Fluorescence densitometry at polymer–polymer interfaces: interdiffusion in polystyrene–poly(cyclohexyl methacrylate) blends

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An experimental set-up is described to determine the concentration profile of a polymer labelled with a fluorescent dye at the interface with a compatible unlabelled polymer. This method is applied to a study of interdiffusion in blends of labelled polystyrene with poly(cyclohexyl methacrylate) and compared with tracer diffusion of labelled polystyrene in the same system.

(Keywords: fluorescence densitometry; interfaces; interdiffusion; blends; polystyrene; poly(cyclohexyl methacrylate))

INTRODUCTION

The number of fully compatible polymer mixtures characterized by a negative Flory–Huggins interaction parameter χ is relatively small. For polystyrene (PS), the most intensely studied mixtures are those with poly(2,6-dimethyl-1,4-phenyl ether) (PPE) and poly(vinyl methyl ether) (PVME) where interdiffusion has also been investigated[1,2]. Neither are ideal model systems for interdiffusion studies since the components have rather different glass transition temperatures T_g. This complicates the analysis of diffusion studies since effects of slow structural relaxation influence diffusional transport in the vicinity of the blend T_g characterized by large motional heterogeneity[3]. Recently, some fully compatible pairs of polystyrenes and polymethacrylates have been discovered[4]. The mixture of PS and poly(cyclohexyl methacrylate) (PCHMA) appeared particularly attractive as a model system since both have the same $T_g = 100°C$ and are available with narrow molecular-weight distributions through anionic polymerization.

Fluorescence microscopy has found wide application, mostly in biological systems (cells, membranes) where structures marked by a fluorescence label are investigated. Fluorescence redistribution after pattern photobleaching (f.r.a.p.p.) is applied to measure tracer diffusion coefficients, also mostly in biological systems[5,6]. Fluorescence densitometry is very similar to i.r. densitometry[7], which has already been applied successfully to tracer and interdiffusion studies in polymer systems[8]. Fluorescence densitometry has the advantage of higher spatial resolution and sensitivity, although it requires the attachment of fluorescent dye labels to the polymer molecules. The influence of the label upon polymer interaction and diffusivity is not negligible (see below). However, the same is true for the deuterated polymers necessary in diffusion studies by i.r. densitometry as well as forward recoil spectrometry and neutron scattering[8]. We have found that PCHMA is incompatible with fully deuterated PS. This may not preclude diffusion studies since partially deuterated PS should still be compatible, but careful studies of the influence of deuteration would be necessary. In the following, we describe the technique of fluorescence densitometry and its application to interdiffusion in the PS–PCHMA system.

EXPERIMENTAL

The experimental set-up is sketched in *Figure 1a*. The 458 nm line of an Ar ion laser is used to excite the fluorescence in the sample. This has some advantages compared with irradiation by the Hg lamp normally used for fluorescence microscopy. In particular, the intensity profile is more homogeneous over the sample, and the intensity can easily be regulated. Since the recording times are short between long annealing periods, the laser can also be used in other experiments. The fluorescence light passes through a filter excluding wavelengths $\lambda \leqslant 490$ nm before entering an amplifying video camera (Hamamatsu) of high sensitivity (~ 0.03 lux). The irradiated laser light usually had a power of 10–20 mW for samples with 300–500 monomer units per dye molecule. The sample could be viewed directly through the microscope (for adjustment) or by the video camera with an 8 bit digitizer card coupled to a computer for image processing.

The sample preparation was somewhat similar to that used in forced Rayleigh scattering experiments[9]. The polymers were pressed (15 bar) into pellets of 8.5 mm diameter and 0.3 mm thickness. To obtain clear samples, the pressure was applied at $\sim T_g + 20$ K and released after slow cooling to $\sim T_g - 20$ K. Both the labelled and the

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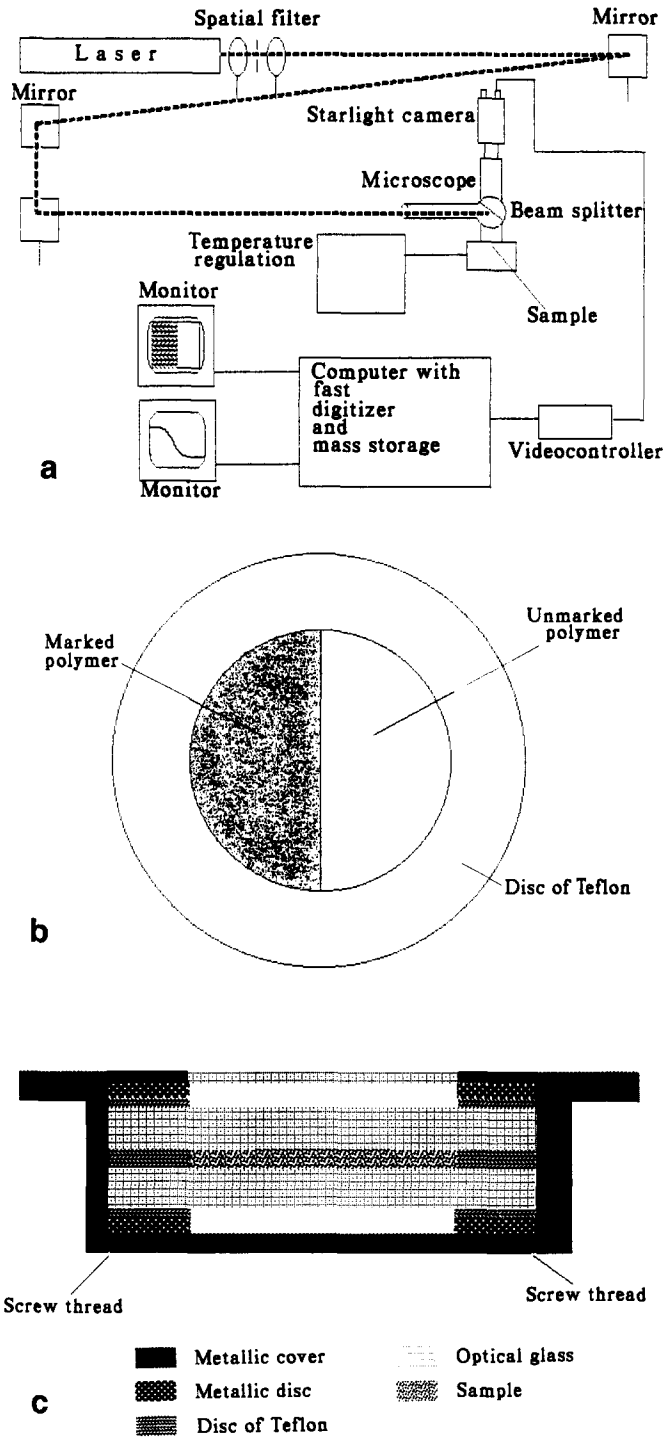

Figure 1 Fluorescence densitometry: (a) experimental set-up; (b) sample, front view; (c) sample, side view

unlabelled pellets were cut in half and assembled in the probe as shown in *Figures 1b* and *1c*. At the interface, the cut edges were polished with a milling cutter (Polycut E of Reichert and Jung). The sample was annealed in a dry-box for up to 24 h at $\sim T_g + 20$ K in order to relax possible internal tensions, and was then heated to the diffusion temperature by the microscope heating system. The interface was smeared over 10–30 μm at time t_0 prior to the diffusion experiment. The concentration profile at t_0 was approximated by a Gaussian error function and attributed to a finite fictitious diffusion time, which was determined as a fitting parameter and added to the real diffusion time when the broadened concentration profiles were evaluated after the diffusion process. The spatial resolution is of the order of the pixel distance of the video camera, corresponding to 1.17 μm in our microscope set-up. To determine one concentration profile $c(x)$, 500 video pictures, each having 24 rows and 620 pixels per row, were averaged. For averaging over the rows it was necessary to adjust the centre $x=0$ by the requirement that:

$$\int_{-\infty}^{0} [1-c(x)]\,dx = \int_{0}^{\infty} c(x)\,dx \qquad (1)$$

where the distance coordinate x is in the space-fixed laboratory system for mixtures with (approximately) constant partial molecular volumes (*Figure 2*).

The PS samples were obtained by anionic polymerization terminated with *p*-dichloromethylbenzene[9] in order to obtain a chloromethyl end-group which could be reacted with the Cs salt of the fluorescence dye 2-dimethylaminocoumarin-4-carboxylic acid (Molecular Probes Co., Eugene, Oregon, USA). One sample of PS with large degree of polymerization, $P_n = 1900$, was statistically chloromethylated[9] to varying degrees of 125, 250 and 500 monomer units per chloromethyl group, respectively. The labelling reaction was the same as in our tracer diffusion studies with photochromic dyes. Some test experiments where acridine yellow was used as fluorescent dye label yielded the same interdiffusion coefficients as are derived when the coumarin label was used (within experimental accuracy). The PCHMA samples were also prepared by anionic polymerization and characterized by g.p.c. All polymer samples had a molecular-weight distribution index (polydispersity) $M_w/M_n < 1.06$. We have found no straightforward method for dye labelling of PCHMA.

RESULTS AND DISCUSSION

The first part of this section is primarily concerned with data analysis and evaluation, It should provide information on the advantages and limitations of the technique exemplified for the PS–PCHMA system. The second part deals with the measured interdiffusion coefficients at different molecular weights and temperatures as compared with expectations from theory.

Concentration profiles

In *Figure 2*, measured concentration profiles for an approximately symmetrical and an unsymmetrical PS–PCHMA pair are shown together with the fit by an error function. A good fit implies that the interdiffusion coefficient D is constant over the whole concentration range. This is certainly not true for the unsymmetrical pair (*Figure 2b*). Here, $D(c)$ can be deterimined as a function of concentration c from the integral[10]:

$$D(c) = -\frac{1}{2t}\left(\frac{dx}{dc'}\right)_{c'=c} \int_{0}^{c} x\,dc' \qquad (2)$$

where x is the inverse of the concentration profile $c(x)$. We have evaluated $D(c)$ numerically after smoothing the measured concentration profile by a polynomial fit. For the profile shown in *Figure 2b*, D increases with increasing concentration of the short PCHMA chains[11]. This indicates that the mobility of the long labelled PS chains in an environment rich in short chains is higher than the mobility of the short PCHMA chains in a PS-rich

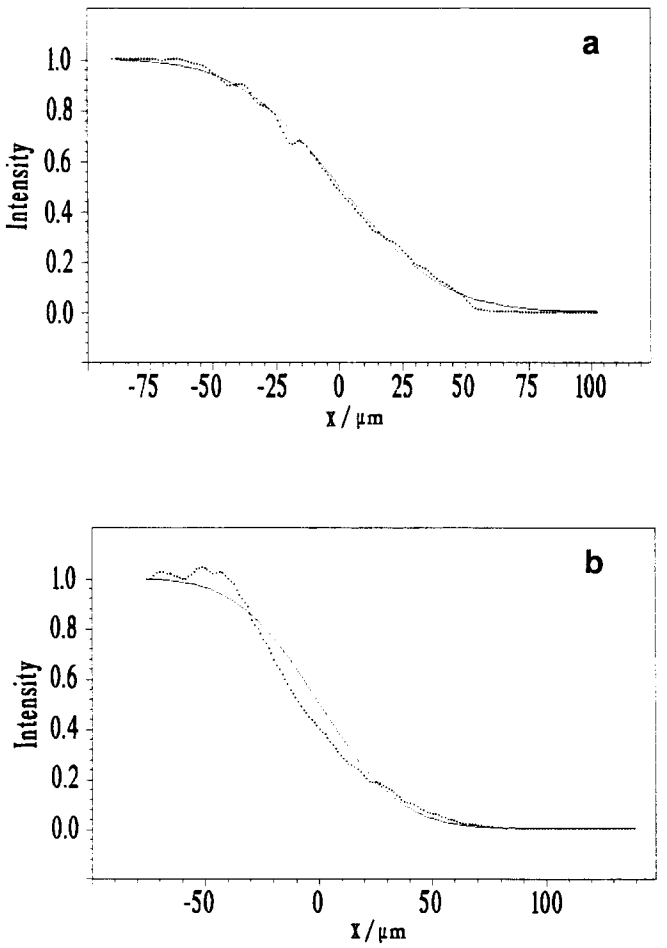

Figure 2 Fluorescence intensity of labelled PS at interface with PCHMA: (a) symmetrical system, PS ($P_n = 491$)–PCHMA ($P_n = 340$), $T = 170°C$, $t = 6.30 \times 10^5$ s; (b) unsymmetrical system, PS ($P_n = 1900$)–PCHMA ($P_n = 200$), $T = 180°C$, $t = 9.28 \times 10^5$ s

environment, A similar situation was found in unsymmetrical blends of long PS and short polymethylstyrene chains[12].

The concentration dependence of D obtained in our experiments[11] is not sufficiently accurate to justify publication since the concentration profiles (proportional to the fluorescence light intensity, cf. *Figure 2*) show relatively large fluctuations, which are probably due to inhomogeneities or dust in our optical set-up. However, the mean interdiffusion coefficients averaged over $D(c)$ are estimated to have an accuracy of about $\pm 30\%$. It should be noted that the averaged D values obtained from concentration profiles determined at different times in the same sample fluctuate within about $\pm 20\%$; D values obtained by fitting the concentration profiles with a Gaussian error function differ in most cases by less than 20% from those obtained by averaging over $D(c)$. Our experimental D values are listed in *Table 1*.

Influence of the label

The influence of dye labels on diffusivity can be minimized by increasing the molecular weight if each macromolecule carries one label. The alternative, namely dilution with unlabelled polymer of the same component[13], results in a ternary system with possibly different diffusion coefficients. Thus, we have found that the D value of 2.0×10^{-11} cm^2 s^{-1} obtained at 453 K for the fully labelled PS ($P_n = 188$) and PCHMA ($P_n = 340$) pair was reduced to 0.8×10^{-11} cm^2 s^{-1} in a sample

Table 1 Average interdiffusion coefficients D (10^{-11} cm^2 s^{-1}) in PS–PCHMA blends at 453 K

	P_n (PCHMA)	
P_n (PS)	200	340
170	–	2.0
188	6.3	2.0
491	4.2	1.6
750	1.2	<0.5[a]
1900	1.3	<0.5[a]

[a] Out of measuring range

where the labelled PS was diluted with two-thirds of unlabelled PS. One should expect that this effect becomes smaller on further dilution provided the mobilities of labelled and unlabelled PS are equal. In order to test this influence we have investigated the PS ($P_n = 1900$) and PCHMA ($P_n = 200$) pair at 453 K with different statistically labelled PS samples. We obtained D values of 0.43, 1.3 and 1.0×10^{-11} cm^2 s^{-1} for samples with an average of 125, 250 and 500 monomers per label, respectively. Thus, we should expect an influence of the label in systems where the number of monomers per label is smaller than about 200.

Molecular-weight dependence

The D values for different molecular weights shown in *Table 1* have qualitatively the expected behaviour in that the largest D value is obtained for the shortest chains of both components and D decreases with increasing chain lengths. A quantitative evaluation seems impossible at present since the experimental accuracy is too low (about $\pm 30\%$) and we have too little information on the tracer diffusion coefficients and the Flory interaction parameter χ, which may also be molecular-weight-dependent.

Temperature dependence

In *Figure 3*, the temperature dependence of inter- and tracer diffusion is shown for the system PS ($P_n = 491$)–PCHMA ($P_n = 340$). The average interdiffusion coefficient

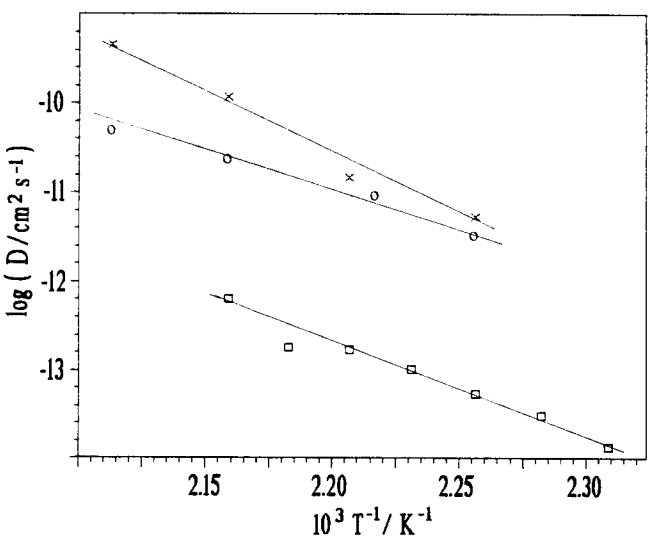

Figure 3 Temperature dependence of diffusion coefficients: (×) interdiffusion coefficient in blend of PS ($P_n = 491$) and PCHMA ($P_n = 340$); (□) tracer diffusion coefficient of labelled PS in the same blend; (○) tracer diffusion coefficient of labelled PS ($P_n = 500$) in a blend with PS ($P_n = 350$)

D was determined as described above. The tracer diffusion coefficient D^*_{PS} was measured in a 1:1 blend by forced Rayleigh scattering using a PS tracer labelled with a photochromic dye label (*o*-nitrostilbene derivative) as in our previous studies on polymer diffusion[14]. For comparison, we also show D^*_{PS} in a pure PS blend of similar chain lengths where PCHMA is replaced by PS. Whereas the slopes of the Arrhenius plots appear reasonable, it is rather surprising that D^*_{PS} in the PS–PCHMA blend is so far below the interdiffusion coefficient. Though it is well known[8,15–17] that D can be much larger than D^* in compatible blends characterized by a negative Flory–Huggins parameter χ, a difference of two decades implies large values of $|\chi|$. However, we know that $|\chi|$ must be very small in our case since we have observed demixing in a blend of PCHMA with deuterated PS, indicating that $|\chi| \lesssim 10^{-3}$ in the protonated system[18]. Let us discuss the consequences of $D \approx 10^2 D^*_{PS}$ and $|\chi| \lesssim 10^{-3}$ from the viewpoint of the 'slow mode' and 'fast mode' models relating the interdiffusion coefficient D with the tracer diffusion coefficients D^*_A and D^*_B in a blend of polymers A and B[8,16,17]:

$$D = \Lambda_0 S(0)^{-1} \tag{3}$$

$$S(0)^{-1} = (N_A \Phi_A)^{-1} + (N_B \Phi_B)^{-1} - 2\chi \tag{4}$$

$$\Lambda_0^{slow} = [(\Phi_A N_A D^*_A)^{-1} + (\Phi_B N_B D^*_B)^{-1}]^{-1} \tag{5}$$

$$\Lambda_0^{fast} = \Phi_A \Phi_B (\Phi_B N_A D^*_A + \Phi_A N_B D^*_B) \tag{6}$$

Here $S(0)$ is the static structure factor at zero wavevector $q=0$, and Φ_i and N_i are the volume fraction and the degree of polymerization of component i (A or B), respectively. If we insert $\Phi_A = \Phi_B = 0.5$, $N_{PS} = 491$, $N_{PCHMA} = 340$, $D/D^*_{PS} = 100$ and $|\chi| \lesssim 10^{-3}$ in these equations, we obtain for the 'slow mode' model the unphysical result $D^*_{PCHMA} < 0$ and for the 'fast mode' model the very large ratio $D^*_{PCHMA}/D^*_{PS} \gtrsim 195$. The 'fast mode' prediction implies that D^*_{PCHMA} is of the order of the interdiffusion coefficient D. On the other hand D^*_{PS} is reduced by two decades in the blend in comparison with the pure PS system (see *Figure 3*). This result is hard to reconcile with the usual considerations relating the molecular mobilities of the components in polymer blends. We have measured self-diffusion in a 1:1 mixture of PS ($P_n = 145$) and PCHMA ($P_n = 60$) using an n.m.r. field-gradient technique[19]. At 200°C, the spin-echo decay functions were dominated by the short spin-relaxation times $T_2 < 1$ ms, and little influence of diffusion was detected at the magnetic gradient of 23.9 T m^{-1} used. At 216°C, the diffusional part of the echo decay could be fitted with two exponentials, where the fast diffusion coefficient D_{fast} was within $(4\text{–}8) \times 10^{-9}$ cm^2 s^{-1} and D_{slow} within $(1\text{–}2) \times 10^{-9}$ cm^2 s^{-1}, possibly with a minor contribution below 1×10^{-9} cm^2 s^{-1}. At 244°C, a corresponding fit yielded $D_{fast} \approx 2 \times 10^{-8}$ cm^2 s^{-1} and D_{slow} within $(1.5\text{–}5) \times 10^{-9}$ cm^2 s^{-1}. At higher temperature, polymer degradation was deduced from the fact that D increased at constant T[20]. If we attribute D_{slow} to PS diffusion, this is indeed below the values expected from extrapolations of previous data in pure PS[9]. However, the difference is less than for the higher molecular weights shown in *Figure 3*. On the other hand, D_{fast} is below the tracer diffusion coefficient expected from the estimate $D^*_{PCHMA} \gtrsim 200 D^*_{PS}$ discussed above. Perhaps, the smaller difference is related to the small degree of polymerization ($P_n = 60$) of PCHMA, but further experiments are necessary in order to substantiate the unexpected difference of component mobilities in PCHMA–PS.

CONCLUSIONS

Fluorescence densitometry can be used as a practicable alternative to i.r. densitometry[7,13,21] for determining interdiffusion coefficients in polymer blends. The spatial resolution is somewhat better[21], owing to the smaller wavelength. However, the problem of preparing a good initial step-function concentration profile at the polymer–polymer interface is comparable in both methods. Labelling of one polymer component with a fluorescent dye is sometimes preferable to deuteration if large isotope effects influence interdiffusion in H/D blends. For the PS–PCHMA system we have observed phase separation in blends of PCHMA with deuterated PS. Labelling of PS with a fluorescent dye has a negligible influence on interdiffusion provided the labelled chains have more than about 200 monomer units per label molecule. Whereas the molecular-weight dependence of interdiffusion in the PS–PCHMA system showed no unexpected behaviour, the tracer diffusion coefficients of PS were found to be surprisingly low (see *Figure 3*). This result cannot be understood in terms of the 'slow mode' model and implies fast PCHMA tracer diffusion if the 'fast mode' model is applied to relating tracer- and interdiffusion[8,16,17].

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