) denote experimental data, and the filled symbols (●) denoted predicted values from eq 5.10.](image-url)
5.2.4 Prediction $T_g$ of Four PVPh-Based Miscible Polymer Blend Systems by the Painter Theory

The majority of the suggested expressions for miscible polymer blend systems with specific interactions, with an exception for the thermodynamic theory of Painter et al.,$^{102}$ have at least one adjustable parameter. The most comprehensive theory predicting the composition dependence of glass transition temperature of miscible polymer blends with specific interactions is given by Painter et al.,$^{102}$ according to which we have the following expression:

$$T_{gm} = \frac{X_A T_{gA} + K_0 X_B T_{gB}}{X_A + K_0 X_B} + q X_A X_B$$ (5.12)

in which $T_{gm}$ is the midpoint of glass transition temperature, as determined from a DSC thermogram, $X_A$ and $X_B$ are the mole fractions of components A and B, respectively, with the subscript B referring to the self-associating component (PVPh in the present study), $T_{gA}$ and $T_{gB}$ are the glass transition temperatures of components A and B, respectively, and $K_0$ is the ratio of heat capacity ($K_0 = \Delta C_{pB}/\Delta C_{pA}$) with $\Delta C_{pB}$ and $\Delta C_{pA}$ being the heat capacities of components A and B, respectively, and $q$ is defined by

$$q = - \frac{X_B \left( [H_B^{H,l}]_{T_{gm}} - [H_B^{H,l}]_{T_{gB}} \right) + \Delta H_m^{H,l}}{X_A X_B (X_A + K_0 X_B) \Delta C_{pA}}$$

$$= - \frac{X_B n_B \Delta h_B \left( [p_{BB}^{o}]_{T_{gm}} - [p_{BB}^{o}]_{T_{gB}} \right) + n_B \Delta h_B \left( p_{BB} - p_{BB}^{o} \right)_{T_{gm}} + n_A \Delta h_{BA} \left( p_{BA} \right)_{T_{gm}}}{X_A X_B (X_A + K_0 X_B) \Delta C_{pA}}$$ (5.13)
The definitions and the physical meanings of the various parameters \( (H_B^{1,1}, \Delta H_m^{1,1}, n_A, n_B, \Delta h_B, \Delta h_{BA}, p_{BB}, p_{BA}, \) and \( p_{BB}^o \) ) appearing in eq 5.13 are given in the Appendix B. Equation 5.12 predicts both positive and negative deviations from the linear mixing rule. For \( q = 0 \), eq 5.12 reduces to the well-known Gordon-Taylor equation.\(^{89}\) For the derivation of eq 5.13, the readers are referred to the original paper.\(^{102}\)

Earlier, Kwei\(^{97}\) proposed an expression that has the same form as eq 5.12, but \( K_0 \) and \( q \) in the Kwei expression are adjustable parameters. Kwei then suggested that the empirical parameter \( q \) in his expression describes the strength of specific interactions with positive values representing strong specific interactions between the constituent components and negative values representing weak specific interactions between the constituent components.

On the other hand, values of composition-dependent \( q \) defined by eq 5.13 can be calculated accurately with the information on the various quantities appearing in the expression, i.e., there are no adjustable parameters in eqs 5.12 and 5.13. Let us consider the four PVPh-based miscible blend systems investigated in this study. Notice that the numerator on the right-hand side of eq 5.13 consists of three terms. The first term
\[
( -X_B n_B \Delta h_B ([p_{BB}^o]_{T_{gm}} - [p_{BB}^o]_{T_{gB}}) )
\]
describes the difference in self-association of PVPh between two different temperatures, one at the midpoint of blend glass transition temperature \( T_{gm} \) and another at the glass transition temperature of neat PVPh \( T_{gB} \); i.e., this term represents the effect of temperature on self-association. The second term
\[
( -n_B \Delta h_B [p_{BB} - p_{BB}^o]_{T_{gm}} )
\]
describes the difference in self-association of PVPh between two situations, one after mixing and another before mixing; i.e., this term represents the
effect of mixing on self-association of PVPh. The third term \((-n_A \Delta h_{BA}[P_{BA}]_{T_{gm}})\)
describes the inter-association (intermolecular attractive interactions) between the
constituent components at \(T_{gm}\). Using the numerical values of the parameters listed in
Tables 5.1 and 5.6 we calculated values of the three terms appearing on the right-hand
side of eq 5.13 for the four PVPh-based blend systems and they are given in Table 5.7.

Table 5.6. Parameters Used to Predict the Composition Dependence of \(T_{gm}\) for Four
PVPh-Based Blend Systems Investigated in This Study

<table>
<thead>
<tr>
<th>polymer</th>
<th>PVAc</th>
<th>PVME</th>
<th>P2VP</th>
<th>P4VP</th>
<th>PVPh</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_A)</td>
<td>86.1</td>
<td>58.1</td>
<td>105.2</td>
<td>105.2</td>
<td>120.2</td>
</tr>
<tr>
<td>(T_{gA}) (°C)a</td>
<td>28</td>
<td>−19</td>
<td>97</td>
<td>153</td>
<td>(T_{gB} = 180)°C</td>
</tr>
<tr>
<td>(\Delta C_pA) (cal/g K)b</td>
<td>0.108</td>
<td>0.142</td>
<td>0.156</td>
<td>0.156</td>
<td>(\Delta C_{PB} = 0.128) cal/g K</td>
</tr>
</tbody>
</table>

aExperimental data. b Obtained by the heat capacity group contribution method.212

The following observations are worth noting in Table 5.7. (1) The magnitude of the
first term on the right-hand side of eq 5.13 is much smaller than that of the other terms,
indicating that the effect of temperature on self-association makes rather small
contributions to the overall values of \(q\) defined by eq 5.13. (2) For the PVPh/PVAc blend
system, the magnitude of the second term on the right-hand side of eq 5.13 is comparable
with or slightly larger than that of the third term, the two terms having opposite signs.
This observation suggests that values of \(q\) (i.e., the sum of the three terms in eq 5.13) can
be even negative for the blends having less than say about 50 wt % of PVPh in
PVPh/PVAc blends, indicating that the self-association of phenolic –OH groups in the
Table 5.7. Values of Three Terms on the Right-Hand Side of Eq 5.13 for Four PVPh-Based Blend Systems Investigated in This Study

<table>
<thead>
<tr>
<th>Blend System</th>
<th>X_B n_B Δh_B</th>
<th>{[p^0_{BB}]<em>{Tgm} - [p^0</em>{BB}]_{TeB}}</th>
<th>-n_B Δh_B [p_{BB} - p^0_{BB}]_{Tgm}</th>
<th>-n_A Δh_{BA} [p_{BA}]_{Tgm}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVPh/PVAc</td>
<td>20/80</td>
<td>0.22</td>
<td>-6.35</td>
<td>5.31</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td>0.74</td>
<td>-8.54</td>
<td>7.52</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>1.13</td>
<td>-7.00</td>
<td>6.69</td>
</tr>
<tr>
<td></td>
<td>80/20</td>
<td>0.97</td>
<td>-3.79</td>
<td>3.92</td>
</tr>
<tr>
<td>PVPh/PVME</td>
<td>20/80</td>
<td>0.19</td>
<td>-7.28</td>
<td>7.98</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td>0.73</td>
<td>-10.58</td>
<td>12.14</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>1.38</td>
<td>-8.50</td>
<td>10.78</td>
</tr>
<tr>
<td></td>
<td>80/20</td>
<td>1.53</td>
<td>-4.27</td>
<td>6.17</td>
</tr>
<tr>
<td>PVPh/P2VP</td>
<td>20/80</td>
<td>0.12</td>
<td>-6.73</td>
<td>9.08</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td>0.25</td>
<td>-10.62</td>
<td>14.68</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>0.28</td>
<td>-8.60</td>
<td>12.11</td>
</tr>
<tr>
<td></td>
<td>80/20</td>
<td>0.18</td>
<td>-4.18</td>
<td>6.28</td>
</tr>
<tr>
<td>PVPh/P4VP</td>
<td>20/80</td>
<td>0.01</td>
<td>-6.14</td>
<td>8.97</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td>-0.12</td>
<td>-9.95</td>
<td>14.52</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>-0.27</td>
<td>-8.68</td>
<td>12.42</td>
</tr>
<tr>
<td></td>
<td>80/20</td>
<td>-0.30</td>
<td>-4.25</td>
<td>6.43</td>
</tr>
</tbody>
</table>
blends would be predominant over the intermolecular attractive interactions between the constituent components. Under such circumstances, \( q \) defined by eq 5.13 does not reflect the strength of intermolecular attractive interactions in miscible PVPh/PVAc blends. (3) For low concentrations of PVPh in the PVPh/PVME blend system, the magnitude of the third term, having a positive sign, on the right-hand side of eq 5.13 are slightly larger than that of the second term having a negative sign, and the magnitude of the third term become larger with increasing concentration of PVPh. This observation indicates that intermolecular attractive interactions between the constituent components in PVPh/PVME blends become predominant over self-association of PVPh in the blends. (4) For the PVPh/P2VP and PVPh/P4VP blend systems, the magnitude of the third term, having a positive sign, on the right-hand side of eq 5.13 is conspicuously larger than that of the second term, having a negative sign, over the entire blend composition. This observation indicates that the intermolecular attractive interactions between the constituent components are predominant over the self-association of PVPh in the PVPh/P2VP and PVPh/P4VP blend systems.

Table 5.8 gives a summary of the values of \( q \) defined by eq 5.13 as a function of composition for all four PVPh-based miscible blend systems investigated. Note in Table 5.8 that the sign of \( q \) can be positive or negative, depending on the sign and the magnitude of the three terms appearing on the right-hand side of eq 5.13 (see Table 5.7). For low concentrations of PVPh (e.g., 20 wt %), since PVPh is surrounded by large amounts of non-self-associating component A, the effect of self-association of PVPh on the values of \( q \) would be small. In this situation, the value of \( q \) reflects the contribution
of inter-association and then a large positive value of \( q \) indicates strong intermolecular interactions in a miscible polymer blend. It can be seen clearly from Table 5.8 that 20/80 PVPh/P4VP blend has a large positive value of \( q \), while 20/80 PVPh/PVAc has a negative value of \( q \). Therefore, we can rank the strength of attractive interactions (SA) in the following order: \( S_{\text{PVPh/P4VP}} > S_{\text{PVPh/P2VP}} > S_{\text{PVPh/PVME}} > S_{\text{PVPh/PVAc}} \). This observation is consistent with that made from the FTIR spectra given in Figure 5.1.

Table 5.8. Values of \( q \) Calculated from Eq 5.13 for Four PVPh-Based Blend Systems Investigated in This Study

<table>
<thead>
<tr>
<th>composition (wt %)</th>
<th>PVPh/PVAc blends</th>
<th>PVPh/PVME blends</th>
<th>PVPh/P2VP blends</th>
<th>PVPh/P4VP blends</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/80</td>
<td>-57.43</td>
<td>65.63</td>
<td>111.35</td>
<td>127.78</td>
</tr>
<tr>
<td>40/60</td>
<td>-10.97</td>
<td>90.04</td>
<td>127.16</td>
<td>131.15</td>
</tr>
<tr>
<td>60/40</td>
<td>27.60</td>
<td>110.34</td>
<td>110.24</td>
<td>100.89</td>
</tr>
<tr>
<td>80/20</td>
<td>46.86</td>
<td>115.06</td>
<td>98.46</td>
<td>81.17</td>
</tr>
</tbody>
</table>

We predicted, via eq 5.12, composition-dependent \( T_{gm} \) and they are summarized in Figure 5.11 (filled symbols), in which the dashed line represents a linear relationship, and the solid line is drawn through the predicted values to guide the eyes. It can be seen from Figure 5.11 that the predicted composition-dependence of \( T_{gm} \) for the four PVPh-based miscible polymer blend systems is in good agreement with experimental results. The details of the procedures employed to calculate \( T_{gm} \) are given in the Appendix B.

What is of great interest in Figure 5.11 is that among the four PVPh-based blend systems investigated, PVPh/P4VP and PVPh/P2VP blend systems have positive
deviation from linearity, while PVPh/PVAc and PVPh/PVME blend systems have slightly negative deviation from linearity. Notice that the PVPh/P4VP blend system has a larger deviation from linearity as compared with the PVPh/P2VP blend system.

Figure 5.11. Composition-dependent glass transition temperatures ($T_{gm}$) for (a) PVPh/PVAc blends, (b) PVPh/PVME blends, (c) PVPh/P2VP blends, and (d) PVPh/P4VP blends, in which the dashed line represents a linear behavior, the open symbols ($\bigcirc$) denote experimental data, and the filled symbols ($\bullet$) denoted predicted values from eq 5.12.
5.3 Linear Dynamic Viscoelasticity of Two Miscible Polymer Blends without Specific Interactions Investigated

5.3.1 Log G’ versus Log G” Plots and Time-Temperature Superposition.

It is reported that PS/PVME blends show a LCST behavior. Plots of log G’ versus log G” begin to exhibit temperature dependence at a temperature below LCST, which is still in the single-phase region according to the phase diagram. Kapnistos et al. ascribed the temperature dependence of log G’ versus log G” to dynamical composition fluctuations near the LCST.

Figure 5.12a gives log G’ versus log G” plots at various temperatures for 70/30 PS/PVME blend. It can be observed from Figure 5.12a that these plots are virtually independent of temperature and have the slope of 2 in the terminal region at T ≤ 110 °C and begin to exhibit temperature dependence at 115 °C. Since T_g for 20/80 PS/PVME blend is only -10 °C, the highest temperature we measured for this blend is only 70 °C (= T_g + 80 °C). No temperature dependence of log G’ versus log G” plots for 20/80 PS/PVME blend was observed (Figure 5.12b). Similar observation can be obtained for 50/50 PS/PVME blend.

The master curve of G’ and G” for PS/PVME blends was given in Figure 5.13, which was prepared by shifting the log G’ versus log ω and log G” versus log ω plots at various temperatures to the data at T_r = T_gm + 50 °C as reference temperature. Note that we only use the data at temperatures where log G’ versus log G” plots show temperature independence. It can be seen from Figure 5.13 that the log G’ versus log a_Tω plots have a slope of 2 and log G” versus log a_Tω plots have a slope of 1 in the terminal region. We
can conclude that TTS is applicable to PS/PVME blends and there is no concentration fluctuation in the range of temperature investigated.

Figure 5.12. Log G’ versus log G” plots for: (a) 70/30 PS/PVME blend at different temperatures (°C): (○) 75, (△) 85, (□) 95, (▽) 105, (◇) 110, (●) 115, (▲) 120; (b) 20/80 PS/PVME blend at different temperatures (°C): (○) 20, (△) 30, (□) 40, (▽) 50, (◇) 60, (●) 70.

From above discussion we can see that the temperature independence of log G’ versus log G” plots warrants an application of TTS. This observation is in agreement with that reported by Han and coworkers\textsuperscript{11,213}.

Similarly, the viscoelastic properties of PSAN/PEMA blends were investigated below their phase separation temperature. It was found that, for four blend compositions, the plots of log G’ versus log G” show temperature independence but the slope in the terminal region is a little bit less than 2, as shown in Figure 5.14. The temperature independency suggests that the morphological state of PSAN/PEMA blends did not change in the range of temperatures investigated.
Figure 5. 13. Plots of log $G'$ versus log $\omega_T$ (open symbols), log $G''$ versus log $\omega_T$ (filled symbols), and log tan $\delta$ versus log $\omega_T$ at various temperatures with $T_r = T_g + 50$ °C as the reference temperature for PS/PVME blends: (a) 20/80: $\bigcirc$ 20 °C, $\triangle$ 30 °C, $\square$ 40 °C, $\triangledown$ 50 °C, $\bigtriangleup$ 60 °C, $\bigcirc$ 70 °C; (b) 50/50: $\bigcirc$ 52 °C, $\triangle$ 62 °C, $\square$ 72 °C, $\triangledown$ 82 °C, $\bigtriangleup$ 92 °C; (c) 70/30: $\bigcirc$ 75, $\triangle$ 85, $\square$ 95, $\triangledown$ 105, $\bigtriangleup$ 110.
Figure 5. 14. Plots of log $G'$ versus log $G''$ at various temperatures for PSAN/PEMA blend (a) 20/80: (○) 100 °C (△) 110 °C (□) 120 °C (▽) 130 °C (◇) 140 °C (●) 150 °C (☉) 160 °C; (b) 40/60: (○) 113 °C (△) 123 °C (□) 133 °C (▽) 143 °C (◇) 153 °C (●) 163 °C; (c) 60/40: (○) 125 °C (△) 135 °C (□) 145 °C (▽) 155 °C (◇) 165 °C (●) 175 °C; (d) 80/20: (○) 132 °C (△) 142 °C (□) 152 °C (▽) 162 °C (◇) 172 °C (●) 182 °C
Since PEMA has a very high molecular weight (ca. 300K) with relatively broad polydispersity (1.60), the PEMA is highly entangled, which leads to the slope in the terminal region less than 2. It can be expected that for lower frequency, the slope would be equal to 2.

Also, TTS is applicable to PSAN/PEMA blends, as shown in Figure 5.15. The above observations are very similar to those reported by Pathak et. al.\textsuperscript{26} and Bousmina et al.\textsuperscript{214} for PSAN/PMMA blends.

The values of $a_T$ for each blend were determined by shifting log $G''$ versus log $\omega$ plots along the frequency ($\omega$) axis. Figure 5.16 gives plots of $a_T$ versus $T - T_r$ for PS/PVME and PSAN/PEMA blends with a reference temperature $T_r = T_{gm} + 50$ °C, showing composition independent correlation, suggesting an iso-free volume state at this reference temperature. Single curve for shift factor for all composition was observed, indicating that TTS is applicable to these two blend systems in the range of temperatures investigated.

TTS is applicable for both blend systems of PS/PVME and PSAN/PEMA at temperatures where plots of log $G'$ versus log $G''$ show temperature independence, even for a very large difference in $T_g$ of constituent components ($\Delta T_g = 120$ °C and 50 °C, respectively) and the width of glass transition ($\Delta w_{T_g}$) is broad. A large $\Delta w_{T_g}$ indicate a large concentration fluctuation\textsuperscript{56}, resulting in a narrow range of temperatures which TTS is applicable.
Figure 5.15. Plots of log $G'$ versus log $\alpha T \omega$ (open symbols), log $G''$ versus log $\alpha T \omega$ (filled symbols), and log $\tan \delta$ versus log $\alpha T \omega$ at various temperatures for PSAN/PEMA blend (a) 20/80: (○) 100 °C (△) 110 °C (□) 120 °C (▽) 130 °C (◇) 140 °C (○) 150 °C (○) 160 °C; (b) 40/60: (○) 113 °C (△) 123 °C (□) 133 °C (▽) 143 °C (◇) 153 °C (○) 163 °C; (c) 60/40: (○) 125 °C (△) 135 °C (□) 145 °C (▽) 155 °C (◇) 165 °C (○) 175 °C; (d) 80/20: (○) 132 °C (△) 142 °C (□) 152 °C (▽) 162 °C (◇) 172 °C (○) 182 °C.
Figure 5.16. Plots of $a_T$ versus $T - T_r$ for (a) PS/PVME and (b) PSAN/PEMA blends with $T_r = T_{gm} + 50 \, ^{\circ}C$ as the reference temperature: (○) 0/100, (△) 20/80, (□) 40/60, (▽) 60/40, (◇) 80/20, and (○) 100/0. Full line is the fit to WLF equation.

5.3.2 Plateau Modulus.

The $G_N^0$ values were obtained from the master curves of $G'$ at the frequency where $\tan \delta$ is at a minimum. The plot of $G_N^0$ versus composition shows a linear function of composition for the PSAN/PEMA blends but a negative deviation from linearity for PS/PVME blends, as shown in Figure 5.17.

Using the relationship $M_c = \rho TR / G_N^0$, the entanglement molecular weight $M_c$ can be calculated. The number of entanglement $N = M_w / M_c$ is also calculated and the results are listed in Table 5.9.

It can be seen from Table 5.9 that the number of entanglement for PEMA is very large ($N = 22$), indicating a high entanglement in PEMA due to the high molecular weight.
Figure 5. 17. Comparison of experimental results (filled symbols) with theoretical predictions for the dependence of $G_N^0$ on composition for (a) PS/PVME blends, (b) PSAN/PEMA blends. Curve (1)–(3) represents the predictions made with eqs 5.14–5.16, respectively. Curve (4) represents the prediction made with eq 5.21.

Table 5. 9. Entanglement Characteristics for Various Polymers Investigated

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$</th>
<th>$G_N^0$</th>
<th>$M_c$</th>
<th>$N = M_w/M_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>$1.32 \times 10^5$</td>
<td>$1.2 \times 10^5$</td>
<td>$2.7 \times 10^4$</td>
<td>4.89</td>
</tr>
<tr>
<td>PVME</td>
<td>$1.64 \times 10^5$</td>
<td>$3.5 \times 10^5$</td>
<td>$8.8 \times 10^3$</td>
<td>18.6</td>
</tr>
<tr>
<td>PSAN</td>
<td>$7.07 \times 10^4$</td>
<td>$2.4 \times 10^5$</td>
<td>$1.5 \times 10^4$</td>
<td>4.71</td>
</tr>
<tr>
<td>PEMA</td>
<td>$3.07 \times 10^5$</td>
<td>$2.3 \times 10^5$</td>
<td>$1.4 \times 10^4$</td>
<td>21.9</td>
</tr>
</tbody>
</table>

Generally, mixing between dissimilar chains tend to reduce the entanglement probability. As a result, a negative deviation from linearity in $G_N^0$ versus blend composition plots can be expected. If the difference in the plateau modulus for two components is small, plateau modulus of blend will shows a linear function of composition. From Table 5.9 we can see that $G_N^0$ of PSAN and PEMA are $2.4 \times 10^5$ and
2.3 \times 10^5$, respectively. That is why the $G_N^0$ shows a linear function of composition for the PSAN/PEMA blends.

There are different expressions for the dependence of $G_{Nb}^0$ on composition.

\[
G_{Nb}^0 = w_1 G_{N1}^0 + w_2 G_{N2}^0
\]

\[
G_{Nb}^0 = \left[w_1 [G_{N1}^0]^{1/2} + w_2 [G_{N2}^0]^{1/2}\right]^2
\]

\[
G_{Nb}^0 = \left[w_1 [G_{N1}^0]^{1/3.4} + w_2 [G_{N2}^0]^{1/3.4}\right]^{3.4}
\]

\[
G_{Nb}^0 = \phi_1 G_{N1}^0 + \phi_2 G_{N2}^0 + \phi_1 \phi_2 (\lambda_e - 1) (G_{N1}^0 + G_{N2}^0)
\]

Equations 5.14–5.16 suggest that the plateau modulus of miscible polymer blends is not influenced by the interaction parameter $\chi$. However, Wu\textsuperscript{21, 28, 116} proposed eq 5.17 based on a simple analysis of entanglement. He suggested that there are three types of entanglement points in a blend: 1-1, 2-2, and 1-2. Assume that every contact between two chains of species $i$ and $j$ has a constant probability of entanglement $p_{ij}$. The number of contacts between two similar chains $k$ is proportional to $\phi_k^{-2}$, and that between two dissimilar chains is proportional to $2\phi_1 \phi_2$. The total number of entanglement points is

\[
N = N_1 \phi_1^2 + N_2 \phi_2^2 + 2N_{12} \phi_1 \phi_2
\]

\[
= N_1 \phi_1 + N_2 \phi_2 + \phi_1 \phi_2 [2N_{12} - (N_1 + N_2)]
\]

where $N_1$ and $N_2$ are the entanglement numbers of pure components 1 and 2, respectively. $N_{12}$ is the entanglement number between two dissimilar chains. The entanglement number is related to the entanglement molecular weight and the plateau modulus by

\[
N = M / M_e = MG_N^0 / \rho RT
\]
where $M$ is the molecular weight, $\rho$ is the density, $R$ is the gas constant, and $T$ is the absolute temperature.

Using eq 5.19 into eq 5.18 gives

$$G_{Nb}^0 = \frac{M_1}{M} G_{N1}^0 \phi_1 + \frac{M_2}{M} G_{N2}^0 \phi_2 + \frac{\phi_1 \phi_2 \rho}{M} [2N_{12} - (N_1 + N_2)]RT \quad (5.20)$$

assume that the density is equal to 1 and molecular weight of two components is similar (i.e. $M_b \approx M_1 \approx M_2$), we have

$$G_{Nb}^0 = G_{N1}^0 \phi_1 + G_{N2}^0 \phi_2 + \frac{2\phi_1 \phi_2 \rho}{M_b} [N_{12} - (N_1 + N_2) / 2]RT \quad (5.21)$$

If we assume that $N_{12} = M_b G_{N12}^0 / \rho RT$ and $G_{N12}^0 = \sqrt{G_{N1}^0 G_{N2}^0}$, eq 5.21 can be reduced to eq 5.15.

Since mixing between dissimilar chains tend to reduce the entanglement probability, the value of $N_{12}$ is less than $(N_1 + N_2)/2$. As a result, a negative deviation of $G_N^0$ from linearity can be expected.

The predictions of $G_{Nb}^0$ obtained with eqs 5.14–5.16 are given in Figure 5.17. The predictions of $G_{Nb}^0$ obtained with eq 5.21 are also given in Figure 5.17 and in good agreement with experimental results for these two blend systems. It is worth noting that the value of $N_{12}$ (13.02) for PSAN/PEMA blends is very close to that of $(N_1 + N_2)/2$ (13.30), which indicates that entanglement in these blends are same as those in each component polymer. On the other hand, for PS/PVME blends, $N_{12}$ (3.46) is much smaller than the value of $(N_1 + N_2)/2$ (11.74), suggesting a less entanglement in blends.
Notice that the third term on the right hand side of eq 5.21 has the form similar to that for calculating the enthalpy of mixing from Flory–Huggins theory, that is,

\[
\Delta H_M = z n \phi_1 \phi_2 \left[ e_{12} - \frac{(e_{11} + e_{22})}{2} \right] = \chi \phi_1 \phi_2 RT
\]  

(5.22)

It is reasonable to consider that the third term \(2\phi_1\phi_2[N_{12} - (N_1 + N_2)/2]RT\) is a function of interaction parameter \(\chi\). Based on this, Wu derives eq 5.17 from eq 5.18 and induces a parameter \(\lambda_e\), which is related to interaction parameter \(\chi\) by \(\lambda_e = 1/(1-7.53\chi)\). It should be pointed out that the relationship between \(\lambda_e\) and \(\chi\) is only an empirical expression.

### 5.3.3 Zero–Shear Viscosity

Figures 5.18 and 5.19 gives plots of log \(\eta'\) versus log \(a_T\omega\) for PS/PVME and PSAN/PEMA blends at iso-free volume state (\(T_g + 50^\circ C\)). The zero–shear viscosity for PS/PVME blends was obtained directly from Figure 5.18. On the other hand, it can be seen from Figure 5.19 that the zero–shear viscosity of PSAN/PEMA blends can not be determined using eq 4.1. It is due to the frequency of oscillatory measurement cannot go lower than 10^{-3} rad/s in our laboratory. However, from the measurement of steady-state shear flow, in which shear strain \(\gamma\) can get as low as 10^{-4} s^{-1}, the zero-shear viscosity can be determined.

Figure 5.20 gives plots of log \(\eta\) versus log \(\dot{\gamma}\) (filled symbols) in steady-state shear flow and plots of log \(\eta'\) versus log \(\omega\) (open symbols) in oscillatory shear flow for pure PEMA at 110 and 170 °C (Figure 5.20a) and PSAN/PEMA blends (Figure 5.20b) at \(T_g + 50^\circ C\), respectively. The Cox–Merz rule seems to work for pure PEMA and is valid approximately for the PSAN/PEMA blends.
Figure 5. 18. Plots of log $\eta'$ versus log $\omega$ for the PS/PVME blend system at $T_g + 50 ^\circ$C: (a) PVME; (b) 20/80; (c) 50/50; (d) 70/30; (e) PS.
Figure 5.19. Plots of log $\eta'$ versus log $\omega$ for the PSAN/PEMA blend system at $T_g + 50$ °C: (a) PEMA; (b) 20/80; (c) 40/60; (d) 60/40; (e) 80/20; (f) PSAN.
Figure 5.20. Plots of log $\eta$ versus log $\dot{\gamma}$ (open symbols) and plots of log $\eta'$ versus log $\omega$ (filled symbols) for (a) PEMA at two different temperatures; (b) PSAN/PEMA blends at $T_r = T_g + 50 ^\circ C$; (c) PVPh/PEMA blends at $T_r = T_g + 50 ^\circ C$.

Figure 5.21. Composition dependence of $\eta_0$ at $T_g + 50 ^\circ C$ for: (a) PS/PVME blends, (b) PSAN/PEMA blends. The straight line represents linear behavior.
The composition dependence of zero-shear viscosities of these two blend systems was shown in Figure 5.21. It is seen in Figure 5.21 that both curves show positive deviation from linearity.

There are several semiempirical mixing rules have been proposed to describe the composition dependence of viscosity for polymer blends. One of the simplest mixing rules is the Arrhenius relation

$$\log \eta_b = x_1 \log \eta_1 + x_2 \log \eta_2$$

(5.23)

where $x_i$ are the mole fractions of components 1 and 2. This mixing rule imposes a linear relation between $\log \eta$ and blend component mole fraction.

Wu$^{21,28,116}$ has proposed a mixing rule of the form

$$\log \eta_b = \phi_1 \log \eta_1 + \phi_2 \log \eta_2 + 2\phi_1\phi_2 \log \lambda_e$$

(5.24)

where $\lambda_e$ is a fitting parameter. This relation can be used to describe the different classes of miscible blend behavior, but the relationship between $\lambda_e$ and molecular parameter is uncertain.

Friedman and Porter$^{218}$ have suggested that a blend of polymers of same chemical structures but different molecular weights should follow the mixing rule:

$$\eta_b^{1/3.4} = w_1 \eta_1^{1/3.4} + w_2 \eta_2^{1/3.4}$$

(5.25)

All the relations proposed above are obtained empirically.

On the other hand, Han and Kim$^{22,23}$ developed a molecular theory to predict the linear viscoelastic properties of binary mixtures of miscible blends, using the concept of the tube model of Doi and Edwards.$^{115}$ It suggests that when the viscosity ratio $\eta_{01}/\eta_{02}$ of the constitutive components is much greater than 1, the $\log \eta_b$ versus blend composition
curves show positive deviations for $\chi \approx 0$. Based on the Flory–Huggins interaction parameters reported in the literatures, we know that $\chi$ values for these two blend systems are very small. Thus, for PS/PVME and PSAN/PEMA blend systems, since the viscosity ratio $\eta_{01}/\eta_{02}$ of the constitutive components is much greater than 1 and $\chi \approx 0$, the log $\eta_{0b}$ versus blend composition curves are expected to show positive deviation from linearity.

5.4 Linear Dynamic Viscoelasticity of Four PVPh-Based Miscible Polymer Blend Systems Investigated

5.4.1 Construction of Reduced Plots of Dynamic Moduli, Composition Fluctuations, and Temperature-Temperature Superposition

Figure 5.22 gives plots of log $G'$ versus log $\omega$ and log $G''$ versus log $\omega$ for 20/80 PVPh/PVME blend at various temperatures ranging from 29 to 79 °C. Similar plots were obtained for other blend compositions. It is seen in Figure 5.22 that both $G'$ and $G''$ decrease with increasing temperature. To obtain temperature-independent generalized (reduced) plots for the dynamic loss modulus $G''$, log $G''$ versus log $\omega$ plots given in Figure 5.22 were shifted along the $\omega$ axis to overlap the log $G''$ versus log $\omega$ plots at a reference temperature $T_r = T_{gm} + 50$ °C with $T_{gm}$ being the midpoint of glass transition temperature of 20/80 PVPh/PVME blend, in which 20/80 refers to the weight percent of the constituent components. The amount of shift made along the $\omega$ axis, which is temperature dependent, is commonly referred to as the “shift factor $a_T$.”
Figure 5.22. (a) Log $G'$ versus log $\omega$ plots and (b) log $G''$ versus log $\omega$ plots for 20/80 PVPh/PVME blend at different temperatures (°C): (○) 29, (△) 39, (□) 49, (▽) 59, (◇) 69, (○) 79.

Figure 5.23a gives reduced plots of log $G'$ versus log $a_T\omega$ and log $G''$ versus log $a_T\omega$ for 20/80 PVPh/PVME blend at various temperatures with $T_r = T_g + 50$ °C. Note that in Figure 5.23a the same values of $a_T$ were used to obtain reduced log $G'$ versus log $a_T\omega$ plots. Similar reduced plots of log $G'$ versus log $a_T\omega$ and log $G''$ versus log $a_T\omega$ for other compositions of PVPh/PVME blends were also given in Figure 5.23. In Figure 5.23 we have temperature-independent log $G'$ versus log $a_T\omega$ plots with curvature in the terminal region for all compositions of PVPh/PVME blends investigated. Before making a general statement, let us observe further whether the reduced log $G'$ versus log $a_T\omega$ plots for three other PVPh-based miscible blend systems investigated in this study would also show the same trend as those for PVPh/PVME blends.
Figure 5. 23. Plots of log $G'$ versus log $\omega$ (open symbols), log $G''$ versus log $\omega$ (filled symbols), and log $\tan \delta$ versus log $\omega$ at various temperatures for PVPh/PVME blends: (a) 20/80: (○) 29 °C, (△) 39 °C, (□) 49 °C, (▽) 59 °C, (◇) 69 °C, (○) 79 °C; (b) 40/60: (○) 54 °C, (△) 64 °C, (□) 74 °C, (▽) 84 °C, (◇) 94 °C, (○) 104 °C; (c) 60/40: (○) 102 °C, (△) 112 °C, (□) 122 °C, (▽) 132 °C, (◇) 142 °C, (○) 152 °C; (d) 80/20: (○) 136 °C, (△) 146 °C, (□) 156 °C, (▽) 166 °C, (◇) 176 °C.
Figure 5.24 gives log $G'$ versus log $a_T\omega$ and log $G''$ versus log $a_T\omega$ plots for PVPh/PVAc blends at various temperatures with $T_r = T_{gm} + 50$ °C. Figure 5.25 gives log $G'$ versus log $a_T\omega$ and log $G''$ versus log $a_T\omega$ plots for PVPh/P2VP blends at various temperatures with $T_r = T_{gm} + 50$ °C. Figure 5.26 gives log $G'$ versus log $a_T\omega$ and log $G''$ versus log $a_T\omega$ plots for PVPh/P4VP blends at various temperatures with $T_r = T_{gm} + 50$ °C. It is clearly seen in Figures 5.23–5.26 that the reduced log $G'$ versus log $a_T\omega$ plots for all four PVPh-based miscible blend systems show temperature independence in the terminal region.

Earlier, Ajii et al.\textsuperscript{30,31} and Kapnistos\textsuperscript{35} reported that the log $G'$ versus log $a_T\omega$ plots in the terminal region of miscible PS/PVME blends without specific interaction varied with temperature and had a curvature in the terminal region. The authors concluded that TTS failed for the PS/PVME blends because log $G'$ versus log $a_T\omega$ plots varied with temperature. If we apply the same rheological criterion, we can conclude that TTS would work well for all four PVPh-based miscible blend systems investigated in the present study. Notice that there is a clear difference in the temperature dependence of log $G'$ versus log $a_T\omega$ plots between the miscible PVPh/PVME blend system with hydrogen bonding and the miscible PS/PVME blend system without specific interaction reported by Kim et al.\textsuperscript{36}
Figure 5. Plots of log $G'$ versus log $a_\tau\omega$ (open symbols), log $G''$ versus log $a_\tau\omega$ (filled symbols), and log tan $\delta$ versus log $a_\tau\omega$ at various temperatures for PVPh/PVAc blends:

(a) 20/80: (○) 74 °C, (△) 84 °C, (□) 94 °C, (▽) 104 °C, (◇) 114 °C, (○) 124 °C; (b) 40/60: (○) 100 °C, (△) 110 °C, (□) 120 °C, (▽) 130 °C, (◇) 140 °C, (○) 150 °C; (c) 60/40: (○) 131 °C, (△) 141 °C, (□) 151 °C, (▽) 161 °C, (◇) 171 °C; (d) 80/20: (○) 162 °C, (△) 172 °C, (□) 182 °C, (▽) 192 °C, (◇) 202 °C.
Figure 5.25. Plots of log $G'$ versus log $a_T\omega$ (open symbols), log $G''$ versus log $a_T\omega$ (filled symbols), and log tan $\delta$ versus log $a_T\omega$ at various temperatures for PVPh/P2VP blends: (a) 20/80: ($\bigcirc$) 151 °C, ($\triangle$) 161 °C, ($\Box$) 171 °C, ($\triangledown$) 181 °C, ($\bigcirc$) 191 °C, ($\bigcirc$) 201 °C; (b) 40/60: ($\bigcirc$) 176 °C, ($\triangle$) 186 °C, ($\Box$) 196 °C, ($\triangledown$) 206 °C, ($\bigcirc$) 216 °C, ($\bigcirc$) 226 °C; (c): ($\bigcirc$) 191 °C, ($\triangle$) 201 °C, ($\Box$) 211 °C, ($\triangledown$) 221 °C, ($\bigcirc$) 231 °C; (d) 80/20: ($\bigcirc$) 201 °C, ($\triangle$) 211 °C, ($\Box$) 221 °C, ($\triangledown$) 231 °C, ($\bigcirc$) 241 °C.
Figure 5.26. Plots of log \(G'\) versus log \(\omega\) (open symbols), log \(G''\) versus log \(\omega\) (filled symbols), and log \(\tan\delta\) versus log \(\omega\) at various temperatures for PVPb/P4VP blends: (a) 20/80: (○) 209 °C, (△) 219 °C, (□) 229 °C, (▽) 239 °C; (b) 40/60: (○) 216 °C, (△) 226 °C, (□) 236 °C, (▽) 246 °C; (c) 60/40: (○) 222 °C, (△) 232 °C, (□) 242 °C, (▽) 252 °C; (d) 80/20: (○) 216 °C, (△) 226 °C, (□) 236 °C, (▽) 246 °C.
Figure 5.27 gives plots of log $a_T$ versus $T - T_r$ with $T_r = T_{gm} + 50 \, ^\circ C$ for the four PVPh-based miscible polymer blend systems investigated, in which symbols represent values of $a_T$ that were obtained by shifting log $G''$ versus log $\omega$ plots along the $\omega$ axis with $T_r = T_{gm} + 50 \, ^\circ C$ for each blend. The solid lines in Figure 5.27 are theoretical predictions from the WLF expression\textsuperscript{108}

$$\log a_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)}$$ \hspace{1cm} (5.26)

In obtaining the solid lines in Figure 5.27, the constants $C_1$ and $C_2$ in eq 5.26 were determined by fitting the experimentally determined $a_T$ to eq 5.26, and the values of the WLF constants determined for each blend system are summarized in Table 5.10. It is seen from Figure 5.27 that plots of log $a_T$ versus $T - T_r$ are independent of blend composition for each blend system, indicating an iso-free volume state at the reference temperature. It can be concluded from Figure 5.27 that an application of TTS to all four PVPh-based miscible blend systems is warranted. It worth noting that by choosing different reference temperature, shift factors for each blend are different. For example, the plots of log $a_T$ versus $T - T_r$ with different reference temperature $T_r$ for 60/40 PVPh/PVME blend are shown in Figure 5.28.
Figure 5. Plots of $a_T$ versus $T - T_r$ with $T_r = T_{gm} + 50$ °C as the reference temperature for (a) PVPh/PVAc blends, (b) PVPh/PVME blends, (c) PVPh/P2VP blends, and (d) PVPh/P4VP blends at various blend compositions: (□) 0/100, (△) 20/80, (□) 40/60, (▽) 60/40, (◇) 80/20, and (○) 100/0. The solid line represents a fit to the WLF expression.
Table 5.10. WLF Constants for Four PVPh-Based Blend Systems Investigated in This Study

<table>
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<th>blends</th>
<th>$C_1$</th>
<th>$C_2$ (°C)</th>
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</thead>
<tbody>
<tr>
<td>PVPh/PVAc blends</td>
<td>7.74</td>
<td>105.88</td>
</tr>
<tr>
<td>PVPh/PVME blends</td>
<td>8.81</td>
<td>140.23</td>
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<tr>
<td>PVPh/P2VP blends</td>
<td>6.76</td>
<td>101.59</td>
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<tr>
<td>PVPh/P4VP blends</td>
<td>5.14</td>
<td>86.49</td>
</tr>
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</table>

Figure 5.28. Reference temperature dependence of shift factor $a_T$ for PVPh/PVME 60/40 blend at different reference temperature: (○) $T_g + 30$ °C, (△) $T_g + 40$ °C, (□) $T_g + 50$ °C, (▽) $T_g + 60$ °C, (◇) $T_g + 70$ °C, and (○) $T_g + 80$ °C.
Earlier Yang et al.\textsuperscript{24} observed that the plots of log $a_T$ versus $T$ were independent of blend composition for PMMA/PSAN blends, but dependent upon blend composition for PMMA/PVDF blends. They further observed that TTS worked very well for PMMA/PSAN blends while TTS failed for PMMA/PVDF blends. One of the differences between PMMA/PSAN blends and PMMA/PVDF blends is that the difference in $T_g$, $\Delta T_g$, between the constituent components of PMMA/PSAN blends is relatively small ($\approx 20^\circ\text{C}$) while PVDF in PMMA/PVDF blends is a semicrystalline polymer. According to the observations made by Pathak et al.\textsuperscript{26} and Friedrich et al.,\textsuperscript{49} TTS would work for miscible polymer blends without specific interaction when $\Delta T_g$ is about $20^\circ\text{C}$ or less. However, the same empirical criterion does not seem applicable to the four PVPh-based miscible blend systems investigated in this study, because $\Delta T_g = 152^\circ\text{C}$ for PVPh/PVAc blends, $\Delta T_g = 199^\circ\text{C}$ for PVPh/PVME blends, $\Delta T_g = 83^\circ\text{C}$ for PVPh/P2VP blends, and $\Delta T_g = 27^\circ\text{C}$ for PVPh/P2VP blends. That is, irrespective of the large differences in $\Delta T_g$ among the four PVPh-based miscible blend systems, log $a_T$ versus $T - T_r$ plots are independent of blend composition (see Figure 5.27) and log $G'$ versus log $a_T\omega$ plots in the terminal region are independent of temperature for all four PVPh-based miscible blend systems (see Figures 5.23–5.26). If we maintain the view that a failure of TTS in miscible polymer blends without specific interaction (e.g., PEO/PMMA blends; PS/PVME; PS/PSαMS blends; PI/PVE blends) is associated with the presence of concentration fluctuations and dynamic heterogeneity, we are then led to conclude that the extent of concentration fluctuations and dynamic heterogeneity in the four PVPh-based miscible
blend systems with hydrogen bonding might be very small, if not negligible, because TTS apparently works.

It is appropriate to discuss at this juncture the previous rheological studies on PVPh-based miscible polymer blends. Akiba and Akiyama\textsuperscript{86} reported on the linear dynamic viscoelasticity of PVPh/PVME and PS/PVME blend systems. They observed that log $a_T$ versus $T - T_r$ plots were virtually identical and the slope of log $G'$ versus log $a_T \omega$ plots in the terminal region was 2 for both PVPh/PVME and PS/PVME blend systems, in spite of the fact that PVPh/PVME blends are expected to form hydrogen bonds. However, Akiba and Akiyama did not present FTIR spectra of the PVPh/PVME blends employed. That is, the study of Akiba and Akiyama did not reveal any difference in linear dynamic viscoelasticity between PS/PVME blends without specific interaction and PVPh/PVME blends with specific interactions. On the other hand, in the present study we have presented, via FTIR spectra (see Figure 5.1a), clear evidence of the formation of hydrogen bonds between the constituent components in the PVPh/PVME blends employed. The only obvious difference between the two studies is the molecular weights of PVPh and PVME; namely, in the study of Akiba and Akiyama $M_w = 5.0 \times 10^3$ for PVPh and $M_w = 7.42 \times 10^4$ for PVME, while in the present study $M_w = 2.16 \times 10^4$ for PVPh and $M_w = 1.64 \times 10^5$ for PVME. Nonetheless, we cannot reconcile the differences between the two studies.

Cai et al.\textsuperscript{87} reported the linear dynamic viscoelasticity of PVPh/PEO blends. Note that PVPh and PEO are known to be miscible for PEO content less than about 60 wt % and form hydrogen bonds.\textsuperscript{79, 121} Cai et al. observed that plots of log $G'$ versus log $a_T \omega$
and log $G''$ versus log $a_T$ with $T_r = T_{gm} + 15 \, ^\circ C$ was independent of temperature and the slope of log $G'$ versus log $a_T$ plots in the terminal region was much smaller than 2. Such experimental results are very similar to those (see Figures 5.23–5.26) obtained for the four PVPh-based miscible polymer blend systems investigated in the present study. However, Cai et al. reported that plots zero-shear viscosity ($\eta_{0,b}$) versus blend composition prepared at $T_r = T_g + 15 \, ^\circ C$ went through a maximum at a weight fraction of PEO ($w_{PEO}$) of about 0.2 and then a minimum at $w_{PEO} \approx 0.25$. We are of the opinion that such a seemingly anomalous composition dependence of $\eta_{0,b}$ of the PVPh/PEO blends might be attributable to the choice of the reference temperature ($T_r$) very close to the $T_g$ of the blends. Further, Cai et al. reported a very strong composition dependence of log $a_T$ versus $T - T_r$ plots at $T_r = T_g + 15 \, ^\circ C$ for the PVPh/PEO blends employed, which is at variance with our results (see Figure 5.27) for the four PVPh-based miscible blends investigated in this study. Again, we are of the opinion that the strong composition dependence of log $a_T$ versus $T - T_r$ plots at $T_r = T_g + 15 \, ^\circ C$ for the PVPh/PEO blends observed by Cai et al. might be attributable to the choice of $T_r$ very close to the $T_g$ of the blends.

5.4.2 Log $G'$ versus Log $G''$ Plots, Composition Fluctuations, and Time-Temperature Superposition.

Log $G'$ versus log $G''$ plots at various temperatures are given in Figure 5.29 for PVPh/PVAc blends in Figure 5.30 for PVPh/PVME blends, in Figure 5.31 for PVPh/P2VP blends, and in Figure 5.32 for PVPh/P4VP blends. In Figures 5.29–5.32
Figure 5. 29. Log $G'$ versus log $G''$ plots for PVPh/PVAc blend at different temperatures: (a) 20/80: (○) 74 °C, (△) 84 °C, (□) 94 °C, (▽) 104 °C, (◇) 114 °C, (◯) 124 °C; (b) 40/60: (○) 100 °C, (△) 110 °C, (□) 120 °C, (▽) 130 °C, (◇) 140 °C, (◯) 150 °C; (c) 60/40: (○) 131 °C, (△) 141 °C, (□) 151 °C, (▽) 161 °C, (◇) 171 °C; (d) 80/20: (○) 162 °C, (△) 172 °C, (□) 182 °C, (▽) 192 °C, (◇) 202 °C.
Figure 5. Log $G'$ versus log $G''$ plots for PVPh/PVME blends at different temperatures: (a) 20/80: (○) 29 °C, (△) 39 °C, (□) 49 °C, (▽) 59 °C, (◇) 69 °C, (○) 79 °C; (b) 40/60: (○) 54 °C, (△) 64 °C, (□) 74 °C, (▽) 84 °C, (◇) 94 °C, (○) 104 °C; (c) 60/40: (○) 102 °C, (△) 112 °C, (□) 122 °C, (▽) 132 °C, (◇) 142 °C, (○) 152 °C; (d) 80/20: (○) 136 °C, (△) 146 °C, (□) 156 °C, (▽) 166 °C, (◇) 176 °C.
Figure 5. 31. Plots of log $G'$ versus log $G''$ for PVPh/P2VP blends at different temperatures: (a) 20/80: (○) 151 °C, (△) 161 °C, (□) 171 °C, (▽) 181 °C, (◇) 191 °C, (☐) 201 °C; (b) 40/60: (○) 176 °C, (△) 186 °C, (□) 196 °C, (▽) 206 °C, (◇) 216 °C, (☐) 226 °C; (c): (○) 191 °C, (△) 201 °C, (□) 211 °C, (▽) 221 °C, (◇) 231 °C; (d) 80/20: (○) 201 °C, (△) 211 °C, (□) 221 °C, (▽) 231 °C, (◇) 241 °C.
Figure 5. 32. Plots of log $G'$ versus log $G''$ for PVPh/P4VP blends annealed at 200 °C for 3 h: (a) 20/80: (○) 209 °C, (△) 219 °C, (□) 229 °C, (▽) 239 °C; (b) 40/60: (○) 216 °C, (△) 226 °C, (□) 236 °C, (▽) 246 °C; (c) 60/40: (○) 222 °C, (△) 232 °C, (□) 242 °C, (▽) 252 °C; (d) 80/20: (○) 216 °C, (△) 226 °C, (□) 236 °C, (▽) 246 °C.
there are three common features in all four PVPh-based miscible polymer blends: (1) log \( G' \) versus log \( G'' \) plots are independent of temperature over the entire range of temperatures investigated, (2) the curvature of log \( G' \) versus log \( G'' \) plots in the terminal region becomes progressively pronounced as the amount of PVPh in each blend is increased from 20 to 80 wt %, and (3) the temperature independence of log \( G' \) versus log \( G'' \) plots is very similar to the corresponding log \( G' \) versus log \( a_T \omega \) plots, especially in the terminal region.

Let us consider the origin of curvature in the terminal region of log \( G' \) versus log \( G'' \) plots given in Figures 5.29–5.32. The factors that could have caused curvature in the terminal region of log \( G' \) versus log \( G'' \) plots are: (1) cross-linking, (2) dynamic heterogeneity, and (3) intermolecular attractive interaction (hydrogen bonding). If there had any cross-linking in any of the four PVPh-based miscible blends, temperature-independent log \( G' \) versus log \( G'' \) plots could not have obtained and thus TTS should have failed. However, from Figures 5.29–5.32 we can conclude that TTS works for all four PVPh-based blend systems. Therefore cross-linking of PVPh cannot be a reason for the curvature in the terminal region of log \( G' \) versus log \( G'' \) plots. It was reported that the PVPh/P4VP blends, for instance, were miscible even on the scale of 2–3 nm,\(^8^2\) suggesting that dynamic heterogeneity may not be a cause for the curvature in the terminal region of log \( G' \) versus log \( G'' \) plots. Then, the curvature in the terminal region of log \( G' \) versus log \( G'' \) plots is most likely due to the presence of intermolecular attractive interactions in the PVPh-based miscible blend systems investigated in this study.

Previously, Zhang and coworker\(^{68,73,74,219-221}\) investigated the dynamics of polymer miscible blends with specific interactions using broadband dielectric relaxation
spectroscopy (DRS). They found that strong intermolecular interactions were able to damp concentrations fluctuations and couple components’ segmental relaxations, which can be clearly observed when the two constituent components have very large T_g difference. Since concentration fluctuation is related to dynamic heterogeneities, it can speculate that dynamic heterogeneity is insignificant in miscible blends with strong specific interactions. In fact, Zhang et al. found that insignificant dynamic heterogeneity in PVPh/P2VP blends.

Recall that referring to Figure 4.5 for neat PVPh, we attributed the curvature in the terminal region of log G’ versus log G” plots to the self-association of phenoxy –OH groups in PVPh (see Figure 4.1 for FTIR spectrum of PVPh). According to Han and coworkers, the temperature independence of log G’ versus log G” plots signifies little or no morphological change occurring in a polymer (or polymer blend) over the range of temperatures investigated, while log G’ versus log G” plots are expected not only to be independent of temperature but also to have a slope of 2 in the terminal region for all homogeneous polymeric liquids including the block copolymers in the disordered state and the liquid-crystalline polymers in the isotropic state. Previously, Ajii et al. reported that log G’ versus log G” plots in the terminal region of PS/PVME blends, which exhibit lower critical separation temperature (LCST) behavior, had little or no temperature dependence at temperatures below LCST (i.e., in the homogeneous state), but had a strong temperature dependence at temperatures above LCST (i.e., in the immiscible state). Nonetheless, the log G’ versus log G” plots in the terminal region for the homogeneous state of PS/PVME blends had a slope much less than 2, which was attributed to significant concentration fluctuations and dynamic heterogeneity. However,
the presence of curvature in the terminal region of log $G'$ versus log $G''$ plots for the four PVPh-based miscible blends investigated in this study must have a different origin because TTS works for those blends and thus significant concentration fluctuations and dynamic heterogeneity might have not occurred in those blends. In other words, the origin of curvature in the terminal region of log $G'$ versus log $G''$ plots for the four PVPh-based miscible blends is attributable to the presence of strong intermolecular attractive interactions (hydrogen bonding).

5.4.3 Plateau Modulus

The $G^0_N$ values were obtained from the master curves of $G'$ at the frequency where tan $\delta$ is at a minimum. The plot of $G^0_N$ versus composition shows a negative deviation from linearity for all four PVPh-based blends, as shown in Figure 5.33. As we discussed above for blends without specific interactions, mixing between dissimilar chains tend to reduce the entanglement probability. As a result, a negative deviation from linearity in $G^0_N$ versus blend composition plots can be predicted.

The predictions of $G^0_{Nb}$ obtained with eqs 5.14–5.16 are given in Figure 5.33. The predictions of $G^0_{Nb}$ obtained with eq 5.21 are also given in Figure 5.33 and in good agreement with experimental results for these four blend systems. It is worth noting that the values of $N_{12}$ for all PVPh-based blends are much smaller than that of $(N_1 + N_2)/2$, suggesting a less entanglement in blends.

It should be pointed out that eq 5.21 is derived from mean-field theory, which might not be applied to blends with specific interactions.
Figure 5.33. Comparison of experimental results (symbol ) with theoretical predictions for the dependence of $G_N^0$ on composition for (a) PVPh/PVAc blends, (b) PVPh/PVME blends, (c) PVPh/P2VP blends, (d) PVPh/P4VP blends. Curve (1)–(3) represents the predictions made with eq 5.14–5.16, respectively. Curve (4) represents the prediction made with eq 5.21.
5.4.4 Zero–Shear Viscosity

Figures 5.34-5.38 gives plots of log $\eta'$ versus log $a_T\omega$ for five neat polymers and four PVPh-based blend systems investigated at iso-free volume state ($T_{gm} + 50^\circ$C). It can be seen from Figure 5.34 that a flat region can be observed at low frequency for all five neat polymers investigated. Therefore, the zero-shear viscosity for five neat polymers can be obtained directly from Figure 5.34. However, from Figures 5.35-5.38 we can see that for some blend compositions, the curves are not flat at low frequency. However, we still take values of $\eta_0$ from these curves. Since $\eta' = G''/\omega$, if $G''$ is proportional to $\omega$, $\eta'$ is constant. From the above discussion we can see that the slope in the terminal region of log $G''$ versus log $a_T\omega$ plots is close to 1. As a result, at low frequency (say $10^{-3}$), $\eta'$ is close to $\eta_0$. (That is, $\eta_0 = \lim_{a_T\omega \to 0} (G''/a_T\omega)$)

The composition dependence of $\eta_0$ for four PVPh-based blend systems investigated was given in Figure 5.39. It is seen in Figure 5.39 that the curves show a positive deviation. Since the real $\eta_0$ can only larger or equal to the values we taken, the trend of positive deviation can not be wrong. As we discussed above, PVPh-based blend systems behave like a physically cross-linked network because of the specific interactions (of course, intermolecular hydrogen bonding is only a transient network with relatively weak bonds compared to covalently cross-linked systems). At low shear rates, the network-like structure must be broken for flow. The extra stress it takes to break the structure is measured as an increase in viscosity at low rates. As a result, the composition dependence of $\eta_0$ shows a positive deviation from linearity.
Figure 5. Plots of log $\eta'$ versus log $a_T\omega$ for (a) PVAc, (b) PVME, (c) P2VP, (d) P4VP, and (e) PVPh.
Figure 5.35. Plots of log $\eta'_b$ versus log $a_\tau \omega$ for PVPh/PVAc blends: (a) 20/80, (b) 40/60, (c) 60/40, (d) 80/20.
Figure 5.36. Plots of log $\eta'$ versus log $a_1\omega$ for PVPh/PVME blends: (a) 20/80, (b) 40/60, (c) 60/40, (d) 80/20.
Figure 5. 37. Plots of log $\eta'$ versus log $a_\tau\omega$ for PVPh/P2VP blends: (a) 20/80, (b) 40/60, (c) 60/40, (d) 80/20.
Figure 5. Plots of log $\eta'$ versus log $\omega$ for PVPh/P4VP blends: (a) 20/80, (b) 40/60, (c) 60/40, (d) 80/20.
Figure 5. Composition dependence of zero-shear viscosity of four PVPh-based miscible blend systems investigated: (a) PVPh/PVAc blends, (b) PVPh/PVME blends, (c) PVPh/P2VP blends, and (d) PVPh/P4VP blends.
5.5 Concluding Remarks

In this chapter, we have presented experimental results for the linear dynamic viscoelasticity of four PVPh-based miscible polymer blend systems with hydrogen bonding. We have confirmed that each of the blend systems investigated had hydrogen bonding between the constituent components as determined by FTIR spectroscopy. It was found that the strength of the hydrogen bonds (SH) in the four PVPh-based miscible blends can be ranked as follows: $SH_{PVPh/P4VP} > SH_{PVPh/P2VP} > SH_{PVPh/PVME} > SH_{PVPh/PVAc}$. We have found that the self-association of the phenoxy –OH groups in PVPh and the inter-association (intermolecular attractive interactions) between the constituent components have a profound influence on the linear dynamic viscoelasticity of the respective blend systems.

We have found that log $G'$ versus log $a_{T-\omega}$ and log $G''$ versus log $a_{T-\omega}$ plots and also log $G'$ versus log $G''$ plots for all four PVPh-based blend systems show temperature independence. Further, we have found that plots of log $a_{T-\omega}$ versus $T - T_r$ with $T_r$ being a reference temperature show composition independence in all four PVPh-based blend system investigated, irrespective of the very large differences in the component glass transition temperatures. Therefore, we conclude that an application of TTS is warranted to the four PVPh-based miscible blend systems with hydrogen bonding. If we apply the same empirical criterion, which has been applied to miscible polymer blends without specific interaction (see the Introduction Section), to the four PVPh-based miscible polymer blends investigated in this study, we can conclude that the effects of concentration fluctuations and dynamic heterogeneity on the
rheological behavior of such miscible polymer blends might be very small, if not
negligible. This conclusion, though tentative, is definitely a distinguishing rheological
characteristic between the miscible polymer blends with specific interaction (hydrogen
bonding in the present study) and the miscible polymer blends without specific
interaction. The apparent absence or negligibly small concentration fluctuations and/or
dynamic heterogeneity in the four PVPh-based miscible polymer blends with hydrogen
bonding can be attributed to the presence of self-association (intramolecular interactions)
and/or inter-association (intermolecular attractive interactions) between the constituent
components. It seems very reasonable to speculate that intermolecular attractive
interactions would suppress concentration fluctuations in miscible polymer blends
forming hydrogen bonds.

However, we have observed curvature in the terminal region of log $G'$ versus log $G''$
plots for all four PVPh-based blend systems investigated, and the severity of curvature
becomes more pronounced as the concentration of PVPh in the respective blend systems
is increased. Specifically, for blends with low concentrations of PVPh (e.g., 20 wt %),
since PVPh is surrounded by large amounts of non-self-associating component A, the
fraction of self-association of phenoxy –OH groups is very small. Most of the phenoxy
–OH groups form the intermolecular hydrogen bonds and the blends are miscible.
However, because of the low concentration of PVPh, the number of hydrogen bonds may
not be sufficiently large. We have shown (see Table 5.2) that the fraction of hydrogen
bonded A groups is small (about 20%). As a result, the effect of specific interactions on
the linear viscoelastic properties would be small and thus the curvature in the terminal
region of log $G'$ versus log $G''$ plots is not discernible. However, as the concentration of
PVPh is increased, there are not only intermolecular hydrogen bonds, but also self-association of phenoxy –OH groups. Hydrogen bonding enhances the friction between different segments. Thus, very strong intermolecular interactions between the constituent components in such miscible polymer blends may suppress concentration fluctuations and thus dynamic heterogeneity. It can then be concluded that the curvature in the terminal region of log G’ versus log G” plots is attributable to both self-association and inter-association in PVPh-based miscible blends when concentration of PVPh exceeds a certain critical value.

It is worth mentioning that the balance between self-association and inter-association in miscible polymer blends with hydrogen bonding would vary depending on their relative strength of hydrogen bonding. Let us consider, for illustration, 60/40 PVPh/PVME blend. From the calculation of the fraction of hydrogen bonds in this blend, we find that about 46.19% of the ether groups in PVME are associated with the phenolic –OH groups in PVPh (see Table 5.2). In addition, the fraction of self-associated phenolic –OH groups is about 59.08%, which is much larger than the fraction (about 37.73%) of inter-associated phenolic -OH groups (these values are calculated from Table 5.2 under the assumption that the mole fraction of functional groups is equal to the weight fraction of the constituent components). It can then be concluded that the predominant hydrogen bonding in this blend arises from self-association. As a result, the curvature in the terminal region of log G’ versus log G” plots for the 60/40 PVPh/PVME blend is attributable primarily to the self-association of PVPh rather than inter-association in the blend.
On the other hand, we know from the FTIR spectra (see Figure 5.1) and the composition dependence of $T_g$ (see Figure 5.11) that P4VP forms stronger intermolecular hydrogen bonds with PVPh, for example, in 60/40 PVPh/P4VP blend than with PVME in 60/40 PVPh/PVME blends. From the calculation of the fraction of hydrogen bonds in the 60/40 PVPh/P4VP blend, we find that about 80.34\% (see Table 5.2) of the pyridine groups in P4VP are associated with the phenolic –OH groups in PVPh. Further, the fraction of self-associated phenolic -OH groups in 60/40 PVPh/P4VP blend is only 37.73\%, and 53.56\% of phenolic -OH groups in PVPh is hydrogen-bonded with the pyridine groups in P4VP. As a result, the curvature in the terminal region of log $G'$ versus log $G''$ plots of 60/40 PVPh/P4VP blend is attributable primarily to the inter-association (intermolecular hydrogen bonding) between the phenolic –OH groups in PVPh and the pyridine groups in P4VP, although some self-association is also involved. Similar arguments can be made to PVPh/PVAc and PVPh/P2VP blend systems investigated in this study.

In summary, for the first time, we have presented experimental results, demonstrating a clear distinction in linear dynamic viscoelasticity between the miscible polymer blends with specific interaction (hydrogen bonding in the present study) and the miscible polymer blends without specific interaction.
CHAPTER VI

MISCIBILITY AND RHEOLOGY OF FUNCTIONALIZED POLYNUORBORNENE-BASED BLENDS

6.1 Synthesis of Functionalized Polynorbornenes

6.1.1 Synthesis of HPNBCOOH

Figure 6.1 gives the FTIR spectra for NBCOOH and NBCOOSiMe3. Referring to Figure 6.1a, the absorption peak at 1780 cm⁻¹ corresponds to the vibration of carbonyl group (C=O), and a broad band between 2500–3500 cm⁻¹ represents the carboxylic acid group. Referring to Figure 6.1b, we observe that the carboxylic peak at 1700 cm⁻¹ and a very broad peak centered at 3000 cm⁻¹ disappear, and the ester peak at 1740 cm⁻¹ appears. Also, the absorptions of CH₃ symmetric bending of Si-CH₃ at 1254 cm⁻¹, CH₃ asymmetric bending of Si-CH₃ at 1418 cm⁻¹, and Si-C stretching at 854 cm⁻¹ appear. These observations suggest that the carboxylic acid group was protected in NBCOOSiMe₃.

Figure 6.2 gives the ¹H NMR spectra for NBCOOH and NBCOOSiMe₃. Note in Figure 6.2a that the spectra at δ = 5.7–6.0 ppm represents C=C double bonds, and a weak absorption peak at δ = 11.8 ppm represents the carboxylic acid group (-COOH). Referring to Figure 6.2b, ¹H NMR spectrum shows an absorption at 0.08 ppm for Si-CH₃
Figure 6. FTIR spectra of (a) NB-COOH and (b) NBCOOSiMe3. The numbers in lower part are the wave numbers corresponding to the indicated bonds. w, m, and s represent that the intensity of absorption band is weak, medium, and strong, respectively.
Figure 6.2. $^1$H-NMR spectrum of (a) NB-COOH and (b) NBCOOSiMe$_3$ in DMSO.
Figure 6.3. FTIR spectra of (a) PNBCOOSiMe3 and (b) HPNBCOOH.

Figure 6.4. $^1$H-NMR spectrum of HPNBCOOH in DMSO. Starred peaks are due to solvent.
vibration, indicating the formation of NBCOOSiMe₃. Thus, Combining the FTIR and \(^1\)H NMR spectra we confirm that the monomer, 5-norbornene-2-carboxylic acid, has the right chemical structure as we expected.

After polymerization, the copolymer was hydrogenated and followed by deprotection to provide HPNBCOOH copolymer. Figure 6.3 gives the FTIR spectra for PNB (1) before hydrogenating, (2) after hydrogenating and removing the protective group. It can be seen from Figure 6.3b that a broad band corresponding to carboxylic acid group at 2500~3500 cm\(^{-1}\) appears again (compare with Figure 6.3a) and the absorption band assigned to Si-CH\(_3\) at 1254 cm\(^{-1}\) disappears, which indicates that the trimethylsilyl protection group was removed. Also, the absorption band at 968 cm\(^{-1}\) assigned to the C-H bonds adjacent to trans double bonds was totally absent from the spectrum, which suggests that the copolymer was totally hydrogenated.

From the \(^1\)H NMR spectrum of the HPNBCOOH (Figure 6.4), we can see that there is no olefinic resonance visible after hydrogenation. That is, the resonances between 5.6 and 6.0 ppm completely disappeared. Thus, we have confirmed, via FTIR and \(^1\)H NMR spectroscopies, the chemical structure of the polynorbornene with carboxylic acid groups, HPNBCOOH.

6.1.2 Synthesis of HPNBOH

Figure 6.5 gives the FTIR spectra for NBOH monomer before and after the protection by trimethylsiloxy group. A specific absorption of \(\nu_{OH}\) at 3400 cm\(^{-1}\) indicates the conversion of carboxylic acid groups into the alcohol groups (Figure 6.5a). After protecting, the peak of hydroxyl group at 3000-3600 cm\(^{-1}\) disappears completely (Figure
Figure 6.5. FTIR spectra of (1) NB-OH and (2) NB-CH₂OSiMe₃. The numbers in lower part are the wave numbers corresponding to the indicated bonds. w, m, and s represent that the intensity of absorption band is weak, medium, and strong, respectively.
Figure 6. $^1$H-NMR spectra of NB-CH$_2$OH and NB-CH$_2$OSiMe$_3$ in DMSO. Starred peak is due to solvent.
6.5b). The absorption peak at 1091 cm\(^{-1}\) indicates the vibrations of C-O-Si stretching, at 1252 cm\(^{-1}\) representing the CH\(_3\) symmetric deformation of Si-CH\(_3\), and at 839 cm\(^{-1}\) representing Si-C stretching and CH\(_3\) rocking.

The \(^1\)H NMR spectra for NBOH and NBCH\(_2\)OSiMe\(_3\) are shown in Figure 6.6. It can be observed from Figure 6.6a that the peak for double bond appears at \(\delta = 5.8–6.0\) ppm; the peak for hydroxyl group (−OH) appears at 1.65 ppm. After protection, an absorption at 0.08 ppm for Si-CH\(_3\) vibration appears, indicating the hydroxyl groups was protected, as shown in Figure 6.6b.

The structures of PNBOSiMe\(_3\) and PNBOH are confirmed by the FTIR spectra as shown in Figure 6.7. Namely, comparison of Figure 6.7a with Figure 6.7b reveals that an absorption band at 3000–3600 cm\(^{-1}\) appears again after hydrolysis, which represents the −OH group. And the absorption peaks at 842 cm\(^{-1}\) (Si-C stretching), 1092 cm\(^{-1}\) (C-O-Si stretching) and 1254 cm\(^{-1}\) (CH\(_3\) symmetric deformation of Si-CH\(_3\)) disappeared. The above observations demonstrate that the trimethylsilyl protection group was removed completely. Also, the absorption of double bonds at 1570 cm\(^{-1}\) and the absorption band at 968 cm\(^{-1}\) assigned to the C-H bonds adjacent to trans double bonds are totally absent from the spectra.
Figure 6. 7. FTIR spectra of (1) PNB-OSiMe₃, (2) PNB-OH, and (3) HPNBOH.

6.1.3 Synthesis of HPNBNH₂

Figure 6.8a gives the FTIR spectra of 5-norbornene-2-amine (NBNH₂) monomer, which shows two N-H stretching bands at 3362 and 3294 cm⁻¹, a broad NH₂ scissoring band at 1574 cm⁻¹, and C-N stretching bands at 1020–1220 cm⁻¹. The structure of 5-norbornene-2-methylphthalimide (NB-MP) was also confirmed by FTIR (Figure 6.8b) [1610 cm⁻¹ (νC=C, vinylic), 1710 cm⁻¹ (νC=O, symmetric), 1768 cm⁻¹ (νC=O, asymmetric), 2930 cm⁻¹ (νC-H, methylene)].

After polymerization, the structure of the copolymer of norbornene and 5-norbornene-2-methylphthalimide (PNB-MP) was confirmed by FTIR (Figure 6.9a) [968 cm⁻¹ (νC-H, double bonds), 1380-1470 cm⁻¹ (δCH₂, methylene), 1710 cm⁻¹ (νC=O, symmetric), 1768 cm⁻¹ (νC=O, asymmetric), 2900 cm⁻¹ (νC-H, methylene)].
Figure 6. FTIR spectra of (a) NBNH₂ and (b) NB-MP. The numbers in lower part are the wave numbers corresponding to the indicated bonds. w, m, and s represent that the intensity of absorption band is weak, medium, and strong, respectively.
Figure 6. 9. FTIR spectra for (a) PNB-MP, (b) HPNB-MP, and (c) HPNB-NH₂.

After hydrogenation, it can be observed from FTIR spectra (Figure 6.9b) that the absorption band at 968 cm⁻¹ assigned to the C-H bonds adjacent to trans double bonds, is totally absent from the spectra.

The hydrogenated copolymer of norbornene and 5-norbornene-2-methylphthalimide (HPNB-MP) was hydrazinolyzed to remove the protection group. The structure was confirmed by FTIR (Figure 6.9c). It can be observed in Figure 6.9c that the νC=O absorption bands at 1714 and 1772 cm⁻¹, which comes from the protective groups, phthalimide, disappear completely. The absorption bands for amine groups appear (3322 cm⁻¹, NH₂ stretch; 1606 cm⁻¹, NH₂ scissors; 1098 cm⁻¹, C-N stretch; 838 cm⁻¹, NH₂ wagging and twisting).
6.1.4 Molecular Characteristics of PNB.

The effect of the amount of catalyst and reaction time on molecular weight was investigated, as listed in Table 6.1, from which we can observe that for a longer period (60 min) of reaction, a high-molecular-weight \( (M_w = 2 \times 10^5) \) PNB with a relatively narrow polydispersity (1.22) was obtained when 0.1 wt% of catalyst was employed. However, when the period of reaction was shortened to 20 min with the same amount of catalyst (0.1 wt %), a low-molecular-weight \( (M_w = 2.3 \times 10^4) \) PBN was obtained and the yield was only 10% and the polydispersity became broader (1.51). On the other hand, when the amount of catalyst was increased to 1 wt % with the period of reaction for 60 min, the molecular weight was decreased. For example, when 1wt % of catalyst was used, the molecular weight was \( 2.3 \times 10^4 \). All these features are consistent with the living nature of ROMP.

Table 6. 1. GPC Characterization of PNBs

<table>
<thead>
<tr>
<th>Reaction time (min)</th>
<th>Catalyst added (wt %)</th>
<th>Measured ( M_w )</th>
<th>Calculated ( M_w )</th>
<th>( M_w/M_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.1</td>
<td>23000</td>
<td>184000</td>
<td>1.507</td>
</tr>
<tr>
<td>60</td>
<td>0.1</td>
<td>202000</td>
<td>184000</td>
<td>1.224</td>
</tr>
<tr>
<td>60</td>
<td>1.0</td>
<td>23000</td>
<td>15000</td>
<td>1.197</td>
</tr>
<tr>
<td>60</td>
<td>0.5</td>
<td>46000</td>
<td>30000</td>
<td>1.069</td>
</tr>
</tbody>
</table>

The thermal stability of the polymers is found to be relatively poor. The decomposition temperature of PNBOH is found to be about 200 °C for low-molecular-weight samples \( (M_w = 2 \times 10^4) \) while it increases to 275 °C for high-molecular-weight samples \( (M_w = 2 \times 10^5) \). On the other hand, the thermal degradation temperature of
HPNBCOOH is found to be only 140 °C, which is the onset point of anhydride formation for carboxylic acid group. As a result, later we could not run rheological measurements at temperatures higher than 140 °C for HPNBCOOH.

6.2. Miscibility of Functionalized Polynorbornene-Based Blends

6.2.1 Miscibility of PC/HPNBCOOH Blends

Blends of HPNBCOOH with polycarbonate (PC) were prepared by dissolving both components in THF. Figure 6.10 gives DSC thermograms at a heating rate of 20 °C/min of PC/HPNBCOOH blend system, showing a broad, single glass transition for each blend composition, in which the arrow upward denotes the onset point (Tg₁), the symbol + denotes the midpoint (Tgm), and the arrow downward denotes the end point (Tge) of the glass transition. A single, though broad, glass transition indicates that the blends are miscible over the entire blend composition.

Figure 6.10. DSC thermograms for PC/HPNBCOOH blends during heating at a rate of 20 °C/min: (1) HPNB; (2) 20/80; (3) 40/60; (4) 60/40; (5) 80/20; (6) PC.
Table 6.2 gives a summary of the values of $T_{gi}$, $T_{gm}$, and $T_{ge}$. Also given in Table 6.2 is the width of glass transition, $\Delta w_{Tg} = T_{ge} - T_{gi}$, for each blend composition. Note in Table 6.2 that the difference in component glass transition temperature, $\Delta T_g$, is 91 °C and $\Delta w_{Tg}$ is about 20 °C, which is larger than that (~10 °C) of the constituent components.

Table 6.2. Summary of the Glass Transition Temperature for PC/HPNBCOOH Blends

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$T_{go}$ (°C)</th>
<th>$T_{gm}$ (°C)</th>
<th>$T_{ge}$ (°C)</th>
<th>$\Delta w_{Tg}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPNBCOOH</td>
<td>56</td>
<td>61</td>
<td>66</td>
<td>10</td>
</tr>
<tr>
<td>20/80</td>
<td>61</td>
<td>72</td>
<td>84</td>
<td>23</td>
</tr>
<tr>
<td>40/60</td>
<td>79</td>
<td>92</td>
<td>100</td>
<td>21</td>
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<tr>
<td>60/40</td>
<td>85</td>
<td>97</td>
<td>106</td>
<td>21</td>
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<tr>
<td>80/20</td>
<td>84</td>
<td>97</td>
<td>104</td>
<td>20</td>
</tr>
<tr>
<td>PC</td>
<td>147</td>
<td>153</td>
<td>156</td>
<td>9</td>
</tr>
</tbody>
</table>

Figure 6.11 gives composition dependence of $T_{gm}$ for PC/HPNBCOOH blends, showing negative deviation from linearity. In general, the negative deviation from linearity in the plot of $T_{gm}$ versus blend composition suggests that the strength of attractive interactions between the constituent components of miscible polymer blends is not strong.\(^88\)

Figure 6.12 gives the FTIR spectra of the carbonyl stretching (1650–1750 cm\(^{-1}\)) vibration region for PC/HPNBCOOH blends. It can be seen that there are two carbonyl bands: one assigned to the hydrogen-bonded carboxylic acid dimers at 1700 cm\(^{-1}\) and another one assigned to the hydrogen bonds formed between the –COOH groups in HPNBCOOH with carbonyl groups in PC at 1730 cm\(^{-1}\). The absorption band at 1730
cm$^{-1}$ is not very obvious, indicating that the specific interaction between PC and HPNBCOOH is not strong.

Figure 6.11. Composition-dependent glass transition temperature $T_{gm}$ for PC/HPNBCOOH blends, in which the solid line represents linear behavior and the dash line is obtained from experimental data.

Figure 6.12. FTIR spectra for PC/HPNBCOOH blends in the carbonyl stretching region at room temperature: (a) PC, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80, and (f) HPNBCOOH.
6.2.2 Miscibility of P2VP/HPNBOOCOOH Blends

Blends of HPNBOOCOOH with P2VP were prepared by dissolving both components in pyridine. Figure 6.13 gives DSC thermograms at a heating rate of 20 °C/min of the P2VP/HPNBOOCOOH blend system, showing a broad, single glass transition for each blend composition. The thermograms indicate that the blends are miscible over the entire blend composition.

Figure 6.13. DSC Thermograms for P2VP/HPNBOOCOOH blends during heating at a rate of 20 °C/min: (1) HPNBOOCOOH, (2) 20/80, (3) 40/60, (4) 60/40, (5) 80/20, (6) P2VP.

Table 6.3 gives a summary of the values of $T_{gi}$, $T_{gm}$, $T_{ge}$, and $\Delta w_{T_g}$ of the P2VP/HPNBOOCOOH blend system, showing that $\Delta T_g$ is 36 °C and $\Delta w_{T_g}$ is about 20 °C.

Figure 6.14 gives composition dependence of $T_{gm}$ for P2VP/HPNBOOCOOH blends, showing small negative deviation from linearity. This observation indicates that the strength of attractive interactions between P2VP and HPNBOOCOOH is stronger than that between PC and HPNBOOCOOH (compare Figure 6.14 with Figure 6.11).
Table 6.3. Summary of the glass transition temperature for P2VP/HPNBOOOH blends

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$T_{go}$</th>
<th>$T_{gm}$</th>
<th>$T_{ge}$</th>
<th>$\Delta w_{Tg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPNBOOOH</td>
<td>56</td>
<td>61</td>
<td>66</td>
<td>10</td>
</tr>
<tr>
<td>20/80</td>
<td>59</td>
<td>68</td>
<td>76</td>
<td>17</td>
</tr>
<tr>
<td>40/60</td>
<td>62</td>
<td>74</td>
<td>83</td>
<td>21</td>
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<tr>
<td>60/40</td>
<td>72</td>
<td>80</td>
<td>88</td>
<td>16</td>
</tr>
<tr>
<td>80/20</td>
<td>81</td>
<td>89</td>
<td>100</td>
<td>19</td>
</tr>
<tr>
<td>P2VP</td>
<td>90</td>
<td>97</td>
<td>101</td>
<td>11</td>
</tr>
</tbody>
</table>

Figure 6.14. Composition dependence of $T_{gm}$ for P2VP/HPNBOOOH blends.

Figure 6.15 gives FTIR spectra in the 1500–1800 cm$^{-1}$ range of P2VP/HPNBOOOH blends with various compositions. The absorption band at 1700 cm$^{-1}$ is assigned to the
hydrogen-bonded carboxylic acid dimmers. As the concentration of HPNBCOOH is increased in the blend, the absorption bands of pyridine groups in P2VP shifts from 1590 to 1600 cm$^{-1}$, which is attributed to the attractive interactions between the nitrogen in the pyridine group in P2VP and the –COOH group in HPNBCOOH.$^{230,231}$ Also, the absorption band at 1725 cm$^{-1}$ is assigned to the “free” carbonyl group liberated when the hydrogen bonding between the acid hydroxyl and the pyridine nitrogen group is formed. Based on above observation, it can be concluded that that the intermolecular hydrogen bonds have been formed between the –COOH groups in HPNBCOOH and the pyridine groups in P2VP.

![FTIR spectra](image)

Figure 6. FTIR spectra in the range of 1500–1800 cm$^{-1}$ for P2VP/HPNBCOOH blends at room temperature: (a) HPNBCCOOH, (b) 20/80, (c) 40/60, (d) 60/40, (e) 80/20, and (f) P2VP.
6.2.3 Miscibility of PC/HPNBOH Blends

Blends of hydrogenated polynorbornene with hydroxyl group (HPNBOH) with PC were prepared by dissolving both components in THF. DSC thermograms of PC/HPNBOH blend system show two glass transition for each blend composition (Figure 6.16), which indicates that PC is immiscible with HPNBOH. However, before hydrogenation, polynorbornene with hydroxyl group (PNBOH) shows partly compatibility with PC, as shown in Figure 6.17. Although two T_g's still can be observed, the values of two T_g's are close to each other: one is about 62 °C and the other is 117 °C, which indicates that the blend is partially compatible.

FTIR spectra (Figure 6.18) for PC/HPNBOH blends show that the absorption band at 1774 cm⁻¹ for carbonyl groups in PC and the absorption band center at 3350 cm⁻¹ has no change at all, which indicates that there are no specific interactions between hydroxyl group in HPNBOH and carbonyl group in PC or the interactions are very weak.

![Figure 6.16. DSC thermograms for PC/HPNBOH blends during heating at a rate of 20 °C/min: (1) 10/90; (2) 50/50; (3) 70/30.](image-url)
Figure 6. 17. DSC thermograms for PC/PNBOH blends during heating at a rate of 20 °C/min: (a) 10/90; (b) 20/80.

Figure 6. 18. FTIR spectra for (a) HPNBOH, (b) 25/75 PC/HPNBOH, (c) 90/10 PC/HPNBOH, and (d) PC.
6.2.4 Miscibility of PA66/HPNBNH₂ Blends

Polyamide 66 has a glass transition temperature of about 61 °C, which is very close to the T_g of HPNBNH₂ (ca. 52 °C). Therefore, the composition dependence of T_g for PA66/HPNBNH₂ blends should show a linear relationship if there are no specific interactions. However, the T_g of 80/20 PA66/HPNBNH₂ blend is about 76 °C (Figure 6.19), which is higher than that of the constituent components, indicating a strong interaction between them.

Figure 6.19. DSC thermogram for 80/20 PA66/HPNBNH₂ blends during heating at a rate of 20 °C/min.

6.2.4 Miscibility of PVPh/HPNBCOOH Blends

We also prepared blends of HPNBCOOH with poly(4-vinylphenol) (PVPh). It is found that 60/40 PVPh/HPNBCOOH blend shows a single T_g (Figure 6.20). FTIR spectra of the hydroxyl stretching vibration region and the carbonyl stretching region for PVPh/HPNBCOOH blends is shown in Figure 6.21. It can be observed that two
vibration bands related to “free” and intra-associated hydroxyl groups appear in neat PVPh at 3530 and 3380 cm\(^{-1}\), respectively. For 60/40 PVPh/HPNBCOOH blend, the center of absorption band for the broad hydrogen bonding shifts from 3380 to 3300 cm\(^{-1}\), which assigns to the interaction between the hydroxyl group of PVPh and the carbonyl group in HPNBCOOH. In the range from 2000 to 1600 cm\(^{-1}\), there are two carbonyl bands: one assigned to hydrogen bonded carboxylic acid dimers at 1700 cm\(^{-1}\), another assigned to hydrogen bonds between carboxylic acid groups in HPNBCOOH with hydroxyl group in PVPh at 1730 cm\(^{-1}\). FTIR spectra in both regions confirm that there are specific interactions in PVPh/HPNBCOOH blend.

![DSC thermogram](image)

Figure 6. 20. DSC thermogram of 60/40 PVPh/HPNBCOOH blend
Figure 6.21. FTIR spectra in the range of (a) 4000 to 2400 (hydroxyl stretching region) and (b) 2000 to 1600 (carbonyl stretching region) cm$^{-1}$ for (1) PVPh, (2) 60/40 PC/HPNBCOOH blend, (3) HPNBCOOH.

6.3 Rheological Behavior of HPNBCOOH-Based Blends

Since the onset of anhydride formation for carboxylic acid group is about 140 °C, the range of temperatures for rheological measurements taken was limited to a very narrow range.

6.3.1 Rheology of PC/HPNBCOOH Blends

Figure 6.22 gives log $G'$ versus log $a_T \omega$ and log $G''$ versus log $a_T \omega$ plots for 20/80 and 40/60 PC/HPNBCOOH blends at various temperatures, in which values of temperature-dependent shift factor $a_T$ were obtained by shifting log $G''$ versus log $\omega$ plots along the $\omega$ axis using $T_r = T_{gm} + 50$ °C as a reference temperature. For the reasons that PC/HPNBCOOH blends undergo thermal degradation at 140 °C and the PC/
HPNBCOOH blends having more than 40 wt % PC has a glass transition temperature ($T_{g(e)}$) of about 100 °C (see Table 6.2), we could not carry out rheological measurements for 60/40 and 80/20 PC/PNBCOOH blends. It can be seen in Figure 6.22 that the reduced plots are virtually independent of temperature over the entire range of temperatures tested. Notice, however in Figure 6.22 that the slope in the terminal region of log $G'$ versus log $\alpha_T\omega$ plots is much smaller than 2, and the slope of log $G''$ versus log $\omega$ plots in the terminal region is much smaller than 1. We attribute this observation to the presence of hydrogen bonding between the –COOH groups in HPNBCOOH and the carbonyl groups in PC.

Figure 6.23 gives log $G'$ versus log $G''$ plots for 20/80 and 40/60 PC/HPNBCOOH blends at various temperatures. The following observations are worth noting in Figure 6.23. The log $G'$ versus log $G''$ plots for both blends are virtually independent of temperatures over the entire range of temperatures tested, but the slope of the plots for the 40/60 PC/HPNBCOOH blend is smaller than that for the 20/80 PC/HPNBCOOH blend. This is attributed to the fact that as the amount of PC is increased from 20 to 40 wt % in the blend, the extent of intermolecular attractive interactions between the –COOH groups in HPNBCOOH and the carbonyl groups in PC becomes stronger. It is worth noting that in Figure 6.23 the slope of log $G'$ versus log $G''$ plots in the terminal region is much smaller than 2, which is attributed to the presence of hydrogen bonding between the –COOH groups in HPNBCOOH and the carbonyl groups in PC. It has been observed that the slope of log $G'$ versus log $G''$ plots in the terminal region are 2 (or very close to 2) for monodisperse homopolymers, block copolymers in the disordered state,
liquid-crystalline polymers in the isotropic state,\textsuperscript{225,226,237} and miscible polymer blends without specific interactions.\textsuperscript{36}

Based on Figures 6.22 and 6.23 we can conclude that time-temperature superposition (TTS) is applicable to PC/HPNBOCOOH blend with hydrogen bonding.

![Graphs](image-url)

**Figure 6.22.** Plots of log $G'$ versus log $a_T\omega$ and log $G''$ versus log $a_T\omega$ for PC/HPNBOCOOH blends at various temperatures with $T_r = T_{gm} + 50 \, ^\circ C$ as the reference temperature: (a) and (b) 20/80: (○) 102 °C (△) 112 °C (□) 122 °C (▽) 132 °C; (c) and (d) 40/60: (○) 122 °C (△) 132 °C (□) 142 °C.
Figure 6.24 gives log $G'$ versus log $a_T\omega$ and log $G''$ versus log $a_T\omega$ plots for 20/80, 40/60, 60/40, and 80/20 P2VP/HPNBOOH blends at various temperatures, in which $T_r = T_{gm} + 50$ °C was used as a reference temperature. The following observations are worth noting in Figure 6.24. In all four compositions of P2VP/HPNBOOH blends both log $G'$ versus log $a_T\omega$ and log $G''$ versus log $a_T\omega$ plots are independent of temperature, very similar to the observations made for PC/HPNBOOH blends (see Figure 6.24). While the slope of log $G'$ versus log $a_T\omega$ plots in the terminal region is much smaller than 2, the degree of the deviation from 2 in the slope of log $G'$ versus log $a_T\omega$ plots in the terminal region appear to vary with blend composition. Specifically, the slope of log $G'$ versus log $a_T\omega$ plots in the terminal region for the 60/40 P2VP/HPNBOOH blend is
smaller than that for the 40/60 P2VP/HPNBCOOH blend. This observation is attributable to the stronger intermolecular interactions between the nitrogen in the pyridine group of P2VP and the −COOH groups in HPNBCOOH in the 60/40 P2VP/HPNBCOOH blend than in the 40/60 P2VP/HPNBCOOH blend (see Figure 6.24). Interestingly, notice that the slope of log $G'$ versus log $a_{\tau \omega}$ plots in the terminal region for the 80/20 P2VP/HPNBCOOH blend is larger than that for the 60/40 P2VP/HPNBCOOH blend. Again, this observation is attributable to the weaker intermolecular interactions between the nitrogen in the pyridine group of P2VP and the −COOH groups in HPNBCOOH in the 80/20 P2VP/HPNBCOOH blend than in the 60/40 P2VP/HPNBCOOH blend (see Figure 6.24). This is because a lesser amount of HPBNCOOH is surrounded by a large amount of strongly polar P2VP in the 80/20 P2VP/HPNBCOOH blend and thus a lesser degree of hydrogen bonding occurred in the blend. It is interesting to observe that the slope of log $G'$ versus log $a_{\tau \omega}$ plots in the terminal region for the 20/80 P2VP/HPNBCOOH blend (see Figure 6.24a) is smaller than that for the 80/20 P2VP/HPNBCOOH blend (see Figure 6.24g). This is attributable to the presence of hydrogen-bonded carboxylic acid dimers (see Figure 6.15) when a larger amount (80 wt %) of HPBNCOOH is surrounded by a lesser amount (20 wt %) of P2VP in the 20/80 P2VP/HPNBCOOH blend.
Figure 6. Plots of log $G'$ versus log $aT\omega$ and log $G''$ versus log $aT\omega$ for P2VP/HPNBCOOH blends at various temperatures with $T_r = T_{gm} + 50$ °C as the reference temperature: (a) and (b) 20/80: (○) 98 °C (△) 108 °C (□) 118 °C (▽) 128 °C; (c) and (d) 40/60: (○) 104 °C (△) 114 °C (□) 124 °C (▽) 134 °C; (e) and (f) 60/40: (○) 110 °C (△) 120 °C (□) 130 °C; (g) and (h) 80/20: (○) 119 °C (△) 129 °C (□) 139 °C.
Figure 6.25. Plots of log $G'$ versus log $G''$ for P2VP/HPNBCOOH blends at various temperatures: (a) 20/80: (○) 98 °C (△) 108 °C (□) 118 °C (▽) 128 °C; (b) 40/60: (○) 104 °C (△) 114 °C (□) 124 °C (▽) 134 °C; (c) 60/40: (○) 110 °C (△) 120 °C (□) 130 °C; (d) 80/20: (○) 119 °C (△) 129 °C (□) 139 °C
Figure 6.25 gives log $G'$ versus log $G''$ plots for 20/80, 40/60, 60/40, and 80/20 P2VP/HPNBOOH blends at various temperatures. It can be seen that the plots are independent of temperature for all four blends over the entire range of temperatures tested, very similar to the observation made for the P2VP/HPNBOOH blends in Figure 6.24. Notice again in Figure 6.25 that the slope of log $G'$ versus log $G''$ plots in the terminal region has curvature especially for the 60/40 and 80/20 P2VP/HPNBOOH blends, which is attributed to the presence of hydrogen bonding between the nitrogen in the pyridine group and the –COOH groups in HPNBOOH.

Based on Figures 6.24 and 6.25 we can conclude that TTS is applicable to PC/HPNBOOH blend with hydrogen bonding.

6.4 Concluding Remarks

In this chapter we synthesized, via ring-opening polymerization, hydrogenated functional polynorbornenes, HPBNCOOH, HBNBOH, and HPNBHNH$_2$. The purpose of having synthesized the polymers was to investigate the rheology of model miscible polymer blends with hydrogen bonding. We have found that blends of HPBNCOOH with PC or P2VP are miscible on the basis of DSC thermograms having a single, broad glass transition and the blends form hydrogen bonds over the entire range of blend compositions investigated. FTIR spectroscopy confirmed the interactions between carboxylic acid groups in HPNBOOH and carbonyl groups in PC or pyridine groups in P2VP. On the other hand, we have found that blends of HBNBOH and PC are immiscible as determined from DSC thermograms. Also, there are no specific
interactions between hydroxyl groups in HPNBOH and carbonyl groups in PC can be observed from FTIR spectroscopy.

It is found that the plots of log $G'$ versus log $G''$ show temperature independence and TTS is applicable to both PC/HPBCOOH and P2VP/HPNBCOOH blend systems, which also suggests these blends are miscible.

It has been the general, though strictly empirical, experimental observations\textsuperscript{24,26,48,49} that TTS is applicable to miscible polymer blends without specific interaction only when the difference in glass transition temperature ($\Delta T_g$) between the constituent components, $\Delta T_g$, is about 20 °C or less and TTS fails when $\Delta T_g$ is larger than about 20 °C. It is the general consensus among researchers that concentration fluctuations\textsuperscript{56,57,238,239} and/or dynamic heterogeneity\textsuperscript{34,37,51,53,55,57,239,240} cause the failure of TTS in the miscible polymer blends without specific interaction when $\Delta T_g$ is larger than about 20 °C. Interestingly, however, in the present study we have observed that TTS is applicable to both PC/HPNBCOOH and P2VP/HPNBCOOH blend systems investigated (see Figures 6.22–6.25), in spite of the fact that $\Delta T_g$ is 91 °C for the PC/PNBCOOH blends and $\Delta T_g$ is 36 °C for the P2VP/PNBCOOH blends. Such an observation leads us to speculate that the presence of hydrogen bonds in the PC/PNBCOOH and P2VP/ PNBCOOH blends must have suppressed concentration fluctuations and/or dynamic heterogeneity.
7.1 Conclusions

In this study, we have shown that intramolecular hydrogen bonding between phenolic groups (self-association) can be formed in STVPh copolymers, as confirmed via FTIR spectroscopy. Both the extent of self-association and the glass transition temperature ($T_g$) of the STVPh copolymers are proportional to the content of vinylphenol (VPh). The rheological properties of STVPh copolymers were studied. It was found that with small contents of VPh, the viscoelasticity of STVPh copolymer is similar to that of homopolymer polystyrene. However, as the content of VPh is increased, log $G'$ versus log $G''$ plots have shown temperature independence but have a slope less than 2 in the terminal region, behavior quite different from that of homogeneous polymer without intramolecular interactions. In addition, TTS was found to be applicable to the STVPh copolymers. We have found that reduced log $G'$ versus log $a_{\tau\omega}$ plots have a slope less than 2 and log $G''$ versus log $a_{\tau\omega}$ plots have a slope less than 1 in the terminal region. To investigate whether the observed curvature in the terminal region of log $G'$ versus log $a_{\tau\omega}$ plot arises from cross-linking, we annealed PVPh specimens at different temperatures for various periods. We have found that STVPh copolymers were not cross-linked at the
temperatures investigated. On the other hand, when a PVPh specimen was annealed at high temperatures for a long period, cross-linking occurred and a temperature dependence of log $G'$ versus log $G''$ plots was observed. Therefore, we conclude that the curvature in the terminal region of log $G'$ versus log $G''$ plots for PVPh arose from self-association.

In this study, we have investigated the linear dynamic viscoelasticity of four PVPh-based miscible polymer blend systems with hydrogen bonding. We have confirmed that each of the blend systems investigated formed hydrogen bonds between the constituent components as determined by FTIR spectroscopy. It was found that the strength of the hydrogen bonds (SH) in the four PVPh-based miscible blends can be ranked as follows: $\text{SH}_{\text{PVPh/P4VP}} > \text{SH}_{\text{PVPh/P2VP}} > \text{SH}_{\text{PVPh/PVME}} > \text{SH}_{\text{PVPh/PVAc}}$.

We have found that each blend investigated in this study shows a single, broad glass transition temperature ($T_g$), indicating that the PVPh-based blends are miscible in the entire range of compositions. Regarding the composition dependence of $T_g$, PVPh/P4VP and PVPh/P2VP blend systems have exhibited positive deviation from linearity, while PVPh/PVAc and PVPh/PVME blend systems have exhibited slightly negative deviation from linearity. The predicted composition dependence of $T_g$ using Painter’s Theory for the four PVPh-based miscible blend systems is found to be in good agreement with experimental results.

We have found that log $G'$ versus log $a_T \omega$, log $G''$ versus log $a_T \omega$ plots, and also log $G'$ versus log $G''$ plots for all four PVPh-based blend systems show temperature independence. Further, we have found that plots of log $a_T$ versus $T - T_r$ with $T_r$ being a reference temperature show composition independence in all four PVPh-based blend...
system investigated, including the PVPh/PVME blend system having a very large
difference in the component glass transition temperature ($\Delta T_g$), 199 °C. Therefore we
conclude that an application of TTS to the four PVPh-based miscible blend systems with
hydrogen bonding is warranted. If we apply the same empirical criterion, which has been
applied to miscible polymer blends without specific interaction, to the four PVPh-based
miscible blends investigated in this study, we can conclude that the effects of
concentration fluctuations and dynamic heterogeneity on the rheological behavior of the
miscible blends might be very small, if not negligible. This conclusion, though tentative,
is definitely a distinguishing rheological characteristic between the miscible polymer
blends with specific interaction (hydrogen bonding in the present study) and the miscible
polymer blends without specific interaction. The apparent absence or negligibly small
concentration fluctuations and dynamic heterogeneity in the four PVPh-based miscible
blends with hydrogen bonding is attributable to the presence of self-association
(intramolecular interactions) and/or inter-association (intermolecular attractive
interactions) between the constituent components. We tentatively conclude that
intermolecular attractive interactions would suppress dynamic heterogeneity and
concentration fluctuations in miscible polymer blends forming hydrogen bonds.

We have observed curvature in the terminal region of log $G'$ versus log $G''$ plots for
all four PVPh-based blend systems investigated, and the severity of curvature becomes
more pronounced as the concentration of PVPh in the respective blend systems is
increased. Specifically, for blends with low concentrations of PVPh (e.g., 20 wt %),
since PVPh is surrounded by large amounts of non-self-associating component, the
fraction of self-association of phenoxy –OH groups is very small. Most of the phenoxy
–OH groups form the intermolecular hydrogen bonds and the blends are miscible. However, because of the low concentration of PVPh, the number of hydrogen bonds may not be sufficiently large. As a result, the effect of specific interactions on the linear viscoelasticity would be small and thus the curvature in the terminal region of log $G'$ versus log $G''$ plots is not discernible. However, as the concentration of PVPh is increased, there are not only intermolecular hydrogen bonds, but also self-association of phenoxy–OH groups. Hydrogen bonding enhances the friction between different segments. Thus, very strong intermolecular interactions between the constituent components in such miscible polymer blends may suppress concentration fluctuations and dynamic heterogeneity. It can then be concluded that the curvature in the terminal region of log $G'$ versus log $G''$ plots is attributable to both self-association and inter-association in PVPh-based miscible blends when concentration of PVPh exceeds a certain critical value.

Using the Painter-Graf-Coleman association model, the fraction of hydrogen bonds was calculated. We found that the balance between self-association and inter-association in miscible polymer blends with hydrogen bonding would vary depending on their relative strength of hydrogen bonding. For example, the predominant hydrogen bonding in 60/40 PVPh/PVME blend arises from self-association. As a result, the curvature in the terminal region of log $G'$ versus log $G''$ plots for the 60/40 PVPh/PVME blend is attributable primarily to the self-association of PVPh rather than inter-association in the blend. On the other hand, the curvature in the terminal region of log $G'$ versus log $G''$ plots of 60/40 PVPh/P4VP blend is attributable primarily to the inter-association (intermolecular hydrogen bonding) between the phenolic–OH groups in PVPh and the
pyridine groups in P4VP, although some self-association is also involved. Similar arguments can be made to PVPh/PVAc and PVPh/P2VP blend systems investigated in this study.

In this study we synthesized, via ring-opening metathesis polymerization, hydrogenated functional polynorbornenes, HPBNCOOH, HPNBOH, and HPNBNH₂. The purpose of having synthesized the polymers was to investigate the rheology of model miscible polymer blends with hydrogen bonding. We have found that blends of HPBNOOH with PC or P2VP are miscible on the basis of DSC thermograms exhibiting a single, broad glass transition. FTIR spectroscopy confirmed the formation of hydrogen bonds between carboxylic acid groups in HPNCOOH and carbonyl groups in PC or pyridine groups in P2VP over the entire range of blend compositions investigated. On the other hand, we have found that blends of HPNBOH and PC are immiscible as determined by DSC. It has been found that log $G'$ versus log $G''$ plots show temperature independence and TTS is applicable to both PC/HPBNOOH and P2VP/HPNCOOH blend systems, in spite of the fact that $\Delta T_g$ is 91 °C for the PC/PNCOOH blends and $\Delta T_g$ is 36 °C for the P2VP/PNCOOH blends. Such an observation leads us to conclude that the presence of hydrogen bonds in the PC/PNCOOH and P2VP/PNCOOH blends might have suppressed concentration fluctuations and dynamic heterogeneity.
7.2 Recommendations

In order to have a better understanding of the effect of specific interactions on rheological properties of miscible polymer blends, we recommend that solid-state NMR spectroscopy be employed to determine the extent of dynamic heterogeneity and concentration fluctuation in four PVPh-based blend systems employed in this study.
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(a) Derivation of System Equations. The equilibrium constants, $K_2$, $K_B$, and $K_A$, appearing in eqs 5.1 and 5.2, are defined by

\[ K_2 = \frac{\Phi_{B_2}}{2\Phi_{B_1}} \]  

(A1)

\[ K_B = \frac{\Phi_{B_{h+1}}}{\Phi_{B_h}\Phi_{B_1}} \left( \frac{h}{h+1} \right) \]  

(A2)

\[ K_A = \frac{\Phi_{B_h A}}{\Phi_{B_h} \Phi_{A_1}} \left( \frac{hr}{h+r} \right) \]  

(A3)

where $\Phi_{B_h}$ ($h \geq 2$) is the volume fraction of a hydrogen-bonded $h$-mer. $\Phi_{B_h A}$ is the volume fraction of hydrogen bonding between $A$ and $B$. Equations A1 and A2 are identical to those defined by Flory.\textsuperscript{241} Equation A3 was obtained in the same manner as eqs A1 and A2 were obtained, as shown below.

For a dynamic equilibrium, we have

\[ B_h + A_1 \rightleftharpoons B_h A_1 \]  

(A4)

The concentration equilibrium constant $K_C$ is defined as
\[ K_C = \frac{[B_h A_1]}{[B_h][A_1]} = \frac{n_{hA}/V}{(n_h/V)(n_{A1}/V)} \]  

(A5)

where \([B_h A_1], [B_h], [A_1]\) etc. represent the molar concentrations of the species, which are equal to the molar number \((n_{hA}, n_h, n_{A1})\) divided by the total volume \((V)\) of the system. And we know:

\[
\Phi_{hA} = \frac{n_{hA} V_{hA}}{V} = \frac{n_{hA}(h V_B + V_A)}{V} 
\]  

(A6)

Then

\[
\frac{n_{hA}}{V} = \frac{\Phi_{hA}}{(h \cdot V_B + V_A)} 
\]  

(A7)

Similarly

\[
\frac{n_h}{V} = \frac{\Phi_h}{h \cdot V_B} 
\]  

(A8)

\[
\frac{n_{A1}}{V} = \frac{\Phi_A}{V_A} 
\]  

(A9)

We have

\[
K_C = \frac{n_{hA}/V}{(n_h/V)(n_{A1}/V)} = \frac{\Phi_{hA}}{\Phi_h \Phi_A} \frac{hr}{h + r} V_B 
\]  

(A10)

Dimensionless constant is:

\[
K_A = \frac{K_C}{V_B} = \frac{\Phi_{hA}}{\Phi_h \Phi_A} \frac{hr}{h + r} 
\]  

(A11)

According to eqs A1 and A2 we have

\[
\Phi_{B2} = 2K_2\Phi_{B1}^2 
\]  

(A12)
\[ \Phi_{B_h} = \frac{h}{h-1} K_B \Phi_{B_{h-1}} \Phi_{B_1} \]  

(A13)

By successive substitution of \( \Phi_{B_{h-1}}, \Phi_{B_{h-2}}, \ldots, \Phi_{B_2} \) we obtain:

\[ \Phi_{B_h} = \frac{K_2}{K_B} h (K_B \Phi_{B_1})^h \]  

(A14)

Further, from eq A3 we have

\[ \Phi_{B_h A} = K_A \Phi_A \Phi_{B_1} \left( \frac{h + r}{hr} \right) \]  

(A15)

Thus, the volume fraction of B units, \( \Phi_B \), in a miscible blend can be written from the material balance by

\[ \Phi_B = \Phi_{B_1} + \sum_{h=2}^{\infty} \Phi_{B_h} + \sum_{h=1}^{\infty} \Phi_{B_h A} \left( \frac{h}{h + r} \right) \]  

(A16)

Substituting eqs A14 and A15 into eq A16, with the aid of the following expression

\[ \sum_{h=1}^{\infty} h (K_B \Phi_{B_1})^{h-1} = \frac{1}{(1 - K_B \Phi_{B_1})^2} \quad (K_B \Phi_{B_1} < 1) \]  

(A17)

we obtain (eq 5.1)

\[ \Phi_B = \Phi_{B_1} \left[ \left( 1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \frac{1}{(1 - K_B \Phi_{B_1})^2} \right] \left[ 1 + \frac{K_A \Phi_A}{r} \right] \]  

(A18)

For \( \Phi_B = 1 \) (neat B), eq A18 reduces to

\[ 1 = \Phi_{B_1}^0 \left[ \left( 1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \frac{1}{(1 - K_B \Phi_{B_1}^0)^2} \right] \]  

(A19)
where $\Phi_{B_1}^o$ is the volume fraction of free monomers in neat B. Similarly, the volume fraction of A units ($\Phi_A$) in a blend is given by

$$\Phi_A = \Phi_{A_1} + \sum_{h=1}^{\infty} \Phi_{B_hA} \left( \frac{r}{h+r} \right)$$

(A20)

Using the following expression

$$\sum_{h=1}^{\infty} (K_B \Phi_{B_1})^{h-1} = \frac{1}{(1 - K_B \Phi_{B_1})} \quad (K_B \Phi_{B_1} < 1)$$

(A21)

we obtain (eq 5.2)

$$\Phi_A = \Phi_{A_1} + K_A \Phi_{A_1} \Phi_{B_1} \left[ \left( 1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \frac{1}{(1 - K_B \Phi_{B_1})} \right]$$

(A22)

(b) Calculation of the Fraction of Hydrogen Bonds Formed. Let us assume that each of the free -OH groups is at one end of a chain and thus it represents a measure of the number of chains present in a blend, as shown below.

Schematic representation of phenol self-association and inter-association.

Then, the fraction of free B molecule ($f_{FB}$) is equal to the total number of B chains divided by the total number of B molecules present in the system and it is expressed by
where $n_{B_h}$ and $n_{B_A h}$ are the number of chains that have $h_B$ units from self-association and inter-association, respectively. We can express these in terms of volume fractions using

$$
\Phi_{B_h} = \frac{n_{B_h} V_{B_h}}{V} = \frac{n_{B_h} hV_B}{V}
$$

where $V_{B_h}$ is the molar volume of an h-mer, $V_B$ is the molar volume of an individual B molecule, and $V$ is the total volume of the system. Similarly, assuming that there is no change in volume upon forming a hydrogen bond, we have:

$$
\Phi_{B_A h} = \frac{n_{B_A h} V_{B_A h}}{V} = \frac{n_{B_A h} (hV_B + V_A)}{V}
$$

where $V_{B_A h}$ is the molar volume of the intermolecular hydrogen bonds formed between A unit and h-mer. Substituting eqs A24 and A25, with the aid of eqs A12, A13, A17, and A21, into eq A23, we obtain (eq 5.3).

$$
f_{FB} = \frac{\left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B} \left(\frac{1}{1 - K_B \Phi_{B_1}}\right)}{\left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B} \left(\frac{1}{1 - K_B \Phi_{B_1}}\right)^2} \left[\frac{1}{1 + \frac{K_A \Phi_{A_1}}{r}}\right]
$$

The fraction of free A molecule ($f_{FA}$) is equal to the number of non-hydrogen-bonded A molecules divided by the total number of A molecules ($f_{FA} = \Phi_{A_1} / \Phi_{A}$). Therefore, the fraction of hydrogen-bonded A groups ($f_{BA}$) is given by (eq 5.4)
\[ f_{BA} = 1 - f_{FA} = \left( 1 - \frac{\Phi_{A1}}{\Phi_A} \right) \]  \hspace{1cm} \text{(A27)}

Using the numerical values of the parameters given in Table 5.1 into eq A18, we can calculate values of \( \Phi_{B1} \) (\( \Phi_{B1} < \Phi_B \) and \( K_B \Phi_{B1} < 1 \)) iteratively using Newton’s method. For 20/80 PVPh/P4VP blend, for example, we obtain \( \Phi_{B1} = 0.0033 \) (another root is 0.0878). Substituting the value into eq A22, we obtain \( \Phi_{A1} = 0.6347 \). Further, substituting those values into eqs A26 and A27, we obtain \( f_{FB} = 0.0166 \) and \( f_{BA} = 0.2067 \).
APPENDIX B

THE THERMODYNAMIC THEORY OF PAINTER

According to Painter et al., the composition dependence of glass transition temperature \( T_g \) of a miscible polymer blend system with hydrogen bonding is given by

\[
T_g = \frac{X_A T_{gA} + K_0 X_B T_{gB}}{X_A + K_0 X_B} - \frac{X_B \left( [H_{B}^{H,1}]_{T_g} - [H_{B}^{H,1}]_{T_{gB}} \right)}{(X_A + K_0 X_B)\Delta C_{pA}} + \Delta H_{m}^{H,1}
\]

where \( X \) is the mole fraction, \( K_0 \) is the ratio of heat capacity increment \( (K_0 = \frac{\Delta C_{pB}}{\Delta C_{pA}}) \), the subscript B denotes the self-association component, \( H_{B}^{H,1} \) is the heat of self-association, and \( \Delta H_{m}^{H,1} \) is the contribution of specific interactions to the heat of mixing in the liquid state, which can be calculated from the following equations:

\[
[H_{B}^{H,1}]_{T_g} - [H_{B}^{H,1}]_{T_{gB}} = n_B h_B \left\{ [p_{BB}^{\circ}]_{T_g} - [p_{BB}^{\circ}]_{T_{gB}} \right\}
\]

\[
\Delta H_{m}^{H,1} = n_B h_B \left( [p_{BB} - p_{BB}^{\circ}]_{T_g} + n_A h_{BA} [p_{BA}]_{T_g} \right)
\]

where \( n_A \) and \( n_B \) are the numbers of moles of A and B segments, respectively, \( \Delta h_B \) is the molar enthalpy of individual B---B hydrogen bond, \( \Delta h_{BA} \) is the molar enthalpy of interassociation, \( p_{BB}^{\circ} \) and \( p_{BB} \) are the probability of forming a hydrogen bond between two B segments in neat B and in the mixture, respectively, and \( p_{BA} \) is the probability of A
segments that are hydrogen-bonded to a B segment. Note that eq B1 can be rewritten as eq 5.13.

From the CGP association model we know that the quantities $p_{BB}$ and $p_{BA}$ are related to the equilibrium constants and the volume fractions $\Phi_{B_1}$ and $\Phi_{A_1}$ by

$$p_{BB} = K_B \Phi_{B_1} \quad \text{(B4)}$$

$$p_{BB}^0 = K_B \Phi_{B_1}^0 \quad \text{(B5)}$$

$$n_A p_{BA} = n_B (1 - K_B \Phi_{B_1}) \left(1 + \frac{r}{K_A \Phi_{A_1}}\right) \quad \text{(B6)}$$

Similar to the above calculation of the fraction of hydrogen bonds, at a temperature $T$, for given composition ($\Phi_B$ and $\Phi_A$) with the values of equilibrium constants ($K_2$, $K_B$, and $K_A$), using eqs A18, A19 and A22 we can obtain $\Phi_{B_1}^0$, $\Phi_{B_1}$ and $\Phi_{A_1}$. Substituting these values into eqs B4–B6, the quantities $p_{BB}$ and $p_{BA}$ can be calculated. Finally, the enthalpic quantities $[H_B^{\text{H,1}}]_{T_{gm}} - [H_B^{\text{H,1}}]_{T_{gB}}$ and $\Delta H_m^{\text{H,1}}$ can be calculated using eqs B2 and B3.

Equation B1 can be rearranged in the following form:

$$f(T_{gm}) = X_A \Delta C_{pA} (T_{gm} - T_{gA}) + K_0 X_B \Delta C_{pA} (T_{gm} - T_{gB})$$

$$+ X_B \{[H_B^{\text{H,1}}]_{T_{gm}} - [H_B^{\text{H,1}}]_{T_{gB}}\} + \Delta H_m^{\text{H,1}} \quad \text{(B7)}$$

Equation B7 is a function of temperature $T_{gm}$. The temperature that makes $f(T_{gm}) = 0$ is the glass transition temperature of the blend sought for. This involves an iterative process.
Let us illustrate the procedures for predicting $T_{gm}$ from eq B7 for 20/80 PVPh/P4VP blend, for which we have $m_A = 0.8$ g and $m_B = 0.2$ g. Assuming that their densities are unity, we have $\Phi_A = 0.8$ and $\Phi_B = 0.2$. Also, $T_{gA} = 153$ °C, $T_{gB} = 180$ °C, $\Delta C_{pA} = 0.156$ cal/(g K), $\Delta C_{pB} = 0.128$ cal/(g K), $M_A = 105.2$, $M_B = 120.2$ ($M_i$ is the segment molecular weight), $r = 0.849$. Then $n_A = 0.0076$, $n_B = 0.0017$, $X_A = 0.82$, and $X_B = 0.18$. Let us first assume that $T_{gm}$ is 170 °C. Using eq 5.5 we have

$[K_2]_{170 \, ^\circ\text{C}} = 0.95$, $[K_B]_{170 \, ^\circ\text{C}} = 3.85$, $[K_A]_{170 \, ^\circ\text{C}} = 21.75$. Using eqs A18, A19 and A22 we obtain $[\Phi^0_{B_1}]_{T_{gm}} = 0.1976$, $[\Phi_{B_1}]_{T_{gm}} = 0.0112$, and $[\Phi_{A_1}]_{T_{gm}} = 0.5548$. Also, $[K_B]_{T_{gm}} = 3.38$ and $[\Phi^0_{B_1}]_{T_{gm}} = 0.2207$. Then we have $n_A[p_{BA}]_{T_{gm}} = 0.00149$,

$[H^H_{B,1}]_{T_{gm}} - [H^H_{B,1}]_{T_{gm}} = -0.1289$, and $\Delta H^m_{m} = -2.724$. Substituting these values into eq B7 we obtain $f(T_{gm}) = -0.8$. Since $f(170 \, ^\circ\text{C}) < 0$, we had to iterate the process by increasing a guestimated value of $T_{gm}$ until $f(T_{gm}) = 0$ is achieved. Finally we obtain $f(175.36 \, ^\circ\text{C}) = -0.0002 \approx 0$. Therefore, the predicted $T_{gm}$ for 20/80 PVPh/P4VP blend is 175.36 °C.