Interdiffusion in blends of polystyrene and polymethylstyrene studied by light scattering after temperature jumps across the phase boundary

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We describe a simple light scattering set-up for measuring interdiffusion coefficients D in polymer blends by generating spinodal decomposition and subsequent dissolution after temperature jumps across the phase boundary. In blends of polystyrene and polymethylstyrene (random copolymer of 60% *m*-methylstyrene and 40% *p*-methylstyrene) D values were obtained between 10^{-11} and $10^{-15}\,\mathrm{cm^2\,s^{-1}}$ at temperatures up to 50 K above the upper critical solution temperature. The results are discussed in relation to tracer diffusion in the same system.

(Keywords: light scattering; phase boundary; interdiffusion; blends; polystyrene; polymethylstyrene)

INTRODUCTION

There is a sizeable literature on temperature jumps into the two-phase region where the time evolution of spinodal decomposition in polymer blends is investigated by light scattering[1–5]. Essentially, the same technique can be applied to studies of interdiffusion in the one-phase regime. Here, one also starts the experiment by performing a T jump from the one-phase into the two-phase regime and observes the increase of light scattering due to spinodal decomposition. This temperature is maintained until sufficient scattering intensity (for detection) is available from the concentration fluctuations. After this preparation of the initial condition for the diffusion experiment, a second T jump is made back into the one-phase region to a temperature T where the interdiffusion coefficient $D(T)$ of the polymer blend is to be measured. Now, the concentration fluctuations originating from spinodal decomposition provide a non-equilibrium state that relaxes towards equilibrium with a time constant $\tau(T)$ related to $D(T)$ by equation (2) as discussed further below. This relaxation process can be monitored by light scattering since the concentration fluctuations are proportional to corresponding fluctuations in the index of refraction.

Previously, interdiffusion coefficients in blends of polystyrene and poly(vinyl methyl ether) have been measured by this method[6,7], but the experiments were not optimized for interdiffusion studies. In the present investigation, we have expended considerable effort to achieve high accuracy, a wide temperature range and a wide dynamic range of accessible interdiffusion coefficients. The potential of the technique is critically discussed in comparison with other methods for investigating interdiffusion in polymer blends. The system, mixtures of polystyrene (PS) and polymethylstyrene (PMS), has been investigated previously in our laboratory by forced Rayleigh scattering[8,9] and photon correlation spectroscopy[10,11]. The components can be obtained with narrow molecular-weight distributions by anionic polymerization. The glass transition temperatures are close for both components, $T_g = 91°\mathrm{C}$ for PMS and 100°C for PS, and a sufficiently wide one-phase region is available above a lower miscibility gap[8]. Since tracer diffusion coefficients of both components have been determined in PS–PMS blends[9,11], the measurement of interdiffusion coefficients should provide a test of alternative theoretical predictions relating tracer and interdiffusion in polymer blends[12–14]. Furthermore, the slowing down of interdiffusion on approaching the critical decomposition temperature T_C is investigated in the present paper.

EXPERIMENTAL

The experimental set-up is sketched in *Figure 1*. A He–Ne laser ($\lambda = 633\,\mathrm{nm}$) is used as a light source. The sample is contained in a heated metal block with narrow openings, 2 mm diameter for the incoming and 19 mm for the scattered laser beam, in order to guarantee a homogeneous temperature over the whole sample. The sample holder is essentially the same as that used in our fluorescence densitometry experiments[15]. The halo of scattered light is observed from a ground-glass plate with a sensitive video camera (Burle Electronix, model TC 654 X). The intensity is digitized and processed using a fast microcomputer. In a typical experiment, the sample is annealed for about 1 day at a temperature T_0 well above the upper critical solution temperature (*UCST*) T_s

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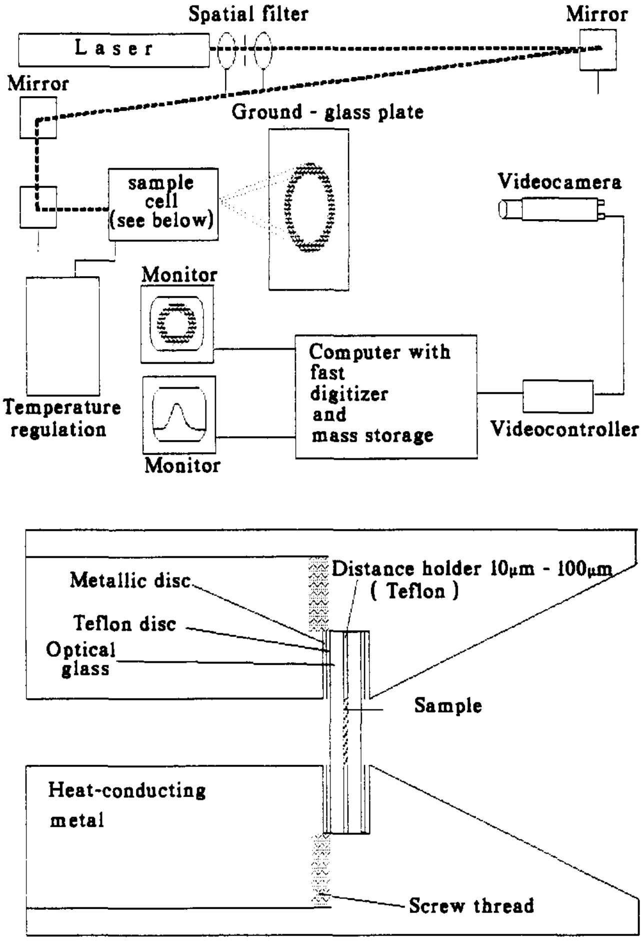

Figure 1 Experimental set-up (above) and sample cell (below)

Table 1 Characterization of polymer samples

Sample	Numer-average molecular weight M_n	Molecular-weight distribution index, M_w/M_n
Polystyrene	15000	1.05
	32200	1.03
	34320	1.03
Polymethylstyrene	38300	1.05
	60300	1.06
	380000	1.07

in order to relax possible inhomogeneities or tensions from sample preparation. After the first T jump to T_1 about 10–15 K below T_s, spinodal decomposition causes the development of a halo where the intensity maximum of the scattered light shifts to lower angles; the scattering intensity also increases[1–7]. In the second T jump, the sample is heated to some temperature T where the diffusive decay of the concentration fluctuations is detected via the decay of the scattering halo. The limitation of the range of accessible temperatures and diffusion constants is discussed along with the results in the next section.

The samples were prepared from dilute solutions (~0.3%) of PS and PMS in tetrahydrofuran by slowly removing the solvent and subsequently drying under vacuum at about 30 K above the glass transition temperature for 1 day. The resulting film was powdered and pressed using a modified i.r. pellet press into a cylinder of 8.5 mm diameter and about 0.1 mm thickness. The polymer samples listed in *Table 1* were prepared by anionic polymerization[8]. The polymethylstyrene (PMS) sample was a random copolymer from a mixture of 60 wt% *m*-methylstyrene and 40 wt% *p*-methylstyrene purchased from Merck (Darmstadt).

RESULTS AND DISCUSSION

We first discuss the procedure for obtaining an interdiffusion coefficient D from light scattering data by describing a typical example, namely, a critical mixture of PS ($P_n = 145$) and PMS ($P_n = 3248$). Here, the *UCST* is $T_s = 182.5°C$ and the critical composition is assumed to be given by the Flory–Huggins expression[16] $\Phi_{PS} = [1 + (N_{PS})^{0.5}]^{-1} = 0.82$. In *Figure 2*, we show a selection of scattering curves recorded after a T jump from 170 to 185°C. The intensity for each angle is integrated over the radially symmetric halo (spinodal ring) of scattered light (*Figure 1*). Typical results are shown in *Figure 2*. It is expected that the decay at short times is influenced by non-Fickian transport but the long-time behaviour is given by an exponential decay of the dynamic structure factor $S(q,t)$[6,7]:

$$S(q,t) = S(q,0)\exp(-t/\tau) \tag{1}$$

$$\tau^{-1} = Dq^2 \tag{2}$$

which is related to the scattering intensity $I(q,t)$ by[7]:

$$I(q,t) = I_\infty(q) + I_0(q)\exp(-2t/\tau) \tag{3}$$

$q = (4\pi n/\lambda)\sin(\theta/2)$ is the value of the wavevector, where θ is the scattering angle, λ the (air) wavelength and n the polymer index of refraction.

Figure 3 shows a fit of an exponential to the long-time limit of $I(q,t)$ determined at $q = 12900\,\mathrm{cm}^{-1}$ corresponding to $\theta = 7.46°$. (It should be noted that the flat cell geometry of our set-up (*Figure 1*) results in the relation:

$$\theta = \sin^{-1}\{n\sin[2\sin^{-1}(\lambda q/4\pi n)]\}$$

between q and the scattering angle θ.)

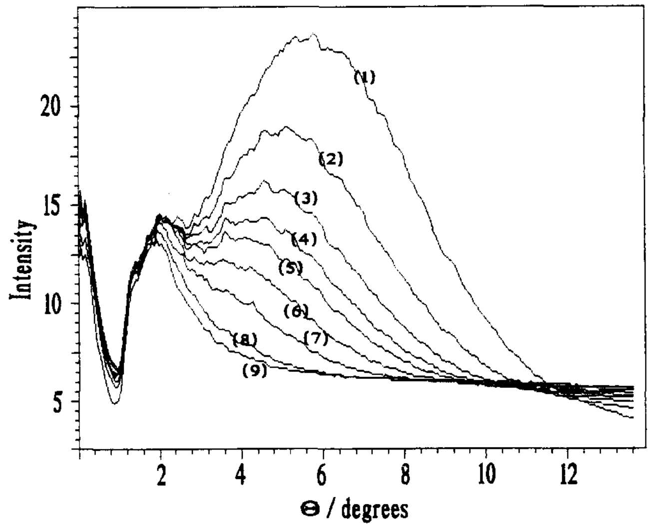

Figure 2 Scattering intensity (in arbitrary units) drawn *versus* the scattering angle θ for different annealing times after the temperature jump into the one-phase region at $T = 185°C$ for a blend of 82 wt% PS ($P_n = 145$) and 18 wt% PMS ($P_n = 3248$). The annealing (developing) times for curves (1) to (9) are 450, 2250, 4500, 6750, 9000, 13500, 22500, 45000 and 67500 s, respectively

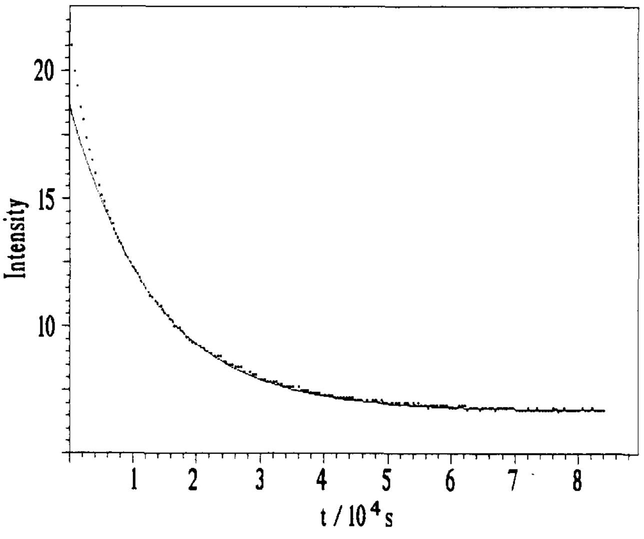

Figure 3 Scattering intensity (in arbitrary units) drawn *versus* the annealing time t at $\theta = 7.45°$ for the system shown in *Figure 2*

There are three possible sources for deviations from exponential decay during the initial time period. First, spinodal decomposition gives rise to fluctuations that imply large changes of the concentration (and the concentration-dependent PS and PMS mobilities[9,11]) over very small distances usually described by a gradient term in the local chemical potential difference[17]. Therefore, one should expect non-Fickian decay until a state sufficiently close to equilibrium at the diffusion temperature in the one-phase region is attained. Secondly, some time ($t \lesssim 1000$ s) is needed after the T jump before a constant sample temperature is reached. Thirdly, thermal expansion during the temperature change can result in convectional flow resulting in deviations from radial symmetry of the scattering halo. It is difficult to discriminate between the different contributions to the deviations from the exponential function. However, we had no difficulties in obtaining stable fits of the long-time regime to an exponential as shown in *Figure 3*. The resulting τ values at different scattering angles were found to be proportional to q^{-2} in the q range relevant to our experiments, as demonstrated in *Figure 4*. This justifies the analysis in terms of the interdiffusion coefficient D from equations (1)–(3).

In *Figure 5*, we show the D values determined in three different PS–PMS mixtures. In all cases, 'critical slowing down'[7] was observed on approaching the *UCST* at 425, 455 and 465 K, respectively. In the symmetric mixture, PS ($P_n = 330$)–PMS ($P_n = 330$), the smallest diffusion coefficient, $D = 1.4 \times 10^{-15}$ cm^2 s^{-1} was determined only about 0.5 K above T_s. The D values deviate from a high-temperature Arrhenius behaviour in a range up to about 15 K above T_s. This is in qualitative agreement with the findings of Momper[18] in mixtures of poly(ethylmethylsiloxane) and poly(dimethylsiloxane). However, we could perform no quantitative comparison with theories of critical dynamics[19], which requires accurate static scattering functions (see below). The broken line shown in *Figure 5* indicates the diffusion coefficients obtained by analysing the decay of concentration fluctuations in a 1:1 mixture of PS ($P_n = 72$) and PMS ($P_n = 70$) by photon correlation spectroscopy[11]. Apparently, the D values are far below the interdiffusion coefficients expected for this short-chain system and they are attributed to 'slow mode' fluctuations[10,11], which are also observed in supercooled low-molecular-weight liquids[20].

The interdiffusion coefficient D can be related to the tracer diffusion coefficients D_A^* and D_B^* of polymer components A and B by alternative 'slow mode' and 'fast mode' models[12–14]:

$$D = \Lambda_0 S(0)^{-1} \tag{4}$$

$$S(0)^{-1} = 2(\chi_s - \chi) = (N_A \Phi_A)^{-1} + (N_B \Phi_B)^{-1} - 2\chi \tag{5}$$

$$\Lambda_0^{\text{slow}} = [(\Phi_A N_A D_A^*)^{-1} + (\Phi_B N_B D_B^*)^{-1}]^{-1} \tag{6}$$

$$\Lambda_0^{\text{fast}} = \Phi_A \Phi_B (\Phi_B N_A D_A^* + \Phi_A N_B D_B^*) \tag{7}$$

N_j, Φ_j and D_j^* are the degree of polymerization, the volume fraction and the tracer diffusion coefficient of the components $j = $ A, B, respectively; χ_s and χ are the Flory–Huggins parameters at the spinodal and the temperature T, respectively.

We have determined the tracer diffusion coefficients

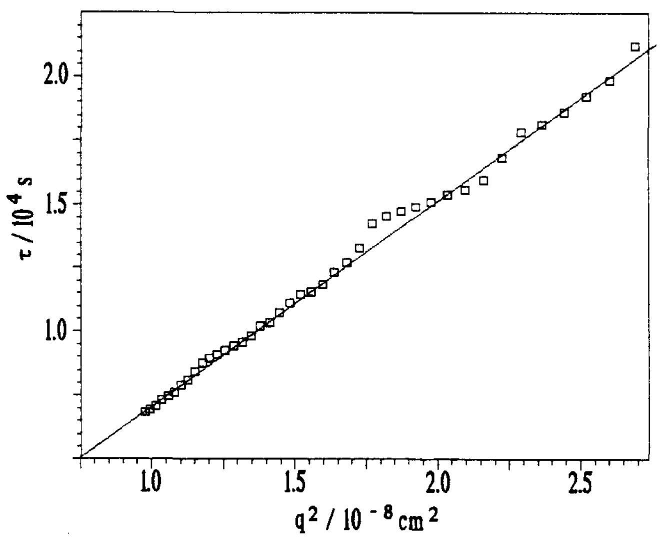

Figure 4 Decay times τ obtained from exponential fits of scattering intensity decay curves (see *Figure 3*) for the system shown in *Figure 2*

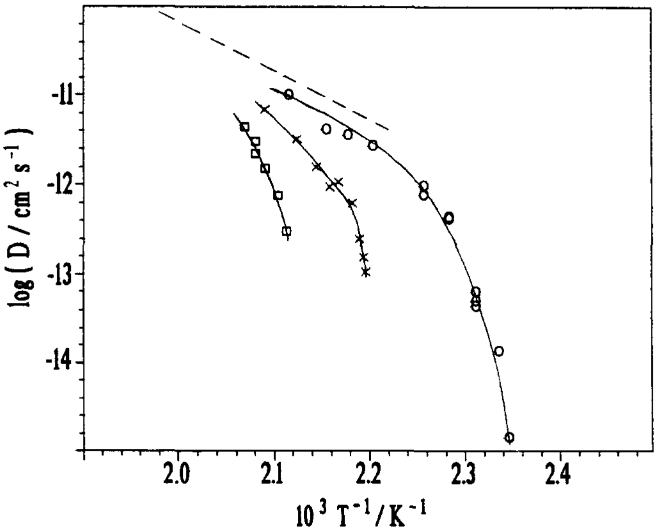

Figure 5 Temperature dependence of interdiffusion coefficients D determined in PS–PMS blends: (○) 50 wt% PS ($P_n = 330$)–50 wt% PMS ($P_n = 330$); (×) 82 wt% PS ($P_n = 145$)–18 wt% PMS ($P_n = 3248$); (□) 50 wt% PS ($P_n = 310$)–50 wt% PMS ($P_n = 520$). The full curves are a guide to the eye. The broken line corresponds to the 'slow mode' in a 1:1 blend of PS ($P_n = 70$) and PMS ($P_n = 72$); see text

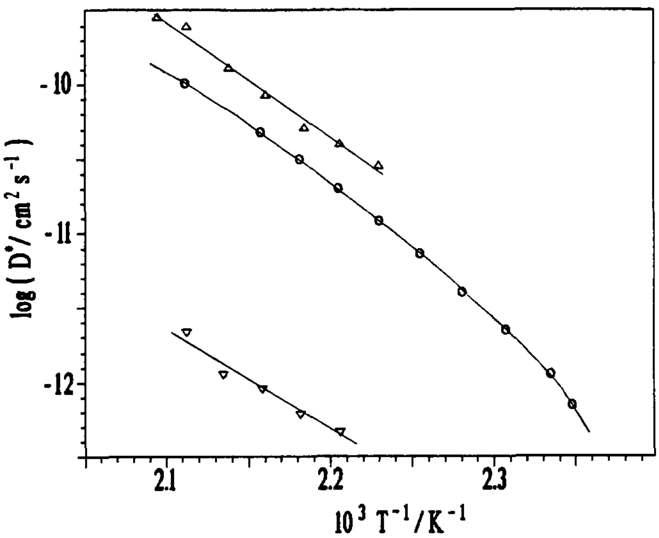

Figure 6 Temperature dependence of tracer diffusion coefficients D^* in PS–PMS blends: (Δ, ∇) D^* of PS ($P_n = 145$) and PMS ($P_n = 3245$), respectively, in the unsymmetrical blend (× in *Figure 5*); (○) equal D^* values of PS ($P_n = 330$) and PMS ($P_n = 330$) in the symmetrical blend (○ in *Figure 5*). The full curves are a guide to the eye

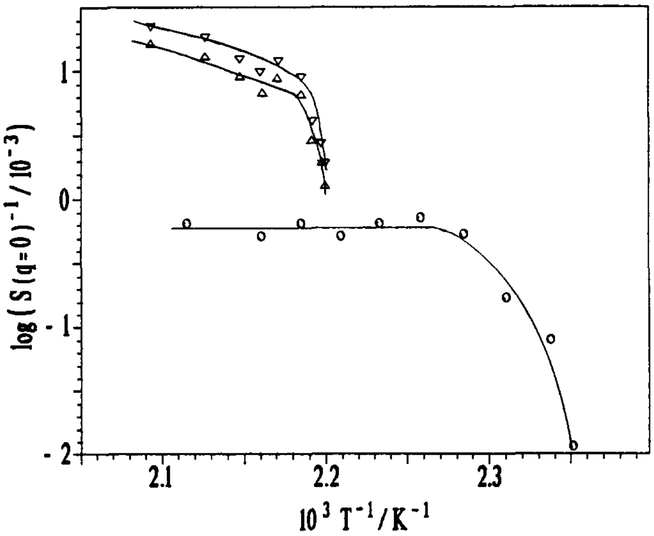

Figure 7 Inverse static structure factor $S(q=0)^{-1}$ determined from equations (4)–(7) (see text): (∇, △) results from 'slow mode' and 'fast mode' model, respectively, for unsymmetrical blend; (○) results for symmetrical blend

D^*_{PS} and D^*_{PMS} in the unsymmetrical mixture PS ($P_n = 145$)–PMS ($P_n = 3248$) using the forced Rayleigh scattering method applied in our previous work[9,11].

The results are shown in *Figure 6* along with the values $D^*_{PS} \approx D^*_{PMS}$ for the symmetric system estimated from our previous measurements in this molecular-weight and temperature range[9,11,21]. From these results we have calculated Λ_0^{slow} and Λ_0^{fast} (equal for the symmetrical system) and have evaluated the static structure factor $S(0)$ at $q = 0$ from equation (4) using the D values from *Figure 5*. The results shown in *Figure 7* indicate a sizeable difference between the slow and fast models, which should allow us to discriminate between both alternatives if $S(0)$ or the χ parameter could be determined independently. We know from neutron scattering measurements in PS–PMS mixtures[21] that the N dependence of $S(0)$ can only be described by equation (5) if the χ parameter is also assumed to depend upon N. From these results, we doubt whether it is possible to obtain sufficiently accurate $S(0)$ values from neutron scattering for a meaningful comparison with the data in *Figure 7*, though the isotope effect of demixing is relatively small if one component is deuterated[22]. It is also possible to determine $S(0)$ by extrapolation to $q = 0$ from static light scattering at equilibrium in the one-phase system[18,19,23]. Unfortunately, we were unable to determine $S(0)$ with the set-up of *Figure 1*. It should be noted that the accurate $S(0)$ values of Fischer and collaborators were obtained with polymer blends of much lower viscosity, which could be prepared free of dust in cylindrical samples[18,19,23]. It is remarkable that the temperature dependence of $S(0)$ as shown in *Figure 7* is rather different for the two blends studied. This is probably related to the assumption that Λ_0 is given by equation (6) or (7) whereas it depends upon the correlation length in the regime of critical slowing down[19,24–26].

Finally, let us briefly compare the T jump method applied above with other techniques[14] for measuring interdiffusion in polymer blends in a range of up to 50 K above a *UCST* or below a *LCST*. There is no doubt that the direct measurement of the dynamics of concentration fluctuations by photon correlation spectroscopy is appropriate, since it also provides the static structure factor $S(0)$[19,23]. However, this technique is restricted to (sufficiently) fluid systems at temperatures far above the glass transition since otherwise the predominance of slow mode scattering[10,11,20] (cf. *Figure 5*) precludes interdiffusion studies. I.r. densitometry, forward recoil scattering (He^{2+}) and neutron scattering techniques require an at least partially deuterated polymer component, which may have different miscibility behaviour from the corresponding hydrogenated compounds. X-ray and EM techniques require one polymer component with electron-rich elements to provide sufficient contrast. All techniques[14,15] where a concentration profile is determined at the interface between the interdiffusing components provide no information on $S(0)$, which is necessary for quantitative analysis in the vicinity of a critical point.

CONCLUSIONS

The light scattering analysis of phase dissolution after temperature jumps across the phase boundary can be used as a simple and accurate method for measuring interdiffusion coefficients in the one-phase region above a *UCST* or below a *LCST* in polymer blends. We have investigated interdiffusion in blends of polystyrene and polymethylstyrene and have compared the results with tracer diffusion coefficients in the same system. The results should, in principle, allow discrimination between alternative theoretical predictions relating inter- and tracer diffusion in polymer blends. However, before this is possible, an independent determination of the static structure factor in the long-wavelength limit is required.

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REFERENCES

1 Hashimoto, T., Kumaki, J. and Kawai, H. *Macromolecules* 1983, **16**, 641
2 Snyder, H., Meakin, P. and Reich, S. *Macromolecules* 1983, **16**, 787
3 Inoue, T., Ougizawa, T., Yasuka, O and Migasuka, K. *Macromolecules* 1985, **18**, 57
4 Wang, Z.-Y., Konno, M. and Saito, S. *J. Chem. Phys.* 1989, **90**, 1281
5 Bates, F. S. and Wiltzius, P. *Macromolecules* 1989, **91**, 3258
6 Kumaki, J. and Hashimoto, T. *Macromolecules* 1986, **19**, 763
7 Sato, T. and Han, C. C. *J. Chem. Phys.* 1988, **88**, 2057
8 Antonietti, M., Lang, S. and Sillescu, H. *Makromol. Chem. Rapid Commun.* 1986, **7**, 415
9 Lang, S. and Sillescu, H. *Makromol. Chem.* 1989, **190**, 797
10 Antonietti, M., Ehlich, D., Sillescu, H. and Wesselmann, M. *Prog. Colloid Polym. Sci.* 1989, **80**, 83
11 Wesselmann, M. and Sillescu, H. *Makromol. Chem.* 1991, **192**, 709
12 Brochard, F., Jouffroy, J. and Levinson, P. *Macromolecules* 1983, **16**, 1638
13 Kramer, E. J., Green, P. and Palmstrom, C. J. *Polymer* 1984, **25**, 473
14 Binder, K. and Sillescu, H. in 'Encyclopedia of Polymer Science and Engineering', Suppl. Vol., 2nd Edn (Eds Mark, Bikales, Overberger and Menges), Wiley, New York, 1989, pp. 297–315 and references therein
15 Best, M. and Sillescu, H. *Polymer* 1992, **33**, 5245
16 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979
17 Binder, K. *J. Chem. Phys.* 1983, **79**, 6387
18 Momper, B. Dissertation, Universität Mainz, 1989
19 Meier, G., Momper, B. and Fischer, E. W. to be published
20 Gerharz, B., Meier, G. and Fischer, E. W. *J. Chem. Phys.* 1990, **92**, 7110
21 Wesselmann, M., Dissertation, Universität Mainz, 1988
22 Lang, S., Dissertation, Universität Mainz, 1986
23 Brereton, M. G., Fischer, E. W., Fytas, G. and Murschall, U. *J. Chem. Phys.* 1987, **87**, 6144
24 Kawasaki, K. in 'Phase Transitions and Critical Phenomena', Vol. 5a (Eds C. Domp and M. S. Green), Academic Press, New York, 1976
25 Bates, F. S., Wiltzius, P. and Heffner, W. R. *Phys. Rev. Lett.* 1988, **60**, 1538
26 Bates, F. S. and Wiltzius, P. *J. Chem. Phys.* 1989, **91**, 3258