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Excimer Fluorescence as a Molecular Probe of Polymer Blend Miscibility. 6. Effect of Molecular Weight in Blends of Poly(2-vinylnaphthalene) with Poly(methyl methacrylate)

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ABSTRACT: Excimer fluorescence is employed to determine the influence of molecular weight and concentration on the miscibility of blends of poly(2-vinylnaphthalene) (P2VN) with poly(methyl methacrylate) (PMMA). Three P2VN guests of molecular weights 21 000, 70 000, and 265 000 and concentrations between 0.3 and 35% are blended by solvent casting from toluene with nine PMMA hosts having molecular weights ranging from 1100 to 350 000. Fluorescence measurements are shown to be more sensitive to the existence of phase separation than either the visual observation of turbidity or the observation of two glass transition temperatures by differential scanning calorimetry. The fluorescence results are used with Flory–Huggins lattice theory to yield a consistent value of the binary interaction parameter of 0.07 ± 0.015 for P2VN/PMMA blends.

Introduction

This report is part of a series of studies on the application of fluorescence techniques to the study of polymer blends.[1-6] Previous work has demonstrated that excimer fluorescence can be used to detect immiscibility in polymer blends at an earlier stage than is possible by measurements of optical clarity[4,5] or differential scanning calorimetry.[5,6] In addition, it has been shown that the simple Flory–Huggins mixing theory could be used to predict the points of immiscibility arising from increases in guest or host molecular weight in blends of poly(2-vinylnaphthalene) (P2VN) with polystyrene (PS).[3] In this paper, the influence of molecular weight is examined for blends of P2VN with poly(methyl methacrylate) (PMMA), which is known to be less miscible than the P2VN/PS series.[1,2]

The first objective of this work is to demonstrate the generality of the method of interpreting excimer fluorescence of blends containing P2VN, which was developed earlier.[6] In so doing we will determine a consistent value of the binary interaction parameter from fluorescence measurements. The second objective is to compare the interaction parameters for P2VN in PS and PMMA extracted from the fluorescence data with those predicted by the regular solution theory of Hildebrand and Scott.[7,8]

Table I
Description of Commercial Polymers

sample(MW)	M_w/M_n	synthesis	supplier	ID or lot no.
PMMA(1100)[a]	1.1	*c*	*e*	QR-537
PMMA(2500)[a]	1.1	*c*	*e*	QR-635
PMMA(12 000)[a]		*d*	*f*	02
PMMA(20 000)[a]		*d*	*e*	Acryloid A-101
PMMA(54 000)[b]	1.07	*c*	*g*	
PMMA(79 000)[b]	1.06	*c*	*g*	
PMMA(92 000)[b]	1.06	*c*	*g*	
PMMA(180 000)[b]	1.1	*c*	*g*	
PMMA(350 000)[b]	1.15	*c*	*g*	

[a] Weight-average molecular weight. [b] Number-average molecular weight. [c] Anionic synthesis. [d] Free radical synthesis. [e] Experimental samples were provided by Dr. D. J. McDonald, Rohm and Haas Co. [f] Scientific Polymer Products, catalog no. 424. [g] Pressure Chemical Co.

The reliability of regular solution theory depends heavily on the accuracy of values of the solubility parameter, δ, which are used to calculate the binary interaction parameter for the blend. In order to obtain δ values which reflect the possibility of specific chemical interactions between guest and host polymers, a separate study has been performed in which δ has been evaluated from intrinsic viscosity measurements of P2VN, PS, and PMMA, each in several classes of solvents.[9] For dilute P2VN/PS blends, the appropriate values should be $\delta_{\mathrm{P2VN}} = 9.5 \pm 0.2$ cal$^{1/2}$/cm$^{3/2}$ and $\delta_{\mathrm{PS}} = 9.20 \pm 0.05$ cal$^{1/2}$/cm$^{3/2}$. For dilute P2VN/PMMA blends, we have proposed that $\delta_{\mathrm{P2VN}} = 9.0 \pm 0.2$ cal$^{1/2}$/cm$^{3/2}$ and $\delta_{\mathrm{PMMA}} = 9.4 \pm 0.2$ cal$^{1/2}$/cm$^{3/2}$, where the change in the effective solubility parameter of P2VN results from the change in matrix from an aromatic to an ester character. In this work, the values of χ_{AB} for P2VN/PS and P2VN/PMMA predicted by the intrinsic viscosity results as well as those predicted by a molar group additivity scheme are compared to the values determined from the fluorescence measurements.

Experimental Section

The PS(2200), P2VN(21 000), P2VN(70 000), and P2VN(265 000) samples have been described previously.[3] The PMMA samples, having molecular weights ranging from 1100 to 350 000, are described in detail in Table I. The tacticity of the PMMA samples is unknown, but we have no reason to believe that there

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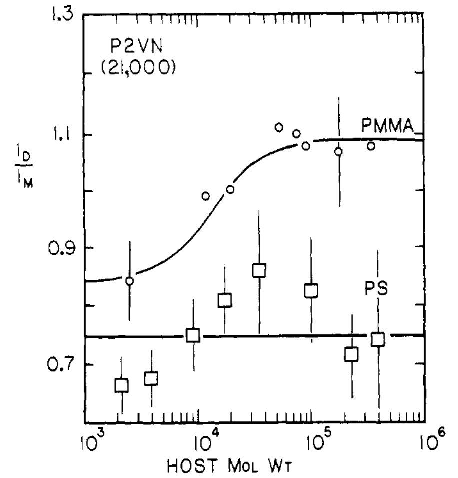

Figure 1. Effect of host molecular weight on I_D/I_M for 0.3% blends of P2VN(21 000) with PMMA (○) and PS(□). The uncorrected excimer and monomer intensities, measured under front-face illumination, have been determined at 398 and 337 nm, respectively. The P2VN/PS results, reproduced from ref 3, have been multiplied by 1.15 to account for the difference between back-face illumination, used previously, and the present method. Filled plotting symbols indicate the film was visibly cloudy; open symbols denote clear films.

are appreciable differences in miscibility with P2VN due solely to variations in PMMA tacticity. The PMMA samples were all used as received without purification. Films of the blends were prepared by casting from toluene onto small glass slides at room temperature, and fluorescence spectra were taken under front-face illumination with exciting light at 290 nm. Residual casting solvent after 1 h of drying has been found to be about 20% for P2VN/PMMA[4] and P2VN/PS[5] films with host molecular weights of approximately 200 000. The solvent content decreases as the host molecular weight, and hence the glass transition temperature drops. After long drying time, residual solvent content in all films is less than 5%. Details of these procedures have been given earlier.[1]

Preparation of P2VN/PMMA blends for examination by DSC followed previous procedures.[5,6] DSC thermograms for the samples were obtained with a Perkin-Elmer DSC-2 calorimeter operating at a rate of 20 K/min. The lower limit temperature was set at 293 K to obtain a sufficient length of the thermogram trace in the PMMA(2500) glassy regime.

Results

1. Fluorescence and Optical Clarity of P2VN/PMMA Blends.

There are two major similarities between the fluorescence spectra of P2VN/PMMA blends and those of P2VN/PS blends which have identical composition and molecular weight. First, the shape and spectral position of the guest monomer and excimer emission are identical in both host polymers. Consequently, the same monomer and excimer wavelengths (337 and 398 nm) were utilized for the determination of I_D/I_M, the ratio of excimer to monomer intensities, for the P2VN/PMMA blends. Moreover, the overall spectral intensity of P2VN fluorescence in both host polymers is roughly similar. It was assumed from this observation that both host polymers were free of quenching impurities.

The P2VN/PMMA blends examined by fluorecence spectroscopy in the following sections were chosen so that the results could be directly compared with those for the counterpart P2VN/PS blends examined earlier.[3,5,6] Through comparison of blends which have identical composition and molecular weights, the effect of the chemical nature of the host polymer on I_D/I_M may be determined.

a. Effect of Molecular Weight at Low P2VN Concentration. Fluorescence results for the three P2VN guest polymers are presented in Figures 1–3, in which I_D/I_M for the guest polymer is plotted against the molecular weight of the host PMMA. For purposes of comparison, the results from the P2VN/PS blend study[3] are also plotted on Figures 1–3. Note that the range of P2VN I_D/I_M values observed for blends with PMMA and PS of different host molecular weights depends upon the molecular weight of the guest, as analyzed in earlier work.[10,12] Thus, the scales of I_D/I_M are quite different in Figures 1–3. I_D/I_M values for the earlier P2VN/PS results have been multiplied by 1.15 to account for the difference in optical arrangement between back-face illumination, used previously, and the front-face illumination employed in the present work. This correction factor was determined experimentally by measuring I_D/I_M for a 0.3% P2VN(70 K)/PS(233 K) film in both front-face and back-face illumination modes. The error bars for the PMMA(2500) and PMMA(180 000) host illustrate one standard deviation for the ratio of two films of these blends; all other P2VN/PMMA data points are single-film values. Error bars are also given for the P2VN/PS blends for cases in which the error exceeds the size of the plotting symbol. The solid lines simply represent smooth curves through the data points, which are

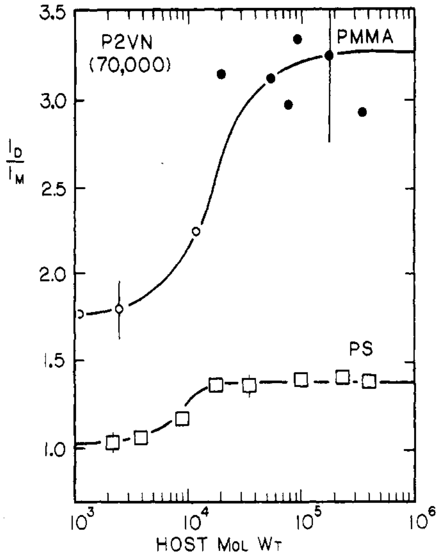

Figure 2. Effect of host molecular weight on I_D/I_M for 0.3% blends of P2VN(70 000) with PMMA (○) and PS (□). See Figure 1 for details.

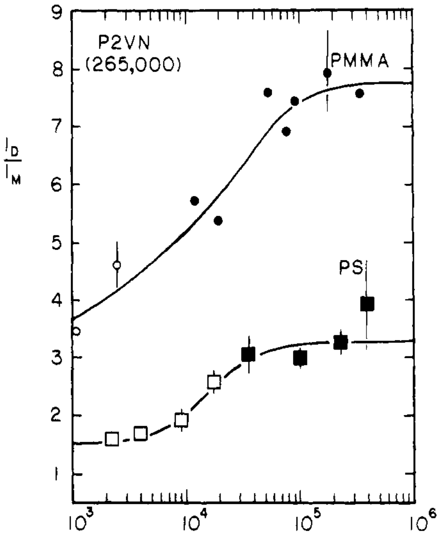

Figure 3. Effect of host molecular weight on I_D/I_M for 0.3% blends of P2VN(265 000) with PMMA (○) and PS(□). See Figure 1 for details.

drawn to be consistent with the measured reproducibility limits. Certainly other lines are possible. However, the subsequent analysis is based on solely on the deviation of I_D/I_M from some lower base line of reference value. No quantitative analysis is made of the significance of the absolute values of I_D/I_M at either the lower or the upper limits.

Figure 1 presents the results for the P2VN(21 000) guest. I_D/I_M increases by 30% between the PMMA(2500) and PMMA(54 000) blends and remains constant for higher PMMA molecular weights. This is in contrast to the P2VN(21 000)/PS blends, where I_D/I_M remains experimentally constant with an average value of 0.75 (corrected to front face) for all PS molecular weights. No significance is attached to the slight apparent maximum in I_D/I_M for the P2VN/PS blends because the samples with PS hosts having molecular weights of 9000, 17 500, and 35 000 tended to crack and craze as the casting solvent evaporated. This generally leads to internal reflection and some self-absorption, which will decrease the monomer signal more than the excimer thus causing an increase in I_D/I_M. This effect was most pronounced for the P2VN(21 000)/PS blends.

Results for the P2VN(70 000) guest are shown in Figure 2. Note the considerable scale change from Figure 1. I_D/I_M appears to be relatively constant for PMMA host molecular weights below 2500. The plateau value at low PMMA molecular weight could conceivably be lower but there are no available hosts which are glassy at the temperature of measurement. Excessive segmental mobility arising from having a T_g close to the measurement temperature would lead to an increase in I_D/I_M due to rotational sampling of excimer forming sites.[2] Between the PMMA(2500) and PMMA(20 000) blends, however, the ratio increases by 80% to a plateau which extends to the PMMA(350 000) blend. This behavior is strikingly similar to that of the PS blends if the magnitudes of the ratios are ignored.

Results for the P2VN(265 000) blends are presented in Figure 3. In contrast to the lower molecular weight guests, I_D/I_M does not appear to become level for PMMA host molecular weights below 2500, and there is no clear-cut point of inflection in the curve. However, the ratio increases to an upper-limit value which is attained at PMMA molecular weights above 80 000. Such an upper plateau is common to all of the I_D/I_M–host molecular weight relationships presented in this work, excluding the P2VN(21 000)/PS results.

In order to determine whether the changes in I_D/I_M for P2VN as a function of PMMA host molecular weight are thermodynamically significant, it is necessary to quantify the results. In earlier work,[10] the fluorescence intensity ratio was shown to be given by

$$\frac{I_D}{I_M} = \frac{Q_D}{Q_M}\left(\frac{1-M}{M}\right) \qquad (1)$$

where Q_D is the ratio of the fluorescence decay constant to the total decay constant for the excimer. In terms of Birks' nomenclature,[11] Q_D is given by $k_{FD}/(k_{FD} + k_{ID})$. Q_M is the corresponding quantity for the monomer, $k_{FM}/(k_{FM} + k_{IM})$, and M is the probability that a photon absorbed by the P2VN guest will decay along a monomer pathway. M has been shown to be a function of concentration and aggregation in the blend.[12,13]

The first step toward quantitative analysis of the P2VN/PMMA blends is to determine whether Q_D and Q_M depend on the host matrix. Because the fluorescence ratio I_D/I_M is directly proportional to Q_D/Q_M, it is conceivable that I_D/I_M for miscible P2VN blends could differ from host to host. For example, the factor Q_D/Q_M for pyrene in acetone solution is 8% larger than in toluene solution;[11] similar results have been obtained for pyrene in a PMMA host relative to PS.[14] It is unclear, however, whether the value of the intramolecular Q_D is affected by the host matrix in the same degree as the intermolecular Q_D. There are few data in the literature for the former quantity, particularly in polymer hosts.

Table II
Influence of Host Matrix on I_D/I_M for 0.3 wt % ββDNP[a] Blends

polymer host	I_D/I_M[b]
PS(2200)	0.0274 ± 0.005
PS(233 000)	0.0265 ± 0.002
PMMA(2500)	0.0267 ± 0.004
PMMA(180 000)	0.0268 ± 0.004
mean	0.027 ± 0.004

[a] ββDNP stands for 1,3-bis(2-naphthyl)propane. [b] I_{398}/I_{337} measured under back-face illumination, corrected for overlap of monomer band into the excimer band.

To demonstrate that Q_D/Q_M is approximately the same in both the PS and PMMA hosts, it is necessary to have an intramolecular excimer forming 2-naphthyl-substituted model compound. Such a compound must be of sufficiently low molecular weight that it is unquestionably miscible with both PS and PMMA. Ideally, it would have been preferable to use an oligomer of P2VN, but none were available. Instead, we used 1,3-bis(2-naphthyl)propane (ββDNP) as the model for the intramolecular excimer forming compound. Although the I_D/I_M value is low at the concentration of 0.3 wt %, we are assured of its miscibility. In a rigid medium, the following expression describes the fluorescence behavior of such a model compound.

$$\left(\frac{I_D}{I_M}\right)_{\text{model}} = \frac{Q_D}{Q_M}\left[\frac{q}{1-q}\right] \qquad (2)$$

The mole fraction of the excimer-forming site, q, should be independent of the host since ββDNP is miscible with PS and PMMA. Thus, any variation of I_D/I_M for the 2-naphthyl excimer caused by differences in the polymer host may be interpreted as a change in Q_D/Q_M.

The fluorescence ratios of the 0.3 wt % ββDNP blends are shown in Table II. The standard deviation is large, approximately 15%, because of the weak intensity of the excimer band and the overlap of the monomer band with the excimer band. Nevertheless, these data show no appreciable difference in I_D/I_M and thus no difference in Q_D/Q_M between the PS and PMMA host polymers. Moreover, Q_D/Q_M is unaffected by host molecular weight, as was assumed previously.[3] Thus, the values of I_D/I_M for P2VN in miscible blends should be independent of whether the host matrix is PMMA or PS.

The second requirement for analysis is that a reference point be established for the fluorescence ratio I_D/I_M for miscible blends. Any deviation from this value, defined as R_{misc}, may then be interpreted in terms of changes in the morphology of the blend. A convenient, albeit arbitrary, method for specifying significant deviations from R_{misc} has been proposed earlier.[6] A quantity R^* is defined such that

$$R^* = (1 + 2W)R_{\text{misc}} \qquad (3)$$

where W is the average relative error determined from all points in the fluorescence data set under consideration. An analogous molecular weight parameter, M^*, is deter-

Table III
R^* and M^* for 0.3 wt % P2VN/PMMA Blends

MW of P2VN	R_{misc}[a]	W,[b] %	R^*[c]	M^*
21 000	0.67	10	0.80	<1000
70 000	1.04	10	1.25	<1000
265 000	1.61	9	1.90	<1000

[a] I_{398}/I_{337} measured under back-face illumination for P2VN/PS(2200) blends, uncorrected for overlap, and multiplied by 1.15 to correct to front-face conditions. See ref 3 for original data. [b] W is the relative error. [c] I_{398}/I_{337} measured under front-face illumination.

mined at the point where I_D/I_M is equal to or greater than R^*. Based on this empirical procedure, it is possible to classify polymer blends on the basis of the I_D/I_M values relative to R^*. Since we are only interested in the *change* in I_D/I_M rather than the absolute value, this seems to be a reasonable approach to correlation of the photophysical observations with the morphology.

It is necessary, however, to determine values for R_{misc} in order to apply eq 3. To some extent, this requires a deeper understanding of the concept of immiscibility at extremely low guest concentrations than is presently available. Unfortunately, it is not possible to distinguish between, e.g., aggregated guest chains or contracted coils solely on the basis of the observed excimer fluorescence. It is likely, however, that the 21 000 and 70 000 P2VN molecular weights are too low to exhibit any appreciable chain expansion as a result of host "solvent" effects. In light of this, and the conclusion that Q_D/Q_M is the same in both PS and PMMA, it seems reasonable to select the P2VN/PS(2100) blends as reference points since these have previously been shown to be miscible.[3,5,6]

The necessary data for computing R^* for the blends of Figures 1–3 are listed in Table III. Values of R_{misc} were reproduced from ref 3, after multiplication by 1.15 to obtain front-face ratios. The increase in I_D/I_M with increasing molecular weight of the P2VN has been analyzed earlier in terms of a one-dimensional energy migration model.[10] This model is applicable for isolated chains in a thermodynamically good matrix. For the purposes of this study, the variation of the low host molecular weight plateau value of I_D/I_M for different P2VN molecular weights is unimportant. Only changes from that level arising from changes in the host molecular weight are of interest.

R^* is computed from R_{misc} by utilizing eq 3. For each of the three figures, the lowest fluorescence ratio is still larger than the corresponding value of R^* in Table III, so that M^* is less than 1000 for all three of the P2VN guests in PMMA. It is intriguing to note that the low plateau values of I_D/I_M for the PMMA blends in Figures 1 and 2 do not represent miscible blends.

These fluorescence results clearly demonstrate that lowering the PMMA host molecular weight increases the miscibility of all three P2VN guests, as was observed for the P2VN/PS series.[3] As confirmation, we note that the P2VN(265 000) and P2VN(70 000) blends are optically cloudy and bluish for PMMA molecular weights greater than or equal to 12 000 and 20 000, respectively. Such behavior is indicated on Figures 1–3 as filled plotting symbols; optically clear films are indicated by open symbols. The fact that all of the P2VN(21 000)/PMMA blends are optically clear neither confirms nor refutes the observation based on excimer fluorescence that these blends are immiscible for large PMMA molecular weights. Further information on the P2VN/PMMA blends may be obtained from studies on the effect of concentration, considered in the next section.

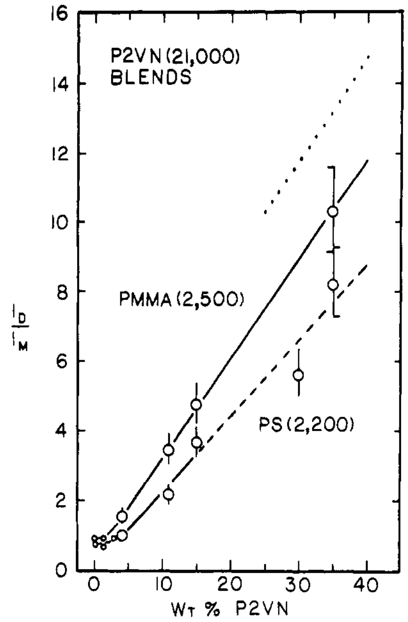

Figure 4. Effect of P2VN(21 000) guest concentration on I_D/I_M for blends with PMMA(2500) and PS(2200). The excimer and monomer intensities are measured at 398 and 337 nm, respectively. The ratio I_D/I_M is corrected for spectral overlap by the relation $(I_D/I_M)_{\mathrm{corrected}} = (I_D/I_M - 0.021)/(1 - 0.020 I_D/I_M)$. Spectra were taken under front-face illumination. Open and filled circles denote optically clear and cloudy blends, respectively. The dashed line represents the data from all three P2VN guests in the PS(2200) host, while the dotted line represents the data from all P2VN guests in the PMMA(2500) host, except P2VN(21 000).

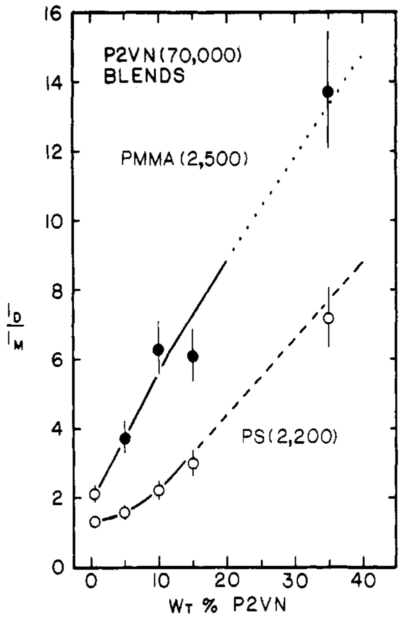

Figure 5. Effect of P2VN(70 000) guest concentration on I_D/I_M for blends with PMMA(2500) and PS(2200). See Figure 4 for details.

b. Effect of P2VN Concentration in the PMMA(2500) Host. PMMA(2500) was selected as the host for the concentration study so that the immiscibility of the P2VN guest might be minimized and so that the results of the fluorescence measurements could be compared with those of a DSC study appearing in a later section. Blends containing up to 35 wt % P2VN were investigated by fluorescence spectroscopy. Because of the limited amounts of PMMA samples, purification of the PMMA hosts was not attempted. Consequently, the P2VN concentration in any PMMA host could not be reduced below 0.3 wt %

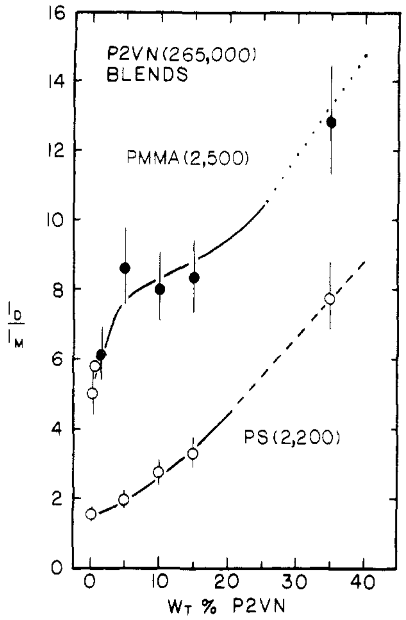

Figure 6. Effect of P2VN(265 000) guest concentration on I_D/I_M for blends with PMMA(2500) and PS(2200). See Figure 4 for details.

due to a small amount of interfering impurity fluorescence.

Fluorescence results for the three P2VN guest polymers are presented in Figures 4–6. In each figure, data for the PS(2200) host polymers are also shown for comparison; the vertical bars represent the typical variation in the ratio for repeated studies. As was true for the molecular weight study, values of I_D/I_M for the PS blends are always lower than those of the comparable PMMA blends, for P2VN compositions between 0.3 and 35 wt %. To facilitate the comparison of different figures, dashed and dotted lines are reproduced in all three figures. The dashed line illustrates the common behavior of all three P2VN guests in the PS(2200) host above 15% P2VN. The dotted line illustrates the common behavior of all except the P2VN(21 000) guest in the PMMA(2500) host above 25% P2VN.

Results for the P2VN(21 000) guest are given in Figure 4. Values of the ratio for the PMMA host are more than 1.26 times larger than I_D/I_M for the PS host over the entire P2VN concentration range shown. Since the P2VN/PS(2200) blends have been shown previously to be miscible,[3,5,6] these data indicate that P2VN(21 000) is immiscible with the PMMA(2500) host for P2VN compositions between 0.3 and 35%. The visual appearance of the PMMA blends does not reveal this immiscibility, however, since all of the blends represented in Figure 4 are clear.

Two additional observations on these fluorescence data may be made. First, I_D/I_M for both hosts increases linearly with P2VN concentration above 8%, and the slope of this trend for the PMMA host is 1.5 times larger than that for the PS host. Second, the slope for the P2VN(21 000)/PMMA blends is the same as the slope of the dotted line which gives I_D/I_M for the higher molecular weight P2VN guests in the PMMA host. While the significance of these linear I_D/I_M–concentration plots will be discussed later, we note from the magnitude of I_D/I_M that the P2VN(21 000)/PMMA blends, while immiscible do not seem to possess the large degree of phase separation exhibited by the higher molecular weight P2VN guests in PMMA.

Fluorescence data for the P2VN(70 000) guest are given in Figure 5. Values of the ratio for the PMMA host are again greater than those for the PS host, considerably larger than the difference observed in Figure 4. Thus, P2VN(70 000) is immiscible with PMMA(2500) for all P2VN concentrations shown. Indeed, blends containing PMMA are optically cloudy for P2VN concentrations greater than 5%. Several observations unique to the fluorescence behavior of the P2VN(70 000) guest may be made. First, the curve for the PMMA host in Figure 5 is roughly linear over the entire concentration range examined. Second, the curve for the PS host does not join the dashed-line asymptote common to all P2VN guests until the P2VN concentration exceeds 12%. These two observations will be discussed later in conjunction with similar observations for the other P2VN guests.

Results for the P2VN(265 000) guest are presented in Figure 6. The PMMA host is quite immiscible with this P2VN guest, since differences in I_D/I_M between the PMMA blends and the (miscible) PS blends are larger than for any other P2VN sample. P2VN(265 000)/PMMA(2500) blends are optically cloudy for P2VN concentrations greater than or equal to 1.5%. The I_D/I_M–concentration curves in Figure 6 show two quite different trends. At one extreme, the curve for the PMMA host increases rapidly at low concentration, reaches a "shoulder" at about 10%, and joins the dotted line at 25% P2VN concentration. At the other extreme, the curve for the PS host, which is quite similar to curves for the other two P2VN guests in PS, joins the dashed-line asymptote at 20% P2VN concentration.

Within the data of Figures 4–6 are several trends which are roughly independent of the molecular weight of the P2VN guest. There are two such trends for the PMMA(2500) host. First, the I_D/I_M–concentration curves are reasonably linear but become somewhat convex as the P2VN molecular weight is increased. Second, the slopes of all these curves are approximately 1.5 times larger than those for all P2VN/PS(2200) blends, for P2VN concentrations greater than or equal to 20%. Similar linear ratio vs. concentration behavior for several P2VN/poly(alkyl methacrylate) systems has been reported.[2] In this earlier work, the magnitude of the slopes of the curves was found to increase in proportion to the difference between the guest and host solubility parameters. Given the results of these previous studies and the observation[1] that P2VN is less miscible in PMMA than in PS, the data presented in this work for the PMMA and PS hosts are quite consistent.

c. Summary. Data on the immiscibility of the P2VN/PMMA blends of the previous sections determined by excimer fluorescence and by visual appearance are collected in Table IV. Again, as found earlier,[3–6] the fluorescence method has superior sensitivity to blend immiscibility relative to visual observation. Because of the greater immiscibility of the PMMA host relative to the PS host, all of the miscible–immiscible transition points M^* and C^* are apparently out of the range utilized in the present work. The lower-limit value of PMMA molecular weight could not be decreased below 1000 because the PMMA would no longer be glassy at room temperature.

2. Differential Scanning Calorimetry of P2VN/PMMA Blends. In this section, the DSC thermograms of pure PMMA(2500) and of 35 wt % P2VN/PMMA(2500) blends will be described and interpreted. Thermograms for the pure polymers PMMA and P2VN are displayed in Figure 7. The results for the PMMA(2500) sample are slightly different from the P2VN thermograms in that a local maximum in the heat capacity does not occur in the PMMA thermogram. T_1 is the point of upward deviation of the heat capacity and appears for both PMMA and P2VN; T_2 represents the point where the high-temperature heat capacity shows a downward devi-

Table IV
Critical Molecular Weight and Concentration for the Apparent Miscible to Immiscible Transition

	immiscibility by technique	
blend	visual	fluorescence ratio
(A) Variable PMMA Molecular Weight		
0.3 wt % P2VN(21 000)	$M > 350\,000^a$	$M^* < 1000^b$
0.3 wt % P2VN(70 000)	$M = 20\,000^a$	$M^* < 1000^b$
0.3 wt % P2VN(265 000)	$M = 12\,000^a$	$M^* < 1000^b$
(B) Variable P2VN Concentration		
P2VN(21 000)/PMMA(2500)	$C > 35\%^c$	$C^* < 0.3\%^d$
P2VN(21 000)/PS(2200)	$C > 35\%^c$	$C^* > 35\%^d$
P2VN(70 000)/PMMA(2500)	$C = 5\%^c$	$C^* < 0.3\%^d$
P2VN(70 000)/PS(2200)	$C > 35\%^c$	$C^* > 35\%^d$
P2VN(265 000)/PMMA(2500)	$C = 1.5\%^c$	$C^* < 0.3\%^d$
P2VN(265 000)/PS(2200)	$C > 35\%^c$	$C^* > 35\%^d$

[a] Blend is cloudy at and above the stated PMMA molecular weight. [b] Blend has ratio $\geq R^*$ at and above the stated PMMA molecular weight. [c] Blend is cloudy at and above the stated P2VN concentration. [d] Blend has ratio $\geq R^*$ at and above the stated P2VN concentration.

ation. The temperatures marked in Figure 7 are listed in Table V. The T_g of PMMA(2500) is almost identical with the value for PS(2200), but the breadth of the transition region for PMMA is more than double that for PS(2200).

Thermograms for the 35 wt % P2VN/PMMA(2500) blends are shown in Figure 8. The transition temperatures have been defined in the same manner as for the pure polymers and are listed in Table V along with previous results[5,6] for blends with PS.

Two glass transitions were observed for all three PMMA blends studied, and the values of T_g recorded for the P2VN and PMMA blend components were shifted from their pure component values by only 10–25 K. As the molecular weight of the P2VN component increases, the T_g of that blend component increases from 401 to 416 K, showing increased immiscibility. These results indicate that all three P2VN/PMMA(2500) blends are immiscible.

The question remains whether these blends were also immiscible before being heated in preparation for the DSC measurement; this heating could alter the morphology of an otherwise miscible blend. The 35% P2VN(70 000)/PMMA(2500) and P2VN(265 000)/PMMA(2500) blends were obviously immiscible, since these blends were cloudy both before and after heating. However, since the 35% P2VN(21 000)/PMMA(2500) blend was initially clear and then turned cloudy during heating, the immiscibility of this blend as determined by the fluorescence ratio could be neither confirmed nor refuted.

A comparison of P2VN/PMMA and P2VN/PS results shows the decreased miscibility of P2VN in the PMMA host relative to the PS host. While both the P2VN(21 000) and P2VN(70 000) guests possess a distinct heat capacity transition in the PMMA host, they do not influence the thermogram for the PS host except to increase the upper temperature T_2 of the host transition. The P2VN(265 000) guest is immiscible with both PMMA and PS, since a guest and a host transition appears in both thermograms. While the temperatures of the host transition differ very little between the PMMA and PS blends, the large change in

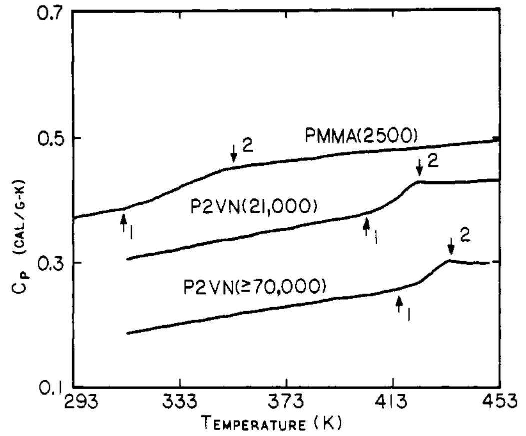

Figure 7. Thermograms for pure polymers. Samples were heated at 20 K/min. The bottom curve is true; each additional curve has been displaced +0.1 cal/g·K from the curve immediately beneath it. See Table V for transition temperatures.

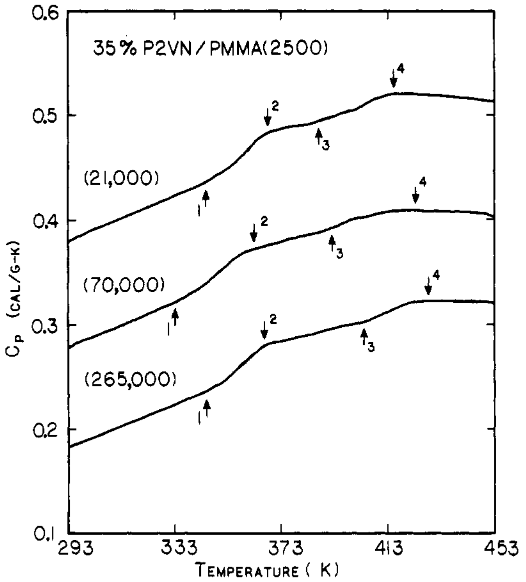

Figure 8. Thermograms for PMMA(2500) films cast from toluene with 35 wt % P2VN. The molecular weight of the P2VN in each blend is given in parentheses. See Table V for temperatures.

Table V
Transition Temperatures for Pure Polymers and Polymer Blends

polymer	T_1	T_2	ΔT	$T_g{}^a$	T_3	T_4	$\Delta T'$	$T_g'{}^b$
PMMA(2500)[d]	312	353	41	333				
PS(2200)[d]	328	345	17	337				
P2VN(21 000)	403	426	23	415				
P2VN(70 000)[c,d]	415	435	20	425				
35% P2VN(21 000)/65% PMMA(2500)	345	368	23	357	387	415	28	401
35% P2VN(70 000)/65% PMMA(2500)[d]	333	363	30	348	392	423	31	408
35% P2VN(265 000)/65% PMMA(2500)	345	367	22	356	404	428	24	416
35% P2VN(21 000)/65% PS(2200)[e]	343	383	40	363				
35% P2VN(70 000)/65% PS(2200)[d]	344	383	39	364				
35% P2VN(265 000)/65% PS(2200)[e]	343	358	15	351	366	400	34	383

[a] $T_g = (T_1 + T_2)/2$. [b] $T_g' = (T_3 + T_4)/2$. [c] The temperatures for P2VN(265 000) are nearly the same as for P2VN(70 000). [d] Reference 5. [e] Reference 6.

the guest transition temperatures quantitatively shows the difference in immiscibility between the PMMA and PS hosts. The breadth of the guest transition in the PMMA host is similar to the transition for pure P2VN(265 000) except for a 10 K decrease in T_g. However, the P2VN(265 000) guest T_g in the PS host is decreased 40 K relative to pure P2VN, and the breadth of the guest transition is increased by 15 K.

The DSC experiments have been useful in judging the miscibility of blends containing high concentrations of P2VN, i.e., in Figures 4–6 for the PMMA host. Whenever high-concentration blends are found by DSC to be miscible, the miscibility of unheated, low-concentration blends can reasonably inferred. Unfortunately, DSC does not shed any light on the question of the miscibility of 0.3% P2VN/PMMA(2500) blends. Consequently, the data obtained by the fluorescence ratio technique on these blends are the only conclusive evidence for their immiscibility.

Discussion

1. Flory–Huggins Lattice Theory of P2VN/PMMA Blends.

The purpose of this section is to determine whether a single value of the binary interaction parameter is sufficient to characterize the P2VN/PMMA blends studied in previous sections. To accomplish this, binodal curves for P2VN/PMMA blends were first generated by the solution of the binodal equations[3] of Flory–Huggins lattice theory. A range of values of the binary interaction parameter χ_{AB} was considered. Then, by comparing the fluorescence results (M^* or C^*) with the binodal curves, a value of χ_{AB} was deduced for each set of P2VN/PMMA blends. An analogous approach was taken earlier.[6]

The introduction of the host polymer PMMA may strain the applicability of the unsophisticated Flory–Huggins theory. The limitations are divided into two types: thermodynamic and kinetic. The main thermodynamic limitation stems from the dissimilarity of P2VN and PMMA and the possibility that the casting solvent may interact preferentially with one of the two polymers. It was assumed previously for the P2VN/PS pair that the casting solvent, toluene, had no such preferences. This assumption meant that the casting solvent could be neglected in the calculation of phase equilibrium, except that the apparent binary interaction parameter χ_{AB} might be reduced from the no-solvent binary parameter by an amount proportional[15,16] to the amount of solvent present in the blend at the solidification point during the casting process. For the moment, we will assume that toluene interacts equally with P2VN and PMMA, if only to allow a direct comparison of the PMMA host and PS host data and their analysis by the Flory–Huggins lattice model. Other minor thermodynamic limitations of the Flory–Huggins theory, namely dilute-blend and equation-of-state corrections, have been discussed previously.[3]

The second type of limitation which occurs for all thermodynamic mixing theories is the kinetic limitation imposed by the enormous bulk viscosity of polymer blends. Strictly speaking, all the P2VN/PS blends[3,5,6] and the P2VN/PMMA blends of the present work have some degree of nonequilibrium character, since the final T_g of the solvent-cast blends is above room temperature. The specific problem for the P2VN/PMMA blends is whether the nonequilibrium character produced by casting from toluene is equal or even comparable to that in the P2VN/PS blends.

The following observations from recent studies support the kinetic similarity of the solvent casting process for the PS and PMMA hosts. First, the value of T_g for PMMA is within 5 K of the value for PS, both at low and high molecular weights. Second, the variation of residual solvent with time for a toluene-cast PMMA film[4] has been found to be quite similar to that for a toluene-cast PS film.[5] Third, the variation of the fluorescence ratio with time during the drying of toluene-cast PS and PMMA films containing 1,3-bis(2-naphthyl)propane (ββDNP) has been found to be identical for PS and PMMA hosts, irrespective of molecular weight.[5] Finally, the time scale of the I_D/I_M–time curves for P2VN/PMMA blends[4] during solvent casting was identical with that for P2VN/PS blends.[5] These results indicate that the solvent content and mobility within toluene-cast PMMA and PS hosts are independent of host during the casting process.

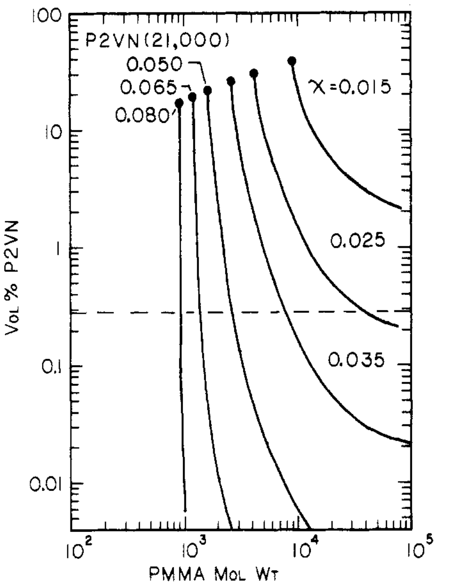

Figure 9. Binodal compositions calculated for P2VN(21 000)/PMMA blends. Results for the P2VN-lean phase are shown as volume percent P2VN vs. PMMA mol wt. The interaction parameter for each curve is given and the critical point is indicated by the filled circle. The dashed line denotes 0.3 wt % P2VN.

Despite the above potential limitations of the Flory–Huggins treatment, we fully expect that the predictions of molecular weight dependence and concentration dependence over a modest concentration range will be qualitatively correct for the P2VN/PMMA pair, since a consistent value of the interaction parameter was found for all P2VN/PS blends.[6]

The binodal curves for P2VN/PMMA blends are presented in Figures 9–11 for the P2VN(21 000), P2VN(70 000), and P2VN(265 000) guests, respectively. These binodals are plotted as P2VN concentration vs. PMMA host molecular weight with the interaction parameter held constant, in the same format utilized earlier.[3] The dashed line in these figures represents a concentration of 0.3 wt % P2VN. A range of interaction parameters from 0.015 to 0.080 was selected for the P2VN/PMMA binodals.

Since the binodal curves for $\chi_{AB} \geq 0.050$ are essentially vertical lines over the P2VN concentration range pictured in Figures 9–11, the important data for large values of χ_{AB} are the locations of the critical point. The P2VN concentration and PMMA molecular weight at the critical point were obtained from eq 4 and 5. The subscripts A and B refer to PMMA and P2VN, respectively; v represents volume fraction and x represents degree of polymerization (based on the reference repeat unit molar volume). For large values of χ_{AB}, the binodal curves shift to

$$v_{B,\mathrm{crit}} = (2x_B\chi_{AB})^{-1/2} \tag{4}$$

$$x_{A,\mathrm{crit}} = x_B[(2x_B\chi_{AB})^{1/2} - 1]^{-2} \tag{5}$$

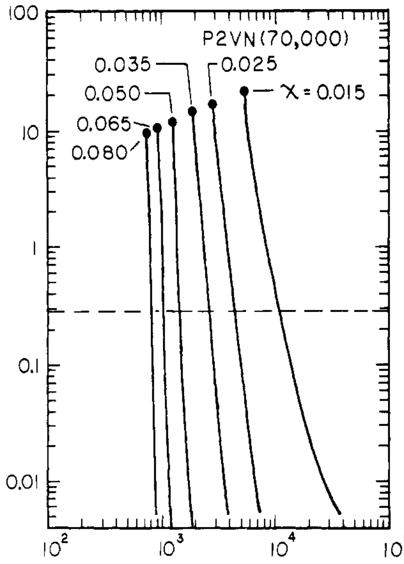

Figure 10. Binodal compositions calculated for P2VN(70 000)/PMMA blends. See Figure 9 for details.

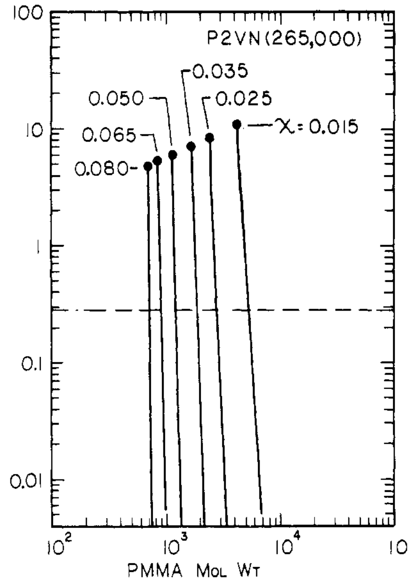

Figure 11. Binodal compositions calculated for P2VN(265 000)/PMMA blends. See Figure 9 for details.

lower host molecular weight, become vertical for high P2VN molecular weights, and become more closely spaced for equal increments in χ_{AB}.

The fluorescence data for the 0.3% P2VN(21 000)/PMMA blends have given $M^* < 1000$, as seen in Table IV. Turning to the binodals of Figure 9, we find through interpolation that $\chi_{AB} = 0.075$ corresponds to $M^* = 1000$. Another value of the interaction parameter may be obtained from the fluorescence data from the variable-concentration P2VN(21 000)/PMMA(2500) blends. Table IV lists $C^* < 0.3\%$ for these blends. Locating $C^* = 0.3\%$ and the host molecular weight of 2500 on Figure 9, one finds that $\chi_{AB} = 0.050$.

Two sets of data are available for the determination of χ_{AB} for blends containing the P2VN(70 000) guest. The first set consists of the PMMA host molecular weight dependence of I_D/I_M in Figure 2. It has been observed that $M^* < 1000$ from these results. Interpolation of the binodals of Figure 10 yields $\chi_{AB} > 0.065$. The second set of experimental I_D/I_M data is obtained from the concentration study in the PMMA(2500) host, presented in Figure 5. The value of C^* was determined to be less than 0.3%. Examination of the binodal curves of Figure 10 gives 0.035 as a lower limit for χ_{AB}.

Finally, we consider blends containing the P2VN(265 000) guest. The fluorescence data for the 0.3% P2VN(265 000)/PMMA blends have given $M^* < 1000$, as seen in Table IV. Corresponding to this value of M^* is the lower-limit value of $\chi_{AB} = 0.057$, found by inspection of Figure 11. Another value of the interaction parameter for the P2VN(265 000) guest is obtained from the fluorescence data from the concentration study in the PMMA(2500) host. Again, the value of C^* was determined to be less than 0.3%. A lower limit of 0.025 for χ_{AB} corresponds to this value of C^* and host molecular weight, as seen in Figure 11.

Values of the interaction parameter χ_{AB} for the six P2VN/PMMA blend systems just examined are compiled in Table VI. Because none of the P2VN/PMMA blends were completely miscible, only a lower limit on χ_{AB} may be determined. In that regard, the best estimate of the interaction parameter occurs for the P2VN(21 000) guest blends, since these blends are closest to miscibility. Thus, we may characterize all the P2VN/PMMA blends by $\chi_{AB} = 0.070 \pm 0.015$.

Table VI
Interaction Parameter χ_{AB} for P2VN/PMMA Blends Solvent Cast from Toluene at Room Temperature

MW of P2VN	wt % P2VN	MW of PMMA	χ_{AB}
21 000	0.3	variable[a]	0.075[c]
21 000	variable[b]	2500	>0.050
70 000	0.3	variable[a]	>0.065
70 000	variable[b]	2500	$\gg$0.035
265 000	0.3	variable[a]	>0.057
265 000	variable[b]	2500	$\gg$0.025

[a] 1100, 2500, 12 000, 20 000, 54 000, 79 000, 92 000, 180 000, and 350 000; $M_w/M_n < 1.15$ for all but 12 000 and 20 000 samples. [b] Between 0.3 and 35 wt %. [c] The P2VN(21 000)/PMMA(1100) blend is considered to give the most accurate lower bound on χ_{AB}, since this blend was the least immiscible of the P2VN/PMMA blends studied. See text.

2. Prediction of the Interaction Parameter χ_{AB}. The objective of this section will be to calculate χ_{AB} for the Flory–Huggins theory by an approach other than fluorescence. The interaction parameter may generally be broken up into two parts

$$\chi_{AB} = \chi_H + \chi_S \tag{6}$$

where χ_H represents the enthalpic contribution and χ_S consists of entropic components not accounted for in the configurational entropy of mixing. In polymer–polymer systems, the free volumes are generally similar so that χ_S would be expected to be small. Furthermore, for the systems considered in this study there are no specific interactions which could cause deviations from random mixing. In earlier work[4] χ_S was estimated to be of the order of 20% of χ_H. It will be ignored in this study.

The enthalpic portion of the interaction parameter under these conditions will be given by[8]

$$\chi_{AB} = \chi_H = \frac{V_r}{RT}(\delta_A - \delta_B)^2 \tag{7}$$

where V_r is the reference molar volume defined as the smaller of the repeat unit molar volumes for the two polymers, δ_i is the solubility parameter of polymer i, and R is the gas constant. The solubility parameter of liquids can be obtained from heat of vaporization data, and ex-

Table VII
Comparison of Interaction Parameters at 298 K for P2VN/PS and P2VN/PMMA Obtained by All Methods

	polymer pair	
method	P2VN/PS	P2VN/PMMA
Small's method[a]	$0.042\,{}^{+0.037}_{-0.025}$	$0.019\,{}^{+0.027}_{-0.015}$[b]
intrinsic viscosity[a]	$0.015\,{}^{+0.028}_{-0.013}$	$0.023\,{}^{+0.044}_{-0.021}$
excimer fluorescence ratio	0.020 ±0.004	0.070 ±0.015

[a] Reference 9. [b] The ester group contribution used by Small[19] appears to be incorrect for methyl esters, and a new value has been proposed in ref 9. If this new value is used, then $\chi_{AB} = 0.002^{+0.013}_{-0.002}$.

tensive tables of solubility parameter values exist in the literature.[8,17,18]

Because the solubility parameter of polymers cannot be obtained in this manner, two other approaches have been developed. In the first approach, due to Small,[19] the solubility parameter is determined from the sum of tabulated values for the chemical groups within the repeat unit of the polymer. The second approach is based on the expansion of a polymer chain, which is maximized in a solvent which has the same solubility parameter as the polymer. This expansion can be determined experimentally from the intrinsic viscosity of dilute polymer solutions or from the swelling of a lightly cross-linked polymer sample in a variety of solvents.

Both approaches to the determination of the solubility parameter were taken in a companion study.[9] The binary interaction parameters obtained from the molar group additivity method and from intrinsic viscosity measurements are compared with the fluorescence results in Table VII.

Small's method produces the poorest estimates of χ_{AB}, particularly since the P2VN/PMMA pair is incorrectly predicted to be more miscible than the P2VN/PS pair. The predicted value of $\chi_{AB} = 0.042$ for P2VN/PS may be reconciled with the fluorescence value of 0.020 if we take $\delta_{P2VN} = 9.38$ cal$^{1/2}$/cm$^{3/2}$, which is within the limits of Small's value of $\delta_{P2VN} = 9.53 \pm 0.18$. In so doing, however, the discrepancy between the predicted values of $\chi_{AB} = 0.019$ for P2VN/PMMA and the fluorescence value of 0.070 becomes larger. Any value of δ_{PMMA} within the range of Small's prediction will give $\chi_{P2VN/PMMA} < \chi_{P2VN/PS}$.

The intrinsic viscosity method, while requiring more effort to apply than Small's method, accurately predicts that the P2VN/PS pair is more miscible than the P2VN/PMMA pair. The predicted value of $\chi_{AB} = 0.015$ for P2VN/PS is quite close to the fluorescence value of 0.020. This slight difference may be removed by increasing δ_{P2VN} slightly from 9.50 to 9.55 cal$^{1/2}$/cm$^{3/2}$. For the P2VN/PMMA pair, the discrepancy between the predicted value of $\chi_{AB} = 0.023$ and the fluorescence value of 0.070 may be removed by setting $\delta_{P2VN} = 8.7$ cal$^{1/2}$/cm$^{3/2}$. This value is slightly outside the range of $\delta_{P2VN} = 8.8$–9.2 cal$^{1/2}$/cm$^{3/2}$ estimated for P2VN in ester solvents but is qualitatively consistent with the observation for PS that δ_{PS} determined in esters is less than δ_{PS} determined in aromatic hydrocarbons.[9] In blends of poly(alkyl methacrylates) with 0.2 wt % P2VN(70 000) it was determined earlier[1,4] from the minimum in the fluorescence ratio that δ_{P2VN} from the intrinsic viscosity method and the fluorescence methods indicates the reliability of the latter.

The failure of a single value of δ_{P2VN} to describe the behavior of P2VN in mixtures both with aromatics and with esters can be understood as part of the larger problem posed by mixtures of polar and nonpolar liquids.[18,20] The energy density of a polar–nonpolar contact is less than the geometric mean of the energy densities of a polar–polar and a nonpolar–nonpolar contact, thus violating the usual assumption made in the derivation of eq 7. For example, carbon disulfide/acetone mixtures exhibit positive deviations from Raoult's law which are greater than the positive deviations predicted from the difference in solubility parameters.[21] Similarly, P2VN/PMMA blends possess a larger interaction parameter than can be obtained from the difference in solubility parameters, whether given by Small's method or determined from small-molecule analogues of the polymers. The value $\delta_{P2VN} = 8.8$ cal$^{1/2}$/cm$^{3/2}$ measured in esters does not describe the energy density of pure P2VN but refers to the ester in which the mixing interaction with P2VN is minimized. Apparently, this mixing process is adequately represented for P2VN/PMMA blends by eq 7 when the value of δ_{P2VN} measured in esters is utilized.

Summary

A broad range of results has been presented for the P2VN/PMMA blends in order to compare the fluorescence ratio approach with the standard techniques of visual appearance and differential scanning calorimetry. Low-concentration P2VN blends containing PMMA were found by all techniques to be less miscible than the analogous PS blends. Only the fluorescence ratio method was useful in determining the immiscibility of 0.3% P2VN/PMMA(2500) blends; all other techniques gave inconclusive results. The comparison of the visual appearance of all P2VN/PMMA blends with fluorescence results confirms the earlier observation made for P2VN/PS blends that the latter approach has superior sensitivity to phase separation of low-concentration P2VN blends.

In addition, methods for the interpretation of the fluorescence ratio of P2VN blends have been presented which allow the experimental determination of the binary interaction parameter. Values of χ_{AB} have been determined for P2VN/PS and P2VN/PMMA which characterize blends of various molecular weights and concentrations for each polymer pair. While the status of χ_{AB} as a completely thermodynamic, solvent-independent quantity has not been fully explored, these characterization methods associated with the fluorescence ratio of aromatic vinyl polymer blends may be useful as a point of departure for future work.

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Spectrum of Light Quasielastically Scattered from Solutions of Very Long Rods at Dilute and Semidilute Regimes

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ABSTRACT: A theoretical model is considered for the effect of anisotropic translational diffusion on the polarized field correlation function $G^1(\tau)$ of light quasielastically scattered from solutions of very long rods. Without solving a coupled translational/rotational diffusion equation, an expression for the first cumulant of $G^1(\tau)$ is derived, which is exactly the same as a recent one by a different approach. The Green function to the coupled diffusion equation in a dilute regime is obtained by two approximations. Since the Green function is characterized only by the sideways (D_1) and lengthways (D_3) translational and the rotational (Θ) diffusion constants, it is applicable to the case of semidilute solutions of rods after simple replacement of these constants with those suitable for a semidilute regime. Using this Green function, we formulate an expression of $G^1(\tau)$ for solutions of very long rods at arbitrary values of $\mu^2 = (D_3 - D_1)K^2/\Theta$ or of its version at a semidilute regime, where K is the length of the scattering vector. Some of simulated $G^1(\tau)$ are presented in order to estimate the accuracy of approximations and to visualize the theory. The present result includes the previous ones for relatively short rod lengths. Our model is easily extendable to the case of a solution of slightly bendable rods. A brief discussion on this context will also be given.

Introduction

Quasielastic scattering of laser light has been extensively applied to dynamic studies of macromolecules in solution. We have been interested in the dynamics of very long and semiflexible (or slightly bendable) filaments in solution. Such filaments include muscle F-actin and its complexes with other muscle proteins,[1–7] bacterial flagella,[8] various kinds of rodlike viruses,[9,10] microtubule,[11] and muscle thin[10] and thick[12] filaments. For example, the thin filament of skeletal muscle is 1 μm in length (L) and 5–8 nm in diameter (d).

To interpret experimental spectra (time correlation functions or power spectra of scattered light) from solutions of such long and semiflexible filaments, theoretical models for rigid rods undergoing translational and rotational Brownian motions are usually applied as the first-order approximation. Because a long rod undergoes anisotropic translation, a coupling between translational and rotational modes of diffusive motions is expected. This effect was once studied with special reference to tobacco mosaic virus (TMV).[13,14] In this case, however, experimental results excluded importance of the coupling effect.[14] And no further study has been made of this effect either theoretically or experimentally for a long time. But, if one wants to study very long rods, one has to take account of the coupling effect. Recently, a multiple time scale asymptotic technique was applied to this problem and experimental data on TMV were reanalyzed, which again gave small anisotropy.[15] More recently, an expression for the first cumulant of the polarized-light field correlation function for a long, thin rod was derived on the basis of a velocity autocorrelation function technique, and experimental data on TMV were analyzed, which gave quite large anisotropy, as large as the theoretically expected one.[16]

In the case of semidilute solutions, one has to take account of an effect of entanglements of long rods. Let c be the number of rods in unit volume. Then, one has to distinguish the two cases, $cL^3 \ll 1$ (dilute regime) and $L/d \gg cL^3 \gg 1$ (semidilute regime). In the case of muscle thin filaments, for example, 1 mg/mL in protein concentration corresponds to $cL^3 = 40$. Doi and Edwards considered the light-scattering spectra from a semidilute solution of relatively short rods.[17] Their model has been tested with (semi-) quantitative success by measurements of, for example, the Kerr effect (long viruses[18a] and a synthetic polymer[26]) and light scattering (long virus[18b] and a synthetic polymer[19]). As far as the light-scattering problem is concerned, the Doi–Edwards model corresponds to the extreme case of anisotropic translation of a rod. In the framework of their model, we can develop a unified theory of light scattering from solutions of long rods at dilute and semidilute regimes. The theories so far proposed for the effect of anisotropic translation on light-scattering spectrum are valid only for solutions of relatively short rods. We will consider a case of very long rods. Under the assumptions we adopted, our theory given below includes the previous ones for shorter rod lengths.

Even if a rod seems (or is believed) to be rigid, it might be semiflexible when it is very long. On electron micrographs of all the above-mentioned filaments, one surely observes *gradually curved images*. Thus, one has to take account of the effect of filament flexibility on the spectra. We have published a paper on the effect of filament flexibility on light-scattering spectra,[20] where neither the coupling nor the entanglement effect was considered.

As the first step to improve our old model,[20] we discuss in this paper a theoretical model for very long rods undergoing anisotropic translation as well as rotation at dilute and semidilute regimes. Because the main aim of this paper is to show gross features characteristic of light-scattering spectra of solutions of very long rods, a very simple model will be adopted and no sophisticated interaction will be considered. The outline of a part of this study has been published.[21]

Model

The polarizability α_3 parallel to the long axis of the rod

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