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Excimer Fluorescence as a Molecular Probe of Blend Miscibility. 3. Effect of Molecular Weight of the Host Matrix

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ABSTRACT: The decrease in polymer-polymer miscibility caused by increases in the host molecular weight has been observed for poly(2-vinylnaphthalene) (P2VN) in dilute solid solutions of monodisperse polystyrene (PS), using the technique of excimer fluorescence. The excimer/monomer fluorescence ratio of the guest P2VN increases rapidly as the molecular weight of the host PS is increased. This change, which occurs before any signs of bulk phase separation are visible, is interpreted as signaling immiscible behavior on a small distance scale. Cloud-point molecular weights and concentrations experimentally measured using excimer fluorescence are predicted with moderate success by Flory-Huggins lattice theory when an empirically determined value of the interaction parameter of 0.010 is used. This experimental value agrees with that predicted by a solubility parameter approach.

Introduction

In recent years considerable attention has been focused on amorphous polymer blends because of the relative ease with which material properties may be modified by physical means.[1-5] Although the morphology of a blend on the distance scale of 100 Å may be all-important in determining the mechanical properties,[6] a clear understanding of the nature of polymer-polymer interactions on the molecular level has proved elusive. Neutron,[7,8] light, and X-ray[9,10] scattering, pulsed NMR,[11,12] and electron microscopy[13] have the required resolving power, but these techniques are generally limited to blends which have at least 1% of the minor polymer component present. The study of blends prepared at even lower concentrations has fundamental significance, however. For example, even when a close chemical "match" of two polymers is made (i.e., a solubility parameter difference of 0.2 $(\text{cal/cm}^3)^{1/2}$ or less) as for polystyrene-poly(methyl methacrylate), the equilibrium solubility of one polymer in the other, estimated for molecular weights of 100000, is 0.1 vol %. Data in the literature for such low-concentration blends are rare, however.[14,15]

Due to their intrinsic sensitivity, fluorescence methods may ultimately prove to be important in the study of such small-scale phase separation and low-concentration miscibility. One method which utilizes energy transfer between suitably labeled blend components has been proposed by Morawetz.[16,17] A second method, used in this and previous[18-23] studies, utilizes excimer fluorescence[24,25] from an aromatic vinyl polymer which is blended as a guest in a matrix of a nonfluorescent host polymer.

A critical feature of the second method is the existence of "excimer-forming sites", which are conformational structures formed when two aromatic rings are nominally situated in a coplanar sandwich, with the ring centers at their equilibrium van der Waals separation. Excitation of one of the rings in the pair by absorption of energy in the near-ultraviolet range may lead to an electronically excited dimer, or excimer.[24,25] The broad structureless fluorescence of the excimer is distinctly different from the structured vibrational progression due to an isolated aromatic ring, or monomer. A convenient experimental measure of excimer fluorescence is the ratio of excimer to monomer emission intensities, I_D/I_M, obtained under photostationary state conditions.

This is part of a series of papers[21-23] in which excimer fluorescence is employed as a molecular probe of thermodynamic compatibility in solid polymer-polymer blends. The guest aromatic vinyl polymers studied have included poly(2-vinylnaphthalene) (P2VN), poly(acenaphthalene), and poly(4-vinylbiphenyl). The host polymers were taken from a homologous series of poly(alkyl methacrylates).

Studies at low guest concentration have shown I_D/I_M to depend upon the enthalpic interactions between guest and host, as reflected in the difference in solubility parameters.[21,22] I_D/I_M was observed to be minimized when the guest and host solubility parameters were equal. For the blends prepared with 0.2 wt % guest polymer in a host polymer, phase separation, as indicated by a bluish or milky tinge, was not visible until the absolute magnitude of the solubility parameter difference exceeded 0.6 $(\text{cal/cm}^3)^{1/2}$, whereas there were significant increases in I_D/I_M for solubility parameter differences of 0.2-0.4 $(\text{cal/cm}^3)^{1/2}$.

Studies on the effect of guest concentration on I_D/I_M have also been performed.[22,23] Regardless of host, a sharp initial rise in I_D/I_M occurs between 0.003 and 0.1 wt % followed by a transition region extending from 0.1 to 1.0 wt % P2VN. Thereafter, a much slower linear rise in I_D/I_M continues as the P2VN concentration increases to 10 wt %. When inspected visually, phase separation for these blends was indicated only for P2VN concentrations greater than 1%.

In both the solubility parameter and concentration studies, increases in the fluorescence ratio I_D/I_M consistently preceded changes in the appearance of the blends as conditions were altered toward greater immiscibility. It seems reasonable to conclude that excimer fluorescence is detecting phase separation which is occurring on a scale too small to be noticed visually.

The objective of this paper is to explore this point further through examination of the dependence of I_D/I_M for a particular guest polymer upon the molecular weight of the host. By lowering the host molecular weight, it should be possible at some point to reduce or even eliminate immiscibility with a particular guest. In this work, three different P2VN guests having molecular weights between 21000 and 265000 are blended with eight different PS hosts having molecular weights between 2200 and 390000. Related studies on the blend polystyrene-poly(methyl methacrylate)[26-28] have shown that when the host molecular weight is large, the guest polymer molecular weight must be lowered to about 4000 to obtain miscible low-concentration blends. Comparable results are obtained in this study.

Experimental Section

One sample of poly(2-vinylnaphthalene) (P2VN) was prepared by bulk thermal polymerization, as described previously,[21] and had a viscosity-average molecular weight, M_v, of 70000. Additional P2VN samples having $M_v = 21000$ and $M_v = 265000$ were pre-

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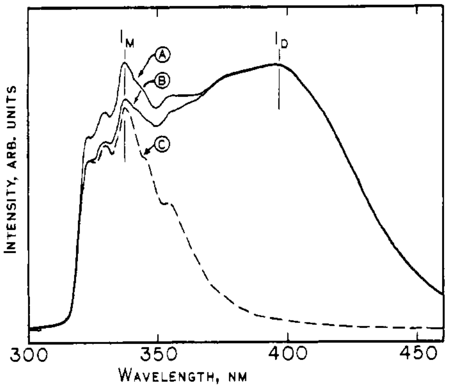

Figure 1. Uncorrected fluorescence spectra of 0.3 wt % P2VN (70 000) and 2-ethylnaphthalene in PS. Excitation wavelength 290 nm. Curve A, P2VN in PS (2200); curve B, P2VN in PS (233 000); curve C, 2-ethylnaphthalene in PS (158 000). The numbers in parentheses refer to the molecular weights. Curve B is normalized to curve A at 398 nm; curve C is normalized to curve B at 323 nm.

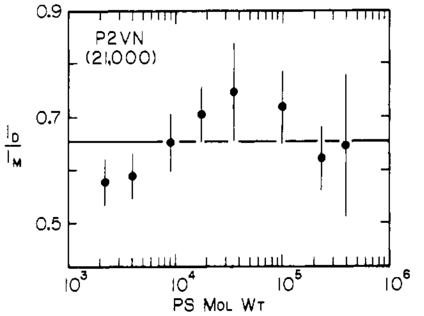

Figure 2. Fluorescence ratio I_D/I_M of 0.3 wt % P2VN (21 000) in PS vs. PS molecular weight. The horizontal line indicates the average value of the eight data points.

pared by solution polymerization with azobis(isobutyronitrile) as initiator.[29] The low molecular weight sample was obtained by using carbon tetrachloride as a chain-transfer agent. The monodisperse polystyrene (PS) was obtained from Pressure Chemical Co. with M_n = 2200, 4000, 9000, 17 500, 35 000, 100 000, 233 000, and 390 000. These polystyrenes had M_w/M_n values less than 1.1. A polydisperse sample of suspension-polymerized PS having M_w = 158 000 was obtained from Polysciences Inc. (lot no 296-3). This host was used only in the concentration study. All polymers were repeatedly precipitated from toluene into methanol, using distilled solvents. The interfering fluorescence from residual impurities in the host polymers remained as the limiting factor, however, for very low concentrations (0.003 wt % or less) of the P2VN guest.

Solid films of the blends were prepared by solvent casting from toluene onto sapphire disks at room temperature to produce a final film thickness of 25 μm. The P2VN guest polymer concentration was 0.3 wt %, except in the concentration study, where the guest concentrations were 0.003, 0.03, 0.1, 0.3, 1.0, 3.0, and 10.0 wt %.

The fluorescence spectrometer has been described previously.[21] All spectra were taken in air, using backface illumination with exciting light at 290 nm.

Results

A. Effect of Molecular Weight on Fluorescence Spectra and I_D/I_M. Uncorrected fluorescence spectra of P2VN, M_v = 70 000, in blends with PS having M_n = 2200 and M_n = 233 000 are shown in Figure 1. Each spectrum is composed of a broad structureless band, corresponding to the excimer emission, superimposed on a structured high-energy (monomer) emission similar to that of 2-ethylnaphthalene. For comparison, the spectrum of 2-ethylnaphthalene in PS is given by the dashed line. The P2VN spectra are normalized at 398 nm. The intensities of the monomer emission, I_M, and of the excimer emission, I_D, were measured at 337 and 398 nm, respectively.

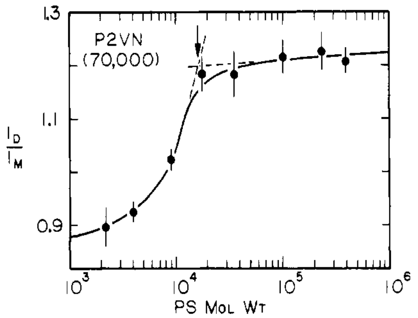

Figure 3. Fluorescence ratio I_D/I_M of 0.3 wt % P2VN (70 000) in PS vs. PS molecular weight. The "knee" of the curve is indicated by the arrow.

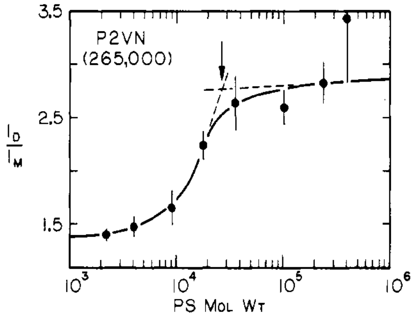

Figure 4. Fluorescence ratio I_D/I_M of 0.3 wt % P2VN (265 000) in PS vs. PS molecular weight. The "knee" of the curve is indicated by the arrow.

Fluorescence results for the three P2VN guest polymers of different molecular weights are presented in Figures 2–4. In each case, the ratio I_D/I_M for the guest polymer is plotted against the molecular weight of the host polymer. The error bars indicate 80% confidence intervals. Figure 2 presents the results for the P2VN guest with the lowest molecular weight, M_v = 21 000. The average of three data points taken from one film of each blend are shown. Although I_D/I_M appears to go through a slight maximum for the PS host with M_n = 35 000, the data are rather scattered and a constant value of I_D/I_M = 0.65 could be reasonably assumed. The results for the P2VN guest having M_v = 70 000 are shown in Figure 3, where the symbols represent the average of six data points taken from two films of each blend. The ratio appears to be relatively constant at very low host molecular weights below M_n = 4000. Between M_n = 4000 and M_n = 17 500, I_D/I_M increases by about 30% to a plateau which extends to M_n = 390 000. The behavior of the highest molecular weight P2VN guest, M_v = 265 000, is qualitatively very similar to that of the P2VN guest with M_v = 70 000. The averages of three data points taken from one film of each blend are shown in Figure 4. Again, the ratio is constant below M_n = 4000, followed by an increase to a plateau value. In this case, I_D/I_M increases about 50%. No significance is attached to the apparent increase in I_D/I_M for the PS host having M_n = 390 000 due to the large scatter in the data for that particular blend.

The features of these results which we wish to explain are the independence of guest I_D/I_M on host molecular weight for P2VN (21 000) and the significance of the increase in I_D/I_M in both P2VN (70 000) and P2VN (265 000) for host molecular weights greater than 4000. Since the experiments involved only photostationary state and no transient measurements, it was not possible to evaluate separately the photophysical rate constants. Thus, the emphasis is on the relative changes in I_D/I_M and not the absolute values. Before we present the morphological interpretation, we review briefly several aspects of the photophysics of the aromatic vinyl polymers.

The excimer to monomer fluorescence intensity ratio, I_D/I_M, depends upon three major factors.[18,23] The first is the electronic stability of the excimer complex, as manifested through the radiative and nonradiative fluorescence decay constants of the excimer and monomer. These photophysical parameters should reflect very short range interactions between the excimer complex on the guest polymer and the local environment in the host matrix. They are not expected to vary appreciably in a given guest–host pair, however. On the other hand, the remaining elements are sensitive to molecular structure.

One of these concerns the number and type of excimer-forming sites.[21-23] The intramolecular site formed between aromatic rings on adjacent repeat units provides information on the conformational statistics of the guest polymer[18,19] and should be independent of the host matrix. The intramolecular site formed between nonadjacent repeat units on the same chain should be sensitive to chain coiling and, thus, to thermodynamic interaction between the guest and host polymers. Finally, the intermolecular site formed between aromatic rings on different polymer chains should also be sensitive to the blend thermodynamics. More specifically, the number of intermolecular sites should increase with the degree of guest chain aggregation in a phase-separated blend.

If the only process leading to excimer fluorescence in the solid-state blends were direct absorption of incident radiation by an aromatic ring in a nominal excimer-forming site, it would be fairly straightforward to infer the molecular morphology from the observed I_D/I_M. In general, however, direct absorption is an insignificant effect due to the small number of excimer-forming sites.[18] The most common situation is that an isolated aromatic ring absorbs a photon of incident radiation followed by a rapid migration of the excitation until competitive trapping occurs at an excimer site. The phenomenon of exciton migration is well-known in the aromatic vinyl polymers.[30] The central question with regard to the blend morphology is the extent to which the efficiency of the exciton migration depends upon the conformational structure of the guest. This is the third major factor to consider.

Guillet[31] has proposed that chain contraction toward Θ dimensions as the thermodynamic solvent quality is reduced should lead to an increased probability of energy migration across loops in the guest polymer random coil. This "short-circuiting" process effectively increases the region of space which may be traversed, thus leading to more efficient sampling of excimer sites. Of course, a similar effect would result from intermolecular clustering.

The difficulties in interpretation of I_D/I_M should now be clear. An increased probability of remote segment contact on the same chain and clustering of segments on different chains have the same qualitative effect on I_D/I_M for both mechanisms. It appears, however, that the relative contributions of the number of excimer-forming sites and the rate at which they are sampled by exciton migration may be clarified by consideration of the efficiency of exciton migration in more detail. If the critical Förster radius[32] for the dipole–dipole energy migration is small or if there is a large separation between aromatic chromophores, exciton migration should be the rate-limiting process for the observed photostationary state fluorescence. If, on the other hand, energy migration is quite efficient, the number of available excimer-forming sites is the rate-limiting feature. In this study, as in the previous papers,[21-23] P2VN is assumed to fall in the second category and the results are interpreted in terms of variation in number of excimer-forming sites. This distinction is not essential to the qualitative assessment of the blend morphology. Only when quantitative results, such as domain size, are required will the precise mechanism become critical.

B. Cloud-Point Concentration for Low-Concentration Blends. Measurement of blend turbidity by light scattering[14] is a common technique for experimental generation of thermodynamic phase diagrams. Thus, it is of considerable interest to determine whether the I_D/I_M fluorescence behavior may be correlated with the optical quality of the film. If this may be done, excimer fluorescence could provide a new tool which would complement existing techniques, particularly at very low concentrations. The use of optical clarity as a method to assess the occurrence of phase separation is subject to a number of experimental difficulties,[4] however. Of course, a necessary prerequisite is that there be a sufficiently large difference between the refractive indices of the blend components. Assuming this to be true, it is still possible to obtain optically clear films if a planar bilayer structure is formed or if the dimensions of any phase-separated domains which are present are small relative to the wavelength of the incident light. Thus, it would be quite possible to obtain an optically clear film for a thermodynamically incompatible blend. If the film is cloudy, however, phase separation is indicated.

The most straightforward correlation of I_D/I_M with optical quality of the blend is made for the results of Figure 4 in which the P2VN guest polymer has the highest molecular weight. Blends prepared with PS of molecular weights 2200, 4000, 9000, and 17 500 were optically clear with no apparent phase separation. All the remaining blends, however, had a bluish tint throughout and contained small regions which were faintly white. Thus, phase separation has assuredly occurred for blends with PS molecular weights of 35 000, 100 000, 233 000, and 390 000. The corresponding increase in P2VN guest I_D/I_M as the PS molecular weight increases must be associated with this phase separation. Presumably, this reflects an increased number of intermolecular excimer-forming sites (or, perhaps, an increased energy migration efficiency). It is interesting to note that I_D/I_M is essentially constant for host molecular weights above and below the transition region. More importantly, the transition is fairly broad, with the initial increase in I_D/I_M occurring at a considerably lower host molecular weight than that which leads to visible phase separation. This suggests that the fluorescence results reflect the growth of phase-separated domains which only become large enough to scatter visible light when the PS molecular weight is 35 000 or larger.

While similar fluorescence trends in I_D/I_M are observed for the P2VN (70 000) guest, all films remain optically clear. Thus, in the absence of the P2VN (265 000) results, it might be argued that no phase separation has occurred for these blends. To follow this point further, an alternative explanation of the P2VN (70 000) I_D/I_M data could be that there is an expansion of the P2VN random coil in the low molecular weight PS host above the Θ dimensions which must exist for the guest coil in the high molecular weight PS.[33] This could result in a decrease of the number of intramolecular excimer sites between nonadjacent segments and could remove alternate energy migration paths, both of which would lower the ratio I_D/I_M.

To evaluate this explanation, we prepared blends using the 70 000 molecular weight P2VN at a concentration of 0.003 wt % in the series of monodisperse polystyrenes. If

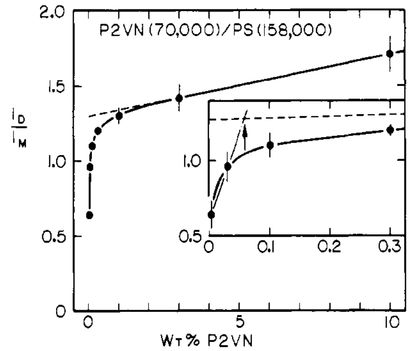

Figure 5. Fluorescence ratio I_D/I_M of P2VN (70 000) in PS (158 000) vs. weight percent P2VN. In the low-concentration detail, the dashed line is an extrapolation of data for concentrations greater than 1 wt % and the "knee" of the curve is indicated by the arrow.

the increase in the fluorescence ratio shown in Figure 3 is caused by the presence of small phase-separated P2VN domains, then the hundredfold reduction in P2VN concentration should reduce or eliminate the immiscibility, causing I_D/I_M to remain constant. On the other hand, if coil expansion is responsible for the change in I_D/I_M, then the reduction in concentration should have little effect and behavior similar to that found in Figure 3 would be expected. In fact, a constant value of $I_D/I_M = 0.67 \pm 0.1$ was recorded for all the PS hosts containing 0.003% P2VN (70 000). Apparently, increased intermolecular excimer formation caused by phase separation is also the reason for the increase in I_D/I_M for P2VN (70 000) as was concluded for P2VN (265 000). The lack of visible cloudiness simply means that the domains are very small.

Finally, we note that all of the blends with P2VN (21 000) are optically clear. Moreover, there is no significant change in I_D/I_M with host molecular weight. Thus, these blends are all assumed to be thermodynamically compatible.

To our knowledge no work has been done on the effect of molecular weight in polymer blends for concentrations less than 1%, although low-concentration cloud points have been determined in several studies on blends of medium and high molecular weight polymers. For example, Yuen and Kinsinger[14] have determined from turbidity and small-angle light scattering measurements as well as from visual appearance that polystyrene is compatible with poly(methyl methacrylate) at or below a concentration of 0.005%. Their blends were prepared by dissolving PS having $M_n = 82\,500$ in methyl methacrylate followed by polymerization at 50 °C, using azobis(isobutyronitrile) initiator.

Anavi, Shaw, and Johnson[15] have recently described a novel method of preparing low-concentration polymer blends. The technique involves the addition of a polymer solution to a polymer melt which is fluxing on a two-roll mill. A simple light scattering device is used to check samples taken from the fluxing polymer blend. They report cloud-point compositions for poly(methyl methacrylate) (100 000) and poly(vinyl acetate) (195 000) dissolved in polyisobutylene (10 000) of 0.4% and 0.03%, respectively. Here the numbers in parentheses refer to the molecular weights.

To extend the similarities between these studies and the present work, we prepared a series of blends to determine the cloud-point concentration of the 70 000 molecular weight P2VN in a medium molecular weight PS matrix. Figure 5 presents the fluorescence ratio vs. P2VN concentration for a single broad molecular weight distribution PS host having $M_w = 158\,000$. The ratio I_D/I_M rises sharply as the P2VN concentration increases from 0.003% to 0.1% and then levels off to a much slower linear increase which begins at 1% and continues until the P2VN concentration reaches 10%. Arbitrarily choosing the "knee" of the fluorescence ratio curve in Figure 5, we obtain an excimer-fluorescence "cloud-point" concentration of 0.05 ± 0.05 wt % P2VN. These blends do not become optically cloudy until the concentration reaches 1%, however. Similar behavior has been observed[23] for P2VN (70 000) in poly(methyl methacrylate) (125 000) and poly(n-butyl methacrylate) (254 000). In this earlier study, cloud-point concentrations measured by excimer fluorescence were 0.1 ± 0.05 and 0.14 ± 0.05 wt %, respectively. Thus, the excimer fluorescence method of determining cloud-point concentrations yields results similar to those obtained from the methods employed by Yuen and Kinsinger[14] and Anavi et al.,[15] given the different methods of preparing the blends.

Discussion

The simplest possible theory for the thermodynamics of mixing two polymers is the Flory–Huggins lattice treatment.[34,35] The pertinent equations required for binodal calculation are

$$\ln v_A'' = (x_A/x_B - 1)(1 - v_A'') - x_A\chi_{AB}(1 - v_A'')^2 - (x_A/x_B - 1)v_B' + x_A\chi_{AB}(v_B')^2 + \ln(1 - v_B') \quad (1)$$

$$\ln v_B' = (x_B/x_A - 1)(1 - v_B') - x_B\chi_{AB}(1 - v_B')^2 - (x_B/x_A - 1)v_A'' + x_B\chi_{AB}(v_A'')^2 + \ln(1 - v_A'') \quad (2)$$

where A and B are the two polymer species, the single prime indicates the B-lean phase of the mixture, two primes indicate the A-lean phase of the mixture, v = volume fraction, x = degree of polymerization = V_m/V_r, V_m = polymer molar volume, V_r = the reference repeat-unit molar volume, taken as the smaller of the two repeat-unit molar volumes of the polymers A and B, and χ_{AB} = binary interaction parameter. Initially, the interaction parameter will be treated simply as an adjustable constant to match the experimental data with the theory. Later, a theoretical estimation of χ_{AB} will be made and compared with experiment. Equations 1 and 2 are written so that an initial guess of the values v_A'' and v_B' can be substituted in the right-hand-side functions to yield improved values of the left-hand-side functions. Successive substitution of v_A'' and v_B' is continued until convergence is reached.

There are several limitations on the application of the Flory–Huggins treatment which should be considered before comparison of theory with experiment. First, the thermodynamics of the solvent-cast blend must be analyzed, strictly speaking, by a ternary phase diagram. As solvent evaporates from the system, the effective glass transition of the blend, T_g, must be lower than the casting temperature, T_c, in order that sufficient mobility remains to allow thermodynamic equilibrium. Further evaporation of solvent will eventually lead to an increase in T_g above T_c and a nonequilibrium blend will be obtained. For polymers which are nearly miscible, different casting solvents can produce both incompatible and compatible blends.[36] Preliminary work with casting solvents other than toluene indicates that moderate differences in the visual appearance and the fluorescence ratio of P2VN/PS blends do occur. Clearly, some nonequilibrium character occurs for the solvent-cast films used in this study, but this is to be expected for any method used to prepare glassy polymer blends. These points are being pursued separately.[37] For the present, the important point is that all films prepared for this study should have the same degree

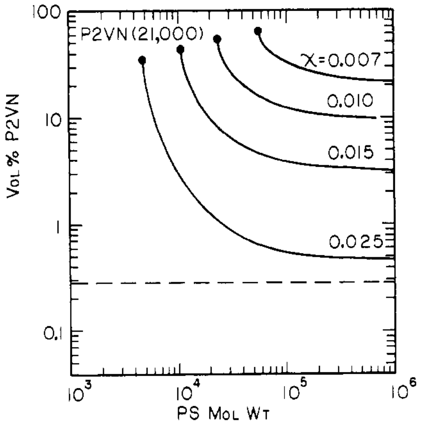

Figure 6. Binodal compositions calculated for P2VN (21 000)/PS blends. Results for the P2VN-lean phase are shown as volume percent P2VN vs. PS molecular weight. The interaction parameter for each curve is given and the critical point is indicated by the filled circle. The dashed line denotes 0.3 wt % P2VN.

of nonequilibrium character since a single casting solvent and method were used to prepare them. Also, since residual solvent in these films is present in amounts typically less than 5%, it should have no significant effect on the apparent interaction parameter.[38,39]

A second objection concerns the limited predictive power of eq 1 and 2 compared with more recent equation-of-state theories of polymer and oligomer mixtures. Flory–Huggins lattice theory generally fails to predict the temperature and concentration behavior of miscible polymer pairs, except for blends of similar copolymers or highly similar polymers.[35] Since this study concerns polymer blends with constant composition which were prepared at constant temperature, we expect that the Flory–Huggins lattice theory will be qualitatively correct in predicting molecular weight effects.

A final objection concerns the problem of dilute-solution thermodynamics. Because of the discontinuous nature of polymer solutions below concentrations of about 1%, additional entropy and enthalpy factors must be added to either the lattice theory or equation-of-state theories. We neglect these factors, again assuming that their qualitative effect will be small.

In summary, although application of the Flory–Huggins theory has definite limitations, there is sufficient justification to believe that the predictions of molecular weight dependence will be qualitatively correct. The approach taken for comparison of theory and experiment is to demonstrate that a consistent binary interaction parameter may be deduced from comparison of the calculated binodal curves with the fluorescence results. This experimental interaction parameter will then be compared with predictions of regular solution theory.

The calculated binodals are presented in Figures 6–8 for the P2VN guests having M_v = 21 000, 70 000, and 265 000, respectively. Note that these binodals are plotted as P2VN concentration vs. PS host molecular weight with the interaction parameter held constant. The usual method of presentation is to give temperature (or interaction parameter) vs. concentration with the host molecular weight held constant. A range of interaction parameters from 0.005 to 0.025 was selected, since these seemed most consistent with the visual appearance and fluorescence behavior of the blends. The dashed line in Figures 6–8 represents the bulk concentration of the guest polymer in the films studied. As the molecular weight of the polystyrene host increases, the concentration of guest in the guest-lean phase at the binodal decreases rapidly. The films in which the host molecular weight is sufficiently large may show phase separation if the guest concentration at the binodal is less than the bulk guest concentration.

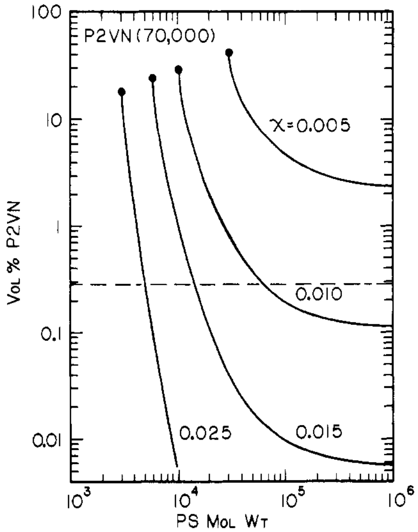

Figure 7. Binodal compositions calculated for P2VN (70 000)/PS blends. See Figure 6 for details.

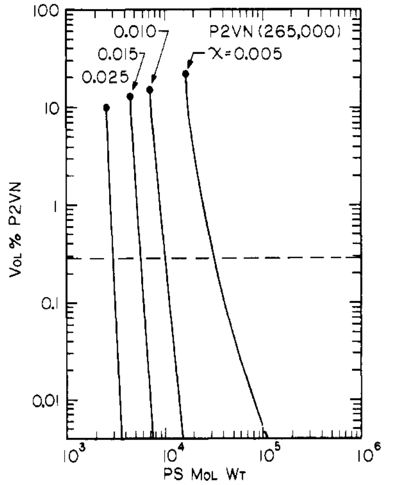

Figure 8. Binodal compositions calculated for P2VN (265 000)/PS blends. See Figure 6 for details.

We first consider blends of P2VN (21 000) and compare the I_D/I_M data of Figure 2 with the binodals of Figure 6. As noted earlier, we infer from the lack of significant change in I_D/I_M with host molecular weight that all blends are miscible. Of course, this arises from the fact that the guest polymer is of relatively low molecular weight. Since none of the binodals calculated for the different interaction parameters intersects the dashed line indicating the bulk film concentration, an upper limit of about 0.027 is established for χ_{AB}.

Two sets of data are available for determination of χ_{AB} for the blends with P2VN (70 000). The first set consists of the host molecular weight dependence of I_D/I_M in Figure 3. The "cloud-point" molecular weight was somewhat arbitrarily selected as the knee formed by the intersection of the dashed lines forming the tangent to the inflection point and the high molecular weight plateau. The choice of this particular point was experimentally convenient and conceptually identical with any other point which could be chosen to characterize the transition. It should be noted, however, that since the P2VN is polydisperse, the transition "point" is in fact a region of phase separation whose breadth probably corresponds to the breadth of the

P2VN molecular weight distribution.[43] The value of the knee is about 16 000 for P2VN (70 000). Selection of this PS molecular weight leads to an interaction parameter of about 0.014 from Figure 7. The second set of experimental I_D/I_M data for this guest polymer is obtained from the concentration study in a host of fixed molecular weight, 158 000, presented in Figure 5. Here the "cloud-point" concentration was determined from the intersection of the straight lines through the lowest concentration data and through the highest data. This value is 0.05% by weight, as noted earlier. Examination of Figure 7 leads to selection of an interaction parameter of about 0.012, in good agreement with the first study.

When the fluorescence data for the P2VN (265 000) blends are treated in the identical manner as for P2VN (70 000), a cloud-point host molecular weight of about 27 000 is obtained. This leads to an interaction parameter of 0.006. It is somewhat surprising that these blends should appear to be more compatible than those for P2VN (70 000). This may reflect nonequilibrium kinetic effects associated with the higher molecular weight guest or simply be an indication of the magnitude of the experimental error. For purposes of comparison with theoretical predictions of χ_{AB}, we will assume an average experimental value of $\chi_{AB} = 0.010 \pm 0.004$.

The simplest approach to theoretical prediction of the binary interaction parameter is due to Scott and Hildebrand, as outlined by Krause.[35] This treatment, based on regular solution theory, yields

$$\chi_{AB} = \frac{V_r}{RT}(\delta_A - \delta_B)^2 \qquad (3)$$

where R = gas constant, T = absolute temperature, V_r = reference volume, and $\delta_{A,B}$ = solubility parameter of polymers A and B. Solubility parameters may be determined experimentally from intrinsic viscosity or swelling measurements or estimated by using the concept of molar group additivity.[35] Krause[35] has shown that the latter approach can work quite well for some homopolymer–homopolymer pairs, particularly when the two polymers have similar polarity and hydrogen-bonding characteristics. On the other hand, Massa[26] and Nishi[41] have observed that empirically determined interaction parameters may differ considerably from that obtained using solubility parameters, as in eq 3.

Since the experimentally determined interaction parameter is rather small, there do not seem to be any specific interactions between P2VN and PS, as would be expected from their similar chemical structures. Thus, eq 3 should work reasonably well. Unfortunately, the precise value of χ_{AB} depends critically on the accuracy of the solubility parameters because χ_{AB} is proportional to the square of the difference in two very similar quantities. Although data in the literature are somewhat scattered, a value of 9.10 $(\text{cal/cm}^3)^{1/2}$ for the solubility parameter of polystyrene seems to be reasonable.[42] No experimental data could be found for P2VN, however. In earlier work[21,22] a value of 8.73 $(\text{cal/cm}^3)^{1/2}$ was obtained from an empirical estimation scheme and experimentally determined densities. This value was consistent with the minimum in I_D/I_M obtained for low-concentration blends (0.2% by weight) in a series of poly(alkyl methacrylate) host polymers.[21] In that study, all of the solubility parameters of the host polymers were estimated by the same procedure as for P2VN. When experimentally determined solubility parameters are used for the host polymer instead of the empirically estimated ones, it appears that a more reasonable value for the solubility parameter of P2VN is 8.85 $(\text{cal/cm}^3)^{1/2}$.

Substitution of $\delta_{PS} = 9.10$ $(\text{cal/cm}^3)^{1/2}$ and $\delta_{P2VN} = 8.85$ $(\text{cal/cm}^3)^{1/2}$ as well as the reference volume, based on polystyrene, of 99.8 cm^3/mol, into eq 3 yields $\chi_{AB} = 0.010 \pm 0.005$. The error limits arise from the uncertainties in component solubility parameters. Clearly, the agreement between the experimental and calculated interaction parameters is very good. This agreement may be fortuitous, however, given the experimental uncertainties and theoretical limitations. Neverless, it appears that the use of excimer fluorescence has considerable potential as a probe of polymer–polymer interactions in the solid state.

Summary

The fluorescence spectra of poly(2-vinylnaphthalene) in dilute solid solutions of monodisperse polystyrene show significant increases in the excimer/monomer fluorescence ratio as the molecular weight of the polystyrene is increased. Increases in the fluorescence ratio consistently precede visible signs of phase separation of the blends, which is consistent with earlier work where miscibility was altered by changing host polymers or concentration. Cloud-point concentrations obtained by using excimer fluorescence are qualitatively similar to other low-concentration cloud points determined in light scattering studies[14,15] for polymer blends. The use of Flory–Huggins lattice theory works reasonably well to describe the effect of molecular weight. An empirically determined interaction parameter was found to be comparable to that predicted by the solubility parameter approach.

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Notes

Configurational Statistics of Polymer Chains Accounting for All Rotational States. General Extension to Finite Chains and Copolymers

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The statistical properties of chain molecules with interdependent rotational potentials may be calculated either within the rotational isomeric state (RIS)[1] scheme or by accounting for all rotational states (ARS scheme).[2] The latter method has been applied hitherto only to infinite chains consisting of equivalent monomer units since these systems allow simplifications in the mathematical procedure (the ring closure of the infinite chain and the evaluation of the partition function through the maximum eigenvalue of the correlation matrix U).[3,4] Copolymer chains have been treated within this framework, but practical expediency only permits fixing of the frequency of occurrence of very short sequences of structural units.[5]

It is the purpose of the present note to show that the matrix correlation techniques employed within either scheme are essentially isomorphic, so that all RIS approaches suggested to treat chains of finite length and/or containing different monomer units in any specified sequence may be easily translated into the ARS language.

The formal equivalence between the two methods follows from the fact that they differ from each other only in the choice of an appropriate set of orthonormal basis functions for the representation of the statistical weight function $w(\varphi_{i-1},\varphi_i)$: Dirac delta functions in one case (RIS) and Fourier components in the other (ARS). Imaginary exponentials may well replace the sine/cosine functions[3] but any other orthonormal basis set could be adopted if appropriate.

From a practical point of view we shall devote particular attention to indicate how to calculate the second moment of the distribution of any vectorial property associated with the chain bonds.

Use is made of definitions already given in ref 2 for what concerns the Fourier method of accounting for all rotational states and in ref 1 for what concerns the step-by-step matrix multiplication to generate the partition function of a polymer chain; the reader is therefore referred to these publications for all details.

In the approximation of first-neighbor correlation we may express the configurational potential energy pertaining to a chain with $N + 1$ bonds in the configuration specified by the values $\varphi_2,\varphi_3,\ldots,\varphi_N$ of the rotational angles as

$$E(\varphi_2,\varphi_3,\ldots,\varphi_N) = E(\varphi_2,\varphi_3) + E(\varphi_3,\varphi_4) + \ldots + E(\varphi_{N-1},\varphi_N) \qquad (1)$$

and the configurational partition function is then given by

$$Z_{N+1} = \int_0^{2\pi}\int_0^{2\pi}\ldots\int_0^{2\pi} w(\varphi_2,\varphi_3)w(\varphi_3,\varphi_4)\ldots w(\varphi_{N-1},\varphi_N)\; \mathrm{d}\varphi_2\, \mathrm{d}\varphi_3 \ldots \mathrm{d}\varphi_N \qquad (2)$$

where

$$w(\varphi_{i-1},\varphi_i) = \exp[-E(\varphi_{i-1},\varphi_i)/RT] \qquad (3)$$

We may expand the periodic function $w(\varphi_{i-1},\varphi_i)$ into a double-Fourier series whose coefficients may be arranged in a matrix $\mathbf{U}_i$ of order $(2\bar{n}_{i-1} + 1) \times (2\bar{n}_i + 1)$, where $\bar{n}_{i-1}$ and $\bar{n}_i$ are the largest Fourier indices pertaining to the expansions along φ_{i-1} and φ_i, respectively;[2] in principle, $\mathbf{U}_i$ may therefore be rectangular but, for simplicity, we shall assume henceforth $\bar{n}_{i-1} = \bar{n}_i = \bar{n}$. The statistical weight function may then be written

$$w(\varphi_{i-1},\varphi_i) = \boldsymbol{\Phi}_{i-1}\mathbf{U}_i\boldsymbol{\Phi}_i^{\mathrm{T}} \qquad (4)$$

where $\boldsymbol{\Phi}_i$ is the row vector defined in eq 7 of ref 2 and $\boldsymbol{\Phi}_i^{\mathrm{T}}$ is its transpose. The multiple integration of eq 2 may be written as in eq 9 of ref 2

$$Z_{N+1} = (2\pi)^{N-3}\int_0^{2\pi}\boldsymbol{\Phi}_2\,\mathrm{d}\varphi_2\,[\prod_{i=3}^{N}\mathbf{U}_i]\int_0^{2\pi}\boldsymbol{\Phi}_N^{\mathrm{T}}\,\mathrm{d}\varphi_N \qquad (5)$$

or

$$Z_{N+1} = (2\pi)^{N-1}\mathbf{J}\prod_{i=3}^{N}\mathbf{U}_i\mathbf{J}^{\mathrm{T}} \qquad (6)$$

where $\mathbf{J}$ is a $(2n + 1)$-dimensioned row vector with the first element equal to 1, all others being equal to 0, and $\mathbf{J}^{\mathrm{T}}$ is its transpose. Comparing eq 6 with eq 24 of ref 1 shows their apparent formal equivalence. Equation 6 may be applied to chains of at least four bonds, while for three-bond systems it becomes

$$Z_3 = 2\pi a_2^{\,0} \qquad (7)$$

where

$$a_2^{\,0} = \frac{1}{2\pi}\int_0^{2\pi} w(\varphi_2)\,\mathrm{d}\varphi_2 \qquad (8)$$

The calculation of the configurational average of any function $f(\varphi_i)$ involves the calculation of an integral of the type $\int_0^{2\pi}\boldsymbol{\Phi}_i^{\mathrm{T}}f(\varphi_i)\boldsymbol{\Phi}_i\,\mathrm{d}\varphi_i$ (see eq 13 of ref 2) which defines a matrix $\boldsymbol{\Psi}_i$ (eq 14 of ref 2); this in turn has the form given

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