Miscibility Study of Poly(vinyl pyrrolidone)/Poly(vinyl butyral) Blends

by

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A thesis submitted to the Faculty of Graduate Studies and Research in Partial fulfillment of the requirements for the degree of
Master of Science

November 1991
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Montreal, Quebec, Canada

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Abstract

The miscibility of poly(vinyl pyrrolidone) PVP with copolymers of vinyl butyral and vinyl alcohol, containing 11% and 19% by weight of vinyl alcohol, has been investigated. To examine how the state of miscibility of these blends varies with the vinyl alcohol content of the copolymers, differential scanning calorimetry (DSC) and solid-state NMR methods were employed. PVP was found to form miscible blends with poly(vinyl butyral) PVB, containing 11 wt% of vinyl alcohol, up to a weight ratio of 40/60(PVP/PVB11). At higher PVP loading, phase separated blends were obtained. In contrast, poly(vinyl butyral) containing 19 wt% vinyl alcohol units was found to be miscible with PVP, over the entire composition range, with an estimated domain size of 2.5 nm. Taken together, the results indicate the importance of the number of hydroxyl groups in achieving miscibility.
Resumé

La miscibilité du poly(vinyl pyrrolidone) PVP avec des copolymères de vinyl butyral et d'alcool vinyle, contenant 11% et 19% en poids d'alcool vinyle, fut étudiée. Pour examiner la variation de l'état de miscibilité de ces mélanges par rapport au contenu d'alcool vinyle des copolymères, des méthodes comme l'enthalpie différentielle et la RMN à l'état solide furent utilisées. Il fut démontré que le PVP forme des mélanges miscibles avec le poly(vinyl butyral) PYB contenant 11%(p/p) d'alcool vinyle, jusqu'à un rapport de 40/60 en poids (PVP/PYB). Au-delà de ce rapport, des mélanges à phases séparées furent obtenus. Par contre, le PVB contenant 19%(p/p) d'alcool vinyle fut trouvé miscible avec le PVP en tout rapport, avec des domaines d'environ 2.5nm. Dans l'ensemble, les résultats ont montré l'importance des groupements hydroxyles pour effectuer cette miscibilité.
Foreword

Polymer-polymer miscibility has attracted the attention of both industrial and academic groups, partly because its potential for providing materials with tailored properties at much cheaper rates than other known procedures, and also because the challenge of understanding why certain polymer pairs form miscible blends while others are immiscible. The work described in this thesis is aimed at elucidating certain aspects of the effects of strong molecular interactions on the phase behavior of polymer blends, and focuses mainly on the effect of the number of interacting groups on miscibility.

The text is divided into four chapters and one appendix. In chapter 1, a general introduction to the subject of polymer-polymer miscibility is given, with special emphasis on the role of specific interactions in achieving miscibility. A discussion on the scope and aims of the work closes the chapter. In chapter 2, a description of the methods and materials used in the thesis is presented. The results are displayed in chapter 3 and discussed, while in chapter 4, some concluding remarks and suggestions for further studies are presented. The thesis concludes with appendix containing the data obtained from differential scanning calorimetry and solid-state NMR techniques.
Acknowledgements

I wish to express my sincere gratitude to Dr. R. St. John Manley for his expert guidance and advice in the course of this work and in the preparation of the thesis.

I also wish to thank the following individuals and institutions:

- Dr. F. Morin for instruction of the use of the solid-state NMR spectrometer.
- Dr. M. Kamal for allowing me to use his DSC-7 calorimeter.
- Dr. T. Kimura for valuable discussions on many aspects of NMR.
- Mr. J-N. Destiné for translating the thesis abstract.
- Mr. A. Parent (Monsanto Canada) for supplying the poly(vinyl butyral) samples.
- Dept. of Chemistry, McGill, for teaching assistantship in 1989 - 1990.
- Pulp and Paper Research Institute of Canada for laboratory accommodation and use of the facilities.
- All my friends in both Otto Mass and Pulp &Paper buildings for making my stay unforgettable.
- Last but not the least, I would like to thank my wife Asha and my children: Mahdi, Muna, and Magan for their patience and understanding.
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Chapter 1

General Introduction
1.1 General remarks

When two polymers A and B are mixed, the resulting physical mixture is called a polymer blend. This mixture is characterized as miscible or immiscible depending whether it exhibits a single homogeneous phase or multicomponent phase behavior. However, many polymers may show partial miscibility, i.e. a variation in miscibility with temperature. Low molecular weight polymers are typically more miscible at higher temperatures and may phase separate on cooling, showing upper critical solution behavior (UCST). Higher molecular weight polymers, which form homogenous mixtures, are typically less miscible at higher temperatures and may phase separate on heating, showing lower critical solution behavior (LCST). Such partial miscibility behavior will be discussed later (see section 1.3).

Mixing of two polymeric components to average or improve their material properties is not new. About a century ago Thomas Hancock mixed natural rubber with gutta percha, in order to obtain materials suitable for waterproofing (1). What is new is the realization that mixing of two polymeric components is the easiest and probably the cheapest way of obtaining materials that satisfy certain demands. Other alternatives, such as, copolymerisation, are known to be expensive both in terms of the capital and the time involved in developing new synthetic procedures. Thus polymer blending has become a very important field in polymer science and engineering. However, for successful blend technology, it is of paramount importance that it be based on a sound scientific basis. This has led to attempts to predict the properties of the resulting polymer blends from the knowledge of the properties of the constituent polymers. Some insights have already been gained and further progress both in theory and application is expected.

It was, historically, believed that polymeric mixtures are generally immiscible, and miscibility of these systems was considered a mere happenstance. However, it is becoming increasingly evident that numerous miscible pairs exist (1-7). This rapid growth, in the
number of miscible polymer-polymer systems, is mainly due to the recognition of certain fundamental thermodynamic and chemical concepts (see section 1.2).

Although the usefulness of a polymer blend does not necessarily require that the system be miscible, it is generally observed that in immiscible systems, the interface between the components is often weak when they are in comparable concentrations in the blend. Therefore these systems have maximum utility when one component is the matrix and the other component is finely dispersed in it; as found, for example, in high impact polystyrene (HIPS) where typically the rubber content is about 8% (8). In contrast, miscible polymer blends offer a latitude of intermediate, if not sometimes better, properties over the whole composition range. This is, in part, the reason behind the interest in searching for new miscible polymer blends.

Since the subject of polymer-polymer miscibility is treated in various books and reviews (1-7), no attempt will be made here to give a thorough examination of all aspects of the subject; however an introductory account of the thermodynamic basis of miscibility will be given, highlighting the importance of specific interactions. Similarly brief notes on some criteria and methods used in characterizing polymer-polymer miscibility will be presented. Finally, the scope and aims of this work will be discussed.
1.2 Basic thermodynamic aspects

Polymer-polymer miscibility, as defined in section 1.1, implies the establishment of thermodynamic equilibrium and the presence of a single homogeneous phase. From the second law of thermodynamics, in the absence of external forces other than the normal pressure, two liquids will mix spontaneously and form a single homogeneous phase, if the free energy of mixing is negative, i.e., $\Delta G_m < 0$. This is a necessary but not sufficient condition for the formation of a homogeneous and stable phase over the whole composition range. The necessary condition for a homogeneous phase to be stable at fixed temperature and pressure is:

$$\langle \delta^2 \Delta G_m/\delta^2 \varphi_2 \rangle_{P,T} > 0$$

1.1

The significance of this condition can be illustrated graphically as shown in figure 1.1, where two typically possible $\Delta G_m /$ composition curves are schematically drawn. In both curves the free energy of mixing is negative over the entire composition range and the first condition of $\Delta G_m < 0$ is satisfied. In curve A, however, there are compositions whose free energy is less negative than the rest. For example, the mixture with the composition corresponding to point x will separate into two phases, with compositions corresponding to the two minima at $\varphi_{2c}$ and $\varphi_{2d}$, to minimize the free energy of the system. On the contrary, in curve B, the free energy curve is concave upward over the entire composition range, and the components are miscible in all proportions; and the stability condition is satisfied.

The free energy of mixing is related to the enthalpy and entropy of mixing as follows:

$$\Delta G_m = \Delta H_m - T \Delta S_m$$

1.2

where $\Delta H_m$ is the enthalpy and $\Delta S_m$ is the entropy of mixing, and $T$ is the absolute temperature. In order to obtain analytical expressions of the enthalpic and entropic terms of
Figure 1.1: Two possible free energy of mixing diagrams for binary mixtures.
the free energy of mixing, theories have been developed. The simplest and most often used model for this purpose is the Flory-Huggins (FH) lattice theory of polymer solutions (9, 10) extended by Scott (11) and Tompa (12) to encompass polymer binary mixtures.

In its original form, the FH model included several assumptions, some of which were relaxed later in the development of the equation of state theories. The main assumptions were as follows:

1) there is no volume change upon mixing, i.e. \( \Delta V_m = 0 \).
2) mixing was assumed random, i.e. no preferential organization of different molecules was allowed. This assumption was invoked to simplify the calculation of the combinatorial entropy of mixing; and limits the applicability of the model to concentrated solutions.
3) the total entropy of mixing can be equated to the combinatorial entropy, i.e., the number of different ways of placing the molecules in the sites of the lattice.
4) the enthalpy of mixing is assumed to be proportional to the energy \( \Delta w_{12} \) associated with creating a new contact of the type 1-2 between segments of component 1 and segments of component 2. It is also assumed that this energy is approximated by the geometric mean of the energies associated with breaking contacts \( w_{11} \) and \( w_{22} \) between the segments of pure components.

According to Tompa (12) and by Patterson (13) the combinatorial entropy of mixing per unit volume of mixture of the two polymeric components is given by:

\[
\Delta S_m / RV = -[(\varphi_1 \ln \varphi_1 / v_1) + (\varphi_2 \ln \varphi_2 / v_2)]
\]

where \( R \) is the gas constant, \( \varphi_i \) and \( v_i \) are volume fractions and molar volumes of the components of the mixture respectively, while \( V \) is the total volume of the mixture. For high molecular weight polymeric mixtures, the molar volumes of the components are very large and in consequence the quantities under parentheses are vanishingly small. The negative value of \( \Delta G_m \) required for miscibility can only come from the enthalpy of mixing.
The enthalpic contribution to the free energy of mixing per unit volume of mixture, computed under the geometric mean assumption, is given by:

\[ \Delta H_m / RTV = (z \Delta w_{12} / kT \nu_1) = (\chi_{12} / \nu_1) \varphi_1 \varphi_2 \]  

where \( z \) is the lattice coordination number corresponding to the number of nearest neighbors to a given segment; \( k \) is the Boltzmann constant; \( \Delta w_{12} \) is the interaction exchange energy; \( \chi_{12} \) is the interaction parameter as defined by Flory:

\[ \chi_{12} = z \Delta w_{12} / kT \]

Recombining equations (1.3) and (1.4) according to equation (1.2) yields the free energy of mixing per unit volume of the mixture:

\[ \Delta G_m / RTV = \left[ \left( \varphi_1 L_1 \varphi_1 \right) / \nu_1 + \left( \varphi_2 L_2 \varphi_2 \right) / \nu_2 + \left( \chi_{12} / \nu_1 \right) \varphi_1 \varphi_2 \right] \]

the first two terms above are due the combinatorial entropy of mixing and as discussed previously are of negligible importance in high molecular weight polymer mixtures and may be approximated to zero. Therefore the free energy of mixing in this case is governed by the heat of mixing term such that:

\[ \Delta G_m / RTV = (\chi_{12} / \nu_1) \varphi_1 \varphi_2 \]  

The sign and the magnitude of the free energy of mixing will depend on the enthalpy of mixing and thus on the type and strength of the interactions between the segments of the two polymeric components. For non-\( \chi \)lar polymeric mixtures where the interaction between segments are of the dispersive type (Van der Waals), the heat of mixing is always positive as given by the solubility parameter model of Hildebrand (14):

\[ \Delta H_m / V = \varphi_1 \varphi (\delta_1 - \delta_2)^2 \]

where \( \delta_i \) are the solubility parameters of the components of the mixture.
As can be seen from equation (1.8), the solubility parameter model can only account for positive, or at best, zero heats of mixing and thus positive free energy of mixing unfavorable for miscibility. When this model is used to predict the state of miscibility of polymer pairs, the polymer components are chosen such that the difference in their solubility parameters is minimum, giving zero heat of mixing. Fortunately, the segmental interactions between two polymers need not be only via dispersive interactions. The components of the mixture can interact via "specific interactions".

By specific interaction, we mean all intermolecular forces which are stronger than the usual dispersive forces but have lesser strength than covalent chemical bonds. They include such intermolecular forces as dipole-dipole, hydrogen-bonding, ion-ion, charge-transfer and acid-base interactions. For polymeric mixtures whose components can interact via one of these interactions, miscibility may be expected. This calls for structural dissimilarity between the component polymers as a prerequisite for miscibility.

From these thermodynamic considerations, we may conclude that miscibility can be expected in two situations:

1) for polymeric mixtures whose components interact via dispersive forces, but their molecular weights are so low such that the combinatorial entropy becomes nonnegligible and may override the positive enthalpy of mixing. This type of miscibility will depend strongly on the molecular weight of the component polymers.

2) miscibility can also be expected if the polymer pair interacts via specific interactions. In this case the miscibility is enthalpy driven and its molecular weight dependence can be considered secondary.

Although the above conclusions may be considered general in scope, there are situations where in the absence of specific interactions between the component polymers, miscibility can still be observed. The most widely studied cases are copolymer/homopolymer and copolymer/copolymer blends. This type of miscibility is known as a "copolymer effect". If a random copolymer A-B is mixed with homopolymer C, it is possible to obtain miscible
and immiscible blends by varying the comonomer ratio in the copolymer. It must also be noted that, what makes this effect seem peculiar is the fact that neither homopolymer A nor homopolymer B need be miscible with C.

There are two opposing views as to the origin of this phenomenon, especially when a recognizable weak interaction is present. The first (15,16,17) is based on the dilution of the intramolecular repulsive interaction forces of the comonomers (positive and unfavorable to mixing) by the presence of the other component, making the overall interaction parameter negative in certain ranges of copolymer composition, as required by the thermodynamics of mixing. The second view (18, 19) is based on the presence of both dispersive and weak specific forces such that at certain copolymer compositions the contribution of the dispersive forces becomes less important, resulting an overall negative interaction parameter.

The proponents of the first view approach the problem via what they call the "binary interaction model" based on the repulsion of comonomer segments in the copolymer. According to this model the heat of mixing per monomer unit calculated for a binary mixture of A-B copolymer and C homopolymer, is given:

\[
\Delta H_m = \phi_{ac} \phi_c \chi_{blend} k T
\]

\[
\chi_{blend} = \phi_a \chi_{ac} + \phi_b \chi_{bc} - \phi_a \phi_b \chi_{ab}
\]

where \(\phi_c\) is the volume fraction of the homopolymer C and \(\phi_{ab}\) is the volume fraction of the copolymer A-B, and \(\phi_a = 1 - \phi_b\) is the volume fraction of comonomer A in copolymer A-B, \(\chi_{ij}\) are the usual FH interaction parameters for ac, bc, and ab monomer-monomer interactions, \(k\) is the Boltzmann constant, and \(T\) is the absolute temperature.

If we consider the case where all \(\chi_{ij}\) parameters are positive, i.e when the heat of mixing of the binaries: A-B, A-C, B-C are positive, the condition for \(\chi_{blend}\) in equation (1.9) and the heat of mixing of the blend to become negative is given by the following inequality.
\[ \chi_{ab} > (\chi_{ac}^{0.5} + \chi_{bc}^{0.5})^2 \]

This signifies that miscible blends of the copolymer A-B and the homopolymer C are likely to form as long as the above inequality is satisfied.

The proponents of the second view suggest that it is not necessary to have recourse to the intramolecular repulsion to explain the effect, but rather base their argument on the fact that the solubility parameter of the copolymer varies linearly with copolymer composition, thus inevitably there will be certain copolymer ratios where the copolymer solubility parameter will match that of the other component. In addition, the presence of even very weak specific interactions will expand the limits of miscibility resulting in the "miscibility window" often observed in this type of systems; using this simple approach, Coleman et al.(19), predicted very well the window of miscibility observed for some systems whose miscibility behavior had previously been explained via the binary interaction model. On this second view, the presence of weak specific interactions offers some tolerance to the unfavorable dispersive interactions which could have led to immiscibility. Actually the argument revolves now on the miscibility of PVC/PE-PVAc blends. The proponents of the first view claim that PVC is immiscible with PVAc(20), while the second group suggest that it is miscible(21) and ascribe the window of miscibility observed for the system to the presence of the increasing number of PVAc units in the copolymer.
1.3 Effect of Temperature on Miscibility

The miscibility of polymeric mixtures varies with temperature. It has been observed (22) that when a miscible polymer blend is heated, it becomes immiscible at a certain temperature. This temperature is called the lower critical solution temperature (LCST). It has also been observed that another critical temperature occurs when some miscible low molecular weight blends are cooled to lower temperatures. The temperature at which this occurs is called the upper critical solution temperature (UCST), because it is the temperature below which the system phase separates and remains immiscible.

These critical temperatures were known to occur in small molecule mixtures (23) and in polymer-solvent systems (24, 25). The upper critical solution temperature (UCST) can be predicted by the FH lattice model via the inverse temperature dependence of the interaction parameter as given by equation (1.5). The miscibility becomes poorer due to the increase of the interaction parameter, as the temperature is lowered. Though it may be predicted, the UCST is not often observed in polymeric mixtures, except for low molecular weight blends. This may be due to the glassy nature and the often associated high viscosities of the polymeric systems below their glass transition temperatures. The effect of the viscosity is important inasmuch as the process of phase separation involves material transport from one phase to another.

The phase separation upon heating can not be accounted for by the FH model in its original form neither in polymer-solvent nor in polymer-polymer systems, therefore more rigorous theories were required. This inspired Flory and coworkers (26-28), Patterson and coworkers (29) and later Sanchez and Lacombe (30), to develop more complex theories known as equation-of-state theories. The details of these theories can be found in the original literature, or any one of the following references (2, 31) and will not be discussed here, but a cursory note on how they explain the LCST phenomenon will be given.
According to the equation of state theories the free energy of mixing of two polymers or a polymer and a solvent can be analysed in terms of three contributions: combinatorial entropy of mixing, an interactional energy term and free volume term. The combinatorial entropy is used as calculated by the lattice model. The free volume term arises from the difference in the thermal expansion coefficients of the component polymers. This free volume difference introduces a net contraction in the volume of the mixture ($\Delta v_m < 0$), which in turn causes a decrease in the entropy and enthalpy of mixing. The net contribution of the free volume term to the free energy of mixing is positive and unfavorable to mixing.

The interactional term is associated with interaction forces involved between the components. These forces can be of the dispersive type making the interactional term positive and unfavorable to mixing, or they can be specific interactions resulting in a negative interaction term favorable to mixing.

The free volume difference of the components increases as the temperature is raised, so does its contribution to the free energy of mixing; Thus the free volume term is always positive and opposes miscibility. As far as the interactional term is concerned, its trend with the temperature depends on the type of the interaction forces involved. If the interaction is of the dispersive type, its contribution becomes less positive by increasing the temperature, while if the interaction is of the specific interaction type, its contribution becomes less negative and unfavorable to mixing.

As mentioned previously, the combinatorial entropy of mixing, for high molecular weight polymeric mixtures, is vanishingly small and does not play any appreciable role in the miscibility in this case. The interactional term, for a miscible polymer-polymer system, is negative (exothermic) at low temperatures and outweighs the positive free volume contribution, but it becomes less negative as the temperature is raised, until at some point in the temperature scan, it will be balanced by the always positive free volume effect. This point is the LCST above which the system will remain immiscible.
Corroborating experimental evidence, in relation to the preceding theoretical discussions, has been found in a variable temperature FTIR study conducted on blends of Poly(ethylene-vinylacetate) copolymer with chlorinated Polyethylene(31). This system manifests a LCST whose location, depending on the composition, varies between 90°-120°C. The presence of hydrogen bonding interactions was deduced from the shift of the acetate carbonyl peak position detectable below 100°C. The shift of the carbonyl peak of the blends, with respect to the same peak position of the pure copolymer, reduces gradually upon heating until the LCST is reached as shown in figure 1.2. This suggests that the hydrogen bonding interactions, responsible for the miscibility of the system, are destroyed upon heating and as consequence, the always positive equation-of-state effects dominate the free energy of mixing and thus phase separation becomes inevitable.

Although the above theoretical considerations, and the accumulated experimental findings(32), will make one conclude that the LCST behavior, in miscible polymer mixtures, is a common phenomenon to be expected, its manifestation may depend on its location relative to the glass transition temperature(Tg) of the blend, and the decomposition temperature of the component polymers. Consider the case where the LCST is located below the the Tg of the blend: one will usually process the blend at temperatures higher than both Tgs(e.g Tg2>Tg1) of the component polymers, and will cool it to ambient temperature. Such a blend is in a two-phase region at processing temperature, and upon cooling passes the glass transition temperature Tg2 of the second component with the subsequent vitrification of that phase. Upon further cooling the blend will reach the LCST below which it should be a homogeneous single phase, but due to the low interdiffusion between components caused by the high viscosity of the medium the blend may remain immiscible. In such a system the LCST will not be observed although the thermodynamics of the situation allows it; and the system will be regarded as immiscible for all intents and purposes.
Figure 1.2  Variation of the carbonyl peak position as a function of temperature in ethylene/vinyl acetate copolymer(right) and in its(80:20 wt%) blend with chlorinated polyethylene(left). Dotted line shows temperature where homogeneous blend phase separates on heating. (from ref. 31)
Another situation where the LCST will not be accessible is when it lies above the decomposition temperature of the blend. This usually happens when strong specific interactions are involved because there is a correlation between the strength of the interaction and the location of the LCST. The stronger the intermolecular interactions the higher the location of the LCST(33, 34).

The presence of a LCST is usually determined optically if the constituent polymers of the blend have a difference in their index of refraction. When an initially clear film of the blend is heated, at a certain point in the temperature scan, the opacity of the film will increase due to the presence of phase separated domains. The observation of a LCST in such an experiment will depend on the wavelength of the light used, the heating rate, and the sample thickness. In the best cases, the presence of a reversible LCST can be used as evidence for thermodynamic miscibility(35).
1.4 The Role of Specific Interactions in Miscibility

As described in the preceding sections, the attainment of miscibility between two high molecular weight polymers is dependent on the presence of specific interactions between the segments of the constituent polymers in a given blend. These specific interactions can be of dipole-dipole, hydrogen bonding, charge transfer, or ion-ion type. The understanding of the importance of these interactions resulted in the discovery of an ever increasing number of miscible polymer blends (3).

The role of these interactions can be appreciated when two potentially immiscible polymers are rendered miscible by modifying the chemical structure of one or both component polymers, such that some chemical groups capable of forming specific interactions are incorporated in them. Incorporation of anions and cations in the component polymers was used by Eisenberg et al (36) to render miscible hitherto immiscible polymeric systems. The same approach of enhancing miscibility is adopted by others using hydrogen bonding as the specific interaction (37). Incorporation of electron donor / acceptor groups on the backbone of inherently immiscible polymer components has been utilized to enhance miscibility via the charge transfer mechanism by Natansohn and coworkers (38).

Among the various specific interactions, hydrogen bonding is the one most frequently used due to its common occurrence in polymers and its ease of characterization spectroscopically. Infrared spectroscopy has been intensively used for that purpose. Shifts in the frequency of absorption of the interacting moieties, are correlated to the presence of these interactions (39). Recently solid state $^{13}$C NMR lineshape differences between the pure polymers and the blend were interpreted to be caused by hydrogen bonding interactions (40, 41, 42, 43).

It has also been observed that these specific interactions have a marked influence on the phase separation behavior of the blends. Kwei et al (34) blended polystyrene incorporating a small number of hexafluoroisopropyl alcohol groups with poly(vinylmethylether).
The system showed a LCST whose location increases with the number of interacting groups in the modified polystyrene as shown in figure 1.3. This means that the more interacting groups there are, the stronger the interactions and thus the larger the thermal energy required to destroy them. This is in concert with the theoretical consideration that an increase of temperature brings about a decrease in magnitude of the interactional contribution. In practical terms, if the presence of a low LCST poses problems of processing of a given polymer blend, probably one way to circumvent that problem would be to modify slightly the component polymers such that interactions become stronger leading conceivably to a LCST higher than the processing temperature, thus assuring one homogeneous phase.

The strength of the intermolecular interaction depends very much on the chemical nature of the interacting groups, i.e., the ease with which a certain hetero-interaction can occur. This in turn depends on the net result of the energetics involved between the self-association(1-1) and the hetero-association(1-2) energies. If, for example, a highly self-associated polymer is blended with less self-associated polymer, it is possible to obtain a miscible or immiscible blend depending on whether the self-associated polymer energetically prefers to interact within itself or intermolecularly with the other component. This may offer an explanation as to why polyamides (very self-associated polymers through intramolecular hydrogen bonding) do not often form miscible blends with other polymers.

Prud'Homme(44), while comparing the miscibility behavior of polyvinylhalides with polyesters, observed that most of the polyesters studied were miscible with Poly(vinyl chloride) (PVC) but all were immiscible with Poly(vinylfluoride) (PVF). The difference in miscibility behavior was suggested to be due to the higher degree of self-association of PVF compared to PVC. The difference in self-association between PVC and PVF was attributed to the presence of the highly electronegative fluorine atoms in the latter competing with the carbonyl group of the polyesters for potential hydrogen bonding.
Figure 1.3  Lower critical phase boundaries for poly(vinyl methyl ether) blended with 1) pure polystyrene; (2) 0.1% hydroxyl group; (3) 0.2 % hydroxyl group; 4) 0.4 % hydroxyl group in the modified polystyrene. (from ref.34)
The efficacy with which these specific interactions cause miscibility depends also on the number of interacting groups. There are several examples in the literature where a given polymer, containing a certain chemical functionality capable of interacting with another moiety in the other polymer, will form miscible or immiscible blends depending whether there are a sufficient number of interacting groups available (45, 46).

Most of these specific interactions have directionally dependent field of force for their efficient juxtaposition. Therefore, it should be expected that the miscibility of polymers will be affected by their stereoregularity. Indeed there are several systems which were examined for that purpose. Polystyrene/Poly(vinylmethylether) was recently studied (47). The study involved the preparation of isotactic and atactic PVME and blending them with polystyrene. It was concluded that the isotactic PVME with its 3₁ helical conformation does not juxtapose very well as the atactic PVME with its zigzag conformation. These findings were based on the observed phase-separation behavior. The LCST was lower for the isotactic form than the atactic form. This was related to the strength of the interactions involved.

In summary, the presence of interacting groups is a necessary but not sufficient for obtaining a miscible polymer blend. Some of the factors mentioned above may be against or in favor of miscibility, and the number of interacting groups must be sufficient to render the blend miscible. The stereochemical structure should be in the right conformation. The strength of the interaction should be such that it outweighs the always present dispersive interactions. All these factors should act in concert in order to obtain miscibility. As one can imagine our knowledge of these factors is very limited therefore the predictive power available at present is at best rudimentary.
1.5 Criteria and Methods of Testing Miscibility

In section 1.2 we implied that miscibility involves thermodynamic equilibrium of a single homogeneous phase. Although the attainment of such an equilibrium state in a polymeric liquid is difficult due to the long relaxation times involved, the task of verifying it seems more difficult. In practical terms, the information obtained from a given test of miscibility will depend on the size of the probe used and its sensitivity. Different techniques are used for ascertaining the miscibility of polymer blends; these techniques can be divided into three main categories depending on what information is provided by them. Some of these give information on the presence or the absence of phases, while from others one can obtain information as to the composition of the phases (if there are any) and some give estimates of the magnitude of the thermodynamic parameters. As the description of these methods can be found in several books (1-4), we will only describe those methods used in the present work, notably the glass transition temperature and the NMR proton relaxation measurements.

1.5.1 Single Glass Transition Temperature Criterion

The glass transition temperature is the temperature at which the immobile backbone sequences of the polymer begin to move. This motion is determined by the structure of the polymer and the surroundings of the chain sequences involved. When a given polymer is mixed with another polymer, if the mixing process is such that the two segments are brought into close proximity the segmental motion will be affected. This is the basis of the glass transition criterion for miscibility.

Two polymers are considered miscible if their blend gives a single glass transition which changes monotonically with the composition. It is also required that the width of the glass transition region of the blend be comparable with that recorded for the pure polymers. The breadth of the glass transition region of the blend may be related to the
presence of local composition fluctuations; thus it may give qualitative information as to the relative homogeneity of the system.

One important question which still remains unanswered is that involving the domain size probed by the single Tg criterion. Earlier attempts by Kaplan(48) suggested that the smallest structural heterogeneity resolvable through glass transition temperature measurements are on the order of 15nm. Although this estimate may be right for the situation examined by him, its universality has been questioned(49, 50). The observation of single Tg is generally associated with the absence of domains larger than 20 to 30nm.

The glass transition temperature is commonly determined by (1) calorimetric measurement, i.e heat capacity as a function of temperature, or (2) dynamic mechanical measurement, i.e the complex modulus as function of temperature. Differential scanning calorimetry (DSC) is the most widely used method of the two due to the simplicity and the small sample requirement and perhaps also the large choice of programmable heating and cooling rates available.

The DSC measures the amount of heat energy needed to raise the sample temperature over that required to heat up a reference material, normally an empty pan, to the same temperature. The change in heat (dq/dt) necessary to maintain this level during a transition is recorded.

The Tg determination by thermal analysis has generally been thought (1,2) to be an ambiguous experimental technique for establishing polymer-polymer phase behavior, if the Tgs of the constituent polymers are similar or differ by only 20 degrees, due to the low resolving power of the DSC. However, recent additions(51-54) to this technique are proving useful, in that it is no longer required that the Tgs of the component polymers be very distant from each other. This new method is based on the well-known phenomenon of enthalpic recovery in glassy polymers(55). When a glassy polymer is heated to a temperature higher than its Tg and quenched to a temperature just below its Tg, and kept at that temperature for a time, and then heated to its glass transition, an enthalpic peak is often
observed at the location of the Tg which is attributed to the recovery of the enthalpy that the glass has lost upon cooling. When a polymer blend whose constituent polymers have similar Tgs is subjected to the above thermal cycles, a single enthalpic peak will be observed if the blend is miscible, while two enthalpic peaks will be observed if the system is immiscible. Due to the long annealing times involved this method is evidently limited to noncrystalline polymers and their blends.

1.5.2 NMR Proton Relaxation Times and Spin Diffusion

Due to the short-range dipolar interactions, NMR can be a useful tool to give information on the spatial proximity of the components in polymer blends. Various solid state NMR techniques are used for this purpose, differing in complexity and material requirements(56). The simplest is the one based on the averaging (or the lack of) of the proton relaxation times(\(T_1, T_{1p}\)). The averaging is brought about by a mechanism known as "spin diffusion". For pure polymers, this process is regarded as a nuisance due to the fact that the otherwise obtainable information from the proton relaxation times of individual protons is hampered by their fast internal spin energy exchange through spin diffusion; as a result all the protons relax with a single relaxation time constant. Fortunately, this fact can be used beneficially in the case of polymer blends(57).

The process of spin diffusion can be thought of as an interconnected water network(58). Let us assume that reservoir A and B, in figure 1.4 depict the behavior of two proton spin population located in different domains A and B, and that valve SD represents the spin diffusion pathway and pipes \(R_a\) and \(R_b\) correspond to the spin-lattice relaxation rates. \(R_b\) being larger than \(R_a\) signifies that the proton spin population B relaxes faster to the lattice(L) than proton spin population A, i.e \(T_{1B} < T_{1A}\). Let us now consider two extreme cases:

1) if the valve SD is fully closed which corresponds to the absence of spin diffusion, reservoirs A and B do not "communicate" and thus they empty to L at a rate commensurate
Figure 1.4 Water network as a spin diffusion analogue.
to the flow rates through pipes $R_a$ and $R_b$. In the parlance of NMR the two domains are said to be weakly coupled and are characterized by different spin-lattice relaxation times.

2) if, on the other hand, the valve SD is fully open, corresponding to the presence of an effective spin diffusion, any instantaneous difference in the levels of the reservoirs will be compensated by a rapid flow through SD, and the two reservoirs will empty at a common rate to the larger reservoir $L$. The magnitude of this common rate of emptying will evidently depend on the intrinsic rates $R_a$ and $R_b$. In this case, the two domains are said to be strongly coupled and are characterized by one spin-lattice relaxation time constant.

Although the usage of the above mass transport analogue may give the impression that spins diffuse through spatial boundaries, in reality what is transferred is energy rather than mass; but for that energy exchange to be effective, it is required that the two spin populations exist in the vicinity of each other in space. Therefore the presence or the absence of the process of spin diffusion can be used as measure of the homogeneity of a given polymeric mixture.

If the two domains are in spatial proximity to each other on the distance scale over which the spin diffusion is efficient, the averaging of the relaxation times is observed. The spin diffusive path length and thus the domain size can be approximately estimated from the following equation (59):

$$L = (6D\tau)^{1/2}$$

where $L$ is the diffusive path length, $\tau$ is time over which spin diffusion takes place and $D$ is spin diffusion coefficient. For solid polymers $D = 10^{-12} \text{cm}^2\text{s}^{-1}$.

Proton $T_1$ is the time constant for the process through which the proton spin system re-establishes equilibrium with the large external magnetic field $B_0$. The proton spin system should dissipate the energy imparted to it by the rf field used to generate the NMR signal.
The process by which the spin system dissipates that energy is called proton spin-lattice relaxation.

In contrast proton $T_{1p}$ is the time constant for the proton spin-lattice relaxation time in the rotating frame of reference. It is the time constant for the process of re-establishing equilibrium with a much lower rf field and thus dissipation of energy through motions of lower frequency than the $T_1$ process.

For the polymers proton $T_1$ is of the order of seconds while $T_{1p}$ is normally in the millisecond range. Substituting these magnitudes for $\tau$ in equation (2.2), it is evident that the domain size given by proton $T_{1p}$ is about one order of magnitude smaller than that probed by $T_1$.

As mentioned previously, miscibility of polymeric systems is relative to the size of the probe used for testing it. The two types of NMR experiments probe different domain sizes. The proton $T_1$ can give information on spatial heterogeneity on the distance scale similar to that of the "single $T_g$ criterion", i.e. 20-30nm, while the $T_{1p}$ probes on a distance scale of a few nanometers. Many polymer systems whose miscibility was established by the $T_g$ criterion show some heterogeneity when subjected to the $T_{1p}$ relaxation criterion.

The experimental conditions required for the measurement of the proton relaxation times in the rotating frame ($T_{1p}$) will be given in chapter 2 of this thesis, nevertheless here we will briefly describe the prerequisites for a given blend system to be studied by this method. In solid-state NMR, the proton relaxation time constants are generally obtained indirectly through the $^{13}C$ signal intensities, it is necessary, therefore, that at least some of the $^{13}C$ resonances of the component polymers be spectrally distinguishable. This will enable us to do the desired comparison of the relaxation behavior of the component polymers in their blended and unblended states and will facilitate the assessment of the degree of miscibility. The observation of exponential decay of the carbon signal is often related to the absence phase-separated domains. The exponential decay of carbon signals can not, however, be taken as an unambiguous evidence of intimate mixing, unless the
proton relaxation time constants of the component polymers differ significantly and at least a factor of two difference may be required.

In summary, the proton relaxation criterion may be used for assessing miscibility of polymer mixtures if the following requirements are satisfied: the CP-MAS spectra of the component polymers must contain at least some spectrally resolvable peaks; some coming from one component and others coming from the other component. It is also required that the proton relaxation time constants of the pure polymers must differ significantly and at least a factor of two difference is required for an unambiguous assessment of exponential decay.
1.6 Scope and Aims of the Investigation

As outlined in section 1.4, the presence of specific interactions is considered important for the miscibility of polymer blend systems. These specific interactions involve functionalities capable of interacting favorably to give rise to a negative heat of mixing as required by the thermodynamics of mixing. One such interaction is hydrogen bonding which involves the proton donating/proton accepting functionalities of the component polymers. Polymers containing hydroxyl, phenol, carboxylic, and sulphonic acid groups are examples of proton donating polymers; while polymers containing ether, nitrile, carbonyl, pyridine groups constitute examples of the proton accepting polymers. A survey of the miscible systems studied thus far demonstrates that a large portion of them contain one type or another of these functional groups.

The number of such proton donor groups plays a very important role in the miscibility of polymer blends. By varying the number of these interacting groups one can map the immiscible, the partially miscible, and the miscible regimes of a given polymer pair, thus making it possible to produce materials of varying but controlled properties. In certain cases, the incorporation of a small number of such proton donors suffices to achieve miscibility of an otherwise immiscible polymer pair(34,62,63).

The ranking of the various proton donor groups according to their efficiency in promoting miscibility has not been thoroughly studied. The acidity (a measure of the ease with which a given proton donor engages in hydrogen bonding interaction with a proton accepting polymer) may, as first approximation, be considered as the main factor affecting the efficiency of these proton donors to enhance miscibility. To test this hypothesis, Morawetz et al (64) incorporated different proton donor groups of varying acid strength into polystyrene and blended with poly(methacrylates). Concurring with earlier studies(34,63), they found that a relatively small number of proton donor groups, in the range of 1-5mole%, is required to achieve miscibility but no correlation was found between
the acid strength of these modified polystyrenes and their efficiency in enhancing miscibility. Vinyl phenol modified polystyrene of relatively lower acid strength, as judged from its pKa of 9, was found to be more efficient in fostering miscibility with poly(methacrylates) than carboxylic acid modified polystyrenes of pKa = 5.

The lack of correlation was later attributed to the relative extent of self-association present in these different proton donors(65). The carboxylic acid groups being more self-associated than the phenolic groups will require that their internal hydrogen bonds be broken before they can engage in hydrogen bonding interactions with the proton accepting polymer. The sign and the magnitude of the overall enthalpy of mixing of such a self-associated polymer with a nonself-associating counter-polymer will depend on three contributions: (1) a positive contribution ($\Delta H_{11}$) resulting from the breaking of the internal hydrogen bonds of the self-associating polymer; (2) a negative contribution ($\Delta H_{12}$) coming from hydrogen bond formation between the self-associated polymer and the other component; (3) a positive contribution coming from the ever present dispersive physical forces ($\Delta H_d$). Apart from $\Delta H_d$, which can be minimized by choosing polymers with similar solubility parameters, the total enthalpy of mixing and thus the attainment of miscibility will depend on the relative magnitudes of $\Delta H_{12}$ and $\Delta H_{11}$. $\Delta H_{12}$ will in turn depend on the acid strength of the proton donor and base strength of the proton accepting polymer, while $\Delta H_{11}$ will depend on the extent of self-association resulting from the presence of acidic and basic units within the proton donor. This suggests that, apart from the acid strength of the proton donor, the extent of self-association is also an important factor affecting the efficiency of these proton donor groups in enhancing miscibility. The more self-associated the proton donor, the less effective it is to foster miscibility. In the absence of self-association, there should be a predictable trend of miscibility enhancement with increasing acid strength because there is an established relationship between the strength of acid-base interactions and the enthalpy associated with them(66,67).
From the foregoing, it may be inferred that a self-associated weakly acidic proton donor will be less effective in promoting miscibility than a nonself-associating proton donor of high acid strength. It is this view that we want to explore in this investigation. It is known for example, that aliphatic alcohols are weaker acids than phenols(68), therefore it can be expected that polymers containing aliphatic hydroxyl groups such as cellulose and poly(vinyl alcohol), which are also known to self-associate through their hydroxyl-hydroxyl internal hydrogen bonding, must contain a large number of hydroxyl groups to achieve miscibility over the whole composition range with a given acceptor polymer. As a matter of fact, while both cellulose(43) and poly(vinyl alcohol) PVA(69-72) form miscible blends with poly(vinyl pyrrolidone) PVP, cellulose diacetate(73) and poly(vinyl butyral) PVB containing about 16% by weight of vinyl alcohol units(74) were found to form partially miscible blends with PVP. This may be a direct consequence of the relatively smaller number of hydroxyl groups present in the derivatives in comparison with cellulose and PVA respectively. It may also imply that, to obtain miscible blends of these aliphatic hydroxyl containing polymers with a proton accepting polymer, a large number of these hydroxyl units would be required.

We, therefore, embarked on an investigation of PVB/PVP blends whose primary objectives were: (1) to study the effect of the hydroxyl content of PVB on its miscibility with poly(vinyl pyrrolidone); (2) to test the hypothesis that a large number of proton donor groups are required to achieve miscibility in this blend system. PVB is actually a copolymer of vinyl alcohol and vinyl butyral obtained by the reaction of PVA and butyraldehyde. Two samples of PVB containing 11% and 19% by weight of PVA were used in this study; the former forms partially miscible blends with PVP while the latter is miscible over the whole composition range. Blends of PVP/PVB11 and PVP/PVB19 covering the entire composition range were prepared by mixing the polymers in chloroform and blend films were obtained by casting. The state of miscibility was assessed by thermal analysis and solid-state NMR.
1.7 References


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Chapter 2

Materials And Methods
2.1 Materials

The poly(vinylbutyral) resins Butvar® B-79 and B-98 were kindly supplied by Monsanto Chemical Company. The poly(vinylpyrrolidone) resin was purchased from Aldrich (cat no. 85,656-8). The molecular characteristics of these polymers are reported on table I.

Table I
Molecular characteristics of the polymers

<table>
<thead>
<tr>
<th>code</th>
<th>[PVA wt%]</th>
<th>PVB wt%</th>
<th>PVAc wt%</th>
<th>$M_w 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butvar(B-98)</td>
<td>19.3</td>
<td>79.2</td>
<td>1.5</td>
<td>6.5$d$</td>
</tr>
<tr>
<td>Butvar(B-79)</td>
<td>10.8</td>
<td>88.2</td>
<td>0.9</td>
<td>5.5$d$</td>
</tr>
<tr>
<td>PVP$c$</td>
<td></td>
<td></td>
<td></td>
<td>4.0$b$</td>
</tr>
</tbody>
</table>

(a) the data pertaining to Butvar(B-98) and Butvar(B-79) were supplied by Monsanto.
(b) $M_w$ of PVP is nominal molecular weight reported by Aldrich.
(c) PVA, PVB, PVAc and PVP stand respectively for poly(vinylalcohol), poly(vinylbutyral), poly(vinylacetate) and poly(vinylpyrrolidone)
(d) these values are typical weight average molecular weights of these commercial resins.

The polymers were used as supplied except for a drying treatment in a vacuum oven at 50°C for 24 hours followed by storage in a desiccator over calcium sulfate until used. The poly(vinylalcohol) content of the poly(vinylbutyral)s was confirmed following the ASTM 1396-73 method and complete agreement between our determinations and those of the supplier was found. The values reported in Table I are those of the supplier.

Spectrograde chloroform, purchased from Aldrich (cat. no. 31,998-8) and dried over 4A type molecular sieves, was used as a mutual solvent for the polymer blend preparation.
The name poly(vinylbutyral) will be abbreviated hereafter to PVB and the number following the symbols will denote the poly(vinylalcohol) content in weight percent. poly(vinylpyrrolidone) will likewise be abbreviated to PVP.
2.2 Experimental Methods

2.2.1 Blend Preparation

Mixtures of either PVB11 or PVB19 with PVP were prepared by dissolving each polymer separately in chloroform at room temperature to form a 5% (weight/volume) solution. After complete dissolution aided by magnetic stirring for over 24 hours, the solutions were mixed in weight ratios of: 90/10 to 10/90 PVP/PVB11 or PVP/PVB19. The resulting mixtures were stirred for several hours.

20g portions of these mixtures were then poured into polypropylene dishes and covered with a large glass chamber under the laboratory fume hood to effect a slow and constant evaporation of the solvent. The polypropylene dishes were employed to prevent adhesion since both polymers stick strongly to glass surfaces. After this initial casting which took about 12 hours, the resulting films were transferred to a vacuum oven for further drying at 75°C to constant weight. The samples were kept in a desiccator over calcium sulfate until tested.

2.2.2 Thermal Analysis

A Perkin-Elmer differential scanning calorimeter DSC-7 equipped with TAS-7 computer accessory was used for the determination of glass transition temperatures of the blends and the pure polymers. The energy output and the temperature were calibrated with ultrapure indium standard (m.p =156.6°C, ΔHf = 28.45J/g°C).

Samples weighing approximately 9-10 mg were placed in standard Perkin-Elmer aluminum pans which were crimped very carefully to insure good contact between the sample and the bottom of the pan to allow uniform heat transfer. All the runs were conducted in a dry nitrogen atmosphere and an empty aluminum pan was used as a reference.
The following heating and cooling scans were adopted:

(1) the samples were heated from 30°C to 200°C at 20°C/min. and kept at 200°C for 5 minutes in order to expel any moisture and to impart the same thermal history.

(2) after that annealing period, the samples were quench cooled to 30°C at a rate of 200°C/min.

(3) after thermal equilibration of the instrument, which takes usually between 2-3 minutes, another heating scan from 30°C to 200°C was effected. This run is designated as the second heat run and all the glass transition temperatures reported are those estimated in this scan.

(4) step 2 was repeated, and then a third heating scan similar to step 3 was conducted for each sample to check the reproducibility of the thermal transitions recorded in step 3. The glass transitions recorded in this third scan and those of the second agreed within the accuracy limits of this determination. i.e ±1°C.

The glass transition temperature (Tg) of each sample was estimated as illustrated schematically in figure 2.1. The Tg was taken at the mid-point of the transition corresponding to the temperature at which the heat capacity change assumes half its total value. This is located by extrapolating the pre-transition and post-transition baselines, corresponding to the glassy and the liquid states of the sample respectively, and dropping a vertical line at the mid-point of the thermogram in the transition region (1).
Figure 2.1 Schematic of Glass Transition Temperature Measurement.
2.2.3 Solid-State NMR Measurements

The measurements were conducted on a Chemagnetics M-100 apparatus operating at resonance frequencies of 100 and 25 MHz for $^1$H and $^{13}$C nuclei respectively. $^{13}$C spectra of all samples were obtained, at room temperature, via the combination of magic angle spinning (MAS), cross-polarization (CP) and dipolar decoupling (DD) with typical spinning rates of 3500-4000 Hz.

Films of the blends and pure polymers were cut into small pieces and packed in a zirconia rotor with Kel-F endcaps. Samples weighed approximately 300 mg. The Hartmann-Hahn match was adjusted using Hexamethylbenzene standard (HMB) prior to every experiment. All the spectra were referenced externally to the methyl resonance of HMB standard (17.4 ppm). A 90° pulse width of 5 μs for both proton and carbon nuclei and contact time of 1 ms were used for all samples with repetition time of 5 s. Typically 500-2500 FIDs were accumulated depending on the sample composition.

The proton spin-lattice relaxation times in the rotating frame $T_{1p}$ measurements were performed by using a $90°_x - τ -$ spin lock pulse scheme (2,3) as depicted in figure 2.2 with a spin-locking field of 50 kHz. A 90° pulse width of 5 μs and contact time of 1 ms were used for all samples. A variable delay of 3 ms to 36 ms were introduced before cross-polarization and at least six values of the variable delay were employed for each $T_{1p}(H)$ experiment. Typically 480 to 1600 FIDs were accumulated depending on the sample composition. After the 1 ms contact time between protons and the carbons, the $^{13}$C magnetization decay was acquired with proton decoupling strength similar to the spin-locking field. The carbon signal intensity decay were fitted to the expression: $I = I_0 \exp[-τ/T_{1p}]$. The proton relaxation times in the rotating frame ($T_{1p}$) were obtained from the slope of a logarithmic plot of the intensity ratio ($I/I_0$) against the delay time ($τ$).
Figure 2.2 Delayed contact pulse sequence for measuring proton $T_{1p}$'s via carbon signal.
Chapter 3

Results And Discussion
3.1 Visual Observations:

Individual solutions of the polymers and their mixtures were transparent and no turbidity signifying liquid-liquid phase separation or complex formation was observed. Pure polymer films of PVP, PVB11, and PVB19 were all optically clear. The blend films prepared from PVP and PVB11 were also transparent except for compositions containing 50 wt % PVP or more, while the blend films prepared from PVP and PVB19 were all clear over the whole composition range.

The presence of opacity in a blend film, whose component polymers are clear, is usually taken as an indication of the presence of phase-separated domains larger than the wavelength of light and thus capable of scattering the incident light. However, the absence of such light scattering does not necessarily translate into the absence of phase-separated domains, because the transparency observed may be due to matched refractive indices of the component polymers, or to the presence of domains much smaller than the wavelength of light.

The slight haziness of some blends films of the PVP/PVB11 system suggests the presence of relatively large phase-separated domains signifying that the system is immiscible, at least in those compositions where hazy films were obtained. However, it can not be concluded from these visual observations, that only these compositions are phase-separated because, as mentioned earlier, it may so happen that the films which appear transparent may do so by virtue of the minuteness of phase-separated domains(if present) relative to the wavelength of the visible light.

From the foregoing, it is obvious that optical clarity is only a rough guide for establishing miscibility of polymer blends and hence more discriminating techniques must be used. In the following, the results of two such experimental techniques will be described and discussed in relation to the miscibility of the systems studied.
3.2 Thermal Analysis

The polymers used in this investigation are all amorphous, thus only one thermal transition is expected above room temperature, namely the glass-rubbery transition (Tg). As outlined in section (1.5.1), the Tg criterion may establish the absence or the presence of domains sizes in the order of 20-30 nm which are much smaller than that resolvable by visual observation, i.e., ca 100 nm (4).

The thermal studies were conducted as described in Chapter two, section (2.2.2). In the first heating scan, almost all samples containing PVP showed a broad endotherm at around 110 - 120°C, consistent with earlier observations (5, 6). This thermal event can be attributed to the presence of moisture in the samples due to the high hygroscopic nature of this polymer. After the first heating scan and the subsequent annealing at 200°C, this transition vanishes and reproducible glass transition temperatures were recorded.

3.2.1 The PVP/PVB11 blend system.

Samples containing 40 wt% PVP or less showed a single glass transition temperature which increases with composition. DSC traces of the pure components and of their blends containing 20, 40, 50, 60, and 80 wt% PVP are reported in figure 3.1. Both the thermograms of 20, and 40 wt% PVP samples show a single Tg in compliance with miscible systems at least on the distance scale resolvable by a single Tg criterion, while all the other thermograms exhibit two glass transition temperatures commensurate with the presence of two phases in the mixture. The lower transition corresponds to a PVB11 rich phase and the higher transition corresponds to a PVP rich phase. The presence of two Tgs for a binary mixture is a definitive indication of the presence of two phases.

In figure 3.2 the Tgs of the blends and the pure polymers are plotted against the composition. The Tg of the blend increases with the PVP content up to 40% by weight, after that two Tgs are recorded for each sample. The Tg of the PVB11 rich phase fluctuates about an almost constant temperature of 85±1°C and that of PVP rich phase hovers about
Figure 3.1 DSC traces of PVP/PVB11 blend system: PVB11(pure), 20, 40, 50, 60, 80wt% PVP and pure PVP (from bottom to top respectively).
164 ±1°C, despite the variation of the overall composition of the blend. The average $T_g$ of the PVB11 rich phase is about 16°C higher than the pure PVB11, while that of the PVP rich phase is only 6°C below the value that it assumes in its pure state. This behavior may be attributed to the existence of a fixed ratio in which the two polymers interact at compositions higher than 40 wt% PVP.

An attempt was made to estimate the relative amount of each component in either phase. The PVB11 rich phase is designated as phase A and the PVP rich phase as phase B. The $T_g$ values of the pure polymers and those corresponding to the compositions with single $T_g$ were fitted to the Gordon-Taylor equation(7):

$$T_g = (w_1 T_{g1} + K w_2 T_{g2}) / (w_1 + K w_2)$$

with a K value of 0.50 as shown by the line in figure 3.2. Calculations were then carried for the 50/50 blend sample by using equation 3.1 rearranged to the following form:

$$T_{gA} = [T_{g1} w_1 + K (1-w_1) T_{g2}] / w_1 + K (1-w_1)$$

where $w_1$ is the weight fraction of PVB11 in phase A and K is the adjustable Gordon-Taylor parameter. $T_{g1}$ is the glass transition temperature of pure PVB11(69°C), $T_{g2}$ is the glass transition temperature of pure PVP(170°C) and $T_{gA}$ is the glass transition temperature of the PVB11 rich phase(85°C).
Figure 3.2 Plot of experimental Tg of PVP/PVB11 blend system: The solid line is a fit based on Gordon-Taylor equation with K value of 0.5 for the blends having a single Tg and those of the pure components.
Substituting these values in the above equation yields $w_1 = 0.73$. A similar calculation on phase B yields a $w_1$ value of only 0.03. This clearly shows that the PVP rich phase is almost pure, while the PVB11 rich phase contains a little less than one-third of its weight of PVP. All the other blends have similar composition as evident in the constancy of their Tg values. This suggests that there is a maximum amount of PVP which can interact with PVB11 and if that amount is exceeded the remaining PVP component, with small inclusions of PVB11 will exist as a separate phase.

This behavior can be understood by considering the fact that the component polymers interact via hydrogen bonding interactions involving the hydroxyl group of the PVB11 and the carbonyl groups of PVP, as evidenced in another study done on PVA/PVP(8). As the PVP weight fraction in the blend increases, more and more of the hydroxyl functionalities of PVB11 will be engaging in hydrogen bonding interaction with the carbonyl groups of the former, until a situation is reached where the excess PVP does not have a counterpart to interact with and resides as a separate phase. This explanation can be tested by blending the same PVP component with a PVB sample having higher hydroxyl content. The results of such an experiment will be presented in the following section.
3.2.2 The PVP/PVB19 blend system

DSC traces of some representative PVP/PVB19 blend samples are reported in figure 3.3. All the traces show a single glass transition temperature increasing systematically with composition. This indicates that the two components are miscible over the whole composition range. For miscible systems, there are several empirical relations which describe the variation of the Tg with composition (7, 9-11). Tg data for the PVP/PVB19 blend system best fits to Gordon-Taylor equation as shown in figure 3.4 with a value of the K parameter of 0.6. Recently Prud’homme and coworkers (12,13) suggested a link between the strength of the interactions between the component polymers in a blend and the magnitude of the parameter, i.e. the higher the value of K the stronger the interactions.

Assuming the existence of such a relationship and judging from the K values of several polymer blend systems (8,14,15) involving PVP and proton donating counter-polymers, it has been suggested (16) that PVP interacts more strongly with hydroxyl containing polymers than with other proton donating polymers such as Poly(vinylchloride). In line with these earlier studies, the K value of 0.6 suggests that the components of the present system interact more strongly with each other than those of the PVP/PVC blend system where the best fit of the corresponding Tg data was found for a K value of 0.34 (17).

The DSC results show that the PVP/PVB19 blend system is miscible over the whole composition range unlike the PVP/PVB11 blend system where partial miscibility was obtained. The different behavior of the two systems may be attributed to the difference in their hydroxyl content. The PVB19 polymer contains approximately 43mole% of PVA units while PVB11 contains about 28mole%. Higher PVA content means more hydroxyl sites for possible hydrogen bonding interactions with the carbonyl groups of PVP and thus a larger range of miscible compositions. This supports the hypothesis alluded to in the previous section concerning the PVP/PVB11 blend system where partial miscibility sets in when a certain blend composition is reached, due to the scarcity of interaction sites.
Figure 3.3 DSC traces of PVP/PVB19 blend system: PVB19 (pure), 10, 30, 50, 70, 90wt% PVP and PVP (from bottom to top respectively)
Figure 3.4 Plot of experimental Tg of PVP/PVB19 blend system: the lines are best fit based on the additivity rule of mixtures, Fox equation, and Gordon-Taylor equation (as indicated by the legend).
The single $T_g$ criterion, adopted in these thermal analyses, is not sensitive to the presence of domains smaller than 20 - 30 nm, it therefore seemed interesting to investigate the blend system by solid state NMR which is sensitive to domain sizes in the range of a few nanometers. In the following the results of such an experiment will be presented.
3.3 Solid-State NMR Studies

The high resolution $^{13}$C solid-state spectra obtainable by the use of CP-MAS techniques(18) has made it possible to investigate the miscibility of polymers at the molecular level(3). For strongly interacting polymer blends, changes in the isotropic chemical shifts can be related to the specific nuclei that participate in the interaction that is responsible for the miscibility of the two components(19,21). These same changes, can give information as to the spatial intimacy of the component polymers in the blend because the shielding effects often responsible of these changes in the isotropic chemical shifts, depend strongly on the distance between the nuclei. Thus if changes in the chemical shift of the interacting functionalities occur upon blending, the component polymers must be mixing at the molecular level.

Another CP-MAS based experiment which can give information about the molecular neighborhood of the component polymers involves the measurement of the proton spin-lattice relaxation time constants in the rotating frame($T_{1p}$) (21-24). If, for example, a blend of two polymers A and B is present, which differ in their CP-MAS spectra, the proton $T_{1p}$ can be separately determined in the environment of the molecules of type A and B respectively by evaluation of the signals from A and B respectively. For a blend miscible at the distance scale of 2-3nm, a common $T_{1p}$ whose value lies between that of the pure components is expected, while for a heterogeneous blend at such a distance scale nonuniform relaxation behavior is observed.

The solid-state NMR results for both the systems under study are reported in figures 3.5 to 3.8. Figure 3.5 shows the $^{13}$C NMR spectra of the pure component polymers namely PVP, PVB11 and PVB19 along with the respective chemical structures of the repeat units. The PVP spectrum shows four $^{13}$C resonances whose assignment is facilitated by reference to published $^{13}$C(25) and proton spectra(26). The carbonyl carbon(f) resonates furthest downfield at 175ppm, the methine carbon(b) on the backbone and the ring carbon(c), both attached to the nitrogen, overlap at 42ppm, while the methylene
Figure 3.5 $^{13}$C CP-MAS spectra of PVP, PVB11 and PVB19 in their unblended state. The labeled peaks correspond to the carbons identified in the accompanying repeat unit chemical structures.
carbon(a) on the backbone and the methylene carbon(e) in the ring overlap at 33ppm. Finally the methylene carbon(d) in the ring resonates further upfield at 19ppm.

The spectra of PVB11 and PVB19 are almost identical although some minor differences are evident especially in their stereosequence. This similarity in the two spectra is not surprising in that the two polymers differ only in the residual PVA units, and as will be apparent shortly, the peaks relative to that part of the polymer overlap with other resonances and thus can not be seen. Also the very small amount of poly(vinylacetate) units present, in the range of 0.9 to 1.25% by weight, does not show up in the spectra and its effect on both the CP-MAS spectra and the relaxation measurements will be neglected.

The spectral assignment of the PVB resonances was made with the help of a published two-dimensional homonuclear correlated spectroscopy(COSY) and $^{13}$C-$^1$H correlated spectroscopy(27). The CP-MAS spectra has more overlapping resonances than the 13C solution counterpart and most of the comonomer sequence information is lacking, but since that aspect of the of the spectra is beyond the scope of the present study, it may suffice to roughly assign the peaks on the basis of the chemical shifts(28).

PVBs are the products of condensation reaction between poly(vinylalcohol)(PVA) and butyraldehyde(BA). The butyraldehyde reacts with adjacent hydroxyl groups of PVA to form butyral rings(30). Depending on the stereochemical structure of the initial PVA, the resulting butyral rings may be in the meso or racemic conformation. These stereosequences can be seen in the solid-state $^{13}$C spectra. Both carbons 6 and 5 show such conformational structures. Carbon 6 of the ring resonates further downfield at ca 102 ppm due to its direct attachment to two oxygens, and it is flanked by another peak(6') at 95 ppm. These peaks are assigned to the anomeric butyral carbon showing the meso and the racemic conformation respectively. Similarly carbon 5 assigned to the butyral ring carbons attached to one oxygen show meso and racemic structures. The main peak at 72 ppm arises from the
meso form while the shoulder at 69 ppm is due to the racemic conformer. Close to this peak at its immediate upfield as a small shoulder, at 64 ppm, is the methine carbon 4 of PVA. The methylene carbon 3 of PVA and the methylenes of the ring overlap at 38 ppm while the methylene carbon 2 overlap with the methyl carbon 1 at 15 - 18 ppm.

The spectra of PVP and PVP19 and two of their blends are shown in figure 3.6. Most of the spectra overlap but fortunately, the carbonyl carbon of PVP (175 ppm) and C6 (102 ppm) and C5 (72 ppm) from the PVB19 are spectrally distinguishable. The carbonyl carbon resonances show a slight broadening and the peak maxima moves slightly to higher ppm relative to the spectrum of the pure PVP. This spectral shift (1 - 2 ppm) to higher ppm suggests that changes in the chemical environment of the carbonyl are occurring as a consequence of the mixing process. Hydrogen bonding interactions involving the carbonyl of PVP and the hydroxyl group of the residual PVA units may result in a decrease in the electron cloud of the carbonyl carbon site although conformational or packing perturbations, which in turn may induce the observed changes in the isotropic chemical shift, can not be ruled out (30). Similar changes in the carbonyl carbon chemical shifts were recently reported by Masson (31) et al when PVP was blended with cellulose, a hydroxyl containing polymer. This was attributed to hydrogen bonding interactions involving the carbonyl group of PVP and the hydroxyl groups of cellulose and in addition to the changes of the carbonyl carbon resonances, other spectral line shape changes were recorded for those carbons attached to the hydroxyl groups of cellulose. Unlike the above case the methine carbon of PVA, most likely affected by the hydrogen bonding interactions, is not spectrally resolvable in this case as it manifests itself as a small shoulder to the C5 resonances (see fig.3.5). This makes the analysis difficult and nothing can be said about its engagement in such potential interactions. Hydrogen bonding interactions are, nevertheless, known to occur between the carbonyl groups of PVP and the hydroxyl groups of PVA as evidenced by FTIR studies done on their blends (8). Furthermore, it has recently been suggested (20) that variation of the chemical shifts observed in the CP-MAS
Figure 3.6: CP-MAS $^{13}$C spectra of PVP and PVB19 and their blends: 70/30 and 30/70 (the first numeral refers to PVP).
spectra may go hand in hand with FTIR frequency shifts often observed for interacting chemical species. In light of the above we tentatively assign the changes observed in the isotropic chemical shifts of the carbonyl carbon of PVP, relative to its chemical shift in the pure state, to hydrogen bonding interactions between the carbonyl functionality of PVP and the hydroxyl moiety of the residual PVA units. Due to the short range requirement of the efficacy of these perturbations, their presence indicates the individual chains are mixed intimately at the molecular level.

As mentioned previously, the homogeneity of a polymer blend can also be assessed through the measurement of the proton spin-lattice relaxation time in the rotating frame ($T_{1p}$) of the component polymers and the blends. The proton $T_{1p}$ of each resolvable carbon peak in the blend spectra was obtained from the slope of semi-log plot of the carbon signal intensities against the pre-contact delay times. All the signals show single exponential decay as shown in figure 3.8 and the $T_{1p}$ values determined for the respective blends are reported in table II. The values of the proton $T_{1p}$ of blends estimated through either the carbons belonging to PVP (175 ppm) or those belonging to PVB19 (102 or 72 ppm) are the same within the experimental accuracy and lie between those of the pure components. This result indicates that the protons of the component polymers are in close proximity and that spin diffusion is adequate to average the relaxation behavior of the component polymers.

In cases like this, an approximate relation proposed by McBrierty et al(32) is often used to estimate the scale of heterogeneity of the blend:

$$<L> = [6Dt]^{1/2}$$

where $<L>$ is the average path length of the spin diffusion, $D$ is the spin diffusion coefficient often approximated to $10^{-12} \text{cm}^2\text{s}^{-1}$ and $t$ is the time taken by the spin diffusion process and set equal to the observed proton $T_{1p}$. Conducting the appropriate calculations through equation 3.3, PVP/PVB19 blends are found to be miscible on a scale of ca 2.5nm.
Figure 3.7 Semilog plot of the carbon signal intensities of PVP and PVB19 and of their blends against the delay time.
Table II
Proton $T_{1p}$ of PVP and PVB19 in their blended and unblended states

<table>
<thead>
<tr>
<th>PVP(weight%)</th>
<th>PVP$^b$</th>
<th>PVB19$^c$</th>
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<tr>
<td>100</td>
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<td>16.2</td>
</tr>
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<td>80</td>
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</tbody>
</table>

a ± 5%
b proton $T_{1p}$ calculated from the carbonyl carbon of PVP(175 ppm)
c proton $T_{1p}$ calculated from either peaks of PVB19 at 102 ppm or 72 ppm.
For the sake of completeness, some proton T<sub>1p</sub> measurements were also conducted on the PVP/PVB11 system. In figure 3.8 the variation of ¹³C signal intensities for the pure polymers and for the 50/50 blend sample are plotted as a function of the delay time. The proton T<sub>1p</sub> s obtained from the slope of these signal intensities are reported in Table III. The PVP pure component was found to have a proton T<sub>1p</sub> of 17.3 ms while the pure PVB11 component has a value of 11.7 ms. For the 50/50 sample the proton T<sub>1p</sub> value depends on the peak used for its evaluation. A value of 14.7 ms is obtained when the PVP peak at 175 ppm is employed while a value of 12.7 ms is obtained when the calculations are conducted on PVB11 peaks at 102 ppm or 72 ppm.

For a miscible blend system, the value of the proton T<sub>1p</sub> should be independent of the peak used for its evaluation. The existence of two T<sub>1p</sub> values in this blend indicates that the spin diffusion path length is much smaller than the phase domains and that the blend is phase separated. The proton T<sub>1p</sub> values of the 50/50 sample, however, are not identical to those of the pure polymers. The proton T<sub>1p</sub> estimated from the intensity variation of the PVP peak is reduced from 17.3 ms (in its pure state) to 14.7 ms in the blend while the value corresponding to PVB11 is increased from 11.7 to 12.7 ms. This suggests that there is some partial mixing of the two component polymers.
Figure 3.8 Semilog plot of the carbon signal intensities of PVP (squares) and PVB11 (circles) in their unblended states and in 50:50 blend against the delay time.
Table III
Proton $T_1\rho$ of PVP and PVB11 in their Blended and unblended states

<table>
<thead>
<tr>
<th>PVP (weight %)</th>
<th>PVP $^b$</th>
<th>PVB11 $^c$</th>
</tr>
</thead>
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</table>

$^a \pm 5\%$
$^b$ proton $T_1\rho$ calculated from the carbonyl carbon of PVP (175 ppm)
$^c$ proton $T_1\rho$ calculated from the PVB11 resonances at 102ppm and 72ppm
Chapter 4

Concluding Remarks and Suggestions for Further Studies
4.1 Concluding Remarks

The DSC and the solid-state NMR techniques used in the present work provide corroborative evidence that the miscibility of PVP with PVB depends on the number of PVA residual units present in PVB. As the number of these PVA units is increased, the composition range of miscibility is extended. PVB containing 11% by weight of PVA units forms miscible blends with PVP up to a weight ratio of 40/60 (PVP/PVB11). At higher PVP loading the system exhibits partial miscibility as shown by the presence of two phases, one rich in PVB and the other rich in PVP. The PVB rich phase was estimated to contain about 30% PVP while the PVP rich phase is almost pure PVP. The Tgs of the two phases do not vary with the overall blend composition, and this was explained on the basis of number of interacting sites in the mixture. The validity of this explanation was further tested by blending PVP with PVB containing a larger number of PVA units. PVB containing about 19% by weight of PVA units was found to be miscible with PVP over the entire composition range.

The systematic change of the isotropic chemical shift of the carbonyl carbon resonance of PVP, as observed in the CP-MAS spectra of its blends with PVB19, was interpreted to be due to hydrogen bonding interactions between the component polymers. From the presence of a single proton T1p for the PVP/PVB19 blends and its compositional dependence, it is concluded that the two components are in close proximity to each other, the upper limit of the domain size is estimated to be 2.5 nm. Proton relaxation measurements on the PVP/PVB11 blend system using a 50/50 sample confirmed the DSC results and two values for the proton relaxation time were obtained commensurate with the existence of phases.

The number of PVA units required to attain miscibility over the entire composition range was shown to be large, i.e about 43 mole % (19 wt%) as anticipated. This expectation was based on the weak acidity of the aliphatic hydroxyl groups and the self-association known to be present in PVB(33). This is in a sharp contrast to the miscibility behavior of
hexafluoroisopropyl alcohol modified polystyrenes, where due to the relatively higher acid strength ($pK_a = 7.4$) and the absence of extensive self-association, a relatively smaller number of these groups was found sufficient to miscibilize polystyrene with a vast array of proton acceptor polymers (34, 35).

It is also worth noting that the efficiency of the proton donors, to promote miscibility, also depends on the basicity of the acceptor polymer. For instance, poly(methyl methacrylate) PMMA does not form miscible blends with PVB19 (33) while PVP, as shown in the present study, forms miscible blends over the whole composition range. PVP being a stronger base than PMMA due to its substituted amide structure interacts strongly with PVB19. This stronger interaction may result in a larger exothermic heat of interpolymer hydrogen bond formation between PVP and PVB19 which overwhelms both the endothermic heats of breaking the internal hydrogen bonds of PVB19 and that due to the dispersive forces. If there were no specific interactions, the solubility parameter approach would have suggested that PMMA ($\delta = 9$) is more likely to form miscible blends with PVB19 ($\delta = 9.3$) than PVP ($\delta = 11$). The solubility parameter difference in the two cases is in favor of PMMA/PVB19 blend. This shows the importance of base strength of the acceptor polymer in achieving miscibility.

Based on what have been learned from this and some other related studies (36, 37), some general trends emerge:

1. In the absence of self-association and for given proton acceptor polymer, the efficiency of miscibility enhancement increases with the acid strength of the proton donor polymer.
2. For a given proton donor polymer, the miscibility depends also on the base strength of the acceptor polymer. Greater enhanced miscibility is achieved with stronger base.
3. Weakly acidic and highly self-associated proton donors are less likely to promote miscibility than strongly acidic proton donors with low degree of self-association.
4.2 Suggestions for Further Studies

In the following, some suggestions for further studies based on these general trends will be presented:

(a) To test the dependence of miscibility on the base strength of the proton acceptor polymer, poly(4-vinyl pyridine) P4VP which is a stronger base than PVP may be blended with PVB11 and PVB19 used in the present investigation. Due to the potentially stronger hydrogen bonding interaction between P4VP and PVBs, it may be expected that a relatively smaller number of PVA units will be required to miscibilize PVB with P4VP than PVP.

(b) The poly(vinyl acetate-co-vinyl alcohol)/PVP blend system shows a nonuniform miscibility dependence on the number of PVA units(38). Miscible blends were obtained over the entire composition for a sample containing 60 mole% PVA; but when a sample containing 70 mole% PVA was used entirely phase separated blends were obtained. It was suggested that this nonuniformity is due to the preferential evaporation of one of the two co-solvents used for the blend preparation. If the lack of a single mutual solvent is circumvented by using a melt blending technique, it may be possible to obtain definitive information regarding the miscibility dependence on the number of PVA units in the copolymer.

(c) Low molecular weight copolymers of styrene and allyl alcohol containing 32 to 40 mole% allyl alcohol units form miscible blends with PVP(15). Although the miscibility may be mainly driven by hydrogen bonding interactions between the carbonyl groups of PVP and the hydroxyl functionalities of the copolymers, favorable entropic contributions resulting from the low molecular weight nature of the copolymers can not be ruled out. Since styrene-allyl alcohol copolymers share with PVB the low acid strength and the presence of extensive self-association, studying blends of high molecular weight copolymers with PVP may provide further evidence that aliphatic hydroxyl groups are less efficient promoters of miscibility.
References

5) Tan, Y. T., and Challa, G., *Polymer* 17 739 (1976)


The following tables contain the data employed for the estimation of the proton $T_{1p}$ of the pure polymers and their blends (Table 1-7). The experimental $T_g$ values used for the construction of figures 3.2 and 3.4 are also reported on Table 8-9.

**Table 1. $^{13}$C signal intensities of 100% PVP**

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Table 2. $^{13}$C signal intensities of 80:20 PVP/PVB19

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Table 3. $^{13}$C signal intensities of 70:30 PVP/PVB19

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Table 4. $^{13}$C signal intensities of 30:70 PVP/PVB19

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Table 5. $^{13}$C signal intensities of 100% PVB19

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Table 6. $^{13}$C signal intensities of 100% PVB11

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<th>Delay times (ms)</th>
<th>102 (ppm)</th>
<th>72 (ppm)</th>
<th>38 (ppm)</th>
<th>15 (ppm)</th>
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<tbody>
<tr>
<td>3</td>
<td>799</td>
<td>1625</td>
<td>1019</td>
<td>2071</td>
</tr>
<tr>
<td>4</td>
<td>725</td>
<td>1393</td>
<td>923</td>
<td>1897</td>
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<td>619</td>
<td>1179</td>
<td>795</td>
<td>1597</td>
</tr>
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<td>995</td>
<td>650</td>
<td>1358</td>
</tr>
<tr>
<td>10</td>
<td>420</td>
<td>844</td>
<td>566</td>
<td>1139</td>
</tr>
<tr>
<td>12</td>
<td>379</td>
<td>705</td>
<td>465</td>
<td>973</td>
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<tr>
<td>15</td>
<td>295</td>
<td>560</td>
<td>372</td>
<td>747</td>
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Table 7. $^{13}$C signal intensities of 50:50 PVP/PVB11

<table>
<thead>
<tr>
<th>Delay times (ms)</th>
<th>175 (ppm)</th>
<th>102 (ppm)</th>
<th>72 (ppm)</th>
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<tbody>
<tr>
<td>5</td>
<td>600</td>
<td>682</td>
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<td>7</td>
<td>533</td>
<td>601</td>
<td>1013</td>
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<tr>
<td>11</td>
<td>406</td>
<td>451</td>
<td>760</td>
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<tr>
<td>13</td>
<td>362</td>
<td>392</td>
<td>660</td>
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<tr>
<td>15</td>
<td>297</td>
<td>297</td>
<td>512</td>
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<tr>
<td>18</td>
<td>256</td>
<td>252</td>
<td>428</td>
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Table 8. The Tg values of PVP/PVBl9 blend system

<table>
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<tr>
<th>Blend Composition&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Tg(°C)</th>
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<tbody>
<tr>
<td>0/100</td>
<td>72</td>
</tr>
<tr>
<td>10/90</td>
<td>78</td>
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<tr>
<td>20/80</td>
<td>86</td>
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<tr>
<td>30/70</td>
<td>94</td>
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<td>40/80</td>
<td>100</td>
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<tr>
<td>50/50</td>
<td>112</td>
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<tr>
<td>60/40</td>
<td>119</td>
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<tr>
<td>70/30</td>
<td>127</td>
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<tr>
<td>80/20</td>
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<tr>
<td>90/10</td>
<td>155</td>
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<tr>
<td>100/0</td>
<td>170</td>
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</tbody>
</table>

<sup>a</sup> PVP/PVP19 (w/w)
Table 9. The Tg values of PVP/PVB11 blend system

<table>
<thead>
<tr>
<th>Blend Composition&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Tg(Blend)</th>
<th>Tg(PVB11) (rich phase)</th>
<th>Tg(PVP) (rich phase)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/100</td>
<td>—</td>
<td>69</td>
<td>—</td>
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<tr>
<td>10/90</td>
<td>75</td>
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<tr>
<td>20/80</td>
<td>81</td>
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<td>—</td>
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<tr>
<td>30/70</td>
<td>85</td>
<td>—</td>
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<tr>
<td>40/60</td>
<td>86</td>
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<tr>
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<td>85</td>
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<tr>
<td>90/10</td>
<td>—</td>
<td>85</td>
<td>164</td>
</tr>
<tr>
<td>100/0</td>
<td>—</td>
<td>—</td>
<td>170</td>
</tr>
</tbody>
</table>

<sup>a</sup> PVP/PVB11 (w/w)