HYDROGEN BONDED POLYMER BLENDS

A Thesis in
Materials Science and Engineering

by
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ABSTRACT

This thesis discusses three topics in the general area of hydrogen bonded polymer blends. The first pertains to the blending of flame retardant polyphosphazenes. Poly[bis(n-alkoxy)phosphazenes] blends with poly(butyl methacrylate-co-4-vinyl phenol) (BMAVPh) were initially studied. These results were compared to BMAVPh blends of analogous poly (vinyl n-alkyl ethers) and the phase behavior was similar. Next, poly[bis(carboxylatophenoxy)phosphazene] blends with a structural polyurethane foam were prepared via reactive mixing. The combustion behavior of these foams was analyzed qualitatively, by a horizontal flame test, and quantitatively, by oxygen index (OI) measurements. Both of these tests indicated a modest increase in flame resistance at loadings of 20 wt% and above. In the second topic, equilibrium constants determined from low molecular weight mixtures were used to successfully predict the phase behavior of analogous polymer blends. Due consideration was given to intramolecular screening and functional group accessibility, factors that are a direct consequence of chain connectivity. In the third topic, polymer blends involving an alternating 1:1 copolymer of tetrafluoroethylene (TFE) and a hexafluoroisopropanol modified vinyl ether (HFIPVE) were studied. This copolymer is interesting for both experimental and theoretical studies of the phase behavior of polymer blends because (1) it is amorphous and has a relatively low glass transition temperature (12°C); (2) it has a relatively low solubility parameter (\(\approx 7 \text{ (cal.cm}^{-3})^{0.5}\)); (3) it is soluble in moderately polar solvents, and (4) it contains the hexafluoroisopropanol group that is a strong hydrogen bond donor. Experimental infrared and thermal analysis studies of polymer blends with (co)polymers containing acetoxy, methacrylate and aliphatic ether groups were studied and compared to theoretical predictions of miscibility maps.
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CHAPTER 1
INTRODUCTION

1.1 Previous Work (An Overview)

The research group directed by Professors Coleman and Painter at Penn State University has been studying the factors that affect the phase behavior of polymer blends for some 20 years. In their 1991 book "Specific Interactions and the Miscibility of Polymer Blends" co-authored with John F. Graf, they describe the development of an equation for the free energy of mixing of hydrogen bonded polymer blends using an association model. These authors also developed computer programs for predicting phase behavior, miscibility windows and miscibility maps for hydrogen bonded polymer blends. The results of experimental studies of the phase behavior of numerous hydrogen bonded (co)polymer blend systems were remarkably consistent with the theoretical predictions.1 Dr. Boris Veytsman, a theoretical physicist, joined the research group in 1993 and discovered that the equation that describes the free energy contribution from hydrogen bonding was thermodynamically flawed.2 This led to a revision of the theoretical equation that describes the free energy of mixing of hydrogen bonded polymer blends and a recognition of the importance of chain connectivity.3-5 Below, these concepts will be considered in more detail.

1.2 Introduction to Miscible Polymer Blends

Polymer blends are physical mixtures of two or more polymers.6 They can be divided into two major classes, miscible and immiscible polymer blends.7,8 Miscible blends are homogeneous single-phase mixtures of two or more polymers, intimately mixed at the molecular level.9 On the other hand, immiscible polymer blends are characterized as being multi-phase consisting of distinct phase domains of the essentially pure or mixed components.9
It is common to find that mixtures of non-polar polymers are immiscible (e.g., binary blends of polyethylene, polypropylene, polybutadiene, polystyrene).\textsuperscript{10} Miscibility is much more likely in polymer blends that contain polar functional groups capable of forming strong intermolecular interactions.\textsuperscript{11,12} Such interactions contribute favorably to the free energy of mixing. A common method for promoting miscibility among non-polar polymers is to incorporate polar functional groups by means of copolymerization or post-functionalization.\textsuperscript{13} For example, to the best of our knowledge high molecular weight polyethylenes are immiscible with all other polymers. However, the addition of a small amount of vinyl acetate into polyethylene produces a copolymer, an ethylene-co-vinyl acetate (EVA), that can now potentially form miscible blends with an appropriate partner.\textsuperscript{5} Using this approach, miscible polymer blend systems can be designed for specific applications from paints and plasticizers to complex macromolecular antioxidants, UV stabilizers, and flame retardants.\textsuperscript{14,15}

1.3 Thermodynamics of Polymer Blends

By simply mixing any two polymers at random the probability of finding a miscible blend system is exceedingly low.\textsuperscript{1} In order to predict if a given pair of polymers is miscible, it is necessary to determine the free energy of mixing as a function of composition at a given temperature. Relevant to the discussions here is the classic free energy equation derived by Flory and Huggins and the modifications of this theory by Painter and Coleman.

1.3.1 The Flory-Huggins Theory

There are two necessary criteria that must be satisfied in order to form a single phase mixture of two (co)polymers.\textsuperscript{15-22} First, the free energy of mixing, $\Delta G_m$, must be less than zero (negative):

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0$$  (1.1)
Second, that the second derivative of the free energy of mixing with respect to composition must be greater than zero (positive) which is the spinodal condition.

\[ \frac{\partial^2 \Delta G_m}{\partial \Phi_i^2} > 0 \]  \hfill (1.2)

The simplest equation for describing the free energy of mixing of two (co)polymers was derived simultaneously by Flory and Huggins and may be expressed as:

\[ \frac{\Delta G_m}{RT} = \left[ \frac{\Phi_1}{M_1} \ln \Phi_1 + \frac{\Phi_2}{M_2} \ln \Phi_2 \right] + \Phi_1 \Phi_2 \chi \]  \hfill (1.3)

where \( \Phi_1, \Phi_2 \) and \( M_1, M_2 \) are the volume fractions and degrees of polymerization of polymers (1) and (2), respectively.\textsuperscript{23-26} The first two bracketed terms correspond to the very small, but favorable contribution to the free energy of mixing from combinatorial entropy. The last term accounts for the presence of "physical" forces in the blend that are generally unfavorable to the free energy of mixing. It is usually expressed in terms of a Flory \( \chi \) parameter which may be estimated from Hildebrand-type solubility parameters using the expression:

\[ \chi = \frac{V_r}{RT} \left[ \delta_1 - \delta_2 \right]^2 \]  \hfill (1.4)

where \( V_r \) is a reference volume (lattice cell size) and \( \delta_1 \) and \( \delta_2 \) are the solubility parameters for (co)polymers (1) and (2), respectively.\textsuperscript{11}

Examining the Flory-Huggins equation, it is immediately clear why most polymers do not intimately mix with one another. The favorable contribution from the combinatorial entropy terms is just too small to compensate for the typically unfavorable \( \Phi_1 \Phi_2 \chi \) contribution for most high molecular weight (co)polymer blends. In fact, the critical value of \( \chi \) for miscibility is < 0.002 for high molecular weight non-polar (co)polymers (or in terms of solubility parameters, the two polymers must be within 0.1 (cal. cm\(^{-3}\))\(^{0.5}\) of each other).\textsuperscript{10} In reality, most (co)polymer mixtures do not meet these criteria and are therefore immiscible.
Generally it more likely that two (co)polymers will be miscible with one another if they contain polar substituents which are capable of forming specific interactions such as dipole-dipole forces, hydrogen bonds, ionic interactions, etc.\textsuperscript{11,12} The presence of such interactions contributes a favorable enthalpic contribution to the free energy of mixing which can drive miscibility.\textsuperscript{1,3} The Flory-Huggins model does not take this into account.

1.3.2 The Painter-Coleman Modification to the Flory-Huggins Equation

Painter and Coleman developed a theoretical equation for the free energy of mixing which takes into account the favorable free energy contribution attributed to the presence of specific hydrogen bonding interactions. According to this model,\textsuperscript{1,3} the free energy of mixing, $\Delta G_m$, for binary mixtures of high molecular weight polymers capable of forming specific interactions can be expressed as:

$$\frac{\Delta G_m}{RT} = \left[ \frac{\Phi_1 M_1}{M_1} \ln \Phi_1 + \frac{\Phi_2 M_2}{M_2} \ln \Phi_2 \right] + \Phi_1 \Phi_2 \chi_{12} + \frac{\Delta G_H}{RT}$$

(1.5)

where $\Phi_1$ and $\Phi_2$, and $M_1$ and $M_2$, are the volume fractions and degrees of polymerization of (co)polymers (1) and (2), respectively. This equation is similar to that of Flory-Huggins, but with an additional term, $\Delta G_H/RT$, that accounts for the changing pattern of hydrogen bonding interactions that occurs in the mixture compared to those occurring in the pure materials.

This free energy of mixing equation (eq. 1.5), can be thought of consisting of three major contributions; combinatorial entropy, a "physical" forces term and a "chemical" forces term. Combinatorial entropy (the first two bracketed terms) contributes a favorable contribution to the overall free energy of mixing, but it is very small due to the high molecular weight of the polymers. The "physical" forces term ($\Phi_1 \Phi_2 \chi$) is the contribution to the overall free energy of mixing from primarily dispersive forces. This is a positive term and is an unfavorable contribution to mixing. Expressed in terms of a Flory $\chi$ parameter, it
can be is estimated from solubility parameters that are calculated from group molar attraction and molar volume constants obtained from carefully selected non-hydrogen bonding compounds.\textsuperscript{1,3} The "chemical" forces term, $\Delta G_H/RT$, contains the contribution to the overall energy of mixing from hydrogen bonding. It is generally favorable to mixing and arises from the change in the distribution of hydrogen bonds found in the blend compared to the pure (co)polymers. Its magnitude can be calculated from spectroscopically determined equilibrium constants, which describe the stoichiometry of hydrogen bonding in the blend.\textsuperscript{1,3}

In order to predict the phase behavior of hydrogen bonded polymer blends, it is necessary to determine the magnitude of the $\Delta G_H/RT$ term. For this a set of equilibrium constants are employed which describe the distribution of hydrogen bonds in a polymer blend. For blends of hydroxyl containing (co)polymers (e.g., poly(4-vinyl phenol) (PVPh) with carbonyl (ester) containing (co)polymers (e.g., poly(vinyl acetate) (PVAc)), two types of equilibrium constants are necessary to adequately describe the hydrogen bonding. The first type describes the formation of hydrogen bonds between “donor” groups (i.e. hydroxyl groups) which is referred to as self-association. The second type of equilibrium constant describes the formation of hydrogen bonds between “donor” and “acceptor” groups (i.e. hydroxyl and carbonyl groups) which is called inter-association.\textsuperscript{1,3} These equilibrium constants provide the link between experimental measurements and theoretical predictions of the phase behavior of polymer blends.
A minimum of two equilibrium constants are necessary to adequately describe the self-association of polymers that contain hydroxyl groups. One describes the hydroxyl-hydroxyl dimer formation \((K_2)\) and the other describes the formation of higher multimers \((K_B)\), as depicted in the following equilibrium scheme:

\[
\begin{align*}
    &K_2 \\
    B_1 + B_1 &\rightleftharpoons B_2 \\
    K_B \\
    B_h + B_1 &\rightleftharpoons B_{h+1}
\end{align*}
\]  

(1.6)

where segments containing the hydroxyl groups are traditionally represented by the letter B.\(^{1,3}\) Self-association equilibrium constants for (co)polymers containing hydroxyl groups are usually determined from appropriate low molecular weight analogs which contain essentially identical chemical structures to that of the repeat units of the polymer. For example, \(K_2\) and \(K_B\) for poly(4-vinyl phenol) (PVPh) has been determined from low molecular weight compounds such as phenol or 4-ethyl phenol.\(^{1,3,27}\) Once an appropriate low molecular weight compound is chosen, infrared spectra are obtained as a function of concentration in a non-hydrogen bonding solvent such as cyclohexane, using standard liquid cells of known thickness.\(^{1,3,28}\) From these spectra, the fraction of free monomers, \(f_{m}^{OH}\), present can be measured at each concentration. The values of \(K_2\) and \(K_B\) are calculated from a least squares fit of the \(f_{m}^{OH}\) data to a previously derived stoichiometric equation which relates \(f_{m}^{OH}\) to the dimensionless equilibrium constants, \(K_2\) and \(K_B\):\(^{1,3}\)

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

(1.7)

where \(\Phi_{B_1}\) is the volume fraction of free hydroxyls.
Self-association equilibrium constants are estimated from low molecular weight analogs simply because polymers like PVPh are not soluble in non-hydrogen bonding solvents such as cyclohexane. It was assumed that these equilibrium constants determined from low molecular weight analogs can be scaled directly to (co)polymers on the basis of their respective molar volume as described by the following equation:1,3

\[ K_i^{\text{Polymer}} = \frac{V_i^{\text{Model}}}{V_i^{\text{Polymer}}} K_i^{\text{Model}} \]  

where \( K_i^{\text{Polymer}} \) and \( K_i^{\text{Model}} \) are the equilibrium constants for the (co)polymer “specific repeat” (defined as the average chemical unit containing only one functional group) and the low molecular weight analogue, respectively. \( V_i^{\text{Polymer}} \) and \( V_i^{\text{Model}} \) are the molar volumes for the polymer “specific repeat” and the low molecular weight analog, respectively.1,3

Inter-association refers to hydrogen bonding between functional groups on two different molecules or (co)polymers, such as the hydroxyl group of vinyl phenol and the carbonyl group of vinyl acetate, according to the following equilibrium scheme:

\[ B_h + A \xrightleftharpoons{K_A} B_hA \]  

where again the letter B represents the segments containing the hydroxyl groups and the letter A represents those containing the carbonyl groups.1,3 In the original studies presented in the 1991 text "Specific Interactions and the Miscibility of Polymer Blends" the authors determined inter-association equilibrium constant values directly from appropriate miscible polymer blends. The experimental determination of \( K_A \) from miscible blends that involve phenolic hydroxyl and ester-type carbonyl groups is relatively straightforward. Using the carbonyl stretching region of the infrared spectrum, two distinct bands are observed that are assigned to “free” and hydrogen bonded carbonyl groups.1,3 The fraction of hydrogen bonded carbonyl groups, \( f_{\text{HB}}^{\text{C=O}} \), can be measured from the relative intensities (areas) of these
two bands taking into account the differences in absorption coefficients.\textsuperscript{3} From the stoichiometric equation:\textsuperscript{1}

\[
f_{\text{HB}}^{\text{CO}} = 1 - \frac{1}{1 + K_A \Phi_{B_1}} \left[ \frac{1}{1 - \frac{K_2}{K_B}} + \left( \frac{K_2}{K_B} \right) \left( \frac{1}{1 - K_B \Phi_{B_1}} \right) \right]
\]

(1.10)

which relates $f_{\text{HB}}^{\text{CO}}$ to the equilibrium constants $K_2$, $K_B$ and $K_A$ and $\Phi_{B_1}$, the volume fraction of isolated B groups. The value of $K_A$ was determined from the least squares fit to eq. 1.10 of the $f_{\text{HB}}^{\text{CO}}$ data obtained from blends of varying composition and could be similarly scaled on the basis of molar volume as described above for the self-association equilibrium constants. It is important to point out that the values of $K_2$ and $K_B$ independently determined from low molecular weight analogs were held constant in the least squares fitting procedure.\textsuperscript{1,3} Using the self-association and inter-association equilibrium constant values obtained in such a manner Painter and Coleman calculated the free energy contribution arising from the $\Delta G_{\text{H}/\text{RT}}$ term (eq. 1.5). It was at this stage that a problem surfaced.

In order to simplify the presentation a less complicated equilibrium scheme depicted below will be employed:\textsuperscript{1}

\[
\begin{align*}
B_h + B_1 & \rightleftharpoons B_{h+1} & K_B \\
B_h + A & \rightleftharpoons B_hA & K_A
\end{align*}
\]

(1.11)

where the distribution of hydrogen bonded species in the polymer blend may be adequately described by two equilibrium constants, one that describes "chain-like" self-association, $K_B$, and the other that describes inter-association, $K_A$. 
\[ \Delta G_{H}/RT \] was expressed as:

\[
\frac{\Delta G_{H}}{RT} = \sum n_{B_i} \ln \left( \frac{\Phi_{B_i}}{h} \right) + \sum n_{B_iA} \ln \left( \frac{\Phi_{B_iA}}{h + r} \right) + n_{A_i} \ln \left( \frac{\Phi_{A_i}}{r} \right) + n_{B}^{h} + n_{A}^{h} + \text{(terms in z and } \sigma) - \\
\left[ n_{B} \ln \Phi_{B} + n_{A} \ln \Phi_{A} \right] - n_{B}^{h} \ln K_{B} - n_{A}^{h} \ln K_{A}
\]

(1.12)

This is the so-called regular solution theory. The interested reader is referred to references (1-3) where the derivation of (eq.1.12) is presented and all the terms are defined. The excess entropy term that is contained in the square bracket of (eq.1.12) is where attention will be focused. Here the parameters \( n_{A} \) and \( n_{B} \) are the number of A's and B's, respectively. Painter and Coleman found, however, that if the set of experimentally determined equilibrium constant values derived from miscible polymer blends was used to calculate the contribution to the free energy of mixing from the \( \Delta G_{H}/RT \) term (eq.1.5), its magnitude was seriously underestimated. The predicted phase diagrams, miscibility windows and miscibility maps calculated from the derivatives of the total free energy of mixing (eq.1.12) were inconsistent with experimental observations of phase behavior.1

Painter and Coleman concluded that the magnitude of the excess entropy term (that contained in the square bracket of (eq.1.13) was the source of the problem, i.e.,

\[ \Delta S_{\text{excess}} = -\left[ n_{A} \ln \Phi_{A} + n_{B} \ln \Phi_{B} \right] \]

(1.13)

This negative contribution from the \( \Delta G_{H}/RT \) term was too small. Using an argument that the above excess entropy term was not applicable to hydrogen bonded polymer blends because one component (B) also form dynamic networks of hydrogen bonded "chains" in the pure state, a modified excess entropy term was introduced:

\[ \Delta S_{\text{excess}} = - \left[ n_{A} \ln \Phi_{A} + \frac{n_{B}^{h}}{h_{o}} \ln \Phi_{B} \right] \]

(1.14)
where $\overline{n}_h$ was the number average length of the hydrogen bonded "chains" formed in pure B. With this modification to the excess entropy (eq. 1.14) in place, the free energies were recalculated and the predicted phase diagrams, miscibility windows and maps for numerous (co)polymer blend systems were found to be remarkably consistent with experimental miscibility data.

All appeared fine until Dr. Boris Veytsman joined the Painter /Coleman research group. In checking the derivation of the new $\Delta G_{\text{f}}/RT$ equation he found that the modification to the excess entropy term (eq.1.14) was actually based upon an incorrect reference state and not theoretically sound. By introducing the $\overline{n}_h$ parameter into the denominator of the second term of (eq.1.14), Painter and Coleman had increased the negative free energy contribution from the $\Delta G_{\text{f}}/RT$ term in (eq.1.12) by an amount that fortuitously brought the theoretical predictions and experimental observations into close agreement. Obviously, something was amiss.

At about the same time, Yun Xu, a graduate student working for Coleman and Painter measured the fraction of hydrogen bonded carbonyl groups present in miscible (single phase) blends of PVPh with poly(ethyl methacrylate) (PEMA) as a function of composition and temperature and compared them to analogous ethyl methacrylate-stat-4-vinyl phenol (EMAVPh) copolymers, polymer solutions of PVPh and ethyl isobutyrate (EIB) and low molecular weight model mixtures of 4-ethyl phenol (EPh) and EIB. There were large differences found in the equilibrium fraction of intermolecular hydrogen bonded carbonyl groups that were formed for equivalent concentrations at the same temperature. This can be conveniently expressed in terms of a standard inter-association equilibrium constant, $K_{\text{Std}}^A$ (at 25°C based upon a standard molar volume of $V_B = 100 \text{ cm}^3/\text{mole}$). Xu obtained $K_{\text{Std}}^A$ values of 38.4, 67.4, 168 and 170 dimensionless units for PVPh/PEMA blends, EMAVPh copolymers, PVPh/EIB solutions and EPh/EIB mixtures, respectively. These are large differences and it was then recognized that the inter-association equilibrium constant values determined experimentally from miscible blends and multifunctional
copolymers reflected the large effect of chain connectivity on the number and distribution of hydrogen bonds in the different systems. In effect, the modification to the excess entropy term (eq.1.14) that was employed to bring the theoretical prediction of phase behavior into concert with experimental observation, was actually compensating primarily for a missing component of the theory, i.e. the effect of chain connectivity.

1.4 The Importance of Chain Connectivity

Once it had been established that there was a major difference in the number and distribution of specific hydrogen bonding interactions occurring in miscible polymer blends compared to that of analogous low molecular weight mixtures, the Painter/Coleman group focused their attention on intramolecular screening and functional group accessibility.\textsuperscript{4,5,13,30-32}

Intramolecular screening is a consequence of chain connectivity.\textsuperscript{13,30-32} The covalent linkages between polymer segments results in an increase in the number of same-chain contacts over that calculated on the basis of a simple random mixing of segments, (as opposed to chains), as the chain bends back upon itself (both locally and through long range effects). This manifests itself in terms of a significant reduction in the number of intermolecular hydrogen bonded carbonyl groups that are formed compared to analogous mixtures (in terms of concentration at the same temperature) of low molecular weight mixtures or polymer solutions. Thus it follows that the values of $K^\text{Std}_A$ obtained experimentally from miscible polymer blends must inherently reflect the presence of intramolecular screening (and, for that matter, any other screening effects that are caused by chain connectivity and which limit the accessibility of functional groups—see below). Since this was not accounted for in the development of an expression for $\Delta G/RT$ (eq. 1.12), it was clear that if experimental values of $K^\text{Std}_A$ are used the favorable contribution to the total free energy of mixing (eq. 1.5) from the $\Delta G/RT$ term must be underestimated.
In a 1997 paper by Painter et al.\textsuperscript{32} the authors presented a theoretical equation for the free energy of mixing of polymers that takes into account intramolecular screening. A parameter, $\gamma$, was introduced, defined as the fraction of same chain contacts that originate from the polymer chain bending back upon itself, primarily through local but also through long range connectivity effects. The results of Monte Carlo simulations performed by Professor Sanat Kumar indicated that the value of $\gamma$ for polymer blends ranged from about 0.30-0.38 for amorphous polymers with molecular weights above 10,000 to infinity.\textsuperscript{32} In brief, the introduction of $\gamma$ modified (eq.1.5) as follows:

$$\frac{\Delta G_m}{RT} = \frac{\Phi_1}{M_1} \ln \Phi_1 + \frac{\Phi_2}{M_2} \ln \Phi_2 + \Phi_1 \Phi_2 (1 - \gamma) \chi_{12} + \frac{\Delta G_H}{RT}$$

(1.18)

Since intramolecular screening effects the number of like and unlike contacts, the parameter $\gamma$ also appears in the "physical" forces or $\chi$ term. Moreover, equilibrium constants $K_B$ and $K_A$ are substituted in eq. 1.12 for $K_B$ and $K_A$ and are defined as:

$$K_B^- = K_B \left[ \frac{\gamma + (1 - \gamma) \Phi_B}{\Phi_B} \right]$$

(1.19)

$$K_A^- = K_A \left[ \frac{1 - (\gamma + (1 - \gamma) \Phi_B)}{\Phi_A} \right] = K_A (1 - \gamma)$$

(1.20)

It is worth noting that $K_B^-$ and $K_A^-$ are “effective” equilibrium constants which correspond to the experimental values determined from miscible blends and inherently reflect effects of intramolecular screening (and other forms of screening—see below). On the other hand, $K_B$ and $K_A$ are the “intrinsic” equilibrium constants (i.e., those that correspond to the values determined from low molecular weight analogs).\textsuperscript{28,30}

In addition to intramolecular screening, George Pehlert, another former graduate student in Coleman and Painter's group, discovered that steric screening, another manifestation of chain connectivity, also significantly affects the number of intermolecular hydrogen bonds formed between complementary polymers in a miscible blend. This effect
has been described under a general heading of functional group accessibility (FGA). Experimental results obtained using a variety of (co)polymers has demonstrated that FGA is affected by the distance between functional groups in the polymer chain and steric hindrance cause by the bulky nature of side groups.4,28

1.5 Outline of Dissertation

In this dissertation, three different hydrogen bonded polymer blend systems will be considered. In Chapter 2, the results of studies performed on a series of a polyphosphazene blends will be discussed. Chapter 3 describes modifications made to the computer programs used to predict the phase behavior of hydrogen bonded polymer blends, taking into account effects of intramolecular screening and functional group accessibility. In Chapter 4, theoretical and experimental studies of blends of a fluoropolymer containing the hexafluoroisopropanol group, which has an inherently low solubility parameter, will be presented. Finally, in Chapter 5, conclusions and suggestions for possible future work are given.
1.6 References


CHAPTER 2
POLYPHOSPHAZENE BLENDS

2.1 Introduction

The development of flame-retardant polymers for a wide range of applications is currently a subject of much interest. The majority of commercial organic polymers have useful structural and mechanical properties, but they are generally flammable. For example, polyurethanes used extensively in the aerospace and construction industries are inherently combustible.\textsuperscript{1-5} Typical approaches used to reduce the flammability of polyurethanes have included the addition of low molar mass flame retardants,\textsuperscript{6-10} and chemical modification of polyurethanes.\textsuperscript{11-15} Both have advantages and disadvantages. Low molar mass flame-retardants are generally inexpensive and relatively easy to incorporate into polymeric systems, but there are problems of migration or leaching. Moreover, during combustion low molar mass additives can decompose and produce toxic vapors. Chemical modification of the polymer structure is generally more costly and has not been embraced industrially. An alternative approach, described in this chapter, involves blending a polyurethane with another polymer that is inherently flame resistant.\textsuperscript{1}

If blends of two or more polymers are to be investigated as potential flame resistant materials, then the phase behavior of the blend is an important factor that must be considered. Phase behavior strongly influences the chemical, physical and mechanical properties of polymer blends.\textsuperscript{16-18} The conditions governing the mixing of polymers are stringent. It is a general rule that if two randomly chosen high molar mass polymers are mixed together the probability of obtaining a single phase (miscible) mixture is exceedingly low.\textsuperscript{17-18} In fact, the mixing of two polymers usually results in a grossly phase separated material. Macromolecular compatibilizers (usually block or graft copolymers) have been used to decrease the domain size of the dispersed phase and produce a more homogeneous dispersion.\textsuperscript{18} In addition, in situ chemical reactions leading
to grafts and cross-links can be used to increase homogeneity as will be shown later in this chapter. However, initially in this work, it was presumed that intimate mixing, exemplified by a single phase (miscible) mixture, would be advantageous for a polyurethane blend containing a macromolecular flame retardant. Known miscible polyurethane blends are unfortunately rare, but the tools are now available to design such systems by incorporating functional groups capable of specific intermolecular interactions.17-19

One class of polymers, the poly(organophosphazenes), with their alternating inorganic nitrogen and phosphorus atoms in the polymer backbone, are known for their relatively good thermal stability. Poly(organophosphazenes) form a large class of macromolecules with the general formula \(-\text{NPR}_2\)\(\text{n}\) and can have a wide variety of organic, organometallic, or inorganic side groups.20-32 These side groups can be tailored to enhance the probability of forming miscible blends as well as optimizing flame resistance.

There is very little in the literature pertaining to poly(organophosphazene) blends. Allcock and his coworkers have studied a few phase separated blends.30-31 Unlike the common purely organic polymers, where data concerning molar attraction and molar volume constant values are readily available,17 in the case of the poly(organophosphazenes) no such data has been generated. This means that the solubility parameters of poly(organophosphazenes) are unknown as they are normally calculated from molar attraction and molar volume constant values.17 Unfortunately, it is not possible to obtain the molar attraction constant values for the -N=P- group from appropriate low molar mass analogs of organophosphazenes—they simply do not exist. Cyclic organophosphazene trimers and tertamers are not suitable as they are crystalline solids with high melting points. Given this situation, it is not possible to use the Painter/Coleman association model approach to predict the miscibility of poly(organophosphazenes) blends. The solubility parameter value is a key factor in
estimating the "physical force" contribution to the free energy mixing (see Chapter 1).17

Faced with this fact, it was decided initially to experimentally study the phase behavior of an homologous series of poly(organophosphazenes) containing alkyl ether side groups in blends with (co)polymers containing 4-vinyl phenol (VPh) and compare the results to analogous poly(vinyl alkyl ether) (PVAE) blends. It was hoped that such studies might lead to an estimation of the solubility parameters of poly(organophosphazenes) and a method for predicting the miscibility of poly(organophosphazenes) blends. As will be seen, there were many complications and this was not successful. This prompted a change in strategy. Attention was then focused on blends of polyurethane foams with poly(organophosphazenes) where significant grafting occurs. As it will be shown, these materials were self-extinguishing, but were not considered outstanding flame resistant materials.

2.2 Experimental

2.2.1 Materials

Tetrahydrofuran (THF), benzene, toluene, methylisobutylketone (MIBK), methyl ethyl ketone (MEK), acetic acid, 2,2'-azobisisobutyronitrile (AIBN), benzyl peroxide (BPO), butyl methacrylate (BMA), tert-butyl-dimethylsilyl chloride, methyltriphenylphosphonium bromide and tetrabutylammonium fluoride (TBAF) were purchased from Aldrich Chemical Co. Inc. AIBN was recrystallized from acetone. THF and benzene were distilled, respectively, from sodium/benzophenone and calcium hydride immediately before use. All other reagents were used without further purification. Propane was obtained from MGI Industries. Vinyl n-propyl ether and vinyl n-butyl ether were purchased from Scientific Polymer Products, Inc. All glassware was oven-dried and then stored under vacuum (.01mm) prior to use.
Five poly(alkyl ether phosphazenes) with molecular weights above 100,000 g/mol, the bis-methoxy (PBMP), the bis-ethoxy (PBEP), the bis-propoxy (PBPP), the bis-butoxy (PBBP) and the bis-pentoxy (PBPeP) were provided by Professor Harry Allock and used without further purification. Professor Allcock also supplied the poly(bis(carboxylato-phenoxy)phosphazene) (PBCPP) used in the polyurethane foam blends. This polymer had a reported molecular weight of $M_n = 2,600,00$ and $M_w = 3,400,00$ g/mol. Poly(vinyl methyl ether) (PVME—30,000 MW and Tg −25°C) and poly(vinyl ethyl ether) (PVEE—20,000 MW and Tg −30°C) were purchased from Scientific Polymer Products, Inc. A two component kit used to produce the polyurethane foam was graciously provided by the Bayer corporation. These materials were used without further purification.

### 2.2.2 Synthesis of Polymers

#### 2.2.2.1 Poly(Butyl methacrylate-co-4-vinyl phenol) (BMAVPh)

Four BMAVPh copolymers containing 44, 50, 60, and 74 mole % VPh [denoted BMAVPh{44}, BMAVPh{50}, BMAVPh{60} and BMAVPh{74}, respectively] were synthesized using the methodology developed in our laboratories by Xu33 and only a brief summary is included here. The monomer 4-(t-butyldimethylsilyloxy)styrene (t-BSOS) was first prepared in two steps; (1) protection of the hydroxyl group and (2) olefination, as shown in scheme 2.1.
Scheme 2.1 Synthesis of 4-(t-butyldimethylsilyloxy)styrene (t-BSOS)

The free radical polymerization of t-BSOS and butyl methacrylate (BMA) was conducted in a glass reaction flask under an argon atmosphere for 4 hours at 70°C as illustrated in Scheme 2.2 below. The reaction was quenched by the addition of methanol and the polymer was recovered by precipitation into excess methanol. Further purification of the polymer was performed by re-precipitation. The concentration of t-BSOS and BMA in the copolymers was determined by H^1NMR.

Scheme 2.2 Synthesis of poly(butyl methacrylate-co-t-BSOS)

Scheme 2.3 summarizes the desilylation procedure for the BMA-co-t-BSOS copolymer. This was essentially the method employed by Xu et al., using tetrabutylammonium fluoride (TBAF). Isolation of the BMAVPh copolymers was
performed by precipitation into a large excess of water followed by filtration and washing with water. The polymers were dissolved in THF and re-precipitated in water. This dissolution/reprecipitation cycle was repeated several times. Finally, the polymers were re-precipitated into hexane and then dried under vacuum at 80°C.

Scheme 2.3 Synthesis of Poly(butyl methacrylate-co-4-vinyl phenol)

2.2.2.2 Poly(vinyl $n$-propyl ether) (PVPE) and Poly(vinyl $n$-butyl ether) (PVBE)

In collaboration with Dr. Steven Fearnley, solution cationic polymerizations of vinyl $n$-propyl ether and vinyl $n$-butyl ether were conducted in liquid propane at -78°C using the initiator boron trifluoroetherate. This was essentially the same published procedure used previously to prepare PVPE and PVBE by the Coleman/Painter group. The chemical structure was confirmed by $^1$H NMR and FTIR spectroscopies. (PVPE 20,000 MW, Tg –40°C) (PVBE 30,000 MW, Tg –47°C).

Scheme 2.4 Synthesis of Poly(viny $n$-propyl ether)
### 2.2.2.3 Polyphosphazene/Polyurethane Foams

Several polyurethane foams containing 5, 10, 15, 20 and 30 wt % poly(bis(carboxylatophenoxy)phosphazene) (PBCPP) were prepared using a two component polyurethane kit supplied by Bayer corporation. This kit employs a two component system containing (1) a low molecular weight (LMW) hydroxyl terminated poly(ethylene oxide) with a slight amount of water and (2) a poly(ether-urethane) LMW prepolymer terminated with isocyanate end groups. In a typical reaction, equal amounts of the isocyanate component and the polyol are mixed and allowed to stand for a period of 2 hours to ensure complete reaction until the material fully hardens. This produces a stiff, yellow, closed foam material.

Incorporation of the PBCPP into the polyurethane was achieved by initially mixing the PBCPP into the polyol component. For example, to generate a 10 wt % PBCPP polyurethane foam, PBCPP (4g) was mixed with the polyol component (16g) and then mixed together with the isocyanate component (20g). This produced a total of 40g of foamed material. To produce samples used to test flame resistance the foam mixture was transferred between two Teflon® coated steel platens spaced 1 cm apart. The foam was allowed to cool for 2 hours before removal. Test bars were made by cutting the cured foam with a sharp knife.

### 2.2.3 Instrumentation and Sample Preparation

Infrared spectroscopic measurements were recorded on a Digilab model FTS45 FTIR spectrometer at a resolution of 2 cm⁻¹. Special attention was paid to ensure that all FTIR samples were sufficiently thin to be within the absorption range where the Beer-Lambert law is obeyed. Polymer blend films for transmission FTIR were cast on KBr windows from ≈ 2% solutions of MEK or MIBK. After the majority of the solvent had evaporated, the films were placed under vacuum at room temperature for at least 24 hours, followed by 2 hours at 150°C, to completely remove residual solvent. ¹H NMR
spectra were obtained on Bruker WP-200 and 300 MHz FT-NMR spectrometers using tetramethylsilane as an internal standard. Deuterated chloroform, deuterated acetone and deuterated dioxane were employed as solvents. Thermal analysis was conducted on a Haake Buckner differential scanning calorimeter (DSC-200C) coupled to a computerized data station. A heating rate of 20°C/min. was used in all experiments and the glass transition temperature was taken as the midpoint of the heat capacity change. Thermal gravimetric analysis was conducted on a Haake Buckner thermal gravimetric analyzer (TGA 400) coupled to a computerized data station. A heating rate of 20°C/min. was used in all experiments.

Vertical flame tests were performed using a simple apparatus. This consisted of two ring stands with clamps. One ring stand held the sample while the other held the Bunsen burner. The foam sample is cut to 1x1x14 cm and marked lengthwise 2 cm from each end. These are used as timing marks for the progression of the flame. The sample is mounted in a clamp in a vertical fashion approximately 20 cm off of the table. A standard Bunsen burner using natural gas is the flame source. The burner is adjusted so that it is 1 cm below the sample and pointed at a 45° angle towards the sample. The flame is adjusted that is no more than 5 cm high and with a slight yellow tip. The experiment begins by adjusting the flame source away from the sample. The ventilation to the fume hood is turned off. The Bunsen burner is moved under the front of the sample for a period of 5 seconds. If the sample does not ignite during those 5 seconds, the flame remains under the sample until it ignites for a period no longer than 30 seconds, after which the burner is removed. The time of progression of the flame from the first mark to the second mark is recorded. Upon completion of the experiment, the ventilation in the fume hood is turned on and the remnants and ashes of the sample are placed in a 1L beaker of water to ensure the flame is extinguished.

Oxygen Index measurements were obtained on an instrument constructed according to ASTM-D-2863-91 using Type C. specimens.
2.3 Comparison of Polyphosphazene and Polyether Blends

2.3.1 Poly(4-Vinyl Phenol) Blends

Poly(vinyl \( n \)-alkyl ethers) (PVAE) superficially resemble poly(bis\( n \)-alkoxy)-phosphazenes) (PBAP) as illustrated below:

\[
\begin{align*}
\text{CH}_3 & \\
\text{CH}_2 & \text{CH}_3 \\
\text{O} & \\
\text{NP} & \text{O} \\
\text{CH}_2 & \text{CH}_3 \\
\text{CH}_2 & \text{CH}_3
\end{align*}
\]

Scheme 2.5 Comparison of PVAE with PBAP

Obviously, there are two alkoxy groups per repeat in the case of PBAP and the \(-\text{N=\text{P}−}\) group is very different chemically to the aliphatic \(-\text{CH}_2-\text{CH}−\) backbone of PVAE. However, both polymer repeat units contain functional ether oxygen groups that can potentially hydrogen bond to proton donators such as phenolic hydroxyl groups. Previous work in our laboratories have demonstrated that poly(4-vinyl phenol) (PVPh) is miscible with PVME and PVEE, but immiscible with PVPE and PVBE.\(^{35}\) The solubility parameter difference between PVPh and these PVAE is large \((\Delta \delta > 2 \text{ (cal. cm}^3)_{0.5}\)) and increases as the number of methylene groups in the side group increases, which indicates a large unfavorable contribution to the free energy of mixing from "physical" forces.\(^{17,36}\) This is offset, in the case of the PVME and PVEE blends, by the large favorable contribution of the free energy from the "chemical" forces that arises from changes in hydrogen bonding of the mixture compared to the pure materials.\(^{17}\) A strong hydrogen bond is formed between the phenolic hydroxyl group of PVPh and the ether oxygen of PVME and PVEE (inter-association) as illustrated in scheme 2.6.
The first question that needs to be addressed is, "does the same type of intermolecular hydrogen bond occur between a phenolic hydroxyl and the ether oxygen in PVPh blends with the PBAP's?" Figure 2.1 shows the hydroxyl stretching region of the infrared spectra of samples of pure PVPh and 20:80 wt % blends of PVPh and PBEP and PBPP recorded at room temperature. The spectrum of the PVPh/PBEP blend shows that significant molecular mixing has occurred. A new band at $\approx 3265 \text{ cm}^{-1}$, assigned to the hydrogen bonded hydroxyl/ether stretching vibration, is observed and this is very similar to the results reported for the analogous PVPh blends with PVME and PVEE. The frequency shift with respect to that of the "free" hydroxyl stretching band is $\approx 260 \text{ cm}^{-1}$ for the phosphazene blend, while it is $\approx 200 \text{ cm}^{-1}$ for the PVME and PVEE blends. This implies that the strength of the hydrogen bond between the phenolic hydroxyl and the ether group of PBEP is significantly greater than that of the analogous PVME and PVEE polymers.
Figure 2.1 The hydroxyl region of the infrared spectrum of blends of PVPh and PBEP and PBPP.
In contrast, the infrared spectrum of the PVPh/PBPP blend suggests that very little mixing has occurred and the results are very similar to those obtained previously on the PVPh blends with PVPE and PVBE.\textsuperscript{35} Thus we can conclude that (a) the ether oxygen in the PBAP polymers is potentially accessible, (b) the range of miscible PVPh/PVAE blends is similar to that of the PVPh/PBAP blends and finally that (c) the solubility parameter of the PBAP polymers cannot be too dissimilar to the analogous PVAE polymers.

However, the hydroxyl stretching region of the infrared spectrum is not amenable to quantitative analysis.\textsuperscript{17,36} Only a qualitative description of molecular mixing can be obtained. For this reason it was decided to synthesize a series of BMAVPh copolymers and study blends with these copolymers with the homologous series of PVAE and PBAB polymers. BMAVPh copolymers have the advantage of containing carbonyl groups and it is possible to quantitatively measure the fraction of carbonyl groups that are hydrogen bonded from the carbonyl stretching region of the infrared spectrum. It was hoped that by determining equilibrium constants that describe the self-association of BMAVPh copolymers a method for predicting miscibility windows and maps could be developed for BMAVPh/PVAE blends, which in turn, by analogy, might lead to a better understanding of hydrogen bonded PBAB polymer blends. However, as will be shown below, this turned out to be a far more complicated than initially thought.

### 2.3.2 Poly(n-butyl methacrylate-co-4-vinyl phenol) (BMAVPh) Blends

Figure 2.2 shows a representative example of the infrared spectrum of a BMAVPh copolymer recorded at room temperature in the region from 500-4000 cm\textsuperscript{-1}. The gross features of the infrared spectra are consistent with those of similar copolymers that have been previously described by Xu et al.\textsuperscript{33} In this work, attention will be focussed on the carbonyl stretching region of the spectrum and those recorded for BMAVPh\{44\}, BMAVPh\{50\}, BMAVPh\{60\} and BMAVPh\{74\}are presented in Figure 2.3.
Figure 2.2 The infrared spectrum of the BMAVPh\{60\} recorded at room temperature.
Figure 2.3 The carbonyl region of the infrared spectrum of the BMAVPh’s recorded at room temperature.
Two obvious and familiar infrared bands are observed which are unambiguously assigned
to the carbonyl stretching vibrations of "free" (non-hydrogen bonded) and hydrogen
bonded carbonyl groups at 1726 and 1701 cm\(^{-1}\), respectively (see Scheme 2.7).\(^{17,33}\)

![Scheme 2.7](image)

**Scheme 2.7** Interactions involving the carbonyl groups in BMAVPh copolymers

Note that the relative contributions of the "free" and hydrogen bonded carbonyl bands changes as the composition of the copolymer varies. Equilibrium considerations dictate that the fraction of carbonyl groups that are hydrogen bonded increases with increasing concentration of VPh in the BMAVPh copolymer. This is generally consistent with the spectral data shown in Figure 2.3, but as the glass transition temperatures (Tg) of the BMAVPh copolymers range from 90 to 128°C the systems cannot be considered to be at equilibrium at room temperature. Only at temperatures well above the Tg can equilibrium conditions be attained.

Figure 2.4 shows the spectra of BMAVPh\{60\} recorded as a function of increasing temperature at intervals of 10° C from 150 to 200° C (above the Tg’s of all the BMAVPh copolymers considered in this work). As expected, with increasing thermal motion the relative intensity of the "free" carbonyl band increases at the expense of hydrogen bonded band.
Figure 2.4 The carbonyl region of the infrared spectrum of the BMAVPh{60} recorded at elevated temperatures.
Spectra were then recorded at the same intervals as the sample was cooled back to 150°C. It was found that the spectra recorded at the same temperature (i.e., on the way up and on the way down) were, within experimental error, identical. This is important because it implies that equilibrium has been attained and there was no significant degradation. For the upcoming quantitative studies of BMAVPh copolymers a temperature of 180°C was chosen, which is well above the Tg of any BMAVPh copolymer considered (by some 50°C). Figure 2.5 shows the carbonyl stretching region of the BMAVPh{44}, BMAVPh{50}, BMAVPh{60} and BMAVPh{74} copolymers recorded at 180°C. The expected trend of increasing relative intensity of the hydrogen bonded carbonyl band as the concentration of VPh in the BMAVPh copolymer increases is qualitatively observed.

The fraction of hydrogen bonded carbonyl groups present at a given temperature for a given BMAVPh copolymer of a specific composition can be determined by curve fitting spectra like those shown in Figure 2.5. The curve fitting procedure is now well established and only a brief summary will be given here. Figure 2.6 shows a typical example of the result obtained by curve fitting the infrared spectrum of BMAVPh{60} recorded at 180°C. Two Gaussian bands were employed in the least squares curve fitting procedure and the areas of the bands calculated. The absorptivity ratio of the "free" to hydrogen bonded bands, (aR = 1.5), is well established and the fraction of hydrogen bonded carbonyl groups, f_{HB}^{C=O}, readily calculated. For the particular spectrum shown in Figure 2.6 a value of f_{HB}^{C=O} = 0.48 was determined. Table 2.1 shows the results obtained from three separate samples of the four BMAVPh copolymers at 180°C. The f_{HB}^{C=O} for BMAVPh{44}, BMAVPh{50}, BMAVPh{60} and BMAVPh{74} was determined to be 0.366 ± 0.004, 0.390 ± 0.007, 0.485 ± 0.000 and 0.555 ± 0.004, respectively. With this information the self-association of BMAVPh copolymers can be described in terms of equilibrium constants.
Figure 2.5 The carbonyl region of the infrared spectrum of the BMAVPh’s recorded at 180°C.
Figure 2.6 An example of the curve fitting of the infrared spectra of BMAVPh\{60\} at 180°C.
<table>
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<th>Copolymer Sample</th>
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<th>Intensity</th>
<th>Width</th>
<th>Area</th>
<th>(f_{\text{HB}}^{C=O})</th>
<th>Ave. (f_{\text{HB}}^{C=O})</th>
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**Table 2.1** The curve fitting data of BMAVPh copolymers at 180°C.
To adequately describe the self-association of BMAVPh copolymers it is necessary to define a minimum of three equilibrium constants. Two describe the interaction of a phenolic group with itself and the third describes the interaction between phenolic hydroxyls and carbonyl groups. Using the nomenclature introduced by Painter and Coleman,\textsuperscript{17,36} the first equilibrium constant, \( K_2 \), describes the formation of phenolic dimers:

\[
\begin{align*}
B_1 + B_1 & \underset{K_2}{\rightleftharpoons} B_2 \\
& (2.1)
\end{align*}
\]

A second equilibrium constant, \( K_B \), describes the formation phenolic multimers:

\[
\begin{align*}
B_h + B_1 & \underset{K_B}{\rightleftharpoons} B_{h+1} \\
& (2.2)
\end{align*}
\]

Standard values of \( K_2^{\text{Std}} = 21.0 \) and \( K_B^{\text{Std}} = 66.8 \) dimensionless units (at 25°C scaled to a common reference molar volume of 100 cm\(^3\)/mol) have previously been determined from low molar mass analogues.\textsuperscript{17,36} A third equilibrium constant, denoted \( K_C \), describes the phenolic hydroxyl/carbonyl interaction:

\[
\begin{align*}
B_h + C & \underset{K_C}{\rightleftharpoons} B_h C \\
& (2.3)
\end{align*}
\]

An experimental value of \( K_C \) for the four different BMAVPh copolymers can be determined from the \( f_\text{HB}^{C=O} \) data given in Table 2.1 from the mathematical relationship:\textsuperscript{17,36}

\[
f_\text{HB}^{C=O} = 1 - \left( \frac{1}{1 + K_C \Phi_{B_h} \left[ \left( 1 - \frac{K_2}{K_B} \right) + \left( \frac{K_2}{K_B} \right) \left( \frac{1}{1 - K_B \Phi_{B_1}} \right) \right]} \right) \]
\]
Since $K_2, K_B, \Phi_{B_1}$, the volume fraction of free hydroxyls, are known, $K_C$ can be readily determined. It is convenient to use the “Fit-K” program written by Dr. John Graf to calculate $K_C$ from the $f_{C=O}^{HB}$ data. As this data was generated at 180° C it is also necessary to have values of the three enthalpies of hydrogen bond formation, $h_2$, $h_B$ and $h_c$. Fortunately, this information is available and using the van't Hoff relationship $K_C$ values can be easily extrapolated to 25°C. Standard $K_C^{Std}$ values of 47, 46, 51 and 51 were calculated for the BMAVPh{44}, BMAVPh{50}, BMAVPh{60} and BMAVPh{74}, respectively. Within the bounds of experimental error these results are identical ($K_C^{Std} = 49 \pm 3$ dimensionless units).

In summary, the values of the three equilibrium constants, $K_2^{Std} = 21.0$, $K_B^{Std} = 66.8$ and $K_C^{Std} = 49$ dimensionless units, and their corresponding enthalpies of hydrogen bond formation, $h_2 = 5.6$, $h_B = 5.2$ and $h_c = 4.1$ cal/mol, describe the self-association of BMAVPh copolymers. Thus the distribution of "free" and hydrogen bonded groups in BMAVPh copolymers can be easily calculated at any given temperature (assuming equilibrium conditions are attained). It is informative to compare the experimental standard equilibrium constant value ($K_C^{Std} = 49$ dimensionless units) obtained from the BMAVPh copolymers to both that obtained for the analogous polymer blend of PVPh with PBMA ($K_A^{Std} = 37$ dimensionless units) and that derived from the analogous mixture of low molecular analogs, ethyl phenol (EPh) and ethyl isobutyrate (EIB), ($K_A^{Std} = 170$ dimensionless units). [Note $K_A^{Std}$ has been used to represent phenolic hydroxyl/ester carbonyl interactions between different molecules or polymers while $K_C^{Std}$ has been used to represent the same interaction occurring in the same compound or (co)polymer.]

Since the experimental results on the BMAVPh copolymers described above were performed, the Coleman/Painter research group at Penn State focused their attention on attempting to understand the reasons why the $K_A^{Std}$ values experimentally obtained from low molecular weight analogs were so much higher than those obtained experimentally from (co)polymer blends ($K_A^{Std} = 170$ versus 37 dimensionless units).
This has led to a complete revision of the equation that describes the free energy of mixing (see Chapter 1) and the introduction of the concepts of intramolecular screening and functional group assessibility. In essence, chain connectivity, the fact that in a (co)polymer the segments are covalently bound together in a chain-like structure, strongly affects the number of like and unlike contacts that are formed in the polymer blend. Thus the experimental values of $K_{A}^{SD}$ (or $K_{C}^{SD}$) determined from polymer blends (or copolymers) reflect the affect of chain connectivity and steric shielding. Pehlert, for example, demonstrated that the value of $K_{A}^{SD}$ rises significantly as functional groups are spaced apart using inert segments in copolymer blends. However, in polymer blends intramolecular screening still remains a dominant factor in limiting the fraction of phenolic hydroxyl/ester carbonyl interactions.

In multifunctional copolymers, like the BMAVPh copolymers studied in this work, chain connectivity is obviously also very important and limits the fraction of phenolic hydroxyl/ester carbonyl interactions formed. How can this be taken into account in any theoretical prediction of polymer blend phase behavior? In Chapter 3 the successful prediction of the phase behavior of hydrogen bonded polymer blends consisting of two (co)polymers that each only contain one type of functional group will be discussed (e.g., dimethylbutadiene-co-4-vinyl phenol (DMBVPh) blends with ethylene-co-vinyl acetate (EVA)). Equilibrium constant values derived from low molar mass analogs are employed and the free energy of mixing is calculated after intramolecular screening and functional group accessibility have been taken into account. Unfortunately, an appropriate way to handle BMAVPh and similar multifunctional copolymers has not yet been established and further experimental work will be necessary to obtain sufficient data to develop a predictive model. It is possible, however, to use a combination of infrared spectroscopy and thermal analysis to study BMAVPh blends of the homologous PVAE series and compare them to analogous PBAB blends.
Figures 2.7 to 2.10 show infrared spectra in the carbonyl stretching region of the pure BMAVPh{44}, BMAVPh{50}, BMAVPh{60} and BMAVPh{74} copolymers, respectively, and those of 50 wt % blends with PVME, PVEE, PVPE and PVBE. First it should be noted that the spectra of the PVPE and PVBE blends are essentially identical to those of the corresponding pure BMAVPh copolymers. This implies that there are few, if any, intermolecular hydrogen bonding interactions between the phenolic hydroxyl and ether oxygen groups and these blends are grossly phase separated. If there were significant mixing between BMAVPh and PVPE or PVBE polymers, competitive equilibria dictates that the ether groups would compete with the BMA carbonyl groups for the phenolic hydroxyls and the fraction of hydrogen bonded carbonyl groups would inevitably decline. Two distinct Tg's were observed in the DSC thermograms of these blends (see Figure 2.11 for representative examples) and this is consistent with a two phase system.

In contrast, the spectra of PVME and PVEE blends are clearly different from those of the corresponding pure BMAVPh copolymers. The fraction of hydrogen bonded carbonyl groups has decreased significantly indicating that intermolecular hydrogen bonding interactions between the phenolic hydroxyl and ether oxygen groups has occurred. This implies molecular mixing, but does not prove that these systems are single phase. Consider, for example, the spectra of the PVME blends with BMAVPh{44} and BMAVPh{74} (Figures 2.7 and 2.10). The hydrogen bonded carbonyl band contribution in the former is very small, whereas in the latter it is significantly larger (although much less than that observed in the spectrum of pure BMAVPh{74}). It is a mistake to conclude that the BMAVPh{44}/PVME blend is single phase and the BMAVPh{74}/PVME blend is two phase from a simple inspection of the infrared spectra.
Figure 2.7 Infrared of the carbonyl region of 50% by weight blends of BMAVPh{44} with some PVAE’s.
Figure 2.8 Infrared of the carbonyl region of 50% by weight blends of BMAVPh{50} with some PVAE’s.
Figure 2.9 Infrared of the carbonyl region of 50% by weight blends of BMAVPh{60} with some PVAE’s.
Figure 2.10 Infrared of the carbonyl region of 50% by weight blends of BMAVPh{74} with some PVAE’s.
Figure 2.11 The DSC of blends of PVEE and PVPE with BMAVPh\{60\}.
This is a competing equilibrium process and the fraction of hydrogen bonded carbonyl groups in a single phase will be determined by the concentration of VPh, BMA and vinyl alkyl ether (VAE) moieties in the blend, the temperature and the values of the *appropriate* standard equilibrium constants that describe self-association ($K_{2}^{\text{Std}}$, $K_{B}^{\text{Std}}$, $K_{C}^{\text{Std}}$) and inter-association ($K_{A}^{\text{Std}}$). By *appropriate*, it is meant those equilibrium constants that are calculated to reflect chain connectivity effects. While it can be confidently stated that the BMAVPh blends with PVME and PVEE are significantly mixed, there is insufficient information to judge whether or not these systems are indeed single phase from the infrared spectral data. However, single Tg's, intermediate between those of the pure components, were observed in the DSC thermograms for all the BMAVPh blends with PVME and PVEE (Figure 2.11). At the probe size measured by thermal analysis this is consistent with single phase (miscible) blends.

Turning our attention to the analogous phosphazene blends, Figures 2.12 to 2.15 show infrared spectra in the carbonyl stretching region of the pure BMAVPh{44}, BMAVPh{50}, BMAVPh{60} and BMAVPh{74} copolymers, respectively, and those of 50 wt % blends with PBEP, PBPP, and PBBP. [Blends with poly(bis(methoxy)-phosphazene) (PBMP) are not shown, because PBMP it is not thermally stable at the temperatures required to produce blend samples.] Commencing with the BMAVPh{60} blends (Figure 2.14), the infrared spectra of the *bis*-proproxy- (PBPP) and *bis*-butoxy-phosphazenes (PBBP) blends suggest that very little mixing has occurred (compare the spectra with that of the pure BMAVPh{60}). This implies two phase systems using the same argument mentioned above. Two distinct Tg's were observed in the DSC thermograms of these blends (see top of Figure 2.16 for representative examples) and this is consistent with a two phase system. On the other hand, the spectrum of the *bis*-ethoxyphosphazene (PBEP) blend shows a marked reduction in the hydrogen bonded carbonyl band that demonstrates significant hydrogen bonding interactions have occurred between phenolic hydroxyl and ethoxy ether groups.
Figure 2.12 Infrared of the carbonyl region of 50% by weight blends of BMAVPh{44} with some PBAP’s.
Figure 2.13 Infrared of the carbonyl region of 50% by weight blends of BMAVPh{50} with some PBAP’s.
Figure 2.14 Infrared of the carbonyl region of 50% by weight blends of BMAVPh{60} with some PBAP’s.
Figure 2.15 Infrared of the carbonyl region of 50\% by weight blends of BMAVPh\{74\} with some PBAP’s.
Figure 2.16 The DSC of blends of PBEEP and PBPrEP with BMAVPh{60}.
This is consistent with molecular mixing and suggests that the blend may be miscible. A representative example is in lower part of figure 2.16 where a single Tg was observed for the blend of PBEP with BMA\{60\}.

Using the infrared and DSC data obtained from the blends of BMAVPh’s with PBAP’s and PVAE’s, it was possible to determine which blends appeared miscible. These results are presented in Tables 2.2 and 2.3. Only PVME, PVEE, and PBEP, are miscible with BMAVPh copolymers examined. It is interesting to note that in blends of PvPh and the four BMAVPh copolymers with the homologous series of PVAE’s, only the methoxy and the ethoxy polyethers are miscible. Blends of the higher homologues, propoxy, and butoxy are immiscible. A similar trend was seen in the analogous PBAP homologous series (although the bismethoxy polymer could not be tested). All other things being equal, this implies that the solubility parameter of the PVAE’s and their PBAP counterparts are similar and the \(-N=P-\) contribution to the solubility parameter is about 8.4 (cal cm\(^{-3}\))\(^{0.5}\). However, recent work by Pehlert\(^{41-43}\) has demonstrated that the accessibility of functional groups in polymer is decreased when flexible substituents groups are attached that contain greater than two carbons (i.e. propyl and greater). Accordingly, the above estimate for the solubility parameter contribution of the \(-N=P-\) group can only be considered to be tentative.

It was hoped at this point in the research, calculations could be preformed to predict the miscibility maps for PBAP blends with polyurethanes. However, with an incomplete understanding of the BMAVPh equilibrium constants and the role of chain connectivity, it was not possible to make such predictions. Thus, it was decided to move ahead and circumvent this problem by making grafts of polyphosphazenes with polyurethanes.
### Table 2.2 Comparison of the Miscibility of Blends BMAVPh copolymers with PVAE’s.

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M = Miscible  
X = Immiscible

### Table 2.3 Comparison of the Miscibility of Blends BMAVPh copolymers with PBAP’s.

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M = Miscible  
X = Immiscible  
N/A = Not Available
2.4 Polyurethane/Polyphosphazene Blends

Grafting a polyphosphazene onto a different organic polymer is an alternative approach to developing highly mixed or miscible blends as potential flame resistant materials. It was postulated that if an inherently flame resistant polyphosphazene, containing functional groups that could be used to chemically graft the polymer to another, it may be possible to produce a flame resistant material that contains only a minor amount of the relatively expensive polyphosphazene. An obvious polymeric material that is found in numerous applications, but is inherently highly flammable is polyurethane foam. Can we make polyurethane foam flame resistant, or at least self-extinguishing, by grafting a polyphosphazene onto the system?

Polyurethane foams can be generated by several different methods, but the most common method employs a two component system containing a low molecular weight (LMW) hydroxyl terminated poly(ethylene oxide) and a poly(ether-urethane) LMW prepolymer terminated with isocyanate end groups. Upon mixing, these two components react to form a high molecular weight polyurethane foam. A phosphazene polymer can be incorporated into the polyurethane foam by introducing one that contains functional groups, such as amines, hydroxyls or carboxylic acids that can also react with the isocyanate groups present in the mixture. Upon surveying the inventory of polymers available from Professor Allock's laboratory, a phosphazene polymer containing carboxylic groups, poly[\text{bis(carboxylatophenoxy)phosphazene}] (PBCPP), was chosen for this work.
As PBCPP contains carboxylic acid groups, these can react with the isocyanate groups present forming a chemical link between the phosphazene and the urethane foam network as illustrated schematically in scheme 2.9.

A series of polyurethane foams containing 0, 5, 10, 15 and 20 wt % PBCPP were initial tested using the vertical flame test described in the Experimental section. The pure polyurethane foam was tested first as a reference material and a photo-montage of the result is included in figure 2.17. As mentioned previously, virgin polyurethane foams are highly flammable. The pure polyurethane ignites readily and the flame progressed to the first mark (at 2 cm) in 5 seconds at which time the Bunsen burner was removed. The flame continued to consume the sample at a rapid rate not unlike that of a firework fuse. The flame progressed to the second mark in 37 seconds and the whole sample was consumed in 40 seconds.
Figure 2.17 Photomontage of the Vertical Flame tests of Polyurethane.
Scheme 2.9 The reaction of PBCPP with an isocyanate end capped polyurethane

Of the polyurethane foams with the different concentrations of PBCPP, only that containing 20 wt % PBCPP exhibited self-extinguishing behavior. In other words, in the case of the 20 wt % PBCPP foam the rate of flame progression was so slow that the flame extinguished before it reached the first mark. This is illustrated in Figure 2.18. The flame of the Bunsen burner was held in place for the full 30 seconds before it was removed. The sample continued to smolder, but the flame did not propagate further. Other blend compositions containing less than 20 wt % PBCPP were not self-extinguishing. However, flame progression rates did decrease somewhat with increasing PBCPP concentration. These initial flame tests were encouraging, but the fact that at least 20 wt % of the polyphosphazene was necessary to attain self-extinguishing was rather disappointing.
Figure 2.18 Photomontage of Polyurethane containing 20% by weight PBCPP
Thermogravimetric analysis (TGA) was employed to study the thermal resistance of the PBCPP/polyurethane foamed materials. One theory of flame progression is that the burning process is fueled by volatile components arising from the breakdown of the burning material. These components when mixed with air are consumed producing more heat and propagating the burning processes. TGA measures the amount of mass lost as a function of temperature at a constant heating rate. While this is only a qualitative measure of flame resistance, TGA data can yield some useful information. Figure 2.19 summarizes the TGA results of the pure polyurethane, pure PBCPP and the polyurethane foam blends containing 5, 10, 15, 20 and 30 wt % PBCPP. These TGA’s were performed from 20°C to 600°C at 20°C/min in air. The shape the curves appear similar. However, with increasing amount of PBCPP the weight loss occurring in the plateau region between 300 and 500°C decreases with increasing PBCPP. Similarly, the loss of material at 600°C also decreases with increasing PBCPP. While the onset temperature for degradation is raised by some 30°C for the 20 wt % PBCPP blend over that of the pure polyurethane foam, this is not considered significant in a practical fire situation. What we appear to be dealing with is a simple rule of mixtures and there appears to be no synergy.

Researchers in the flame retardant field favor a limited oxygen index test because they feel it more accurately correlates with real life fires.\textsuperscript{10-13} This test determines the percent of oxygen required in the atmosphere to sustain combustion of the material under study.\textsuperscript{44} A material which burns in air would have a maximum limited oxygen index value of 18 since air contains 18 wt % oxygen. Materials are considered to be good flame resistant materials when they have a limited oxygen index of > 40.\textsuperscript{44} In collaboration with Dr. J. Taylor the limiting oxygen index of the PBCPP/polyurethane foams were determined. The results were frankly disappointing. For example, even the 30 wt % PBCPP foam only had a limiting oxygen index value of 22. This, at best, is only marginally flame resistant.
Figure 2.19 TGA’s of Polyurethane Foams containing PBCPP sorted by % weight.
2.5 References


44. ASTM-D-2863-91 Standard
CHAPTER 3

THE PREDICTION OF HYDROGEN BONDED POLYMER BLEND
PHASE BEHAVIOR FROM ANALOGOUS LOW MOLAR MASS
EQUILIBRIUM CONSTANTS

3.1 Introduction

In Chapter 1 the difference between “effective” equilibrium constants, $K_B$ and $K_A$, which correspond to the experimental infrared spectroscopic values determined from miscible blends, and “intrinsic” equilibrium constants, those determined from appropriate low molar mass mixtures, was discussed. The values of the "effective" equilibrium constants reflect factors attributed to chain connectivity, such as intramolecular screening and functional group accessibility, which limit the number of intermolecular interactions formed in the blend. It follows that the hydrogen bonding contribution to the free energy of mixing for polymer blends could be determined from “intrinsic” equilibrium constants if the affects of chain connectivity are taken into account. Such equations have been developed and were briefly introduced in Chapter 1. In this chapter theoretical results will be presented that were obtained from a computer program that includes intramolecular screening and functional group accessibility affects. This program, which is a modification of Dr. J. F. Graf original Macintosh computer program (commonly referred to as “Phase Calculator”), calculates the fraction of hydrogen bonded functional groups, the individual contributions to the free energy of mixing, phase diagrams, miscibility windows and miscibility maps etc.
3.2 Modifications to the Phase Calculator Program

To reiterate, the Phase Calculator program originally written by Dr. John Graf was based upon the equation:

\[
\frac{\Delta G_m}{RT} = \left[ \frac{\Phi_1}{M_1} \ln \Phi_1 + \frac{\Phi_2}{M_2} \ln \Phi_2 \right] + \Phi_1 \Phi_2 \chi_{12} + \frac{\Delta G_H}{RT} \tag{3.1}
\]

where \( \Phi_1 \) and \( \Phi_2 \), and \( M_1 \) and \( M_2 \), are the volume fractions and degrees of polymerization of (co)polymers (1) and (2), respectively, and \( \chi_{12} \) is the Flory interaction parameter.

Recall that the free energy contribution from hydrogen bonding, \( \Delta G_H/RT \), contained what is now recognized was an incorrect excess entropy term (that contained in the square brackets of eq. 3.2):

\[
\frac{\Delta G_H}{RT} = \sum n_{b_i} \ln \left( \frac{\Phi_{b_i}}{h} \right) + \sum n_{b_i, A} \ln \left( \frac{\Phi_{b_i, A}}{h + r} \right) + n_{A_i} \ln \left( \frac{\Phi_{A_i}}{r} \right) + n_{BB}^h + n_{AB}^h + \text{(terms in } z \text{ and } \sigma \text{)} - \left[ \frac{n_B \ln \Phi_B + n_A \ln \Phi_A}{h_0} \right] - n_{BB}^h \ln K_B - n_{AB}^h \ln K_A \tag{3.2}
\]

Accordingly, the first trivial modification to Graf’s program was to set the parameter \( h_0 \) to unity, which adjusts the excess free energy term to that corresponding to simple solution theory (eq. 1.13). The next step was introduce the intramolecular screening parameter, \( \gamma \). For the sake of clarity, the relevant equation for the free energy of mixing is reproduced below:

\[
\frac{\Delta G_m}{RT} = \frac{\Phi_1}{M_1} \ln \Phi_1 + \frac{\Phi_2}{M_2} \ln \Phi_2 + \Phi_1 \Phi_2 (1 - \gamma) \chi_{12} + \frac{\Delta G_H}{RT} \tag{3.3}
\]

The parameter \( \gamma \) appears both in the \( \chi \) and \( \Delta G_H/RT \) terms. The former was a trivial modification to Graf’s program, but the latter required the writing of a new
subroutine, since the values of the equilibrium constants used to calculate the free energy contribution from hydrogen bonding vary with composition. For example, in the case of blends systems containing phenolic and acetate groups, two self-association and one inter-association equilibrium constants are calculated according to the eqs. 3.4, 3.5 and 3.6:

\[
\tilde{K}_2 = K_2 \left[ \frac{\gamma + (1 - \gamma)\Phi_B}{\Phi_B} \right] \tag{3.4}
\]

\[
\tilde{K}_B = K_B \left[ \frac{\gamma + (1 - \gamma)\Phi_B}{\Phi_B} \right] \tag{3.5}
\]

\[
\tilde{K}_A = K_A \left[ \frac{1 - (\gamma + (1 - \gamma)\Phi_B)}{\Phi_A} \right] = K_A (1 - \gamma) \tag{3.6}
\]

Pehlert in studies of dimethylbutadiene-co-vinyl phenol (DMBVPh) blends with ethylene-co-vinyl acetate (EVA) copolymers showed that the spacing between phenolic groups in DMBVPh copolymers and the corresponding spacing between acetoxy groups in EVA copolymers has a significant effect on the values of the experimental standard equilibrium constants. Pehlert et al. derived an empirical equation that describes the effect on standard equilibrium constant values as a function of spacing in phenolic/acetoxy blends (eq. 3.7):

\[
\tilde{K}_A = K_A \left[ \frac{1630}{V_1} + \frac{4100}{V_2} \right] \tag{3.7}
\]

where \(V_1\) and \(V_2\) are molar volumes of the specific repeat unit for polymer (1) and (2) respectfully. Equation 3.7 was introduced into the modified Phase Calculator program with an appropriate radio button.
3.3 The Prediction of Polymer Blend Phase Behavior

3.3.1 The PVPh - PVAc Blend System

In order to test whether or not intrinsic equilibrium constant values obtained from low molecular weight model analogs can be used to predict the phase behavior and miscibility maps of hydrogen bonded blends, it was decided to start with a well established miscible polymer blend system composed of two amorphous homopolymers, poly(4-vinyl phenol) (PVPh) and poly(vinyl acetate) (PVAc). Dimensionless standard equilibrium constant values (based on a common reference molar volume \( V_B = 100 \text{ cm}^3/\text{mol} \)) have previously been determined from appropriate low molecular mass analogues [4-ethylphenol (EPh) and ethyl isobutyrate (EIB)].\(^8\) These standard equilibrium constants \( K_{2\text{std}} = 21.0; K_{B\text{std}} = 66.8 \) (self-association) and \( K_{A\text{std}} = 170 \) (inter-association) describe the fraction of the various hydrogen bonded species present in a solution of EPh/EIB as a function of composition at 25°C. This represents the case where there are no effects due to chain connectivity and all the values remain constant regardless of blend composition (depicted in Figure 3.1; \( \gamma = 0 \)).

As mentioned previously, intrinsic equilibrium constant values are modified by chain connectivity effects. Intramolecular screening is accounted for through the parameter, \( \gamma \). The relevant equations are presented above (eqs. 3.4 through 3.6) and it is probably sufficient to simply state that new self-association equilibrium constants \( \tilde{K}_B \) (and \( \tilde{K}_2 \)) are calculated that are now a function of blend composition \( (\Phi_B) \). Typical results are depicted in Figure 3.2 using an appropriate \( \gamma \) value for high molecular polymer blends of 0.30.\(^5\) On the other hand, the new inter-association equilibrium constant, \( \tilde{K}_A \), is not a function of blend composition, but has a reduced constant value of 170 \( (1 - \gamma) = 119 \) dimensionless units. Switching on FGA (eq. 3.7) further reduces the value of \( \tilde{K}_A \) to 55 dimensionless units.
Figure 3.1 Equilibrium constant values for the PVPh-PVAc blend system without the effect of screening or FGA.
Figure 3.2 Equilibrium constant values for the PVPh-PVAc blend system with the effect of screening or FGA.
This closely corresponds to the "effective" value determined experimentally from PVPh/PVAc blends.\textsuperscript{7}

It is now a relatively straightforward task to employ the relevant stoichiometric equations using the above different sets of equilibrium constant values and calculate the theoretical equilibrium fraction of hydrogen bonded acetoxy groups present in a single phase mixture of PVPh and PVAc as a function of blend composition at 25°C. The results are displayed in Figure 3.3. The top curve denotes the fraction of hydrogen bonded carbonyl groups for the $\gamma = 0$ case (calculated using composition invariant values of $K_2^{\text{Std}} = 21.0; K_B^{\text{Std}} = 66.8$ and $K_A^{\text{Std}} = 170$ dimensionless units). If intramolecular screening is now "switched on" by introducing a $\gamma$ value of 0.30, (now the self-association equilibrium constants, $\bar{K}_2$ and $\bar{K}_B$, are compositionally dependent, but the interassociation equilibrium constant is not and has a constant value of $\bar{K}_A = 119$ dimensionless units), the middle curve is obtained. Note that the fraction of hydrogen bonded carbonyl groups has decreased significantly over that calculated in the absence of intramolecular screening, especially for blends that are compositionally rich in PVPh. There are further substantial decreases when functional group accessibility (FGA) effects are taken into account through eq. 3.7 and this is depicted in the lower curve (here $\bar{K}_2$ and $\bar{K}_B$ are still compositionally dependent and $\bar{K}_A$ now has a constant value of 55 dimensionless units).

Comparing, for example, the theoretical fraction of hydrogen bonded carbonyl groups present in a single phase 60:40 wt % PVPh – PVAc blend for the three different cases, values of approximately 0.67 ($\gamma = 0$), 0.58 ($\gamma = 0.30$) and 0.45 ($\gamma = 0.30 + \text{FGA}$) are obtained. These are large differences that have profound repercussions on the amount of favorable free energy that is available from the changing pattern of the hydrogen bonds formed in the mixture relative to the pure components.
Figure 3.3 Calculated fraction of hydrogen bonded acetoxy carbonyls groups for the PVPh-PVAc blend system at 25°C.
It is important to stress that chain connectivity effects (including intramolecular screening and functional group accessibility) cannot be ignored if the phase behavior of polymer blends is to be successfully predicted.

The theoretical equation for the free energy of mixing for hydrogen bonded polymer blends that was derived using an association model and incorporates intramolecular screening was presented above in eq. 3.3. As stated before, phase behavior is dominated in hydrogen bonded polymer blends by the balance between the $\chi$ and hydrogen bonding contributions. In the current version of the computer program options have been introduced that display the total free energy, together with the three contributions, combinatorial entropy, the $\chi$ term and the hydrogen bonding term. As in Graf's original program,7 necessary inputs include information pertaining to the polymer segments (molar volume, molecular weight and solubility parameter, all calculated from group contributions) and the degrees of polymerization of both polymers (default values of $M_A = M_B = 500$ are commonly employed in the absence of explicit information). In addition, standard equilibrium constant values are required (in dimensionless units based upon a standard molar volume of 100 cm$^3$/mol at 25°C) that describe the self-association and interassociation of the low molar mass analogs (in this case, $K_{2}^{\text{Std}} = 21.0$; $K_{B}^{\text{Std}} = 66.8$ and $K_{A}^{\text{Std}} = 170$).8 Later, for calculations at temperatures other than 25°C, values of the enthalpies of hydrogen bond formation ($h_2 = -5.6$, $h_B = -5.2$ and $h_A = -4.1$ kcal/mol) will be required.

Figure 3.4 shows the calculations performed for PVPh – PVAc blends in the absence of intermolecular screening or functional group accessibility effects (i.e. $\gamma = 0$ and no FGA). As anticipated, combinatorial entropy makes a negligible contribution to the total free energy.
Figure 3.4 Contributions to the free energy for the PVPh-PVAc blend system at 25°C for the case of no intermolecular screening ($\gamma = 0$).
The hydrogen bonding term dominates and is a smooth negative (concave upward) curve with a maximum contribution of $\approx -3.8$ cal/ml for the 50/50 wt % blend. Conversely, the $\chi$ term is a smooth positive (concave downward) curve having a maximum value of only $\approx +0.3$ cal/ml. Accordingly, the total free energy curve is only slightly less negative than that of the hydrogen bonding contribution and is a negative (concave upward) curve. The second derivative of the free energy with respect to composition (Figure 3.5) is positive and this implies a single phase system throughout the entire composition range (the definition of true miscibility at this particular temperature, 25°C).

What now happens if intramolecular screening is taken into account? Figure 3.6 shows the free energy calculations for a $\gamma$ value of 0.30. The trends are similar except that the free energy contribution from the hydrogen bonding term has been reduced to a maximum of $\approx -3.1$ cal/ml. This is offset somewhat by a 70% reduction (eq. 3.3) in the maximum value of the $\chi$ term. In any event, the total free energy curve is again only slightly less negative than that of the hydrogen bonding contribution and is a strong negative (concave upward) curve. While intramolecular screening reduces the overall negative free energy of mixing in the PVPh – PVAc blend system, the magnitude of the hydrogen bonding term remains overwhelming and a very strong driving force for mixing. With a positive second derivative throughout the entire composition range a single phase system is indicated (Figure 3.7).

If “spacing” or FGA effects are now added using a $\gamma$ value of 0.30 and accounting for FGA effects through eq. 3.7 the results shown in Figure 3.8 are obtained. Recall, FGA effects are most discernible when the functional groups are in close proximity along their respective polymer chains, as they are in the case of the PVPh and PVAc homopolymers.
Figure 3.5 Second derivative of the free energy of mixing for the PVPh-PVAc blend system at 25°C ($\gamma = 0$).
Figure 3.6 Contributions to the free energy for the PVPh-PVAc blend system at 25°C for the case with intermolecular screening ($\gamma = 0.3$).
Figure 3.7 Second derivative of the free energy of mixing for the PVPh-PVAc blend system at 25°C with intermolecular screening ($\gamma = 0.3$).
Figure 3.8 Contributions to the free energy for the PVPh-PVAc blend system at 25°C for the case with intermolecular screening ($\gamma = 0.3$) and function group accessibility.
Now the maximum value of the hydrogen bonding contribution is reduced to $\approx -1.8$ cal/ml, a substantial reduction over that calculated in the absence of FGA effects. Nonetheless, this is still sufficient to completely overwhelm the positive contribution from the $\chi$ term. Again, a positive second derivative of the total free energy throughout the composition range (Figure 3.9) indicates a single phase system.

The calculated spinodal phase diagram for the PVPh – PVAc blend system from -100 to 300°C is not shown because there are no two-phase compositions calculated throughout the entire ranges of temperature and composition. Given the dominance of the hydrogen bonding contribution to the free energy of mixing shown in Figures 3.4, 3.6 and 3.8, this is hardly surprising. It was decided to move on to a description of the results obtained for PVPh blends with an ethylene-co-vinyl acetate random copolymer containing 45 wt % vinyl acetate (EVA[45])—a system where the balance between the contributions from the $\chi$ and hydrogen bonding terms is more closely balanced.$^{4,6}$

### 3.3.2 The PVPh – EVA[45] Blend System

In replacing PVAc with EVA[45], there are two important changes. First, the average non-hydrogen bonding solubility parameter changes from 9.6 to 8.6 (cal. cm$^{-3}$)$^{0.5}$, which significantly increases the value of $\chi$ [as it is proportional to the square of the difference with respect to that of PVPh = 10.6 (cal. cm$^{-3}$)$^{0.5}$]. Second, the magnitude of the hydrogen bonding contribution decreases for a particular blend composition (the ratio of phenolic hydroxyls to acetoxy carbonyls increases, but we have also to consider the “dilution” effect of the ethylene segments). All this is automatically taken into account in the computer program by the introduction of the specific EVA[45] repeat parameters (i.e. the molar volume, molecular weight and solubility parameter of the average repeat containing one VAc group).
Figure 3.9 Second derivative of the free energy of mixing for the PVPh-PVAc blend system at 25°C with intermolecular screening (γ = 0.3) and function group accessibility.
For the case where intramolecular screening is assumed to be absent (i.e., \(\gamma = 0\)) the results shown in Figure 3.10 were obtained. Once again, combinatorial entropy makes a negligible contribution to the total free energy. The hydrogen bonding term is a negative (concave upward), slightly skewed curve with a maximum contribution close to -1 cal/ml. On the other hand, the \(\chi\) term is a positive (concave downward) curve having a maximum value of about +1 cal/ml. These two contributions are almost balanced and the total calculated free energy resembles a sine wave with negative and positive lobes. The second derivative of the free energy with respect to composition is shown in Figure 3.11, which reveals negative second derivatives at compositions greater than \(\approx 40\) wt % PVPh. Thus above 40 wt % PVPh the PVPh – EVA[45] blend system is predicted to be two-phase at 25°C.

In Figure 3.12 are shown the free energy calculations performed taking into account intramolecular screening for PVPh – EVA[45] blends using a \(\gamma\) value of 0.30. The hydrogen bonding curve is similar to that obtained above (i.e., for \(\gamma = 0\)), except that it is more symmetrical and the maximum value is somewhat less at \(\approx -0.9\) cal/ml. The \(\chi\) term remains a positive (concave downward) curve with a reduced maximum value of about +0.7 cal/ml. In contrast to case where \(\gamma = 0\) (Figure 3.10), the total free energy curve is negative. However, it is not concave upward over the entire composition range. The second derivative of the free energy with respect to composition is shown in Figure 3.13. This reveals negative second derivatives at compositions between \(\approx 55\) and 85 wt % PVPh. Actually, this predicts that a somewhat broader range of single-phase compositions at 25°C compared to the case when \(\gamma = 0\). But this is before we add the effect of "spacing" or FGA.
Figure 3.10 Contributions to the free energy for the PVPh-EVA[45] blend system at 25°C for the case of no intermolecular screening (γ = 0).
Figure 3.11 Second derivative of the free energy of mixing for the PVPh-EVA[45] blend system at 25°C.
Figure 3.12 Contributions to the free energy for the PVPh-EVA[45] blend system at 25°C for the case of intermolecular screening ($\gamma = 0.3$).
Figure 3.13 Second derivative of the free energy of mixing for the PVPh-EVA[45] blend system at 25°C when intermolecular screening (γ = 0.3).
Figure 3.14 shows the free energy calculations for PVPh – EVA[45] blends after the FGA or “spacing” effect has been added. Note that the maximum value of the hydrogen bonding contribution is now reduced to approximately half that calculated in the absence of FGA effects. The positive contribution from the $\chi$ term is greater than that of the negative hydrogen bonded term, leading to an overall positive total free energy of mixing. This, together with the second derivative information (Figure 3.15), of course, implies that the system is grossly phase separated at 25°C.

It was mentioned above that a spinodal phase diagram may be readily calculated if values of the enthalpies of hydrogen bond formation are available.\textsuperscript{2,7} Entering the appropriate values ($h_2 = -5.6$, $h_B = -5.2$ and $h_A = -4.1$ kcal/mol) into the computer program permits the calculation of the individual equilibrium constants and the Flory interaction parameter $\chi$ at any given temperature using, respectively, the well established van’t Hoff and inverse temperature relationships.\textsuperscript{2,7} Using the two criteria for a single phase—that the free energy of mixing must be less than zero and the second derivative of the free energy must be positive—phase diagrams can be calculated. The results of such calculations for the case of $\gamma = 0.3$, with and without FGA, are displayed in Figure 3.16. It is apparent that there is no temperature in the experimentally accessible range (between say ambient and 200°C) where a single phase is predicted at equilibrium across the entire blend composition. The FGA (“spacing”) effect simply increases the composition range over which two phases are predicted.

Finally, the predicted PVPh – EVA[45] phase diagram shown above [which to reiterate was calculated after taking into account intramolecular screening and “spacing” (FGA) effects using equilibrium constants obtained from low molar mass analogues] closely parallels experimental reality.\textsuperscript{7}
Figure 3.14 Contributions to the free energy for the PVPh-EVA[45] blend system at 25°C for the case of intermolecular screening ($\gamma = 0.3$) and FGA.
Figure 3.15 Second derivative of the free energy of mixing for the PVPh-EVA[45] blend system at 25°C with intermolecular screening (γ = 0.3) and FGA.
Figure 3.16 Spinodal phase diagram for the PVPh-EVA[45] blend system.
Moreover, it is very similar to that calculated using the original equations presented in the monograph of Coleman, Graf and Painter,\textsuperscript{7} a reproduction of which is shown in Figure 3.17. Recall that this calculation used "effective" experimental equilibrium constants derived from appropriate miscible polymer blends and that the free energy equation contained an empirical correction factor in the hydrogen bonding free energy term. It is now recognized that this empirical correction factor was compensating primarily for intramolecular screening.\textsuperscript{7}

### 3.3.3 Miscibility Windows and Maps

A miscibility window summarizes the overall phase behavior at a particular temperature for blends of a single polymer with a series of copolymers in which the copolymer composition is systematically varied. Following on from the results described immediately above, the next logical step would be to consider the miscibility window for PVPh with the complete range of EVA copolymers from PVAc to essentially polyethylene. In common with the methodology described in Coleman, Graf and Painter's book,\textsuperscript{7} the segment information for PVPh and PVAc is inputted into the computer program together with that of the “diluent”, in this case the ethylene segment (i.e., two methylene groups). The computer program systematically “synthesizes” EVA copolymers of increasing ethylene content and calculates the relevant average segment information. The free energy of mixing of each of the EVA copolymer blends with PVPh is then calculated at intervals across the entire blend composition. A single phase again requires that the free energy of mixing is negative and that the second derivative with respect to blend composition is positive, and this defines the spinodal boundary between the single and two phase regions in the miscibility window.
Figure 3.17 Spinodal phase diagram for the PVPh-EVA[45] blend system predicted by the original “Phase Calculator” program.
Figure 3.18 shows the results of such a calculation with $\gamma = 0.30$, with and without the effect of “spacing” or FGA. The results predict that only EVA copolymers containing greater than $\approx 55$ wt % VAc are truly miscible with PVPh at 25°C (i.e., a single phase across the entire composition range) and it is evident that the “spacing” or FGA effect appears to make a meaningful difference in this case. As mentioned previously, the FGA effect is greatest when the functional groups of both components are in close proximity along their respective (co)polymer chains (i.e., for the PVPh blends with PVAc). As the ethylene content of the EVA copolymers is increased the effect diminishes, but still remains appreciable for say a PVPh – EVA[50] blend because the VPh groups in PVPh are very close together. The prediction illustrated in Figure 3.18 is consistent with the known experimental data and while there are subtle differences in the form (shape) of the spinodal boundaries the results are similar to the predictions calculated using the original equations.\(^7\) [It is important to note, however, that this is an equilibrium calculation for amorphous (co)polymers and does not take into account kinetic problems that may arise from a high glass transition temperatures of the blends or the presence of any ethylene-type crystallinity].

Finally, presented in Figures 3.19 and 3.20 are the predicted miscibility maps for styrene-co-4-vinyl phenol (STVPh) and 2,3-dimethylbutadiene-co-4-vinyl phenol (DMBVPh) copolymers in blends with EVA copolymers calculated at 100°C. In essence, a miscibility map summarizes the overall phase behavior at a particular temperature for blends of copolymers in which the copolymer composition is systematically varied in both. In other words, we systematically “dilute” both polymers containing the VPh and the VAc segments, calculate the free energy of mixing and test whether or not the particular blend is miscible (a single phase across the whole blend composition range).
Figure 3.18 Miscibility window for the PVPh-EVA blend system at 25°C.
Figure 3.19 Miscibility map for the ST-co-PVPh and EVA blend system at 100°C. Small dots: predicted; large circles: experimental.
Figure 3.20 Miscibility map for the DMB-\textit{co}-PVPh and EVA blend system at 100°C. Small dots: predicted; large circles: experimental.
This methodology has again been described in detail, and the necessary input into the computer program is the segment information for PVPh and PVAc together with those of the two “diluents”, styrene (or 2,3-dimethylbutadiene) and ethylene. The computer program systematically “synthesizes” STVPh (or DMBVPh) and EVA copolymers of increasing ST (or DMB) and ethylene content, respectively, and calculates the relevant equilibrium constants and average segment information. The free energy of mixing of each of the STVPh or DMBVPh copolymer blends with EVA is then calculated at intervals across the entire blend composition at a given temperature. A single phase again requires that the free energy of mixing is negative and that the second derivative with respect to blend composition is positive throughout the composition range, and this defines the spinodal boundary between the miscible and immiscible regions in the miscibility map.

The small black dots in Figures 3.19 and 3.20 correspond to predicted immiscible blends calculated using the initial equilibrium constants derived from the low molar mass analogues and using a $\gamma$ value of 0.30. The small unshaded dots represent the additional immiscible blends predicted when “spacing” or FGA effects are included. As expected, the latter appear more prevalent in blends containing the VPh and VAc rich copolymers. The larger black and white circles represent experimentally determined immiscible and miscible blends, respectively. The agreement to the theoretically predicted miscibility map is very good.

3.4 Conclusion

The most important conclusion to be gained from the above study is that the phase behavior of hydrogen bonded polymer blends can successfully be predicted using equilibrium constants determined from appropriate low molar mass analogs if intramolecular screening and functional group accessibility effects are included.
3.5 References


CHAPTER 4

INFRARED AND THERMAL CHARACTERIZATION OF HYDROGEN BONDED FLUOROETHER COPOLYMER BLENDS.

4.1 Introduction

The primary focus of the infrared spectroscopic research performed by the Coleman/Painter research group at Penn State during the past 15 years has been hydrogen bonding and its effect upon the phase behavior of polymer blends. More recently, the ability to predict phase behavior and take into account effects due to intermolecular screening, functional group accessibility and polymer chain architecture has occupied most attention. The phase behavior of hydrogen bonded polymer blends is dominated by the balance of two major contributions to the free energy of mixing. The first, a "chemical" driving force, is generally favorable to mixing and derived from the changing pattern of hydrogen bonding interactions occurring in the mixture compared to the pure components. The magnitude of this contribution is affected by such factors as the volume fraction of interacting species and "strength" of hydrogen bonding in self-association compared to that of inter-association. The second, a "physical" driving force that is almost always unfavorable to mixing, is a positive contribution to the free energy of mixing and is most conveniently expressed in terms of differences in the non-associative solubility parameters. Naturally, if a single phase (miscibility) is desired one would seek polymer blend systems where the difference in solubility parameters between the two components of the polymer blend is small and the magnitude of hydrogen bonding contribution is large.

Recently, a copolymer of tetrafluoroethylene (TFE) and a hexafluoroisopropanol modified vinyl ether (HFIPVE) was synthesized at DuPont. This copolymer is particularly interesting for theoretical and experimental studies of hydrogen bonded
polymer blends. Polymers containing fluoroalcohol groups have been recognized as potential binders for photolithography at extremely short wavelengths (e.g. 157 nm) for the patterning of semiconductor chips. The copolymer is an essentially alternating 1:1 copolymer of TFE and HFIPVE (designated TFE-$alt$-HFIPVE).

![Scheme 4.1 TFE-$alt$-HFIPVE](image)

This copolymer is soluble in THF and other moderately polar solvents and has a relatively low glass transition temperature (12°C), which facilitates attaining equilibrium conditions in mixtures. The hexafluoroisopropanol (HFIP) group is an excellent hydrogen bonding donor that does not strongly self-associate to the same extent as phenolic or aliphatic hydroxyls, but does form strong hydrogen bonds with acceptors like acetoxy or ester carbonyls, ether oxygens, etc. Moreover, the presence of the fluoromethylene and fluoromethyl groups contribute to bringing the overall average solubility parameter of the copolymer down to a range of approximately 6.8-7.2 (cal. cm$^{-3}$)$^{-0.5}$, which suggests that blends with aliphatic (co)polymers containing ester, acetoxy, or ether groups may potentially be miscible.
4.2 Experimental

The TFE-alt-HFIPVE copolymer was kindly supplied by the DuPont company. The synthesis was performed by Dr. Andrew Feiring and his colleagues using the following procedure. A 200 mL Hastelloy pressure vessel was charged with 42.9 g (0.16 mol) of \(\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{OCH}_2\text{C(CF}_3)_2\text{OH}\), \(40 \text{ mL of tert-butanol, 30 mL of methyl acetate, 0.5 g of potassium carbonate and 0.4 g of Vazo\textsuperscript{52} initiator. The vessel was closed, cooled in dry ice, evacuated and charged with 24 g (0.24 mol) of tetrafluoroethylene (TFE). Caution! TFE is a deflagrating explosive and an experimental carcinogen. All work with this monomer should be conducted in appropriately barricaded and ventilated facilities by trained individuals.}

The vessel contents were agitated at 50 °C for 18 hr. The vessel was cooled to room temperature and vented. The viscous polymer solution was removed using acetone to rinse. The polymer solution was added slowly to excess ice water in a blender. The precipitated solid polymer was filtered and washed with water in a blender. Drying in a vacuum oven at 44 °C overnight gave 38.9 g (58 %) of polymer. \(^1\)H NMR (δ, THF-d8) 2.4 - 2.8 (m, 2H), 3.6-3.9 (m, 6H), 4.4 (bs, 1H), 6.8 (s, 1H). \(^{19}\)F NMR (δ, THF-d8) -77.2 (CF\(_3\)), -110 to -125 (CF\(_2\)). From integration of fluorine absorbances, the polymer composition was calculated to be 50:50. GPC (THF): \(\text{Mn} = 173000, \text{Mw} = 329000, \text{Mw/Mn} = 1.90\). \(\text{Tg} = 12 \degree\text{C (DSC)}\). Elemental Analysis—Found: C, 32.70; H, 3.01; F, 51.03. From % C the polymer composition was calculated to be 49 % TFE and 51 % vinyl ether.

The other polymers used in this study have been previously described.\(^3\),\(^13\),\(^14\) Poly(vinyl acetate) (PVAc), poly(n-butyl methacrylate) (PBMA) and polytetrahydrofuran (PTHF) were purchased from Polysciences. The ethylene-co-vinyl acetate copolymers containing 70 and 40 weight % vinyl acetate, (EVA[70] and EVA[40], respectively), poly(n-hexyl methacrylate) (PHMA), poly(n-decyl methacrylate) (PDMA) and poly(vinyl methyl ether) (PVME) were purchased from Scientific Polymer Products. Poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA) and
tetrahydrofuran (THF) were purchased from the Aldrich Chemical Company. Poly(vinyl ethyl ether) (PVEE) was purchased from Monomer-Polymer & Dajac Laboratories. Poly(vinyl \textit{n}-propyl ether) (PVPE) and poly(vinyl \textit{n}-butyl ether) (PVBE) was synthesized in our laboratories (see Chapter 2) at Penn State.\textsuperscript{13,14}

Conventional infrared spectra were recorded on a Digilab Model FTS-45 Fourier Transform Infrared (FTIR) spectrometer using a minimum of 32 coadded scans at a resolution of 2 cm\(^{-1}\). Spectra recorded at elevated temperatures were obtained using a horizontal transmission cell equipped with a heating jacket mounted inside the sample chamber. Temperature was regulated by a Harrick digital process controller that has a reported accuracy of ±0.1 °C.

Thin films of the TFE-\textit{alt}-HFIPVE copolymer were cast at room temperature from THF onto potassium bromide windows (or glass petri dishes in the case of the samples for DSC analysis) and placed in a vacuum oven for 4 hours to ensure complete removal of the solvent. Blends of these copolymers with PVAc, the EVA copolymers, the poly(\textit{n}-alkyl methacrylates) and the polyethers were cast onto KBr windows at room temperature from a 1\% (w/v) solution in a common solvent (THF). Following air drying at room temperature, the windows were placed in a vacuum oven overnight at 100°C to remove the solvent. All films were thin enough to be within an absorbance range where the Beer-Lambert law is obeyed. Thermal analysis was performed on a Seiko DSCU220 differential scanning calorimeter. A heating rate of 20°C min\(^{-1}\) was used and glass transition temperatures calculated as the midpoint of the heat capacity change.

4.3 Infrared Characterization of TFE-\textit{alt}-HFIPVE

The copolymer TFE-\textit{alt}-HFIPVE is a new material and there has not been any previously published infrared studies. Figure 4.1 shows the FTIR spectra of the pure TFE-\textit{alt}-HFIPVE copolymer. Very intense characteristic bands associated with C-F stretching vibrations of the CF\(_3\) and CF\(_2\) groups (1120-1350 cm\(^{-1}\)) dominate the overall
The HFIPVE unit contains two ether oxygen atoms (see Scheme 4.1) and it would be expected that relatively strong absorptions from the C–O stretching vibrations would occur in roughly the same envelope, but they are not obvious and appear to be swamped by C–F stretching modes. Bands associated with the C–H stretching and O–H stretching modes are relatively weak, but clearly identified, in the 2800-3000 and 3200-3800 cm⁻¹ regions, respectively. Finally, a very weak "free" (non-hydrogen bonded) O–H stretching band is discernable at approximately 3600 cm⁻¹ on the high frequency side of the broad hydrogen bonded O–H band centered at ≈ 3500 cm⁻¹. These two bands will be featured prominently later.

Figure 4.2 shows the effect of temperature on the infrared spectra of TFE-alt-HFIPVE in region from 600-1800 cm⁻¹. The changes observed as the temperature is raised from 40°C to 200°C are quite subtle. As expected, the bands broaden slightly and there are minor changes in intensity in the modes occurring between 1100 and 1200 cm⁻¹. The latter is presumably caused by changes in the conformationally sensitive C–O stretching modes, as the C–F stretching vibrations are anticipated to be insensitive to such changes. Figure 4.3 shows the corresponding scale expanded spectra recorded in the O–H stretching region. Here the familiar changes of the broad, self-associated, hydrogen bonded O–H band as a function of temperature are observed.
Figure 4.1 Infrared spectrum of TFE-\textit{alt}\nobreakdash-HFIPVE recorded at room temperature.
Figure 4.2 Infrared spectrum of TFE-alt-HFIPVE recorded as a function of temperature in the region from 600-1800 cm\(^{-1}\).
Figure 4.3 Infrared spectrum of TFE-\textit{alt}-HFIPVE recorded as a function of temperature in the region from 3100-3700 cm\(^{-1}\).
There is a shift of the peak maximum to higher frequency (which reflects a decrease in the average strength of the hydroxyl-hydroxyl hydrogen bonds) and an overall narrowing of the band (which reflects a change in the distribution of the chain-like hydrogen bonded species).\textsuperscript{1,2,6,7,9-11} The "free" (non-hydrogen bonded) O–H stretching band remains essentially at the same frequency (≈ 3600 \text{cm}^{-1}) as the temperature is raised from 40-200°C. However, the relative intensity of the "free" band increases, reflecting an increase in concentration of "free" over hydrogen bonded hydroxyl groups. This is, of course, an equilibrium process. The fraction of "free" hydroxyl groups can be quantitatively determined if one has a knowledge of the magnitude of the two equilibrium constants that describe the formation of hydroxyl-hydroxyl dimers and multimers (K_2 and K_B), together with their respective enthalpies of hydrogen bond formation (\( h_2 \) and \( h_B \)).\textsuperscript{1,2}

**Self-Association**

**Hydroxy–hydroxy**

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**Hydroxy–ether**

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\textbf{Scheme 4.2} Self Association of TFE-\textit{alt}-HFIPVE
The presence of the two ether oxygen atoms in the side chain of the HFIPVE unit was a source of concern, as hydroxyl groups can potentially form strong hydrogen bonds to aliphatic ether groups (see Scheme 4.2), increasing the complexity of theoretical calculations. It would require that we include additional equilibrium constants to account for hydrogen bonding interactions between hydroxyl groups and ether oxygen atoms (similar to the problems mentioned in Chapter 2 for the BMAVPh copolymers). Only then could we fully describe the self-association of TFE-alt-HFIPVE. Fortunately, the spectroscopic evidence suggests that there are no significant hydrogen bonding interactions involving the hydroxyl and ether oxygen groups in pure TFE-alt-HFIPVE.

Figure 4.4 compares the O–H stretching region of the infrared spectra of pure TFE-alt-HFIPVE and several compositionally lean blends of this copolymer with various polyethers. Although Figure 4.4 will be discussed in more detail later in this work, for now attention will be focused on the three blends where a high degree of molecular mixing has obviously occurred (those containing PTHF, PVME or PVEE) and compare them to the one which is obviously grossly phase separated (PVBE). In the case of the former, an infrared band centered at \( \approx 3210 \text{ cm}^{-1} \) is clearly observed which can be assigned unambiguously to hydroxyl groups that are hydrogen bonded to the ether oxygen groups present in the PTHF, PVME and PVEE polymers.\(^{11}\) The relatively large downfield frequency shift of this band from that of the "free" hydroxyl band (\( \Delta \nu \approx 400 \text{ cm}^{-1} \)) indicates that the hydroxyl-ether oxygen interaction has a much stronger hydrogen bond than the average hydroxyl-hydroxyl interaction (\( \Delta \nu \approx 125 \text{ cm}^{-1} \)). However, in the case of the PVBE blend there is no discernable difference between the blend spectrum in the hydroxyl region and that of pure TFE-alt-HFIPVE. Here we can infer that there is an absence of any hydroxyl-ether oxygen hydrogen bonding interactions and that the two polymers essentially exist in separate phases.
TFE-\textit{alt}-HFIPVE/Polyether Blends

1:4 Molar

\textbf{Figure 4.4} Infrared spectra of 1:4 molar TFE-\textit{alt}-HFIPVE blends with PVME, PVEE, PVBE and PTHF recorded at room temperature in the region 3000-3700 cm$^{-1}$.
Accordingly, it is also possible to conclude that the hydroxyl group of pure TFE-\textit{alt}-HFIPVE does not significantly interact with the ether oxygen atoms present in the HFIPVE side group.

A simple space-filling model of a capped unit of TFE-\textit{alt}-HFIPVE is shown in Figure 4.5. Accepting that this is only a crude visualization of the configuration of a TFE-\textit{alt}-HFIPVE segment, it is nonetheless intuitively obvious that steric shielding caused by the relatively large fluorine atoms in both the CF$_2$ and CF$_3$ groups could prevent the hydroxyl group of one HFIPVE unit from forming a hydrogen bond with either of the ether oxygen atoms of another HFIPVE unit. In any event, it is fortunate hydroxyl-ether oxygen hydrogen bonding interactions are not significant when describing the self-association of TFE-\textit{alt}-HFIPVE.

### 4.4 Miscibility Map Simulations for TFE-\textit{alt}-HFIPVE Blends

In previous work involving the HFIP moiety\textsuperscript{9} it was established from infrared studies of the model compound 1,1-di(trifluoromethyl)-pentane-1-ol (HFMP), standard self-association equilibrium constant values of $K_{2}^{\text{Std}} = 5.0$ and $K_{B}^{\text{Std}} = 11.2$ dimensionless units (at 25°C, scaled to a reference volume of 100 cm$^3$/mol). HFMP is an appropriate model for the TFE-\textit{alt}-HFIPVE copolymer. Moreover, standard inter-association equilibrium constants, $K_{A}^{\text{Std}}$, for the hydrogen bonding interactions between the HFIP hydroxyl group and the carbonyl groups of acetoxy and methacrylate groups were determined to have values of 22.2 and 11.7 dimensionless units.\textsuperscript{11} In Chapter 3 modifications to the original Macintosh computer program (referred to as “Phase Calculator”) written by Dr. J. Graf were described. Using equilibrium constants obtained from appropriate low molar mass mixtures it was shown that the hydrogen bonding contribution to the free energy of mixing of analogous polymer blends could be determined after due consideration had been taken of factors attributed to chain connectivity.
Model Unit of TFE-\textit{alt}-HFIPVE

\textbf{Figure 4.5} Space filling model of the TFE-\textit{alt}-HFIPVE unit.
The equations used to calculate the overall free energy of mixing for hydrogen bonded polymer blends, taking into account such factors as intramolecular screening, functional accessibility, chain architecture etc., have been described in this thesis. To predict miscibility maps for TFE-\textit{alt}-HFIPVE blends it is necessary to input molar volume and solubility parameter values for an average repeating unit that contains one HFIP moiety. Using group contributions\textsuperscript{1,9,11} the molar volume of the TFE-\textit{alt}-HFIPVE segment is estimated to be 225 cm\textsuperscript{3} mol\textsuperscript{-1} and the solubility parameter 7.0 (cal cm\textsuperscript{-3})\textsuperscript{0.5}. Armed with these values, together with the value for the intermolecular screening parameter, $\gamma = 0.3$\textsuperscript{6,7} and the appropriate molar volume and solubility parameter values of the segments of the other (co)polymer components in the blends,\textsuperscript{11} a prediction of the miscibility maps for TFE-\textit{alt}-HFIPVE blends can be made.

4.4.1 Ethylene-co-Vinyl Acetate Blends

Figure 4.6 summarizes the results of spinodal phase behavior calculations performed at 25°C for TFE-\textit{alt}-HFIPVE blends with a series of ethylene-co-vinyl acetate (EVA) copolymers starting at poly(vinyl acetate) (PVAc—0% ethylene) and progressing through the series of EVA copolymers of decreasing ethylene content to polyethylene (PE—100% ethylene). The filled circles, which were calculated using the initial estimate of the solubility parameter for TFE-\textit{alt}-HFIPVE blends of $\delta = 7.0$ (cal cm\textsuperscript{-3})\textsuperscript{0.5}, will be considered first. To reiterate, a miscible system is defined as one that is a single phase over the whole blend composition range. As seen in Figure 4.6 miscible TFE-\textit{alt}-HFIPVE blends are predicted for EVA copolymers containing approximately 40-70% vinyl acetate (VAc). While the calculations suggest that TFE-\textit{alt}-HFIPVE rich blends with VAc rich EVA copolymers may be single phase, the range of two phase blend compositions would be predicted to be much larger had binodal phase diagrams been calculated.
TFE-HFIPVE Blends with EVA at 25°C

\[
\begin{align*}
K_2^{\text{Std}} &= 5.0 \\
K_B^{\text{Std}} &= 11.2 \\
K_A^{\text{Std}} &= 22.2 \\
\gamma &= 0.3
\end{align*}
\]

One Phase

Figure 4.6 Predicted miscibility window for TFE-\textit{alt}-HFIPVE blends with EVA
In order to determine just how sensitive the predictions of miscibility are to the value of the TFE-\textit{alt}-HFIPVE solubility parameter employed, calculations were also performed at $\delta = 7.2$ and 6.8 (cal cm$^{-3}$)$^{0.5}$, denoted by the open circles and squares, respectively. At $\delta = 7.2$ (cal cm$^{-3}$)$^{0.5}$ the "miscibility window opens" for EVA copolymers to about 30-80% VAc (20-70% ethylene), while at $\delta = 6.8$ (cal cm$^{-3}$)$^{0.5}$ it "closes" to approximately 45-55% VAc. In the forthcoming experimental studies with PVAc, EVA[70] and EVA[40] one might anticipate from these relatively crude predictions that only EVA[70] has a good chance of being truly miscible.

### 4.4.2 Poly(n-Alkyl Methacrylate) Blends

Figure 4.7 summarizes the results of spinodal phase behavior calculations performed at 25°C for TFE-\textit{alt}-HFIPVE blends with a homologous series of poly(n-alkyl methacrylates (PAMA) starting at poly(methyl methacrylate) (PMMA—0 methylenes) and progressing through the series of PAMA polymers with increasing numbers of methylenes in the PAMA side group, up to poly(n-dodecyl methacrylate) (PDoMA—10 methylenes). Again the filled circles are a result of the calculations using the initial estimate for the TFE-\textit{alt}-HFIPVE solubility parameter of $\delta = 7.0$ (cal cm$^{-3}$)$^{0.5}$. Only poly(n-butyl methacrylate) (PBMA) and poly(n-pentyl methacrylate) (PPeMA) are predicted to be potentially miscible. In actual fact, the calculations are so sensitive to the value of the TFE-\textit{alt}-HFIPVE solubility parameter used that any predictions of miscibility that prove correct should be considered simply fortuitous. At $\delta = 7.2$ (cal cm$^{-3}$)$^{0.5}$ the "miscibility window opens" and PAMA homopolymers from poly(ethyl methacrylate) (PEMA) to poly(septyl methacrylate) are predicted to be miscible. In marked contrast, calculations (not shown) using a value of $\delta = 6.8$ (cal cm$^{-3}$)$^{0.5}$ predict that none of the PAMA polymers are miscible with TFE-\textit{alt}-HFIPVE and in fact are grossly phase separated!
TFE-HFIPVE Blends with PAMA at 25°C

\[ K_2^{\text{Std}} = 5.0 \quad K_B^{\text{Std}} = 11.2 \quad K_A^{\text{Std}} = 11.7 \quad \gamma = 0.3 \]

Figure 4.7 Predicted miscibility window for TFE-alt-HFIPVE blends with a homologous series of poly(\(n\)-alkyl methacrylates) at 25°C.
This is not promising, in that if the initial estimate of the solubility parameter of TFE-\textit{alt}-HFIPVE is reasonably accurate ($\delta = 7.0 \text{ (cal cm}^3\text{)^{0.5}}$), then this would predict that only PBMA has a chance of being truly miscible.

### 4.5 Infrared and Thermal Studies of TFE-\textit{alt}-HFIPVE Blends

#### 4.5.1 Ethylene-co-Vinyl Acetate Blends

Figure 4.8 shows the infrared spectra of 4:1 molar TFE-\textit{alt}-HFIPVE blends with PVAc and the EVA copolymers recorded at room temperature in the carbonyl stretching region. Two characteristic bands are plainly observed, attributed to "free" (non-hydrogen bonded) acetoxy carbonyl groups at $\approx 1740 \text{ cm}^{-1}$ and carbonyl groups that are hydrogen bonded to HFIP hydroxyl groups at $\approx 1715 \text{ cm}^{-1}$. The obvious presence of a notable fraction of hydrogen bonded carbonyl groups indicates that significant molecular mixing has occurred, but it does not prove the system is single phase. It is important to recognize that an immiscible blend may be composed of two distinct phases of different blend compositions yielding an aggregate fraction of hydrogen bonded carbonyls at equilibrium. If the spectra shown in Figure 4.8 are curve resolved using established methodology$^{1,2,12}$ (see example in Figure 4.9) taking into account the differences in absorptivity of the "free" and hydrogen bonded bands ($a_R = 1.41$)$^{1,2,11}$ values of 0.48, 0.57 and 0.49 are obtained for the fraction of hydrogen bonded carbonyl groups in the 4:1 molar blends of TFE-\textit{alt}-HFIPVE with PVAc, EVA[70] and EVA[40], respectively. Now these experimental values can be compared to those calculated assuming a completely miscible blend system.
TFE-\textit{alt}-HFIPVE Blends with EVA at 25°C

4:1 Molar

![Infrared spectra of 4:1 molar TFE-\textit{alt}-HFIPVE blends with PVAc, EVA[70] and EVA[40] recorded at room temperature in the carbonyl stretching region from 1600-1850 cm\textsuperscript{-1}.]

\textbf{Figure 4.8} Infrared spectra of 4:1 molar TFE-\textit{alt}-HFIPVE blends with PVAc, EVA[70] and EVA[40] recorded at room temperature in the carbonyl stretching region from 1600-1850 cm\textsuperscript{-1}. 
Figure 4.9  An example of curve fitting using the infrared spectrum of the 4:1 molar TFE-alt-HFIPVE blend with EVA[70].
Employing the appropriate values of the molar volumes and standard self-association and interassociation equilibrium constants, the fraction of hydrogen bonded carbonyl groups in a single phase system can be readily calculated as a function of blend composition using the modified Phase Calculator program discussed in Chapter 3. Figure 4.10 shows the results of such a calculation. There are subtle differences in the curves for the different blends, primarily reflecting the differences in molar volume of the average repeat units of the acetoxy containing (co)polymers, but to all extent and purpose, under equilibrium conditions, ≈ 60% of the acetoxy carbonyl groups should be hydrogen bonded in truly miscible 4:1 TFE-alt-HFIPVE blends with PVAc, EVA[70] and EVA[40] at 25°C. Thus it can be concluded that the TFE-alt-HFIPVE blends with PVAc, and EVA[40] are well mixed, but phase separated (the experimental values of the fraction of hydrogen bonded carbonyl groups, 0.48 and 0.49, respectively, are outside the 10% range of maximum estimated error in measurement.) In the case of the TFE-alt-HFIPVE blends with EVA[70], the experimental value of the fraction of hydrogen bonded carbonyl groups is close to the theoretical value, 0.57 vs. 0.60. This is within the error limits and one would have to conclude that the blend is a single phase or, at least, very close to it.

Thermal analysis of a 50:50 wt % TFE-alt-HFIPVE blends with EVA[70] reveals single glass transition temperature, \( T_g \), of -7°C, intermediate between that of pure EVA[70] \( (T_g = -15°C) \) and pure TFE-alt-HFIPVE \( (T_g = 12°C) \). This result (Figure 4.11), together with the optical clarity of the film, is strong evidence for a single phase system, which is consistent with the infrared data.

In the case of the PVAc blend, however, the conclusion is not so clear cut. The DSC thermogram reveals that there is again only a single \( T_g \) at ≈ 31°C, intermediate between that of pure PVAc \( (T_g = 43°C) \) and pure TFE-alt-HFIPVE \( (T_g = 12°C) \).
Figure 4.10 Theoretically calculated fraction of hydrogen bonded carbonyl groups in single phase mixtures as a function of blend composition at 25°C for TFE-alt-HFIPVE blends with PVAc, EVA[70] and EVA[40].
Figure 4.11  DSC thermograms of 50:50 TFE-\textit{alt}-HFIPVE blends with PVAc, EVA[70] and EVA[40], together with those of the pure materials.
For many working in the field this would normally be enough to conclude that the blend system is miscible (single phase). But the infrared results clearly indicate that while the system is highly mixed it exists in two phases. It is not difficult to reconcile this apparent inconsistency. Assume that the blend exists in two phases with compositions that are reasonably close to each another (say, hypothetically, 55/45 and 45/55 A/B). The T_g's of these two individual phases would not be very different, and consequently, what would be observed in the DSC thermogram is an unresolved, relatively broad, apparently single, T_g. On the other hand, the fraction of hydrogen bonded carbonyl groups determined from the infrared experiment is very sensitive to subtle changes that exist between a truly single phase and a mixture of two phases with closely matched compositions.

The DSC scan of the TFE-alt-HFIPVE blends with EVA[40] is complicated by the presence of some polyethylene-type crystallinity observed in the thermogram at temperatures above 30°C. However, the thermogram of the 50:50 blend exhibits a broad transition at about -12°C that is intermediate between T_g's of pure EVA[40] at -24°C and TFE-alt-HFIPVE at 12°C. It is not possible to unambiguously determine whether or not there is one T_g or two T_g's contributing to this transition. Certainly the DSC results imply a significant degree of molecular mixing and this is consistent with the infrared data.

4.5.2 Poly(n-alkyl methacrylate) Blends

Figure 4.12 shows the infrared spectra of 4:1 molar TFE-alt-HFIPVE blends with PMMA, PEMA, PBMA, PHMA and PDMA recorded at room temperature in the carbonyl stretching region. Again, the two characteristic bands are observed attributed to "free" methacrylate carbonyl groups at \( \approx 1730 \text{ cm}^{-1} \), and those carbonyl groups that are hydrogen bonded to HFIP hydroxyl groups at \( \approx 1712 \text{ cm}^{-1} \).
TFE-$alt$-HFIPVE Blends with PAMA at 25$^\circ$C

Figure 4.12 Infrared spectra of 4:1 molar TFE-$alt$-HFIPVE blends with PMMA, PEMA, PBMA, PHMA, and PDMA recorded at room temperature in the carbonyl stretching region from 1600-1850 cm$^{-1}$. 
Curve resolving the spectra shown in Figure 4.12 yields values of 0.51, 0.51, 0.48, 0.28 and 0.10 for the fraction of hydrogen bonded carbonyl groups in the 4:1 molar blends of TFE-alt-HFIPVE with PMMA, PEMA, PBMA, PHMA and PDMA, respectively. Using the same procedure as described above, the theoretical fraction of hydrogen bonded carbonyl groups in truly miscible blends of TFE-alt-HFIPVE with PAMA was calculated as a function of blend composition (Figure 4.13). Under equilibrium conditions, ≈ 48% of the methacrylate carbonyl groups should be hydrogen bonded in the truly miscible 4:1 molar TFE-alt-HFIPVE blends at 25°C. Thus it can be concluded from the infrared data that the 4:1 molar TFE-alt-HFIPVE blends with PMMA, PEMA and PBMA are essentially single phase mixtures (the experimental values of the fraction of hydrogen bonded carbonyl groups, 0.51, 0.51 and 0.48, respectively, are, within error, the same as the theoretically calculated value of 0.48). In contrast, the experimental values of the fraction of hydrogen bonded carbonyl groups obtained from the spectra of the TFE-alt-HFIPVE blends with PHMA and PDMA, 0.28 and 0.10, respectively, fall far below the theoretical value for single phase systems. Accordingly, it can be confidently concluded that these two blend systems are two phase.

Thermal analyses of TFE-alt-HFIPVE blends with the different poly(n-alkyl methacrylates) were performed. For the 50:50 blends with PMMA, PEMA and PBMA single, relatively broad, T_g's were observed at 60, 45 and 20°C, respectively. These are intermediate between those of pure TFE-alt-HFIPVE (T_g = 12°C) and pure PMMA, PEMA and PBMA (T_g's = 104, 74 and 32°C, respectively). Again, strong evidence for single phase systems and consistent with the infrared data. The T_g's of TFE-alt-HFIPVE and PHMA (which appears particularly broad) overlap and it was not possible to determine whether or not one or two T_g's exist in the thermogram of the blend. However, the infrared results in this case clearly establish that TFE-alt-HFIPVE blends with PHMA are phase separated.
Figure 4.13 Theoretically calculated fraction of hydrogen bonded carbonyl groups in single phase mixtures as a function of blend composition at 25°C for TFE-\textit{alt}-HFIPVE blends with PMMA, PEMA, PBMA and PHMA.
4.5.3 Polyether Blends

For completeness, we now return to Figure 4.4, which shows the infrared spectra in the hydroxyl stretching region of 1:4 molar TFE-\textit{alt}-HFIPVE blends with various polyethers recorded at room temperature. Here, unlike the carbonyl stretching region of the spectrum, it is unfortunately not possible to compare the theoretical fraction of hydroxyl-ether hydrogen bonds formed in a miscible blend system with an experimental value derived from the hydroxyl stretching region. A value for the interassociation equilibrium constant that describes hydrogen bond formation between HFIP hydroxyls and ether oxygen atoms is not available. But even if a value of $K_A^{\text{Std.}}$ existed, the hydroxyl stretching region is too complex\textsuperscript{1,2} and not appropriate for the quantitative determination of the fraction of hydrogen bonded ethers. Accordingly, only qualitative judgements can be made as to whether or not a particular TFE-\textit{alt}-HFIPVE blend with a polyether is potentially miscible, well mixed or obviously grossly phase separated. Looking at Figure 4.4, we can confidently state that TFE-\textit{alt}-HFIPVE blends with PVBE (and PVPE, the spectrum of which looks identical to PVBE and is not shown) are grossly phase separated (there is no significant difference between these spectra and that of pure TFE-\textit{alt}-HFIPVE). On the other hand, the spectra of the 1:4 molar TFE-\textit{alt}-HFIPVE blends with PVME, PVEE and PTHF display a large contribution from a hydrogen bonded hydroxyl stretching band centered at $\approx 3210$ cm$^{-1}$, a band that can be unambiguously attributed to HFIP hydroxyl groups that are hydrogen bonded to ether oxygen atoms. It can be confidently stated from the infrared data that these blends are highly mixed at the molecular level with a high probability that they are truly miscible. Thermal analyses of the blends are consistent with the infrared results, with single $T_g$'s observed for the 50:50 TFE-\textit{alt}-HFIPVE blends with PVME, PVEE and PTHF, and two $T_g$'s for the blends with PVPE and PVBE (see Figure 4.14 for representative examples).
Figure 4.14 DSC thermograms of 50:50 TFE-\textit{alt}-HFIPVE blends with PVME and PVBE, together with those of the pure materials.
Why the TFE-\textit{alt}-HFIPVE blends with PVPE and PVBE are grossly phase separated is not completely understood. If reasonable values of $K_{\text{Std.}}^A$ are assumed\textsuperscript{17} and miscibility maps calculated similar to those shown in Figures 4.6 and 4.7, consistently single phase systems are predicted. It is thought that there maybe a functional group accessibility problem in forming a hydrogen bond with poly(vinyl alkyl ethers) when the side group exceeds two carbons. It was noted in the beginning of this section that the ether oxygen atoms of pure TFE-\textit{alt}-HFIPVE are effectively shielded from forming a hydrogen bond with the HFIP hydroxyl group and it is possible that similar shielding is occurring in the case of poly($n$-propyl vinyl ether) and the higher homologues. But this is speculation and further work will be necessary to resolve this apparent anomaly.

### 4.6 Conclusions

In summarizing the results of the infrared and thermal analysis studies of the TFE-\textit{alt}-HFIPVE blends it can be confidently concluded that miscible systems are formed at ambient temperature with PMMA, PEMA, PBMA, EVA\textsuperscript{[70]}, PVME and PVEE. Blends with PVAc and EVA\textsuperscript{[40]} are well mixed at the molecular level, but exist as two phase systems. The PVPE and PVBE blends are grossly phase separated.
4.7 References


CHAPTER 5
CONCLUSION AND FUTURE WORK

5.1 Conclusions

The overall objective of the research presented in this thesis was to better understand the factors that affect miscibility in hydrogen bonded polymer blends. This increased understanding would allow us to make more accurate predictions of miscibility. In the course of this research, polyphosphazenes blends were explored for there was little known about their phase behavior. Several blends with poly(butyl methacrylate-co-4 vinyl phenol) were found to be miscible and the phase behavior of poly(bis(n-alkoxy) phosphazene) was found to be similar to that of analogous poly(vinyl n-alkyl ethers). Blends of polyphosphazenes with polyurethanes produced a modest increase in the flame resistance. The phase behavior of hydrogen bonded polymer blends can be successfully predicted using equilibrium constants determined from appropriate low molar mass analogs if intramolecular screening and functional group accessibility effects are included. This is an important discovery for the prediction of polymer blends because it permits the use of equilibrium constants derived from analogous small molecules. Finally, infrared and thermal analysis studies of poly(tetrafluoroethylene-alt-hexafluoroisopropanol vinyl ether) (TFE-alt-HFIPVE) blends showed that a number of miscible systems are formed at ambient temperature. The results were reasonably consistent with the predictions made, reinforced using equilibrium constants derived from low molecular mass analogues.

5.2 Future Work

The experimental values of the self-association equilibrium constants obtained for butylmethacrylate-co-vinyl phenol (BMAVPh) copolymers remains poorly understood. Since intramolecular screening, a significant factor in determining the number of hydrogen bonds formed in miscible polymer blends is not applicable in the case of pure copolymers
containing multifunctional groups, other screening factors must be involved that reduce the number of phenolic ester hydrogen bonds. It is suggested for future work that a similar methodology to that employed by Pehlert\textsuperscript{1} be used to study the functional group accessibility in multifunctional copolymers. A future researcher might study terpolymers with varying concentrations of an inert diluent to determine the effect of “spacing” upon the measured equilibrium constants. From this a mathematical relationship may be obtained which could be implemented into the phase calculator program. The goal being a program that could be made to predict the miscibility of complex multifunctional copolymer blends.

5.3 Reference

Kevin Guigley was born in Reading, Pennsylvania on April 3, 1970. After graduating from Emmaus High School in May 1988, he attended the Pennsylvania State University at University Park, PA. There he graduated with two simultaneous B.S.’s in Chemistry and Polymer Science and Engineering in May 1992. In the summer of 1992, he began his master studies at the University of Illinois at Urbana-Champaign in the Department of Chemistry. After receiving his M.S. in Chemistry in December 1994, he began his doctoral studies at the Pennsylvania State University in the Department of Materials Science and Engineering specializing in Polymer Science and Engineering.