1-1-1987

Miscibility and molecular interactions in multi-component polymer systems :: characterization at the molecular level via NMR/

Jerome F. Parmer
University of Massachusetts Amherst

Follow this and additional works at: http://scholarworks.umass.edu/dissertations_1

Recommended Citation

This Open Access Dissertation is brought to you for free and open access by the Dissertations and Theses at ScholarWorks@UMass Amherst. It has been accepted for inclusion in Doctoral Dissertations 1896 - February 2014 by an authorized administrator of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.
MISCIBILITY AND MOLECULAR INTERACTIONS IN MULTI-COMPONENT POLYMER SYSTEMS: CHARACTERIZATION AT THE MOLECULAR LEVEL VIA NMR

A Dissertation Presented

by

JEROME F. PARMER

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 1987

Polymer Science and Engineering
MISCIBILITY AND MOLECULAR INTERACTIONS IN MULTI-COMPONENT POLYMER SYSTEMS: CHARACTERIZATION AT THE MOLECULAR LEVEL VIA NMR

A Dissertation Presented
by
JEROME F. PARMER

Approved as to style and content by:

Roger S. Porter
Prof. Roger S. Porter, Chairman

William J. MacKnight
Prof. William J. MacKnight, Member

Thomas R. Stengle
Prof. Thomas R. Stengle, Member

L. Charles Dickinson
Dr. L. Charles Dickinson, Member

Edwin L. Thomas
Prof. Edwin L. Thomas, Department Head
I would like to thank my advisor, Prof. Roger S. Porter, for the support, advice, and encouragement that enabled me to complete this dissertation. Profs. MacKnight and Stengle deserve thanks for their help and willingness to discuss the questions that invariably come up during a research program. I would especially like to acknowledge the help of Dr. Dickinson with the solid state NMR work. Thanks are also due Prof. Chien, who was a part of many valuable discussions.

No Ph.D. is ever completed without the help of other students. In my case, the other members of Prof. Porter's research group were always ready to help with an experiment or a derivation. Eric Beckman, ace thermodynamicist and Paul Lucas, FTIR whiz, were especially helpful. Dr. Jean-Marc Lefebvre provided scientific and culinary inspiration. Matt Muir has been both a good friend and colleague. Rick, Young-Chul, Kevin, J.P., and Ravi were always ready to discuss a problem or have a beer. I hope I will be forgiven for not mentioning everyone else in the department by name, but please know that everyone's help was very much appreciated.

I would be remiss if I did not also thank my parents for their help, encouragement and love. My family has been an important part of this work in many ways.

My biggest debt is to my wife, Dr. Toni Ann Gestone Parmer. Her support and love mean more to me than anything else ever could.
ABSTRACT

MISCIBILITY AND MOLECULAR INTERACTIONS IN MULTI-COMPONENT POLYMER SYSTEMS: CHARACTERIZATION AT THE MOLECULAR LEVEL VIA NMR

MAY 1987

JEROME F. PARMER, B.S., UNIVERSITY OF CALIFORNIA AT SANTA BARBARA
Ph.D., UNIVERSITY OF MASSACHUSETTS

Directed by: Professor Roger S. Porter

A series of multi-component polymer systems were studied using Nuclear Magnetic Resonance and other characterization techniques. An evaluation of the effect of systematic polymer structural and compositional changes on molecular interactions and miscibility was carried out. The systems studied included polystyrene cosolvent ternary solutions, and a series of poly(alky methacrylate)/poly(vinyl chloride) (PVC) blends.

For the polystyrene/acetone/ethyl ether and polystyrene/acetone/methylcyclopentane cosolvent systems, polymer-solvent molecular interactions were evaluated using $^{13}$C NMR. It was determined that preferential polymer-solvent interactions are present in the PS/acetone/diethylether cosolvent system. No apparent interactions were observed in the PS/acetone/methylcyclopentane system, hence such interactions are not a prerequisite for the observation of cosolvency.

The poly(alky methacrylate)/PVC blends were studied using differential scanning calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), and light scattering methods. The FTIR results indicated that methacrylate carbonyl - PVC interactions are relatively
unaffected by the structure of the methacrylate polymer ester group. The DSC results showed all of the methacrylate polymers to be miscible with PVC, with the exception of the poly(benzyl methacrylate). Light scattering indicated LCST behavior for the PMMA/PVC system.

Solid state CP-MAS NMR was used to study several spectral parameters for the methacrylate/PVC blends. Carbon T₁ relaxation times indicated that the PVC had no effect on the MHz frequency motional processes of the methacrylate polymers in the blends. The C chemical shifts and T₁ρ data did not show significant changes after blending. Proton spin-lattice relaxation times were measured for the blends and component polymers. Proton T₁ρ results were used to establish an upper limit to the scale the scale of heterogeneity for PMMA/PVC and PCHMA/PVC blends at = 50.0 Å. The H T₁ρ results indicated the PBenMA/PVC blend to be phase separated.

Intermolecular cross-polarization in blends incorporating deuterated polymers was used to study polymer-polymer miscibility on a molecular scale for several homopolymer blend systems. Cross-polarization dynamics and relative C peak intensities provided information as to the extent of mixing and carbon-proton dipolar interactions. Miscible d-8 PMMA/PVC, d-8 PMMA/PEO, d-8 PMMA/PMMA showed extensive intermolecular cross-polarization. Immiscible d-8 PMMA/PS and d-8 PS/PMMA showed only minimal intermolecular CP. Cross-polarization dynamics were also studied and found to be consistent with the miscibility of the blends.
# Table of Contents

ACKNOWLEDGEMENTS ................................................................. iv
ABSTRACT ................................................................................ v
LIST OF FIGURES ........................................................................ ix
LIST OF TABLES ........................................................................... xii

Chapter

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

II. NMR STUDIES OF MOLECULAR INTERACTIONS IN POLYSTYRENE COSOLVENT SYSTEMS ........................................................................ 11

   Introduction .............................................................................. 11
   Experimental Methods ........................................................... 12
   Results .................................................................................... 16
   Discussion ................................................................................. 38

III. CHARACTERIZATION OF POLY(ALKYL METHACRYLATE)/POLY(VINYL CHLORIDE) BLENDS ............................................................... 44

   Introduction .............................................................................. 44
   Experimental Methods ........................................................... 45
   Results .................................................................................... 51
   Discussion ................................................................................. 76
   Conclusions .............................................................................. 85

IV. SOLID STATE NMR STUDIES OF POLY(ALKYL METHACRYLATE)/POLY-(VINYL CHLORIDE) BLENDS ...................................................... 86

   Introduction .............................................................................. 86
   Experimental Methods ........................................................... 87
   Results .................................................................................... 91
   Discussion ................................................................................. 129
   Conclusions .............................................................................. 136

V. INTERMOLECULAR CROSS-POLARIZATION AS A PROBE OF MISCELLIBILITY IN BLENDS INCORPORATING DEUTERATED POLYMERS ...................................................... 138

   Introduction .............................................................................. 138
   Experimental Methods ........................................................... 141
   Results .................................................................................... 142
   Discussion ................................................................................. 168
   Conclusions .............................................................................. 177
VI. FUTURE RESEARCH .............................................................. 179

APPENDIX
   A. Sample Calculations for Determination of Association
      Constants in Polymer Solutions Using NMR ................. 183
   B. Model Used for Domain Size Calculations in NMR Studies... 185

REFERENCES .............................................................................. 189
1.1 Schematic Phase Diagram for a Polymer-Cosolvent System........... 4
2.1 $^{13}$C Spectrum of Polystyrene in CCl$_4$/Acetone Solvent............. 18
2.2 $^{13}$C Chemical Shift vs. Solvent Composition for Polystyrene 
p-Phenyl Resonance in Acetone/Diethylether Cosolvent............ 19
2.3 $K_a$ Determination for Polystyrene p-Phenyl Resonance.............. 22
2.4 $^{13}$C Chemical Shift vs. Solvent Composition for Polystyrene 
o,m-Phenyl resonance in Acetone/Ether Cosolvent................... 24
2.5 $K_a$ Determination for Polystyrene o,m-Phenyl Resonance............ 26
2.6 $^{13}$C Chemical Shift vs. Solvent Composition for Polystyrene $\alpha$-
Methylene Resonance in Acetone/Diethylether Cosolvent............ 27
2.7 $^{13}$C Chemical Shift vs. Solvent Composition for Polystyrene $\alpha$-
Methylene Resonance in CCl$_4$/Acetone Binary Solvents.......... 29
2.8 $^{13}$C Chemical Shift vs. Solvent Composition for Polystyrene 
o,m-Phenyl Resonance in Acetone/CCl$_4$ Binary Solvents......... 30
2.9 $K_a$ Determination for Polystyrene in Acetone/CCl$_4$ Binary 
Solvents................................................................. 32
2.10 $^{13}$C Chemical Shifts vs. Solvent Composition for Polystyrene 
o,m-Phenyl Resonance in Acetone/MCP Cosolvents.................... 33
2.11 $^{13}$C Chemical Shift vs. Solvent Composition for Polystyrene 
$\alpha$-Methylene Resonance in Acetone/MCP Cosolvents............. 35
2.12 $K_a$ Determination for Polystyrene in Acetone/MCP Cosolvents... 37
3.1 Poly(alkyl methacrylate) Structures........................................ 47
3.2 DSC Scans for PMMA, PVC, and a PMMA/PVC Blend......................... 53
3.3 Glass Transition Temperature vs. PMMA/PVC Blend Composition... 54
3.4 Glass Transition Temperature vs. PEMA/PVC Blend Composition... 55
3.5 Glass Transition Temperature vs. PBMA/PVC Blend Composition... 56
3.6 DSC Scans for PCHMA, PVC, and a PCHMA/PVC Blend................. 58
3.7 Glass Transition Temperature vs. PCHMA/PVC Blend Composition... 59
3.8 DSC Scans for PBenMA, PVC, and a PBenMA/PVC Blend.................. 61
3.9 Glass Transition Temperature vs. PMMA/PVC-co-VC Blend Composition.............................................. 62
3.10 Glass Transition Width vs. PMMA/PVC Blend Composition........... 66
3.11 Glass Transition Width vs. PMMA/PVC-co-VC Blend Composition..... 67
3.12 Glass Transition Width vs. PCHMA/PVC Blend Composition........... 68
3.13 Thermogravimetric Analysis of a PMMA/PVC Blend.................. 72
3.14 Light Scattering Determination of Cloud Point Temperature for a PMMA/PVC Blend Sample.......................... 74
3.15 Cloud Point Temperature vs. PMMA/PVC Blend Composition........ 75
3.16 FTIR Spectrum of PMMA Carbonyl Region........................................ 82
4.1 Solid State CP-MAS NMR Pulse Sequences.............................. 90
4.2 CP-MAS $^{13}$C NMR Spectrum of PVC................................. 93
4.3 CP-MAS $^{13}$C NMR Spectrum of PMMA................................. 94
4.4 CP-MAS $^{13}$C NMR Spectrum of a PMMA/PVC Blend.................. 96
4.5 CP-MAS $^{13}$C NMR Spectrum of a PEMA/PVC Blend................... 98
4.6 CP-MAS $^{13}$C NMR Spectrum of a PBMA/PVC Blend................... 100
4.7 CP-MAS $^{13}$C NMR Spectrum of a PCHMA/PVC Blend.................. 102
4.8 CP-MAS $^{13}$C NMR Spectrum of PBenMA and a PBenMA/PVC Blend..... 104
4.9 Spin-Lattice $^{13}$C Relaxation Time Determination for PMMA....... 110
4.10 Rotating Frame Spin-Lattice $^{13}$C Relaxation Time Determination for PMMA and a PMMA/PVC Blend............... 112
4.11 Rotating Frame Spin-Lattice Proton Relaxation Time Determination for PBenMA.................................. 115
4.12 Proton T$_{1p}$ Relaxation Time Determination for PMMA, PVC, and a PMMA/PVC Mixture............................. 118
4.13 Proton T$_{1p}$ Relaxation Time Determination for PMMA/PVC Blends... 120
4.14 Proton T$_{1p}$ Relaxation Time Determination for PMMA/PVC Blend... 122
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.15</td>
<td>Proton $T_1^p$ Relaxation Time Determination for PCHMA/PVC Blends</td>
<td>124</td>
</tr>
<tr>
<td>4.16</td>
<td>Proton $T_1^p$ Relaxation Time Determination for PBenMA/PVC Blends</td>
<td>126</td>
</tr>
<tr>
<td>5.1</td>
<td>Schematic for Proton-Carbon Cross-Polarization Process</td>
<td>140</td>
</tr>
<tr>
<td>5.2</td>
<td>CP-MAS $^{13}$C Spectra of PVC, PMMA, d-8 PMMA, and a d-8 PMMA/PVC Blend</td>
<td>146</td>
</tr>
<tr>
<td>5.3</td>
<td>CP-MAS $^{13}$C Spectra of d-8 PMMA, and blends of d-8 PMMA/PVC and d-8 PMMA/PEo.</td>
<td>147</td>
</tr>
<tr>
<td>5.4</td>
<td>CP-MAS $^{13}$C Spectra of d-8 PS, PVME, PS, and d-8 PS/PVME Blend.</td>
<td>149</td>
</tr>
<tr>
<td>5.5</td>
<td>CP-MAS $^{13}$C Spectra of d-8 PS/PMMA Blends</td>
<td>151</td>
</tr>
<tr>
<td>5.6</td>
<td>Variable CP Contact Time Spectra for PMMA</td>
<td>153</td>
</tr>
<tr>
<td>5.7</td>
<td>Variable CP Contact Time Intensity Plot for PMMA</td>
<td>154</td>
</tr>
<tr>
<td>5.8</td>
<td>Variable CP Contact Time Spectra for PMMA/PVC Blend</td>
<td>156</td>
</tr>
<tr>
<td>5.9</td>
<td>Variable CP Contact Time Intensity Plot for d-8 PMMA/PVC, PMMA, and a d-8 PMMA/PS Blend</td>
<td>160</td>
</tr>
<tr>
<td>5.10</td>
<td>Variable CP Contact Time Spectra for d-8 PS/PVME Blend.</td>
<td>162</td>
</tr>
<tr>
<td>5.11</td>
<td>Variable CP Contact Time Intensity Plot for d-8 PS, and d-8 PS/PVME d-8 PS/PMMA Blends</td>
<td>164</td>
</tr>
<tr>
<td>5.12</td>
<td>Variable CP Contact Time Intensity Plot for PS and d-3 PS</td>
<td>166</td>
</tr>
<tr>
<td>5.13</td>
<td>Variable CP Contact Time Intensity Plot for PS, d-5 PS, and a d-8 PS/PVME Blend</td>
<td>167</td>
</tr>
<tr>
<td>5.14</td>
<td>Variable CP Contact Time Intensity Plot and Theoretical Fit for pure PMMA</td>
<td>174</td>
</tr>
</tbody>
</table>
List of Tables

2.1 Summary of $K_a$ Values Determined Via NMR............................. 34
3.1 Poly(alky methacrylate) Molecular Weights............................ 48
3.2 Fourier Transform Infrared Carbonyl Band Shifts.................... 69
4.1 PMMA and PMMA/PVC Blend $^{13}$C $T_1$ Relaxation Times........... 106
4.2 PEMA and PEMA/PVC Blend $^{13}$C $T_1$ Relaxation Times........... 107
4.3 PCHMA and PCHMA/PVC Blend $^{13}$C $T_1$ Relaxation Times........... 107
4.4 PBMA and PBMA/PVC Blend $^{13}$C $T_1$ Relaxation Times........... 107
5.1 $^{13}$C Signal Intensities for d-8 PMMA, d-8 PMMA/PVC and
d-8 PMMA/PEO......................................................... 171
Chapter I

A REVIEW OF POLYMER MISCIBILITY AND INTERACTIONS IN POLYSTYRENE COSOLVENT AND POLY(ALKYL METHACRYLATE)/POLY(VINYL CHLORIDE) SYSTEMS

Introduction

The complex relationship between polymer structure and resultant material properties is an important concern. Improving the understanding of the basic principles which govern the properties of multi-component macromolecular systems is a significant priority. The material in this initial chapter will provide the necessary background information as well as a review of the literature relevant to the specific polymer solutions and blends investigated. Prior to a discussion of these areas, the specific research goals will be briefly outlined.

The basic objectives of this research, which has focused on the study of polymer miscibility in blends and solutions, are as follows:

1. Improve the understanding of the relationship between molecular-level and macroscopic properties in multi-component polymer systems.
2. Develop and utilize Nuclear Magnetic Resonance (NMR) methods to evaluate the effects of structural and compositional changes on molecular interactions and miscibility.

3. Coordinate NMR methods and results on polymer miscibility with information provided by other characterization techniques.

Two types of polymer systems were chosen for study. The first, polymer-cosolvent ternary solutions, have been demonstrated to exhibit interesting and unusual phase behavior. The effect of polymer structure and solution composition on molecular interactions and phase behavior was evaluated via NMR methods. Cosolvent systems are also of interest because of their analogous behavior to certain copolymer-homopolymer blends. The second area of investigation involved a series of polymer blends in which the molecular structure of one component was varied in a systematic and controlled fashion. The effect of polymer structural changes was probed on both a macroscopic and a molecular level, using a variety of techniques. The following material provides a review of the important related literature for each of these systems.

Polymer-Cosolvent Systems

Polymer-cosolvent systems exhibit interesting and unusual phase behavior. A polymer-cosolvent solution is one in which a given polymer, insoluble in either of two low-molecular weight nonsolvents, becomes soluble in binary mixtures of the two at intermediate compositions. An
idealized representation of such a system is depicted in Figure 1.1, for a fixed arbitrary polymer concentration. The solid line represents the cloud point boundary as a function of temperature and binary cosolvent composition. The interior of the circular area represents the single-phase region, the exterior area is the immiscible or two phase region. The increased miscibility of the polymer at intermediate solvent compositions is manifested by the increased separation of the upper and lower cloud point temperatures. (Several examples of this type of phase behavior have been reported.\textsuperscript{1-8}) Additional evidence for increased polymer solubility are higher viscosities, expanded polymer chain dimensions, and lower polymer-mixed solvent interaction parameters ($\chi_{ms}$) at intermediate cosolvent compositions.

Various explanations as to the origins of cosolvency have been proposed, and are summarized in a review paper by Cowie and McEwen.\textsuperscript{9}

Arguments based on solubility parameter ($\delta$) considerations, which state that the cosolvent solubility parameter more closely matches that of the polymer, have been shown to be inapplicable to several cosolvent systems (i.e., both of the cosolvent components had $\delta$'s above or below that of the polymer).

Wolf and Molinari\textsuperscript{10} proposed that the observed solubility enhancement of the polymer is due to the excess positive enthalpy of mixing for the two cosolvent components. They argue, based on a Scott single-fluid approximation, that a lower polymer-mixed solvent interaction parameter ($\chi_{ms}$) results due to the relative values of the polymer-solvent and solvent-solvent interaction terms. They discount
Figure 1.1: Representation of a typical cosolvent phase diagram, as a function of temperature and binary cosolvent composition at an arbitrary constant polymer volume fraction.
the possibility of preferential molecular interactions as a reason for cosolvency.

Cowie and McEwen have shown through the application of Prigogine-Patterson-Flory theory, that the polymer cosolvent interaction parameter does decrease at intermediate cosolvent compositions. They demonstrate that the entropic (free volume) contribution to $\chi_{ms}$ increases at intermediate cosolvent compositions, while the enthalpic term decreases sufficiently to more than compensate for the unfavorable entropic term. Cowie and McEwen propose the enthalpic nature of this phenomenon is due to the influence of preferential polymer-solvent component interactions. They suggest that each of the cosolvent molecules have preferred polymer interaction sites, and that when these sites are different, the overall number of favorable polymer-solvent interactions is increased at intermediate solvent compositions. This synergistic effect would thereby promote miscibility of the polymer. They also suggest that systems in which the solvents compete for the same polymer site would not show cosolvency.

Schuster and Cantow have also advanced an explanation for cosolvency based on molecular interactions. They argue that in a mixture of polar and non-polar solvents, interactions between the polymer and the polar solvent component are enhanced by the presence of the non-polar solvent component. They cite the polysytrene/acetone/cyclohexane cosolvent system as an example, theorizing that the addition of cyclohexane acts to break up "acetone
aggregates" and promote polystyrene miscibility by increasing the number of more favorable polystyrene-acetone contacts.

Although there have been several studies of polymer cosolvency of a general nature, no attempt to our knowledge has been made to directly study molecular interactions in these systems. Most of the previous work has been concerned with determination of phase diagrams and analysis of the thermodynamic aspects. If explanations for cosolvency based on preferential molecular interactions are to be accepted, proper experimental investigation of such interactions is required. The polystyrene/acetone/diethyl ether and acetone/methylcyclopentane cosolvent systems are ideal for such a study, as discussed in Chapter II.

Nuclear Magnetic Resonance spectroscopy provides the means for the study of molecular interactions in polymer systems. Several studies have demonstrated the utility of $^{13}$C NMR as a means of quantitative analysis of molecular interactions.\textsuperscript{14-20} The use of high resolution NMR offers certain advantages over other techniques, one being the ability to investigate polymer-solvent interactions on a site-specific basis. Each resonance in the $^{13}$C spectrum of a given polymer has the potential to be used as a probe of molecular interactions at that site. Despite the low natural abundance of carbon-13 nuclei, the sensitivity of modern Fourier-Transform spectroscopic methods permit the study of samples of low polymer concentration. (Several reviews of $^{13}$C FT-NMR methods are available, c.f. references 21-25.) The specific approach used to study
the polystyrene cosolvent systems in this instance is discussed in detail in Chapter II.

**Polymer Structure: Interactions and Blend Miscibility**

As with polymer solutions, the question as to the effect of molecular structure on polymer interactions and blend miscibility is also important for blends. In order for two polymers to be miscible, two thermodynamic criteria must be met. The Gibb's Free Energy of mixing ($\Delta G_{mix}$) must be negative,

$$
1. \Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} < 0 \quad (1.1)
$$

and the second partial derivative of $\Delta G_{mix}$ with respect to composition must be greater than zero. (Where $\phi_i$ is the volume fraction of component 1.)

$$
2. \frac{\partial^2 \Delta G_{mix}}{\partial \phi_i^2} > 0 \quad (1.2)
$$

In a mixture of two high molecular weight polymers, the entropic contribution to the Gibb's Free Energy of mixing ($\Delta S_{mix}$) becomes negligible as the Mw's approach infinity. Hence, the driving force for polymer mixing must necessarily be enthalpic in origin. This means that there must be a favorable interaction between the two components which is of sufficient magnitude to outweigh the dispersive forces, whereas in a polymer-solvent system, the larger $\Delta S_{mix}$ does not make this an
absolute requirement. (Recall that the critical interaction parameter is higher for a polymer-solvent system.) This simple explanation outlines the single most important point: the relationship between polymer structure and the thermodynamics of polymer-polymer miscibility. Several theoretical treatments of polymer blend thermodynamics and review articles explore the subject in more detail.\textsuperscript{26-30}

There are several examples of blends in which different types of polymer-polymer interactions promote miscibility. Many miscible blends have shown evidence for intermolecular hydrogen-bonding interactions.\textsuperscript{31-33} Other polymer blends are possibly stabilized due to the formation of intermolecular acid-base complexes, polymer-polymer charge transfer interactions have also been reported.\textsuperscript{34} In some instances, the structural features which are responsible for such interactions are obvious; in other blends the mode of interaction is more difficult to ascertain.

Despite the seeming ease with which the thermodynamic considerations governing polymer-polymer miscibility can be explained, translation of these principles into accurate descriptions of physical reality is not quite so simple. There are no straight-forward rules which can correlate polymer structure and enthalpic interaction terms. Predicting which polymer pairs will form miscible blends, while an extremely desirable goal, remains an elusive one.

The series of poly(alky methacrylate)/poly(vinyl chloride) (PVC) blends detailed in Chapters III and IV provide an opportunity to investigate the effect of a systematic change in structure for one
component on blend miscibility and molecular interactions. Poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(butyl methacrylate) (PBMA), poly(cyclohexyl methacrylate) (PCHMA), and poly(benzyl methacrylate) (PBenMA) differ only in that the polymer ester side group is changed. This series of blends was chosen for study primarily for this reason.

Previous work on certain of the methacrylate/PVC has been limited, with one or two exceptions. A report by Schurer et al claimed that the PMMA/PVC system was miscible only when PVC content was greater than 60% w/w,\textsuperscript{35} although a second group claimed that the PMMA/PVC system was immiscible.\textsuperscript{36} A more recent study by Ten Brinke and coworkers demonstrated that the degree of miscibility in PMMA/PVC blends depended on the tacticity of the PMMA component.\textsuperscript{37} Other work indicated the atactic PMMA/PVC system to be at only partially miscible.\textsuperscript{38,39} Obviously, there has been a certain degree of controversy regarding this particular system.

Little work has been done with the other methacrylate/PVC blends in this series. Reports by Walsh and McKeown,\textsuperscript{39} and Tremblay and Prud'homme,\textsuperscript{40} indicate that PEMA, PPMA, and PBMA are miscible with PVC, although in both cases only one blend composition was investigated for each system. The two research groups disagreed as to the miscibility of poly(n-hexyl methacrylate) with PVC. There are no apparent studies involving blends of poly(cyclohexyl methacrylate) and PVC.

The disagreement among researchers regarding the miscibility of these systems, and other blends in general, is rather more commonplace
than might be expected. The difficulty arises due to differences in polymer molecular weights, tacticities, and sample histories. Additional complications result from the fact that different experimental methods are often used to establish miscibility. Differential scanning calorimetry does not always agree with dynamic mechanical analysis or optical clarity results, even for the same sample. In studying this series of methacrylate/PVC blends, all of the critical information regarding the specific samples, preparation methods, and experimental techniques has been provided. In addition, an attempt has been made to study certain of the samples on a variety of levels. By employing different characterization techniques, such as solid state NMR, it is possible to probe these systems on a distance scales ranging from angstroms to microns.
CHAPTER II

Nuclear Magnetic Resonance Studies of Molecular Interactions in Polystyrene Cosolvent Systems

Introduction

As discussed in Chapter I, one of the principle objectives of this research is the study of the relationship between molecular interactions and macroscopic behavior in multicomponent polymer systems. With respect to polymer cosolvent systems, this objective is defined by the question as to the possible influence of site-specific polymer-solvent interactions on enhanced polymer miscibility at intermediate cosolvent compositions. No previous work has been done to either confirm or disprove the existence of preferential polymer-solvent interactions in cosolvent systems on a molecular level. This is an important point which has not been investigated experimentally. In order to address this problem, two polymer-cosolvent systems were chosen for study, (as well as other polymer-mixed solvent systems).

Polystyrene/acetone/diethylether and polystyrene/methyl cyclopentane/acetone ternary solutions have been demonstrated to exhibit cosolvent behavior. (Cloud-point diagrams for both the acetone/diethyl ether and acetone/MCP systems have been determined, both systems show typical cosolvency behavior.) These particular systems are of interest for several reasons. Solution properties of polystyrene have
been well studied in these specific cosolvent mixtures.\textsuperscript{39,40} Polystyrenes of various molecular weights and narrow polydispersity are readily available. In addition, the aromatic and main-chain structural groups give rise to easily distinguishable NMR spectral features, which allows the straightforward analysis of interactions at those sites. Hence these particular systems are good choices for study.

Although other techniques such as Fourier Transform Infrared (FTIR) spectroscopy can be used to study molecular interactions, the use of NMR spectroscopy is particularly advantageous in the polystyrene cosolvent systems. FTIR methods are limited in the case of polystyrene by the absence of suitable bands for analysis. Infrared spectroscopy is usually applied to systems with carbonyl or amide bands which are sensitive to hydrogen bonding or acid-base types of interactions. In most cases, \textsuperscript{13}C NMR spectra contain resonances for every carbon in a given polymer. Thus polymer-solvent interactions at the various polymer sites can be studied by analysis of changes in chemical shifts as a function of temperature and solvent composition.

\textbf{Experimental}

\textbf{Sample Preparation}

Polystyrene of M\textsubscript{w} = 17,500 and M\textsubscript{w}/M\textsubscript{n} = 1.04 was obtained from Pressure Chemical Company and used for the majority of the experiments. Reagent grade anhydrous diethylether was obtained commercially and used without further purification. Commercially obtained reagent grade
acetone was dried over $K_2CO_3$ and stored over 3A molecular sieves. Reagent grade methylcyclopentane (MCP), carbon tetrachloride and benzene were all used as received. Reagent grade chloroform was washed with concentrated $H_2SO_4$ and distilled to remove ethanol.

Polymer-cosolvent solutions were prepared by weighing polystyrene into 10 ml volumetric flasks and adding previously prepared binary solvent mixtures or single solvents. Solutions were magnetically stirred for 24-48 hours prior to use. All solutions were approximately 5% polystyrene by volume and were clear in appearance.

NMR Measurements

All $\textsuperscript{13}C$ measurements were performed on a Varian XL-200 spectrometer equipped with variable temperature control. The $\textsuperscript{13}C$ frequency was 50.3 MHz. A 12 msec pulse width was employed, followed by 0.9 sec accumulation time and a pre-acquisition delay of 1 second. Digital resolution was 0.4 Hz. All peak positions (resonance frequencies) are reported in Kilohertz relative to an external dioxane/D$_2$O reference and lock. A concentric sample tube geometry was used in which the polymer solutions were placed in an outer 10 mm tube, and the reference/lock solutions placed in an inner coaxial 4 mm tube. Spectra were generated using a minimum of 1,000 transients, and in general the signal-to-noise ratio was quite good despite the low polymer concentration.
Analysis of NMR Data

Measurement of polymer-solvent interactions in binary solvents is based on a simple model for interactions in the ternary solutions. The assumption is made that each site along the polymer chain can form either a polymer-solvent "A" contact or a polymer-solvent "B" contact. Solvation of the polymer sites by the two solvent components is considered to be a dynamic process, in which polymer-solvent contacts are constantly created and destroyed. The tendency of a solvent component to favorably interact with the polymer can be described by a deviation away from the random exchange limit. This situation can be described by Equation 2.1:

\[
\frac{[A][PS-B]}{[B][PS-A]} = K_a
\]

where \([A]\) and \([B]\) represent the solvent concentration in the bulk solution, \([PS-A]\) and \([PS-B]\) represent the concentration of polymer solvent "A" and "B" contacts respectively, and \(K_a\) is an "association constant" describing the relative proportion of each type of interaction. Thus, a polymer solvent "A" contact is created at the expense of a polymer-solvent "B" contact.

Measuring the change in \(^{13}C\) chemical shift for a given polymer peak as a function of solvent composition (in a binary mixture of two solvents "A" and "B") allows the relative number or ratio of polymer-solvent "A" contacts to polymer-solvent "B" contacts to be determined. If the chemical shifts for the various polystyrene resonances in each
pure solvent are known, (possible in this case due to the use of lower molecular weight polymer) these values can be assumed to be the appropriate resonance frequencies for each type of polymer-solvent contact (i.e. $\delta_B$ is given by the resonance frequency in pure solvent "B"). If the solvent exchange process in the binary solvent mixture is rapid on the NMR time scale, the following equation can be written:

$$x_{PS-A} = (\delta_{obs} - \delta_B)/(\delta_A - \delta_B)$$  \hspace{1cm} (2-2)

where $\delta_{obs}$ is the observed resonance frequency, $x_{PS-A}$ is the mole fraction of polymer-solvent "A" contacts, and $\delta_A$ and $\delta_B$ are the resonance frequencies in the pure solvents. Rearranging Equation 2-1, and plotting $[PS-A]/[PS-B]$ as a function of $[A]/[B]$, allows determination of $K_a$ from the slope of the resultant line. For a system having no preferential interactions, the polymer-solvent contacts are random and proportional to solvent composition, in which case $K_a$ is unity. If polymer-solvent "A" contacts are dominant, $K_a$ is greater than one; if polymer-solvent "B" contacts dominate, then $K_a$ is less than one. Thus, differences in polymer-solvent interactions at any polymer site with a resolvable NMR signal can be studied. For the polystyrene systems, differences in interactions at the phenyl ring and the main chain methylene groups can thus be measured.
Results

Polystyrene/Acetone/Diethylether

Figure 2-1 shows a typical $^{13}$C spectrum of polystyrene in an acetone/diethylether solvent mixture. The solvent peaks are labeled appropriately, as are the polystyrene resonances. Line widths for all of the polystyrene carbon resonances are fairly narrow, on the order of 1-2 ppm at 1/2 height. The signals for the ipso, ortho-meta and para phenyl carbons are well resolved in the aromatic region. The fact that the o,m-phenyl carbons appear as a single peak is due to the experimental conditions. (In better solvents at higher temperatures, the ortho and meta resonances give rise to separate peaks.) The $\alpha$-methine resonance is seen clearly at 39 ppm. The $\beta$-methylene carbon is seen as a rather broad low-intensity peak at 42-46 ppm. The intensities of the solvent peaks varied according to solvent composition.

Interactions between the polystyrene phenyl ring and the solvent components can be followed by measuring the change in chemical shift as a function of solvent composition for each of the various aromatic peaks. Figure 2-2 shows the $^{13}$C chemical shift for the p-phenyl resonance as a function of acetone/diethylether cosolvent composition. (It should be noted that high MW polystyrene is insoluble in pure acetone and pure ether. However, the 17,500 MW polystyrene used in this case enabled dissolution in the pure components). The $^{13}$C NMR experiments were run at two temperatures, 20° and 30° C. At 30° C, the p-phenyl resonance frequency varies linearly from 3.02 to 2.99 KHz. The
Figure 2.1: $^{13}$C spectrum of polystyrene dissolved in a binary solvent mixture of carbontetrachloride and acetone.
Figure 2.2: $^{13}$C chemical shift vs. solvent composition for polystyrene p-phenyl resonance in acetone/diethyl ether cosolvent mixtures; • T = 20 C; ○ T = 30 C.
change in chemical shift is proportionate to the cosolvent composition. Volume additive behavior is represented by the solid line in Figure 2-2. Such behavior can be described by

\[ \delta_{\text{obs}} = \phi_A \delta_A + \phi_{\text{DEE}} \delta_{\text{DEE}} \]  

(2.2)

where \( \phi_A \) and \( \phi_{\text{DEE}} \) are the volume fractions of acetone and diethylether; \( \delta_A \) and \( \delta_{\text{DEE}} \) are the chemical shifts in pure acetone and pure diethylether. This type of chemical shift versus solvent composition behavior is indicative of random interactions between the PS-phenyl ring and the two solvent components. Dropping the temperature to 20\(^\circ\)C alters the chemical shift behavior. At the lower temperature, there is a negative deviation of the p-phenyl \(^{13}\)C resonance frequency at intermediate solvent compositions, towards the shift value observed in pure ether. This is consistent with a preferential interaction between the PS phenyl ring and the diethylether cosolvent component.

The \(^{13}\)C NMR data for the PS p-phenyl resonance can be treated according to the model presented earlier. Use of Equations 2-1 and 2.2 allows determination of the relative number of PS-acetone and PS-ether contacts and hence determination of \( K_a \) values. This result is shown in Figure 2-3. (For sample calculations, refer to appendix A) At 20\(^\circ\)C, a \( K_a \) value of 0.7 ± 0.1 is obtained. Raising the temperature to 30\(^\circ\)C yields \( K_a = 1.0 \pm 0.1 \). The model predicts a straight line fit, which is indeed observed. A linear least squares fit gives correlation coefficients in excess of 0.98 for the \( K_a \) plots at both temperatures.
Figure 2.3. Association constant ($K_a$) plot for polystyrene p-phenyl resonance in acetone/diethyl ether cosolvent mixtures; • $T = 20$ C; ○ $T = 30$ C.
The graph shows a plot of [Acetone]/[Ether] against [PS-Acetone]/[PS-Ether]. Two straight lines are drawn, one with a slope of 1.0 and the other with a slope of 0.7. The x-axis represents [PS-Acetone]/[PS-Ether] ranging from 4 to 2 and then 2 to 0, while the y-axis represents [Acetone]/[Ether] ranging from 6 to 4 and then 4 to 2.
The results obtained for the polystyrene o,m-phenyl peak were consistent with the results found for the p-phenyl resonance. Figure 2-4 shows the change in chemical shift vs. solvent composition for the o,m-phenyl peak. At 20° C, a negative deviation towards the resonance frequency obtained in pure ether is observed at intermediate solvent compositions. Raising the temperature to 30° C results in volume additive shift behavior.

Analysis of the data for the o,m-phenyl resonance yields the $K_a$ plot shown in figure 2-5. As with the p-phenyl data, the $K_a$ value of 0.6 ±0.1 at 20° C indicates an interaction between the PS phenyl ring and the ether. The fact that the results for the two different aromatic peaks are consistent is a further indication that there is indeed such an interaction present in the system.

The same treatment was applied to the shift data for the polystyrene α-methine resonance. In this case, the results were not as clear as those obtained for the polystyrene aromatic ring. An accurate $K_a$ plot was not possible with this data. Figure 2-6 gives the 13C chemical shift for the α-methine resonance as a function of solvent composition. No obvious trend is apparent, due to the excessive scatter of the NMR data points. This could possibly be due to the rather small magnitude of the overall change in resonance frequency for the α-methine peak in the two different solvents.
Figure 2.4: $^{13}$C chemical shift vs. solvent composition for polystyrene o,m-phenyl resonance in acetone/diethylether cosolvent mixtures; • $T = 20 \, \text{C}$; ○ $T = 30 \, \text{C}$. 
Figure 2.5: $K_a$ plot for polystyrene o,m-phenyl carbons in acetone/diethyl ether cosolvent mixtures; $\bullet$ $T = 30$ C; $\circ$ $T = 20$ C.
Figure 2.6: $^{13}$C Chemical shift vs. solvent composition for polystyrene $\alpha$-methine resonance in acetone/diethylether cosolvent mixtures; 
- $T = 20$ C;  
- $T = 30$ C.
Polystyrene/Acetone/Carbon tetrachloride

Due to the inconclusive results obtained for the polystyrene methine group, a series of NMR experiments were run for polystyrene dissolved in acetone/CCl$_4$ mixtures. As CCl$_4$ is an isotropic solvent, interactions between the polystyrene and the acetone in this system might be consistent with those for the acetone/ether cosolvent.

Figure 2-7 shows the chemical shift data for the polystyrene o,m-phenyl resonance in acetone/CCl$_4$ mixtures at 20°C. The data follows volume additivity, as shown by the solid line. Figure 2-8 shows chemical shift vs. solvent composition for the a-methine resonance. In this case, there is a negative deviation towards the NMR frequency in pure CCl$_4$.

The $K_a$ plot shown in figure 2-9 summarizes the results for the PS/acetone/CCl$_4$ system. At 20°C, the association constant for the polystyrene methine unit is 0.6 ±0.1, indicating preferential solvation by the carbon tetrachloride. The $K_a$ value for the PS phenyl ring is 0.9 ±0.1, which is consistent with random polymer-solvent interactions.

Polystyrene/Acetone/Methylcyclopentane

The PS/acetone/MCP cosolvent system, as with the PS/acetone/ether system, is characterized by enhanced miscibility of the polystyrene at intermediate cosolvent compositions. The results of the $^{13}$C NMR shift versus cosolvent composition experiments for the PS o,m-phenyl resonance are shown in figure 2-10. The solid line represents the chemical shift behavior expected based on volume additivity. Although there is an
Figure 2.7: $^{13}$C chemical shift vs. solvent composition for polystyrene $\alpha$-methylene resonance in acetone/CCl$_4$ binary solvent mixtures; $T = 20^\circ C$. 
Figure 2.8. $^{13}$C chemical shift vs. solvent composition for polystyrene o,m-phenyl resonance in acetone/CCl$_4$ binary solvent mixtures; T = 20 C.
Figure 2.9: $K_a$ plot for polystyrene in acetone/CCl$_4$ binary solvent mixtures; ● o,m-phenyl; ⊗ α-methylene unit; $T = 20$ C.
Figure 2.10: $^1$H Chemical shifts vs. solvent composition for polystyrene o,m-phenyl peak in acetone/MCP binary cosolvent mixtures; $T = 20$ C.
initial negative deviation at high MCP volume fractions, the overall change in chemical shift is essentially linear. Figure 2-11 shows the same type of behavior for the $^{13}$C α-methylene resonance.

The resulting $K_a$ plots are shown in figure 2-12. For both the polystyrene phenyl ring and the backbone groups, the calculated $K_a$ values are equal to unity within experimental error. Hence the data suggests that no significant polymer-solvent preferential interactions are present in this system.

Table 2.1: Summary of association constants determined via NMR for polystyrene in binary mixed solvent systems.

<table>
<thead>
<tr>
<th>Solvent Mixture</th>
<th>PS Interaction Site</th>
<th>$K_a (± 0.1)$</th>
<th>Temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone/ether</td>
<td>p-phenyl</td>
<td>0.7</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>30.0</td>
</tr>
<tr>
<td></td>
<td>o,m-phenyl</td>
<td>0.6</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.9</td>
<td>30.0</td>
</tr>
<tr>
<td>acetone/CCl₄</td>
<td>o,m-phenyl</td>
<td>0.9</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>α-methine</td>
<td>0.6</td>
<td>20.0</td>
</tr>
<tr>
<td>acetone/MCP</td>
<td>o,m-phenyl</td>
<td>1.0</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>α-methine</td>
<td>1.1</td>
<td>20.0</td>
</tr>
</tbody>
</table>
Figure 2.11: $^{13}C$ chemical shift vs. solvent composition for polystyrene α-methylene resonance in acetone/MCP cosolvent mixtures; $T = 20$ C.
Figure 2.12: $K_n$ plot for polystyrene in acetone/MCP binary cosolvent mixtures; ○ methine carbon; ● o,m-phenyl carbons; $T = 20$ C.
Discussion

Model for Polymer-Solvent Interactions

In discussing the experimental results of this work, the validity of the model used to represent polymer-cosolvent interactions and treat the NMR data should be reviewed. As presented in chapter one, the basic premise is that the polymer, when dissolved in a binary cosolvent mixture (solvents "A" and "B"), can interact with either solvent component preferentially at different sites along the polymer chain. In the case of a favorable interaction, e.g. one in which the polymer-solvent "A" contact energy is lower than the polymer-solvent "B" contact energy, there are proportionately more polymer-solvent "A" contacts. The extent to which the polymer site is preferentially solvated by solvent "A" is represented by the association constant $K_a$. This model has been shown to fit the experimental data quite well. However, a couple of points should be kept in mind. Solvation of the polymer in the binary cosolvent mixture is a highly dynamic process. Polymer-solvent contacts or interactions are in a constant state of flux, and hence a "polymer-solvent "A" contact" should not be viewed as a long lived species. In addition, there is really no precise definition as to exactly what constitutes a polymer-solvent "contact" or "interaction". Physical reality is quite likely more complex than the somewhat simplistic model used to represent it. However, such a model is still a useful concept. The association constant gives a quantitative manner in which to describe the extent to which a specific polymer site interacts
with a given solvent component. Such information can be valuable, as in the case of the polymer-cosolvent systems.

There are other models that have been used to describe molecular interactions in solution. For example, formation of charge-transfer complexes can be represented by \(^{42,43}\)

\[
A + D \xrightleftharpoons{} K \rightarrow AD
\]

(2-3)

where A and D are acceptor and donor molecules, and AD is the charge-transfer complex. Using the same assumptions regarding NMR measurements of chemical shifts that yields equation 2-2, the resulting expression

\[
\frac{\delta_A - \delta}{C_D} = K(\delta_A - \delta_{AD}) - K(\delta_A - \delta) \quad (2-4)
\]

is obtained, where K is the equilibrium constant for complex formation, \(\delta_A\) and \(\delta_{AD}\) are the NMR shifts for the acceptor and complex respectively, \(\delta\) is the observed shift, and \(C_D = x_D + x_{AD}\). This is known as the Scatchard equation. \(^{44}\) Other similar expressions have been developed by Scott, \(^{45}\) and Benesi and Hildebrand. \(^{46}\) These treatments are useful for systems which are forming strong charge-transfer complexes. However, systems having only weak interactions are not suitable for analysis using this approach. This is because weak AD "complexes" require relatively high donor concentrations in order to reach a measureable degree of complex formation. Hence the use of the "solvent exchange"
model (equation 2-1) provides a better description of the weak polymer-solvent interactions in the polymer-cosolvent systems.

Polystyrene/Acetone/Diethylether

The $^{13}$C NMR experiments showed evidence for a preferential interaction between the polystyrene phenyl ring and the diethylether at intermediate cosolvent compositions. Both the $p$-phenyl and $o,m$-phenyl NMR peaks showed a negative deviation away from volume additive behavior of chemical shift vs. solvent composition at $20^\circ C$. The resulting $K_a$ values of less than one for all of the PS aromatic resonances support this interpretation. The magnitude of the negative deviation in the chemical shifts vs. cosolvent composition is not very large, which suggests that the interaction between the phenyl ring and the diethylether is relatively weak in comparison to hydrogen bonding or charge transfer types of interactions. Such interactions are generally evidenced by larger shifts in NMR frequencies. Although this is a qualitative observation, it is also supported by the $K_a$ results obtained at $30^\circ C$. Raising the temperature only 10 degrees results in $K_a$ values of unity for the aromatic resonances. NMR studies of systems in which hydrogen bonding occurs, such as in haloform-ether mixtures, show that significant deviations in NMR shift vs. solvent composition behavior occur in the $30-40^\circ C$ temperature range. Typical values for the enthalpy of haloform-ether hydrogen bonding interactions are on the order of 3-4 Kcals/mole, and have been confirmed by both NMR and GLC techniques. The polystyrene phenyl ring-diethylether interactions are
undoubtedly weaker than such H-bonding interactions. Although additional experiments at other temperatures were run, it was not possible to establish a more accurate temperature dependence of the interactions($K_a$ values) due to poor NMR spectral resolution at temperatures lower than 15°C. Conversely, higher temperatures resulted in excessive loss of solvent due to evaporation of the highly volatile ether/acetone mixture.

The $^{13}$C NMR data for the polystyrene $\alpha$-methine resonance frequency as a function of cosolvent composition was less than ideal. Figure 2-6 shows significant scatter in the resonance frequency vs. solvent composition plot. This is probably due to poorer resolution of the $\alpha$-methine resonance and a small difference in the absolute chemical shifts in each of the two pure solvents (less than 12 Hz). It was therefore not possible to extract meaningful $K_a$ values from this data.

**Polystyrene/Acetone/Carbon tetrachloride**

Because of the scatter present in the NMR shift data for the $\alpha$-methine resonance in acetone/ether mixtures, a series of $^{13}$C NMR experiments were performed on polystyrene dissolved in binary mixtures of acetone and carbon tetrachloride. (This system has not been shown to exhibit any cosolvent effects.) As CCl$_4$ is an isotropic solvent, polymer-acetone interactions in this ternary system might be expected to be consistent with interactions in the PS/acetone/ether system.

The $K_a$ results depicted in figure 2-9 show no preferential interaction between the acetone and the polystyrene phenyl ring. For
the polystyrene methine group, the $K_a$ value of $0.6 \pm 0.1$ indicates that CCl$_4$ interacts more favorably at this site than does the acetone.

This result is not consistent with the proposal that there are "cooperative" preferential interactions between the solvent components and different sites on the polymer in the acetone/diethylether/polystyrene cosolvent system. If this were the case, an interaction between the acetone and the PS $\alpha$-methine unit would be expected in this system. However, the results obtained with the acetone/CCl$_4$ system should only be compared to the PS/acetone/ether system on a qualitative basis.

**Polystyrene/Acetone/Methylcyclopentane**

The polystyrene/acetone/MCP system was chosen for study in order to provide a comparison with the PS/acetone/diethylether cosolvent system. If cooperative preferential polymer-solvent interactions are a prerequisite for the observation of cosolvency, they should be evident in this system as well. The $^1$H NMR experiments, however, contradict this quite clearly. Figures 2-10 and 2-11 show that the $^1$H chemical shift vs. solvent composition behavior for both the p-phenyl and the $\alpha$-methine resonances does not significantly differ from that expected based on simple volume additivity. There appears to be a slight negative deviation in the acetone-rich portion of the graph ($\phi_{\text{MCP}} < 0.3$) but not in a significant fashion. The $K_a$ plots resulting from this NMR data (figure 2-12) show slopes of unity for both the phenyl and methine polystyrene sites, and in both cases the fit is very good. This is an
interesting result, as this system does exhibit cosolvent behavior despite the apparent lack of any significant polymer-solvent interactions. The obvious conclusion is that such interactions are not required in order for cosolvency to occur in all systems.
Chapter III

CHARACTERIZATION OF POLY(ALKYL METHACRYLATE)/POLY(VINYL CHLORIDE) BLENDS

Introduction

Poly(alkyl methacrylate) (MMA)/poly(vinyl chloride) (PVC) blends were chosen for study for several reasons. Firstly, this particular set of polymers affords the opportunity to explore the effect of a systematic change in the structure of one component on miscibility in polymer blends. The effect of structure on polymer-polymer interactions is also an important question which can be studied with this series of polymers. Also, there are commercially-available methacrylate polymers with a fairly wide variety of alkyl ester side group structures. Another factor is that the component polymers are readily soluble in a variety of solvents, which makes blend preparation a simple matter. The various functional groups of the component polymers provide NMR spectral features that are well resolved. This is important for the spectroscopic characterization discussed in Chapters III and IV. Finally, there is commercial interest in methacrylate/PVC blends, as evidenced by recent patent applications.47,48

The work presented in this chapter is concerned primarily with the characterization of the MMA/PVC blends by DSC and FTIR methods. Some additional results from low angle laser light scattering measurements of cloud points are also discussed. The experiments discussed in this
chapter provide useful information in their own right, and in addition provide essential background information on the blends required for solid-state NMR experiments. In addition, the results from techniques such as DSC and FTIR can be compared and contrasted to information gained through the use of solid state NMR techniques. This is one of the objectives mentioned in Chapter I. Much of the previous work described in the literature on blends of poly(vinyl chloride) and methacrylate polymers does not provide sufficient information about these specific systems. Sample histories, molecular weights, blend preparation and characterization methods are seldom consistent from one laboratory to another. Hence it is not always appropriate to rely on characterization results reported in the literature as the basis for additional studies.

**Experimental**

**Sample Preparation**

The various poly(alkyl methacrylate) polymers were obtained commercially through Aldrich Chemical Co. The repeat unit structures and corresponding abbreviations are shown in Figure 3-1. The molecular weights for the polymers are shown in Table 3-1. The methacrylate polymers were polymerized via free-radical initiators and hence are not monodisperse. The PMMA was shown to be atactic by proton NMR methods; the other methacrylate polymers were reported to be atactic materials as well.
Figure 3.1: Repeat unit structures and corresponding abbreviations for the various alkyl methacrylate polymers used in these studies.
Table 3.1: Molecular weights and polydispersities for the methacrylate polymers used in this study.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$ *</th>
<th>$M_n$ *</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>105</td>
<td>60</td>
<td>1.80</td>
</tr>
<tr>
<td>PEMA*</td>
<td>340</td>
<td>126</td>
<td>2.83</td>
</tr>
<tr>
<td>PBMA#</td>
<td>320</td>
<td>74</td>
<td>4.30</td>
</tr>
<tr>
<td>PCHMA**</td>
<td>280</td>
<td>110</td>
<td>2.7</td>
</tr>
<tr>
<td>PBEnMA**</td>
<td>$&gt;100$</td>
<td>$&gt;60$</td>
<td>---</td>
</tr>
</tbody>
</table>

*(g/mole x $10^{-3}$)

**Gel Permeation Chromatography

# As reported by Aldrich

The poly(vinyl chloride) used throughout the study was supplied by B.F. Goodrich, and was reported to be additive-free atactic material. Gel Permeation Chromatography was used to determine a $M_w = 66,800$ and $M_n = 54,200$, which yields a polydispersity of 1.24.

The blends were prepared by dissolving appropriate amounts of the component polymers in tetrahydrofuran (THF) to obtain 5% w/w solutions. The solutions were stirred for a minimum of 24 hours prior to precipitation into methanol. After vacuum filtration and 2-4 hours air drying, the samples were placed in a vacuum oven at $50^\circ$C for 48 hours. Oven temperature was then increased to $130^\circ$C for an additional 3-4 hours. In addition, blend films were prepared by slow casting from THF onto glass petri dishes, followed by the same drying procedure as for
the blends prepared via precipitation into methanol. The films were used for infrared spectroscopy and light scattering experiments.

**Differential Scanning Calorimetry**

Scanning calorimetry (DSC) measurements were performed with a Perkin-Elmer DSC-4 equipped with a TADS microcomputer and software for data analysis. Temperature was calibrated using an indium standard. Samples of approximately 4-7 mg were sealed in aluminum sample pans. Glass transition temperatures were obtained on second heating at a scan rate of 20 °C/minute. Midpoint values are reported except where otherwise noted. The \( T_g \) widths were obtained from plots of the first derivative of the \( C_p \) vs. temperature plot, the initial and final changes in slope of the \( C_p \) vs. temperature scan were used as the limits of the glass transition.

**Fourier Transform Infrared Spectroscopy**

FTIR spectra of the MMA/PVC blend films (80% PVC in all cases) were obtained using an IBM IR-98 spectrometer. The spectra were recorded using 2 cm\(^{-1}\) resolution and 500 scans. Infrared spectra for the methacrylate polymers dissolved in PVC analog solvents were obtained using an IBM IR-30S bench-top spectrometer using triangular apodization, 2 cm\(^{-1}\) resolution, and 30 scans. All solution spectra were obtained using a Harrick Inc. cell equipped with KBr windows. Polymer concentrations in solution were approximately 3-4%.
Thermogravimetric Analysis

Weight loss as a function of temperature was measured for the various blends and component polymers using a Perkin-Elmer DSC-4 TGA unit interfaced with a TADS data analysis station. Heating rate was 40°C/minute under a helium flow. Degradation temperatures are reported at 5% weight loss.

Light Scattering

Cloud points for the PMMA/PVC and PCHMA/PVC blends were obtained using a standard low-angle laser light scattering apparatus. Blend films (1% dioctyltin Thermolite® stabilizer was added to prevent degradation) were cast onto microscope slides and mounted in a temperature controlled Mettler hot stage. Incident light was supplied by a Hughes Aircraft Co. 5 mW helium-neon laser. Scattered intensity was monitored by an SSR Instrument Co. quantum photon detector placed at a 20° angle to the exit beam, interfaced with an SSR digital synchronous photon counter. Temperature scan rate was 2°C/minute, and all reported cloud point temperatures are the average of a minimum of three runs obtained on first heating.
Results

DSC Studies: Tg Measurements

**Poly(methyl methacrylate)/PVC**

Differential scanning calorimetry was used to measure the T_g values of PMMA/PVC blends as a function of blend composition. Figure 3.2 shows typical 2nd heating traces for pure PMMA, a 50/50 PMMA/PVC blend, and for pure PVC. All three samples show readily identifiable jumps in the C_p vs. temperature plot corresponding to the respective glass transition temperatures. The trace for the 50/50 blend exhibits a single transition intermediate between those for the pure component polymers. This indicates that the 50/50 blend is miscible. The results of other DSC glass transition measurements for PMMA/PVC blends of various compositions are depicted in Figure 3.3. The dashed line represents the transition behavior expected based on simple weight additivity. The actual results deviate from this line slightly, showing a somewhat sigmoidal shape. There is a small negative deviation in the PMMA rich region, and a small positive deviation in the PVC rich region. These results indicate this blend to be miscible for all compositions.

**Poly(ethyl methacrylate)/PVC**

Figure 3-4 shows the T_g behavior as a function of blend composition for a series of PEMA/PVC blend samples. The dashed line represents weight additive behavior. Although there is a small amount of scatter
Figure 3.2: Typical DSC traces obtained for samples of poly(methyl methacrylate), poly(vinyl chloride) and a 50/50 PMMA/PVC blend.
Figure 3.3: Glass transition temperature vs. weight fraction PMMA for PMMA/PVC blends, as determined by DSC.
Figure 3.4: Glass transition temperature vs. weight fraction PVC for PEMA/PVC blends as determined by DSC.
Figure 3.5: Glass transition temperature vs. blend composition for PBMA/PVC blends as determined by DSC.
Figure 3.6: DSC traces for poly(cyclohexylmethacrylate), poly(vinyl chloride) and a 50/50 w/w PCHMA/PVC blend.
Figure 3.7: Glass transition temperature vs. weight fraction poly(cyclohexylmethacrylate) for PCHMA/PVC blends as determined by DSC.
Figure 3.8: DSC traces for samples of poly(benzyl methacrylate), poly(vinyl chloride) and a 50/50 w/w PBenMA/PVC blend. The middle trace for the blend shows evidence of two Tg's.
Figure 3.9: Glass transition temperature vs. weight fraction PMMA for PMMA/PVC-co-VC blends as determined by DSC.
of the data points, this system appears to show a positive deviation at intermediate blend compositions. Despite the relatively small difference in $T_g$'s for the component polymers, the DSC measurements indicate a miscible blend system.

**Poly(butyl methacrylate)/PVC**

Blends of PBMA and PVC show $T_g$ versus composition behavior similar to that seen for the PMMA/PVC blends. Figure 3-5 shows that the PBMA/PVC system follows essentially weight additive behavior, as represented by the dashed line, at PVC contents greater than 40 wt%.

Glass transition measurements were obtained for blends having greater than 40 wt% PVC content. Films cast from THF at both PVC rich and PBMA rich compositions were optically transparent. There is sufficient experimental data to conclude this to be a miscible blend system.

**Poly(cyclohexyl methacrylate)/PVC**

Figure 3-6 shows typical DSC results obtained for samples of pure PCHMA, pure PVC, and a 50/50 blend. The glass transitions are readily observable, and there is a single transition for the blend. The scanning calorimetry results for the entire series of PCHMA/PVC blends are shown in Figure 3-7. There is a strong positive deviation in $T_g$ at intermediate blend compositions. Again, the dashed line represents weight additive behavior. The overall change in $T_g$ with composition shows no indication of more than one transition.
Poly(benzyl methacrylate)/PVC

Figure 3.8 shows DSC scans for pure PBenMA, pure PVC, and a 50/50 blend. Despite the relative proximity of the glass transition temperatures for the component polymers, two overlapping glass transitions are observable for the 50/50 blend. Results obtained on other PBenMA/PVC blends of varying compositions showed the same results, with the relative magnitudes of the $\Delta C_p$'s changing proportionate to the amounts of each polymer in the blend. In addition, films cast from THF and benzene showed a rather mottled appearance indicative of a phase separated system.

PMMA/Poly(vinyl chloride-co-vinylidene chloride)

This series of blends exhibits thermal transition behavior consistent with miscibility. The results shown in Figure 3.9 show $T_g$'s for the blends which are intermediate between those of the component polymers. The observed behavior for the blends follows that predicted by simple weight additivity (solid line).

Glass Transition Widths

Figure 3-10 shows the width of the glass transition plotted against blend composition for a series of PMMA/PVC blends. There is some scatter in the data points, but it is still quite easy to see a distinct increase in $\Delta T_g$ in the blends at PMMA contents above 60 wt%. Below 50 wt% PMMA, the transition widths are identical to those of the pure
components, within experimental error. The maximum transition width is approximately $30^\circ$ and occurs at a PMMA content of 80% w/w.

The PMMA/PVC-co-VC blends show similar $\Delta T_g$ behavior in comparison with the PMMA/PVC blends, as seen in Figure 3.11. Again there is a significant increase in $\Delta T_g$ at PMMA contents above 50 weight percent, with a maximum transition width of $30^\circ$ at 80% PMMA.

Figure 3.12 shows the $\Delta T_g$ behavior for PCHMA/PVC blends. These blends exhibit an initial increase in $\Delta T_g$ with increasing PCHMA content. At about 50 wt% PCHMA, there is a sudden drop in transition width, which thereafter remains constant at approximately $15^\circ$, as the PVC content decreases. The maximum transition width is approximately $20^\circ$ and occurs at 50% PCHMA content. This behavior differs considerably from that of the two blends discussed previously (PMMA/PVC and PMMA/PVC-co-VC).

FTIR Studies

The carbonyl bands for the various methacrylate polymers were studied in terms of the effect of PVC and PVC analog compounds on band position and width. Band shifts to lower absorption frequencies in these solvents as compared to isotropic solvents gives an indication as to the extent of Lewis acid-base types of interactions. The maximum shift of $-7 \text{ cm}^{-1}$ was seen for the methacrylates dissolved in chloroform, relative to the $\text{CCl}_4$ reference solvent. A small shift of approximately $1-2 \text{ cm}^{-1}$ was seen for polymers dissolved in the 1,3-dichlorobutane.
Figure 3.10: Width of $T_g$ vs. PMMA/PVC blend composition as determined by differential scanning calorimetry.
Figure 3.11: Width of T\text{g} vs. PMMA/poly(vinylchloride-co-vinylidene chloride) blend composition as determined by DSC. (PVC-co-VC polymer had 5% vinylidene chloride content)
Figure 3.12: Width of $T_g$ vs. polycyclohexylmethacrylate/PVC blend composition, as determined by differential scanning calorimetry.
Similarly, the carbonyl band shift in the blends with PVC showed only a minimal shift of about 1-2 cm\(^{-1}\). The larger shift for the CHCl\(_3\) solvent is not entirely surprising, as the lone proton is of stronger Lewis acid character than the \(\alpha\)-protons of the 1,3-dichlorobutane or PVC.

Table 3.2: Infra red carbonyl band frequencies for various methacrylate polymers dissolved in PVC analog solvents, and in PVC blends.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>CCl(_4)</th>
<th>PVC</th>
<th>1,3 dichlorobutane</th>
<th>CHCl(_3)</th>
<th>(\Delta \nu^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-PMMA</td>
<td>1734</td>
<td>1732</td>
<td>1733</td>
<td>1728</td>
<td>6</td>
</tr>
<tr>
<td>a-PMMA</td>
<td>1735</td>
<td>1732</td>
<td>1734</td>
<td>1729</td>
<td>6</td>
</tr>
<tr>
<td>PEMA</td>
<td>1733</td>
<td>1731</td>
<td>1732</td>
<td>1727</td>
<td>6</td>
</tr>
<tr>
<td>PtBMA</td>
<td>1724</td>
<td>--</td>
<td>--</td>
<td>1717</td>
<td>7</td>
</tr>
<tr>
<td>PBMA</td>
<td>1730</td>
<td>--</td>
<td>--</td>
<td>1732</td>
<td>7</td>
</tr>
<tr>
<td>PCHMA</td>
<td>1725</td>
<td>1723</td>
<td>1723</td>
<td>1718</td>
<td>7</td>
</tr>
<tr>
<td>PBenMA</td>
<td>1730</td>
<td>1730</td>
<td>1730</td>
<td>1725</td>
<td>5</td>
</tr>
</tbody>
</table>

*Difference in band positions for polymers in CHCl\(_3\) relative to CCl\(_4\).*

Light Scattering for Cloud Point Determination

Prior to the use of low-angle laser light scattering to determine cloud points, thermogravimetric analysis was carried out on PMMA, PCHMA, PVC, and their respective blends in order to determine onset of degradation temperatures. Figure 3.13 shows a typical TGA curve for a 50/50 blend of PCHMA and PVC. Two distinct weight loss shoulders can be seen, one at \(-140^\circ\) C, and a second at \(-280^\circ\) C. TGA experiments on the pure components showed that the PVC was degrading at \(140^\circ\) C, followed by
the methacrylate polymer at 280 °C. Similar results were obtained for the PMMA/PVC blends. In neither case were the degradation temperatures for the component polymers significantly affected by blending. These results indicated the use of a thermal stabilizer was required to prevent PVC degradation from interfering with the cloud point measurements.

Figure 3.14 shows a plot of the natural log of the scattering intensity as a function of temperature for three samples of an 80/20 blend of PMMA/PVC. The scattered intensity remains fairly constant until approximately 200 °C, when it starts to increase. The cloud point was taken from the intersection of the slopes of the two lines drawn through the experimental points. The reported cloud point temperatures are averages obtained from a minimum of three runs for each blend composition.

Figure 3.15 is a plot of cloudpoint temperature as a function of blend composition for the PMMA/PVC system. There is a distinct LCST curve apparent at compositions containing greater than 50 wt% PMMA. The PCHMA/PVC blends, however, showed no apparent phase separation prior to onset of degradation under similar experimental conditions.
Figure 3.13: TGA weight loss vs. temperature plot for a 50/50 blend of poly(cyclohexylmethacrylate) and poly(vinyl chloride).
Figure 3.14: Scattering intensity at 20° angle for determination of cloud point for a PMMA/PVC 80/20 blend. Thermal scan rate was 2 degrees/minute. Triangles represent temperature taken as the cloud point for each run.
Figure 3.15: Cloud-point curve for PMMA/PVC blends determined by light scattering; LCST behavior is evident at PMMA contents greater than 50%.
Discussion

The scanning calorimetry studies of the methacrylate/PVC blends provide some interesting and somewhat surprising results. Initially it was expected that the change in methacrylate alkyl ester structure would result in a decrease in miscibility for the polymers having bulkier side groups. This prediction was based on an earlier report which indicated that poly(n-hexyl methacrylate) and poly(n-octyl methacrylate) formed immiscible blends with PVC. Hence it might be expected that certain of the methacrylate polymers, such as poly(cyclohexyl methacrylate), would be immiscible with PVC as well. However the results showed that each of the methacrylate/PVC blends studied had a single $T_g$ intermediate between those of the pure components, with the sole exception being the poly(benzyl methacrylate)/PVC blends which showed two distinct $T_g$'s corresponding to those of the pure components.

The $T_g$ vs. blend composition data provides more information than is possibly gained by just looking at a single blend composition, as is often the case in the literature. The results reported here indicate that there are significant variations in the glass transition as a function of blend composition behavior, depending on the methacrylate ester group structure.

The PMMA/PVC blends, as shown in Figure 3-3, exhibit an S-shaped deviation away from the weight additive case represented by the dashed line, which can be described by Equation 3-1:
\[
T_g = w_1 T_{g1} + w_2 T_{g2} \tag{3-1}
\]

where the glass transition temperature of the blend is proportional to the relative amounts \(w_1\) and \(w_2\) of each component. More typically, a miscible blend will follow a slightly negative deviation from the weight additive case across the entire range of blend compositions. Such behavior can be described by a number of empirically derived expressions, perhaps the most well known being the Fox equation \(^{50}\)

\[
1/T_g = w_1/T_{g1} + w_2/T_{g2} \tag{3-2}
\]

The usual explanation for stronger negative deviations than are predicted by equation 3-2 is based on the premise that there is less than ideal mixing in the system. This may also be accompanied by a broadening of the transition at intermediate compositions, which can be indicative of local compositional fluctuations or microheterogeneity. However, this is an essentially qualitative explanation and has not been rigorously confirmed. For the case of the PMMA/PVC system, the breadth of the glass transition does increase at the same blend compositions which show a negative deviation (above 50 wt% PMMA). The observation that the PMMA/PVC blends show LCST behavior for PMMA contents greater than 50 wt% is consistent with the DSC data, in the sense that taken together it is indicative of greater miscibility or single phase stability for the PVC-rich region.
The PCHMA/PVC blends, in addition to showing single glass transition temperatures at intermediate compositions, exhibit a surprisingly strong positive deviation overall. Explanations for positive deviations have been proposed which are based on strong molecular interactions between the blend components. For example, if the two polymers have strong exthermic specific interactions, a negative volume of mixing or densification may result at intermediate blend compositions. This negative $\Delta V_{\text{mix}}$ would result in a higher than expected glass transition temperature due to a reduction in free-volume. However, differential scanning calorimetry measures only the macroscopic thermal properties of the system in question. Although interpretations of the results may involve microscopic level phenomena such as crystallization, molecular interactions, and molecular motions associated with $T_g$, it must be remembered that DSC is not a molecular level probe of the system. Hence positive deviations in $T_g$ at intermediate blend compositions are not adequate proof of strong polymer-polymer interactions. Such deviations can be explained by other considerations. For example, one possible reason for positive deviations is related to the relative expansivities of the component materials. The Kelley-Bueche expression is given as $^{53-55}$

$$T_g = \frac{[T_g + (KT_g^2 - T_g)\phi_2]/[1 + (K - 1)\phi_2]}$$

where $K = \Delta \alpha_1 / \Delta \alpha_2$. The terms $\Delta \alpha_1$ and $\Delta \alpha_2$ are defined as the difference in the thermal expansivities above and below the glass transition
temperature for each component polymer. The PCHMA/PVC blend $T_g$ vs. composition behavior can be fit using the Kelley-Bueche expression along with a $K$ value of $= 2.0$ (for $T_g^1 = 358$ K and $T_g^2 = 388$ K). This would indicate a larger $\Delta \alpha$ for the PCHMA, however this has not been verified experimentally.

A more recent approach by Couchman relates the $T_g$-blend composition behavior to differences in the relative heat capacities above and below the glass transition for the component polymers. The general expression is given as

$$T_g = (M_1\Delta C_p^1\ln T_g^1 + M_2\Delta C_p^2\ln T_g^2)/(M_1\Delta C_p^1 + M_2\Delta C_p^2) \quad (3.4)$$

where $M_1$ and $M_2$ are the mass fractions of polymers 1 and 2, and the $\Delta C_p$'s are the difference in heat capacities above and below the glass transition for the blend components. Positive deviations for systems such as the PCHMA/PVC blends would hence be due to the relative $\Delta C_p$ values for each polymer.

Both equations can be used to fit the $T_g$ data for the PCHMA/PVC blends. However, it is not possible to establish the validity of the fitting parameter in either case. Both of these treatments, the Kelley-Bueche and the Couchman equations, rely on the assumption that the $\Delta C_p$'s and the $\Delta \alpha$'s for the component polymers are unaffected by the blending process. This may be the fortuitous truth for some systems, but it is not always the case. This is seen for the PMMA/PVC blend, which exhibits a sigmoidal $T_g$ vs. composition curve. Although it may be
possible to fit the data using either of these treatments, the result may still be somewhat empirical.

The other methacrylate/PVC blends showed varying $T_g$-composition behavior. Poly(methyl methacrylate) blended with PVC-co-VC showed essentially the same behavior as the PMMA/PVC blends. The poly(ethyl methacrylate)/PVC blends showed a positive deviation, although the close proximity of the two $T_g$'s renders this interpretation subject to more uncertainty than for the other systems. The poly(butyl methacrylate)/PVC blends exhibited weight additive behavior, up to a PBMA content of 60 wt%.

The FTIR results were rather interesting, especially in view of the DSC results regarding positive $T_g$ deviations for some of the methacrylate blends. The infrared carbonyl absorption band for each of the methacrylate polymers was monitored for changes in frequency and bandwidth after dissolution in PVC analog solvents. This was also done for methacrylate polymers blended with PVC. It has been well documented that shifts in carbonyl band position to lower absorption frequencies, and increases in bandwidth, can be correlated with the strength of Lewis acid-base types of interactions.\textsuperscript{57-59} Fowkes and coworkers have demonstrated for PMMA and other ester-containing polymers that the magnitude of the carbonyl shift to lower frequencies is directly proportional to the strength of the interaction as determined by calorimetric studies.\textsuperscript{57} Carbonyl groups dissolved in stronger Lewis acids show larger low-frequency shifts, and smaller shifts in weaker Lewis acids. However, these low-frequency shifts are not necessarily
Figure 3.16: FTIR spectra showing carbonyl band region for syndiotactic PMMA dissolved in various PVC analog solvents and in a PVC blend.
Carbonyl Band for Syndiotactic PMMA in PVC and Analogous Solvents

- CCl₄
- PVC and CH₃CCH₂CH₂Cl
- CHCl₃

Sample Name: SAMPLE 032266E, S-PMMA in CCl₄
Sample Form: NOT GIVEN
Operator: JERRY PARKER
Apodization: TRIANGULAR
Resolution: 2 cm⁻¹
Created: 3/23/86 14:10:40
Scans: 30
indicative of hydrogen-bonding interactions. True hydrogen bond formation may actually result in the formation of a second distinct absorption band, although this is a matter of some controversy.

For the various methacrylates in this study, the carbonyl band shift in the PVC analog solvents was of the same magnitude no matter what the ester group structure. The same result was found for the blends with PVC, with the exception of the poly(benzyl methacrylate). The results are summarized in Table 3.2.

The FTIR results are consistent with the conclusion that the methacrylate alkyl ester group does not significantly affect the ability of the carbonyl group to interact with weak Lewis acids. It is fairly well established that such an interaction is at least partially responsible for the miscibility of a wide variety of polyesters and methacrylates with various chlorinated polymers. The fact that the methacrylate ester group does not inhibit such interactions is entirely reasonable, as the alkyl group is neither strongly electron withdrawing or donating insofar as the carbonyl group is concerned. It might be argued that steric factors could come into play, with the bulkier groups inhibiting carbonyl interactions, but that does not appear to be the case for these systems.

The observation that carbonyl group Lewis acid interaction potentials remain constant for the various methacrylate polymers contradicts possible explanations for positive deviations in blend Tg's based on arguments of stronger polymer-polymer interactions. If the observed positive deviations for the PEMA/PVC and PCHMA/PVC blends were
due to stronger interactions, it would be reflected in the FTIR results. The differences in $T_g$ vs. blend composition behavior among the various blends can be related to differences in heat capacities ($\Delta C_p$) or thermal expansivities as discussed in reference to Equations 3.3 and 3.4.

The laser light scattering results seem to indicate a higher degree of single-phase stability for the PCHMA/PVC blends in comparison with the PMMA/PVC blends. The cloud point measurements for the PMMA/PVC blends clearly showed LCST behavior, whereas the PCHMA/PVC blends did not phase separate prior to the onset of degradation at 250 °C. Although the IR results indicate no differences in polymer-polymer carbonyl-PVC interaction strengths, such a result can still be explained. Lower critical solution phenomena are a result of an increasingly positive contribution to $\Delta G_{mix}$ by the free-volume or entropy contribution to the polymer-polymer interaction parameter.\(^{61}\) This is generally thought to be a result of increasingly disparate free volumes for the component polymers as the temperature is increased, as a result of different thermal expansivities for each polymer. It is quite possible that the difference in $\alpha$'s, and hence in free volumes at higher temperatures is of less significance for the PCHMA/PVC system due to a better match of thermal expansivities. Thus it is not necessary to invoke stronger interactions for the PCHMA/PVC system in comparison to the PMMA/PVC blends as a cause for greater single phase stability.
Conclusions

In summary, it has been demonstrated that a systematic change in the structure of the methacrylate alkyl ester group has a definite impact on the properties of the polymer itself as well as in the PVC blends. However, the effects are somewhat surprising. The methyl and n-butyl methacrylate/PVC blends show a linear change in glass transition temperature proportionate to the weight fraction of each component. The ethyl and cyclohexyl methacrylate/PVC blends show a strong positive deviation. On the scale of the DSC measurement, (≈ 300 A) the bulkier ester groups do not inhibit miscibility with poly(vinyl chloride). The single exception was for the poly(benzyl methacrylate), which was immiscible with PVC as indicated by DSC.

The FTIR results showed that interactions between the carbonyl groups of the various methacrylate polymers and PVC as well as PVC analog compounds are unaffected by ester group structure. The magnitude of the carbonyl band shifts was 1-2 cm\(^{-1}\) in the PVC blends and 6-7 cm\(^{-1}\) in chloroform. This result contradicts possible explanations for the observed positive deviations in \(T_g\) vs. blend composition behavior based on stronger polymer-polymer interactions for the PCHMA/PVC and PEMA/PVC systems.

The laser light scattering experiments showed LCST behavior for only the PMMA/PVC blends. This result is consistent with the conclusion that the bulkier methacrylate ester groups do not inhibit miscibility with PVC.
Chapter IV

SOLID STATE NUCLEAR MAGNETIC RESONANCE STUDIES OF POLY(METHYL METHACRYLATE)/POLY(VINYL CHLORIDE) BLENDS

Introduction

In order to evaluate the effects of structural changes in polymer blend components on molecular scale phenomena such as molecular interactions and segmental mixing, experimental techniques must be used which are direct probes of the system at the molecular level. The use of solid state NMR provides this ability. The various parameters measured with NMR depend on both polymer structure and the local environment of the nucleus. Blending two different polymers can alter the local magnetic field at the nucleus to the extent that changes in chemical shift occur. Carbon-13 relaxational processes may be affected by changes in molecular motions brought on as a result of blending. Diffusion of spin energy between domains of the blend components may also change proton relaxation times of the component polymers. The study of these parameters can offer information on distance scales ranging from the molecular level to the 400-500 ångström range depending on the specific system in question.  

The initial problem that must be addressed when undertaking studies of this nature involves appropriate parameter selection. In other words, which of the many possible solid state NMR experiments will
provide the best or most interesting information? The available literature provides good background information for the selection of appropriate SS-NMR experimental procedures, however, the field is still new enough at this point in time to make it difficult to choose the best experiment a priori for every system. A judicious choice of experimental techniques and conditions must be determined to some extent by trial and error. The type of information gained by each of the various NMR experiments is fairly well established, which does improve the situation. For example, experiments which monitor \textsuperscript{1}H spin diffusion properties are often the best way to estimate domain sizes or extent of phase segregation in blends, provided the intrinsic proton relaxational processes of the components are amenable to such experiments. This chapter will outline various solid state NMR experiments and results for the series of poly(alkyl methacrylate)/PVC blends.

**Experimental**

The alkyl methacrylate polymers and the poly(vinyl chloride) used for these experiments were the same polymers used in the DSC and FTIR studies. Molecular weight and other information is provided in the experimental section of Chapter 3 page 48.

The polymer blends were prepared by dissolving appropriate amounts of the component polymers in THF to make \(\approx 5\%\) w/w solutions. After stirring for 24 hours, samples were precipitated into methanol, vacuum
filtered and washed with additional methanol. All samples were dried in vacuo at 50\(^\circ\)C for 48 hours, followed by an additional 3-4 hours under vacuum at 130\(^\circ\)C.

All solid state NMR experiments were performed using an IBM AF-200 spectrometer equipped with variable temperature control and magic-angle spinning. The spectrometer utilized an Oxford superconducting magnet with a proton resonance frequency of 200 MHz and a carbon frequency of 50 MHz. The solids probe was manufactured by Doty Scientific Inc. A preamp blanking circuit was added to prevent preamp overloading. Samples were packed in a cylindrical sapphire rotor equipped with Vespel or Kel-f endcaps. Spinning rates were generally 3.5-4.5 KHz; spinning rate adjustments were made as necessary for removal of spinning sidebands. A 90° pulse width of 5 usec was employed. The spectral width was 20,000 Hz with a digital resolution of 9.7 Hz. The minimum number of FID accumulations was usually 256, although longer acquisitions were used when needed to improve signal-to-noise (S/N) ratios. The Hartman-Hahn match was adjusted prior to every spectral acquisition using a ditertbutyl benzene standard. Adamantane was used to adjust field homogeneity. The various pulse sequences used for the relaxation experiments are shown in Figure 4.1. All spectra were obtained at ambient temperature, except where noted otherwise.
Figure 4.1: Pulse sequences used to determine solid state carbon and proton relaxation times.
Results

Solid State $^{13}$C Spectra

Figure 4.2 shows a solid state $^{13}$C spectrum of poly(vinyl chloride), obtained with a 2 msec cross-polarization (CP) contact time and 256 FID accumulations. Two distinct resonances are clearly visible. The downfield resonance (b) at = 51 ppm is due to the chlorinated carbon. The upfield resonance at 46 ppm (a) is the methylene or CH$_2$ carbon. The peak widths are broader than usual in comparison to other glassy polymers, possibly due to carbon-chlorine quadrupolar coupling. However, the coupling is not of sufficient magnitude to significantly inhibit resolution of the two resonances.

Figure 4.3 shows a typical solid state $^{13}$C spectrum of pure poly(methyl methacrylate), obtained with a 2 msec CP contact time and 256 FID scans. The resolution and signal-to-noise ratio are quite good. The resonances (from high to low field) are due to the α-CH$_3$, quaternary, methoxy, and carbonyl carbons respectively. The CH$_2$ resonance is not visible.

A representative $^{13}$C spectrum for a PMMA/PVC 20/80 blend is shown in figure 4.4. The PVC resonances overlap with the quaternary and methoxy resonances of the PMMA. (The O-CH$_3$ signal is seen as a small peak midway between the two more intense signals at 44 and 51 ppm.) The PMMA resonances are correspondingly less intense in comparison with the PVC resonances due to the smaller amount of PMMA in the blend. In this instance, the signal-to-noise ratio is low due to the smaller amount of
Figure 4.2: Solid state CP-MAS $^{13}$C NMR spectrum of poly(vinyl chloride), obtained with 2 msec CP contact time and 256 scans.
Figure 4.3: Solid state CP-MAS $^{13}$C NMR spectrum of poly(methyl methacrylate), obtained with 2 msec CP time and 256 scans.
Figure 4.4: Solid state CP-MAS $^1$C NMR spectrum of a 20/80 w/w blend of poly(methyl methacrylate) and poly(vinyl chloride).
Figure 4.5: Solid state CP-MAS $^{13}$C spectrum of a 50/50 blend of poly(ethyl methacrylate)/poly(vinyl chloride).
Figure 4.6: CP-MAS $^{13}$C spectrum of a 50/50 blend of poly(butyl methacrylate)/PVC, obtained with 2 msec CP time and 256 scans.
Figure 4.7: Solid state CP-MAS $^1$C NMR spectrum of a 50/50 w/w blend of poly(cyclo hexylmethacrylate) and poly(vinyl chloride).
Figure 4.8: Top CP-MAS $^1$C spectrum is of poly(benzyl methacrylate). Bottom spectrum is of a 30/70 w/w PBenMA/PVC blend.
material packed into the rotor.

Additional solid state spectra and peak assignments for the other MMA/PVC blends are shown in Figures 4.5-4.8. Peak assignments are as listed in the accompanying captions.

\[ ^{13}C \text{ Spin Lattice Relaxation Time Measurements} \]

A Spin Lock-90\( _x \) -(\( \tau \))-90\( _x \) pulse sequence (as shown in Figure 4.1) was used to measure \(^{13}C\) spin lattice relaxation times (\( T_1 \)) for PVC, the methacrylate polymers, and the respective blends. Spectra were obtained for several values of delay time \( \tau \), usually a minimum of 8 spectra were generated for each \( T_1 \) determination. When using the above pulse sequence, the carbon signal intensity as a function of delay time \( \tau \) is given by

\[ M_I = M_0 \exp(-\tau/T_1) \]  

(4.1)

where \( M_I \) is the observed intensity at delay time \( \tau \), \( M_0 \) is the initial maximum signal intensity at \( \tau = 0 \), and \( T_1 \) is the carbon spin lattice relaxation time. \( T_1 \) values were obtained from the slope of a semi-log plot of \( \ln(M_I/M_0) \) vs \( \tau \). Although exponential fitting programs were readily available as part of the IBM spectrometer software package, such programs proved unreliable for accurate estimation of appropriate \( T_1 \) values. (Multi-component decay behavior was difficult to detect using the IBM software fitting program).
Figure 4.9 shows a series of PMMA $^{13}$C spectra as a function of delay time for each of the various carbon resonances. The slope of the signal intensity vs. delay time plots obtained for each PMMA resonance yield the T$_1$ relaxation times, and show single component (linear) decay for each carbon. The results for additional $^{13}$C T$_1$ experiments on the various methacrylate polymers and respective blends with PVC are summarized in Tables 4.1 - 4.4. In general, there do not appear to be significant changes in the methacrylate polymer relaxation times after blending with PVC. For example, the carbonyl groups in all of the methacrylate materials have spin lattice relaxation times on the order of 10 to 11 seconds, and these relaxation times remain essentially constant after blending with PVC. The PVC resonances for the α and β carbons overlap with the methacrylate methoxy and quaternary resonances, hence the T$_1$ values reported for the 45 and 51 ppm peaks in the various blends reflect contributions from both polymers, the relaxation times reported for the pure PVC excepted.

Table 4.1: Carbon spin lattice relaxation times for PMMA and PMMA/PVC blends as determined via solid state NMR methods.

<table>
<thead>
<tr>
<th>Group (PPM)</th>
<th>PMMA</th>
<th>50/50</th>
<th>20/80</th>
<th>PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-CH$_3$</td>
<td>15.8</td>
<td>&lt; 0.4</td>
<td>&lt; 0.4</td>
<td>&lt; 0.4</td>
</tr>
<tr>
<td>-C-</td>
<td>44.7</td>
<td>5.8</td>
<td>5.3</td>
<td>6.3</td>
</tr>
<tr>
<td>O-CH$_3$</td>
<td>52.0</td>
<td>7.5</td>
<td>6.8</td>
<td>7.1</td>
</tr>
<tr>
<td>C=O</td>
<td>177.0</td>
<td>11.0</td>
<td>8.4</td>
<td>9.2</td>
</tr>
</tbody>
</table>
Table 4.2: Carbon spin lattice relaxation times for poly(ethyl methacrylate) and PEMA/PVC blends as determined via solid state NMR.

<table>
<thead>
<tr>
<th>Group</th>
<th>(PPM)</th>
<th>PEMA 50/50</th>
<th>PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\text{CH}_3)</td>
<td>13.8</td>
<td>1.6</td>
<td>---</td>
</tr>
<tr>
<td>-C-</td>
<td>44.6</td>
<td>4.6</td>
<td>4.9</td>
</tr>
<tr>
<td>O-(\text{CH}_2^-)</td>
<td>60.3</td>
<td>5.4</td>
<td>6.3</td>
</tr>
<tr>
<td>C=O</td>
<td>176.9</td>
<td>9.7</td>
<td>9.9</td>
</tr>
</tbody>
</table>

Table 4.3: Carbon spin lattice relaxation times for poly(cyclohexylmethacrylate) and PCHMA/PVC blends as determined via solids NMR.

<table>
<thead>
<tr>
<th>Group</th>
<th>(PPM)</th>
<th>PCHMA 50/50</th>
<th>PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-CH</td>
<td>60.2</td>
<td>5.8</td>
<td>4.0</td>
</tr>
<tr>
<td>C=O</td>
<td>176.0</td>
<td>9.7</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Table 4.4: Carbon spin lattice relaxation times for poly(butyl methacrylate) and PBMA/PVC blends as determined via solid state NMR.

<table>
<thead>
<tr>
<th>Group</th>
<th>(PPM)</th>
<th>PBMA 50/50</th>
<th>PVC</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\text{CH}_3)</td>
<td>14.1</td>
<td>1.3</td>
<td>1.6</td>
</tr>
<tr>
<td>-C-</td>
<td>44.7</td>
<td>3.8</td>
<td>4.7</td>
</tr>
<tr>
<td>-(\text{CHCl}^-)</td>
<td>56.8</td>
<td>---</td>
<td>6.7</td>
</tr>
<tr>
<td>C=O</td>
<td>177.0</td>
<td>9.7</td>
<td>8.8</td>
</tr>
</tbody>
</table>
The pulse sequence used to determine $^{13}$C $T_1\rho$ relaxation times is shown in Figure 4.1. Measurements of $T_1\rho$ values were made for pure PMMA and for several blends of PMMA and PVC. Additional experiments were run on PMMA samples having various thermal and preparative histories. Determination of accurate carbon $T_1\rho$ times proved difficult. Seemingly good exponential fits of the carbon signal intensities as a function of delay time ($\tau$) were obtained using the IBM fitting program, which fits the $^{13}$C signal decay to equation 4.1 (substituting $T_1\rho$ for $T_1$).

However, semi-log plots of normalized signal intensity vs. $\tau$ showed definite non-exponential decay behavior. Figure 4.10 illustrates the $^{13}$C $T_1\rho$ results for the carbonyl group of pure PMMA, and the PMMA carbonyl group in a blend with PVC. There are clearly both fast and a slow components to the $T_1\rho$ decay process. In general it was found that semi-log plots of signal intensity as a function of delay time were the best way to establish if single component relaxation was occurring.

There was no significant difference for the pure PMMA and PMMA/PVC blend samples. This type of result was also obtained for the other PMMA samples; sample history did not appear to have a significant effect on the $T_1\rho$ relaxation times. (The samples were annealed for various lengths of time at 125°C from 1/2 to 6 hours; precipitated, as received, and freeze dried PMMA were used.) Due to the nature of these results, no further experiments with other methacrylate polymers were attempted.
Figure 4.9: Series of $^{13}$C spectra for PMMA obtained at varying delay times ($t$) for determination of carbon $T_1$ relaxation times.
Figure 4.10: Carbonyl signal intensity vs. delay time ($\tau$) of poly(methyl methacrylate) and a 60/40 w/w PMMA/PVC blend, for determination of carbon-13 rotating frame spin lattice relaxation time.
Chemical shifts for the various methacrylate resonances were measured before and after blending with PVC. Particular attention was given to the resonance frequencies of the methacrylate carbonyl bands. Although there were changes in the chemical shifts of the PMMA carbonyl resonances before and after blending with PVC, there did not appear to be any consistent pattern to these changes. This observation was repeated for the other blends as well. Any shifts in the peak positions which may be occurring due to polymer-polymer interactions must therefore be smaller than the resolution limits of the spectrometer.

Proton Spin Lattice Relaxation

Measurements of rotating frame spin-lattice relaxation times ($^1H T_1^p$) were made using the 90-$\tau$-SL pulse sequence illustrated in Figure 4.1. Use of this procedure allowed the determination of the $^1H T_1^p$ values for the blends and component polymers by monitoring the change in carbon signal intensities as a function of delay time ($\tau$). This method provides more detailed information regarding the proton relaxation behavior than techniques which measure proton relaxation times directly. (Although this method is more time consuming) Depending on the $^{13}C$ peak studied, the nature of the proton spin-lattice relaxational process in the immediate vicinity of either blend component can be studied and compared to the relaxation behavior in the pure components.

Figure 4.11 shows the results of a solid state proton $T_1^p$ 90°-$\tau$-SL experiment on a sample of pure poly(benzyl methacrylate). The
Figure 4.11: Normalized $^{13}$C signal intensity vs. delay time ($\tau$) for poly(benzyl methacrylate) resonances, for determination of $T_1^p$ relaxation times.  

- $\circ$ carbonyl;  
- $\bigcirc$ aromatic C$_1$;  
- $\bigotimes$ aromatic C$_{2-6}$;  
- $\bullet$ methyl.
normalized carbon signal intensities for each of the PBenMA resonances are plotted on a semi-log scale against delay time (τ). The slope of each line yields the proton $T_1^p$ time determined via each of the different carbon signals. In this example, all of the carbon resonances decay at the same rate, yielding a proton spin lattice relaxation time of approximately 8.0 msec. The fact that the identical $^1H$ relaxation time is obtained from each carbon resonance indicates a tightly coupled spin system, that is, spin diffusion among the different protons in the homopolymer is an efficient process. This averages out the overall proton decay rate to a single value, despite the presence of different types of protons in the polymer. Each of the different methacrylate polymers as well as the PVC showed this type of behavior.

Solid state proton $T_1^p$ experiments were concentrated primarily on three different blend systems. Based on the DSC results and the different ester group structures, the PMMA/PVC, PCHMA/PVC, and PBenMA/PVC systems were selected for study. The blends chosen provide a good basis for comparisons and evaluation of the technique as applied to each of the methacrylate/PVC blend systems. Proton $T_1^p$'s were measured for each of the component polymers and for blends of various compositions.

Figure 4.12 depicts the results of the $^1H$ $T_1^p$ measurements for PMMA, PVC, and a phase separated mixture of the component polymers prepared by simply mixing the polymer powders in the sample rotor. The pure PMMA exhibited a proton $T_1^p = 9.3$ msec, as determined from the slope of the carbonyl signal decay. The pure PVC showed a faster
Figure 4.12: Proton T$_1$ decay plots for poly(methyl methacrylate), poly(vinyl chloride), and a simple mixture of the two powders.
Figure 4.13: Proton $T_1^p$ decay plots for PMMA, PVC, a 60/40 w/w blend and a 30/70 w/w blend. Temperature = 333 K.
Figure 4.14: Proton $T_1$ decay plots for poly(methyl methacrylate), poly(vinyl chloride), and a 50/50 PMMA/PVC blend. ($T = 295 \text{ K}$)
Figure 4.15: Proton $T_1$ plot for poly(cyclo hexylmethacrylate), poly(vinyl chloride, a 80/70 w/w blend and a 60/40 w/w blend.
Figure 4.16: Proton $T_1^*$ decay plot for poly(benzyl methacrylate), poly(vinyl chloride), and a 30/70 w/w blend.
relaxation, \( T_1^p \) was \( \approx 7.3 \) msec. Interestingly, the PVC \( \alpha \)-carbon signal intensity shows what appears to be two component decay behavior. There is an initial rapid drop in signal intensity, followed by a regime which relaxes somewhat more slowly. The \( T_1^p \) result for the 50/50 mixture of the two polymers indicates no change in the \( T_1^p \) decay as determined via the PMMA carbonyl resonance.

An identical series of experiments run with the PMMA/PVC blends at ambient temperature (see Figure 4.14) showed a small change in \( ^1H \ T_1^p \) after blending, but the decay rates for the pure PMMA and PVC were very close. Increasing the temperature resulted in a larger difference in the \( T_1^p \) values of the components, which provided better definition of the intermediate decay rates for the blends.

Figure 4.13 summarizes the proton \( T_1^p \) results obtained at 333 K for pure PMMA, pure PVC, a 60/40 and a 30/70 wt% blend. In this case, the \( ^1H \ T_1^p \) relaxation behavior is very different from that of the PMMA/PVC mixture. The decay rates of the pure component polymers are \( \approx 7.3 \) msec for the PVC and 9.3 msec for the PMMA. However, after blending, there is a definite change in the observed relaxation time. As the PVC content in the blend is increased, the proton \( T_1^p \) time as measured via the PMMA carbonyl signal decreases. Both of the blend samples have proton \( T_1^p \) times intermediate between the relaxation times for the pure components. In addition, there appears to be no evidence for multicomponent decay in either of the blends. The signal intensity vs. \( \tau \) plots show a linear slope for both blends, and hence a single
component relaxation process. These results indicate efficient communication of spin energy between the two blend components.

The results of the proton $T_1^p$ measurements on the PCHMA, PVC and poly(cyclo hexylmethacrylate)/PVC blends are shown in Figure 4.15. (Both PCHMA and PCHMA/PVC blend relaxation times were determined via the carbonyl signal). The pure PCHMA exhibited a proton $T_1^p$ time of $= 2.4$ msec; the PVC relaxation time was again $= 7.3$ msec. The $T_1^p$ results for the PCHMA/PVC blends were similar to those observed for the PMMA/PVC blends. The PCHMA/PVC blend relaxation times were found to be intermediate between those of the pure component polymers. As the PCHMA content was increased, the blend $T_1^p$ relaxation time approached the value observed for pure PCHMA. For the 30/70 blend, however, the signal decay did appear to exhibit a slight two-component character. The difference between the fast and slow rates is very small, but this could possibly indicate less than 100% efficiency in the spin diffusion process in the 30/70 blend.

The poly(benzyl methacrylate)/PVC blend results were very different from those for the PMMA and PCHMA blends. Figure 4.16 shows the results of the proton $T_1^p$ measurements for pure PBenMA, pure PVC, and a 30/70 blend. Despite the excess of PVC present in the blend, no significant change in the slower PBenMA relaxation time is observed. Because the $T_1^p$ measurement was obtained via the PBenMA carbonyl signal, this indicates no spin diffusion between the two blend components.
Discussion

The most basic NMR experiment is simply the acquisition of a spectrum for a given compound. The types of results obtained with the solid state $^{13}$C CP-MAS spectrometer demonstrate the utility of the CP-MAS technique for this purpose. For each of the samples, the resolution of the various polymer carbon units is quite good. The broad range of $^{13}$C resonance frequencies (220 ppm) makes differentiation of the individual resonances much easier than would be possible for proton spectra in the solid state. The $^{13}$C peak assignments were based on either published solution spectra or expected shifts for the various functional group carbons. The spectra for some of the poly(alkyl methacrylate)/PVC blends had overlapping peaks, as the PVC α and β carbon signals at 45 and 61 ppm were coincidental with the methoxy and quaternary peaks.

The fact that the PVC peaks were = 2-3 times broader than the peaks for the other polymers is probably due to moderate carbon-chlorine quadrupolar coupling. This could cause broadening due to unresolved $^{13}$C-Cl splittings, or possibly shorter Cl $T_1$ processes affecting the carbon $T_2$ behavior. The $^{13}$C $T_1$ measurements showed that the PVC carbons have comparable spin-lattice relaxation times to those of the methacrylate polymers, and hence differences in the MHz range motional processes can not be a significant factor.

The $^{13}$C $T_1$ experiments were undertaken in order to evaluate the effect of methacrylate polymer structure and blending with PVC on the
carbon spin-lattice relaxation behavior, with the thought that information on interactions or miscibility might be provided on a site-specific basis. The results as summarized in Tables 4.1 - 4.4 seem to indicate that the methacrylate polymer carbon $T_1$ relaxation behavior is not significantly affected by blending with PVC. In order to explain this result, the basic factors which contribute to the carbon spin lattice relaxation process must be considered.

Because of the low natural abundance of the $^{13}C$ nuclei (sometimes referred to as S Spins), spin-spin interactions between carbons are negligible. Proton (I spins) carbon spin-spin interactions are also not a significant factor in the $^{13}C T_1$ process, due to the large difference in the Larmor frequencies for the two different nuclei. This effectively isolates the two spin systems, which means that the dominant factor governing the efficiency of the $T_1$ relaxation is the spectral density of molecular motions at or near the Larmor frequency. Fluctuating dipolar fields in this frequency range control the coupling of the S spin system to the lattice. For $^{13}C$ nuclei, this comprises motions in the MHz frequency range. The small amplitude of such motions in solid polymers results in carbon $T_1$ times which are typically much longer than those found in solution. This is seen in the results obtained in this study, with the $T_1$ values for the polymers ranging from less than 0.4 seconds to 10 seconds.

The fact that the methacrylate polymer $T_1$ times remain substantially unchanged after blending is likely due to relatively little alteration of the motional processes in the MHz regime, either in terms
of the spectral densities or amplitudes. In retrospect, this is not a surprising result. All of the carbon $T_1$ measurements were made at ambient temperature, which is well below the glass transitions for all of the blends. Polymer molecular motions in the MHz frequency range have been proposed to be of a short range torsional nature, and hence can still be present in polymer systems which are well below $T_g$. The longer range cooperative main chain motions in the kilohertz frequency range, which are more likely to be affected by blending, are not a factor in the $T_1$ process.

Any specific interactions between the blend components apparently do not affect the short range MHz motions to any significant degree.

The results of the $^{13}$C $T_1\rho$ experiments did not provide any conclusive information regarding the effect of methacrylate structure on blend miscibility. Although the carbon $T_1\rho$ relaxation is strongly dependent on molecular motions in the KHz range, there are other factors which complicate the relaxation process. There are explanations for this based on I spin/S spin cross relaxation resulting from the strong coupling of the proton dipolar fields to the lattice. This results in multicomponent decay behavior, such as that observed in our experiments. However, there is controversy regarding the interpretation of carbon $T_1\rho$ data. The results obtained of the PMMA/PVC system indicated that further $^{13}$C $T_1\rho$ measurements would be inadvisable.

Changes in the NMR resonance frequency for a given compound can sometimes be correlated with intermolecular interactions. This is because such interactions can perturb the local magnetic field at the
observed nucleus, resulting in shifts in resonance frequency. Changes in chemical shifts have been used to study molecular interactions in a variety of systems, mostly in solution (see Chapter II). It might be expected that similar effects would be present in solid state spectra as well, and some reports indicate this to be the case. The results for the poly(alkyl methacrylate)/PVC blends showed no significant or consistent changes in carbon resonance frequencies that could be attributed to polymer-polymer interactions. Although favorable specific interactions must be present in order to induce blend miscibility, and even though the FTIR studies indicate carbonyl-PVC interactions in these systems, the effect on solid state $^{13}$C chemical shifts is negligible. Any changes which may be present are below the resolution limits of the spectrometer.

The measurements of the $^1$H $T_1\rho$ relaxation times for the PMMA, PCHMA, PBenMA, PVC, and respective blends proved to be particularly valuable. The utility of the proton relaxation measurements lies in their ability to probe blend miscibility on a much smaller scale than is possible using methods such as DSC. Given the appropriate experimental conditions, establishment of hetero or homogeneity is possible on a distance scale ranging from 25 - 500 Å. The evaluation of how polymer structure or blend composition affects blend miscibility may in many cases require characterization at small distances, as changes are not necessarily detectable with DSC or other such methods.

Because of the high natural abundance of the protons, I spin-spin coupling is an important process. For example, this is the reason for
the observation of a single \( ^1 \text{H} T_1 \rho \) for all of the various protons in the PBenMA (Figure 4.11) and other polymers. The I spin system reaches internal equilibrium much more rapidly than it reaches equilibrium with the surrounding lattice. The strong coupling between nearby protons results in efficient transfer of spin energy. (Both intra and intermolecular coupling can be significant) This process can just as easily occur between different polymer molecules, depending on the scale of mixing. If two blend components are intimately mixed, a single relaxation time for the blend may be observed. The proton \( T_1 \rho \) behavior for the PMMA/PVC and PCHMA/PVC blends showed single component relaxation rates intermediate in value between those of the component polymers. This is an important result. The fact that a single intermediate relaxation time for the blend is observed means that intermolecular transfer of proton magnetization is an efficient process on the same time scale as the decay process.

On the basis of strong spin diffusion coupling between the two blend components, the observed \( T_1 \rho \) times should follow the expression\(^7^0\)

\[
K_B = K_1 (N_1/N_T) + K_2 (N_2/N_T)
\]  

\[ (4.2) \]

where \( K_B \) is the relaxation rate for the blend (\( K_B = 1/T_1 \rho \)), \( K_1 \) and \( K_2 \) are the spin-lattice relaxation rates for the component polymers, \( N_1 \) and \( N_2 \) are the number of component protons, and \( N_T \) is the total number of protons in the blend. The \( K_B \) values for the PMMA/PVC and PCHMA/PVC blend roughly follow this expression, however the difference in the
relaxation rates of the components is not large. However, the fact that there is only a single component decay observed for the blends does establish the existence of strong diffusion coupling. In addition, the fact that the procedure used monitors proton relaxation behavior via the carbon signals provides a more detailed picture of the blend system. This type of experiment follows the behavior of the protons in the immediate vicinity of the polymer chain to which the carbon signal belongs. Hence changes in relaxation behavior are more sensitive to the immediate environment of the given blend component than those measured by following the bulk proton signal in the solid state. (The relaxation rates of the two blend components must differ by at least a factor of two in order to accurately evaluate the existence of spin diffusion.) Direct measurement of proton relaxation behavior may provide faster data accumulation, but it is a less elegant approach.

The transfer of magnetization from one "domain" to another is a simple gradient driven diffusional process, and is exactly analogous to heat flow or any other such process. Hence, it is possible to estimate the distance over which energy transport takes place if the time scale of diffusion and the diffusion coefficient are known. Although the $T_{1p}$ experiment does not directly measure the characteristic diffusion time constant, an upper limit can be established on the basis of the observed $T_{1p}$ for the blend. (Only if intermediate single component decay is present) An upper limit to the distance over which spin diffusion occurs can be estimated using Equation 4.3. 

65,71
\[ \langle x \rangle^{1/2} = (2D\tau)^{1/2} \]  \hspace{1cm} (4.3)

where \( x^2 \) is the mean square transport distance occurring during a time \( \tau \), and \( D \) is the diffusion coefficient. Substituting a value of \( 5.0 \times 10^{-12} \) for \( D \) and 8 msec for \( \tau \), the PMMA/PVC system yields \( \langle x \rangle^{1/2} \) of \( 30 \) \( \text{Å} \). A similar calculation for the PCHMA/PVC system using \( \tau = 6.0 \) msec yields \( \langle x \rangle^{1/2} = 25.0 \) \( \text{Å} \).

The accuracy of the calculated mean square transport distances depends on the validity of the particular model used to derive Equation 4.3. When reporting such numbers, two points should be noted. First, the calculated \( \langle x \rangle \) is actually an upper limit to the scale of heterogeneity in the blend. This is because the \( ^1H\ T_1\rho \) experiment is not measuring the actual time constant for spin diffusion (\( \tau \)), and the calculation is based on the assumption that \( \tau \) must be the limiting factor for the observation of intermediate single component \( T_1\rho \) decay in the blends as compared to the component polymers. Secondly, the model from which Equation 4.3 is derived may not necessarily be the best representation of the actual blend morphology. (For more discussion on this, refer to Appendix B) However, detailed studies of various models by Packer and coworkers as well as VanderHart and Havens have shown that this approach does provide good estimates of the scale of phase separation in random two-phase systems. In their experiments which measure \( \tau \) directly, the calculated mean square diffusion distance for a series of semi-crystalline polymers was shown to correlate very well with data obtained from small angle X-ray scattering. The estimated
error in the long period spacings determined via NMR was \( \pm 6.0 \) Å. The long period is given by

\[
L = 2\langle x \rangle^{1/2}
\]

In our case the potential error is likely to be somewhat higher, as upper limit values are the actual quantity determined. The values probably overestimate \( L \) by 10-20%.

Conclusions

The use of solid state NMR to study poly(alkyl methacrylate)/poly(vinyl chloride) blends has provided some important insights into the effects of polymer structure on the molecular level properties of these blends.

Solid state \(^{13}\)C \(T_1\) relaxation time measurements indicated no significant changes in the \( T_1 \) behavior for the methacrylate polymers after blending with PVC. This is consistent with minimal changes in the polymer molecular motional processes in the MHz range.

The carbon \(^{13}\)T\(_1\) experiments showed significant multicomponent decay process for the polymers before and after blending, indicating that cross-relaxational processes are a factor in these systems.

The \(^{13}\)C chemical shifts did not exhibit any significant or consistent changes as a result of blending. This indicates that the
polymer-polymer specific interactions are either weak or simply do not produce shifts beyond the resolution limits of the spectrometer.

The proton $T_1^p$ experiments proved to be extremely valuable for the evaluation of blend miscibility. In both the PMMA/PVC and PCHMA/PVC blends, single component relaxation times (on the order of 7-8 msec) intermediate between those of the pure polymers were observed. Application of spin diffusion considerations allowed an upper limit to heterogeneity of 50 Å to be established. The PBenMA/PVC blend system showed no evidence for spin diffusion between the components. The relaxation process was unaffected by blending, and hence it was established that there is significant phase separation above the 50 Å level for these blends.
CHAPTER V

Intermolecular Cross-Polarization as a Probe of Miscibility in Blends
Incorporating Deuterated Polymers

Introduction

An excellent method for the characterization of blend miscibility involves solid state NMR cross-polarization (CP) studies in mixtures of deuterated and protonated polymers. This technique has been used to study mixing in polymer-plasticizer mixtures and for measuring interfacial mixing in block copolymer systems. Intermolecular cross-polarization studies can also provide useful information about miscibility at the molecular level for homopolymer/homopolymer blends, which have not been studied previously using this technique. An added advantage is the ability to study blends in which one component polymer is present in small quantities (less than 5 wt%).

Typically, a solid state $^{13}$C spectrum is obtained with the aid of CP and magic angle spinning (CP-MAS). Cross-polarization involves irradiating the protons in the system at an appropriate frequency such that the Hartman-Hahm condition is met. During the time period in which the two spin systems are brought into contact, magnetization is transferred from the abundant protons to the $^{13}$C nuclei. This permits more rapid data acquisition and enhances the carbon signal intensity.
The efficiency of this process depends on the strength of the proton-carbon dipolar coupling, which to a first approximation in a static system depends on the relative proximity of the protons to the $^{13}$C nuclei.\textsuperscript{78,79} Carbons with directly attached protons will cross-polarize more rapidly than non-protonated carbons, and the intensities of the peaks will also depend on the strength of the proton-carbon coupling. Of course, the absence of protons in a system precludes the use of this technique. Hence, a completely deuterated polymer will yield a featureless carbon spectrum in a standard CP-MAS experiment.

Cross-polarization need not occur only through intramolecular pathways. It is quite possible for intermolecular CP to occur, in a system with sufficient intermolecular magnetic dipolar coupling between the protons of one molecule and the $^{13}$C nuclei of another molecule. This situation can occur in systems in which the average proton-carbon internuclear distances are sufficiently small, on the order of 10 Å or less. Thus if a deuterated polymer is mixed with a second protonated component, $^{13}$C spectral features may be observed if the system is sufficiently miscible on a molecular scale. The study of intermolecular CP processes in these types of systems can thus yield important information about miscibility.
Figure 5.1: Schematic illustration of proton-carbon cross-polarization used in solid state MAS NMR experiments.
The deuterated polymers were obtained from Polymer Laboratories Ltd. and were used without further purification or treatment. The d-8 poly(methyl methacrylate) was of Mw = 57,000 and Mw/Mn = 1.08. The d-8 polystyrene was of Mw = 110,000 and Mw/Mn = 1.04. Both polymers had isotopic purities of greater than 98%. Additive-free poly(vinyl chloride) was supplied courtesy of the B.F. Goodrich Co., and was of Mw = 66,000 and Mn = 54,200. The poly(ethylene oxide) was purchased from Aldrich Chemical Co. and had a Mw = 100,000. The PVC-co-vinylidene chloride polymer was purchased from Scientific Polymer Products Co. and (5 mole% vinylidene chloride) had an inherent viscosity of 0.86. The poly(vinyl methyl ether) (PVME) was of Mw = 100,000. The partially deuterated polystyrenes were prepared from monomers obtained from Cambridge Isotopes Inc. Both the d-3 and d-5 materials were polymerized anionically using sec-butyl lithium initiator. Molecular weights were on the order of 1.4 x 10^6, and polydispersities (Mw/Mn) were less than 1.30.

Polymer blends were prepared by weighing the appropriate amounts of polymer into Erlenmeyer flasks and dissolving in sufficient THF to form 3% solutions. Blends were then precipitated into MeOH, filtered, and washed with additional MeOH. The blends were dried in vacuo at 60° C for 48 hours, followed by an additional 4 hours under vacuum at 130° C.

The solid state IBM 200-AF spectrometer specifications are provided in Chapter II. The variable CP contact time experiments were performed
using a standard $^{13}\text{C}$ observe pulse sequence in conjunction with a sequential contact time prior to acquisition. All experiments were run at ambient temperature except where noted.

**Results**

**Blend Spectra**

PMMA/PVC: Solid state $^{13}\text{C}$ spectra of the pure component polymers were obtained using a standard CP-MAS pulse sequence in conjunction with 2 msec CP contact time and 256 FID acquisitions. Figure 5.2a and 5.2b show the $^{13}\text{C}$ spectra for regular (protonated) PVC and PMMA, respectively. Peak assignments are identical to those given in Chapter III (see pages 93-94). The $^{13}\text{C}$ spectrum shown in Figure 5.2c is for the d-8 PMMA, and was obtained using 2 msec CP time and 4,110 scans. Only minimal signal intensities were observed for the carbonyl, methoxy and quaternary carbons. These weak signals are due to the presence of residual protons in the perdeuterated polymer. (In comparing the spectra for the H PMMA and d-8 PMMA, it should be noted that spectral intensities are not normalized to account for sample weight or number of scans in this case.)

Cross-polarization in the d-8 PMMA is not an effective process, due to the lack of protons in the sample. Figure 5.2d shows a $^{13}\text{C}$ CP-MAS spectrum obtained for a blend of 95% d-8 PMMA and 5% PVC. The spectrum was obtained with 2 msec CP time and 2,000 FID acquisitions. In this case, there is a dramatic increase in the carbon signal intensity for
the d-8 PMMA in comparison to the pure sample. This result indicates that there is substantial intermolecular cross-polarization between the PVC protons and the carbons of the deuterated PMMA. This experiment was repeated using d-8 PMMA/PVC blends having 10 and 20 wt% PVC, and extensive intermolecular cross-polarization was observed for these samples as well.

Figure 5.3 compares $^{13}$C spectra for d-8 PMMA, 95/5 d-8 PMMA/PVC, and 97/3 d-8 PMMA/PEO. The PEO/PMMA and PVC/PMMA blends at these compositions have identical proton densities. Both blends exhibit a dramatic increase in $^{13}$C signal intensity as a result of intermolecular cross-polarization. The d-8 PMMA normalized signal intensities in the PVC blend are somewhat larger than in the PMMA/PEO blend.

Polystyrene/poly(vinyl methylether): Figure 5.4a shows a $^{13}$C spectrum of pure d-8 polystyrene, obtained with 2 msec CP time and 4,000 FID acquisitions. The only visible signal occurs in the aromatic region at 126 ppm, and is no doubt attributable to the aromatic phenyl ring carbons ($C_2$). As with the d-8 PMMA, residual protons are responsible for the weak carbon signals in the spectrum of the pure d-8 PS. The spectrum shown in Figure 5.4b is of solid PVME, obtained using direct carbon polarization and 256 FID scans. The resonances are due to the methylene, methine, and methoxy carbons, going from low to high field. Direct polarization was used because pure PVME is well above $T_g$ at room temperature, and the liquid-like motions of the PVME chains preclude the use of cross-polarization. (PVME yields a featureless spectrum under CP conditions.) Figure 5.4c is a $^{13}$C spectrum of solid polystyrene. The
main chain methine resonance is visible at 39 ppm, the C₆ aromatics are seen at 126 ppm, and the unprotonated aromatic resonance is visible at 145 ppm. Figure 5.4d shows a CP-MAS spectrum of a 65/35 blend of d-8 PS and PVME prepared by slow-casting from toluene. In comparison with the spectrum of the pure d-8 PS, there is a very large (factor of 12) increase in the carbon signal intensity of the deuterated polymer after blending. There is apparently significant intermolecular cross-polarization between the PVME protons and d-8 PS carbons.

It should also be noted that the PS/PVME blend spectrum shows resonances attributable to the PVME carbons. Due to the fact that there is significant liquid-like motion of the PVME chains at room temperature, solid state carbon spectra cannot be obtained using cross-polarization methods. Hence the spectrum of the pure PVME was obtained using direct carbon polarization. The PS/PVME blend spectrum was obtained using normal cross-polarization, hence the PVME motional processes in the blend must have been inhibited significantly compared to the pure PVME.

d-8 PS/PMMA and d-8 PMMA/PS: Intermolecular cross-polarization in two immiscible blends of d-8 PS/PMMA and d-8 PMMA/PS was investigated. Figure 5.5a shows a ¹³C spectrum of a simple 65/35 w/w mixture of d-8 PS and PMMA powders. The PMMA resonances are readily visible, along with a weak aromatic signal at 126 ppm from the d-8 PS. The aromatic signal intensity is identical to that of the pure d-8 polystyrene. (There may also be a weak d-8 PS methine signal which is obscured by the 45 and 51 ppm PMMA resonances.) The spectral detail (5.5b) shown for
Figure 5.2: Solid state CP-MAS $^{13}$C spectra of: a, poly(vinyl chloride); b, poly(methyl methacrylate); c, deuterated (d-8) poly(methyl methacrylate); d, a 95/5 w/w blend of d-8 PMMA/PVC.
Figure 5.3: Solid state CP-MAS $^{13}$C spectra of d-8 PMMA, a 95/5 w/w d-8 PMMA/PVC blend, and a 97/3 w/w d-8 PMMA/PEO blend.
Figure 5.4: Solid state CP-MAS $^{13}C$ spectra of: a, deuterated (d-8) polystyrene; b, poly(vinyl methylether); c, polystyrene; d, a 65/35 w/w d-8 PS/PVME blend.
Figure 5.5: Solid state CP-MAS $^{13}$C spectrum of a 65/35 physical mixture of d-8 polystyrene and PMMA (spectrum a). Details in the aromatic region show: b, aromatic signal after blending the d-8 PS/PMMA; c, aromatic region of a 65/35 d-8 PS/PVME blend (reduced by a factor of 1/2).
the aromatic region was obtained after blending the two polymers by co-dissolution in THF and precipitation into MeOH. It can be seen that there is a slight (x 2) increase in the d-8 PS aromatic signal intensity as a result of the blending. The detail of the aromatic region in the d-8 PS/PVME blend (5.5c) is shown for comparison. Obviously, the post-blending increase in aromatic intensity is much greater for the d-8 PS/PVME blend.

A similar series of spectra were obtained for a blend of d-8 PMMA incorporating 25 wt% polystyrene. As with the d-8 PS/PMMA system, only minimal increases in d-8 PMMA $^{13}$C signal intensity were observed after blending. However, there were differences in the dynamics of the CP process, which will be discussed in the next section.

### Cross-Polarization Dynamics

A series of variable CP contact time experiments were run in order to study the dynamics of the cross-polarization process. Both pure component materials as well as blends were studied.

Figure 5.6 shows the results of a typical variable CP contact time experiment on poly(methyl methacrylate). The length of the CP time was varied incrementally from 0.1 msec to 10.0 msec; 256 FID acquisitions were made for each spectrum. At short CP contact times, the $^{13}$C signal intensity increases rapidly with increasing contact time. The signal intensities reach a maximum at ~ 2 msec, yielding the optimal contact time to be used for a normal spectral acquisition. As the CP time is
Figure 5.6: Variable contact time $^{13}$C solid state NMR experiment for pure poly(methyl methacrylate).
Figure 5.7: Carbon-13 signal intensity vs. cross-polarization contact time for the various PMMA resonances.
Figure 5.8: CP-MAS $^{13}$C spectra of a 95/5 w/w d-8 PMMA/PVC blend at three different cross-polarization contact times.
increased beyond 2 msec, the PMMA signal intensity decreases.

A more quantitative presentation of the results for the PMMA cross-polarization kinetics are depicted in Figure 5.7. The PMMA $^{13}$C signal intensities for each carbon are plotted on a semi-log scale against CP contact time. This more clearly shows the dynamics of the CP process, and permits a better comparison of the behavior for each carbon. It is apparent that both of the carbons with directly bonded protons (the OCH$_3$ at 51 ppm and the $\alpha$-CH$_3$ at 16 ppm) cross-polarize more rapidly than the unprotonated carbons. At longer contact times (> 2 msec), all of the PMMA resonances lose magnetization at the same rate, indicating a uniform proton $T_1^p$ process.

Cross-polarization dynamics for the various blend systems were also studied. Figure 5.8 shows $^{13}$C spectra of a 95/5 d-8 PMMA/PVC blend obtained with CP contact times of 0.5, 1.0, and 7.0 msec. At 0.5 msec contact time, the PVC peaks at 51 and 44 ppm are at almost maximum intensity. A weak resonance at 176 ppm and a shoulder between the two PVC resonances are due to the d-8 PMMA. Increasing the contact time to 1.0 msec yields stronger d-8 PMMA signals, although they are still weak in comparison to the PVC peaks. (The peak labeled "b" is attributable to the d-8 PMMA methoxy resonance.) The last spectrum, obtained with a CP contact time of 7.0 msec, shows all of the d-8 PMMA resonances quite clearly. The signal-to-noise ratio is very good for this particular spectrum. This experiment demonstrates that the rate of cross-polarization for the d-8 PMMA in the blend is slower than for either pure PMMA or for the PVC carbons.
The differences in CP kinetics for PMMA, d-8 PMMA/PVC and d-8 PMMA/PS blends are pictured in a quantitative fashion in Figure 5.9, which shows the various PMMA carbonyl signal intensities as a function of CP contact time. (Carbonyl signal intensities were normalized to H-PMMA, with sample weights and number of scans taken into account.) As was also seen in Figure 5.7, the PMMA carbonyl shows a rapid increase in signal intensity at short CP times, with a $T_{CH} = 0.20$ msec. Maximum signal intensity is attained at $= 1.0$ msec contact time. For the carbonyl resonance in the d-8 PMMA/PVC blend, the carbonyl signal intensity increases at a slower initial rate as compared to the pure H-PMMA. Maximum intensity is reached at $= 5.0$ msec contact time. Note also the lower maximum intensity in comparison to the protonated PMMA. Lastly, the CP rate for the carbonyl group in the d-8 PMMA/PS blend is observed to be slower than that of either the PMMA or the d-8 PMMA/PVC blend. The phase separated d-8 PMMA/PS blend also shows the weakest maximum signal intensity overall.

The $T_{CH}$ times for the three systems can be ranked in decreasing order: d-8 PMMA/PS > d-8 PMMA/PVC > PMMA. Maximum signal intensities have the opposite order. (The other PMMA resonances show similar behavior to that exhibited by the carbonyl group.)

The effect of CP contact time on the $^{13}$C spectra of the 65/35 w/w d-8 PS/PVME blend is shown in Figure 5.10. In this case, there is a slower CP rate for the deuterated polystyrene in comparison to the protonated PVME carbons. Maximum d-8 PS signal intensity occurs at $= 5.0$ msec contact time, and for the PVME at $= 2.0$ CP time. The fact that
Figure 5.9: Normalized carbonyl signal intensity vs. CP contact time for pure PMMA, a 95/5 d-8 PMMA/PVC blend, and a 75/25 d-8 PMMA/PS blend.
Figure 5.10: CP-MAS $^{13}$C spectra of 65/35 w/w d-8 PS/PVME blend at three different cross-polarization contact times.
the PVME peaks are observed under CP conditions in this blend is also noteworthy. Recall that the pure PVME $^{13}$C spectrum had to be obtained using direct carbon polarization, due to liquid like chain motions at room temperature.

Figure 5.11 shows normalized PS aromatic (127 ppm) signal intensities as a function of CP contact time for 65/35 d-8 PS/PVME, 65/35 d-8 PS/PMMA, and pure d-8 PS. The miscible d-8 PS/PVME blend shows the most rapid increase in signal intensity, as well as the most intense signal overall. In comparison, the signal intensity of the aromatic peak in the immiscible d-8 PS/PMMA blend increases at a much slower rate, and has a much lower maximum signal intensity. The CP dynamics of the weak aromatic signal for the pure d-8 PS is shown for reference.

The T\textsubscript{CH} times for these three systems can be ranked in decreasing order as d-8 PS > d-8 PS/PMMA > d-8 PS/PVME.

Some additional solid state NMR experiments were performed in order to examine the CP dynamics of some selectively deuterated polystyrene samples. Figure 5.12 compares the CP dynamics for the 127 ppm and 39 ppm resonances of protonated polystyrene to d-3 main chain deuterated polystyrene. The results are interesting, as they provide an excellent means for looking at the effect of carbon-proton internuclear distances on CP efficiency, as the $^1H$-$^{13}C$ distances for the main chain deuterated PS are obviously larger than for the regular PS.

The results show no difference in the CP rate or maximum intensity for the aromatic resonances of the two samples. However, the results
Figure 5.11: Normalized $^{13}$C polystyrene aromatic signal intensity vs. CP contact time for a 65/35 d-8 PS/PVME blend, a 65/35 d-8 PS/PMMA blend, and pure d-8 PS.
Figure 5.12: Normalized $^{13}$C signal intensities vs. CP contact time for polystyrene and chain deuterated (d-3) polystyrene.
Figure 5.13: Normalized $^{13}$C polystyrene aromatic signal intensity vs. CP contact time for PS, a 65/35 d-8 PS/PVME blend, and ring (d-5) deuterated PS.
for the deuterated PS main chain methine resonance at 39 ppm are quite different from that of the regular polystyrene methine resonance. The d-3 PS shows a slower CP rate for the methine resonance, and a lower maximum intensity as well.

Figure 5.13 compares the cross-polarization dynamics of the aromatic polystyrene carbons to that for a 65/35 d-8 PS/PVME blend and a sample of ring deuterated d-5 polystyrene. The important result in this comparison is the difference, or lack thereof, in the CP dynamics of the d-5 PS and the d-8 PS/PVME blend. It is apparent that the \( T_{CH} \) time for the aromatic carbons of the d-5 sample is comparable, if not equal, to that for the aromatic carbons in the d-8 PS/PVME blend. This provides a convenient yardstick for the comparison of \( ^1H-^{13}C \) dipolar interaction coupling in these systems.

**Discussion**

As mentioned in the introductory part of this chapter, solid state intermolecular cross-polarization methods have the potential to provide a molecular level probe of polymer-polymer miscibility. The results of the experiments for the systems studied show this to indeed be the case. Perhaps the most graphic illustration lies in the comparison of the results obtained for the solid state \( ^{13}C \) spectra of the perdeuterated polymers before and after blending with the protonated polymers. The spectra for the d-8 PMMA/PVC and d-8 PS/PVME blends, shown in Figures 5.2 and 5.4 respectively, are excellent examples. In both cases, the
minimal signal intensities of the pure perdeuterated polymers are dramatically enhanced by the addition of the protonated material. The increased $^{13}$C peak intensities in these blends indicate that intermolecular cross-polarization is occurring between the protonated and deuterated polymers. This demonstrates conclusively that there is substantial mixing of a segmental scale in these blends.

The conclusion regarding intimate mixing in the PS/PVME and PMMA/PVC blends can be justified based on the nature of the cross-polarization process. Cross-polarization is normally used in a solid state MAS experiment to enhance the signal intensity of the low-abundance $^{13}$C nuclei (S spins) by transfer of magnetization from the abundant protons (I spins). This is done by the application of resonant RF fields after a $90^\circ$ $^1$H pulse such that the Hartman-Hahn condition is fulfilled:

$$Y_I^H I = Y_S^H S$$

(5.1)

where $Y_I$ and $Y_S$ are the nuclear magnetogyric ratios and $H_I^I$ and $H_S^S$ are the resonant RF fields. This permits the exchange of magnetization via mutual spin flips between the two spin systems. However, the magnetic IS dipolar interaction is very short range; the IS dipolar Hamiltonian term is proportional to $1/r_{ij}^6$, where $r_{ij}$ is the $^1H - ^{13}C$ internuclear distance. Hence in a rigid system, the strength of the proton-carbon dipolar coupling drops rapidly as the internuclear distance increases. This means that the observation of $^{13}$C resonances
for the deuterated polymers in the blends comes about only in the event that there is a substantial degree of intermixing on a distance scale of 10 Å or less. This result was observed for the d-8 PMMA/PVC, d-8 PMMA/PEO, d-8 PMMA/PMMA, and d-8 PS/PVME blend systems.

The $^{13}$C spectrum of the d-8 PS/PVME blends show an additional result that is both interesting and informative. In order to obtain a solid state spectrum of the PVME, direct carbon polarization had to be used, as the liquid-like motion of the pure PVME prevented efficient proton-carbon cross-polarization. However, the blend spectrum obtained using cross-polarization only, shows peaks arising from the PVME. This must be a result of the main chain motions of the PVME being restricted by the more rigid polystyrene chains. This is consistent with the conclusions that the intermixing in this blend occurs on a molecular scale.

In addition to the miscible blends studied, $^{13}$C spectra were obtained for two immiscible blends of deuterated and protonated polymers. The 75/25 d-8 PS/PMMA blend spectrum is shown in Figure 5.5. As might be expected for such a blend, the increase in $^{13}$C signal intensity for the d-8 PS is minimal in comparison to that seen for the d-8 PS blended with poly(vinyl methylether). However, the fact that there is still a small increase is noteworthy. There have been electron microscopy studies which show the PMMA/PS system to be extensively phase separated. Despite the phase separation, there must still be some interfacial mixing on a segmental level, as indicated by the small increase in signal intensity for the d-8 PS aromatic resonance. Similar
results were obtained with the 75/25 d-8 PMMA/PS system, which showed only a minor increase in signal intensity for the d-8 PMMA after blending. The change in intensity appeared to be smaller for the d-8 PMMA, perhaps suggesting a lower degree of interfacial mixing for the PS rich composition.

Direct comparisons of $^{13}$C intensities for the deuterated polymers may be made in order to evaluate the relative extent of segmental mixing in two different blends, provided the deuterated polymer is the same in both cases and in acquisition conditions are identical. This was done for a d-8 PMMA/PVC and a d-8 PMMA/PEO blend. The weight fractions of the protonated polymers were adjusted so as to create identical proton concentrations in both samples. The normalized d-8 PMMA signal intensities are given in Table 5.1.

Table 5.1: Normalized d-8 PMMA $^{13}$C signal intensities for pure d-8 PMMA, 95/5 d-8 PMMA/PVC, and 97/3 d-8 PMMA/PEO blends.

<table>
<thead>
<tr>
<th>Peak</th>
<th>d-8 PMMA</th>
<th>d-8 PMMA/PVC</th>
<th>d-8 PMMA/PEO</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O</td>
<td>0.97</td>
<td>4.83</td>
<td>4.74</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>2.31</td>
<td>7.75</td>
<td>7.94</td>
</tr>
<tr>
<td>-C-</td>
<td>2.56</td>
<td>9.41</td>
<td>11.15</td>
</tr>
<tr>
<td>$\alpha$-CH$_3$</td>
<td>1.30</td>
<td>2.00</td>
<td>2.56</td>
</tr>
</tbody>
</table>

The overall intensities of the PMMA peaks are approximately the same for both blends, indicating a similar degree of mixing. The relative intensity of the carbonyl peak to the other carbons in each blend is
slightly higher for the d-8 PMMA/PVC blend. This could be indicative of stronger $^1H-^{13}C$ dipolar interactions for the carbonyl group with the PVC protons as compared to the PEO protons. However, this is not a conclusive, as the differences in signal intensity ratios are not large.

The dynamics of inter and intramolecular CP processes can also provide useful information. The contact-time dependency of the signal intensities can be correlated with the average $^1H-^{13}C$ distances and dipolar coupling. In general, the kinetics of the CP process can be described by three time constants: $T_1^p (^1H)$, $T_1^p (^{13}C)$, and $T_{CH}$. The cross-polarization time constant, $T_{CH}$ governs the rate at which magnetization is transferred to the carbon nuclei from the protons. The proton $T_1^p$ and carbon $T_1^p$ rotating frame spin-lattice relaxation times describe the rate of loss of magnetization to the lattice. (See Figure 5.1 for a schematic representation of the situation.) Usually, $T_1^p$ is much longer than the other two time constants and can hence be neglected. The resultant expression describing carbon magnetization as a function of CP contact time (t) is given as

$$I = I_o / T_{CH} \left[ \exp\left(-t/T_1^p (^1H)\right) - \exp\left(-t/T_{CH}\right) \right] / \left[ T_{CH}^{-1} - T_1^p (^{13}C) \right]$$ (5.2)

where $I_o$ is the maximum signal intensity. This equation predicts an initial increase in $I$ at short contact times at a rate given by $T_{CH}^{-1}$, followed by an eventual decay in $I$ at longer contact times regulated by the proton spin-lattice relaxation rate. This type of behavior can be
clearly seen for the semi-log I vs. t plots (Figures 5.11 through 5.13) presented in the experimental section of this chapter.

The results of a variable CP time experiment on regular poly(methyl methacrylate) shown in Figure 5.6, and in quantitative fashion in Figure 5.7, prove that the I vs. t behavior predicted by equation 5.2 is indeed observed for each of the PMMA carbons. It is possible to estimate the $T_{CH}$ and $T_1^\rho$ relaxation times by fitting the $^{13}C$ data to equation 5.2. An example of a typical fit is shown in Figure 5.14 for the H-PMMA carbonyl peak. The parameters obtained in this specific instance were $T_{CH} = 0.60$ msec and $T_1^\rho = 90.0$ msec. The agreement between the experimental data and Equation 5.2 is quite good.

The significance of the analysis of the CP kinetics lies in the ability to compare $T_{CH}$ obtained for one system or carbon to another. The magnitude of the time constants for CP is a direct reflection of the strength of the $^1H-^{13}C$ dipolar coupling. For example, carbons with directly bonded protons cross-polarize more rapidly than those carbons without directly attached protons. This is seen for the PMMA sample, in which both the OCH$_3$ and $\alpha$-CH$_3$ carbons have shorter $T_{CH}$ times than the carbonyl or quaternary carbons. A similar result was obtained for the polystyrene sample as well. The slowest $T_{CH}$ time was obtained for the unprotonated ipso-phenyl carbon.

The results of the CP dynamics experiments for the various blends of deuterated and protonated polymers were particularly interesting. For example, Figure 5.9 illustrates the $^{13}C$ carbonyl signal intensity as a function of contact time for PMMA, 95/5 d-8 PMMA/PVC, and 75/25 d-8
Figure 5.14: Poly(methyl methacrylate) carbonyl signal intensity vs. cross-polarization time (open circles). Solid line (triangles) represent best fit using a two-parameter fit.
PMMA/PS. The differences in behavior reflect the extent of the $^1H-^{13}C$ dipolar interactions in each system. The PMMA sample has the shortest $T_{CH}$ time, due to the close proximity of the protons on the $\alpha$-CH$_3$, CH$_2$, and OCH$_3$ groups. The miscible d-8 PMMA/PVC blend shows a somewhat slower increase in $^{13}C$ signal intensity than the PMMA. Although there is extensive segmental mixing in this system, the average $^1H-^{13}C$ internuclear distances are obviously greater than those in the pure PMMA. The slowest $T_{CH}$ time is seen for the phase separated d-8 PMMA/PS system. This is a result of still larger average proton-carbon distances in the interfacial regions.

Figure 5.11 shows the contact-time dependent aromatic signal intensity for 65/35 d-8 PS/PVME, 75/25 d-8 PS/PMMA, and d-8 PS. Again it is observed that the CP rate for the miscible blend is much faster than for the immiscible blend. The d-8 PS/PVME reaches a maximum signal intensity at $= 2.0$ msec, whereas the aromatic signal in the d-8 PS/PMMA blend is still increasing at $5.0$ msec CP time. The data for the pure d-8 polystyrene is provided as a reference. Note the overall lower intensity and long $T_{CH}$, reflecting the proton-starved nature of the deuterated carbons.

An even more quantitative demonstration of the effect of $^1H-^{13}C$ internuclear distance on $T_{CH}$ can be seen in the results of the variable CP time experiments on the selectively deuterated polymers. Figure 5.12 shows the results of a variable contact time experiment for regular polystyrene and for main-chain deuterated PS. The intensity vs. CP time behavior for the aromatic resonance (127 ppm) of the H-PS and d-3 PS is
identical. There is no difference in the $^1H - ^{13}C$ coupling for the two polymers. However, this is not the case for the main chain methine resonances at 39 ppm. The d-3 ps methine carbons show a much slower cross-polarization rate compared to the regular PS. The maximum signal intensity is also somewhat smaller for the d-3 material. The only source of magnetization for the main chain d-3 carbons is via the aromatic protons. These protons are at a greater distance from the methine $^{13}C$ nuclei than the directly bonded protons in the regular PS. Hence the longer $T_{CH}$ time is a direct result of the larger internuclear proton-carbon distance.

The use of selectively deuterated polymers can provide information regarding miscibility as well. The data in Figure 5.13 compares the cross-polarization kinetics of the aromatic PS carbons of ring deuterated d-5 PS to that of the aromatic carbons in a 65/35 d-8 PS/PVME blend. The most striking feature is the fact that the CP process for the aromatic carbons in the blend appears to be more efficient than that for the selectively deuterated polystyrene. This occurs even though the proton density for the blend is nearly the same as that of the deuterated sample. This is consistent with the interpretation of extensive segmental mixing in the blend, as the $^1H - ^{13}C$ internuclear distances for the d-5 PS and the d-8 PS/PVME blend must be comparable.
Conclusions

In summary, the use of solid state CP-MAS Nuclear Magnetic Resonance in conjunction with blends of deuterated and protonated polymers has been shown to be a valuable method for the study of miscibility in multicomponent polymer systems. This technique has allowed characterization on a molecular level, which complements and enhances information gained through other techniques such as DSC and proton spin relaxation measurements.

The PMMA/PVC blends showed results indicative of significant mixing on a segmental scale. Solid state CP-MAS $^{13}$C spectra of d-8 PMMA showed negligible signal intensities due to the lack of protons for cross-polarization. After blending with PVC (5 wt%) the d-8 PMMA $^{13}$C signal intensities increased by a factor of 10, a result consistent with extensive intermolecular cross-polarization. Similar results were observed for blends of d-8 PMMA/PEO, d-8 PMMA/PMMA, and d-8 PS/PVME.

Immiscible blends of d-8 PMMA/PS and d-8 PS/PMMA showed only minimal intermolecular cross-polarization. The signal intensities of the deuterated polymers increased by only a factor of 2, despite the presence of 25 wt% protonated polymer. The fact that there was a small amount of signal enhancement is likely due to interfacial mixing in the otherwise phase separated systems.

The CP dynamics were found to be consistent with the degree of intermixing for the various blends as indicated by the signal intensity results. The rate of cross-polarization was proportional to the extent
of intermolecular cross-polarization. The miscible d-8 PMMA/PVC, d-8 PS/PVME, and d-8 PMMA/PEO blends had $T_{CH}$ times which were 8-10 times shorter than those observed for the immiscible d-8 PMMA/PS and d-8 PS/PMMA blends.
Polymer Cosolvent Systems

The results presented in Chapter II demonstrate the utility of Nuclear Magnetic Resonance methods for the study of molecular interactions in cosolvent systems. The role of such interactions in the enhancement of miscibility in the PS/acetone/diethylether and PS/acetone/methylcyclopentane cosolvent systems was evaluated. It was concluded that preferential polymer-solvent interactions as measured by NMR are not a prerequisite for the observation of cosolvent-type phase behavior. There are, of course, additional avenues for experimental investigation that would be both interesting and worthwhile. Some possibilities are outlined below.

1. NMR analysis of other polymer-cosolvent systems could provide additional information regarding the role of polymer-solvent interactions in promotion of miscibility. The polystyrene systems discussed in this work were ideal for study as representative examples. The $^{13}$C NMR results for both systems indicated only weak molecular interactions between polymer and solvent components. However, it could be that other cosolvent systems might show evidence for stronger interactions. For example, PMMA has been reported to show enhanced solubility in binary mixtures of methanol/cyclohexane and
neither of the two alcohols or the cyclohexane
dissolve the polymer singly. The carbonyl unit of the PMMA has the
potential for hydrogen-bonding interactions with the hydroxy-proton of
the alcohol solvent component in the binary cosolvent mixtures.
Comparisons of interactions in the two PMMA cosolvent systems with other
PMMA ternary systems would be interesting, the NMR techniques would be
easy to apply.

There are other systems that could be possible candidates for NMR
analysis of molecular interactions as well, such as
PS/cyclohexane/acetone, PS/dimethylcyclohexane/acetone, and
PS/methylcyclohexane/acetone.81

2. The effect of polymer tacticity on cosolvency and polymer-
cosolvent interactions would be a second possible area for study. The
polystyrene samples used in this work were all atactic materials. The
strength of molecular interactions could be different for syndio or
isotactic polymers. There are a number of companies that offer iso and
syndiotactic polystyrene and poly(methylmethacrylate). With sufficient
spectral resolution, it might even be possible to study differences in
interactions at different dyad sites in a give atactic sample. (This was
not possible with the polystyrene systems in this work, but it might be
possible in others.)

3. Ionmers such as zinc sulfonated ethylene propylene polymers and
sulfonated polystyrene show cosolvent-type behavior.83-85 Cloud-point
diagrams for these systems have not been determined; the cosolvent effects are manifested by significant decreases in viscosity with the addition of a second solvent component to insoluble ionomer gels. Typical binary cosolvents for ionomers are made up of hydrocarbons mixed with alcohols, amines, amides, and ester-group containing solvents. It has been hypothesized that the polar cosolvent component interacts strongly with the polymer ionic groups, thereby reducing ion pair self-association. NMR techniques could easily be applied to these types of systems to study solvation effects as a function of cosolvent composition.

**Polymer Blends: Molecular Structure and Miscibility**

The studies of the poly(alkyl methacrylate)/PVC blends provided interesting and useful results regarding the effect of a systematic change in component molecular structure on polymer-polymer miscibility and interactions. Particularly valuable was the combined use of solid state NMR with other standard characterization methods to probe the blends on different distance scales. In some cases, the changes in blend behavior brought about by altering polymer molecular structure can be subtle. For example, the fact that the replacement of the methyl ester group in PMMA with the cyclohexyl ester group does not inhibit miscibility with PVC was unexpected. This conclusion would not have been reached without the combined use of DSC and solid state NMR techniques. There are many possible opportunities for additional work along these lines. Some suggestions are listed below.
1. Polymer tacticity would be an interesting variable to investigate. Work by Ten Brinke\textsuperscript{37} et al showed that the tacticity of PMMA affected miscibility with poly(vinyl chloride). This factor has not been examined for the other alkyl methacrylate polymers in the series. It would be possible to synthesize iso and syndiotactic ethyl, butyl and cyclohexyl methacrylate polymers. Miscibility and interactions in blends with PVC might also reveal changes depending on the tacticity of the methacrylate polymer. The solid state \textsuperscript{1}H T\textsubscript{1}p NMR experiments would be particularly interesting to do with such systems.

2. There has been substantial interest in the behavior of random copolymer-homopolymer blends.\textsuperscript{87,88} Blends in which a given homopolymer is miscible with an AB copolymer, but immiscible with the corresponding A or B homopolymers have been reported.\textsuperscript{87} The copolymer/homopolymer systems have a "window" of miscibility for random copolymers of intermediate compositions. This effect would be particularly interesting to study using NMR methods. The effect of copolymer composition on miscibility and segmental mixing would be an obvious route of investigation. Solid state proton relaxation studies could be used to estimate the scale of heterogeneity. If suitable copolymers were found that could be blended with deuterated homopolymers, intermolecular cross-polarization experiments could be utilized to study segmental mixing. This would be an extremely interesting series of experiments.
Appendix A

Sample Calculations for Determination of $K_a$ Constants from $^{13}$C NMR Data

As outlined in Chapter II, equation 2-1 can be used to determine the mole fraction or ratio of polymer-solvent "A" contacts to polymer-solvent "B" contacts. A sample calculation is presented below for the polystyrene p-phenyl $^{13}$C data in acetone/diethylether at 20°C. Calculation results are summarized in Table A-1.

The mole fraction of polystyrene p-phenyl-acetone contacts is given by

$$x_{PS-A} = \frac{(\delta_{obs} - \delta_{DEE})}{(\delta_{DEE} - \delta_A)}$$

where

$$\delta_{DEE} = 2990 \text{ Hz} \quad \delta_A = 3019.4 \text{ Hz}$$

then $x_{PS-A}$ can be converted to [PS-A] for use in Equation 2.1.

For polystyrene in a binary acetone/ether mixture of molar ratio 7.49, the p-phenyl resonance frequency ($\delta_{obs}$) was 3015.0 Hz. Hence

$$x_{PS-A} = \frac{(3015 - 2990)}{(3019.4 - 2990)} = 0.8416$$

The results for other experiments in solvent mixtures of different composition are shown in table A-1.
Table A-1: Results for $K_a$ calculations for polystyrene p-phenyl resonance in acetone/diethylether binary cosolvent mixtures.

<table>
<thead>
<tr>
<th>[Acetone]/[Ether]</th>
<th>[PS]*</th>
<th>$\delta_{obs}$</th>
<th>$\chi_{PS-A}$</th>
<th>[PS-A]/[PS-DEE]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure acetone</td>
<td>0.3344</td>
<td>3019.7</td>
<td>1.000</td>
<td>Infinite</td>
</tr>
<tr>
<td>7.49</td>
<td>0.3382</td>
<td>3015.0</td>
<td>0.842</td>
<td>5.32</td>
</tr>
<tr>
<td>4.47</td>
<td>0.3248</td>
<td>3012.4</td>
<td>0.754</td>
<td>3.07</td>
</tr>
<tr>
<td>3.02</td>
<td>0.3562</td>
<td>3010.0</td>
<td>0.673</td>
<td>2.06</td>
</tr>
<tr>
<td>2.13</td>
<td>0.3494</td>
<td>3008.0</td>
<td>0.606</td>
<td>1.54</td>
</tr>
<tr>
<td>1.42</td>
<td>0.2712</td>
<td>3003.3</td>
<td>0.448</td>
<td>0.81</td>
</tr>
<tr>
<td>0.95</td>
<td>0.3053</td>
<td>2999.5</td>
<td>0.320</td>
<td>0.47</td>
</tr>
<tr>
<td>0.36</td>
<td>0.3285</td>
<td>2993.8</td>
<td>0.128</td>
<td>0.15</td>
</tr>
<tr>
<td>pure ether</td>
<td>0.2894</td>
<td>2990.0</td>
<td>0.000</td>
<td>0.00</td>
</tr>
</tbody>
</table>

* Units of mole/liter.

# Frequency in Hertz from dioxane reference.

Plotting the values in the last column as a function of the acetone/ether solvent ratios yields a straight line, with a slope of 0.72±0.10. Correlation coefficient for a linear least squares fit of the data was 0.982.

This approach was used to determine $K_a$ values for all of the polymer solutions discussed in chapter II.
A Model for the Estimation of Spin Diffusion Distances in Polymer Blends

The results of proton $T_1^P$ measurements on the poly(alkyl methacrylate)/PVC blends described in Chapter IV were used to estimate an upper limit to heterogeneity in the various systems. The model used to obtain Equation 4.3 is based on the following assumptions:

1) A lamellar morphology of two regions A and B, having infinite parallel boundaries. The domain spacing $L$ is equal to the combined thickness of the two regions, as shown below

\[ L = 2x \quad \text{(A.1)} \]

2) The diffusion of magnetization within each region is isotropic, i.e. there is no directional dependence of the diffusion coefficient.

3) Spin temperature within the slow-relaxing phase is constant.
Normally, this model is used in conjunction with Goldman-Shen types of pulse sequences which create a magnetization gradient in a two-phase system and then measure the time constant ($\tau$) for spin diffusion. The experimental determination of $\tau$ can then be used along with a knowledge of the diffusion constant $D$ to estimate $L$ by first solving

$$\frac{\partial M(r,t)}{\partial t} = D(r)\nabla^2 M + R(r)[M_{\text{eq}} - M] \quad (A.2)$$

where $M$ is the magnetization as a function of coordinates $r$ and time $t$, $M_{\text{eq}}$ is the equilibrium magnetization, $D$ is the diffusion coefficient and $R$ is a parameter characterizing magnetization loss to the lattice via $T_1$ processes.

The result is

$$\langle x^2 \rangle = (2Dt)^2 \quad (A.3)$$

where $\langle x^2 \rangle$ is the mean square distance over which energy transport occurs in a time $\tau$. This solution is obtained by using numerical methods to solve the general diffusion equation for the lamellar model pictured above.\(^7\)

A reasonable estimate for $D$ can be obtained for rigid hydrocarbon systems by experimentally measuring proton linewidths for a given sample. This is possible because $D(r_{ij})$ is given by

$$D(r_{ij}) = W(r_{ij})r_{ij}^2 / 6 \quad (A.5)$$
where $W_{ij}$ is the probability of a mutual spin-flip for two adjacent protons at a distance $r_{ij}$. (This is explained in detail in references 8 and 9.)

Then, from (A.5)

$$D = 2r_o^2/T_2$$  \hspace{1cm} (A.4)

where $r_o$ is the Van der Waal radius of hydrogen and $T_2$ is the proton spin-spin relaxation time.

There are further considerations which should be mentioned when using the results of the above model to estimate the scale of mixing or heterogeneity in amorphous polymer blends. First, how legitimate is the value used for $D$? This is a critical factor in the estimation domain spacings. A reasonable estimate for a rigid hydrocarbon system can be made by measuring $T_2$ directly. Several other workers\textsuperscript{6-9} have shown that for a typical polymer, $D$ is on the order of $5.0 \times 10^{-12}$ cm$^2$/second. This varies slightly depending on the proton density of the specific polymer, and is proportional to the cube root of the proton density. A second consideration is the validity of the application of a model based on a lamellar morphology to a system which may consist of a random distribution of domain sizes and interdomain distances. What must be remembered, however, is that the calculation determines an upper limit to heterogeneity in the blend. No attempt is made to state that a lamellar morphology of uniform thickness $L$ is the actual physical state of the system. The fact that single component intermediate proton relaxation times are observed for a blend establishes a maximum value
for the diffusion time \( t \). This means that there is no significant or detectable phase separation on a distance given by Equation (A.2).

Keeping in mind the realization that physical reality likely involves a distribution of interdomain spacings, the statement that such a distribution does not encompass a significant fraction of distances greater than the calculated value for \( L \) is certainly reasonable.
References


12. K.S. Siow, G. Delmas, and D. Patterson, Macromolecules 5, 29 (1972)


35. J.W. Schurer, A. de Boer, and G. Challa, Polymer, 16, 201 (1975)


37. G. Ten Brinke, Private Communication 1984


47. Patent Application #82/196,589 Chem. Abstracts 101:172417m


56. P.R. Couchman, Macromolecules, 11, 1156 (1978)


64. A. Abragam "Principles of Nuclear Magnetism" Oxford Press, Oxford 1961


66. A.N. Garroway, W.B. Monits, and H.A. Resing, ACS Symposium Series #103, page 1, 1978


73. L.A. Belfiore, Polymer, 27, 80 (1986)


81. See reference 1

82. R.D. Lundberg, to be published


