tencies. In particular, it is not clear which value of R should be used in the evaluation of τ according to the present treatment in order to match the conditions of the two-phase model used in the other paper. Therefore conclusions concerning the dipole moment and its relaxation behavior of polyelectrolytes based on the mechanism discussed previously[3] and on the numerical values of τ derived here should be considered with proper care.

References and Notes

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Excimer Fluorescence as a Molecular Probe of Blend Miscibility. 4. Effect of Temperature in Solvent Casting

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ABSTRACT: Excimer fluorescence from poly(2-vinylnaphthalene) (P2VN) is utilized in conjunction with observations of optical clarity to assess the thermodynamic state of blends of P2VN with poly(*n*-butyl methacrylate) (PnBMA), poly(ethyl methacrylate) (PEMA), or poly(methyl methacrylate) (PMMA). When blends are prepared by solvent casting at temperatures greater than the glass transition temperature of the binary polymer 1/polymer 2 system, followed by quenching to an examination temperature below T_g, the fluorescence and optical properties are characteristic of the morphology in thermodynamic equilibrium at the casting temperature. The phase relationships for such equilibrium P2VN/PnBMA blends are described quite well by a Flory–Huggins treatment with a temperature-dependent binary interaction parameter. All P2VN/PMMA and P2VN/PEMA blends prepared by solvent casting below T_g are in nonequilibrium states; apparent miscibilities for the P2VN/PMMA blend are much higher than predicted by the Flory–Huggins treatment.

Introduction

Due to the relative ease with which material properties may be modified by physical blending, considerable attention has been focused recently on the thermodynamics of amorphous polymer blends.[1-5] Although a number of sophisticated experimental techniques, including neutron, light, and X-ray scattering, pulsed nuclear magnetic resonance, differential scanning calorimetry, and electron microscopy, have been used to observe phase separation, none provides detailed information on the segmental level. Moreover, the existing methods lack the sensitivity for detection of blend components at concentrations less than about 10%.

This is part of a series of papers in which a relatively new spectroscopic method, excimer fluorescence, is used as a molecular probe of polymer blend morphology. A critical requirement for application of the excimer probe technique is the existence of "excimer-forming sites", which result when two identical aromatic rings in their electronic ground states are physically apposed in a coplanar sandwich arrangement at the equilibrium van der Waals separation distance.[6] Excitation of one member of this paired structure by direct absorption of light or by energy transfer from a nearby excited ring may lead to the formation of an electronically excited complex, the excimer. Since the ground state of the excimer is repulsive, there is no absorption spectrum characteristic of the complex; the excimer may be examined only by fluorescence methods.

Excimer fluorescence has been observed in a wide variety of aromatic vinyl polymers in which the excimer-forming site may result from intramolecular association between aromatic rings on adjacent or nonadjacent repeat units or from intermolecular association between rings on different polymer chains. Excimer-forming sites are of great photophysical importance in aromatic vinyl polymers, even at low concentration, because the electronic excitation energy can migrate from chromophore to chromophore. This migration takes place nonradiatively by resonance transfer between an electronically excited chromophore and a ground-state chromophore. Radiationless energy transfer has been reviewed for aromatic molecules in general by Förster[7] and Berlman[8] and for aromatic vinyl polymers in particular by Klöpffer.[9]

In this work, as in previous studies, excimer fluorescence from an aromatic vinyl polymer introduced as a guest in a matrix of a nonfluorescent host polymer is used to study low-concentration miscibility and small-scale phase separation. Previous papers focused on three variables important to polymer–polymer miscibility: enthalpic segmental interaction between guest and host polymer,[10] concentration of the guest polymer in the host matrix,[11] and molecular weights of the guest and host polymers.[12] The objective of this study is to determine the effect of casting temperature. Major emphasis is placed on two series of blends in which the guest aromatic vinyl polymer is poly(2-vinylnaphthalene) (P2VN) and the nonfluorescent host polymer is either poly(*n*-butyl methacrylate) (PnBMA) or poly(methyl methacrylate) (PMMA). A smaller amount of work is performed on blends of P2VN with poly(ethyl methacrylate) (PEMA). These particular hosts were selected because the enthalpic interactions with P2VN are sufficiently dissimilar to yield distinctly different phase relationships, and the glass transition temperatures differ widely, providing an opportunity to study nonequilibrium aspects of solvent casting.

Experimental Section

P2VN was prepared by bulk thermal polymerization and purified by precipitating three times from toluene by addition of methanol.[10] PnBMA and PMMA were obtained from Polysciences (PnBMA, catalog no. 2061, lot no. 21-38-7; PMMA, catalog no. 4553) and purified by precipitating three times from acetone by addition of deionized water. The sample of PEMA was an Elvacite acrylic resin type 2043 obtained from du Pont and purified in the same manner as PnBMA and PMMA. It was not a pure homopolymer, as indicated by the manufacturer's notation that it was

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Table I

	$[\eta]$,[a] dL/g	$\bar{M}_v$[b]	ρ,[c] g/cm³	T_g, K	α_p,[d] K⁻¹	δ,[e] cal^1/2 cm^-3/2
PnBMA	0.581	254 000	1.045	293	3.60×10^{-4} 6.35×10^{-4}	8.71
PMMA	0.390	125 000	1.172	378	2.69×10^{-4}	9.21
PEMA	0.186	68 000	1.107	338	3.14×10^{-4} 6.1×10^{-4}	
P2VN	0.219	71 400	1.124	405	4.5×10^{-4}	8.85

[a] In benzene at 303 K for PnBMA and PMMA; in toluene at 303 K for P2VN; in MEK at 296 K for PEMA. [b] Using $[\eta] = KM^a$: $K = 4.0 \times 10^{-5}$, $a = 0.77$ for PnBMA; $K = 2.8 \times 10^{-5}$, $a = 0.79$ for PEMA; $K = 5.2 \times 10^{-5}$, $a = 0.76$ for PMMA; $K = 1.48 \times 10^{-5}$, $a = 0.66$ for P2VN. [c] At 303 K using density gradient column. [d] Measured using TMS-1 in the temperature range 273–373 K. For PnBMA and PEMA below and above T_g; for PMMA and P2VN below T_g. [e] Estimated with Hoy's values for PnBMA and PMMA. See text for P2VN. No value is listed for PEMA because the identification of the molecular structure is equivocal (see text).

"modified for improved pigment wetting and adhesion". In spite of the difficulties associated with complete characterization, it was included in this study to reinforce the qualitative correlation between fluorescence behavior and optical quality of solvent-cast films; cf. seq. Intrinsic viscosities and viscosity-average molecular weights are reported in Table I along with the Mark–Houwink constants and other physical parameters.

Solid films of the host polymers and of blends were prepared by solvent casting from spectrophotometric grade toluene supplied by Aldrich. Initial solution concentration was 8.8% polymer by weight for PMMA, 10.4% for PEMA, and 7.1% for PnBMA hosts. Films were cast at five temperatures: 295, 313, 333, 353, and 373 K. The first step in casting at elevated temperature was to heat the casting solution, the glass plate, the cover (which is used to retard the evaporation rate), and the casting pipet to the desired temperature in the oven. All items were then removed from the oven, a known amount of the heated solution was spread over a premeasured area of the casting plate, and the plate was re-covered and placed back in the oven. The film was allowed to dry at the casting temperature for 24 h, after which it was placed under vacuum at room temperature and dried further to constant weight. Final film thickness was 15–20 μm.

Polymer film densities were determined with a density gradient column filled with a water–ethanol–zinc chloride mixture. Glass transition temperatures were determined by thermal mechanical analysis with a Perkin-Elmer TMS-1 in the probe penetration mode. Thermal expansion coefficients were determined in the probe expansion mode.

The spectrofluorimeter has been described previously.[10] All spectra were taken at room temperature using backface illumination with exciting light at 290 nm. Simple envelope intensities taken in regions of minimal overlap of the excimer and monomer bands, e.g., 398 nm for the excimer and 331 nm for the monomer, were used for calculation of I_D/I_M. The ratios were not corrected for the spectral response of the spectrofluorimeter.

Results

1. Host Matrix and Concentration Dependence. The most important experimental parameter for this study is the ratio of excimer to monomer emission intensities, I_D/I_M. For randomly dispersed chains of P2VN in a matrix of a glassy host polymer, an earlier analysis[13] showed that

$$\frac{I_D}{I_M} = \left[\frac{k_{FD}}{k_{FM}}\frac{k_E}{k_D}\right]\left[\frac{f_R}{1-f_R}\right] \quad (1)$$

where k_{FD} and k_{FM} are the fluorescence rate constants for excimer and monomer emission, k_D is the overall excimer decay constant given by $k_D = k_{FD} + k_{ID}$ in which k_{ID} is the rate constant for nonradiative decay, k_E is the rate constant for excimer formation resulting from energy migration along the chain, and f_R is the fraction of aromatic rings in excimer-forming sites.

Although it is possible to calculate f_R for the case where excimer formation occurs only between adjacent repeat units on the same polymer chain, a phase-separated blend will also contain nonadjacent intramolecular and intermolecular sites. The intramolecular sites will be independent of the bulk concentration whereas the intermolecular sites will depend directly upon concentration.[11] Furthermore, as the local concentration of aromatic rings increases, the probability of exciton migration occurring across loops in the same chain or between different chains will increase. Thus, the random walk executed by the hopping exciton could change from a one-dimensional to a three-dimensional process.[14]

The simple Birks' kinetic scheme from which eq 1 is derived has recently been shown to be inappropriate for naphthalene-containing polymers in solution.[15-17] Nevertheless, the functional form of the $f_R/(1 - f_R)$ factor is identical with that obtained from a simple treatment of a three-dimensional random walk, although the rate constant factor is altered.[18] The thrust of this paper is to develop an empirical relationship between I_D/I_M and the morphology. Thus, eq 1 is presented here for illustrative purposes and is not used explicitly in the analysis. Preceding papers have demonstrated that a number of features of molecular structure may be inferred from trends in the observed I_D/I_M values. Hence, it is worthwhile to review briefly the earlier results and their interpretation.

In blends of high polymers, the entropic contribution to the free energy of mixing is generally overshadowed by the enthalpic contribution. A convenient means of obtaining an estimate of the latter quantity for blends in which the segmental interactions between the two polymers are mainly dispersive, with no hydrogen bonding or polar interaction, is to use

$$\Delta H_{12} = RT\chi_{12}v_1v_2 \quad (2)$$

where v_1 and v_2 are volume fractions and χ_{12} is the binary interaction parameter given by

$$\chi_{12} = \frac{V_r}{RT}(\delta_1 - \delta_2)^2 \quad (3)$$

in which V_r is the reference repeat unit molar volume, taken to be the smaller of the two repeat unit molar volumes, R is the gas constant, T is the absolute temperature, and δ is the Hildebrand solubility parameter.[19] The solubility parameters may be determined from intrinsic viscosity or swelling measurements or estimated by using the concept of molar group additivity. The latter approach has been recommended by Krause[20,21] and has been used in this work.

Since the solubility parameters of the guest and host polymers are reasonably close together, as seen in Table I, the accuracy of the individual values is an important concern. For this reason, better density measurements have been used to recalculate the host solubility parameters for the homologous series of poly(alkyl methacrylates) examined in the first study.[10] The ratio of excimer to monomer emission intensities, I_D/I_M, for the guest P2VN is replotted vs. the corrected host solubility parameter in Figure 1. The hosts of major interest for this work, PnBMA and PMMA, are highlighted to emphasize their positions relative to the minimum. Similar behavior has been observed for blends of poly(4-vinylbiphenyl) and polyacenaphthalene in the same host series.[11]

The minimum in I_D/I_M was initially interpreted as resulting from a minimum in the number of excimer-forming sites at the point where the guest solubility parameter

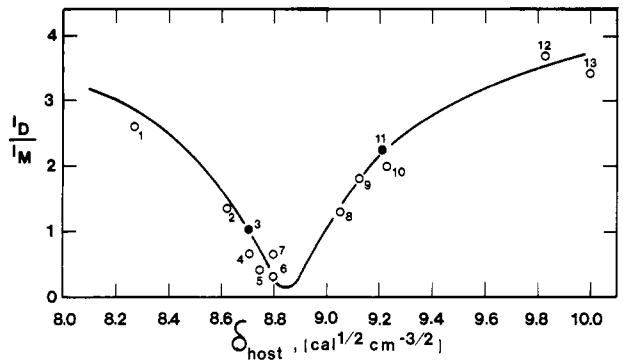

Figure 1. Dependence of I_D/I_M fluorescence ratio on the host solubility parameter. The number beside each point refers to the host polymer: (1) PIBoMA; (2) PiBMA; (3) PnBMA; (4) PtBMA; (5) PiPMA; (6) PsBMA; (7) PnPMA; (8) PCMA; (9) PS; (10) PBzMA; (11) PMMA; (12) PVAc; (13) PPhMA. The acronyms are interpreted in ref 10.

matches that of the host.[10] At the minimum there is maximum interpenetration of the guest polymer coils with the host polymer chains which will result in a local dilution of aromatic rings and will reduce the number of intermolecular excimer sites. Similarly, the number of intramolecular sites between aromatic rings on nonadjacent repeat units should decrease if the radius of gyration of the guest P2VN increases above the Flory value in the good host polymers. An alternative explanation, leading to the same qualitative effect on I_D/I_M, is that there is a decreased efficiency of energy migration in good hosts.[14]

In spite of this ambiguity, the I_D/I_M vs. solubility parameter curve is directly analogous to a plot of intrinsic viscosity of polymer solutions prepared from different solvents or of the inverse swelling ratio of a cross-linked polymer in different solvents. As such, the solubility parameter for P2VN as a guest in a poly(alkyl methacrylate) host matrix should be taken as 8.85 cal$^{1/2}$ cm$^{-3/2}$, which differs slightly from that previously reported.[10] This new value was used in the preceding paper[12] and will also be used in the present study. It should be noted, however, that δ(P2VN) may not be the same if measured in another homologous host series having widely differing dispersive, polar, or hydrogen bonding interactions.

The effect of concentration on the observed I_D/I_M ratio for solvent-cast blends of P2VN with PnBMA and PMMA hosts prepared at 295 K is shown in Figure 2.[11] The vertical bars represent standard deviations. The accuracy of the fluorescence data is reduced for the very low concentration blends because of interference from the slight background fluorescence. The observed I_D/I_M for the blends in this very low concentration range was corrected for possible interference from light scattering or impurity fluorescence by subtracting the contribution to the monomer and excimer band intensities of a blank host film. Both fluorescence spectra of the host and the blend films were obtained under the same experimental conditions. The corrections amounted to 15% of I_M and 5% of I_D for the P2VN/PMMA blends and 30% of I_M and 10% of I_D for the P2VN/PnBMA blends.

The common value of I_D/I_M for the two hosts at infinite dilution indicates that the P2VN guest polymer coils are effectively isolated from one another, forcing excimer formation to be totally intramolecular between adjacent repeat units. Such interactions should be independent of matrix, whereas intramolecular excimer formation between nonadjacent rings may exhibit a matrix dependence. The initial rise in I_D/I_M for PMMA may reflect a change in the mode of energy migration associated with local guest chain

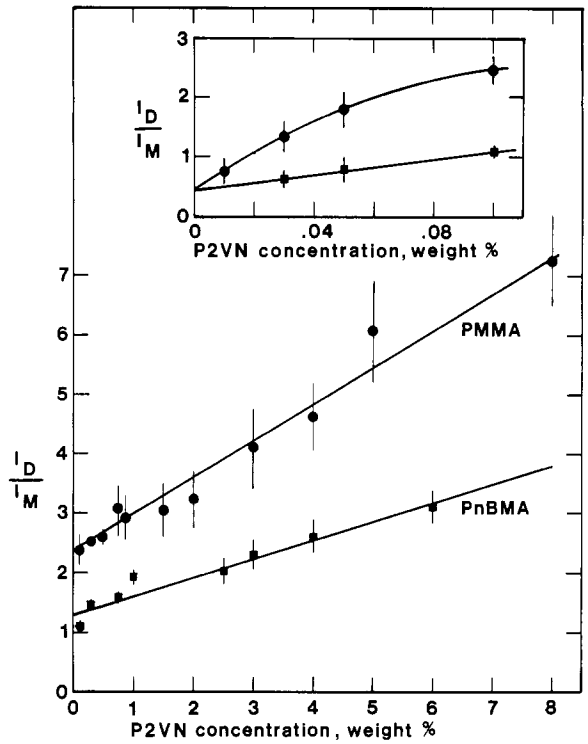

Figure 2. Dependence of I_D/I_M fluorescence ratio on bulk concentration of poly(2-vinylnaphthalene) (P2VN) as a guest in poly(methyl methacrylate) (PMMA) and poly(*n*-butyl methacrylate) (PnBMA) hosts. Films were cast and examined at 295 K.

aggregation prior to macroscopic phase separation. The increase in I_D/I_M at higher concentration would be expected if either new intermolecular excimer sites were being created or additional pathways for energy migration were being established. A consistent interpretation of both the host matrix and concentration studies is that I_D/I_M may be correlated qualitatively with guest chain aggregation.

2. Generation of Experimental Phase Diagrams Using I_D/I_M Contours. Although enthalpic interactions and guest concentration may be varied in a straightforward fashion, an analogous examination of the effect of temperature presents considerable difficulties. Certainly, thermodynamic equilibrium may be ensured in the blend if fluorescence measurements are made sufficiently above the glass transition temperature. Unfortunately, such an experiment introduces two new factors. The first arises as a direct consequence of the increase in segmental mobility. The formation of an excimer in the glassy state as a result of competitive trapping of the migrating singlet exciton, termed migrational sampling, has already been discussed. In addition, excimer formation may result from rotational sampling in which the residence time of the excitation at a particular aromatic ring is long enough for segmental motion to cause a second aromatic ring to move into the proper position to form an excimer. Since this process depends upon the local viscosity, the rate will increase with temperature, thus increasing the observed excimer fluorescence. The increase due to this cause, however, will bear no relation to any changes in molecular structure arising from alteration of the phase relationships. The second difficulty in use of temperature as a variable is that the nonradiative component of the overall excimer decay constant, k_{ID}, also depends strongly on temperature.[6] Hence, I_D/I_M will change simply due to excimer complex destabilization. Again, this does not reflect any change

in the blend thermodynamics.

A strong incentive thus exists to perform all fluorescence measurements at the same temperature and, preferably, in the glassy state. In order to do this and still accomplish the objective of using excimer fluorescence to determine the temperature dependence of blend miscibility, the blend is prepared by solvent casting at an elevated temperature, T_c, and then quickly cooled before the fluorescence measurement is made. The intent is to "freeze in" the morphology resulting from the evaporation of the solvent at the casting temperature, at least for a length of time sufficient to determine I_D/I_M. Since this approach is essential to the subsequent analysis, the solvent casting process is examined in some detail in the Appendix.

The important conclusion from the casting studies is that the molecular structure in P2VN/PnBMA blends cast 20 K above the T_g of the binary blend and subsequently quenched should represent thermodynamic equilibrium at the casting temperature. This includes all of the P2VN/PnBMA blends with the possible exception of some of those prepared at 293 K. On the other hand, all of the P2VN/PMMA blends were prepared at casting temperatures less than or equal to T_g of the binary blend and, thus, are in nonequilibrium states. A similar situation applies to the P2VN/PEMA blends in which the host T_g is in the midrange of casting temperatures.

The standard procedure for describing equilibrium binary phase relationships is with a phase diagram including the binodal curve which is the locus of temperature and composition points for which the chemical potential of a particular component is equal in the two phases. A common experimental method for determining the binodal is to perform cloud point measurements in which the turbidity of a blend at a particular composition is monitored as a function of temperature and the onset of cloudiness noted. The locus of temperature–composition points for which visible phase separation may be established reversibly defines the binodal. Although light scattering methods are, in general, quite powerful, the simple test of optical clarity often used is subject to considerable ambiguity. In order to see any cloudiness at all, there must be a sufficient difference in refractive indices between the two polymers. Assuming this to be the case, the observation of cloudiness or opacity gives reasonable assurance of two-phase behavior. Observation of a clear film does not necessarily mean that the blend is miscible, however, because a bilayer structure might form or the phase domains may be too small to scatter the incident light.

In spite of the difficulties in the use of visual appearance as a morphological tool, it is of interest to explore the point further because some of the P2VN/PnBMA, P2VN/PEMA, and P2VN/PMMA blends were cloudy and obviously phase separated while others were clear. For example, all P2VN/PMMA blends cast at 293 K are visibly cloudy and phase separated for concentrations in excess of 0.5 wt %, while films prepared at lower concentrations are optically clear. The corresponding concentrations separating clear and cloudy films for the P2VN/PEMA and P2VN/PnBMA blends cast at 293 K are considerably larger at about 3 and 5%, respectively. Thus it appears that the PnBMA host provides a more thermodynamically compatible matrix than either the PMMA or PEMA host.

The morphological observations on optical quality for all of the blends are included in Figures 3–5, in which I_D/I_M is used to parameterize the results. Each data point in these figures corresponds to a particular film with a given composition and casting temperature. The open points represent optically clear films and the solid ones refer to those which were cloudy. Half-filled points are in a transition region.

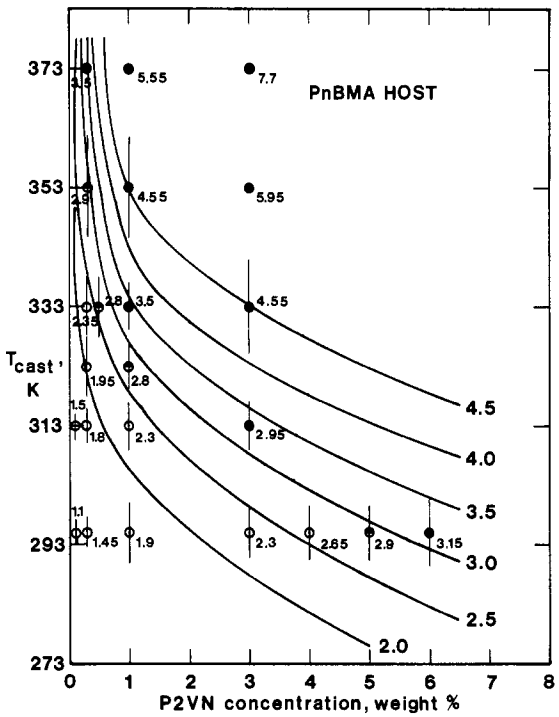

Figure 3. Generation of experimental phase diagram for P2VN/PnBMA blends. The I_D/I_M value for a given casting temperature and P2VN concentration is indicated next to each point. Closed circles represent cloudy films and open circles represent clear films. Each solid contour line represents a constant I_D/I_M value which is indicated next to each line.

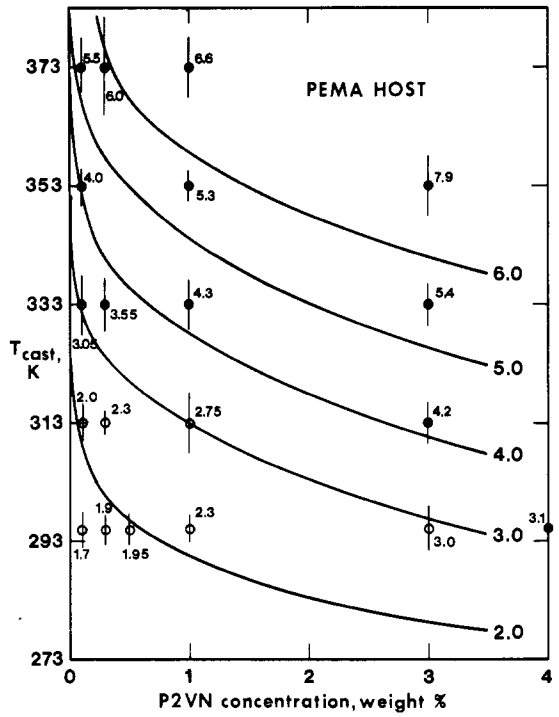

Figure 4. Generation of experimental phase diagram for P2VN/PEMA blends.

The results for the PnBMA host in Figure 3 are particularly significant because, if the quenching procedure is accepted as a valid means of freezing in the phase structure, the P2VN/PnBMA visual and fluorescence data reflect the equilibrium morphology present at the casting temperatures. Thus, it is reasonable to treat the

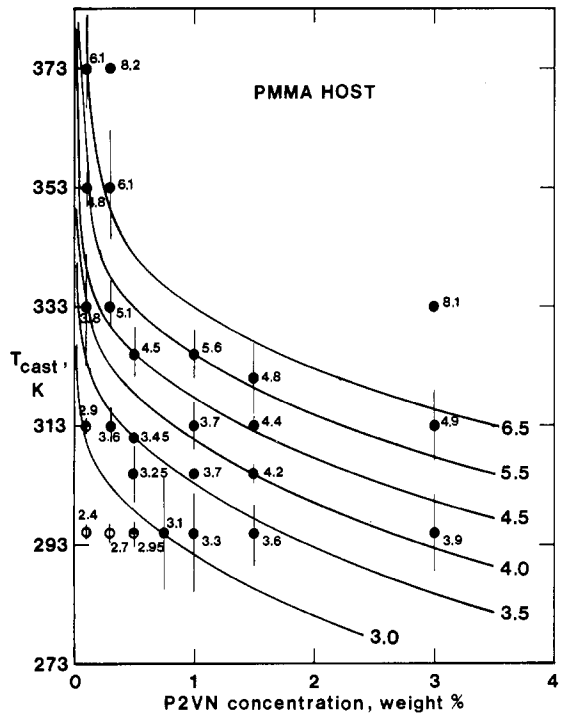

Figure 5. Generation of experimental phase diagram for P2VN/PMMA blends.

P2VN/PnBMA data points in the same manner as is done for the traditional cloud point measurements and to denote the line separating the clear and cloudy films as the binodal. After this is done, a most interesting correlation is observed—the cloud point curve coincides approximately with an interpolated fluorescence contour line based upon a constant value of $I_D/I_M = 3.0 \pm 0.5$. In other words, most films with I_D/I_M greater than 3.0 are cloudy while those with smaller I_D/I_M values are clear. Similar contour lines for other values of I_D/I_M were prepared; the nominal values are listed beside each solid curve. The fluorescence results for PEMA and PMMA hosts are correlated in the same fashion in Figures 4 and 5. Again, a contour line of $I_D/I_M = 3$ is a reasonable representation of the demarcation between clear and cloudy films in both cases.

The significance of these observations may be wide ranging. Whereas the clear/cloudy demarcation is both qualitative and macroscopic, the I_D/I_M ratio could, in principle, provide a semiquantitative measure of chain clustering at the molecular level, if a complete model for the photophysics were available. Although this is not the case at the present time, we infer from the coincidence of a particular value of I_D/I_M with the onset of visible phase separation that the local concentration of aromatic rings in the P2VN-rich domains appears to be the same for all the poly(alkyl methacrylate) blends at the point where the domain sizes are large enough to scatter visible light. It is interesting to note, however, that the I_D/I_M value which correlates with the clear/cloudy demarcation is far below the neat film I_D/I_M ratio of about 20. This may mean that kinetic restrictions in the highly viscous casting solution have prevented complete demixing on the short-range scale, of the order of 10^2 Å, although sufficient segregation has occurred to lead to a refractive index difference and visible phase separation on a large scale, of the order of 10^4 Å. This point is under further study.

Discussion

1. Binary Interaction Parameter. In order to demonstrate that the solvent casting method employed in this work is, under appropriate conditions, suitable for establishing experimental phase diagrams, it is necessary to compare the experimental cloud point curve with thermodynamic predictions. As noted earlier, the most important contribution to ΔG_{mix} for blends of high polymers is due to enthalpic effects represented by the binary interaction parameter. In the original Flory–Huggins treatment[22-25] χ_{12} is assumed to be independent of temperature, concentration, pressure, and molecular weight. There is compelling experimental evidence which indicates that those assumptions are oversimplifications, however, and χ_{12} is now generally considered to be dependent upon both temperature and concentration. A number of empirical approaches, such as those of Tompa[26] and Koningsveld,[27] have been taken to explain the thermodynamic behavior of specific polymer mixtures.

One factor which was largely ignored in such approaches is the possible existence of a noncombinatorial component to the entropy of mixing. Of course, the classical combinatorial entropy contribution to ΔG_{mix} is calculated assuming complete randomness of orientation and rigid molecules.[22-25] The actual distribution of molecules will not be perfectly random, however, particularly if there are any specific interactions. Moreover, for nonrigid molecules there is an influence of the surrounding on the average randomness of orientation of a segment in a polymer chain relative to the orientation of the preceding segment. Experimental evidence has clearly confirmed the existence of a noncombinational contribution to the entropy of mixing.[28] Huggins, in his new theory, accounted for these nonrandom factors by suggesting that the interaction parameter should consist of an entropic part in addition to the enthalpic part.[29-31]

A similar approach, which is of more direct usefulness for this study, was used by Koningsveld.[32] He obtained a closed expression for the concentration dependence of χ_{12} for mixtures of homopolymers, given by

$$\chi_{12}(T,v_2) = \left[\alpha + \frac{\beta}{1 - \gamma\epsilon v_2}\right] \tag{4}$$

The significant aspect of eq 4 is that there are two contributions to χ_{12}: an empirical entropy correction, α, and an enthalpic contribution, β, related to the heat of mixing. In the second term of eq 4, $\beta = (Z-2)\Delta w_{12}/RT$, in which Z is the coordination number of the lattice, Δw_{12} is the interchange energy between segments of polymer 1 and polymer 2, $\gamma = 2/(Z-2)$ relates the number of pairs of unlike neighbors in the lattice to the volume fractions of the two polymers, and $\epsilon = (1/x_1 - 1/x_2)$, in which x is the deree of polymerization. ϵ is related to the probability of having unlike neighbors with an upper limit of unity for a solvent–polymer mixture and a lower limit of zero for a mixture of two infinitely high molecular weight polymers.

The analysis employed in this work was inspired by Koningsveld's development of eq 4 and the application of Flory–Huggins lattice theory to blends by Krause.[21] If the coordination number in eq 4 is between 6 and 12, γ has a value of the order unity. In addition, for the particular polymers of this work, ϵ is 1.58×10^{-3} for the P2VN/PnBMA blend and 5.48×10^{-4} for the P2VN/PMMA blend. Thus, for low concentrations with v_2 below 0.10, the concentration-dependent term $1 - \gamma\epsilon v_2$ in eq 4 is essentially unity. If, following Krause,[21] β is taken equal to the interaction parameter expected for regular solutions, eq 4 then reduces to

$$\chi_{12}(T) = \chi_S + \chi_H \tag{5}$$

where $\chi_S = \alpha$ and χ_H is given by eq 3. Since α is an

empirical constant used to fit the experimental data, it is convenient to carry through the calculation of ΔG_{mix} assuming first that $\alpha = 0$ and then that it has some finite value. It will be shown that, in fact, the enthalpic contribution χ_H is considerably larger than χ_S.

Of prime importance is the temperature dependence of χ_{12} which is contained explicitly in the RT factor in χ_H as well as implicitly in the solubility parameter. The latter dependence arises because in the molar group additivity approach the solubility parameter is estimated from the relation

$$\delta = \rho \sum F_i / M^0 \tag{6}$$

where ρ is the bulk density, F_i is a tabulated[21] molar contribution resulting from a particular chemical moiety in the repeat unit, and M^0 is the molecular weight of the repeat unit. Krause has shown that this technique works well for polymer–polymer pairs with similar polarity and hydrogen bonding requirements.[21] The bulk density in eq 6 is, of course, temperature dependent. The temperature dependence of δ may then be estimated readily by using experimental measurements of ρ at 303 K and of the thermal expansion coefficient.

Conceptual justification for this approach may be derived from aspects of the equation-of-state theory developed by Flory and co-workers.[33,34] McMaster[35] has applied Flory's theory to mixtures of polystyrene and poly(vinyl methyl ether) and has concluded that the thermal expansion coefficient plays an important role in determining polymer–polymer miscibility; a small difference in pure-component thermal expansion coefficients is sufficient to cause blends of two high molecular weight polymers to exhibit a lower critical solution temperature. The incorporation of the thermal expansion coefficient to account for the temperature dependence of δ in this work provides a qualitative physical link between the two approaches.

Even stronger justification for our approach comes from the work of Biros, Zeman, and Patterson.[36] They noted that the solubility parameter method can incorporate dissimilarities in free volume, important to the equation-of-state theories, as well as dissimilarities in contact energies, which form the basis for the classical Flory–Huggins treatment, if the solubility parameters are assumed to be temperature and pressure dependent. The proposed dependencies are of the form

$$[\partial \ln \delta / \partial T]_p \cong -\alpha_p \tag{7}$$

$$[\partial \ln \delta / \partial P]_T = \beta_T \tag{8}$$

where α_p and β_T are the coefficients of thermal expansion and isothermal compressibility. Note that differentiation of eq 6 leads to

$$[\partial \ln \delta / \partial T]_p \cong -\alpha_p / (1 + \alpha_p \Delta T) \tag{9}$$

which reduces to eq 7 for small values of $\alpha_p \Delta T$. Biros et al. compared the predictions of both the equation of state and modified solubility parameter approaches for the dependence of the binary interaction parameter on temperature, pressure, solvent chain length, and polymer flexibility. Both treatments gave qualitatively similar predictions with values of χ based upon solubility parameters always lower than the equation-of-state predictions. Quantitative agreement between the two approaches could be achieved if an entropic correction term, represented by α in eq 4, were employed. Thus, the Flory–Huggins approach as modified in this work should provide a good representation of the equilibrium thermodynamic state of the blends.

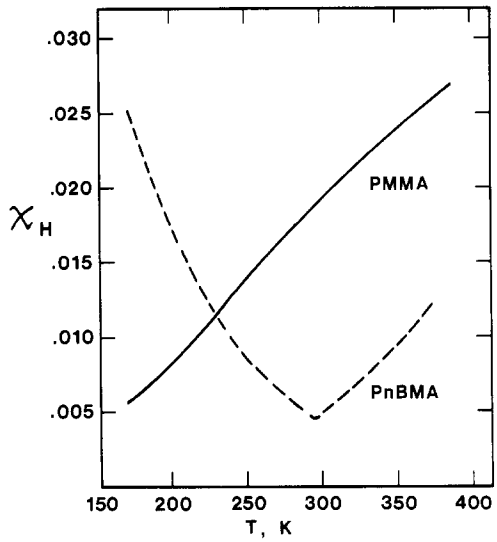

Figure 6. Estimated temperature dependence of the binary interaction parameter for P2VN/PnBMA (dashed line) and P2VN/PMMA (solid line).

Of course, the precise value of the interaction parameter depends critically on the accuracy of the solubility parameters because χ_H is proportional to the square of the difference of two very similar quantities. The values estimated for PnBMA and PMMA at 295 K listed in Table I seem to be very reasonable compared to the literature values of 9.25 $cal^{1/2}\ cm^{-3/2}$ for PMMA and 8.70 $cal^{1/2}\ cm^{-3/2}$ for PnBMA.[37] No experimental data could be found in the literature for P2VN.

Figure 6 shows the temperature dependence of χ_H for the PMMA and PnBMA host systems. For the PMMA host matrix χ_H increases continuously with temperature over the temperature range 173–373 K. On the other hand, χ_H for the PnBMA host first decreases, reaches a minimum at T_g, and then increases over the same temperature range. Detailed thermodynamic calculations were not performed for the P2VN/PEMA blends because the lack of knowledge of the molecular structure of the "modified" commercial host polymer prevented an accurate estimate of the solubility parameter.

The increase of χ_H with temperature above 293 K for PnBMA and PMMA host matrices and the observation that films prepared at higher casting temperatures are cloudy whereas those cast at lower temperatures are clear support the earlier suggestion that phase separation is occurring for blends prepared at higher casting temperatures. To quantify this statement, it is necessary to compare the observed fluorescence results with calculations of phase equilibria. This is the subject of the next section.

2. Calculated Phase Diagrams. The fundamental quantity necessary for calculation of the phase relationships is the free energy of mixing. In the Flory–Huggins treatment, the free energy of mixing per lattice site is given by

$$\frac{\Delta G}{RT} = \frac{v_1}{x_1} \ln v_1 + \frac{v_2}{x_2} \ln v_2 + \chi_{12} v_1 v_2 \tag{10}$$

where $x_{1,2}$ is the degree of polymerization. Preliminary characterization of the equilibrium thermodynamics of the P2VN/PnBMA and P2VN/PMMA blends may be obtained through calculation of $\Delta G/RT$ in which the binary interaction parameter is obtained from eq 3 and 5, assuming $\alpha = 0$. A necessary but insufficient condition that the blend be miscible is that $\Delta G/RT$ is negative. From Figure 7 it is seen that $\Delta G/RT$ is initially negative in the

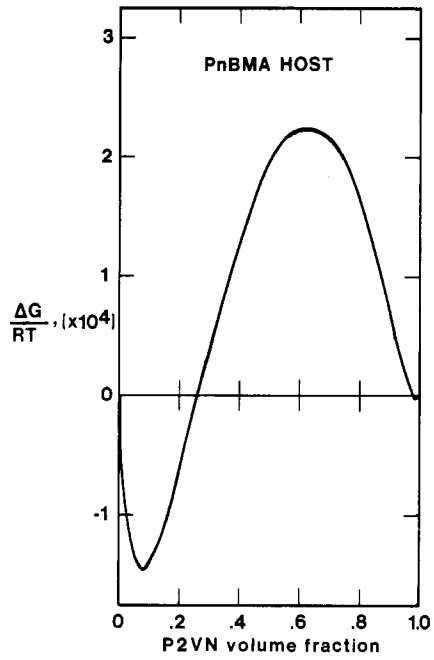

Figure 7. Concentration dependence of Flory–Huggins free energy of mixing for P2VN/PnBMA blends.

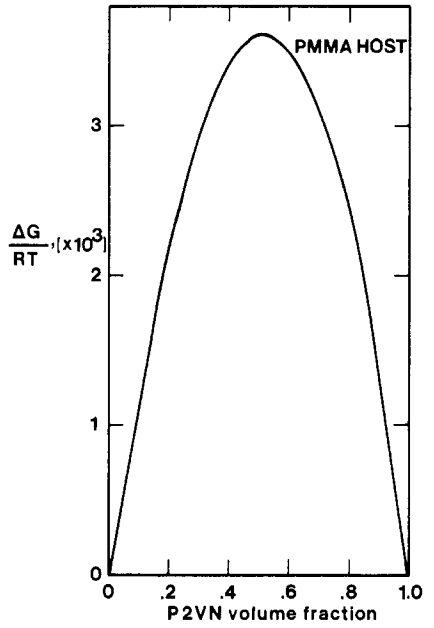

Figure 8. Concentration dependence of Flory–Huggins free energy of mixing for P2VN/PMMA blends.

P2VN/PnBMA blends for P2VN concentrations up to about 25% and positive thereafter. Thus, the P2VN/PnBMA blend may be miscible for low guest concentrations. In Figure 8, $\Delta G/RT$ is always positive in the P2VN/PMMA blends except for extremely low guest concentrations and, hence, these blends are expected to be immiscible over almost the whole concentration range.

It is of interest to consider briefly the possible type of phase behavior which is expected for polymer–polymer systems. McMaster[35] concluded from his equation-of-state calculations of binodal and spinodal curves for simulated polymer pairs that lower critical solution (LCS) behavior is actually more common than upper critical solution behavior in polymer–polymer blends. He also concluded that small positive values for the interaction parameter can lead to hourglass-shaped binodal and spinodal curves and that increasing the molecular weight of either polymer may also

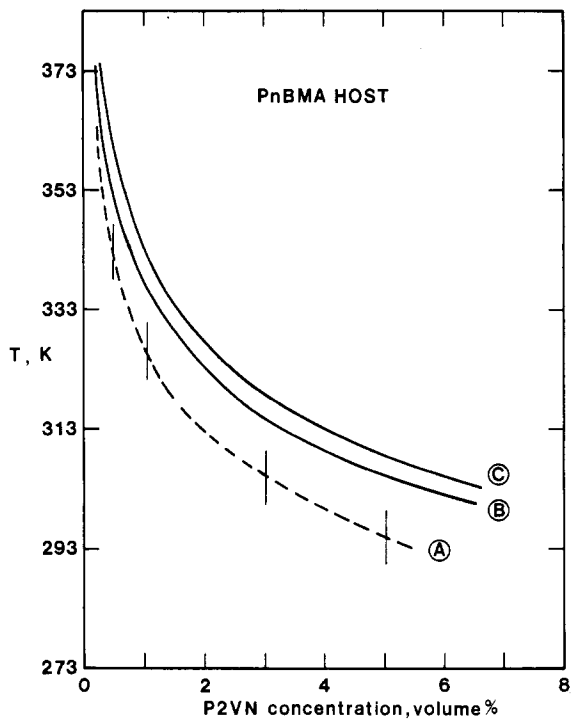

Figure 9. Calculated and experimental binodal curves for the P2VN/PnBMA blends. Curve A represents the $I_D/I_M = 3$ contour line, curve B represents the calculated binodal for a solvent-free blend, and curve C represents the calculated binodal for a blend with 5% solvent.

eliminate the LCS behavior and replace it with a limited miscibility binodal over the entire temperature range. With this as background, the Flory–Huggins treatment, modified by use of a temperature-dependent interaction parameter, may be used to calculate the binodal curves. The working equations have been described previously.[12]

The calculated Flory–Huggins binodal for the binary P2VN/PnBMA blends, which should represent equilibrium states at the casting temperatures, is shown as the solid curve B in Figure 9. The experimental cloud point curve, which coincides with the $I_D/I_M = 3.0$ contour, is the dashed curve A. Since, as will be shown in the Appendix, residual solvent is present in the cast films of all hosts, the thermodynamic calculations should actually be based on a ternary guest polymer/host polymer/casting solvent system. Scott[38] considered the presence of a solvent with two other polymers and suggested that the presence of solvents will work to reduce χ_{12}. Thus, the effective interaction parameter should be given by $\chi_{12}(1 - v_s)$, where v_s is the volume fraction of solvent. Curve C in Figure 9 is the binodal curve corresponding to a 5% by volume residual solvent concentration.

The experimental and calculated binodals for P2VN/PnBMA blends are relatively close, assuming that α in eq 3 is zero. However, curve C can be made to superpose exactly on curve A by selecting an entropy correction term $\alpha = 0.001\,31$ which is independent of temperature. Since this term is only about 20% of χ_H, the overall approach seems quite reasonable.

The experimental cloud point curve for the P2VN/PMMA/toluene system is compared to calculated binodals for a range of solvent volume fractions in Figure 10. The behavior of the PMMA host is considerably different from that of the PnBMA. Although the residual solvent concentration is considerably higher than for PnBMA, at about 19 vol %, comparison of the experimental cloud point curve and calculated binodals would imply that the

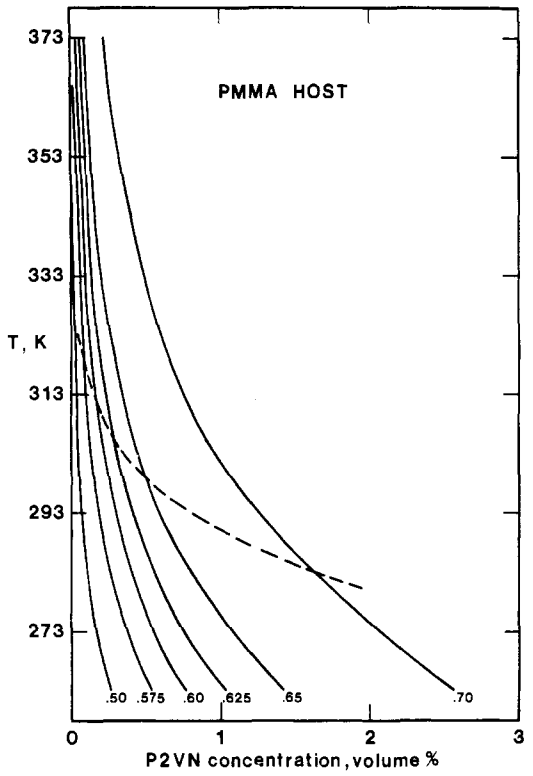

Figure 10. Calculated binodal curves for P2VN/PMMA blend in the presence of different amounts of solvent. The volume fraction of solvent is indicated beside each curve. The dashed line represents the $I_D/I_M = 3$ contour line.

solvent composition is much higher and quite variable. The explanation for this strange behavior is, of course, that all P2VN/PMMA films represent nonequilibrium states. The calculated binodal suggests that in the absence of solvent the guest and host are highly incompatible and the blend would separate into two pure phases if true thermodynamic equilibrium could be reached. The high T_g of the blend prevents the system from attaining equilibrium and, hence, results in total disagreement between theory and experiment.

Summary

A central objective of this paper has been to continue the development of the excimer fluorescence technique as a molecular probe of structure in amorphous polymer blends. In establishing the feasibility of any new experimental method for providing more detailed information about a physical phenomenon, it is necessary to compare the new approach with existing classical techniques. The optical clarity has served as such a classical method for comparison in this work. Viewed in its most limited sense, the discussion of phase relationships could have been developed by using only the crude visual morphological observations. At this level, the major contribution of this paper would be in the combined use of solvent casting and a modified Flory–Huggins theory to treat the equilibrium thermodynamics.

It has been shown that solvent casting at temperatures greater than T_g for the ternary polymer 1/polymer 2/solvent system, followed by rapid quenching to a temperature below T_g, can quench in the morphology characteristic of the casting temperature. Assuming the morphology to represent an equilibrium state at the casting temperature, the solubility parameter approach has been shown to give a temperature-dependent χ_{12} which, when used in the Flory–Huggins theory, provides a good fit to the experimental binodal. Even better agreement is obtained if a small empirical entropic contribution is applied to χ_{12}.

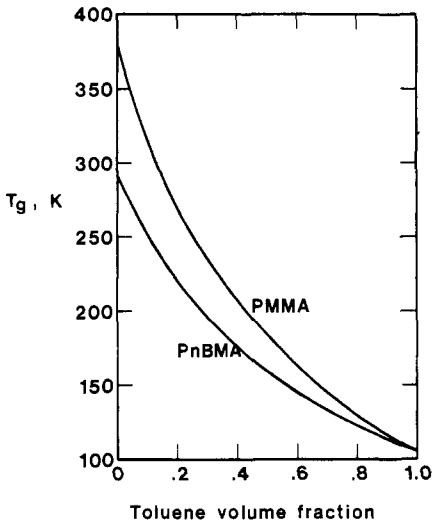

Figure 11. Effect of solvent and concentration on glass transition temperature of PnBMA/toluene and PMMA/toluene systems.

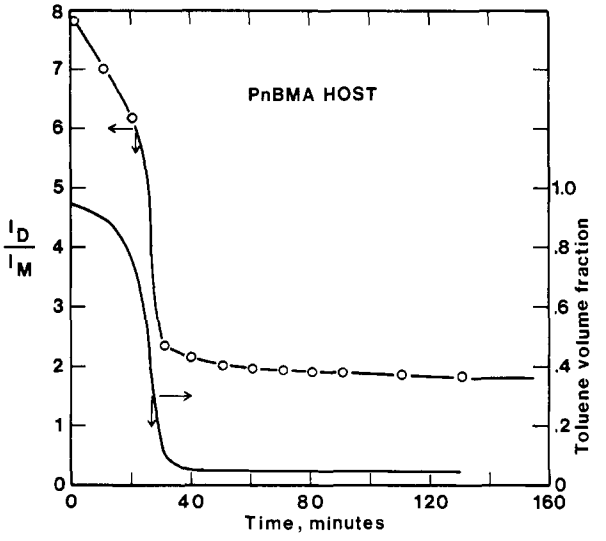

Figure 12. I_D/I_M ratio and solvent composition during drying of 1% P2VN/PnBMA/toluene system. Initial solution concentration was 6.67 g of polymer/dL of toluene.

The major limitation of the optical morphological technique is, of course, the ambiguity associated with the existence of apparently clear blends which are, in fact, thermodynamically incompatible. Because of this, the fluorescence results have considerably broader significance for more detailed study of the morphology on the molecular level. When a photophysical model which can treat both one- and three-dimensional energy migration is developed, it may be possible to determine the size of the guest-rich domains and, indeed, to follow the kinetics of domain growth during phase separation.

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Appendix. A Critique of Solvent Casting

An important parameter for solvent casting is the glass transition temperature, T_g, for the ternary mixture, which depends strongly upon the amount of solvent present. At

high solvent concentration, T_g will be quite low and molecular motion will be facile. Thus, there should be no kinetic limitation to achieving thermodynamic equilibrium. As the solvent evaporates, the solution viscosity will increase and mobility will be reduced, although equilibrium may still be achieved on a reasonable time scale as long as the temperature of measurement is greater than T_g for the system. After complete solvent evaporation, the T_g should be that of the binary blend. The possibility of multiple T_g's resulting from phase separation will be ignored for a practical reason—classical methods for determining multiple T_g's, such as differential scanning calorimetry of dynamic mechanical spectroscopy, require the concentration of the minor component to exceed 10%; all blends in this study are at lower concentration.

An estimate of the change in T_g in the plasticized blend as a function of solvent concentration may be obtained by the Bueche relation[39]

$$T_g = \frac{T_{gp} + (KT_{gs} - T_{gp})v_s}{1 + (K-1)v_s} \tag{11}$$

where T_{gp} and T_{gs} are the glass transition temperatures of polymer and solvent, v_s is the volume fraction of solvent, and K is the ratio of the difference in volume coefficients of expansion for the liquid and glassy states of the solvent to that for the polymer. A value of 2.5 was used for K, as recommended by Bueche.[39] The estimated T_g's for the PnBMA/toluene and PMMA/toluene solutions are shown in Figure 11.

Of critical significance to the use of solvent casting for freezing the blend morphology is the value of T_c relative to T_g of the binary system. If T_c is appreciably greater than T_g for the blend, and the blend is held at T_c long enough, there should be sufficient molecular mobility, even after complete evaporation of the solvent, in order for the blend to achieve its thermodynamic equilibrium state at T_c. This is the situation for P2VN/PnBMA blends as long as T_c is greater than about 300 K, as is clear from Figure 11. Rapid quenching of the blend to a temperature below T_g should then eliminate any further coil translational diffusion and large-scale cooperative motion, although localized segmental motion and pendant group rotation will still be possible. Thus, with regard to the excimer probe, the distribution of intermolecular excimer-forming sites will appear frozen whereas there may be readjustment of the intramolecular site population. Since the former type of site predominates at higher concentration and in the phase-separated blends, T_c may be treated as a "fictive" temperature to characterize the thermodynamic state of the sample.

Of course, the extent to which the morphology remains "frozen" depends upon T_g and the storage or examination temperature. In practice, since T_g for the low-concentration P2VN/PnBMA blend is close to that for the host PnBMA, about 293 K, subsequent fluorescence measurements following quenching from T_c were done within 24 h to minimize relaxation effects. Repetition of the casting process for other values of T_c, also above T_g for the solvent-free binary blend, will then allow the temperature component for the equilibrium phase relationships to be examined.

An alternative possibility is that T_c is less than T_g for the binary blend, which is the case for the P2VN/PMMA system. At some point in the casting of these samples, T_g of the ternary system will exceed T_c and the polymer blend will be in a glassy state. Note that these samples could contain appreciable residual solvent. Although continued solvent loss from the glassy blend will occur at a very slow rate, there will be insufficient mobility for further large-scale motion of the polymer chains, such as would accompany phase separation. Thus, the blend morphology which is frozen into such a sample at T_c is that characteristic of a ternary system with appreciable residual solvent.

Since the presence of casting solvent has a strong influence on both the thermodynamic state of the final blend and the kinetic processes associated with blend preparation, the casting process was characterized by performing two types of measurements. First, the weight loss from a typical casting solution was monitored in an analytical balance under drying conditions similar to the spectrofluorimeter sample chamber. In addition, I_D/I_M was measured as a function of time for the same sample solution in the spectrofluorimeter. Typical results for a P2VN/PnBMA solution are shown in Figure 12.

The first important observation is that the residual solvent composition after 60 min of drying is about 5%, as compared to 19% for an analogous experiment with a P2VN/PMMA casting solution. It is interesting to note that, although the accuracy of the Bueche estimation procedure may not justify the comparison, the residual solvent composition for both systems corresponds to that present when the T_g of the solution reaches 20 K below the casting temperature.

Also of interest is the correlation of the fluorescence behavior with the solvent loss. At high solvent concentration, I_D/I_M is largely due to the combined action of energy migration and segmental motion in sampling of excimer-forming sites. As the solution becomes more concentrated, the viscosity increases and rotational motion is reduced. The rate of decrease of I_D/I_M slows dramatically as the residual solvent composition approaches its minimum value. Presumably, both observations are related to the glass transition of the blend; both the rate of segmental motion and that of solvent diffusion will be reduced dramatically below T_g. Although subsequent changes in I_D/I_M do occur, they are quite small. This is a clear demonstration of the ability to freeze in a particular phase morphology for both the P2VN/PnBMA and P2VN/PMMA blends.

As a final point, the effect of solvent evaporation rate was examined briefly. This is of interest because the increased solvent volatility at elevated casting temperatures causes much more rapid evaporation for films prepared there than at room temperature. A possible rate dependence might be expected if phase separation were to occur at a solvent concentration at which highly viscous solutions would result. On the other hand, no rate dependence would be expected if the ternary system were to remain miscible down to very low solvent concentration or if phase separation were to occur in the solution at moderate or high solvent content. In fact, casting of a P2VN/PMMA solution at a solvent evaporation rate which was 10 times slower than that represented in Figure 12 led to identical residual solvent composition and I_D/I_M. Although it is possible that the range of rates was too narrow to observe any dependence, a more likely explanation, given that most of the P2VN/PMMA blends were obviously immiscible, is that phase separation occurred at a solvent composition where the viscosity was still low enough for bulk motion.

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Equation of State of Pressure-Densified Glasses of Poly(vinyl chloride)

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ABSTRACT: Volumetric data of poly(vinyl chloride) glasses formed from the liquid state by isobaric cooling at a constant rate under pressures of 1, 150, 300, and 500 kg cm^{-2} are reported. The pressure–volume–temperature relations of the glasses are shown to be described with the principle of corresponding states. The characteristic volume and entropy are not affected by the pressure densification, while the characteristic temperature, pressure, and internal energy increase with increasing glass-forming pressure. Some theoretical equations of state for polymer liquids are applied to the glasses, but they are in serious disagreement with the experiments. Also discussed is an equation of state derived from cell theory by introducing a distribution of the cell size in its simplest form, which gives results quite close to the experimental *PVT* data and the internal energy. The presented results suggest that the localized energy field may play an important role in the molecular motions and the configurational properties of the glass.

I. Introduction

It is well-known that the density of a glass depends on its thermodynamic history. Many investigators have shown that formation of organic,[1,2] inorganic oxide,[3] and polymer[2,4-13] glasses by lowering the temperature at elevated pressures leads to samples which are more dense. Effects of pressure densification on the pressure–volume–temperature (*PVT*) relations of the glasses were first studied by McKinney and Goldstein,[12] who obtained *PVT* data for two glasses of poly(vinyl acetate) (PVAc) by using the same isobaric cooling rate at 1 and 800 bars. The *PVT* surfaces of the pressure-densified glasses are illustrated schematically in Figure 1.

The liquid and various glass surfaces are continuous only through their respective glass transition intersection line, the $T_g(P)$ line in Figure 1. The $T_g(P)$ line approximately corresponds to the isorelaxation time line on which a mean volume relaxation time is essentially constant as pressure is varied.[14-16] The intersection line of the liquid and P_0 glass surface is shown as the iso-free-volume line in Figure 1. Similar lines are available for the other glasses. If the glass transition is determined in terms of one ordering parameter, e.g., the free volume, the iso-free-volume lines should be identical with the $T_g(P)$ line. This is, in fact, not realized,[12] as illustrated in Figure 1. Therefore, the glassy state cannot be described in terms of a single ordering parameter.

Theoretical approaches to the equation of state of polymer glasses have been demonstrated by Somcynsky and Simha[17] and Nose,[18] who employed hole theory. In their treatments, the glass is viewed as the state where the rearrangements of holes are forbidden. Below the glass transition temperature, their hole theories become equivalent to traditional cell theories.[19,20] However, Quach and Simha[21] showed that the assumption of a constant hole fraction in the glassy state was an oversimplification. Later McKinney and Simha[22] introduced a notion of gradual freeze-in of the hole fraction, treated the hole fraction as an adjustable, pressure- and temperature-dependent parameter to be obtained by experiment, and analyzed the *PVT* data of PVAc glasses.[12] They deduced that the partial freeze-in of the hole fraction was due to a size distribution of hole clusters.

The purpose of this paper is first to give detailed *PVT* data of the pressure-densified glasses of poly(vinyl chloride) (PVC), second to elucidate the correspondence among

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