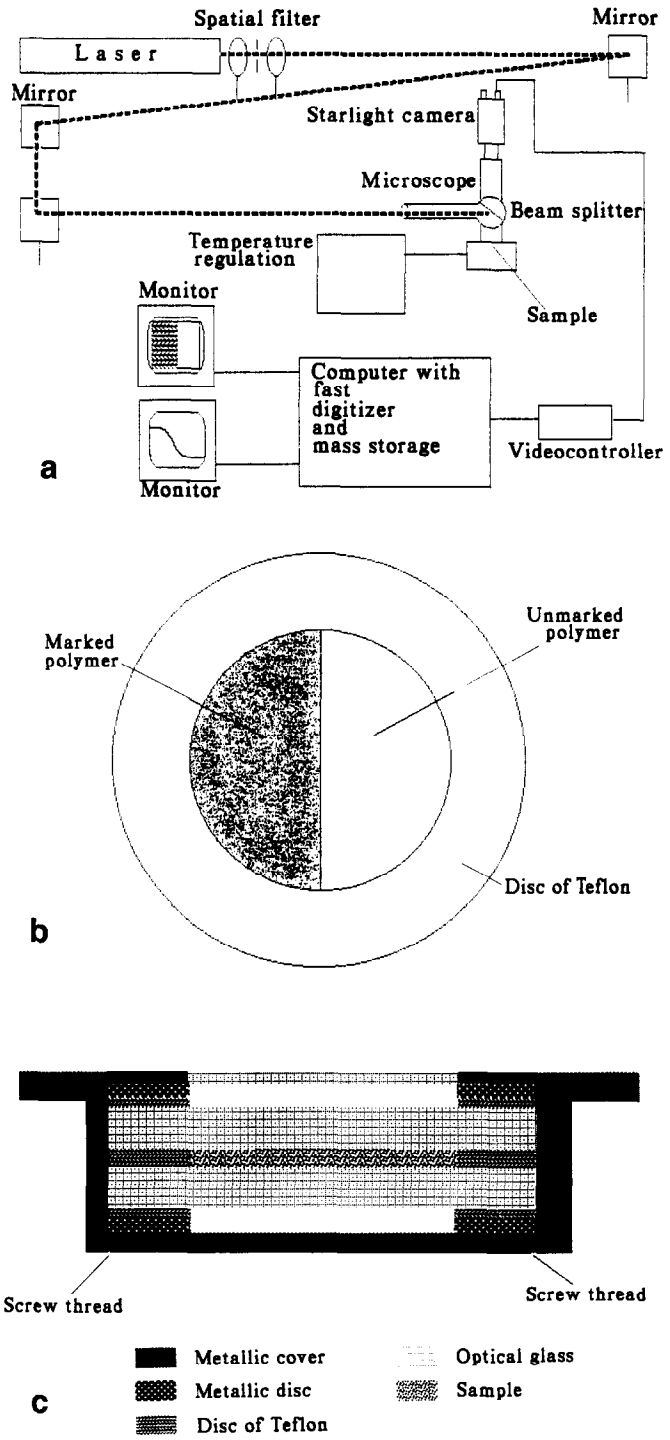

Figure 1 Fluorescence densitometry: (a) experimental set-up; (b) sample, front view; (c) sample, side view

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

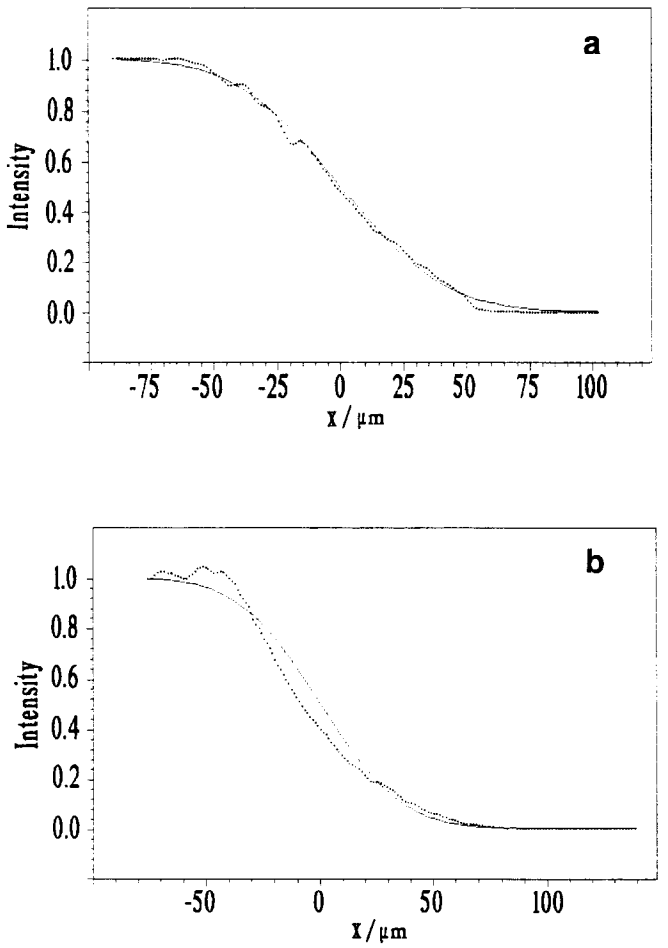

Figure 2 Fluorescence intensity of labelled PS at interface with PCHMA: (a) symmetrical system, PS ($P_n = 491$)–PCHMA ($P_n = 340$), $T = 170°C$, $t = 6.30 \times 10^5$ s; (b) unsymmetrical system, PS ($P_n = 1900$)–PCHMA ($P_n = 200$), $T = 180°C$, $t = 9.28 \times 10^5$ s

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

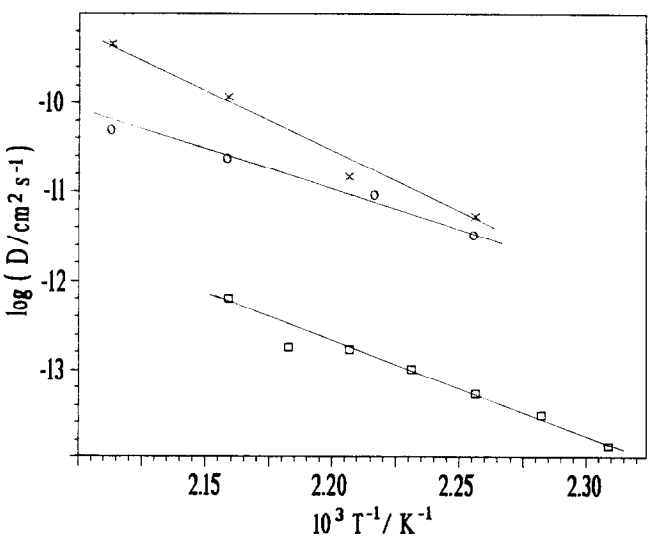

Figure 3 Temperature dependence of diffusion coefficients: (×) interdiffusion coefficient in blend of PS ($P_n = 491$) and PCHMA ($P_n = 340$); (□) tracer diffusion coefficient of labelled PS in the same blend; (○) tracer diffusion coefficient of labelled PS ($P_n = 500$) in a blend with PS ($P_n = 350$)