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Characterization of Polymer Compatibility by Nonradiative Energy Transfer. Application to Binary Mixtures Containing Anionically Prepared Polystyrene, Anionically Prepared Poly(α-methylstyrene), or Poly(2,6-dimethyl-1,4-phenylene ether)

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ABSTRACT: Polystyrene (PS) and poly(α-methylstyrene) (PMS), prepared by anionic polymerization, and poly(2,6-dimethyl-1,4-phenylene ether) (PPO) were labeled with carbazole or anthracene residues. The compatibility of polymer pairs labeled with the donor and acceptor chromophores, respectively, was characterized by nonradiative energy transfer in blends of PS with PMS, PPO with PS, and PPO with PMS. The technique demonstrates a slight departure from random mixing even in the PPO–PS system, which has been previously described as perfectly compatible.

In a previous report from this laboratory[2] a new method was demonstrated by which the compatibility of two polymers can be characterized. In this technique the first polymer was labeled with a fluorescent residue (the "donor") whose emission spectrum overlapped the absorption spectrum of another fluorescent moiety (the "acceptor") attached to the second polymeric species. Energy absorbed by the donor can then be transferred by a nonradiative process to the acceptor over distances of the order of 2 nm so that the relative donor and acceptor emission intensities of a sample irradiated in the donor absorption band is a measure of the spacing of donor and acceptor groups and thus dependent on the mutual interpenetration of the two polymeric species.

In this previous work the fluorescent labels were introduced into the polymers by copolymerization. In the present study we have developed techniques by which such labels may be attached to preexisting aromatic polymers. This allowed us to use polystyrene and poly(α-methylstyrene) with narrow molecular weight distributions prepared by the "living polymer" polymerization technique. It allowed us also to investigate the compatibility characteristics of poly(2,6-dimethyl-1,4-phenylene ether), which had been studied previously by a variety of methods.[4-8]

Experimental Section

Polymers. Polystyrene (PS) and poly(α-methylstyrene) (PMS) were prepared by anionic polymerization, using potassium naphthalene as the initiator. The molecular-weight distribution was characterized by GPC, yielding for PS $\bar{M}_n = 11.3 \times 10^4$ and $\bar{M}_w = 17.1 \times 10^4$ and for PMS $\bar{M}_n = 9.49 \times 10^4$ and $\bar{M}_w = 11.9 \times 10^4$. The polymers were twice dissolved and reprecipitated to remove residual naphthalene. Poly(2,6-dimethyl-1,4-phenylene ether) (PPO) was a gift from Dr. D. Fox of the General Electric Co. It had $[\eta] = 0.49$ dL/g in chloroform at 25 °C.

Attachment of Fluorescent Labels. PS and PMS were chloromethylated as described by Jones.[9] With 1 wt % of $ZnCl_2$ added to a 10% polymer solution in chloromethyl methyl ether, chlorine contents of 0.85 wt % in PS and 0.53 wt % in PMS were obtained after 10 min at room temperature. To ensure complete removal of the $ZnCl_2$, the modified polymers were dissolved in dioxane and reprecipitated in water.

The chloromethylated PS and PMS were condensed with potassium carbazole as described by Gibson and Bailey.[10] The polymer was dissolved and reprecipitated five times with intermittent washing by the precipitant until the absorption in the 270–320-nm range, characteristic of carbazole, stopped decreasing.

Anthracene-labeled PS and PMS were prepared by treating the chloromethylated polymers with (9-anthryl)methanol (Aldrich) and sodium hydride by the procedure used for the benzylation of carbohydrates.[11] This method is based on the observation[12] that benzyl chloride does not react with sodium hydride below 170 °C.

The fluorescent labels were attached to poly(2,6-dimethyl-1,4-phenylene ether) (PPO) by first slightly chlorinating the polymer in refluxing chloroform and then reacting the chloromethyl groups with potassium carbazole or (9-anthryl)methanol as described above.

The content of carbazole and anthracene moieties in the polymers was determined by UV spectroscopy, using dioxane solutions for labeled PS and PMS and chloroform solutions for labeled PPO. The extinction coefficients were assumed to be the same as those of 9-benzylcarbazole (ϵ 16 070 and ϵ 16 210 $cm^{-1}\,M^{-1}$ at 294 nm in dioxane and chloroform, respectively) and (9-anthryl)methanol (ϵ 8460 and ϵ 8530 $cm^{-1}\,M^{-1}$ at 365 nm in dioxane and chloroform, respectively). The absorption spectra of the labeled polymers in the region characteristic of the carbazole and anthracene moieties were identical with those of the low molecular weight derivatives.

Sample Preparation and Fluorescence Measurements. Films were cast from tetrahydrofuran solutions containing PS–PMS blends and from methylene chloride solutions containing PPO–PS or PPO–PMS blends. In all cases the labeled polymers

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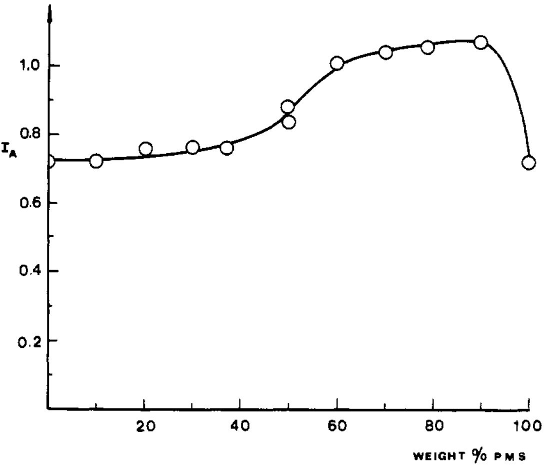

Figure 1. Dependence of I_C/I_A on the composition of polystyrene blends with poly(α-methylstyrene).

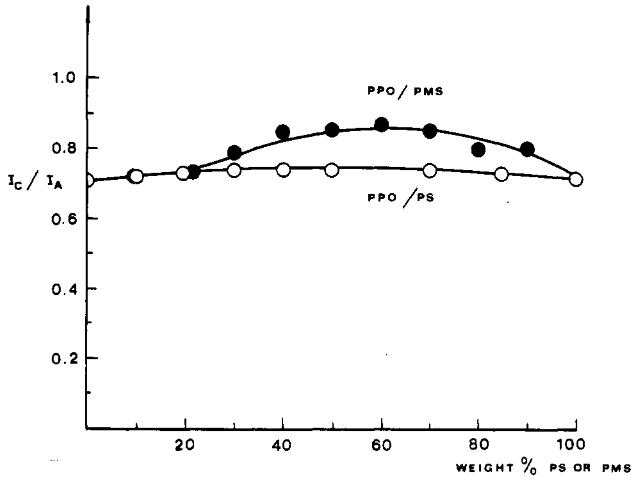

Figure 2. Dependence of I_C/I_A on the composition of blends of PPO with polystyrene or poly(α-methylstyrene).

were diluted with the corresponding unlabeled polymer so as to arrive at 0.01 M concentration of carbazole and anthracene residues in the film. Reflectance fluorescence spectra of films irradiated in the carbazole absorption band at 297 nm were recorded as previously described.[2] The nonradiative energy transfer was characterized by the ratio of the emission intensities of the donor, carbazole, at 365 nm (I_C) and the acceptor, anthracene, at 413 nm (I_A).

In the study of PS–PMS blends, the PS was labeled with 2.63 mol % carbazole and the PMS with 1.62 mol % anthracene. For reference, donor-labeled PS was mixed with PS carrying 1.76 mol % anthracene residues, and acceptor-labeled PMS was mixed with PMS containing 1.78 mol % carbazole residues. The studies of PPO blends employed PPO labeled with 1.83 mol % anthracene with the carbazole-labeled PS or PMS. For reference, the acceptor-labeled PPO was blended with PPO containing 2.13 mol % carbazole. The samples were not annealed before fluorescence measurement, since we found previously that annealing produces no significant change in the emission spectra.

DSC measurements were carried out with a Perkin-Elmer Type 1B instrument. Samples were rapidly cooled from a temperature above the highest T_g and the DSC trace was recorded at a heating rate of 8°/min.

Results and Discussion

The ratios of the carbazole and anthracene emission intensities, I_C/I_A, in blends of polystyrene and poly(α-methylstyrene) are presented in Figure 1 as a function of the composition of the blend. The carbazole moiety has an extinction coefficient 23 times as high as the anthryl group at the excitation wavelength, and when solutions of *N*-benzylcarbazole and (9-anthryl)methanol of equal optical densities were excited at 297 nm, the ratio of the emission intensities at 365 and 413 nm was 5. Thus, $I_C/I_A \sim 114$ would correspond to an absence of energy transfer in a system containing equimolar concentrations of donor and acceptor chromophores. The value $I_C/I_A = 0.72$ observed in blends in which the donor and the acceptor are both attached to PS or both attached to PMS corresponds, therefore, to very extensive energy transfer in these homogeneous systems.

Blends of donor-labeled PS and acceptor-labeled PMS exhibit generally higher I_C/I_A, but the plot shows that relatively large amounts of PMS may be added to PS with little demixing, while even small amounts of PS added to PMS lead to systems in which the polymeric species are segregated to some extent. It is possible that a dissymmetry of the phase diagram is a result of the lower molecular weight of the PMS used in our study and this point should be further investigated. For all the blends, I_C/I_A retains a rather low value, suggesting that phase separation is not extensive or else that the phase domains are small compared to the characteristic distance for energy transfer of the donor–acceptor pair used in this study, which has been estimated[2] as 2.9 nm. This ambiguity in the interpretation of energy-transfer data has been discussed in our previous report on the use of this technique for the study of polymer compatibility.[2] Our results indicating phase separation in blends with a high PMS content are consistent with those of Robeson et al.[13] They used polymers of higher molecular weight and observed by mechanical-loss measurements on such blends the glass transitions characteristic of both PS and PMS. Dunn and Krause[14] found no evidence of phase separation in blends containing 60 or 80 wt % PMS, but a blend of equal weights of PS and PMS exhibited two glass transition temperatures.

The compatibility of PPO with PS has been established in the past by a variety of techniques[5,15] and it was then of special interest to characterize this system by the energy-transfer method. Figure 2 shows, as expected, that I_C/I_A is almost independent of the composition of PPO–PS blends. Yet, a slight increase in I_C/I_A resulting from a mixing of the two polymeric components is found consistently in all our data and we consider it, therefore, to be experimentally significant. Our previous work[2] demonstrated that the spectroscopic method can detect variations in local concentrations which are not made evident by the appearance of two glass transition temperatures. Wetton et al.,[16] who studied blends of PPO with styrene–4-chlorostyrene copolymers, concluded that such local variations lead to a broadening of dielectric relaxation spectra in systems which appeared homogeneous by other criteria. Our technique has the advantage that it provides a basis of comparison with a system which is necessarily homogeneous, i.e., a blend of identical polymers labeled with a donor and an acceptor, respectively.

Figure 2 also shows a plot of I_C/I_A for blends of PPO with poly(α-methylstyrene). At low concentrations, the compatibilities of PS and PPO and PMS with PPO seem to be indistinguishable, while at higher concentrations PMS is clearly much less miscible with PPO. Since the compatibility of PPO with PS is reduced by substitution of either a chlorine in the ortho or para position[7,16] or a methyl in the α position of the styrene residue, it would be tempting to assume that the compatibility of the PPO–PS system is due to a matching of the cohesive energy densities,[2] a compatibility which is destroyed when the styrene residues are modified so as to make them more or less polar. However, the observation[7] that PPO is compatible with 4-chlorostyrene–2-chlorostyrene copolymers within a certain composition range shows that

Table I
Glass Transitions in Blends of PPO with Polystyrene or Poly(α-methylstyrene)

PPO wt fraction	T_g, °C PS blends	PMS blends
0.0	100	185
0.2	107–122	177–193
0.4	122–143	177–200
0.6	142–167	187–197
0.8	152–202	207–217
1.0	227	227

such an interpretation is greatly oversimplified. This is not surprising, since it has been known for a long time[17] that use of a single parameter (such as the cohesive energy density) to characterize the components of a mixture is inadequate for the prediction of the heat of mixing in systems in which dipole interactions are important, and this point has also been made specifically for the prediction of polymer compatibility.[18]

Table I lists the results of a DSC study of the PPO–PS and PPO–PMS systems. It may be seen that in both these systems a single glass transition temperature was detected for the various blends, so that calorimetry would have provided no evidence for a reduced compatibility when the styrene residues are methylated in the α position. The present study thus confirms our previous conclusion[2] that the energy transfer between fluorescent labels provides a more sensitive criterion of compatibility than calorimetric data.

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Low-Temperature Crystallization of Poly(dimethylsiloxane) from Solution

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ABSTRACT: Poly(dimethylsiloxane) (PDMS) has been crystallized from solution in hydrocarbons at about −90 °C. It is shown that the temperature of crystallization is independent of the hydrocarbon medium. X-ray diffraction studies show the degree of crystallinity of the low molecular weight PDMS to be greater than that of the high molecular weight material. Proton NMR has been used to detect the phase separation and to confirm the X-ray observations. It is shown that the crystallization of PDMS from solution is a bulk phenomenon and not surface-induced.

It has recently been reported[1,2] that poly(methyl methacrylate) particles that are stabilized by poly(dimethylsiloxane) (PDMS) flocculate both on heating and on cooling when dispersed in *n*-alkanes. The upper critical flocculation temperature (UCFT) was found to correlate qualitatively with the Θ temperature associated with the lower critical solution temperature (LCST) of the respective PDMS + *n*-alkane solutions.[3,4] However, the lower critical flocculation temperature (LCFT) was found to be essentially independent of the nature of the dispersion medium and occurred at a temperature far above the Θ temperature associated with the upper critical solution temperature (UCST) that has been estimated for these solutions.[5] It has been suggested[6] that the LCFT in these systems is due to surface-induced crystallization of PDMS, which allows the attractive van der Waals forces between the particles to become operative, thereby causing the particles to flocculate. It has been shown recently,[7] from low-temperature X-ray diffraction studies on PDMS-stabilized particles, that crystallization of PDMS occurs at about −90 °C, well above the suggested Θ temperature of about −173 °C for these systems.[5]

In order to investigate the requirement of the presence of a particle surface for the crystallization of PDMS to occur, we have carried out low-temperature X-ray and NMR measurements on PDMS, dissolved in two hydrocarbon liquids. We report the first measurements on the crystallization behavior of PDMS from solution, which is

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