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thesis entitled

SYNTHESIS AND CHARACTERIZATION OF HYDROGEN BONDED INTERPOLYMER COMPLEXES

presented by

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has been accepted towards fulfillment
of the requirements for

M.S. degree in Chem. Engr.

Alan Scranton
Major professor

Date 11/17/92

SYNTHESIS AND CHARACTERIZATION OF

HYDROGEN BONDED INTERPOLYMER COMPLEXES

By

Carl Lawrence Aronson

A THESIS

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

1992

ABSTRACT

Synthesis and Characterization of

Hydrogen Bonded Interpolymer Complexes

By

Carl Lawrence Aronson

Macromolecular complexes of poly(4-vinyl phenol) (PVPh) with poly(N,N-dimethylacrylamide) (PDMA) and poly(ethylene glycol) (PEG) with poly(methacrylic acid) (PMAA) were synthesized and characterized. In the first system, PVPh is a proton donor and PDMA is a proton acceptor and the two form relatively strong hydrogen bonded complexes. The complex was isolated by precipitation from alcohol solutions. The composition of the complex was determined, using high resolution ^{1}H NMR spectroscopy and elemental analysis, and was correlated with the homopolymer feed ratio. The glass transition temperature of the complex was found to be substantially higher than either of the two constituent homopolymers. A variety of solvents dissolved both constituent homopolymers but would not dissolve the complex. However, strong hydrogen bonding solvents, such as N,N-dimethylformamide, dimethyl sulfoxide and pyridine, appear to break the complex upon dissolution. The complexation of PEG with PMAA was studied in dilute aqueous solutions. Complexation was detected by NMR relaxation experiments at lower PEG molecular weights than previously reported.

DEDICATION

to Cynthia Jean

My Wife and Inspiration

ACKNOWLEDGMENTS

I would like to thank my advisor, Professor Dr. Alec Byron Scranton, for his guidance, encouragement, and support. He was a constant source of knowledge and help throughout this work.

I am grateful to the College of Engineering and the Department of Chemical Engineering at Michigan State University for providing a fellowship for myself as well as the fine facilities to carry out this work. I am grateful to the State of Michigan for providing financial research support my in the form of grants through the Research Excellence Funds at Michigan State University. I am also very grateful to the Michigan Polymer Consortium for a graduate fellowship.

I am grateful to Hope College for the valuable knowledge that I gained in my undergraduate years. I am also grateful for the research experience in chemistry that I was afforded.

I wish to thank Lori A. Murphy, Kelley R. Copes, Cheryl R. Harned, Maryam Hooshmand, Richard L. Bost and Krista J. Jenison who diligently worked in the lab as undergraduate research assistants. I wish to thank the staff at the Max T. Rogers NMR facility at Michigan State University for their encouragement and consultation. I appreciate the help of Cynthia J. Aronson, my wife, and Dr. Jay A. Siegel of the Department of Criminal Justice at Michigan State University for their help with solubility, refractive index and FT-IR measurements. I appreciate the help of my wife, Cynthia J. Aronson, in putting together this thesis. I also wish to thank Dr. Jay A. Siegel for the use of his lab and equipment. I would like to thank Professors Eric A. Grulke and

R. Mark Worden of the Department of Chemical Engineering at Michigan State University, for their encouragement, guidance and stimulating discussions about my research and graduate education.

My sincere thanks are given to the many friends, old and new, I have at Michigan State University and in East Lansing, Michigan. My appreciation goes to the members of Dr. Scrantons's laboratory including graduate students Scott Coons and Eric Nelson for their input into my research. Special appreciation goes to Arvind Mohan Mathur, my office mate and friend. He has been a great support to me during these past two years. I surely enjoyed the discussions concerning science, engineering, research, religion and marriage.

I wish to thank my wife Cynthia Jean (Schutt) for marrying me, putting up with my idiosyncrasies and loving me so much. I wish to acknowledge my family, who have helped much more than words can express. To them I give my deepest love and gratitude. I wish to thank my parents-in-law for giving me their daughter, a great set of extended relatives; and especially for their love, support and generosity. I particularly wish to thank my father and mother, Dr. Lawrence D. Aronson and Mrs. Joan Kelly for being my friends as well as my teachers. Thank you mom and dad for giving me the desire to learn, the discipline to accomplish a task and the wisdom to know that God is in charge of my life.

I wish to thank the Lord for giving me the mind, health and perseverance to finish this work. Only He is able to keep us from all evil.

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CHAPTER 1

INTRODUCTION

Polymer complexes are formed by the association of two or more complementary polymers, and may arise from electrostatic forces, hydrophobic interactions, hydrogen bonding, van der Waals forces or combinations of these interactions (1-4). Due to the long-chain structure of the polymers, once one pair of complementary repeating units associate to form a segmental complex, many other units may readily associate without a significant loss of translational degrees of freedom. Therefore the complexation process is cooperative, and stable polymer complexes may form even if the segmental interaction energy is relatively small (1,4). A schematic representation of polymer complexation is shown in Figure 1. The formation of complexes may also strongly affect the polymer solubility, rheology, conductivity and turbidity of polymer solutions. Similarly, the mechanical properties, permeability and electrical conductivity of the polymeric systems may be greatly affected by complexation.

The use of macromolecular complexation for the development of novel polymeric materials is an area of unexplored potential. The specificity and reversibility of polymer complexes make them useful for providing some control of a materials structure and properties. Because macromolecular complexes often exhibit chemical and physical properties that are drastically different than those of the individual constituent polymers, complexation may be used to modify the properties of polymeric materials (1-2,4). However few examples have been reported in the literature. Only recently, hydrogen bonded molecular complexes have been exploited for the formation of environmentally sensitive materials (5,6), while ionic complexes have been used for development of

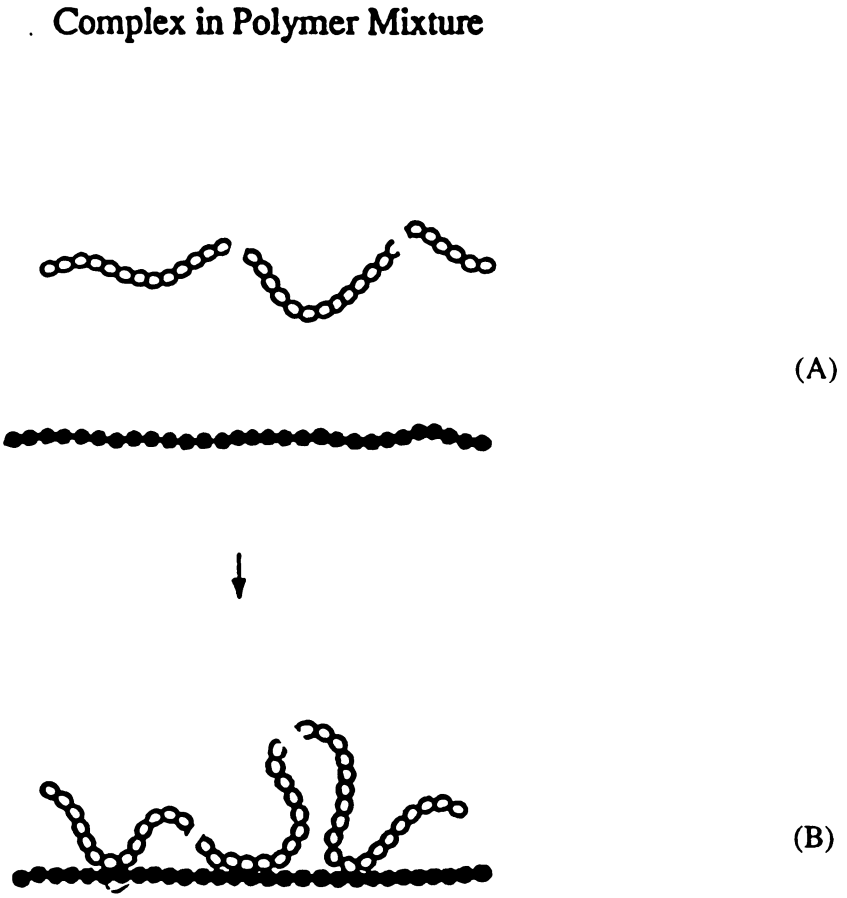


Figure 1: Schematic representation of polymer complexation. (A) Two different polymer species uncomplexed. (B) Segmental interactions to form polymer complexes.

materials which will contract upon an increase in temperature, or the application of electrical potential (3).

Compared to complexes between complementary polyelectrolytes, complexes formed by hydrogen bonding between complementary polymeric Lewis acids and bases (1-4) typically dissociate under a wider variety of conditions. Hydrogen bonding occurs between a Lewis acid containing an electron deficient proton and a Lewis base containing a lone pair of electrons. Hydrogen bonds are distinctly directional and specific, and are more localized than any other type of weak intermolecular interaction (7). In associating polymer systems the equilibrium between complexed (hydrogen bonded) and uncomplexed polymers in solution may be highly sensitive to surrounding conditions, such as pH, temperature, solvent composition and polymer concentration. Molecular structural parameters such as molecular weight and polymer architecture may also influence the complexation equilibrium.

Many interesting properties of macromolecular complexes arise from the cooperative nature of the complexation process (1-2,4). Unlike small molecules, macromolecules can accommodate many energetically favorable segmental interactions without undergoing a large change in entropy. For this reason, stable macromolecular complexes may form even if the segmental interaction energy is relatively small, and the complex stability is highly dependent upon the polymer chain lengths. In fact, many systems exhibit a critical chain length below which complexation is not detected (1-2,4).

We have investigated the use of macromolecular complexation for developing materials which exhibit an enhanced glass transition temperature and increased solvent resistance. We have used a model system of poly(4-vinyl phenol) (PVPh) with poly(N,N-dimethylacrylamide) (PDMA). In this system, PVPh is a proton donor, PDMA is a proton acceptor, and the two form relatively strong hydrogen bonded complexes. The PVPh/PDMA complex was isolated by precipitation from solution with

yields of over 95 mass percent under optimum conditions. The PVPh /PDMA was characterized in solution and in solid polymer blends. The thermal, optical and solution characteristics of the complex were correlated with composition.

We have also investigated the role of macromolecular complexation in responsive polymers whose physical properties depend on external conditions such as temperature and pH. The model system used was hydrogen bonded complexes of poly(methacrylic acid) (PMAA) and poly(ethylene glycol) (PEG). Here, PMAA is a Lewis acid or proton donor, and PEG is the Lewis base or proton acceptor. The system was studied using nuclear magnetic resonance (NMR) spectroscopy to investigate whether spin-spin relaxation studies could be used to detect complex formation. The spin-spin NMR relaxation times of dilute poly(ethylene glycol) (PEG) solutions were determined using spin-echo pulse sequences. PEG samples with higher molecular weight had shorter spin-spin NMR relaxation times. Spin echo experiments were also done on mixtures of two PEG species of different molecular weight. Regression analysis with two decaying exponentials successfully characterized the mass fraction of each constituent. The complexation of PEG with poly(methacrylic acid) was studied in dilute aqueous solutions. Complexation in dilute solution was detected by NMR relaxation time experiments at lower PEG molecular weights than previously reported.

CHAPTER 2

BACKGROUND

2.1 Polymer Complexation

Polymer complexation, interassociation or adduct formation has received considerable attention in recent years. For example, several authors have reported that the miscibility of two polymers is drastically affected by complex formation (8-13). A number of modified Flory-Huggins thermodynamic models which incorporate strong interactions such as hydrogen bonding have been proposed (8-11). In general, the entropy of mixing for two polymers is small, therefore the enthalpy of mixing must be negative for the two polymers to be miscible. For this reason, the overriding thermodynamic requirement for polymer compatibility is a large enthalpic interaction to produce a negative free energy of mixing. Various types of secondary intermolecular binding forces have been investigated for producing miscible blends, including hydrogen bonding (14-20), acid-base interactions (21), charge transfer (22,23), and ion-dipole interactions (24). Hydrogen bonded complexes are particularly attractive for this purpose because a variety of organic constituents may participate in hydrogen bonding. Hydrogen bonding occurs between a proton donor group containing an electron deficient proton, and a proton acceptor group containing an electron lone pair (e.g. O, N and S). Hydrogen bonds are distinctly directional and specific, and are more localized than any other type of weak intermolecular interaction (7). Hydrogen bond energies are typically in the range of 1-10 kcal/mol. Coleman et al. (25) recently published a concise guide to polymer miscibility enhanced by hydrogen bonding.

2.1.1 Complexes with Poly(4-vinyl phenol)

In the past few years, several authors have studied macromolecular complexes of poly(4-vinyl phenol) (PVPh), also named poly(4-hydroxyl styrene) (PHOST), with a variety of complementary polymers. Moskala and co-workers (26,27,28) used infrared spectroscopy to investigate complexes of PVPh with poly(vinyl acetate), poly(lactones), poly(vinyl alkyl ethers), poly(ethylene oxide) and poly(vinyl pyrrolidone). In all cases the strength of the hydrogen bonding interaction directly correlated with the polymer-polymer miscibility. Meftahi and Frechet (29) investigated the effect of complex formation on polymer miscibility by studying the compatibility of poly(vinyl pyridine) with copolymers of PVPh. They observed that a critical fraction of 4-vinyl phenol (VPh) units copolymerized with styrene was necessary to achieve complete miscibility with poly(vinyl pyridine). Qin et al. (30,31) investigated amorphous blends of PVPh with poly(vinyl methyl ketone) and poly(ethylene glycol) using solid state ^{13}C nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FT-IR). Again physical properties such as miscibility, glass transition and melting temperature varied directly with the degree of complexation. Zhang et al. (32) have recently studied the composition dependence and phase structure of blends between poly(4-vinyl phenol) and poly(ethylene oxide) or poly(ethylene glycol). Carbon-13 (^{13}C) resonance and proton spin diffusion NMR results gave evidence for intermolecular hydrogen bonding phase structure as well as domain size. Ting et al. (33) have investigated hydrogen bonding between copolymers of styrene and (4-vinyl phenol) with poly(ethylene oxide). An enhanced glass transition temperature as well as infrared resonance effects gave evidence of hydrogen bonded interaction equilibrium attributed primarily to the acidity of the phenol group (33).

Other studies of PVPh complexes with complementary polymers have focussed on polymer-polymer miscibility and glass transition temperatures. Serman et al. (34,35) recently studied the hydrogen bonded complexation of PVPh with polyethers and poly(n-alkyl methacrylate). These authors constructed spinodal polymer-polymer phase diagrams and established association equilibrium constants using FT-IR. Jong et al. (36) reported limited miscibility in blends of poly(styrene-co-vinyl phenol) with poly(n-butyl methacrylate) based on the amount of 4-vinyl phenol (VPh) monomer units in the copolymer. Results of ^{13}C solid state NMR, DSC, FT-IR and cloud point experiments showed the domain size for homogeneity is also proportional to the number of VPh monomer units. French and Machado (37-39) have investigated blends of poly(styrene-co-vinyl phenol) with polyacetal. In the initial study of low molecular weight analogs, hydrogen bonding was detected between 4-ethyl phenol and dimethoxymethane in the infrared spectrum (37). These authors obtained an interaction parameter by melting point depression (38) that agreed well with interaction parameters obtained for the low molecular weight analogs (39). The polymer blends exhibited a single glass transition temperature over a wide composition range indicating miscibility (39). In addition, the degree of crystallinity in the polyacetal phase decreased upon blending with the poly(styrene-co-vinyl phenol) random copolymer (39). Coleman et al. (40) used infrared spectroscopy and thermal analysis to determine miscibility maps between copolymer-copolymer blends of poly(styrene-co-4-vinyl phenol) and poly(ethylene-co-methacrylate). These experimentally determined miscibility maps compared favorably with those theoretically calculated using the Flory-lattice model for hydrogen bonded polymer interactions.

Landry and Teegarden (41) measured the heats of mixing of small molecular weight analogs of PVPh and poly(N,N-dimethylacrylamide) (PDMA). These studies revealed that the hydrogen bonding interaction in this system is strong compared to

typical systems. Based upon differential scanning calorimetry (DSC) and FT-IR studies, these researchers established complete miscibility for the PVPh/PDMA blend over the entire composition range. Wang et al. (42) examined the effect of PVPh molecular weight in complexes with PDMA, and investigated a variety of solvents for synthesizing the blend. Here, all the blends showed a single Tg which was enhanced relative to either constituent polymer. Wang et al. (42) characterized the PVPh/PDMA complex stoichiometry through FT-IR and elemental analysis and found an azeotrope at 46 mole percent PVPh in the feed irrespective of synthesis solvent (42). Suzuki et al. (43,44) characterized the PVPh/PDMA blend using solid state ^{13}C NMR and observed a shift of 3 ppm in the phenolic carbon resonance peak due to hydrogen bonding.

2.1.2 Complexes of Poly(ethylene glycol) (PEG) with Poly(methacrylic acid) (PMAA)

The properties of dilute aqueous solutions of PEG and PMAA or PAA have been studied by a number of investigators using viscometry, turbidimetry and potentiometric titration (1-4,45-49). These studies have shown that the complexed polymer fraction depends strongly upon the molecular weight of the complementary polymers. In experiments with PAA or PMAA of high molecular weight, a critical PEG molecular weight was identified below which no complexes were observed. A critical molecular weight of about 2000 was reported for the PEG/PMAA system, while a value of around 6000 was reported for the PEG/PAA system (46-48). Several investigators (1-4,45-49) found that both atactic PAA and PMAA complexed with PEG in a 1:1 repeating unit molar ratio while isotactic PAA formed complexes with a 2:3 carboxylate:ether molar ratio. Finally, all investigators found that the complex stability increased with decreasing pH, although there are discrepancies in the value of the critical pH for complexation. For

example, based upon turbidimetry Ikawa (49) reported a critical pH for PMAA/PEG complexation of 3.0 in contrast to a value of 5.6 obtained previously using viscometry and potentiometry.

Several authors have investigated the hydrophobic stabilization of PEG/PMAA complexes. The earliest evidence for hydrophobic stabilization in aqueous media arose from the temperature dependence of the complex stability. PMAA/PEG complexes increase in strength with increasing temperature (45,46), whereas those of PAA/PEG do not change appreciably. These trends suggest that the PEG/PMAA complexes are hydrophobically stabilized, perhaps due to the α-methyl group which is present on PMAA. Further evidence of hydrophobic stabilization of PMAA/PEG complexes was reported by Ikawa et al. (49). For PMAA systems the critical chain length of PEG increased significantly when the solvent was changed from water to a water/methanol mixture; while it remained relatively constant for the PAA/PEG system. Similarly, Osada and collaborators (48,50) found the temperature dependence of complex stability to be opposite in ethanol/water mixtures from that in pure water, due to disruption of hydrophobic interactions in the former case. These results were supported by measurements made by Papisov et al. (51) who found that complexation of PMAA and PEG in water is endothermic with a positive entropy change.

Recently the complexation of PAA and PMAA with PEG were studied using fluorescent spectroscopic techniques (52-58). Morawetz and coworkers (56,57) studied PAA association with PEG using PAA labeled with dansyl chromophores. These chromophores exhibit a fluorescent intensity change and spectral shift when moved from a hydrophilic to a hydrophobic environment. Large peak intensity changes upon addition of PEG to dansylated PAA revealed that the chromophore ends up in an environment largely devoid of water. Frank and collaborators (52-55) used fluorescence spectroscopy to investigate the complexation of pyrene end-labeled PEG with PMAA and PAA. Examination of the pyrene excimer to monomer ratio of sparsely tagged PEG allowed

intramolecular end-to-end contact to be characterized, while experiments with fully tagged PEG provided information about both intra- and intermolecular contacts. These studies confirmed previous observations that complexation is highly dependent upon chain length, facilitated by low pH, reduced by neutralization of the acid and reduced by the addition of methanol. However, in contrast to earlier results, complexes of the PEG with PMAA and PAA were detected for PEG molecular weights as low as 1850 and 4200, respectively (52-55).

Investigations of the complex stoichiometry by fluorescence spectroscopy yielded mixed results. Based upon studies using the previously described chromophores, Morawetz and collaborators (56,57) and Frank and collaborators (52-55) found the extent of complexation in the PEG/PAA system increased as the number of acid moieties was increased past a 1:1 molar ratio. In fact, for low molecular weight PAA, the formation of intermolecular excimers plateaued at the PAA/PEG repeating unit ratio of around 3:1 (55). In contrast, Heyward and Ghiggino (58) used fluorescence polarization studies of acenaphthylene labeled PAA to show that complexation is maximized for the 1:1 molar ratio of repeating units.

The affinity of PMAA and PAA for polymeric Lewis bases can depend quite strongly upon the structure of the base. For example, PMAA will bind more strongly with poly(vinyl pyrrolidone) (PVP) than with PEG (1-4,59). In fact, PVP will displace PEG of similar molecular weight from a complex with PMAA. Interestingly, PEG of much larger molecular weight than the PVP can displace PVP from a complex with PMAA. Similarly the Lewis acid poly(itaconic acid monomethyl ester) will form a hydrogen-bonded complex with PVP, but not with PEG. Other polymeric Lewis bases with which poly(carboxylic acids) will form complexes include poly(acrylamide), poly(dimethoxyethylene), poly(vinyl methyl ether), poly(vinylbenzo-18-crown-6) and poly(vinyl alcohol).

2.1.3 Applications of Poly(ethylene glycol) (PEG) / Poly(methacrylic acid) (PMAA) Complexes

Complexes of PEG and PMAA have been used to design novel polymeric systems. For example, PEG complexes with PMAA have been used to form membranes with controlled permeability (60). Addition of PEG to water-swollen PMAA membranes at low pH gave rise to large reversible shrinkage of the membranes. The shrinkage increased with PEG concentration and with temperature. PEG with a molecular weight as low as 2000 gave rise to shrinkage (61), while addition of alcohols or base to shrunken membranes broke the complexes and resulted in swelling. Osada and coworkers (62,63) used these membrane systems as chemical valves with controllable permeability. The porous PMAA membranes were fixed in frames so that when shrinkage and swelling were induced, the pores would open and close, thereby regulating solute flux. A similar concept was studied by Nishi and Kotaka (64). End-linked PEG gels were swollen with acrylic acid, which was subsequently polymerized. The resulting interpenetrating networks showed pH responsive swelling and permeability similar to that described above. The flux of solute macromolecules was varied by changing the pH of the surrounding medium.

Polymer complexation has been exploited in our laboratory for the design of responsive polymeric materials which exhibit sharp transitions in swelling and permeability in response to small changes in pH, temperature or solvent composition (6,65). This approach is based upon the fact that material properties under complex-promoting conditions may be dramatically different than those under complex-impeding conditions.

2.1.4 Theoretical Models of Polymer Complexation

The complexation of complementary polymers has been modeled theoretically by Kabanov and collaborators (4,47,66). In this analysis the total free energy of complexation was divided into two contributions: one arising from the specific interactions between complexing functional groups, and a second arising from configurational changes of the system upon complexation. The authors typically assumed that in the complexed state, the polymer of the shortest chain length (the PEG) was completely bound with all repeating units participating in hydrogen bonds. This assumption greatly simplified the calculation of the number of system configurations in the complexed state. According to these models the extent of complexation can change very abruptly near critical values of polymer molecular weight or free energy of complexation due to cooperative effects in the complexation process. Calculations based on the model also agreed at least qualitatively with other experimentally observed trends. For example, the equilibrium bound fraction depended strongly upon chain length and stable complexes formed even with weak segmental interactions.

Several authors have modeled the association of biological polymers (67-70). The various models differ in the manner in which the polymer conformation in the complexed state is considered. One approach incorporates the assumption that a complexed polymer has only one possible conformation, that in which all repeating units are bound to the complementary polymer. Examples include models for the complexation of poly- and oligo-nucleotide (67,68). In contrast, models of the double-stranded helix complexes of long-chain nucleic acids have included the possibility of loops in the conformation of a complexed chain (69,70). In these models, which are reviewed by Poland and Scheraga (70), it is typically assumed that the loops are fairly long (> 20 units) when calculating the loop entropy.

Mathematical techniques based on sequence generating functions have been proposed for efficient formulation of the statistical mechanical partition functions of polymeric systems. For example, Lifson (71) reported a procedure for evaluating the canonical partition function of long-chain polymers with repeating units existing in two or more distinct states, while Eichinger et al. (72) reported a generating function technique for the evaluation of the partition functions of a long polymer chain absorbed onto a planar surface. Both of these methods were applicable in the limit of infinite chain length. Scranton et al. (73) used a similar generating function technique to describe the complexation thermodynamics of free and graft oligomers with complementary polymers. Since the long chain assumption was not required, this analysis was applicable to short and intermediate chain lengths.

In summary, polymeric acids may form complexes with a number of polymeric Lewis bases (including PEG) in water. The extent of complexation increases with polymer concentration, polymer molecular weight and with reductions in pH. The extent of complexation may increase, decrease or remain essentially unchanged with changing temperature depending upon the contribution of hydrophobic interactions to the complex stability. Recent spectroscopic measurements suggest that complexes may take place at lower molecular weights than previously determined using viscometry, turbidimetry or titration. In addition, some complexes previously thought to form with a 1:1 repeating unit stoichiometry may not do so in every case. Certain detection techniques may be more sensitive to complexation than others, perhaps accounting for the discrepancies in critical chain length and complex stoichiometries.

CHAPTER 3

OBJECTIVE

Although significant advances in the area of polymer blending via complexation have been made, analysis of the literature reveals relatively few contributions utilizing polymer complexation for the purpose of creating materials with enhanced solvent resistance and an enhanced glass transition. Most researchers have concentrated their efforts on enhancing miscibility through secondary interactions.

The work with the poly(4-vinyl phenol) (PVPh)/poly(N,N-dimethylacrylamide) (PDMA) system addresses important fundamental aspects of interpolymer hydrogen bonded complexation and establishes composition-property relationships for a model hydrogen bonded interpolymer system.

The first broad objective of this work was to synthesize hydrogen bonded complexes of poly(4-vinyl phenol) with poly(N,N-dimethylacrylamide) with varying initial feed composition. In particular, the following specific objectives were established:

(i) to optimize the synthetic yield of the PVPh/PDMA complexes with respect to feed composition, and solvent;

(ii) to characterize the composition (stoichiometry), degree of hydrogen bonding and thermal properties of the PVPh/PDMA complex using spectroscopic, thermal, optical and elemental analysis techniques;

(iii) to test the solubility of the PVPh/PDMA complexes in a wide variety of solvents in order to investigate enhanced solvent resistance due to complexation as well as to

establish a relationship between the solubility of the polymer complex and the energy of the hydrogen bonded interaction; and

(iv) to investigate any enhancement of the glass transition temperature (T_g) without a change in the melting or degradation temperatures with respect to the uncomplexed homopolymers.

The second broad objective of this work was to investigate whether nuclear magnetic relaxation could be used as a tool in detecting hydrogen bonding. Here, the system used is complexes of poly(ethylene glycol) with poly(methacrylic acid). More specifically, the major objectives of this work were:

(i) to investigate the correlation between spin-spin relaxation time (T_2) and molecular weight of monodisperse poly(ethylene glycol) samples;

(ii) to investigate the determination of mass fraction of a single polymeric species in the midst of a mixture using nuclear magnetic relaxation spin echo techniques; and

(iii) to investigate the detection of a critical molecular weight for complexation through nuclear magnetic relaxation spin echo experiments.

CHAPTER 4

COMPLEXATION OF POLY(4-VINYL PHENOL) (PVPh) WITH POLY(N,N-DIMETHYLACRYLAMIDE) (PDMA)

4.1 Synthesis of the PVPh/PDMA Complexes

Poly(4-vinyl phenol) (PVPh) and poly(N,N-dimethylacrylamide) (PDMA) were used as received from the supplier (Polysciences, Inc., Warrington, PA). The structures of PVPh and PDMA are shown in Figures 2 and 3 respectively. The nominal molecular weight of the PVPh as reported by the supplier was 30,000 g/mol. The molecular weight of the PDMA was measured by viscometry. The intrinsic viscosity of the PDMA at 25°C in methanol was 1.33 dL/g. Based upon the Mark-Houwink parameters reported for PDMA by Trossarelli and Meirone (74), the weight average molecular weight was determined to be 510,000 g/mol.

For complex synthesis, separate solutions of PVPh and PDMA were prepared by dissolving appropriate amounts of the polymers in a solvent. Acetone, methanol and ethanol were investigated with polymer concentrations of 1 or 3 weight percent. Precipitate formed immediately upon mixing solutions of the component polymers at room temperature. The opaque complex precipitate was allowed to settle for 1 hour and then the supernatant was decanted off. The complex precipitate was placed in a 65°C oven for one week in order to evaporate off all residual solvent. After a week the red-orange complex was weighed to determine the yield of the complex.

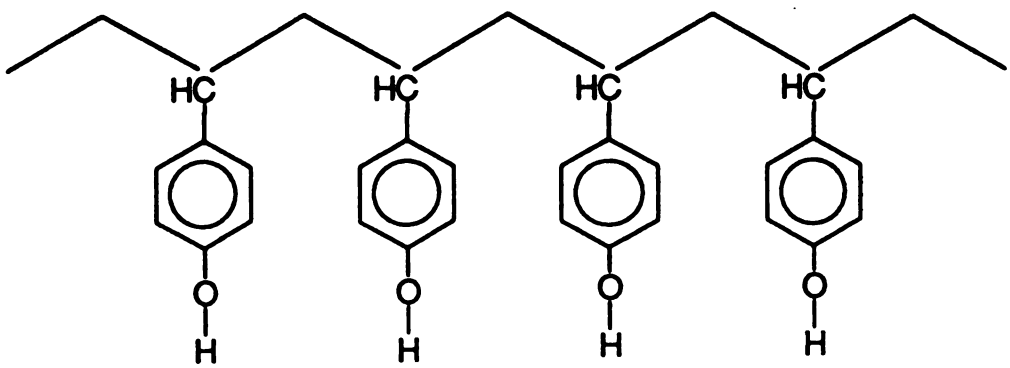


Figure 2: Structure of Poly(4-vinyl phenol) (PVPh).

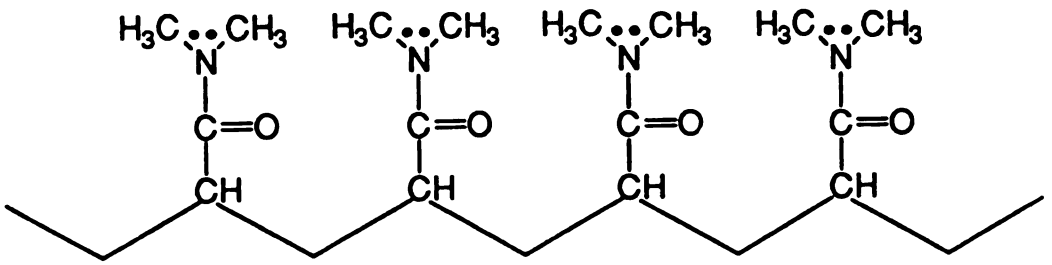


Figure 3: Structure of Poly(N,N-dimethylacrylamide) (PDMA).

4.2 Characterization of the PVPh/PDMA Complexes

4.2.1 Elemental Analysis Studies

The composition of the complex was determined by elemental analysis. Elemental analysis was performed on a CHN analyzer. The mass percents of hydrogen, carbon and nitrogen were determined for each sample.

4.2.2 Nuclear Magnetic Resonance Studies

. Solution state ^1H NMR spectroscopy was performed using a VXR-300 spectrometer (Varian, Palo Alto, CA). Deuterated dimethyl sulfoxide (DMSO-d_6, 99.96% D, Isotec, Inc., Miamisburg, OH) was used as the solvent in all the experiments. NMR samples had concentrations between 0.5 and 0.8 weight percent polymer. All experiments were performed with a controlled temperature of 40°C, using a transmitter frequency of 299.949 MHz. Experiments were conducted at an elevated temperature in order to reduce the viscosity of the sample and obtain narrower linewidths. The 180 degree pulse was measured for each sample and varied between 34.4 and 35.2 microseconds. The delay between successive pulses was at least 30 seconds. At least 200 transients were collected before Fourier transformation. Peak assignments for the proton spectrum of PVPh are as follows (Figure 4): ethylene protons showed in a broad peak centered at 1.4 ppm; aromatic protons were displayed by a peak centered at 6.5 ppm and the hydroxy hydrogen was observed at approximately 9 ppm. For PDMA (Figure 5), the peak for the backbone ethylene protons came at 1.5 ppm and the peaks

corresponding to the 6 methyl protons for the two CH_3 groups attached to the nitrogen were centered at 2.8 ppm. It should be noted that in the ^1H NMR spectrum of PDMA, the peak corresponding to the 6 methyl protons, of the two CH_3 groups attached to the nitrogen, are likely split because of hindered rotation around the N-CO bond due to the presence of the carbonyl group. Rotation around the N-CO bond is likely slower than the NMR timescale. In the spectrum of the PVPh/PDMA complex (Figure 6), the peak due to the methyl groups attached to the nitrogen for PDMA and the peak due to the aromatic protons meta and ortho to the hydroxyl group on the aromatic ring of PVPh were integrated to determine composition (Figure 5). The hydroxyl peak of the PVPh appeared at the same location for the complex and the pure PVPh.

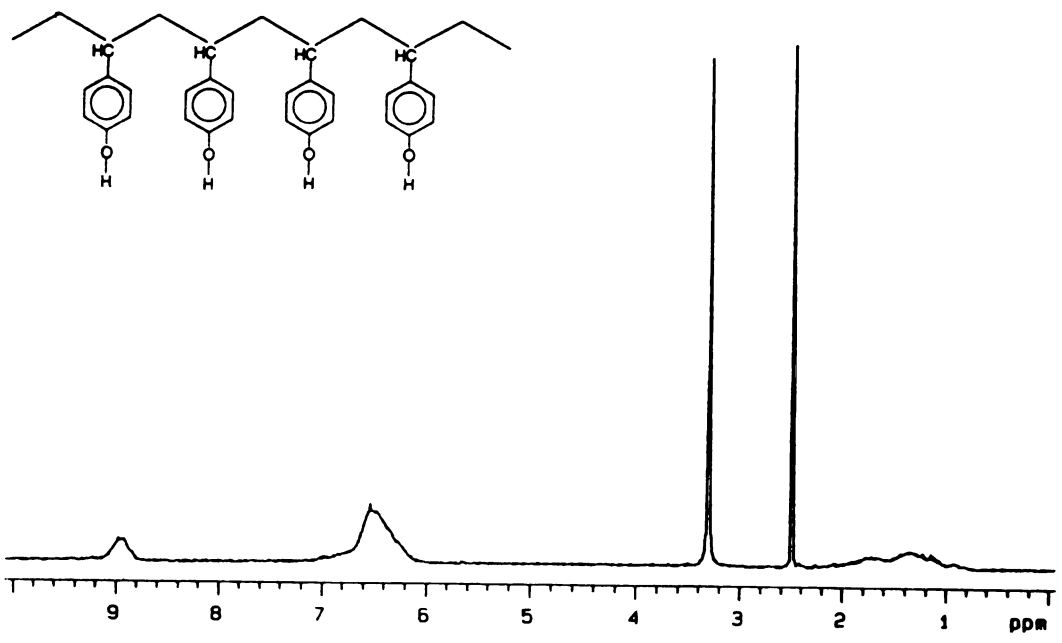


Figure 4: High resolution ^{1}H NMR spectrum of poly(4-vinyl phenol) (PVPh) in DMSO-d_6 at 40°C.

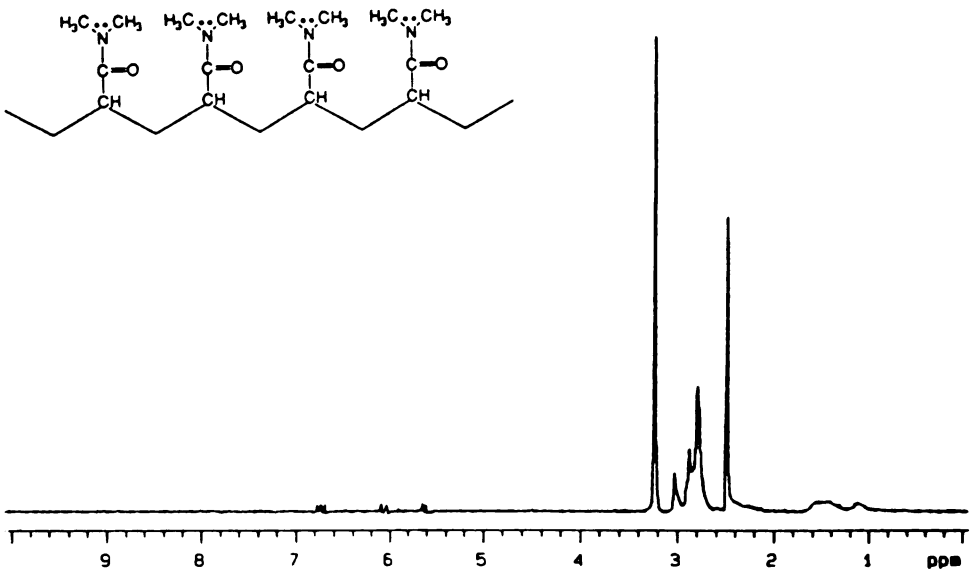


Figure 5: High resolution ^{1}H NMR spectrum of poly(N,N-dimethylacrylamide) (PDMA) in DMSO-d_6 at 40°C.

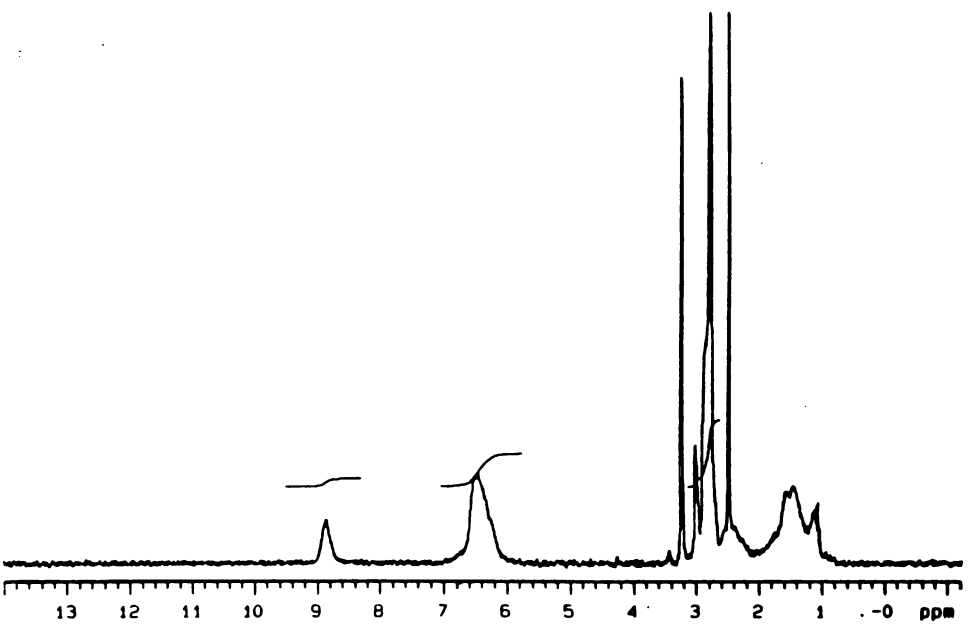


Figure 6: High resolution ^{1}H NMR spectrum of PVPh/PDMA complex in DMSO-d_6 at 40°C.

4.2.3 Refractive Index Studies

Refractive index (n_i) measurements were performed using the Becke line method. The sample and refractive index standard liquid were heated using a Mettler-FP52 hot stage and the Becke line was observed to fade at a specific temperature. Using light filters the refractive indices relative to the sodium C (λ_{max}=651.2 nm), sodium D (λ_{max}=588.0 nm) and sodium F (λ_{max}=486.3 nm) lines were accurately measured. The standard deviation for the refractive index measurements was less than 0.001. Blends of PVPh with PDMA in methanol were prepared by film casting for refractive index calibration. The solutions were dried for 7 days at 70°C to remove most of the solvent. The samples were then placed in a vacuum oven at 70°C under a vacuum of 28 inches of mercury for 12 hours to drive off residual solvent. The refractive indices of each sample were measured relative to the sodium C, D, and F lines.

4.2.4 Fourier Transform-Infrared Studies

Samples for infrared analysis were prepared by mixing the dried complex with potassium bromide (KBr) at a concentration less than 1 weight percent. The mixture was pressed into pellets under pressure. Infrared spectra were acquired on a Nicolet 5DXB Fourier Transform infrared spectrometer in transmittance at a resolution of 4 cm^{-1}. The frequency scale was internally calibrated with a reference helium-neon laser to an accuracy of 0.2 cm^{-1}. At least 200 scans were signal averaged and the spectra were stored on a disk system. A Beckman-RIIC TEM 1C automatic temperature controlled cell mounted in the spectrometer was used to obtain elevated temperature spectra. The temperature of the cell was checked by an external temperature sensor and was accurate to within +/-0.5°C.

4.2.5 Solubility Studies

The solubility of the complex was investigated by mixing equal amounts of successively dilute homopolymer solutions of 1.0, 0.1 and 0.01 mass percent polymer in methanol, and then observing for precipitate formation. The solubility of the complex as compared to the individual homopolymers was also determined in a wide range of solvents. The complex or one of the homopolymers was placed in a solvent at polymer concentrations between 0.1 and 0.5 mass percent polymer. The resulting solutions were vortex mixed and observed at room temperature for at least 14 days for dissolution of the polymer.

4.2.6 Characterization of Thermal Properties

The thermal properties of the complexes were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC and TGA were performed on a DuPont 9900 instrument, with a heating rate 10^{o}C/minute in both cases. The sample size was between 10 and 20 mg for both DSC and TGA. For the DSC experiments, two runs were conducted on each sample. The initial run to 250^{o}C was performed to drive off any residual solvent. The glass transition temperature (Tg) was taken as the inflection point in the change in heat capacity with temperature for the second run. All complexes exhibited a single Tg. In the TGA experiments, the temperature for the onset of degradation as well as the temperature of 25.00% weight loss were measured for each sample heated under nitrogen purge. Both the DSC and TGA measurements were repeated at least twice on samples from identical batches and the variance between samples was less than 10^{o}C for both the Tg and the 25.00% degradation temperatures.

4.3 Results and Discussion

The complexes were synthesized by precipitation from solutions containing 1 or 3 weight percent of each of the constituent polymers. Alcohols such as methanol and ethanol are particularly useful for this synthesis method because, although both homopolymers are soluble in these liquids, the complex is not. Therefore, the complex may be isolated in a purified form containing no uncomplexed homopolymers.

Ethanol and methanol were chosen as the optimum solvents for synthesizing the PVPh/PDMA complexes. For synthesis runs containing 1:1 4-vinyl phenol (VPh)/N,N-dimethylacrylamide (DMA) repeating unit mole ratios, the mass percent yield of the complex was consistently over 95% of the total polymer in the feed for both ethanol and methanol. These alcohols were chosen as synthesis solvents largely because of their volatility, allowing them to be evaporated off easily. Precipitation of the complex from methanol was observed at concentrations as low as 0.01 weight percent polymer.

4.3.1 Composition of Complexes

Table 1 contains data for the composition of PVPh/PDMA complexes as a function of the corresponding feed composition. These complexes were synthesized by mixing solutions containing 1 weight percent of each homopolymer in ethanol. The values in the first column of the table report the percentage of the polymer repeating units in the synthesis mixture (both complexed and uncomplexed) which are vinyl phenol (VPh) (the solvent is ignored for this calculation). The second column reports the mole percentage of polymer repeating units in the complex which are vinyl phenol, as determined by elemental analysis for nitrogen. The values in this column were checked

using high resolution, solution state ^{1}H NMR and the agreement between the two methods was very good above 30 mol% VPh in the complex as shown in Table 2. Below 30 mol% VPh in the complex, the two methods do not agree well with each other. This is probably due to the insensitivity of the NMR integration for relatively broad peaks with low intensity. Therefore, the elemental analysis data are probably more trustworthy at these concentrations.

Table 1: Composition of the PVPh/PDMA Complexes

Overall mol% VPh Repeating Units	mol% VPh Repeating Units in Complex, Elemental Analysis
3.39	16.8
7.33	30.9
11.9	31.8
17.4	39.6
32.2	43.2
42.5	44.7
55.9	45.4
74.0	53.4

Table 2: Comparison of Compositional Results for the PVPh/PDMA Complexes as determined by Elemental Analysis and ^1H NMR

Overall mol% VPh Repeating Units	mol% VPh Repeating Units in Complex, Elemental Analysis	mol% VPh Repeating Units in Complex, NMR
3.39	16.8	2.30
7.33	30.9	14.1
11.9	31.8	29.1
17.4	39.6	39.6
32.2	43.2	43.0
42.5	44.7	45.0
55.9	45.4	48.5
74.0	53.4	52.6

Data from Table 2 are plotted in Figure 7. The diagonal line in the figure corresponds to compositional azeotropes which would occur if the composition of the complex were the same as that of the feed. The data appears to intersect the diagonal at about 45 mol% VPh, suggesting that the system exhibits an azeotrope at this composition. It is clear from Figure 6 that below the azeotrope, the complex is enriched in VPh relative to the feed. As the mol% VPh in the feed is increased to 74 mol%, the percentage of VPh in the complex approaches a plateau at around 53 mol percent. These trends are in qualitative agreement with those reported by Wang et al. (42).

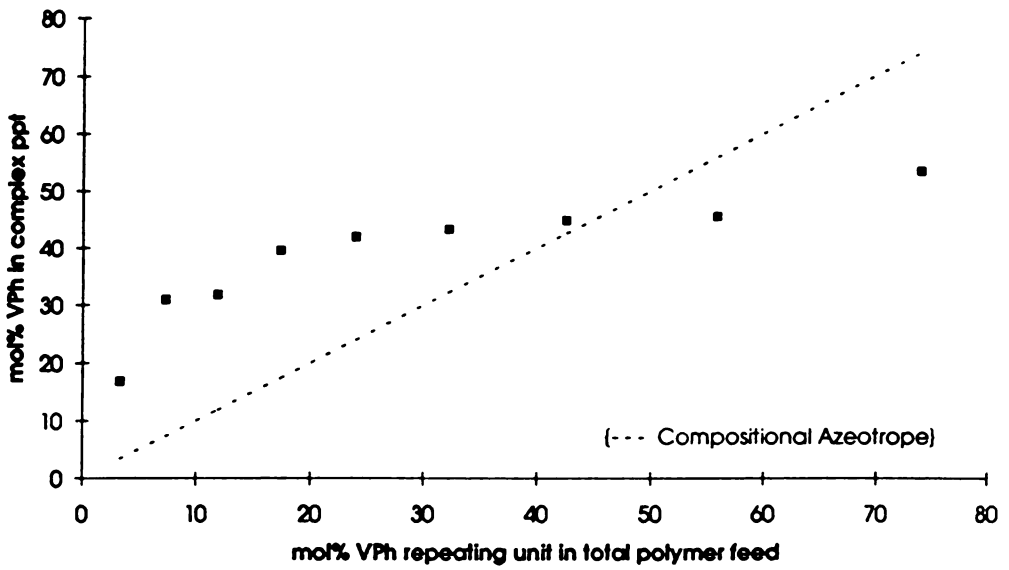


Figure 7: Composition of the complexes as determined by elemental analysis for nitrogen. The diagonal line corresponds to compositional azeotropes.

The reason for this trend arises in part from the molecular weight differences between the PDMA and PVPh used in this study. The PDMA, which has a molecular weight of about 510,000 g/mol, contains over 5,000 repeating units per chain; while the PVPh (M.W. 30,000) contains only about 250 repeating units per chain. Therefore, each PDMA chain is capable of accommodating twenty fully bound PVPh chains. It could accommodate even more if the PVPh chains were partially bound with dangling ends. It is unclear how many PVPh chains must be bound to a PDMA chain before it becomes insoluble and precipitates. For a system which is lean in PVPh, the complex is enriched in PVPh relative to the solution suggesting that a threshold number of bound chains may be required for precipitation. As the VPh/DMA repeating unit ratio increases, the complex stoichiometry approaches a value near 1:1 with the VPh mol% in the complex plateauing at 53%. In this regime, the solution contains excess PVPh chains, and the complex contains PDMA chains completely covered with PVPh. The plateau clearly implies that once a PDMA chain is consumed in the complex (fully covered with PVPh), it cannot accommodate more PVPh. Therefore an increase in the PVPh concentration in the solution does not lead to an increase in the PVPh content of the complex.

4.3.2 Refractive Index of Complexes

The refractive index measurements on the polymer blends prepared by film casting indicated that the refractive index of the blends varied linearly with the molar composition. Therefore, refractive index measurements were proposed to provide an alternative method for determining the composition of the complexes. Data for the refractive indices of the complex are shown in Table 3, 4 and 5 for the sodium C, D and F lines respectively. The first column of each table represents the mole fraction of VPh

repeating units in the complexes as determined by ^{1}H NMR. The second column in each table represents the experimentally determined refractive index of the complex, while the third column shows the value calculated as the pure component values multiplied by the corresponding mole fractions. The excellent agreement between the experimental and predicted values demonstrates that the refractive index varies linearly with the molar composition and may be used to estimate the composition of the complexes.

Table 3: Refractive Index of the PVPh/PDMA Complexes using the Sodium C line

mol% VPh Repeating Units in Complex	Experimental Refractive Index	Calculated Refractive Index
0	1.513	1.513
2.30	1.514	1.515
14.1	1.522	1.527
29.1	1.532	1.543
41.9	1.544	1.555
43.0	1.551	1.557
45.0	1.568	1.559
48.5	1.557	1.562
52.6	1.561	1.566
100	1.615	1.615

Table 4: Refractive index of the PVPh/PDMA Complexes using the Sodium D line

mol% VPh Repeating Units in Complex	Experimental Refractive Index	Calculated Refractive Index
0	1.515	1.515
2.30	1.518	1.518
14.1	1.525	1.530
29.1	1.531	1.545
41.9	1.544	1.558
43.0	1.552	1.559
45.0	1.571	1.565
48.5	1.560	1.567
52.6	1.562	1.569
100	1.618	1.618

Table 5: Refractive Index of the PVPh/PDMA complex using the Sodium F line

mol% VPh Repeating Units in Complex	Experimental Refractive Index	Calculated Refractive Index
0	1.523	1.523
2.30	1.523	1.525
14.1	1.533	1.538
29.1	1.539	1.555
41.9	1.558	1.568
43.0	1.563	1.570
45.0	1.579	1.575
48.5	1.573	1.577
52.6	1.574	1.580
100	1.632	1.632

4.3.3 Fourier Transform-Infrared Spectra of the Complexes

The infrared (IR) spectra of PVPh, PDMA and the PVPh/PDMA complex were measured at room temperature. The room temperature infrared spectra of PVPh as shown in Figure 8 had several distinguishing features. The absorbances at 825, 1100, 1170, 1445, and 1602/1609 cm^{-1} were due to the aromatic ring of the pendant group. The absorbance at around 870 cm^{-1} is due to the para substitution on the phenyl ring. Absorbances from 1200-1400 cm^{-1} are the -OH deformation and C-O stretching vibrations mixed together to some degree. The absorbance band from 3800 to 3000cm^{-1} (maximum absorbance at 3381 cm^{-1}) is due to -OH stretching vibrations. The -OH stretching region of the spectra (3800 to 3000 cm^{-1}) of PVPh collected at 60°C is shown in Figure 9. There is still not much resolution of the complexed and free -OH groups. However, Moskala et al. (26) reported that at elevated temperatures above 100°C, two components contained in this band can be identified. In the -OH stretching region (3800 to 3000 cm^{-1}), the relatively broad band can be attributed to hydrogen bonded -OH groups. This broadening is due to the hydrogen bonds being associated in aggregates of various sizes and shapes, producing a variety of different extents of interactions and bond strengths. While the narrower band is due to free, non-hydrogen bonded hydroxyl groups. Increasing the temperature causes the intensity of the absorbance due to free -OH groups to increase relative to the hydrogen bonded absorbance (26). The IR spectral assignments for PVPh presented for the data here are similar to those presented by Moskala et al. (26) as well as Wang et al. (42).

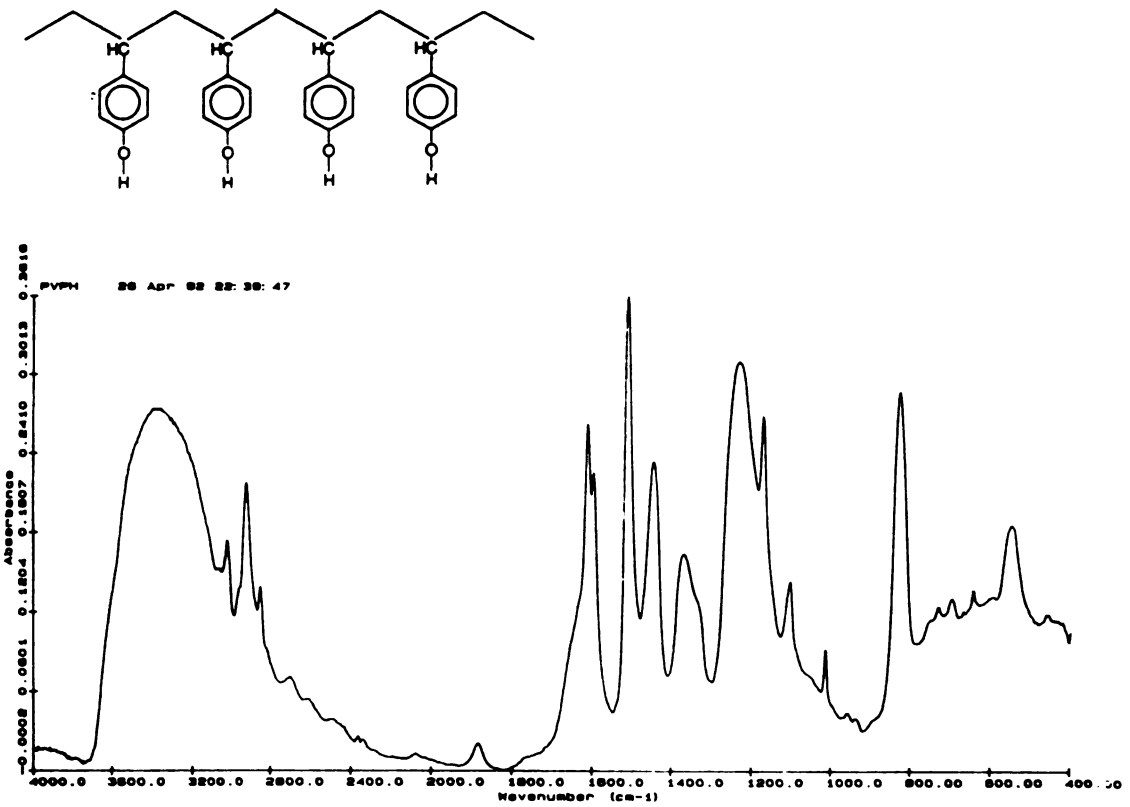
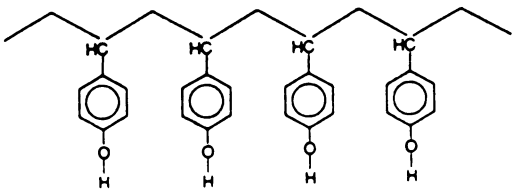


Figure 8: Infrared spectra of PVPh at room temperature (20°C).



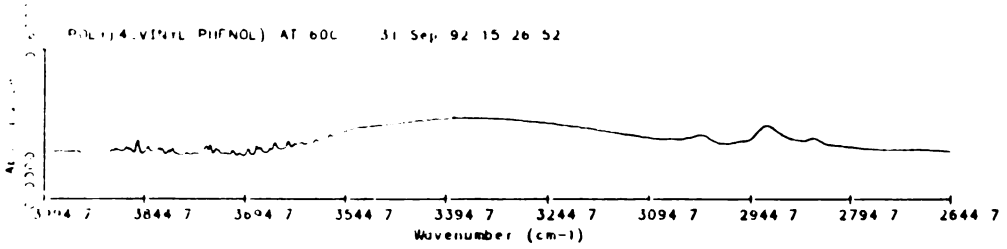


Figure 9: Infrared Spectra of PVPh at 60°C.

The IR spectra at room temperature of PDMA as shown in Figure 10 also showed characteristic group absorbances. The absorbances between 1759 and 1547 cm^{-1}, with a maximum at 1639, are due to carbonyl group (C=O) stretching. Yang et al. (14) have shown that at elevated temperatures it is readily apparent that this C=O band contains two components. The peak centered at 1639 cm^{-1} is due to free, non-hydrogen bonded C=O groups and the peak centered at 1624 cm^{-1} is due to hydrogen bonded C=O groups. The spectral assignments here for PDMA are similar to those given by Yang et al. (14). Yang et al. (14) have shown that at elevated temperatures it is readily apparent that this C=O band can be quantitatively resolved into both free and hydrogen bonded C=O components.

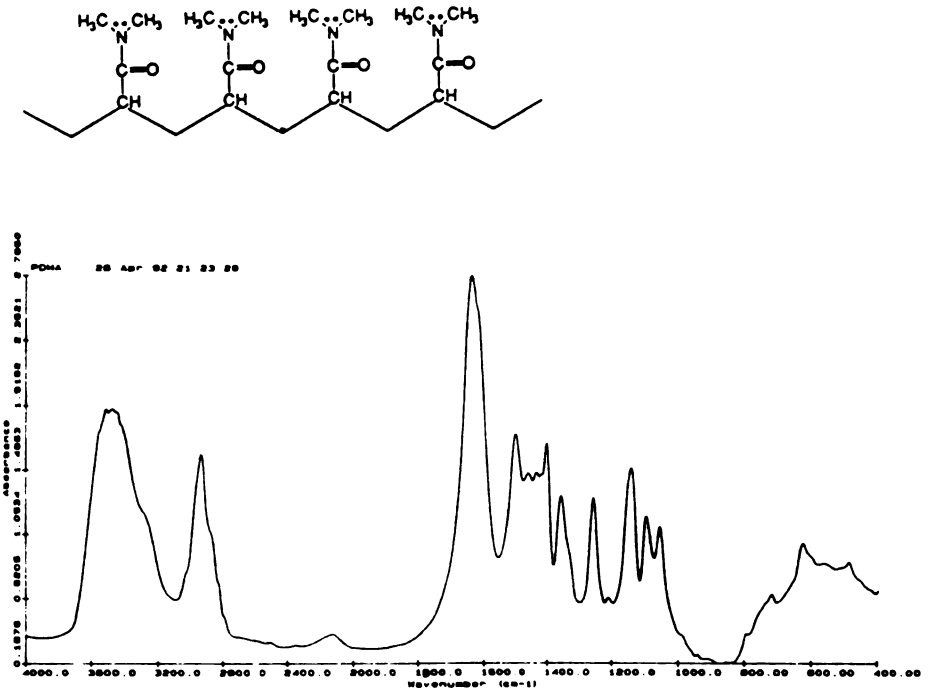


Figure 10: Infrared spectra of PDMA at room temperature (20^{o}C).

The room temperature IR spectrum of the PVPh/PDMA complexes contained components from both constituent homopolymers as well as features due to interpolymer complexation. The absorbance peak at 1630 cm^{-1} in Figure 11 is due to the C=O moiety of PDMA. The absorbance from 3800 to 3000 cm^{-1} is due to the para substituted -OH moiety of PVPh. According to Landry and Teegarden (41), absorbances at 1612 and 1592 cm^{-1} correspond to ring vibrations in PVPh. At room temperature the free hydrogen bonded components of the C=O and -OH absorbances were not able to be resolved. The spectral assignments for the PVPh/PDMA complex given here are similar to those presented by Landry and Teegarden (41). These authors have shown that at elevated temperatures, IR absorbances due to hydrogen bonding were visible (41). These authors show that the absorbance of the non-hydrogen bonded (free) -OH as well as both the peak due to the $(C=O)_{free}$ fraction and the absorbance of the $(C=O)_{hydrogen\ bonded}$ fraction were able to be resolved (41). This is due to the decrease in hydrogen bonding at higher temperatures and hence a narrowing of the corresponding peak. Landry and Teegarden also have shown a change in the phenol intensity and $(C=O)_{hydrogen\ bonded}$ fraction with a change in PVPh concentration in the complex (41). Absorptions due to hydrogen bonding stretching are moved to longer wavelengths (lower frequencies) accompanied by increased intensity and band broadening. Landry and Teegarden used the linear relationship between the change in absorbance frequency upon hydrogen bonding and the enthalpy of interaction to obtain an experimental enthalpy of mixing for the PVPh/PDMA complex (41).

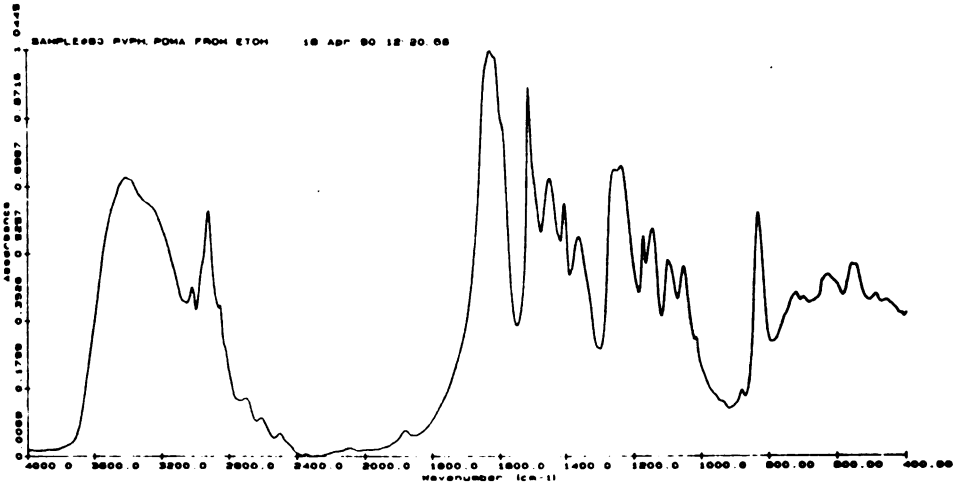


Figure 11: Infrared spectra of PVPh/PDMA complex (53 mol% VPh repeating unit in the complex) at room temperature (20^{o}C).

4.3.4 Thermal Properties of Complexes

Table 6 shows the glass transition and degradation temperatures of the complex over a range of compositions as determined by elemental analysis for nitrogen. Each complex exhibited a single glass transition, indicating that the complexes are homogeneous. The data from the first two columns of Table 6 are shown in Figure 12. The Tg value obtained for pure PDMA (108°C) is somewhat lower than that reported by previous authors (118°C-122°C) (41,42,43,44). The Tg value obtained for PVPh is 156°C. The dotted line in Figure 11 represents a weighted average between the Tg values for PDMA and PVPh. In general, the value of Tg increases as the mol% of 4-vinyl phenol (VPh) increases from 0% to 45%. For systems containing more than 30 mol% VPh in the complex, the Tg of the complex is substantially above the weighted average. In fact, for systems containing more than 40 mol% VPh in the complex, the Tg of the complex is greater than that of either homopolymer. Similar trends have been reported by previous investigators (41,42). Hydrogen bonding can lead to an enhanced glass transition temperature because these interactions act as physical cross-links (42), and additional energy must be provided to the hydrogen bonds for the individual polymer chains to gain enough mobility to become rubbery. As illustrated in Table 6, the degradation temperature steadily decreases as the PVPh content of the complex increases. The degradation steadily decreases as the mol% VPh increases. We observed no enhancement of the degradation temperature due to complexation. The TGA experiments are void of the effects of hydrogen bonding since these experiments are primarily sensitive to the breaking of covalent bonds.

Table 6: Thermal Properties of the PVPh/PDMA Complexes

mol% VPh Repeating Units in Complex	Glass Transition Temperature, ^{o}C	Degradation Onset Temperature, ^{o}C	25.00% Weight Loss Temperature, ^{o}C
0.00	108	421	431
16.8	108	404	430
30.9	147	392	412
31.8	144	406	420
39.6	156	376	411
43.2	167	378	404
44.7	182	376	409
45.4	169	397	411
53.4	175	374	419
100.0	156	386	399

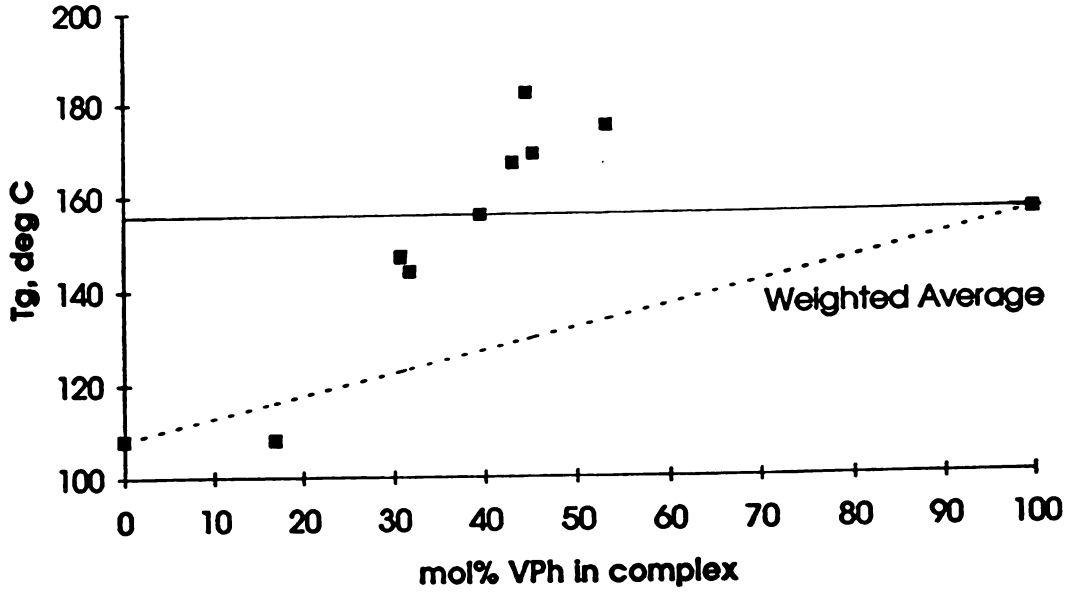


Figure 12: Glass transition temperature of the PVPh/PDMA complex over a composition range.

4.3.5 Solubility of Complexes

Table 7 contains data for the solubility of the complex and the constituent homopolymers in a wide variety of solvents. These studies were performed using a rather low concentration of 0.1 to 0.5 weight percent polymer in solvent to characterize solubility. In the table a "+" denotes solubility while a "-" denotes insolubility. It is interesting to note that eleven of the solvents investigated will dissolve both constituent homopolymers but will not dissolve the complex. Complexation may drastically affect polymer-solvent miscibility because in the complex, polar polymer functionalities are interacting strongly with one another, and are unavailable to interact with the solvent. It was hoped that nonpolar solvents would dissolve the complex while leaving the hydrogen bonds intact. However, only three solvents were found which dissolved the complex, and all three are strong hydrogen bonding solvents. Therefore, it is likely that these solvents disrupted the hydrogen bonds and broke apart the complexes during dissolution. The fact that the ^{1}H NMR PVPh hydroxyl peak occurred in the same location for the complex and the pure PVPh indicates that DMSO indeed disrupts the polymer-polymer complex.

Table 7: Solubility of the PVPh/PDMA Complex, PVPh and PDMA

Solvent	Complex	PVPh	PDMA
Methanol	-	+	+
Ethanol	-	+	+
1-Propanol	-	+	+
2-Propanol	-	+	+
Water	-	-	+
HCl/H2O pH 4.0	-	-	+
HCl/H2O pH 2.0	-	-	+
HCl/H2O pH 1.5	-	-	+
Acetone	-	+	+
Methyl ethyl ketone	-	+	+
Formaldehyde	-	-	+
Hexanes	-	-	-
Cyclohexane	-	-	-
Formamide	-	+	+
Dimethylformamide	+	+	+
Tetrahydrofuran	-	+	+
Dimethyl sulfoxide	+	+	+
Carbon tetrachloride	-	-	-
Chloroform	-	-	+
Methylene chloride	-	-	+
Benzene	-	-	-
Toluene	-	-	-
Phenol	-	+	+
Pyridine	+	+	+
Dioxane	-	+	+
Acetonitrile	-	+	+

Drago et al. (75) have developed a double-scale, four-parameter equation for predicting enthalpies of hydrogen bond formation. This equation can be used to correlate the enthalpies of interaction in donor-acceptor chemical systems. We have calculated enthalpies of complex formation from the Drago parameters between eligible donor (acid) and acceptor (base) constituent group pairs for the homopolymers and various solvents used in Table 7. The predicted enthalpies of hydrogen bond formation and the associated standard deviations are shown in Table 8.

The segmental enthalpy of hydrogen bonding for the PVPh/PDMA system can be modeled by considering interactions between the low molecular weight analogs of the polymer pendant groups on PVPh and PDMA, phenol and N,N-dimethylformamide respectively. The value of the enthalpy of hydrogen bond formation between phenol and N,N-dimethylformamide using Drago parameters is -6.42 +/- 0.24 kcal/mol. In comparison to the phenol/N,N-dimethylformamide system only the solvents that dissolved the PVPh/PDMA complex, pyridine and dimethyl sulfoxide, showed a more negative or more favorable enthalpy of interaction with the phenol group than N,N-dimethylformamide of the solvents listed in Table 8. These calculations suggest that the PVPh/PDMA complex is probably broken during dissolution and are in agreement with the ^{1}H NMR results using dimethyl sulfoxide as the solvent. In order to dissolve the complex the acceptor group has to displace the N,N-dimethylformamide pendant groups hydrogen bonded to the PVPh. This PVPh/solvent complex would then displace the interpolymer PVPh/PDMA complex during the dissolution process. The other acceptor groups (Lewis base solvents) listed in Table 8 had a less favorable or higher enthalpy of hydrogen bonding, using Drago's parameters, than N,N-dimethylformamide with phenol. These solvents in actuality did not dissolve the PVPh/PDMA complex. Thus, there is a correlation between the interaction enthalpy as calculated by Drago parameters and the solubility of the complex. These results also suggest that the solubilities of the

PVPh/PDMA complex in a solvent can be correlated to Drago's parameters. Thus, the Drago parameters could be used to try and predict solubility trends of interpolymer complexes.

Table 8: Enthalpies of Hydrogen Bond Formation Calculated from Drago Parameters

Acid / Base	-ΔH, kcal/mol +/- standard deviation
phenol / N,N-dimethylformamide	6.42 +/- 0.24
phenol / pyridine	7.89 +/- 0.14
phenol / dimethyl sulfoxide	7.06 +/- 0.13
phenol / tetrahydrofuran	6.12 +/- 0.13
phenol / acetone	5.30 +/- 0.12
chloroform / dimethylformamide	4.44 +/- 0.25
phenol / acetonitrile	4.43 +/- 0.09
phenol / benzene	2.42 +/- 0.12

CHAPTER 5

NMR RELAXATION STUDIES OF POLY(ETHYLENE GLYCOL) (PEG)/ POLY(METHACRYLIC ACID) (PMAA) COMPLEXES

5.1 NMR Relaxation

Nuclear magnetic relaxation may be resolved into two components - relaxation along an axis parallel to the external magnetic field and that in the plane perpendicular to the field. The former is called spin-lattice or longitudinal relaxation, while the latter is called spin-spin or transverse relaxation. These nuclear magnetic relaxations are characterized by the exponential time constants T_1 and T_2 respectively. Relaxation ultimately arises from fluctuating magnetic fields experienced by the nuclei as they interact with other molecules while undergoing random thermal motion. Fluctuating magnetic field components of the proper frequency lead to nuclear magnetic relaxation. Because the frequencies of the fluctuating fields are dependent upon the mobility of the nuclei, so are the relaxation times, T_1 and T_2. In general T_2 decreases monotonically as the mobility decreases, while T_1 passes through a minimum. This behavior is due to the fact that transverse relaxation relies upon low-frequency contributions to the spectral density function for efficient relaxation, while longitudinal relaxation relies upon higher frequency contributions (76,77).

5.2 NMR Sample Preparation

Monodisperse samples of poly(ethylene glycol) (PEG) (Polysciences) with molecular weights ranging from 200 to 20,000 as well as polydisperse samples of larger molecular weight were used as received from the supplier. The structure of PEG is shown in Figure 13. The molecular weights and polydispersity of the PEG samples used in this study are listed in Table 9 in the Results and Discussion section of this chapter. NMR samples were prepared by dissolving appropriate amounts of the PEG in D_2O (99.9%, Cambridge Isotope Laboratories). The concentration of the NMR samples was 0.1 +/-0.01 weight percent polymer.

5.2.1 Synthesis and NMR Sample Preparation of PEG/PMAA Complexes

Poly(methacrylic acid) (PMAA) for NMR samples was synthesized at 40°C by reacting 20 vol% MAA monomer in water with 0.50 wt% of both sodium bisulfite and ammonium persulfate based upon the total mass. The polymer product was dialyzed with D_2O to exchange H^+ with D^+, and the resulting polymer was dried in vacuo. The resulting PMAA was used for NMR relaxational studies of PEG complexed with PMAA. The structure of PMAA is shown in Figure 14. Samples containing both species were prepared by dissolving appropriate amounts of each constituent in D_2O. The concentration of the NMR samples was approximately 0.1 weight percent polymer. These samples were typically prepared by first forming dilute solutions of each polymeric species separately, and then mixing the solutions in appropriate proportions.

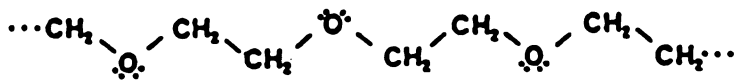


Figure 13: Structure of poly(ethylene glycol) (PEG).

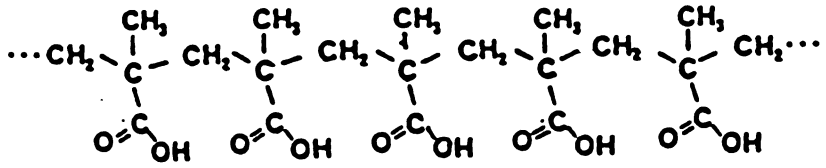


Figure 14: Structure of poly(methacrylic acid) (PMAA).

5.3 Spin-Echo NMR Experiments

High resolution ^1H NMR relaxational studies were conducted using a VXR-300 spectrometer (Varian, Palo Alto, CA) located in the Max T. Rogers NMR facility at Michigan State University or a Gemini-300 spectrometer (Varian) at the Dow Chemical Company (Midland, Michigan). These experiments were performed with a controlled temperature of 25°C, using a transmitter frequency of 299.949 MHz. The 180 degree pulse was measured between 30.0 and 31.8 microseconds. The delay between successive pulses was at least fifteen seconds (T_1 by inversion recovery was less than two seconds). At least 16 transients were added before Fourier transformation. Spin-spin relaxation times were measured using a Carr Purcell Meiboom Gill (CPMG) pulse sequence (78) with a Levitt Freeman 180 degree composite refocussing pulse (79). The sequence is shown below.

$$90^o\ (\tau\ 180^o\ 2\tau\ 180^o\ \tau)_n \text{ acquire.}$$

The CPMG pulse sequence effectively removed relaxational effects due to magnetic field heterogeneity and greatly limited the effects of diffusion, while the composite pulse was used to remove pulse imperfections (79) and off-resonance effects. The NMR tube was not allowed to spin during the spin echo experiments. The solution state ^1H NMR spectrum of PEG in D_2O is very simple with all of the ethylene protons occurring in one peak at 3.6 δ (Figure 15). The D_2O solvent peak occurred at 4.6 ppm. For each polymer sample the intensity or integral of the ethylene peak was measured as a function of total time for relaxation (equal to $4n\tau$).

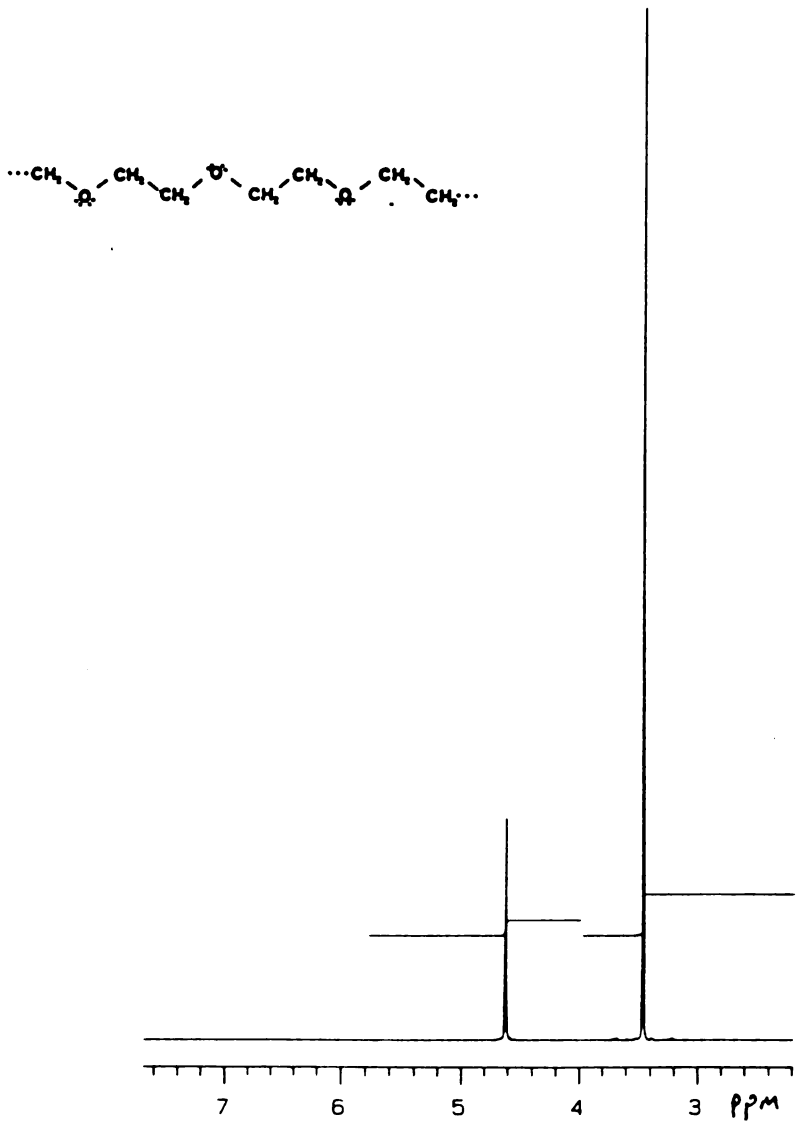


Figure 15: High resolution ^{1}H NMR Spectra of poly(ethylene glycol) (PEG) in D_2O at 25°C.

5.4 Results and Discussion

5.4.1 Spin-Spin Relaxation Times of PEG Ethylene Protons

The spin-spin relaxation of dilute PEG solutions were determined using spin echo pulse sequences. The spectral results are shown in Figure 16. These experiments were performed on solutions of 0.1 wt% PEG in D_2O. The data for the intensity of the ethylene peak as a function of the total time for relaxation were fit by non-linear least squares regression to a single decaying exponential, thereby providing a value for T_2. In all cases the error in the value of T_2 was less than 5%. Results for a series of experiments with different PEG molecular weights are shown in Table 9. These results serve as a basis of comparison for the subsequent experiments using complexed PEG. As expected, the value of the spin-spin relaxation time decreased as the molecular weight of the PEG decreases. As illustrated in Table 9, the incremental decrease in the relaxation time with increasing molecular weight is most pronounced for the smallest molecular weights. This trend probably arises from a diminishing incremental decrease in mobility with increasing chain length for long polymer chains.

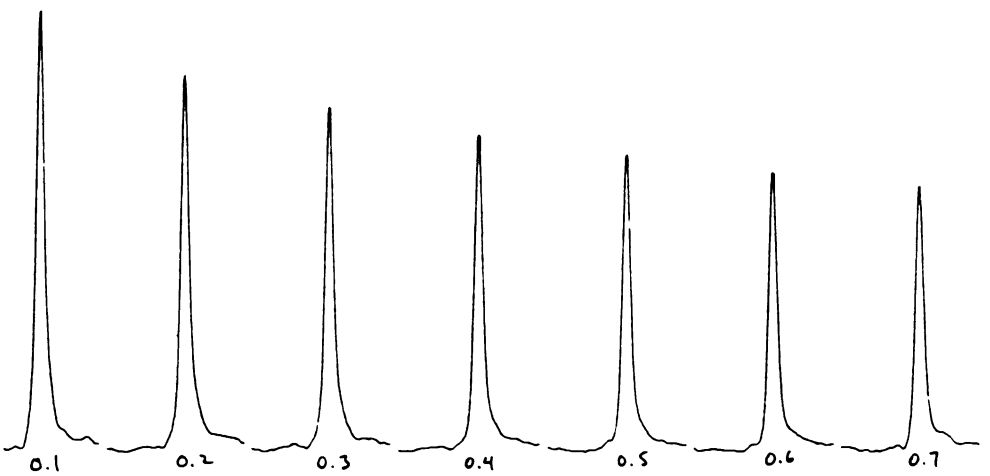


Figure 16: Ethylene protons of PEG (^{1}H NMR) as a function of total time for delay using spin echo pulse sequence.

Table 9: NMR Spin-Spin Relaxation Times of the PEG Ethylene Protons

Molecular Weight	Polydispersity	Relaxation Time (sec)
62	1.00	3.70
202	1.05	0.99
600		0.64
1500	1.05	0.61
5000	1.05	0.55
11, 000	1.04	0.48
20,000	1.13	0.47
5,000,000		0.45

5.4.2 Spin Echo Experiments on Mixtures of Different Molecular Weight PEG

Mixtures of two different molecular weight PEG species were prepared by dissolving known amounts of the two PEG species in D_2O. The total polymer concentration was 0.1 wt% PEG. Spin echo NMR experiments were performed on these solutions of two different molecular weight PEG chains in D_2O. The ethylene peak for both the lower and higher molecular weight PEG species showed at the same chemical shift (Figure 17). Therefore, the integral for the peak containing both species was measured.

When the data for the composite integral of the ethylene peak as a function of total time for relaxation was fit to a single decaying exponential, there was a significant amount of error in determining a single T_2 for the mixture (Figure 18). A computer program (see Appendix) was written in order to carry out a non-linear least squares fit to three parameters: mass fraction and the spin-spin relaxation time for each species. The equation used in the regression analysis is shown here:

$$(\text{Composite Integral}) = (\text{mass fraction}_1)\,(e^{-t/T_{21}}) + (\text{mass fraction}_2)\,(e^{-t/T_{22}}). \quad (1)$$

In this equation, the left side is the value for the integral of the NMR peak containing both PEG species. The right hand side contains terms for both PEG species including mass fractions and spin-spin relaxation time. The variable "t" stands for the total delay time for relaxation in the spin echo experiments. Figure 19 is a graphical representation of equation 1 showing a relative contribution from each molecular weight polymer chain to the overall NMR relaxation data. The ethylene proton peak of PEG for samples containing 62 and 5,000,000 molecular weight PEG are shown in Figure 17.

Two experiments were carried out on samples containing two different molecular weight PEG. The results are shown in Table 10. The known mass fraction for each polymer species is given in column 2 of Table 10. A computer program was supplied with initial guesses for individual spin-spin relaxation times (T_{21}, T_{22}) for each PEG species as well as an initial guess for the mass fractions (m.f.$_1$, m.f.$_2$). Supplied with these initial values, the non-linear least squares regression program produced values for mass fraction shown in the third column of Table 10. The best fit was shown to be independent of initial guess for the mass fractions. This was shown to be true even for initial guesses with large deviations away from the known mass fraction values. The value obtained by regression analysis for the spin-spin relaxation time of each PEG species was within 10% of the T_2 value obtained for the individual species in D_2O reported in Table 9. However, the T_2 value in the mixture cannot necessarily be expected to match the T_2 value obtained for the individual PEG species alone, due to the dependence of spin-spin relaxation time on concentration and molecular weight.

Figure 17: Ethylene protons of a mixture of 62 and 5,000,000 molecular weight PEG (^{1}H NMR) as a function of total time for delay using spin echo pulse sequence.

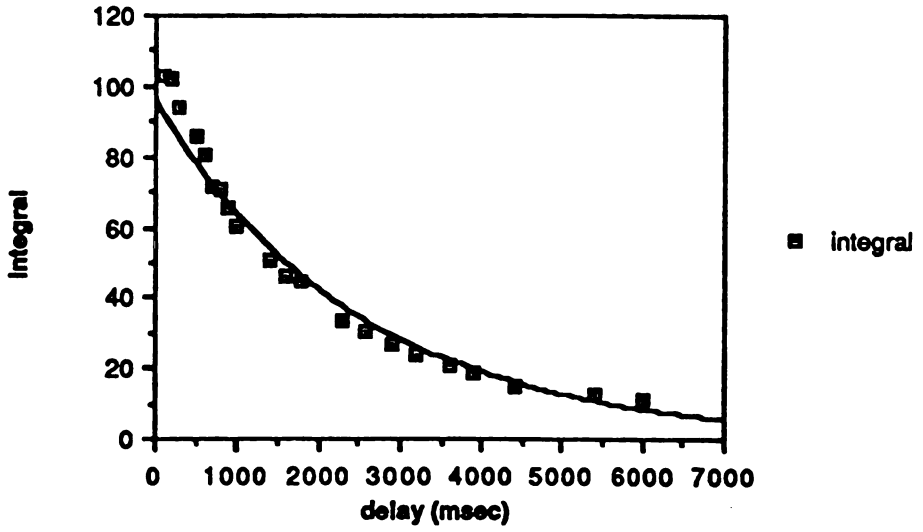


Figure 18: Data of composite integral versus total time for delay for the spin echo pulse sequence on mixtures of 62 and 5,000,000 molecular weight PEG.

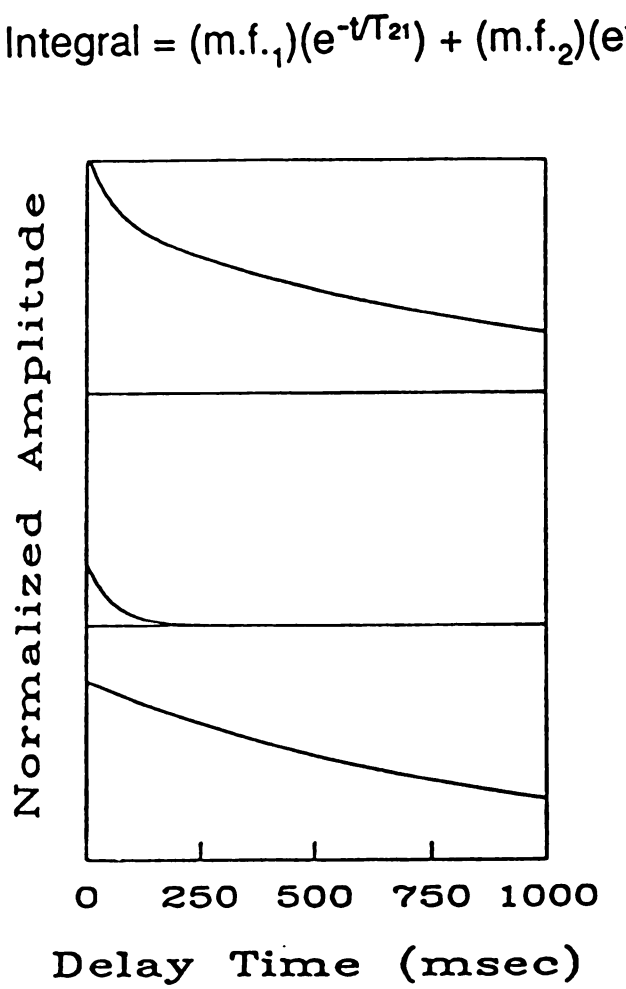


Figure 19: Graphical representation of equation 1 with contribution from each molecular weight polymer in the mixture.

When the data were fit to these two decaying exponentials (equation 1), there was agreement between the known and calculated mass fractions as shown in Table 10. Table 10 shows the results of the spin echo measurements of two mixtures containing 202 and 62 molecular weight PEG; and 62 and 5,000,000 molecular weight PEG chains.

Table 10: Spin Echo Measurements for Mixtures of Different Molecular Weight PEG

Molecular Weights	mass fractions (actual)	mass fractions (regression)
62, 202	0.45. 0.55	0.42, 0.58
62, $5X10^6$	0.40, 0.60	0.40, 0.60

The two species fit the proposed two decaying exponential model. Shorter T_2 values were consistently calculated for the higher molecular species in the mixture. In both cases there was good agreement between regression and actual mass fractions. Spin echo measurements on mixtures of three different molecular weight PEG species were also performed. However, non-linear least squares regression analysis was unsuccessful. The program did not give fitted mass fractions that were within an acceptable (+/-10%) error limit when compared to known values. Therefore improved fitting techniques will need to be employed when trying to analyze multicomponent samples. Fitting the spectrum of relaxation time, as a function of delay time, to an inverse Laplace transform (80) is currently being investigated in our laboratory as a method for resolving polydisperse polymer samples.

5.4.3 Spin-Spin Relaxation Times of PEG/PMAA Complexes

Relaxational studies were also performed on PMAA and on PEG/PMAA complexes. Solutions of 0.1 wt% PMAA and 0.01 wt% PEG were formed by dissolving appropriate amounts of these polymers in D_2O, while solutions of PEG/PMAA complexes were formed by dissolving 0.1 wt% PMAA and 0.01 wt% PEG in the same tube. Again, values of the spin-spin relaxation time were obtained by fitting the data for the peak integrals as functions of the time for relaxation to a single decaying exponential. The relaxation times of both the α-methyl and methylene protons on PMAA were less than 10 msec, while values for PEG are shown in Table 11. The relaxation time for complexed PEG chains is expected to be shorter than that for uncomplexed chains because complexation effectively decreases the mobility of the chains, thereby enhancing the low frequency contributions to the spectral density function. In fact, if irreversible complexes were formed, the T_2 value for the complexed chains would likely approach that of the PMAA protons (approximately 10 msec), an order of magnitude lower than the values for uncomplexed PEG (over 500 msec). However, the complexes are reversible and the PEG chains undergo rapid exchange relative to the NMR relaxation timescale. Therefore the observed relaxation time is a weighted average of the values for the complexed and uncomplexed chains (81). As shown in Table 11, although the presence of the PMAA has a relatively small effect on the T_2 value of PEG of molecular weight 1500, it has a pronounced effect on the T_2 value of PEG of molecular weight 5000. These results suggest that the spin-spin relaxation is indeed sensitive to the formation of complexes, and that there is a measurable chain length effect on the complex stability between PEG molecular weights of 1500 and 5000. For the 1500 molecular weight PEG, the ten percent decrease in T_2 from 570 msec to 511 msec provides evidence for complexation even at this relatively short chain length.

Table 11: T_2 Values for Complexed and Uncomplexed PEG

Molecular Weight	Uncomplexed (msec)	Complexed (msec)
1500	570	511
5000	530	310

The experimental results may be explained in terms of the statistical thermodynamic description of the complexation equilibrium reported by Scranton et al. (73). These authors considered the complexation thermodynamics of dilute solutions of free and graft oligomers with complementary polymers. The total free energy change upon complexation was divided into two contributions which were considered separately. An internal contribution to the free energy accounted for the conformational degrees of freedom as well as the segmental binding interactions, while an external contribution accounted for the configurational (translational) degrees of freedom. The external contribution could be evaluated from combinatorial considerations, while the internal canonical and grand canonical partition functions were formulated in terms of sequence generating functions for trains, tails and loops. A simple random walk model was used to evaluate statistical weights of those generating functions. Details of these calculations may be found in reference 73.

In agreement with the experimental results reported here and in the literature, the theoretical simulations revealed a marked dependence of the equilibrium bound fraction on the segmental binding free energy and the PEG chain length. Moreover, simulation results indicated that covalently attaching the complementary polymers to one another promotes the formation of complexes primarily due to a decrease in the configurational entropy change upon complexation. If the complementary polymers are covalently

attached to one another, they are effectively immobilized and are in close proximity prior to complex formation. This result corroborates NOE experiments done in this laboratory (6) which indicate the lack of critical chain length for graft copolymers. Other simulation results indicate that the loops may be important in the conformation of a complexed oligomer, and that the conformational averages for the ungrafted case asymptotically approach those for the grafted case as the segmental binding free energy, polymer concentration and PEG chain length increase.

CHAPTER 6

CONCLUSIONS and RECOMMENDATIONS

6.1 Complexes of PVPh with PDMA

In the first system, complexes of poly(4-vinyl phenol) (PVPh) with poly(N,N-dimethylacrylamide) (PDMA) were synthesized by precipitation from alcohol solutions and were characterized as to their composition, solubility, thermal properties and refractive index. A compositional azeotrope in which the feed solution and the complex exhibited the same composition was observed at about 45 mole% vinyl phenol repeating units. For overall vinyl phenol mole fractions below the azeotrope, the complex was enriched in PVPh relative to the feed, while above the azeotrope the mole% of vinyl phenol in the complex plateaued at a value of about 53 mol%. These results suggest that a minimum coverage of PDMA by PVPh is required for precipitation, and that once a PDMA chain is completely covered with PVPh, an increase in the PVPh concentration in the solution does not lead to an increase in the PVPh content of the complex. The refractive index of the complex varied linearly with the composition.

Solubility studies revealed that many solvents can dissolve both constituent homopolymers, but cannot dissolve the complex. These results illustrate that macromolecular complexation can drastically change polymer-solvent interactions since polar functionalities are associated with one another in the complex, and are therefore inaccessible to the solvent. Only strongly hydrogen bonding solvents could dissolve the complex, and the polymer-polymer hydrogen bonds were apparently disrupted during

dissolution. Complexes containing more than 30 mole percent VPh repeating units exhibited glass transition temperatures higher than either homopolymer. This trend is due to the fact that hydrogen bonds act as physical crosslinks which must be overcome for the transition from the glassy state to the rubbery state to occur. The degradation temperature decreased as the VPh content was increased, with no enhancement due to complexation.

The future work on the PVPh/PDMA system should include incorporating both complementary species into one molecule. This should be done by synthesizing random, block and graft copolymers. The synthesis of graft copolymers could be carried out by using a macromonomer. Copolymerization would allow further investigation into the underlying mechanism of complexation between PVPh and PDMA. Copolymerization could also form a tougher material than the homopolymer complex. The complex should be molded for the purpose of thermomechanical analysis, dynamic mechanical analysis, tensile testing, and izod testing. These mechanical tests would complete the picture as to the strength, processability and range of application for the PVPh/PDMA complex. Since it has been difficult to melt the constituent homopolymers, the first attempt in this area might be to solution cast the complex in a volatile solvent. The use of ultra violet-visible (UV-Vis) and fluorescence spectroscopy for detecting complexation as well as quantitative determination of the stoichiometry of hydrogen bonding should also be investigated. Because of the aromatic substituent groups in PVPh, the compound should fluoresce.

The synthesis of these complexes should also be carried out at different concentrations in order to see if the apparent complex compositions change. Using more dilute homopolymer solutions for synthesis of the complexes than are used here (0.1 or 0.01 wt% polymer) would allow further investigation into complexation equilibrium and entrainment phenomena. The synthesis of the PVPh/PDMA complexes should be

studied at different temperatures because hydrogen bonding equilibria is greatly affected by temperature. The concentration of the supernatant, decanted off during isolation of the complex precipitate, could be measured by ^1H NMR. These data would provide further confidence in the determination of the complex composition by assuming conservation of mass.

Fourier transform infrared (FT-IR) spectroscopy could be used as a method for quantitative determination of complexation stoichiometry. Wang et al. (42) have shown that the absorbance due to the para substitution on the aromatic ring of PVPh at approximately 870 cm^{-1} can be used to establish compositions of the complex and stoichiometry of hydrogen bonding. This can be accomplished due to the lack of any absorbing group in this area on PDMA. FT-IR could also be used to establish the degree of hydrogen bonding by resolving both the free and hydrogen bonded carbonyl (C=O) and hydroxyl (-OH) moieties of the constituent homopolymers in the complex. This would require the fitting of spectral peaks. These types of methods are outlined in detail in the book by Coleman et al. (25). In order to obtain the resolution between intermolecularly complexed and uncomplexed carbonyl and hydroxyl groups, spectra will have to be collected at elevated temperatures. Moskala et al. (26) and Landry and Teegarden (41) have shown that at elevated temperatures the absorbances due to hydrogen bonding interactions are distinguishable and can be resolved.

The glass transition temperature for the complex could be fit to the Kwei (82), Gordon-Taylor and Fox models for polymer blends. Between these three equations, the Kwei equation has been shown to be most applicable to hydrogen bonding polymer systems. Fitting to these models would require the collection of a few more data points preferably covering the entire composition range for the complex. The simplified Kwei equation (41,83) requires a relatively small number of data points. This equation has one adjustable parameter (q) which represents the stabilization energy in the polymer

backbone due to molecular interaction. When the data here for the PVPh/PDMA complex was fit to the simplified Kwei equation, the value obtained for q was between 150 and 200. This value is misleading due to the limited number of data points collected and the limited composition range covered by the data. Suzuki et al. (44) and Landry and Teegarden (41) both obtained q values near 100.

Molecular simulations using packages such as POLYGRAF^{R} (Molecular Simulations, Inc., Waltham, MA) could provide in depth understanding to the underlying interpolymer hydrogen bonding mechanism. By doing molecular dynamics and molecular mechanics simulations on the PVPh/PDMA system, probable donor and acceptor moieties could be identified and the stoichiometry of complexation could be theoretically calculated.

The complexation chemistry should be applied to complementary polymer systems in which the interaction is even stronger than PVPh/PDMA such as poly(4-vinyl phenol) (PVPh) with poly(allyl diphenyl phosphine oxide) (PADPO). These materials should have greater toughness and more enhanced thermal properties.

6.2 NMR Analysis of PEG/PMAA Complexes

The spin-spin nuclear magnetic resonance time (T_2), as measured by spin echo experiments, decreased as the molecular weight of the poly(ethylene glycol) (PEG) chain was increased. The individual mass fractions of two PEG samples with differing molecular weight were obtained by regression analysis from spin echo data. However, regression analysis for individual mass fractions on mixtures of three different molecular weight PEG samples was unsuccessful. Complexation between poly(ethylene glycol) and poly(methacrylic acid) in dilute aqueous solution was detected by NMR relaxation spin echo experiments. The change in spin-spin relaxation time (T_2) was correlated with a change in mobility of the PEG upon complexation. Complexation was detected at lower poly(ethylene glycol) molecular weights than previously reported.

The future work on the characterization of polymers by spin echo NMR relaxation should include analysis of systems with many molecular weights (polydisperse). To accomplish this task, an improved data fitting technique will be needed. The analysis of spin echo experiments yields the relative contributions of species with different spin-spin relaxation times by fitting the peak integral as a function of delay time to multiple decaying exponentials. This technique worked well for the system used here in which the total number of components making up the sample was known. Resolution of overlapping peaks based upon relaxation rate constant could be performed by taking the inverse Laplace transform of the data for integral as a function of delay time (80). The relaxation rate is the inverse of the spin-spin relaxation time (T_2). The inverse Laplace transform technique would be useful in determining the number of components contained in the NMR peak, and could provide useful information concerning the distribution of the relaxation rate constants. Use of this technique would require

obtaining the inverse Laplace transform of a discrete data set. In addition, acceptable resolution in the relaxation rate domain would require a large number of experiments to be performed (80).

The conditions of the spin echo experiments could also be varied to help broaden the T_2 range. The temperature, oxygen content, concentration, viscosity and solvent are some of these variables. The most valuable application of this method would in the analysis of the molecular weight distribution and other useful characteristics of biological protein chains such as heparin (84). The use of spin echo NMR experiments to detect complexation should also be applied to other complementary polymer systems such as the strongly associating systems suggested in section 6.1.

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APPENDIX

Computer Program with IMSL Subroutine for Calculating the NMR Spin-Spin Time Constant (T_2) by Non-Linear Least Squares Regression Using Equation 1 on page 60.

```
c       Carl Aronson
c       Computer Program with IMSL subroutine for
c       Non-linear Regression to solve for best fit to two
c       Decaying exponentials
        integer    ldr,nobs,nparm
        parameter (nobs=22, nparm=10, ldr=nparm)
        integer    ideriv, irank,nout
        real       dfe,exampl, r(ldr,nparm),sse, theta(nparm),
     k           xdata(nobs),ydata(nobs)
        common     /xydata/xdata,ydata
        external   exampl,rnlin,umach,wrrrn
c
        data theta/46.44,-0.2857,0.0,-0.3,0.0,-.34,-56.76,-1.0,0.0,-1.26/
        call umach (2,nout)
        ideriv=0
        call rnlin(exampl,nparm,ideriv,theta,r,ldr,irank,dfe,sse)
        write(nout,*) 'theta= ', theta
        write(nout,*) 'irnk= ', irank, '  dfe= ',dfe, '  sse= ',sse
c
        call wrrrn('r',nparm,nparm,r,ldr,0)
        end
c
        subroutine exampl (nparm,theta,iopt, iobs,frq,wt,e, de,iend)
        integer  nparm,iopt,iobs,iend
        real   theta(nparm),frq,wt,e,de(1)
        integer  nobs
        parameter(nobs=22)
        real   exp, xdata(nobs), ydata(nobs)
        common /xydata/ xdata,ydata
        intrinsic exp
c
        if (iobs .le. nobs) then
           wt=1.0e0
           frq=1.0e0
           iend=0
        e= ydata(iobs) - (theta(1)*exp(theta(2)*xdata(iobs))+
     k  theta(3)*exp(theta(4)*xdata(iobs))+theta(5)*exp(xdata(iobs)*
     k  theta(6))+theta(7)*exp(xdata(iobs)*theta(8))+theta(9)*exp(xdata
     k    (iobs)*theta(10)))
c
        else
        iend=1
        end if
        return
        end
        block data xy
        integer nobs
        parameter (nobs=22)
c
        real   xdata(nobs),ydata(nobs)
        common    /xydata/ xdata, ydata
c
        data xdata/0.1,0.2,0.3,0.4,0.5,0.6,0.7,0.8,0.9,1.0,1.4,1.6,1.8,
     k      2.3,2.6,2.9,3.2,3.6,3.9,4.4,5.4,6.0/
c
        data ydata/103.2,101.999,93.79,82.12,85.7728,80.278,71.5402,
     k  70.9128,65.2595,60.2525,50.9971,45.9541,44.6843,33.8635,30.3355,
     k      27.119,23.74,20.7712,18.4181,14.8399,12.3019,10.9268/
c
        end
```

VITA

Carl Lawrence Aronson was born in Bethesda, Maryland, United States of America on January 17, 1968 to two ecstatic Jewish parents. He grew up in several places throughout the USA due to his father's extensive medical training. These places included Bethesda, Maryland; Santa Barbara, California; Cumberland, Maryland; East Lansing, Michigan; Tulsa, Oklahoma and East Grand Rapids, Michigan. In the Spring of 1990, he graduated from East Grand Rapids, Michigan High School in the top ten of his class. In the Fall of 1990, he entered Hope College, Holland Michigan with the help of Presidential and Dow Chemical Company scholarships. During four summers at Hope, he engaged in chemistry research with financial support from the Dow Chemical Company, Midland, Michigan. After four years in Holland, he graduated Cum Laude from Hope College in June of 1990 with a Bachelor of Science in Chemistry and a Bachelor of Arts in Music (Trumpet Performance) as well as a Mathematics minor.

During the Summer of 1989, Carl did research under Dr. R. Mark Worden in the Department of Chemical Engineering at Michigan State University, East Lansing, Michigan. Due mainly to this research experience, he decided to attend graduate school at Michigan State University in Chemical Engineering. He accepted an assistantship from Michigan State University and entered graduate school in Chemical Engineering eight days after graduating from college. In the Summer of 1991, he received a four year graduate fellowship from the Michigan Polymer Consortium. During his graduate research, Carl studied under the tutelage of Professor Alec Byron Scranton. Carl is the first student to earn an advanced degree under Dr. Alec B. Scranton.