Characterization of Polymer Compatibility by Nonradiative Energy Transfer. Applications to Binary Mixtures of Homopolymers and to Homopolymer–Block Copolymer Blends

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ABSTRACT: Polystyrene (PS), poly(α-methylstyrene) (PMS), poly(*p-tert*-butylstyrene) (PtBS), and block copolymers of styrene with α-methylstyrene (PS–PMS) or with *p-tert*-butylstyrene (PS–PtBS) were labeled with carbazole or anthracene. The compatibility of the binary systems PS + PS–PMS, PMS + PS–PMS, PS + PtBS, and PtBS + PS–PtBS and of the ternary system PS + PMS + PS–PMS was characterized by energy transfer between carbazole donors attached to the block copolymers and the anthracene acceptor carried by the homopolymers. Data were also obtained for the homopolymer blends PS + PMS and PS + PtBS, where one of the species was labeled with carbazole and the other with anthracene. These various systems were also studied by DSC. It was found that the energy-transfer technique is more sensitive than DSC in characterizing polymer miscibility. The specific homopolymer interaction with a similar block of the block copolymer was also reflected by the data.

In previous reports from this laboratory[2-5] the compatibility of polymers was studied by the nonradiative energy transfer between a polymer labeled with a fluorescing donor whose emission spectrum overlapped the absorption spectrum of a fluorescing acceptor attached to a second polymer. In the case of carbazole donors and anthracene acceptors the characteristic distance for the transfer of half of the radiation absorbed by the donor was found,[3] according to the theory of Förster,[6] to be 2.8 ± 0.1 nm. As expected, energy transfer was favored by the interpenetration of the polymeric species and was, therefore, a sensitive indicator of polymer compatibility.

In the early work[2,3] the labeling was accomplished by copolymerization with monomers carrying the desired label. However, this approach could not be used with systems containing anionically polymerized styrene or α-methylstyrene, and in this case the label had to be attached to the polymers after a light chloromethylation.[4] The same approach was used in the present investigation, in which anionically prepared homopolymers and block copolymers were studied. The polystyrene–poly(α-methylstyrene) system (and the corresponding block copolymer) was used as characteristic of a pair that is relatively close to compatibility while the polystyrene–poly(*p-tert*-butylstyrene) system (and the corresponding block copolymer) was taken as characteristic of strongly incompatible pairs.

Experimental Section

Polymers. Polystyrene (PS) and poly(α-methylstyrene) (PMS) were prepared by anionic polymerization initiated by potassium naphthalene. The block polymers were obtained by anionic polymerization initiated by butyllithium. Average molecular weights of the homopolymers were determined by GPC and viscosimetry. The composition of block copolymers (Table I) was obtained by IR spectroscopy (using the band at 1233 cm^{-1} for PMS and at 902.5 cm^{-1} for PS[7]) and by NMR analysis.[8] A Varian XL-100 was employed for NMR analysis using 10 wt % polymer solutions in tetrachloromethane at 60 °C. From intrinsic viscosities in benzene at 25 °C for PS and at 30 °C for PMS, average molecular weights were obtained with $[\eta] = K\bar{M}_v^a$ with $K = 9.18$ mL/g and $a = 0.743$ for PS[9], and $K = 10.3 \times 10^{-3}$ mL/g and a = 0.72 for PMS.[10] GPC measurements were carried out by Dr. Pokorny in an apparatus constructed at the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, using silica gel (Rechinay Saint Gobin) columns and tetrahydrofuran solutions. Polystyrene standards obtained from Waters Associates were used for calibration, treating the block polymers like polystyrene. The polymer designations (e.g., PS-80A) specify $10^{-3}\bar{M}_w$ obtained from GPC and the nature of the fluorescent label (A for anthracene and C for carbazole).

Table I
Characterization of Homopolymers and Block Copolymers Employed

polymer[a]	$\bar{M}_w/\bar{M}_n$[b]	$10^{-3}\bar{M}_v$	mol % styrene		mol % label
			IR	NMR	
PS-80A	1.43	74			1.82
PS-403A	2.08	355			1.53
PMS-48A	1.58	43			1.56
PMS-157A	1.20	152			1.37
PS-PMS-53C	1.22		45	43	0.93
PS-PMS-155C	1.23		46	42	1.05
PS-PtBS-104C	1.37			33	1.82
PtBS-58	1.59				
PtBS-172C	1.60				0.86
PtBS-380C	1.40				0.88

[a] The number specifies $10^{-3}\bar{M}_w$; A and C symbolize labeling by anthracene and carbazole, respectively. [b] From GPC.

Attachment of Fluorescent Labels. PS, PMS, and PS block copolymers with PMS (PS–PMS) and poly(*p-tert*-butylstyrene) (PS–PtBS) were lightly chloromethylated and labeled with either carbazole or anthracene as previously described.[4] Poly(*p-tert*-butylstyrene) (PtBS) labeled with the donor or acceptor chromophore was prepared by a free radical copolymerization with 2-*N*-carbazoylethyl methacrylate or (9-anthryl)methyl methacrylate.[4] The content of the labels in the homopolymers was obtained by UV spectroscopy with extinction coefficients reported previously.[4] It was assumed that the chloromethylation of the blocks in copolymers proceeds at the same relative rate as in the corresponding homopolymers. Since the chloromethylation rates of PS and PMS are identical, the labels are assumed to be uniformly distributed in PS–PMS. On the other hand, chloromethylation of PtBS takes place at a negligible rate compared to that of PS, and the PS–PtBS may then be assumed to carry all the labels on the PS block. Table I lists the label content of all the polymers used. The labeled and unlabeled PtBS polymers were prepared by free radical polymerization and fractionated at 25 °C. For preparation of polymer blends, fractions were used that had the most similar molecular weights.

Sample Preparation and Fluorescence Measurement. Films of polymer blends were cast from 8% toluene solutions at ambient temperature in a drybox under a nitrogen atmosphere. After 24 h they were vacuum-dried at 3 Pa to constant weight. Labeled polymers were diluted with unlabeled polymers so as to arrive at a concentration of 10 mM of the carbazole and anthracene

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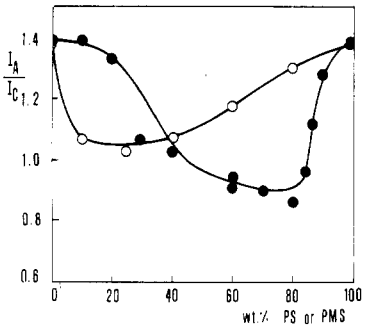

Figure 1. Dependence of I_A/I_C on the composition of blends of block copolymer PS–PMS-155C with PS-403A (●) or PMS-157A (○).

chromophore. Reflectance fluorescence spectra with excitation at 297 nm were obtained[4] with a Hitachi Perkin-Elmer MPF-2A or MPF-44 fluorimeter. Nonradiative energy transfer was characterized by the relative emission intensity of the anthracene acceptor at 413 nm (I_A) and the carbazole donor at 365 nm (I_C).

DSC. A DuPont thermal analyzer 990 with a 910 DSC module was calibrated according to the manufacturer's instructions. Samples of blends were prepared by coprecipitation of 6.5% benzene solutions into methanol. The measurements were carried out on 5–20-mg samples. They were first heated above the highest T_g; DSC measurements were made in a stream of argon at a heating rate of 10 K min^{-1} after cooling at the same rate. The breadth of the glass transition was defined as follows: T_g was taken as the temperature at which half of the heat capacity change during the glass transition had occurred. The lower and the upper ends of the glass transition interval, T_{g1} and T_{g2}, were defined as the intersections of the tangent to the inflection point of the DSC trace with the extrapolated traces of the glassy and rubbery regions, respectively. The breadth of the transition was characterized by $\Delta T_g = T_{g2} - T_{g1}$ as suggested by Krause et al.[23]

Results and Discussion

Blend of PS or PMS with the Block Copolymer PS–PMS. The I_A/I_C ratio for blends of PS-403A or PMS-157A with PS–PMS-155C are plotted as a function of the composition of the blend in Figure 1. Similar data are obtained with the lower molecular weight polymers and block copolymers. These should be compared with $I_A/I_C \sim 0.0088$ expected in the absence of nonradiative energy transfer as calculated from the extinction coefficients and the relative quantum yields of the donor and acceptor fluorescence[4] and $I_A/I_C = 1.39$ found for the homogeneous blend of donor- and acceptor-labeled PS. (It should be understood that some energy transfer will be expected even for incompatible polymer blends if the phase domains are sufficiently small, particularly since such blends are known[5] to be characterized by "fuzzy" phase boundaries.)

The plot in Figure 1 shows that PMS is more compatible than PS with the block copolymer PS–PMS although high PMS contents in blends with PS–PMS lead to partial phase separation as previously reported by Robeson.[11] This is also consistent with out previous finding[4] that small concentrations of PMS are more easily accommodated in PS than small concentrations of PS in PMS. The effect is probably not produced by the different molecular weights of PS and PMS since similar compatibility differences were observed when PS-80A or PMS-48A, which differ much less in molecular weight, were blended with PS–PMS-53C. The energy transfer in blends of the donor-labeled block copolymer with the acceptor-labeled homopolymers is somewhat less than in blends of similar homopolymers labeled with the donor and the acceptor, respectively. This is not surprising since each homopolymer would be expected to mix freely only with one of the blocks of the block copolymer. Thus, the labels attached to the other block should have a smaller probability of participating in energy transfer.

Table II
Glass Transitions in Blends of Block Copolymer PS-PMS-155 with Polystyrene PS-403 or Poly(α-methylstyrene) PMS-157

PS or PMS wt fraction	PS blends T_g, K	PS blends ΔT_g, K	PMS blends T_g, K	PMS blends ΔT_g, K
0.0	404	31	404	31
0.2	399, 449[a]	29	418	35
0.4	393, 451[a]	13	423	40
0.6	383	14	432	30
0.8	381	12	442	23
1.0	375	6	441	13

[a] Two transitions are indicated.

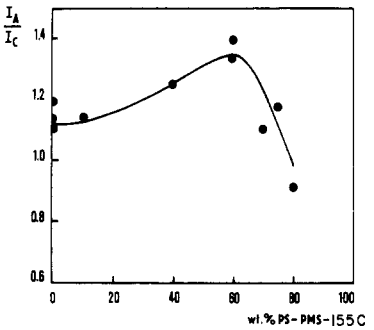

Figure 2. Dependence of I_A/I_C on the weight fraction of the block copolymer PS–PMS-155C in blends with equal weights of PS-403A and PMS-157A.

It was of interest to compare the results of energy transfer with DSC data. Results obtained with DSC traces for blends of PS-403A and PS–PMS-155C and for blends of PMS-157A with PS–PMS-155C are listed in Table II. The T_g values of 375 K for PS and 440 K for PMS agree with previous results.[11] The block copolymer PS–PMS-155C behaves like a homogeneous system. It has been reported[7,11,13–17] that PS–PMS block copolymers may form a single phase or two-phase systems, depending on their composition or molecular weight. Of our two PS–PMS block copolymers, the one with the higher molecular weight had a broader glass transition range, ΔT_g (31 K for PS–PMS-155C and 24 K for PS–PMS-53C). Both these ΔT_g values are much greater than those recorded for the homopolymers and than those expected for really homogeneous blends.[18] With most of the blends a single T_g transition was observed, which shifted with the composition of the blend.[24] The broadening of the T_g for block copolymers and for their blends with PS or PMS may indicate that the miscibility does not extend to the molecular level[18–20] as is also indicated by the lower I_A/I_C values. The domain dimension required for the appearance of a macroscopic property such as T_g is still uncertain;[18] Kaplan[21] estimates it to be about 15 nm. The energy-transfer technique is highly sensitive but its interpretation is somewhat ambiguous, since the phenomenon is sensitive to both compatibility and the interphase area.

The effect of the block copolymer PS–PMS-155C on the miscibility of equal weights of PS-403A with PMS-157A is illustrated on Figure 2. It may be seen that energy transfer between the block copolymer donor and the homopolymer acceptors is maximized at 60 wt % of the block copolymer, while it decreases precipitously when the block copolymer content is increased beyond this point. This may be interpreted as follows: As long as its concentration is low, the block copolymer will form a thin layer between the two homopolymer domains, and the donor attached to the block copolymer will lie close to the ac-

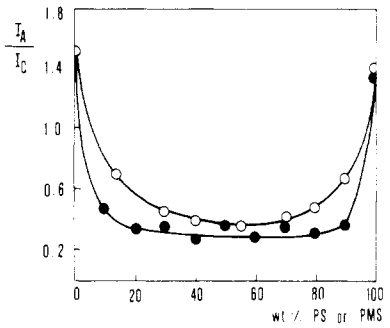

Figure 3. Dependence of I_A/I_C on the composition of blends of PS-403A with PtBS-380C (●) and of PMS-157A with PtBS-172C (○).

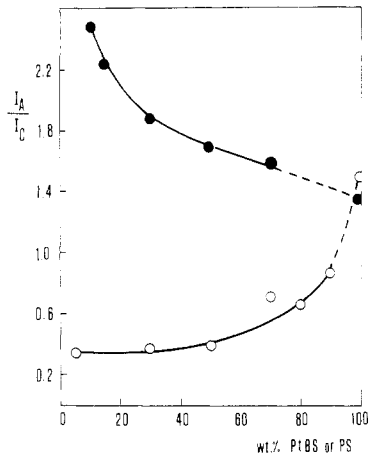

Figure 4. Dependence of I_A/I_C on the composition of blends of PS-80A with PS–PtBS-104C (●) and of PtBS-58A with PS–PtBS-104C (○).

ceptor attached to the homopolymers. When the block copolymer concentration is high, the block copolymer will form relatively large domains, and the donor chromophores attached to it will be increasingly shielded from the acceptors attached to the homopolymers.

Blends of PS or PMS with PtBS and Ternary Systems PS + PtBS + PS–PtBS. While the blends described above were close to compatibility on the molecular level, the systems to be dealt with now are clearly incompatible. A plot of the I_A/I_C ratio in blends of PS-403A with PtBS-380C and of PMS-157A with PtBS-172C is shown on Figure 3 as a function of the ratio of the components. The plot passes through very low I_A/I_C values, reflecting the segregation of the two polymeric species into separate phases. The dependence of I_A/I_C on the composition of blends of PS-80A or PtBS-58A with the block copolymer PS–PtBS-104C is shown on Figure 4. In this case we must take account of the fact that the carbazole label is attached only to the PS block of the block copolymer. For low concentrations of PS-80A, the homopolymer is effectively mixed with the donor-labeled PS block of the block copolymer and the energy transfer is highly efficient. As the homopolymer concentration is increased, more and more of it is removed from the block copolymer, and the efficiency of the energy transfer decreases.

The behavior of the blends of PtBS-58A with the block copolymer PS–PtBS-104C is strikingly different. In this case, a low concentration of the homopolymer leads to low I_A/I_C ratios since the acceptor-labeled PtBS mixes with the PtBS block of the block copolymer, in which the concentration of donor labels is negligible. As the PtBS homopolymer concentration is raised, it comes increasingly in contact with the donor-labeled PS block of the block copolymer, leading to a rise in the energy-transfer efficiency. Thus, the difference in the behavior of the PS–PtBS blends with PS and PtBS, respectively, is a consequence of the asymmetric labeling of the block copolymer. The effect is enhanced by the microphase separation in the PS–PtBS, which was confirmed by DSC.

For blends of PS-403 with PtBS-380 and of PMS-157 with PtBS-172 two T_g's were observed. In blends of PS-403 with PtBS-380 the T_g of the PtBS was 416 K (as against 419 K in pure PtBS), and in blends of PMS-157 with PtBS-172 the T_g of PMS was on the average raised by more than 10 K. The breadth of T_g did not change significantly in these blends, which were all microphase separated. The microphase-separated block copolymer PS–PtBS-104 exhibits T_g at 379.5 and 420.5 K, somewhat higher than for PS and PtBS, respectively. Two T_g transitions were also found in blends of PS-80 with PtBS-58, which could all be characterized as incompatible.

Concluding Remarks

Energy transfer between labeled polymers or block polymers was found to yield data on miscibility that were qualitatively in agreement with DSC data. The energy-transfer method is more sensitive and allows more detailed conclusions to be reached, particularly in the case of blends of homopolymers with block copolymers. Nevertheless, the interpretation of energy-transfer data is limited since they depend not only on the extent of interpenetration of donor- and acceptor-labeled polymers but also on the dimensions and geometry of phase domains.[5] The greatest problem is that of sample preparation.[5,22] In film casting one cannot be sure of obtaining thermodynamic equilibrium, and the properties of the film prepared from solutions of mixed polymers may depend on the polymer–solvent interactions, on the point at which the system becomes glassy during drying, and on the rate of the drying process.

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Registry No. PS, 9003-53-6; PS–PMS, 9011-11-4; PMS, 25014-31-7; PtBS, 26009-55-2; PS–PtBS, 26124-34-5.

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(24) However, Krause et al.[23] found that ΔT_g was generally larger in the microphase of block copolymers than in a corresponding homopolymer.

Ionic Conductivity of Polyether–Polyurethane Networks Containing Alkali Metal Salts. An Analysis of the Concentration Effect

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ABSTRACT: The ionic conductivity of poly(oxyethylene)–polyurethane networks containing either sodium tetraphenylborate or lithium perchlorate was studied as a function of the salt concentration at constant reduced temperature $T - T_g$. Two different types of networks, based on poly(oxyethylene) of molecular weight 400 and 1000, respectively, were investigated. The log–log plots of the conductivity vs. the salt concentration at constant reduced temperature were linear with slopes close to unity. These results are explained by assuming complete dissociation of the salt under most conditions studied.

The increasing interest in ion-containing polymers is directly related to their properties. Polyether–alkali metal salt systems have been thoroughly studied in view of their potential applications as solid electrolytes in electrochemical solid-state primary or secondary generators. Wright first reported high ionic conductivity for mixtures of poly(oxyethylene) and alkali metal salts.[1] Armand et al. have extensively investigated their electrical properties and their behavior as solid electrolytes.[2] Our interest in this field has focused on polyether–polyurethane *networks* containing sodium or lithium salts. In previous papers we demonstrated the important role played by the glass transition temperature on their ionic conductivity[3] as well as on their viscoelastic properties.[4,5] The overall effect of an increase in the salt concentration on the viscoelastic properties of these networks (with $NaBPh_4$) is to increase the glass transition temperature,[4] as expected on the basis of free volume considerations. Indeed, at constant reduced temperature $T - T_g$ there is no noticeable effect of the salt concentration on the viscoelastic properties.[4] Similar considerations, based on a free volume diffusion model for the ions, lead us to a WLF relationship to describe the conductivity behavior with temperature at constant salt concentration.[3,7] We were also able to establish a direct correlation between the viscoelastic properties of these networks and their ionic conductivity, as predicted by theoretical considerations.[7,8] ^{7}Li spin–spin relaxation times (T_2) were also found to correlate well with the respective ionic conductivities.[6] This is not surprising since all the transport properties of the materials, e.g., viscoelastic, ionic conductivity, and spin–spin relaxation properties, are a consequence of the local segmental mobility, which, in turn, depends on free volume through classical relationships.

In the present paper we examine the variations of the conductivity with the salt concentration, at constant free volume fraction, i.e., at constant reduced temperature, for two types of materials: urethane-cross-linked poly(oxyethylene) (POE), $M = 400$, containing $NaBPh_4$ and urethane-cross-linked poly(oxyethylene), $M = 1000$, containing $LiClO_4$.

Experimental Section

The preparation and conditioning of the membranes have been described in previous papers.[4,6] Conductivities were measured either on an Alcatel Model 2531 impedance meter or on a Solartron 1174 frequency response analyzer controlled by an Apple II computer. The conductivity is obtained from the complex impedance diagram.[9] ^{7}Li broad-line NMR analysis was carried out on a Bruker WP-100 spectrometer. Loss-tangent measurements and the corresponding peak temperatures ($T_{\delta_{max}}$, Table I) at 11 Hz were made on a Rheovibron DDV II viscoelastometer.[1,4] The glass transition temperatures were measured on a DuPont 990 thermoanalyzer. The main characteristics of the samples are shown in Table I. The $T_{g,DSC}$ (Table I) values reported correspond to the lower temperature of the transition zone.[10] The conductivity values at a given reduced temperature were obtained by interpolation on log σ vs. T diagrams.

Results and Discussion

Since we have shown in previous papers that the ionic conductivity follows a WLF relationship at constant salt concentration,[3,6,7] we assume here that measurements at constant reduced temperature relate to iso-free-volume conditions. This assumption is in agreement with the fact that the C_1 and C_2 constants of the WLF relationships found for different materials similar to those used in this study are almost independent of the salt concentration.[11,12] As shown respectively for POE 400–$NaBPh_4$ and POE 1000–$LiClO_4$ networks in Figures 1 and 2, the log–log plots of the conductivity vs. the salt concentration are reasonably linear. Moreover, the slope of these lines is close to unity. This implies that the conductivity increases linearly with salt concentration at constant free volume, at least in the temperature and concentration ranges studied here. This observation can be rationalized by assuming that the degree of disssociation α of the ionogenic functions is con-

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