Characterization of Polymer Miscibility by Fluorescence Techniques. Blends of Styrene Copolymers Carrying Hydrogen Bond Donors with Polymethacrylates[1]

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ABSTRACT: A styrene copolymer with a small proportion of *N*-carbazolylethyl methacrylate (CEM) and styrene terpolymers with CEM and methacrylic acid (MA), methacryloyl glycine (MAG), styrenesulfonic acid (SSA), *p*-(hexafluoro-2-hydroxylisopropyl)styrene (HHIS), or *p*-vinylphenol (VP) were prepared. Films of these polymers blended with copolymers of methyl methacrylate, ethyl methacrylate, or butyl methacrylate with 9-anthrylmethyl methacrylate (AMM) were cast from toluene, dioxane, or chloroform solution and the intimacy of the mixing of the components of these blends was characterized by nonradiative energy transfer (NET) from the carbazole to the anthracene fluorophore. The miscibility of the polymers depended strongly on the casting solvent and was much better for styrene copolymers with HHIS or VP than for styrene copolymers with MA, MAG, or SSA. Stronger excimer emission was observed in polystyrene blends with poly(ethyl methacrylate) than in blends with poly(methyl methacrylate), although NET indicated a better miscibility with poly(ethyl methacrylate); this was interpreted as due to the lesser rigidity of poly(ethyl methacrylate).

Introduction

Many years ago, Gee[2] pointed out that the mixing of long-chain molecules leads to a negligible entropy change, so that the mixture can be stable only if the mixing process is exothermic. In the absence of specific interactions, the ΔH is usually positive[3] and this is the reason why most polymer pairs resist mixing, so that even dilute solutions containing two polymers in a common solvent form two phases.[4] In a previous study from this laboratory[5] it was shown that such phase separation in solutions containing polystyrene (PS) and poly(methyl methacrylate) (PMMA) can be avoided if a small concentration of vinylpyridine is incorporated into the PS and if the PMMA is modified by a small concentration of methacrylic acid residues, so that the exothermic acid–base interaction overwhelms the unfavorable enthalpy characterizing the mixing of PS with PMMA. Later studies of polymer blends in bulk, carried out in many laboratories, demonstrated that a variety of immiscible polymers can be rendered compatible by utilizing the interactions of small numbers of acid and base,[6] ion pair and dipole,[7] hydrogen bond donor and acceptor,[8] or electron donor and acceptor[9] substituents.

In the mixing of polymer pairs for which the driving force for phase separation is relatively small, "fuzzy" phase boundaries are obtained, since the chains of each polymer penetrate some distance into the region in which the other polymer is the main component. The phase boundaries will gradually sharpen as the mixing of the polymers becomes more unfavorable[27] and the size of the phase domains will increase with an increasing interfacial energy. Different experimental techniques for the characterization of polymer miscibility may lead to different conclusions, since each technique will require some minimum size of phase domains to detect phase separation. Thus, Albert et al.[10] found that nonradiative energy transfer between fluorescent labels attached to poly(vinyl chloride) and syndiotactic PMMA decreased gradually with an increasing PMMA content in the blend, indicating some separation of the two polymers, although an earlier study[11] had reported a single T_g for blends containing up to 80 wt % PMMA. More recently, Shah[8c] reported that the introduction of acidic groups into polyacrylates renders their blends with poly(*N*-vinylpyrrolidone) optically transparent, because of the hydrogen bonding of the two polymers, while microphase separation is still demonstrated by electron microscopy.

In this report we describe results obtained on blending styrene copolymers containing various hydrogen bond donor residues (as shown in Figure 1) with polymers of methyl, ethyl, and butyl methacrylate (PMMA, PEMA, and PBMA) where the carbonyl group acts as a hydrogen bond acceptor. Two fluorescence techniques were used to characterize the compatibility of the blends.

(a) When the polymethacrylates were labeled with anthracene and the styrene copolymers with carbazole, the overlap between the carbazole emission and anthracene absorption spectra led to nonradiative energy transfer (NET)[12] so that on irradiation of a sample in the carbazole absorption band the ratio of carbazole and anthracene emission intensity, I_C/I_A, decreased with an increasingly intimate mixing of the two polymers.[13] The efficiency of NET is given by

$$\text{eff} = [1 + (r/R_0)^6]^{-1} \qquad (1)$$

where r is the distance between the donor and acceptor fluorophore and the characteristic transfer distance R_0 has been determined to be 2.8 nm for the carbazole–anthracene pair.[13] The technique should be sensitive to phase separation involving phase domains exceeding this dimension.[28]

(b) In a homogeneous blend of PS with a nonfluorescing polymer, excimer emission has been shown[14] to increase relatively slowly with the PS concentration, indicating that excimer formation is predominantly intramolecular, requiring a statistically improbable conformation between two consecutive monomer residues in the ground state. On the other hand, PS in bulk exhibits only excimer emission, since phenyl residues attached to different chains can interact to form the excimer. This contrasting behavior can be exploited to characterize phase separation in polystyrene blends, as demonstrated by Gelles and Frank.[14] We have tried to determine whether the ratio of the emission intensities of the excimer and the monomer band, I_e/I_m, of PS can also be used as a measure of polymer miscibility in our systems.

Experimental Section

Materials. 9-Anthrylmethyl methacrylate (AMM) and 2-(*N*-carbazolyl)ethyl methacrylate (CEM) were synthesized as previously described.[13] Methacryloyl glycine (MAG) was prepared from glycine and methacryloyl chloride in the presence of sodium hydroxide and phenothiazine polymerization inhibitor and *p*-(hexafluoro-2-hydroxylisopropyl)styrene (HHIS) was synthesized by the method of Pearce et al.[8a] *p*-Acetoxystyrene (AS) from Allied

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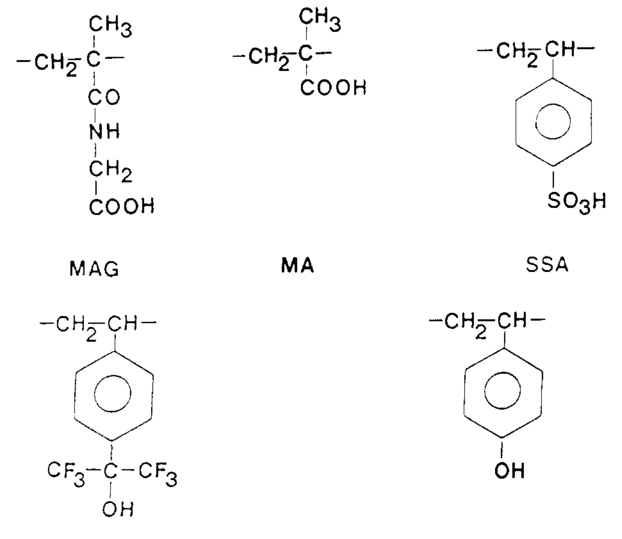

Figure 1. Styrene comonomers used as hydrogen bond donors.

Chemical Co. was vacuum distilled before use. Sodium styrene sulfonate was purchased from Polysciences Inc.

Polymers. Polymerizations were carried to low conversion at 60 °C in dioxane solution (except for the terpolymers containing sodium styrene sulfonate, for which a dioxane mixture with methanol was used) with ABIN as initiator. Sodium styrenesulfonate terpolymers were converted to the acid form by passing HCl gas through the solution and filtering off the NaCl. Styrene terpolymers with AS were converted to the *p*-vinylphenol terpolymers in a mixture of dioxane and hydrazine hydrate, storing the solution for 4–5 h at room temperature. A dioxane solution of HCl was added to the product and the terpolymer was purified by several redissolutions in dioxane and precipitations into a large excess of methanolic HCl. The CEM and AMM contents of fluorophore-labeled polymers were determined by UV spectroscopy as previously described.[13] The content of carboxyl and sulfonic acid groups in styrene terpolymers was determined by titration with sodium methoxide in a 4:1 mixture of benzene and methanol with phenolphthalein as end point indicator. The content of AS residues in their terpolymers was determined in chloroform solution from the intensity of the carbonyl 1740 cm^{-1} IR band (allowing for the contribution from the CEM residues) by using poly(*p*-acetoxystyrene) as a standard. The data were consistent with the reactivity ratios for the copolymerization of styrene with AS as reported by Arshady et al.[15] The conversion of AS residues into vinyl phenol VP residues was followed by the disappearance of the carbonyl IR band. The composition of the HHIS terpolymer was obtained from the fluorine content by elemental analysis. The compositions and intrinsic viscosities of the labeled polymers are listed in Table I. The unlabeled polystyrene, poly(methyl methacrylate), poly(ethyl methacrylate), and poly(butyl methacrylate) had intrinsic viscosities (in dioxane at 25 °C) of 0.76, 0.98, 0.42, and 0.41 dL/g, respectively.

Sample Preparation and Fluorimetry. Films were cast from 8% solutions containing equal weights of the two polymers in a blend, unless specified otherwise. After evaporation of the solvent, the films were dried for at least a week under vacuum and were stored under vacuum up to the time of fluorescence measurement. Reflection spectra were recorded on a Perkin-Elmer MPF-44B fluorimeter using an excitation wavelength of 296 nm for blends of CEM and AMM labeled polymers. Energy transfer was characterized by I_C/I_A, the ratio of the carbazole emission intensity at 365 nm and the anthracene emission intensity at 413 nm. For unlabeled blends of polystyrene with polymethacrylates, excitation at 260 nm was used and the ratio I_e/I_m, of excimer emission at 340 nm and monomer emission at 285 nm, was recorded as a function of the composition of the blend.

DSC measurements were carried out by using a Du Pont Model 9900 DSC instrument. After heating at a rate of 10 °C/min up to 140 °C, the sample was quenched and the thermal behavior was recorded from 0 to 140 °C under nitrogen.

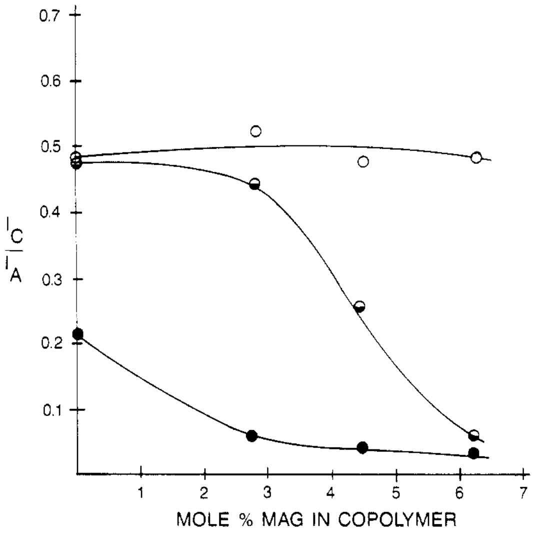

Figure 2. Ratio of donor and acceptor fluorescence in blends of PEMA with S–MAG. Films cast from chloroform (○), dioxane (◒), and toluene (●).

Table I
Characterization of Fluorophore-Labeled Polymers

polymer	mol % H bonding comonomer	mol % CEM	mol % AMM	[η], dL/g, dioxane, 25 °C
PS		0.46		0.56
S-MA	3.3	0.45		0.43
S-MA	3.9	0.48		0.45
S-MA	5.4	0.48		0.45
S-MA	6.6	0.47		0.52
S-MAG	2.8	0.50		0.44
S-MAG	4.4	0.51		0.43
S-MAG	6.2	0.52		0.43
S-SSA	1.2	0.48		0.25
S-SSA	1.9	0.51		0.21
S-SSA	2.8	0.51		0.17
S-HHIS	0.9	0.51		0.38
S-HHIS	1.4	0.51		0.36
S-HHIS	2.3	0.53		0.38
S-HHIS	4.6	0.53		0.39
S-HHIS	6.2	0.48		0.45
S-VP	0.94	0.50		0.39
S-VP	1.9	0.53		0.40
S-VP	3.8	0.51		0.43
S-VP	4.9	0.53		0.45
PMMA			0.49	0.66
PEMA			0.44	1.27
PBMA			0.51	1.11

Results and Discussion

Nonradiative Energy Transfer. For all the blends used in this study, the NET characterized by I_C/I_A depended on the solvent from which the film was cast. This feature is illustrated in Figure 2 for blends styrene–methacrylylglycine copolymers with poly(ethyl methacrylate). Compatibility is optimized by casting from toluene solutions; more segregation of the components of the blend was observed for films cast from dioxane which competes with PEMA as a hydrogen bond acceptor. For blends cast from chloroform, no improvement of compatibility was found when MAG residues were introduced into PS, presumably because the solvent supplanted completely the MAG as a hydrogen bond donor. It should be noted, however, that the dependence of compatibility on the casting solvent is also observed for the blend of the PS and PEMA homopolymers, where no hydrogen bonding is involved. It has been observed in various systems that the same polymer blend may lead to homogeneous or phase-separated films, depending on the solvent from which the film is cast[16] as would be generally expected if the solvent interacts much

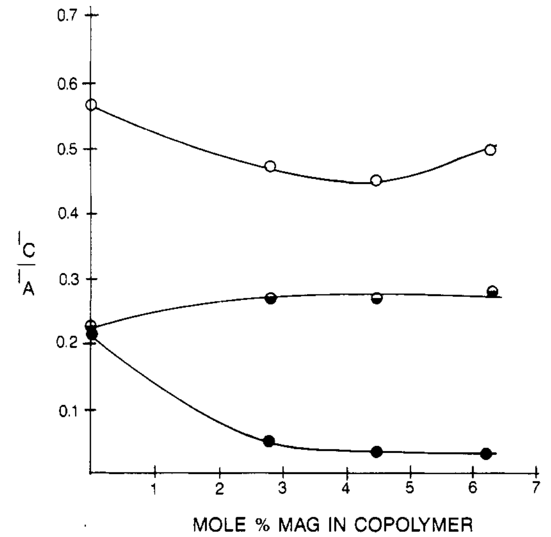

Figure 3. Ratio of donor and acceptor fluorescence in blends of S-MAG with PBMA (○), PMMA (◒), and PEMA (●). Films cast from toluene.

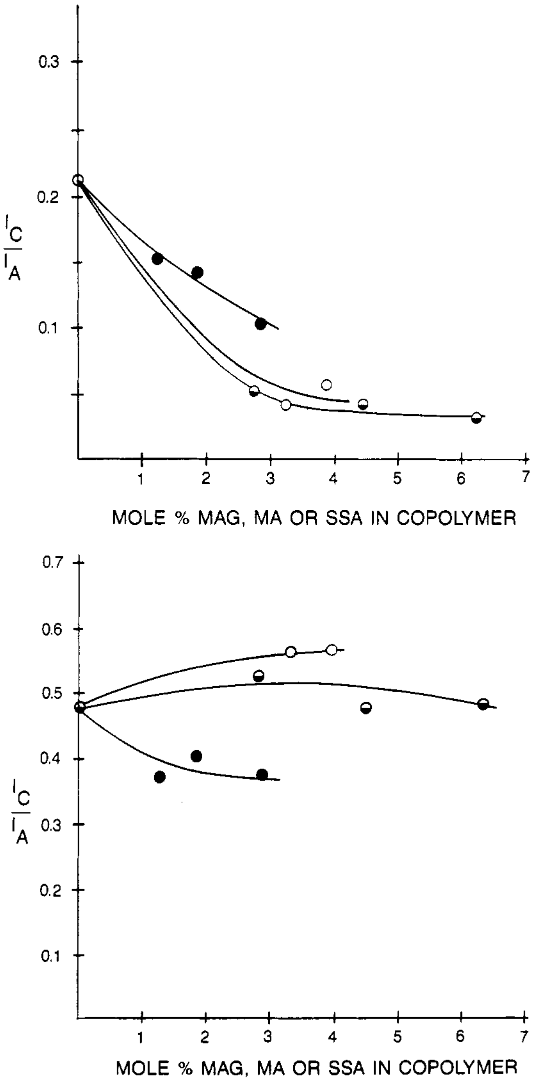

Figure 4. Ratio of donor and acceptor fluorescence in blends of PEMA with S-MA (○), S-MAG (◒), and S-SSA (●). (Top) Cast from toluene; (bottom) cast from chloroform.

more strongly with one component of the polymer pair.[17] If we use the difference between the Hildebrand solubility parameters[18] of the polymer, δ_p, and the solvent, δ_s, as a measure of polymer solvation, we find that with $\delta_p = 8.99$ for PEMA, $\delta_p = 9.04$ for PS,[19] $\delta_s = 8.9$ for toluene, and $\delta_s = 10.0$ for dioxane,[18] the $\delta_p - \delta_s$ are very similar for the two polymers in both casting solvents, so that no phase separation would be expected on the basis of a preferential solvation of one of the components of the blend. It seems then that a better mixing on the segmental level is brought about when casting the polymer blend from a strongly solvating medium (i.e., from toluene, characterized by a small value of $\delta_p - \delta_s$). On the other hand, if we compare blends of PS and styrene copolymers with different polymethacrylates, then the extent of phase separation is clearly correlated with $\Delta\delta_p$, the difference in the solubility parameters of the two polymers. For PS blends with PMMA, PEMA, and PBMA the $\Delta\delta_p$ are[19] 0.26, 0.05, and 0.56 and the data in Figure 3 show that, as expected, the PS-PEMA is closest and the PS-PBMA furthest from compatibility.

We were particularly interested in the relative efficiency of various styrene comonomers functioning as hydrogen bond donors in promoting compatibility with polymethacrylates. The MAG residue would be expected to be much more acidic than a methacrylic acid (MA) residue,[20] and since its carboxyl group is further from the chain backbone, it should be more accessible to the hydrogen bond accepting carbonyls of the polymethacrylates. Yet, we found in most experiments little difference in the compatibility of S-MAG and S-MA copolymers with polymethacrylates. The relative effectiveness of carboxyl and sulfonic acid groups in promoting compatibility was found to depend both on the polymethacrylate with which the styrene copolymer was blended and on the solvent from which the blend was cast. In blends of styrene copolymers with PEMA, the sulfonic acid was less efficient for films cast from toluene, while it clearly promoted compatibility for films cast from chloroform, where the MAG and MA comonomers were completely ineffective (Figure 4). In blends with PBMA, the sulfonic acid was more effective in compatibilizing PS films cast from either solvent (Figure 5). Unfortunately, the data for styrene copolymers carrying carboxyl and sulfonic acid groups are not strictly comparable, because of the much shorter chain length of the S-SSA copolymers as indicated by the intrinsic viscosity values in Table I. This difference in molecular weight was due to the difference in polymerization conditions: It was difficult to find a solvent medium for mixtures of styrene and sodium styrene sulfonate, so that the S-SSA copolymers had to be prepared in much more dilute solution than the other styrene copolymers. We tried to avoid this difficulty by sulfonating the styrene-CEM copolymer, but this procedure led to a change in the spectroscopic properties of the fluorophore.

The HHIS fluorophore, first shown by Pearce et al.[8a] to be a powerful agent for rendering polystyrene compatible with polymers functioning as hydrogen bond acceptors, proved incomparably more efficient than MA, MAG, and SSA comonomers. This can be seen in comparing Figures 2 and 6—it is particularly striking that blends of S-HHIS with PEMA achieve a high degree of compatibility even when cast from chloroform. The degree of mixing on the segmental level which leads to optically clear films was obtained when the NET was characterized by $I_C/I_A < 0.1$; this was observed in films cast from toluene solutions for blends of PEMA or PBMA with a styrene copolymer containing as little as 0.9 mol % Of HHIS residues.

The incorporation of VP residues into styrene copolymers was also found to be very effective in promoting compatibility with polymethacrylates. This is illustrated in Figure 7 for blends of S-VP copolymers with the three polymethacrylates cast from toluene and in Figure 8, which

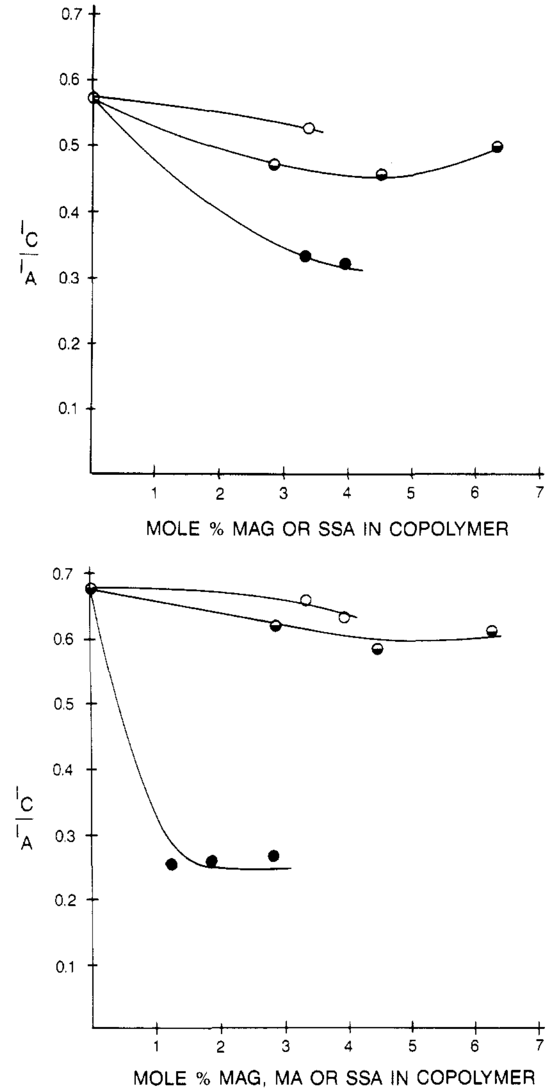

Figure 5. Ratio of donor and acceptor fluorescence in blends of PBMA with S-MA (○), S-MAG (◒), and S-SSA (●). (Top) Cast from toluene; (bottom) cast from chloroform.

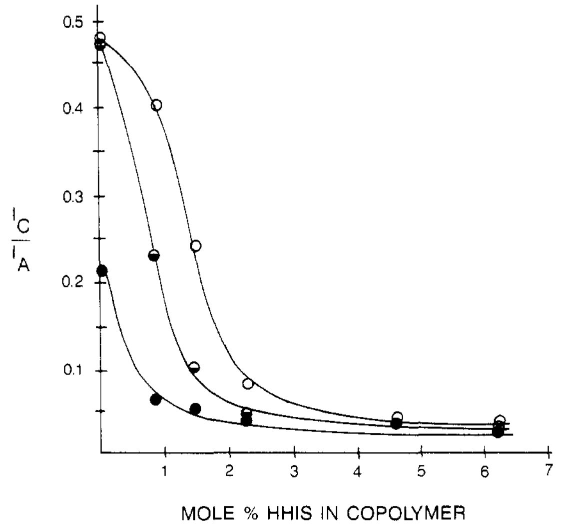

Figure 6. Ratio of donor and acceptor fluorescence in blends of PEMA with S-HHIS. Cast from dioxane (○); cast from chloroform (◒); cast from toluene (●).

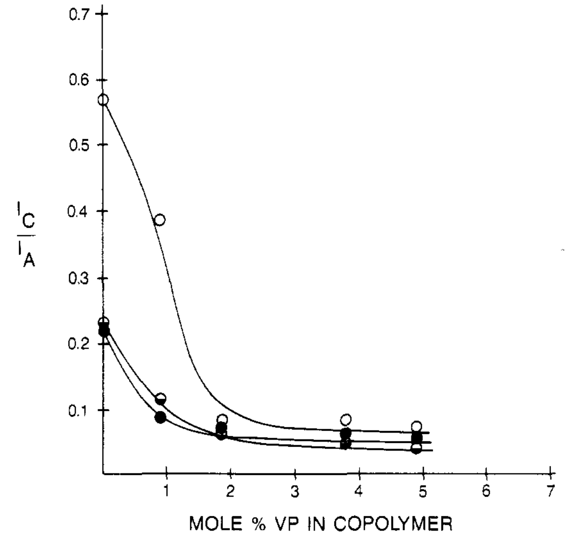

Figure 7. Ratio of donor and acceptor fluorescence in blends of S-VP with PBMA (○), PMMA (◒), and PEMA (●). Films cast from toluene.

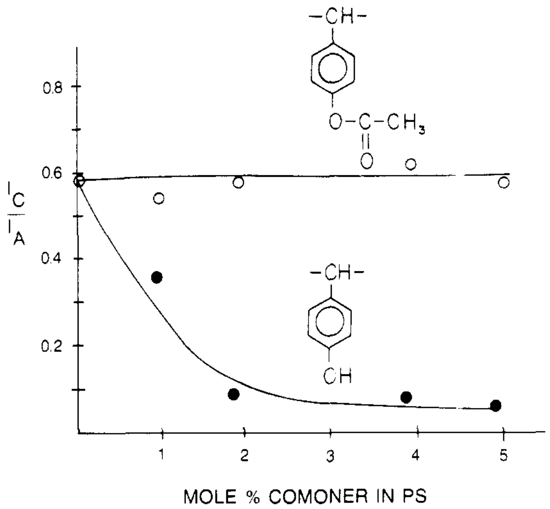

Figure 8. Ratio of donor and acceptor fluorescence in blends of PBMA with styrene copolymers with p-acetoxystyrene compared with this ratio after conversion of the p-acetoxystyrene to p-vinylphenol residues.

shows that whereas the acetoxy substituent has no effect on the compatibility of PS with PBMA, the efficiency of NET increases dramatically when the acetoxystyrene residues are converted to VP residues. However, our NET data showed that S-VP copolymers with a VP content above 70% are immiscible with PBMA. Here, the self-association of the phenolic residues dominates the hydroxyl-ester association.[24]

The interaction of VP residues with polymers acting as hydrogen bond acceptors was first studied by Moskala et al.[26] who used FT-IR spectroscopy to characterize hydrogen bonding in blends of the VP homopolymer with poly(vinyl acetate) and ethylene-vinyl acetate copolymers. Blends of poly(4-vinylpyridine) (PVPy) with S-VP copolymers were studied by de Meftahi and Fréchet,[21] who found that they required relatively high concentrations of VP residues to avoid phase separation (for instance, two T_g were observed in a blend of equal weights of PVPy and a styrene copolymer containing 30 mol % VP). These authors were apparently unaware of the effect of the casting solvent on the homogeneity of the film and since they cast their films from pyridine, a preferential solvation of the VP copolymer would be expected to have favored phase separation. In contrast with the results of de Meftahi and Fréchet, the fact that we found less than 1 mol % of VP residues in a S-VP copolymer to be sufficient to produce compatible films with PMMA and PEMA is striking. Only in blends with PBMA was the HHIS co-

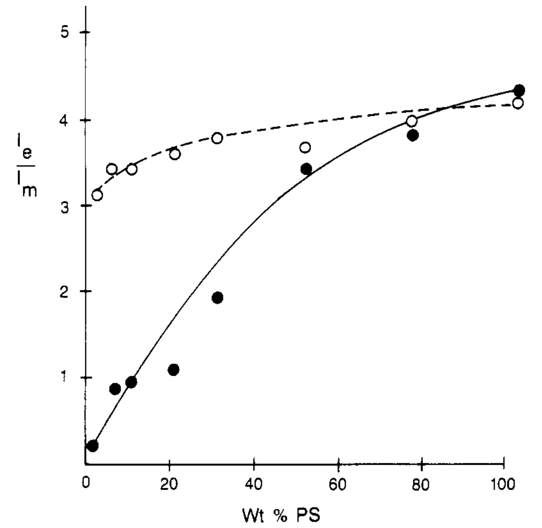

Figure 9. Ratio of excimer and monomer emission intensity in blends of PS with PMMA. Films cast from dioxane (○) and from toluene (●).

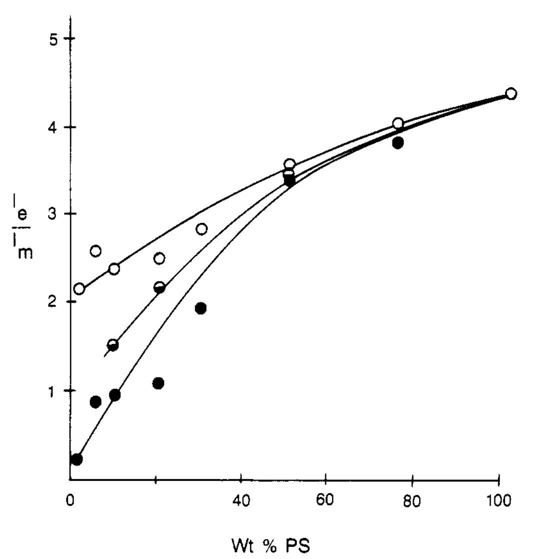

Figure 10. Ratio of excimer and monomer emission intensity in blends of PS with PBMA (○), PEMA (⊖), and PMMA (●). Films cast from toluene.

monomer more efficient than VP in promoting PS compatibility.

Excimer Emission. It has been shown by Gelles and Frank[14,22] that in blends of PS with poly(vinyl methyl ether) (PVME) the relative emission intensity of the excimer and the monomer, I_e/I_m, increases with the degree of phase separation. Two causes contribute to this effect: (a) Excitation energy migration becomes more efficient if it does not have to travel along the contour of the polymer chain but can hop from one polymer molecule to another. Thus, the probability that this excitation will reach a pair of monomer residues with a conformation favorable for excimer formation is enhanced. (b) As the concentration of PS in a phase increases, excimers may also be formed by the interaction of phenyl groups appended to different chains but placed in close proximity.

As expected, blends of PMMA containing moderate concentrations of PS are characterized by substantially higher I_e/I_m in films cast from dioxane than in films cast from toluene (Figure 9). This agrees with the result obtained by NET, which showed that toluene-cast films are more homogeneous. However, when we compared blends of PS with PMMA, PEMA, or PBMA cast from toluene (Figure 10), we found I_e/I_m to follow the order PBMA > PEMA > PMMA, although the NET data showed convincingly that PEMA is most compatible with PS (Figure 3). We believe that this discrepancy is due to the fact that PEMA is closer to its glass transition (T_g = 70 °C) than PMMA (T_g = 100 °C). Thus, the lower rigidity of the blends of PS with PEMA allows neighboring styrene residues somewhat more freedom to acquire the excimer conformation. We conclude that NET, which should not be sensitive to variations in polymer rigidity, is a more reliable measure of PS compatibility with other polymers than excimer emission. The I_e/I_m ratio is also unsuitable for the study of effects of hydrogen-bonding comonomers in increasing PS compatibility, since even low concentrations of these comonomers reduce substantially excimer emission.

Differential Scanning Calorimetry. The compatibility of PS with PMMA cannot be studied by the DSC method, since T_g is close to 100 °C for both these polymers. Even with blends of PEMA ($T_g \sim 70$ °C) with PS, the small value of ΔT_g renders the evaluation of the DSC traces difficult. Nevertheless, the effect of the casting solvent on the phase behavior could be demonstrated; for instance, a PEMA blend with S–MA containing 3.3 mol % of methacrylic acid residues exhibited a single glass transition, at 90 and 81 °C respectively, when cast from toluene or dioxane, but two glass transitions, at 70 and 102 °C, when cast from chloroform. In the case of blends of PBMA (T_g = 30 °C) with the S–MA, S–MAG, and S–SSA copolymers, all the blends yielded DSC traces indicating two glass transitions, i.e., phase separation. Even with the S–HHIS copolymers, a content of 4.2 mol % of the acidic comonomer was required before the blend exhibited a single T_g.

Concluding Remarks. A significant result of this study is the demonstration that the hydrogen bond donor efficiency is not determined by the acidity. Thus, the hexafluoroisopropyl alcohol group with a pK[23] = 9 and the phenolic group with a similar acidity were found to aid the compatibility of PS with polymethacrylates much more than carboxyl groups. It is true that carboxyl is both a hydrogen bond donor and acceptor and that in its latter role it may compete, in principle, with the carbonyl groups of polymethacrylates,[24] but in view of the much larger concentration of ester groups in the systems which we have studied, it seems unlikely that this is a significant factor in explaining the relatively low efficiency of MA and MAG comonomers in promoting PS miscibility with polymethacrylates. In fact, the lack of correlation between the acidity and the efficiency of donating a hydrogen bond has a corollary in the absence of a correlation between hydrogen bond acceptance and the basicity, with dimethylacetamide being a more powerful hydrogen bond acceptor than pyridine.[25]

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Registry No. (CEM)(S) (copolymer), 116910-77-1; (CEM)(S)(MA) (copolymer), 116910-78-2; (CEM)(MAG)(S) (copolymer), 116910-79-3; (CEM)(HHIS)(S) (copolymer), 116910-80-6; (AMM)(MMA) (copolymer), 33773-67-0; (AMM)(EMA) (copolymer), 78949-80-1; (AMM)(BMA) (copolymer), 116910-83-9.

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1983, *16,* 753) that with blends involving copolymers specific group interactions need not be required to achieve miscibility. This is due to the fact that unfavorable energetic interactions between the comonomers in a copolymer are relieved by dilution, leading to the exothermicity of mixing. Shiomi et al. (Shiomi, T.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1986,** *19,* 2274, 2644) have listed a number of systems in which compatibility was due to this principle.

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(28) We have recently demonstrated (Horsky; Morawetz, H. *Macromolecules,* submitted for publication) that some of the energy transfer observed in blends of donor and acceptor labeled polymers is radiative, i.e., independent of the spacial distribution of the fluorescent labels. Thus, energy transfer data cannot be interpreted in terms of the dimensions of phase domains as suggested by Albert et al. in ref 10.

Fluorescence Study of the Complexation of Poly(acrylic acid) with Poly(*N*,*N*-dimethylacrylamide-*co*-acrylamide)

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ABSTRACT: Complex formation of poly(acrylic acid) (PAA) with the *N*,*N*-dimethylacrylamide (DAAm) homopolymer and its copolymers with acrylamide (AAm) in water solution was characterized by the enhancement of fluorescence of dansyl labels attached to the PAA. The complexation was more pronounced at pH 3 where the acrylamide residues seemed to contribute to complex stability, while at pH 4 no complex was formed with a copolymer containing 55 mol % AAm. The ratio of monomer residues in PAA and the copolymer in the complexes was independent of the copolymer composition. A number of arguments contradict the concept that polymer complexation in water solution by cooperative hydrogen bonding requires the interaction of long sequences of contiguous monomer residues.

Introduction

Many investigations have been reported on polymer complexation by cooperative hydrogen bonding.[1] If such complexation takes place in aqueous solution, there is only a small difference between the strength of the interpolymer hydrogen bond and the hydrogen bonds of the two polymers with water. It is then not surprising that a large number of interpolymer bonds must be formed to yield a stable complex. It has been claimed[1a] that such complexation involves "noninterrupted linear sequences of bonds" between monomer residues of the hydrogen bond donor and the hydrogen bond acceptor polymer, but it was pointed out that this would involve prohibitive steric strain.[2] It has also been shown that alternating copolymers of carboxylic acids with maleic anhydride form stable complexes with poly(*N*-vinylpyrrolidone) (PVP) in aqueous solution.[3]

Whereas the results obtained with alternating copolymers demonstrate that hydrogen-bonded polymer complexes may form in water solution even if the interacting groups are not attached to neighboring monomer residues, a study of the complexation of a homopolymer with a series of random copolymers containing varying concentrations of inert monomer residues should shed additional light on factors determining complex stability. Bimendina et al.[4] studied complexation of poly(methacrylic acid-*co*-methyl methacrylate) containing 63.6–76.8 mol % of the acid monomer residues with PVP, but this system could only be investigated in water containing 30% ethanol. Iliopoulos et al.[5] considered partially ionized poly(acrylic acid) (PAA) as a random copolymer of hydrogen-bonding and inert monomer residues and studied the complexation of PAA at varying degrees of ionization with poly(oxyethylene) or PVP.

Unfortunately, the introduction of a comonomer into one of the partners of complex forming polymers can never be considered a "structure defect"[5] only, since it will affect the complex stability in various other ways: This may involve hydrophobic interactions stabilizing the complex,[6,12] or in the case of partially ionized PAA, a strong interaction of the anionic acrylate residues with water, which would be expected to weaken the cohesion of the interacting polymer chains. To minimize this difficulty, we chose for our study the complex formation of PAA with

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