Poly-β-CD-A shows higher polarization of fluorescence than β-CD. The polymer complex may rotate slowly and further the rigidity of the complex may contribute to increase the rotational relaxation time of TNS.

From our experimental results, it may be concluded that the fluorescence enhancement of TNS caused by binding is ascribable to the restriction of intramolecular rotation in the rigid environment and/or to the exclusion of solvent relaxation.

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LCST Behavior in Polymer Blends

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ABSTRACT: Lower critical solution temperature (LCST) behavior has been established for five miscible polymer blend systems, and for four of these the loci of cloud points observed on heating has been determined as a function of blend composition. These systems include: polycarbonate–poly(ε-caprolactone) and mixtures of poly(vinylidene fluoride) with poly(methyl acrylate), poly(ethyl acrylate), poly(methyl methacrylate), and poly(ethyl methacrylate). The effect of adding a compatible plasticizer, dimethyl phthalate, on the cloud point curve for the poly(methyl methacrylate)–poly(styrene-*co*-acrylonitrile) was also studied. The prior literature documents LCST behavior for only four polymer blend systems even though several theories predict this to be a general phenomenon in blends.

Recent theories of mixing, such as the "equation of state" approach by Flory[1–5] and Sanchez's[6–8] "lattice fluid" model, predict that polymer–polymer blends which are miscible at lower temperatures are likely to exhibit phase separation at higher temperatures[5,8] in contrast to the predictions of the classical Flory–Huggins theory.[9] However, to date apparently such lower critical solution temperature (LCST) behavior has been reported for only four blend systems, viz., poly(methyl methacrylate)–poly(styrene-*co*-acrylonitrile);[10,11] polystyrene–poly(vinyl methyl ether);[12–16] poly(ε-caprolactone)–poly(styrene-*co*-acrylonitrile);[5] and chlorinated rubber–poly(ethylene-*co*-vinyl acetate).[17] The question of whether LCST behavior is a general phenomenon of miscible blends or is a peculiar characteristic of the specific systems mentioned above led us to examine more closely several systems, whose miscibility at lower temperatures was under investigation in our laboratory, for any LCST type behavior they might exhibit. In our search for this behavior some of these blends were heated to temperatures higher than normally required or expected in conventional studies or sample preparation. This leads to certain problems of polymer thermal stability but nevertheless yields interesting and useful information. This preliminary investigation has resulted in the observation of LCST behavior for five additional blend systems as reported here. This return for our modest effort leads us to the conclusion that LCST behavior is rather common for blend systems as predicted.

Two different molecular weight samples of one of the

Table I
Description of Polymer Samples

Polymer	Designation used here	Commercial designation (source)	Mol wt information	Ref
Poly(vinylidene fluoride)	PVF_2	KYNAR 301 (Pennwalt)	$\overline{M}_n$ = 88 000 $\overline{M}_w$ = 197 000	*a*
Poly(methyl methacrylate)	PMMA-1	ELVACITE 290 (Du Pont)	$\overline{M}_n$ = 45 600 $\overline{M}_w$ = 92 000 $\overline{M}_z$ = 145 100	11
	PMMA-2	V-415 (Rohm and Haas)	$\overline{M}_n$ = 190 000	*a*
	PMMA-3	V(811)-100 (Rohm and Haas)	$\overline{M}_n$ = 110 000	*a*
Poly(ethyl methacrylate)	PEMA	(Bulk polymerized by benzoyl peroxide)	$\overline{M}_w$ = 762 000	27
Poly(methyl acrylate)	PMA	(Bulk polymerized by benzoyl peroxide)	Not available	20
Poly(ethyl acrylate)	PEA	(Bulk polymerized by benzoyl peroxide)	Not available	20
Poly(styrene-*co*-acrylonitrile) 28% AN by wt	SAN	RMD-4511 (Union Carbide)	$\overline{M}_n$ = 88 600 $\overline{M}_w$ = 223 000 $\overline{M}_z$ = 679 600	11
Poly(ϵ-caprolactone)	PCL-300	PCL-300 (Union Carbide)	$\overline{M}_n$ = 10 000	*b*
	PCL-700	PCL-700 (Union Carbide)	$\overline{M}_w$ = 40 000	*b*
Polycarbonate	PC	LEXAN 310 (General Electric)	$\overline{M}_w$ = 29 200	*c*
Poly(vinyl acetate)	PVAc	AYAF (Union Carbide)	Not available	
High-density polyethylene	HDPE	DNDJ (Union Carbide)	Melt index = 4.8	*a*
Low-density polyethylene	LDPE	DYNF-3 (Union Carbide)	Melt index = 2.8	*a*
Poly(ethylene terephthalate)	PET	(Fiber Industries)	$\overline{M}_v$ = 19 200	*a*
Copolyester (see text)	PET	KODAR A150 (Tennessee Eastman)	Not available	

[a] Molecular weight information provided by supplier. [b] Provided by J. V. Koleske. [c] From solution viscosity.

components were used for two of the systems reported here. In addition, the effect of adding a compatible plasticizer to form a ternary system was examined in one case.

Experimental Section

The various polymers used in this study are listed in Table I along with their sources, trade designations, and available characterizing information. Some blends were made by melt mixing in a Brabender Plasti-Corder while others were solvent cast, and in some cases both techniques were used. The details of blend preparation for each system are given in the following sections.

Samples used in the cloud point measurements were thin disks, approximately one centimeter in diameter, cut from either compression molded or solvent cast films whose thicknesses varied from 0.01 to 0.05 cm. Within this range, sample thickness did not affect the temperature at which the cloud point was judged to occur. The apparatus for cloud point measurements, except as noted below, consisted of an aluminum base plate, 1.25 cm thick, placed on top of a hot plate used as a heat source. Another aluminum plate, 0.3 cm thick, was placed over the base plate, and a hole 4.0 cm in diameter in its center served as a cavity for the blend sample which was sandwiched between two glass cover slips. A Pyrex glass sheet was laid over the aluminum plates to retard heat losses while allowing the sample to be viewed from above. Sample temperature was measured by a thermometer inserted into a hole drilled into the side of the aluminum base plate such that its bulb was directly below the sample and very near the top surface of the base plate. Heating rates could be easily varied within the range of 5 to 15 °C/min by adjusting the voltage to the hot plate. Heating rates within this range did not seem to affect the observed cloud point, and so a nominal rate of 10 °C/min was typically used for convenience. Visually observed melting points of several standard compounds using this apparatus checked closely with published values.

The temperature at which the first faint opalescence appeared on heating was designated as the cloud point. All samples became completely opaque ca. 10–20 °C beyond this point.

In several instances, the cloud point was near or above the thermodynamic ceiling temperature of one of the components. The extent of depolymerization can be evaluated by the weight loss of the sample after heating. Weight changes were monitored for all systems and were always less than 2% except for blends containing poly(ethyl methacrylate) whose decompositions are described more fully below. In several instances, samples were heated rapidly to just below the expected cloud point and then transferred to this apparatus for closer inspection to minimize decomposition problems.

Results for Binary Blends

(1) Poly(methyl methacrylate)–Poly(styrene-*co*-acrylonitrile) This system has been studied extensively by Stein et al.[10] and McMaster[11] and was selected for restudy in order to evaluate the reliability of our techniques. The SAN and the PMMA-1 shown in Table I are identical with the materials used by McMaster and thus should provide a direct comparison with his results. The PMMA-2 has a higher molecular weight but the details of its distribution are not available. Blends of SAN and both PMMA's were solvent cast from 1,2-dichloroethane by evaporating the solvent at room temperature and pressure followed by heating for 1 h at 70 °C. Subsequent heating in a vacuum oven for prolonged times failed to change any characteristics of these blends which were always clear.

In order to minimize oxidation, cloud points for these blends were initially determined in a vacuum oven; however, subsequent measurements using the procedure described above gave identical results. The data for both PMMA samples are shown in Figure 1. McMaster's cloud point curve is reproduced here as shown. Our data for PMMA-1, the solid points, agree with it very well and thus demonstrate the reliability of the present procedures. The cloud points for PMMA-2 with SAN depend less on composition, but no further interpretation of these trends can be made without more complete information on the molecular weight distribution for this sample which evidently is the only factor differing between the two PMMA's.

Interestingly, the phase separation induced on heating for this system is not reversed on cooling for the range of cooling

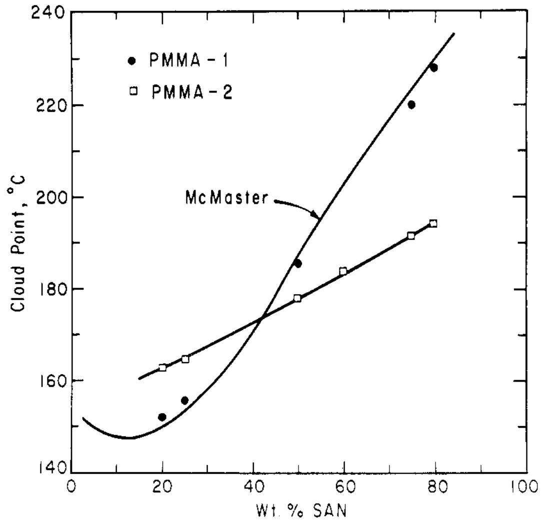

Figure 1. Cloud point curves for SAN-PMMA blends. For PMMA-1, the solid line shows results obtained by McMaster while the points show data obtained here.

rates used here, ca. 5 °C/min, as evidenced by the fact that the samples remained cloudy.

(2) Polycarbonate–Poly(ϵ-caprolactone). These two polymers have been judged to be miscible because their blends show a single glass transition[18] which has also been found for block copolymers of these components.[19] Blends of polycarbonate with PCL-700 were prepared by melt mixing, and through normal processing it became evident that this system showed LCST behavior. Blends using PCL-300 were cast from methylene chloride solutions and dried in vacuo at 60 °C.

Cloud points for this system are shown in Figure 2. The curve for PCL-300 lies above that for PCL-700 as one might expect[16] based on its lower molecular weight. The cloud points lie above the melting point of the polycarbonate.[18] At these temperatures, the polymers, particularly PCL, are not very stable; however, through the procedures used here these observations are meaningful. Reversibility of the phase separation was rapid in this system because the blends become clear again immediately upon cooling below the cloud point observed on heating.

(3) Poly(vinylidene fluoride)–Poly(methyl acrylate). Observations on the transitional behavior of this system[20] are in agreement with the conclusion that these polymers are miscible. The PMA used here was polymerized by Wahrmund[20] and no molecular weight characterization is available. Blends containing 25, 50, and 75% PVF_2 by weight were prepared by melt mixing while compositions other than these were prepared by dissolving one of these blends in dimethylformamide and adding additional PVF_2 followed by solvent removal under vacuum at 120 °C for several hours.

The cloud point curve observed for this system is shown as the top curve in Figure 3. This curve is relatively independent of composition, but it apparently has a minimum at low PVF_2 content. The cloud point temperatures are substantially above the melting point of PVF_2, and the blends are transparent at temperatures between these limits. Blends which have been heated above the cloud point become clear again as the temperature is reduced below the cloud point. Evidently the ceiling temperature of PMA is quite high[21] compared to the methacrylic esters described later since decomposition was no real problem even at these high temperatures. PVF_2 is quite thermally stable.

(4) Poly(vinylidene fluoride)–Poly(ethyl acrylate). The transitional behavior of this system also is in agreement with the conclusion of miscibility confirmed here.[20] The details of PEA polymerization and blend preparation are the same as for PMA above. No molecular weight information is available for the PEA.

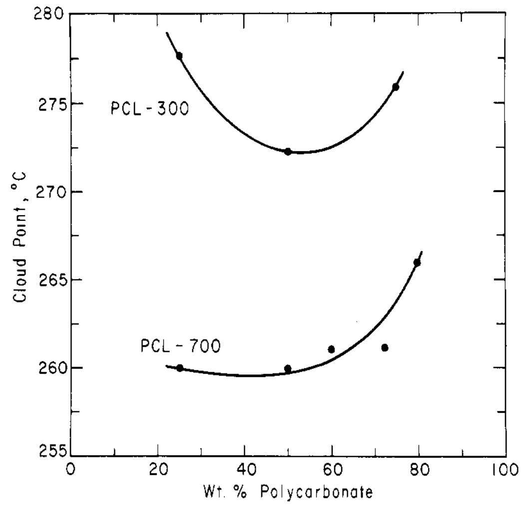

Figure 2. Cloud point curves for blends of polycarbonate with PCL-300 and PCL-700.

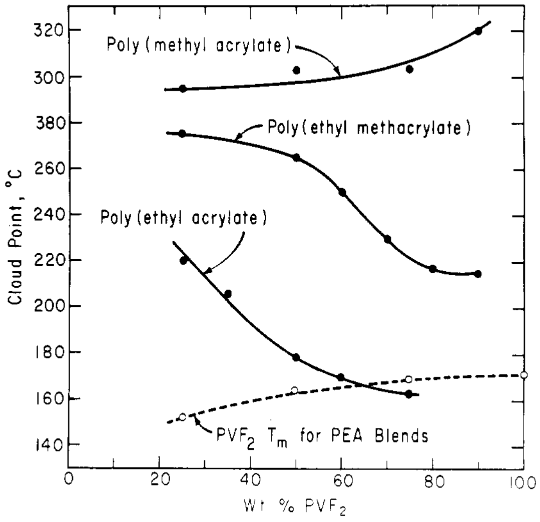

Figure 3. Cloud point curves for blends of poly(vinylidene fluoride) with acrylate and methacrylate polymers. Dotted line shows PVF_2 melting point in PEA blends; similar curves exist for other blends.

The cloud points for this system form the lower solid curve in Figure 3 and apparently there is a minimum at high PVF_2 concentrations. The dotted line in Figure 3 shows the melting point of PVF_2, observed by DTA, which is depressed somewhat[20] by addition of PEA. Similar curves were observed for PVF_2 blends containing the other components described here. At high PVF_2 contents, the cloud point curve dips below the melting point curve. The 75% PVF_2 cloud point was only observable by rapid quenching and reheating to avoid the opacity which results from crystallinity. Beyond the PVF_2 content where T_m is higher than the cloud point, the PEA–PVF_2 blends were opaque at all temperatures because of either PVF_2 crystallinity below T_m and/or liquid–liquid phase separation above the cloud point. When these samples were heated, there was a noticeable increase in opacity at about 150 °C which evidently is related to the cloud point phenomenon. Blends containing less than about 65% PVF_2 were observed to be clear between T_m and the cloud point. The intersection of these two different mechanisms of phase separation has interesting ramifications. If the diffusional mobility below T_m

is low, melt mixing could not be used to make homogeneous amorphous phases below T_m (when T_m > cloud point) even though this represents the equilibrium state at say 25 °C; whereas, solvent casting may permit this.

(5) **Poly(vinylidene fluoride)–Poly(methyl methacrylate).** This system has been studied rather extensively[22–24] and it is agreed that these components are completely miscible in the amorphous phase. Melt mixed blends, containing PMMA-3, from a previous investigation were used here.

These transparent, when molten, blends showed no evidence of a cloud point until heated to the very high temperature of about 350 °C. Since the ceiling temperature for PMMA is ~220 °C, decomposition is a severe problem in this range. It was not possible to quantify these observations very closely, but there is no doubt that a cloud point does exist in this general temperature range as shown by the following. An 80% PVF_2 blend was placed directly onto the hot plate device set at 350 °C. In a few seconds, the blend went from clear to opaque. Within 4 min, the sample began to yellow and develop quite a few bubbles. After about 5 min the sample became clear again suggesting that all the PMMA had disappeared and the sample was no longer a blend. Repeatedly, it was observed that samples which had turned opaque on the 350 °C hot plate would become clear again if removed and, therefore, cooled. These same samples would become opaque again when returned to the 350 °C surface. Blends placed on the hot plate at settings of 330 °C or less always remained clear even though bubbling still occurred. The opacity at 350 °C was not an artifact of the bubbles. While depolymerization of PMMA prohibits a more careful documentation, there is no question that this system also exhibits LCST behavior.

(6) **Poly(vinylidene fluoride)–Poly(ethyl methacrylate).** This system has also been studied rather extensively,[22,25,26] and these components are believed to be completely miscible in the amorphous phase although it has been proposed[26] that an UCST lies between T_m and T_g at high PVF_2 contents. The PEMA used here was polymerized by Imken[27] and has a rather high molecular weight as shown in Table I. Melt mixed blends prepared for this earlier work[27] were used here.

The middle curve in Figure 3 represents the observed cloud points which appear to exhibit a minimum at high PVF_2 levels. This is reasonable in view of the high molecular weight of the PEMA.

Like PMMA, PEMA has a low ceiling temperature,[27] and its depolymerization was evident in these studies. Blends which originally contained 10, 40, 50, and 70% PEMA were found to have undergone total sample weight losses of 1.8, 2.5, 6.3, and 22% respectively during the cloud point measurements. No doubt, the quantitative nature of the cloud point curve in Figure 3 reflects this problem; however, there is no question about the semiquantitative validity of these observations.

(7) **Poly(vinylidene fluoride)–Poly(vinyl acetate).** This system is presently under investigation in our laboratory.[28] Blends containing 40, 50, and 75% PVF_2 were cast from dimethylformamide solutions and dried in vacuo at 120 °C for 1 h. Above the PVF_2 melting point these blends were always clear and showed no evidence of a cloud point up to 350 °C. These observations could mean that this system (a) is miscible and any theoretical cloud point that should occur exists in a higher, inaccessible temperature range or (b) is largely immiscible but is clear because of a fortuitous combination of size and refractive indices of the phases. Studies in progress should decide between these alternatives.

(8) **Polycarbonate–Aromatic Polyesters.** Blends of polycarbonate with poly(ethylene terephthalate) and a copolyester of 1,4-cyclohexane dimethanol with a mixture of terephthalic and isophthalic acids have also shown evidence of partial or total miscibility.[18,29] The severe decomposition problems for these polyesters above their melting points made the search for cloud points inconclusive; however, apparently none exist for these systems below 350 °C.

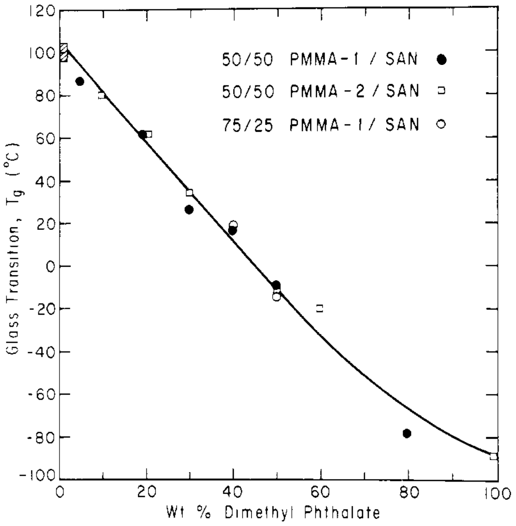

Figure 4. Glass transitions for PMMA/SAN/DMP mixtures. Because of the similarity of the T_g's for PMMA and SAN (see shaded box at 0% DMP) one curve adequately describes this relation for all PMMA/SAN ratios.

(9) **High-Density Polyethylene–Low-Density Polyethylene.** One 50/50 melt mixed blend of HDPE and LDPE was examined. Above the melting point, the blend became clear and showed no evidence of a cloud point up to 350 °C.

Results for the Ternary System PMMA–SAN–Plasticizer

Since polymers are frequently solution processed or used in a plasticized state it was of interest to learn what effect a compatible low molecular diluent might have on the cloud point of a blend showing LCST behavior.[30] The PMMA–SAN system was selected for this determination since it has been thoroughly studied before and recent neutron scattering results[31] have confirmed its miscibility in an elegant manner. Dimethyl phthalate, DMP, was chosen as the diluent since it is compatible with both polymers. Mixtures of either pure polymer with DMP showed no evidence of cloudiness in the range from 20 to 240 °C.

Ternary mixtures of PMMA–SAN–DMP were prepared by dissolving all three components in 1,2-dichloroethane which were removed by evaporation at atmospheric conditions for several days and then at 70 °C for 1 h. Since PMMA and SAN have similar glass transitions, the T_g of their blends are substantially independent of component proportions. However, blends diluted with DMP have considerably lower values of T_g as expected. Figure 4 shows the glass transitions (measured by DTA at 10 °C/min) of several ternary mixtures as a function of DMP content. One curve adequately describes all PMMA/SAN ratios for both PMMA samples. Pure DMP showed a T_g of −88 °C compared to the reported value of −78 °C.[32] The DMP crystallized at −14 °C and then melted at +7 °C while heating at 10 °C/min.

Figure 5 shows the effect on the cloud point of adding DMP to blends of fixed PMMA/SAN ratios while Figure 6 shows the effect of varying the polymer proportions at fixed DMP content. Interestingly, addition of DMP first *lowers* the cloud point but further addition causes the cloud point to increase. More detailed thermodynamic information would be required to understand fully this unanticipated behavior; however, several factors are undoubtedly involved. First, the larger free

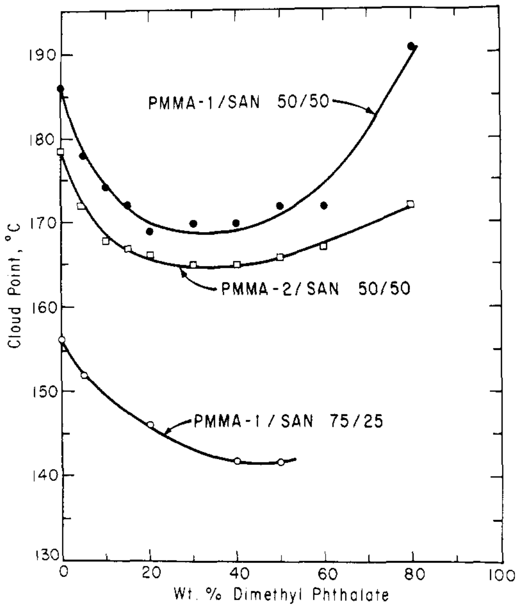

Figure 5. Effect of DMP on the cloud points of blends at fixed PMMA/SAN ratios.

volume, and probably higher thermal expansion coefficient, of the DMP than the two polymers increases the "equation of state" contributions for the mixture which are now believed to be largely responsible for LCST behavior.[1,5,8] Second, the lower molecular weight of DMP certainly increases the entropy of mixing for the ternary system beyond that of the binary polymer blend. However, it is perhaps too simplistic and premature to suggest that it is precisely these two factors working in opposition which cause the minima observed in Figure 5. In any case, these unique observations have interesting implications for blend processing and use.

Blends that contained 15% or more DMP became clear again when cooled below the cloud point at rates less than 10 °C/min. When cooled at fast rates, the phase separation was not reversed.

Summary

The present observations have expanded by more than twofold the number of blend systems known to show LCST behavior and lead to the conclusion that experimentally observable LCST behavior is a fairly general result for miscible blends. It would be interesting to compare the cloud points observed with those predicted by the various theories now available; however, before this can be done, more complete PVT behavior of the component polymers must be determined experimentally. In addition, the cloud points are rather sensitive to the molecular weight and molecular weight distributions of each polymer. Nishi and Kwei[16] have addressed this problem, but it is clear that the effect of molecular weight distribution is not yet fully understood. In view of this, it would be preferable to employ monodisperse polymers in any experimental study designed for this type of comparison. Most of the polymers used here are poorly characterized with respect to molecular weight distribution and even average molecular weight in some cases. Simple analyses show that the composition at which the critical solution temperature occurs is skewed toward the lower molecular weight component while more involved treatments[33] show that certain composition dependent interactions may cause the opposite result. Very often the critical point does not coincide with the minimum in the cloud point curve. It has not been possible to determine this critical point for the present systems, but in some cases it is possible to justify the direction of skewness in terms of the component molecular weights.

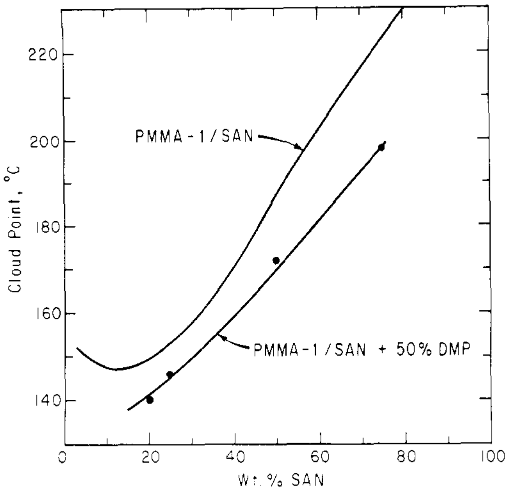

Figure 6. Cloud point curves for plasticized (50% DMP) PMMA-1/SAN blends. Unplasticized curve shown for comparison.

While the observed cloud points cannot be directly translated into fundamental measures of component interactions for the reasons outlined above, some semiquantitative trends do seem to exist. Other factors being equal, the cloud points should shift to higher temperatures as the specific interaction responsible for miscibility becomes larger, i.e., as the heat of mixing becomes more negative. Thus, it appears that the interaction with PVF_2 is stronger for the methacrylic polymers than the acrylics and is greater when the alkyl group is a methyl than when it is an ethyl group. A more quantitative comparison of these effects based on heats of mixing derived from melting point depressions is under way.[28]

It is interesting that the phase separation on heating is readily reversed on cooling for some systems but not others, e.g., SAN–PMMA. This is no doubt a result of the diffusive mobility of the components within the mixture. It will be recalled that when more than 15% DMP plasticizer was added to the SAN–PMMA system the cloudiness did disappear readily on cooling which is consistent with this argument. The kinetics of reversibility could be a critical issue in the phase structure of products melt processed from blends showing LCST behavior.

It is often difficult to prove that a blend is, in fact, miscible. The most frequent approach is to investigate the glass transition behavior, but this is futile when both components have nearly the same value as in the SAN–PMMA case or complicated when one or both components crystallize. In the melt state, techniques for such proof are quite limited and often clarity has been the only practical indicator; however, the possibilities of similar refractive indices or domains smaller than the wavelength of light render such observations ambiguous. However, the fact that a clear melt becomes cloudy on heating, i.e., exhibits LCST behavior, provides positive a posteriori evidence that complete miscibility did exist below that temperature. A state of miscibility must prevail for all lower temperatures, including the glassy state, until an UCST (if it exists) is reached. By this reasoning, the present results provide us with convincing proof of miscibility for several systems whose transitional behaviors alone do not permit such definitive conclusions.[20]

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The Effect of Good Solvents on Molecular Motion of Nitroxide Free Radicals in Covalently Labeled Polystyrene and Poly(methyl methacrylate)

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ABSTRACT: Poly(methyl methacrylate) and polystyrene in linear and lightly cross-linked latex form were covalently labeled with a nitroxide amine free radical. In all cases the nitroxide was attached to a methacrylate unit through an amide linkage. The temperature dependence of the ESR spectrum of labeled, solid PMMA shows that at room temperature the nitroxide is relaxed by motion about the terminal C–N bond in the nitroxide moiety. The ESR spectra were measured as a function of solvent composition using the thermodynamically good solvents chloroform, benzene, and dimethylformamide. All six polymer–solvent systems showed qualitatively similar behavior. At low concentration of solvent the nitroxide motion was unaffected by the presence of solvent. In the intermediate concentration region two distinct populations of nitroxide motions were observed which were not interconverting on the ESR time scale. One population was being relaxed by terminal bond motion. The faster moving nitroxides were being relaxed predominately by local mode main chain motion which correlated with the effect of solvent on the monomeric friction coefficient. At high dilution all nitroxides were relaxed by the local mode mechanism.

Molecular motions in an amorphous polymer at temperatures considerably below its glass transition (T_g) are predominantly limited local motions such as side chain motion, terminal group rotation, and local mode relaxation or crankshaft motions.[1] Correlated backbone motion, having a much higher apparent activation energy than side chain motion, rapidly increases as the temperature is raised and above T_g approaches the relaxation frequency of side chain motions.[1–3] The addition of solvent or plasticizer to a glassy polymer lowers T_g. The lowering is dependent on the amount of diluent added and on the nature of the polymer–solvent pair.[4,5] A solvent thus lowers the temperature at which significant correlated main chain motion begins to occur. Above T_g low frequency relaxations, i.e., correlated backbone motions, are affected similarly by solvent and temperature. Although the monomeric frictional coefficient changes dramatically as diluent is added, a shift factor will bring low-frequency temperature and diluent relaxation data to a common curve.[1,6] Below T_g the motions are thought not to be describable by a monomeric frictional coefficient,[1] and the superposition of low-frequency temperature-diluent relaxation data does not seem to have been attempted.

The ESR spectrum of a nitroxide free radical is sensitive to the rotational motion of the nitroxide over a wide range of rotational correlation times (10^{-6}–10^{-11} s). We have given preliminary accounts of the effect of solvents on nitroxide motion in labeled polystyrene (PS) and poly(methyl methacrylate) (PMMA)[7–9] and a more extensive study of the effect of nonsolvents.[9] In this manuscript the detailed results are presented for the effect of thermodynamically good solvents on motion of nitroxide spin labels covalently attached to PS and PMMA.

Experimental Section

Labeled Polymers. Linear poly(methyl methacrylate), PMMA (linear), had a nominal molecular weight of 100,000 and unknown polydispersity (Monomer-Polymer Laboratories, Inc.). Cross-linked PMMA spheres, PMMA (latex), and polystyrene spheres, PS (latex), were prepared by emulsion polymerization of the respective monomer