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Miscibility in blends of polystyrene and poly(methyl methacrylate) studied by nonradiative energy transfer

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Summary

The miscibility of anthracene-labelled polystyrene (PS) in blends with carbazole-labelled poly(methyl methacrylate) (PMMA) was examined by the nonradiative energy transfer (NET) technique. It was found that the miscibility is relatively insensitive to the PMMA component molecular weight which has the range from 4.70×10^5 to 2.36×10^6. However, the miscibility is sensitive to the PS component molecular weight which has the range from 8.22×10^4 to 4.68×10^5. The observation from transmission electron microscopy is consistent with the results obtained from NET.

Introduction

A fluorescence technique, based on the phenomenon of nonradiative energy transfer (NET), has been developed for studying the miscibility of polymer blends (1). When the overlap integral between the normalised emission spectrum of one chromophore (donor) and the absorption spectrum of another chromophore (acceptor) is sufficiently high, the excitation energy absorbed by the donor can be transferred to the acceptor over large distances, as a result of dipole-dipole interactions between the donor and acceptor.

The efficiency of this nonradiative energy transfer, E, is directly related to the distance, r, between the donor and acceptor, according to the Förster equation (2),

$$E=R_0^6/(R_0^6+r^6) \tag{1}$$

where R_0 is the so-called Förster distance for which transfer and spontaneous decay of the excited state of the donor are equally probable.

The distance-dependent efficiency of energy transfer has been used as a sensitive probe of the average distance between donors and acceptors attached to polymers, allowing investigation of mutual interpenetration of polymeric species in blends. With a suitable choice of donor and acceptor chromophores, such as carbazole (donor) and anthracene (acceptor) for example, an R_0 value of about 2 nm can be obtained (1). Therefore, the ratio of the fluorescence emission intensities of the donor and acceptor chromophores in polymer blends can be related to the magnitude of the chain miscibility of labelled polymers on a molecular scale of about 2 nm.

In the previous work, the nonradiative energy transfer technique has been applied to binary polymer pairs which are considered to be miscible by the classical definition or which have a similar molecular structure, so that changes in the miscibility on the molecular scale may be sensitively detected (3, 4).

In the present work, the miscibility of the blends of a carbazole-labelled poly(methyl methacrylate) (PMMA) and an anthracene-labelled polystyrene (PS), which are considered

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to be immiscible by the classical definition (5), were investigated by the nonradiative energy transfer technique. The main object of this work was to observe the effect of the molecular weight of the two polymers on the miscibility of the blend. Although molecular weight can have a strong influence on polymer properties, the role of molecular weight has often been overlooked in studies of polymer blends (6).

Experimental

Fluorescent Precursors. N-(2-hydroxyethyl) carbazole was prepared from carbazole and ethylene oxide in the presence of sodium hydroxide. 2-N carbazolylethyl methacrylate (CEMA) was obtained by the reaction of N-(2-hydroxyethyl) carbazole and methacryloyl chloride (7). 9-Anthrylmethanol was obtained from 9-anthrylmethaldehyde with $NaBH_4$ (8). 9-Anthrylmethyl chloride (AMC) was obtained from 9-anthrylmethane with Lucas reagent (9).

Polystyrene (PS). PS was prepared by radical polymerization initiated by AIBN at 80°C. The process of fractional precipitation was used for PS fractionation, in which methyl ethyl ketone was used as a solvent and methanol as a nonsolvent. Polymer molecular weights were obtained from the intrinsic viscosities of toluene solutions at 30°C, using the Mark-Houwink constants, $K=9.2\times10^{-3}$ mL/g and $a=0.72$ (10). PS was labelled with the anthracene chromophore by Friedel-Crafts acylation (11). The anthracene moiety was attached to the PS chain by reaction with AMC using $SnCl_4$ as a catalyst. The reaction was carried out under anhydrous conditions, in ortho-dichlorobenzene at 25°C for 6 hours. The content of the anthracene chromophore label in the PS was obtained by UV spectroscopy, using 9-anthrylmethane as a corresponding low molecular weight reference analogue (1).

Poly(methyl methacrylate) (PMMA). Copolymers of MMA and CEMA and the homopolymer of MMA were prepared by radical polymerisation initiated by AIBN at 60°C, keeping the conversion below 10%. The process of fractional precipitation, in which chloroform was a solvent and petroleum ether was a nonsolvent, was used for sample fractionation. The average molecular weight of the polymers was obtained from intrinsic viscosities in benzene at 25°C, with $K=5.5x10^{-3}$ mL/g and $a=0.76$ (12). The content of the carbazole chromophore label in PMMA was obtained by UV spectroscopy, using N-ethyl carbazole as a corresponding low molecular weight reference analogue (1).

Sample Preparation and Fluorescence Measurement. Films of PS/PMMA blends were cast from 2% dichloromethane solution at ambient temperature. After 24 hours they were vacuum-dried to constant weight. Labelled polymers were diluted with unlabelled polymers so as to arrive at concentrations of 10^{-2} M for both the carbazole and anthracene chromophores (13). Reflectance fluorescence spectra with excitation at 296 nm were obtained with a Hitachi-850 spectrofluorophotometer. The efficiency of the energy transfer was characterised by the relative emission intensity of the anthracene acceptor at 413 nm (I_A) and the carbazole donor at 347 nm (I_C).

Transmission Electron Microscopy (TEM). A staining method consisting of two steps was used to prepare the TEM samples of PS/PMMA blends (14). In the first step, the thin solution cast film of a PS/PMMA blend on a microscope grid was immersed into 2% wt. allylamine aqueous solution for 2 minutes and the excess allylamine was then desorbed in vacuo for 48 hours. In this step, the allylamine was absorbed in the PMMA phase. In the second step, the samples were exposed to OsO_4 vapour for 1 hour and 30 minutes at 50°C, so that the adsorbed allylamine reacted with OsO_4, thus preferentially staining the PMMA phase. Transmission electron micrographs were obtained with a Hitach-600 transmission electron microscope.

Results and Discussion

Four PS samples and five PMMA samples were obtained with different average molecular weights. The molecular weight and percent label for the various polymer samples are shown in Table 1.

Table 1. Characteristic of Polymers

Sample	wt.% label	M_V (labelled)	M_V (unlabelled)
PS-1	0.58	8.22×10^4	8.22×10^4
PS-2	1.75	1.71×10^5	1.71×10^5
PS-3	0.50	2.64×10^5	2.64×10^5
PS-4	1.43	4.69×10^5	4.69×10^5
PMMA-1	0.75	4.45×10^5	4.70×10^5
PMMA-2	0.79	7.04×10^5	6.55×10^5
PMMA-3	0.80	1.16×10^6	1.19×10^6
PMMA-4	0.80	1.54×10^6	1.56×10^6
PMMA-5	0.80	2.42×10^6	2.36×10^6

The reference ratio corresponding to the maximum energy transfer between donor and acceptor was obtained using a homogeneous blend of donor- and acceptor labelled PMMA (15). The I_C/I_A value obtained was 0.24, which is representative of a completely miscible system. The other reference ratio, corresponding to the absence of energy transfer between donor and acceptor, was obtained by using donor-labelled PS and acceptor-labelled PMMA films (16). The I_C/I_A value obtained was 64, which is representative of a completely phase-separated system.

The I_C/I_A ratio for blends of PS-1 and PS-4 with the different PMMA samples are plotted as a function of the blend composition in Figure 1. The I_C/I_A values are higher than those expected for blend systems in which the binary blend pairs have similar molecular structure, such as polystyrene/poly(α-methylstyrene) (4) and poly(methyl methacrylate)/poly(ethyl methacrylate) (1). Compared with the reference ratio corresponding to a completely miscible system ($I_C/I_A = 0.24$), we may concluded that the PS/PMMA blends are immiscible. This is consistent with previous studies using other experimental techniques (17). Figure 1 also shows that there is little or no change in I_C/I_A with a change in the composition of the blend. There is only a slight increase in the I_C/I_A value when the PS content of the blend is about 20 wt.% for the blends of PS-2 with the different PMMA samples. Therefore, the miscibility of these PS/PMMA blends are insensitive to the composition of the blend.

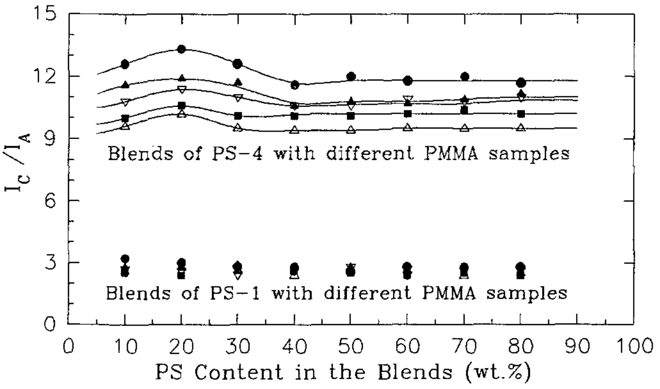

Figure 1. I_C/I_A versus PS content in blends of PS-1 and PS-4 with different PMMA samples: ▵ PMMA-1, ■ PMMA-2; ▿ PMMA-3; ▲ PMMA-4; ○ PMMA-5.

The I_C/I_A values for the blends of PS-1 with the different PMMA samples are very similar, indicating that there is little variation in miscibility with the molecular weight of the PMMA, for this system. On the other hand, when PS-4 was blended with the different PMMA samples, an increase in the molecular weights of the PMMA component causes an increase in the I_C /I_A value, and thus the miscibility of the system decreases.

Figure 2 shows the change in the I_C /I_A values of PS/PMMA blends in which the composition weight ratio of PS/PMMA in the blend is 50:50 wt.%. This plot shows that the miscibility of the blends of PS-1 or PS-2 with PMMA are relatively insensitive to the molecular weight of the PMMA component. However, I_C /I_A increases linearly with an increase in the PMMA molecular weights for the PS-3 or PS-4 blends. Table 2 shows the slope of a plot of I_C /I_A verses PMMA molecular weight for blends of the different PS samples with PMMA. When the molecular weight of the PS sample increases, the slope increases. Thus the miscibility of these blends is more sensitive to changes in the PMMA molecular weight.

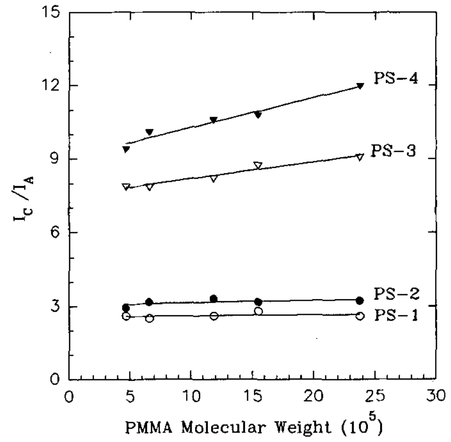

Figure 2. I_C/I_A versus PMMA molecular weight for blends of 50:50 wt.% composition.

Table 2. Slope of I_C/I_A with PMMA Molecular Weights

PS Sample	PS-1	PS-2	PS-3	PS-4
M_V	8.22×10^4	1.71×10^5	2.64×10^5	4.69×10^5
Slope	4.7×10^{-8}	1.0×10^{-7}	6.8×10^{-7}	1.2×10^{-6}

According to the Huggins-Flory theory (18), the free energy of mixing, ΔG_M, for a binary mixture containing A and B polymers can be written as:

$$\Delta G_M = RT\left(\frac{W_A}{M_A}\ln\phi_A + \frac{W_B}{M_B}\ln\phi_B + \chi\phi_A\phi_B\right) \tag{2}$$

where W_A and W_B are the weights of polymer A and B in the blend, respectively. M_A and M_B are the molecular weights of polymer A and B, respectively. Φ_A and Φ_B are the volume fractions of the polymer A and B in the blend, respectively, and χ is the binary interaction parameter.

Equation (2) shows that with the decrease of the molecular weight of the blend components, the free energy of mixing for the binary blend decreases, and thus the miscibility of the blend increases.

From equation (2),

$$\frac{\partial \Delta G_M}{\partial M_i} = -\frac{RTW_i\ln\phi_i}{M_i^2} \tag{3}$$

where i represents component A or B.

From equation (3) we conclude that the lower the molecular weight of one of the components, the more sensitive is the free energy of mixing to a change of the molecular weight of that component. Therefore, when two polymers of different molecular weight are blended, the miscibility is more sensitive to changes in the molecular weight of the lower molecular weight component than it is for the higher molecular weight component. From Table 1 we find that the range of the molecular weights of the five PMMA samples is from 4.70×10^5 to 2.36×10^6. However, the range of the four PS samples is from 8.22×10^4 to 4.69×10^5, so that the molecular weight of the PS sample having the highest molecular weight is similar to that of the PMMA sample having the lowest molecular weight. Hence, the miscibility of the blends will be less sensitive to a change in the molecular weight of the PMMA than it will be to a change in the molecular weight of the PS. Thus, as the molecular weight of the PS component of the blends is raised, the molecular weights of the two components approach one another, and the miscibility of the blend becomes less sensitive to the molecular weight of the PMMA component.

Figure 3 shows the change in the I_C /I_A values for PS/PMMA blends with PS molecular weights in which the composition weight ratio of PS/PMMA blend is 50:50. The miscibility of the blends is sensitive to a change in the PS molecular weight. For every PMMA sample there are obviously two stages. When the PMMA samples were blended with PS-1 or PS-2, the I_C /I_A values are in the range of 2 to 4. However, when the PMMA samples were blended with PS-3 or PS-4, which have higher molecular weight, the I_C /I_A values are increased to over 7. Therefore, there is obviously a critical molecular weight for PS which lies between the molecular weights of PS-2 and PS-3, in which the phase structure of the blend undergoes some sudden change.

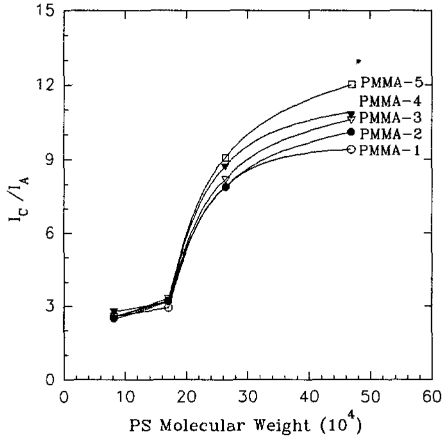

Figure 3. I_C/I_A versus PS molecular weight for blends of 50:50 wt.% composition.

Previously we have shown that blends of PS and PMMA form an immiscible system. Therefore, it may be considered that there is phase separation when PS-3 or PS-4 are blended with the different PMMA samples. However, as the molecular weight of the PS is reduced, there is a critical molecular weight below which the PS phase and PMMA phase have some degree of interpenetration, and thus the miscibility of the binary blend system is "improved", and the I_C /I_A values are correspondingly lower.

The transmission electron microscopy (TEM) has been applied to investigate the morphology of this blend system. Figure 4 shows the TEM photographs for the blends of PMMA-5 with the PS-1 and PS-3 polymers. When PMMA-5 was blended with PS-3 (Figure 4 (b)), there are obviously two phases (the PMMA phase is black and the PS phase is white). However, if the molecular weight of the PS component is decreased, the "miscibility" of the binary blend system is increased. From Figure 4 (a), we find that when PS-1 is blended with PMMA-5, the phase sizes for the PS phase and the PMMA phase have been obviously reduced. The PS phase and PMMA phase thus have some degree of interpenetration. This is consistent with the observed change in the I_C /I_A values. PS/PMMA blends prepared by melt mixing in an elastic melt extruder have been found to have a morphology consisting of two continuous phases (5). From Figure 4 we also find that there is some degree of the continuity between the PS and PMMA phases when the molecular weights of the PS component in the PS/PMMA blends are small.

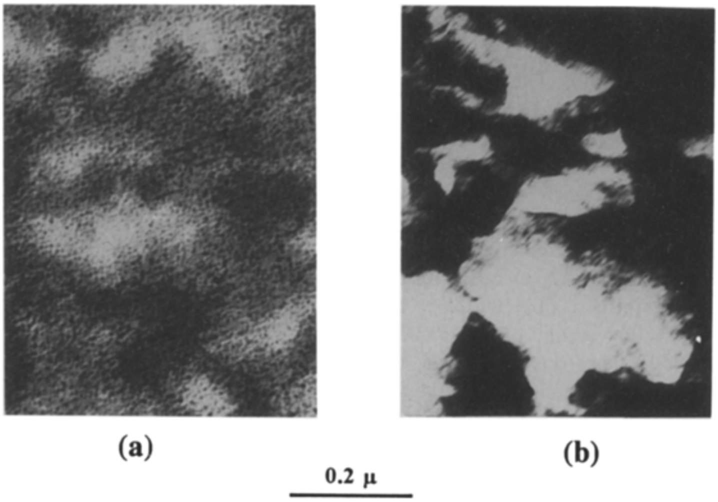

Figure 4. The TEM photographs of the blends, (a) PMMA-5 with PS-1 and (b) PMMA-5 with PS-3.

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