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Dynamics of Composition Fluctuations in Statistical Copolymer Solutions

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ABSTRACT: Dynamic properties of styrene−methyl methacrylate (MMA) statistical copolymer solutions in benzene, a solvent isorefractive with MMA, were studied by dynamic light-scattering spectroscopy (DLS) and by pulsed-field-gradient NMR (PFG-NMR). Two separate dynamic processes were found from the DLS results in the semidilute region. The fast process was related to the cooperation diffusion mode. The slow diffusive process was attributed to the dynamics of composition fluctuations. The diffusion coefficient of the slow process has the magnitude similar to the self-diffusion coefficient determined by PFG-NMR. Dynamic property of the slow "polydispersity" mode were qualitatively interpreted in terms of the theory developed for diblock copolymers.

Introduction

In 1986, Akcasu et al.[1] and Benmouna et al.[2] published a theory of dynamic light scattering (DLS) from ternary mixtures of two homopolymers and a solvent based on the random phase approximation. The main result of the theory is a prediction of the existence of two relaxation processes, which were interpreted as cooperative and interdiffusion modes. The physical meaning attributed to the two modes that characterize the dynamic behavior of ternary polymer systems has been discussed by Akcasu and co-workers.[3,4] The theory was subsequently extended to homogeneous semidilute solutions of monodisperse diblock copolymers.[5,6] In copolymer solutions the first dynamic mode is the cooperative diffusion of the physical network, identical to that observed in semidilute homopolymer solutions.[7,8] The corresponding component of the scattered light intensity I_c and the cooperative diffusion coefficient D_c for good solvents and $q\xi \ll 1$ are given by

$$I_c \propto (n_c^{\,2} - n_s^{\,2})^2 \Phi^{-0.3} \tag{1a}$$

$$D_c \approx k_B T / 6\pi\eta_s \xi \tag{1b}$$

where Φ is the copolymer volume fraction, n_c and n_s are the average refractive indices of the copolymer and the refractive index of the solvent, respectively, η_s is the solvent shear viscosity and ξ is the correlation length. In the semidilute region, I_c should decrease and D_c increase with increasing Φ.

The second internal mode is related to the relative motion of one block with respect to the other and is therefore a characteristic feature of diblock copolymers. In the low-q limit ($q^2R_g^{\,2} \ll 1$) the internal mode is the q-independent relaxation mode. This internal relaxation mode has been experimentally observed both in bulk[9−11] and in semidilute solutions.[12−20]

Dynamic light-scattering (DLS) experiments on disordered diblock copolymer melts[9−11,21,22] and semidilute copolymer solutions[16−20,23−27] revealed the presence of an additional slow diffusion mode. The origin of this mode is related to the dynamics of concentration fluctuations due to the composition polydispersity of copolymers. It was shown[9,17−19,24−27] that these fluctuations relax via a diffusive mechanism of exchange of diblock chains of different composition. For disordered semidilute block copolymer solutions, the scattered intensity, I_h, and the characteristic diffusion coefficient, D_h, of this so-called "heterogeneity" or "polydispersity" mode are respectively given by[17]

$$I_h = (n_A^{\,2} - n_B^{\,2})^2\, \kappa_o N v \Phi / (1 - 2\chi N \kappa_o \Phi^{1.59}) \tag{2a}$$

and

$$D_h = D_s(N,\Phi)\,(1 - 2\chi N \kappa_o \Phi^{1.59}) \tag{2b}$$

where χ is the Flory−Huggins segment−segment interaction parameter, n_i is the refractive index of i-block of the diblock, v is the average segmental volume, N is the total number of segments ($N = \langle N_A + N_B\rangle$), $D_s(N,\Phi)$ is the self-diffusion coefficient of diblock chains in semidilute solutions, and κ_o is a measure of the composition polydispersity of the diblock:

$$\kappa_o = (\langle N_A^{\,2}\rangle\langle N_B^{\,2}\rangle - \langle N_A N_B\rangle^2)/N^2\,\langle(N_A+N_B)^2\rangle \tag{3}$$

Note that a finite κ_o as well as high concentration Φ are necessary for an experimental observation of the polydispersity dynamic mode in block copolymer solutions.

Since random copolymers show polydispersity both with respect to molecular weight and also with respect to chemical composition (composition polydispersity), we anticipated that the above-described heterogeneity mode could also be observed in semidilute solutions of statistical copolymers. It is plausible to expect that the amplitude of the internal relaxational mode, which has been observed in block copolymer melts and solutions, is very low because of the random structure of the copolymers.

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The high molecular weight polydispersity of studied statistical copolymers (M_w/M_n = 2.5−3.5) could be responsible for an additional slow dynamic process in the semidilute solutions.[2] To simulate the effect of polydispersity on the dynamics of semidilute solutions Benmouna et al.[2] theoretically considered the case of a semidilute solution containing two identical polymers differing in their respective molecular weights. Using the random phase approximation they were able to show that two dynamic processes exist in such a system leading to a bimodal autocorrelation function. The cooperative diffusion coefficient and the interdiffusion coefficient could be isolated from the correlation functions. The existence of bimodal time correlation functions was experimentally proven using ternary solutions of two polyisobutylenes in chloroform.[28−30] So far, the slow dynamic mode has not been corroborated for semidilute solutions of polydisperse homopolymers in thermodynamically good solvents.

The above survey indicates that the fast cooperative diffusion mode and the slow mode, which relaxes by translational diffusion and is due to chain-to-chain fluctuations in composition or molecular weight, should dominate the solution dynamics of random copolymers in thermodynamically good solvents. To the best of our knowledge, no experimental analysis of the dynamic behavior of semidilute solutions of statistic copolymers has been published so far.

In this paper, experimental evidence of these two modes in semidilute solutions of styrene (S)−methyl methacrylate (MMA) statistical (S-*s*-MMA) copolymers in benzene is revealed by DLS spectroscopy. Benzene is a solvent isorefractive with MMA, which provides a sufficient optical contrast for styrene. The S-*s*-MMA copolymers were selected because they were frequently studied in the past, and therefore, conditions for their preparation and their properties are quite well known.[31] The slow process was shown to be dominated by the heterogeneity mode. The results of DLS measurements are compared with the self-diffusion results obtained by means of pulsed field gradient NMR. Theoretical expressions for the amplitude and relaxation rate of the heterogeneity mode was used to qualitatively describe the observed slow dynamic process.

Experimental Section

Sample Preparation. Both the monomers styrene (S) and methyl methacrylate (MMA) were purified by removing the inhibitor and were mixed together to obtain desired initial composition ranging from 10 to 50 vol % of styrene. The reaction mixtures were filtered through PTFE membrane filters with the 0.2 μm pore diameter into ampules, free oxygen in three freeze−thaw cycles, and sealed under vacuum. The polymerization was initiated thermally[32] by heating the samples for 18 h at 120 °C followed by 8 h at 150 °C. On completion of the polymerization, the ampules were slowly cooled to room temperature. The conversions exceeded 98%.

Semidilute solutions of the copolymers in benzene were prepared from filtered dilute solutions with copolymer volume fraction $\Phi = 0.02$ directly in the dust-free light-scattering cells by slow evaporation of benzene. The concentration of solutions was determined by weighting the resulting solutions.

Molecular-weight distribution of copolymers was determined by the GPC method in tetrahydrofuran solutions at 25 °C. All copolymers used in this study showed a single broad M_w distribution. The molecular characteristics of the copolymer samples are given in Table 1.

Table 1. Sample Characteristics

code	composition vol % of styrene	$M_w \times 10^5$, g mol^{-1}	M_w/M_n
sm1/9	10	16.4	3.5
sm2/8	20	9.0	3.3
sm3/7	30	5.9	3.1
sm4/6	40	4.9	2.8
sm5/5	50	4.3	2.7

Dynamic Light Scattering (DLS). Polarized DLS measurements were made in the angular range of 30−120° using a light scattering apparatus equipped with an Ar ion laser (λ = 514.5 nm) and an ALV 5000, multi-τ autocorrelator covering approximately 10 decades in delay time *t*. By using the assumption of homodyne scattering and the Siegert relation the electric field autocorrelation functions $g^{(1)}(t)$ were obtained and fitted to a sum of single exponential and stretched exponential functions:

$$g^{(1)}(t) = A_f \exp(-[t/\tau_f]) + A_s \exp(-[t/\tau_s]^{b_s}) \tag{4}$$

where τ_i are characteristic decay times, i stands for the subscripts f (fast) and s (slow), A_i relative scattering amplitudes; $A_f + A_s = 1$. The exponent b_s ($0 \le b_s \le 1$) is a measure of the width of the corresponding distribution of the relaxation times τ; the smaller the value of b_s, the broader the distribution is. The DLS results are presented through the paper using the normalized intensity autocorrelation functions $g^{(2)}(t) = (g^{(1)}(t))^2$.

The mean relaxation time, τ_{sm} of the slow mode is given by

$$\tau_{sm} \equiv (\tau_s/b_s)\,\Gamma(1/b_s,) \tag{5}$$

where $\Gamma(1/b_s)$ is the gamma function. The apparent diffusion coefficients, D_i, were calculated from the equations

$$D_f = 1/\tau_f\, q^2 \tag{6a}$$

$$D_s = 1/\tau_{sm}\, q^2 \tag{6b}$$

where $q = 4\pi n_o[\sin(\theta/2)/\lambda_o]$ is the magnitude of the scattering vector, with n_o the refractive index of the solvent and λ_o the wavelength of the incident light.

Static Light Scattering (SLS). Static light scattering measurements were performed using a light-scattering goniometer equipped with a vertically polarized Ar ion laser (λ = 514.5 nm) in the angular range of 30−150°. The scattered intensity I_h were calculated from the total scattering intensity, I_t, using the relation

$$I_h = I_t\, A_s/(A_f + A_s) \tag{7}$$

I_t data were corrected for the change in scattering volume.

Pulsed-Field-Gradient NMR (PFG NMR). The pulsed-field-gradient NMR measurements were carried out with a custom-built spectrometer at a resonance frequency of 400 MHz.[33] For the NMR measurements, the polymer was dissolved in fully deuterated benzene to suppress the NMR signal of the solvent.

In PFG-NMR, the self-correlation function of the protons in the system is monitored. In the present experiments the root-mean-squared displacements of the protons within the diffusion time *t* are much larger than the radius of gyration of the chain molecules; hence, the self-diffusion coefficient D_s of the center of mass of the chain molecules is measured. Further details about the method are available.[34−36]

The stimulated echo pulse program ($\pi/2$-τ-$\pi/2$-τ-$\pi/2$-τ-echo) was used. The time τ was always 3 ms. In the experiment, the magnitude *g* of the field gradient pulses (between the first two $\pi/2$ rf pulses and the third $\pi/2$ rf pulse and the echo) was varied between 0 and 25 T/m. The width δ of the field gradient pulses (maximum value 2 ms) and the diffusion time *t* (between 20 and 500 ms) was chosen such that at g = 25 T/m a sufficient echo attenuation was reached with a still detectable echo. The echo attenuations measured for the sample sm3/7 are shown in Figure 1.

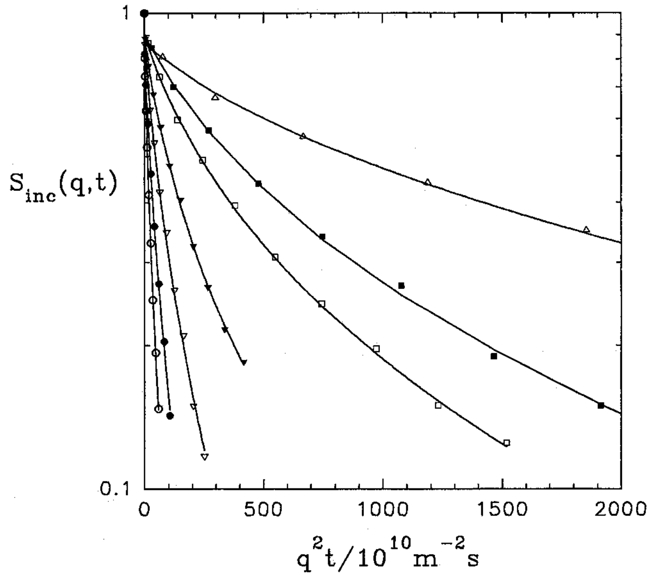

Figure 1. Echo attenuation plots, i.e. $S_{inc}(q,t)$ vs q^2t, for the sample sm3/7 dissolved in deuterated benzene with the concentrations Φ of 0.02 (○), 0.03 (●), 0.005 (▽), 0.07 (▼), 0.1 (□), 0.125 (■), and 0.15 (△).

In the diffusion limit the echo attenuation is equivalent to the incoherent intermediate scattering function $S_{inc}(q,t)$[36]

$$S_{inc}(q,t) = \exp(-q^2D_st) \qquad (8)$$

for a system with one self-diffusion coefficient $D_sq = \gamma\delta g$ is a generalized scattering vector with γ denoting the gyromagnetic ratio of the proton. In the present samples, however, a distribution of chain lengths results in a distribution of self-diffusion coefficients and, hence, to a superposition of exponentials given by eq 8. For the fitting of the measured echo attenuations $S_{inc}(q,t)$ the same procedure as in the DLS data analysis was used, i.e. the results were fitted to a stretched exponential function:

$$S_{inc}(q,t) = a\exp(-(q^2D_st)^b) \qquad (9)$$

The quantity $a < 1$ takes into account a small part of fast-diffusing low molecular traces (e.g. residual protons in the deuterated solvent) in the solution. The averaged (apparent) self-diffusion coefficients are calculated from the fitted parameters D_s and b using the relation equivalent to eq 5:

$$D_{s,av} = bD_s/\Gamma(1/b) \qquad (10)$$

Results and Discussion

In contrast to the semidilute solutions of linear monodisperse homopolymers in a good solvent where the dynamics is dominated by a single cooperative diffusion mode,[7,8] the dynamics in solutions of statistical S-*s*-MMA copolymers is more complex. This is demonstrated in Figure 2 where the normalized autocorrelation functions, $g^{(2)}(t)$, are plotted against the logarithm of the delay time t for several S-*s*-MMA copolymer samples with styrene contents from 10 to 50 vol % at copolymer volume concentration $\Phi \approx 0.09$. The autocorrelation functions show a fast initial single exponential decay which is followed by long time tail which can be fitted by a stretched exponential function of t (cf. Figure 3). Inset of Figure 3 shows that the distribution of residuals is random. This finding agrees with the prediction given by Semenov *et al.*[37] that the stretched exponential relaxation is expected for the broad distribution of the molecular weight. The scattering amplitude ratios A_s/A_f, obtained by fitting of experimental correlation functions from Figure 2 are given in Table 2. The ratio A_s/A_f decreases with the increasing content of styrene in copolymer samples. The decay rates of the fast, Γ_f, and slow Γ_s, modes are plotted as a function of

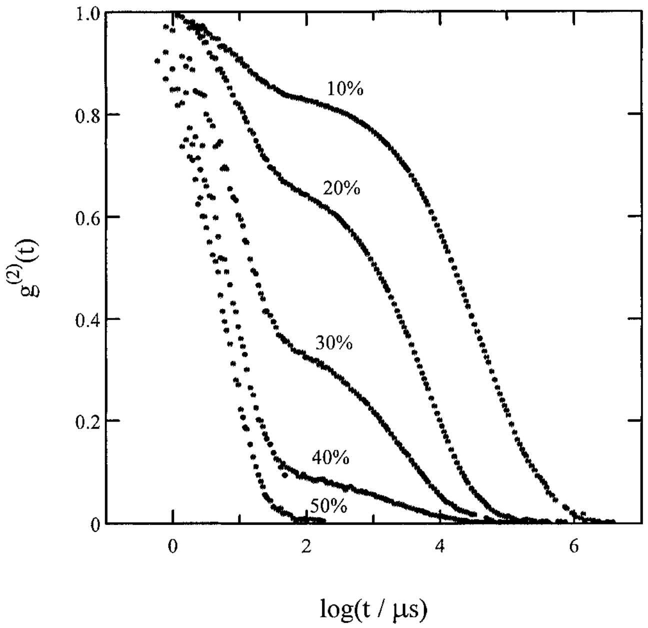

Figure 2. Normalized intensity autocorrelation functions, $g^{(2)}(t)$, measured for the semidilute solutions of copolymers with styrene volume fractions as indicated; $\Phi \approx 0.09$, the scattering angle $\theta = 90°$.

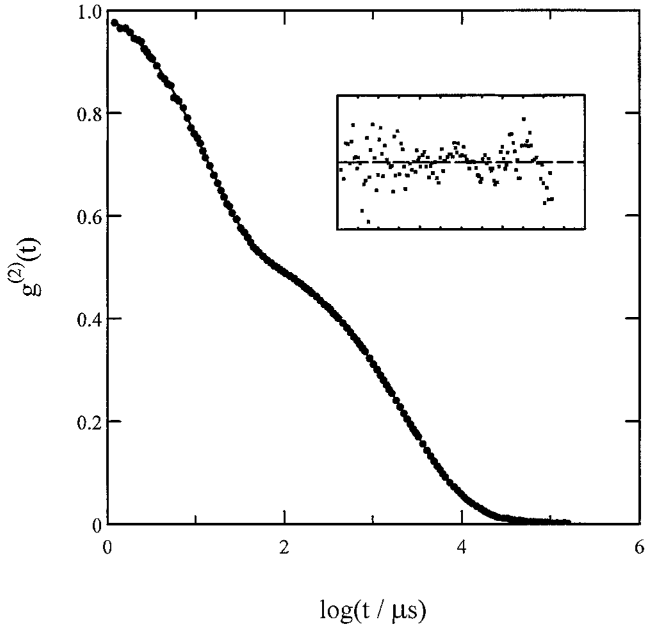

Figure 3. Normalized intensity autocorrelation function, $g^{(2)}(t)$, for a 6.3 vol % solution of sm2/8 measured at $\theta = 90°$ fitted to the sum of one single and one stretched exponential functions. The insert shows the respective residuals.

Table 2. Ratio of Scattering Amplitudes and Composition Polydispersity

sample	A_s/A_f	$[A_s(n_c^2 - n_s^2)^2/A_fN] \times 10^6$	$2\chi N\kappa_o$[a]	$\kappa_o \times 10^3$ [a]	$2\chi N\kappa_o$[b]	$\kappa_o \times 10^3$ [b]
sm1/9	11	0.2	13	2.6	16.5	3.3
sm2/8	4.3	1.1	17	6.6	20	7.8
sm3/7	1.5	1.5	2.2	1.2	3.2	1.7
sm4/6	0.4	1.0	–	–	–	–
sm5/5	~0	~0	~0	~0	~0	~0

[a] Data from Figure 7a. [b] Data from Figure 7c.

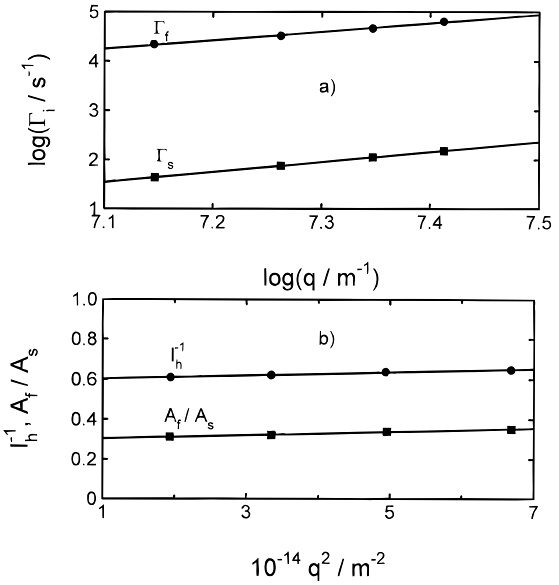

Figure 4. (a) The log Γ vs log q plot for fast (Γ_f) and slow (Γ_s) decay rates found for a 6.3 vol % solution of sm2/8 and (b) The q^2 dependence of $(I_h)^{-1}$ and A_f/A_s.

the magnitude of the scattering vector, q, in Figure 4a. Since both the decay rates are q^2-dependent for all samples and concentrations used, the fast and slow diffusion coefficients were calculated according to eqs 6a and 6b, respectively. The fast diffusion coefficient is assumed to correspond to the cooperative diffusion in the physical network and is identical with D_c. Its magnitude is similar to the magnitude of cooperative diffusion coefficients in equivalent semidilute solutions of homopolymers and was found to be independent of the sample molecular weight. The slow diffusion coefficient should have two contributions: one resulting from the compositional (chemical) and other from the molecular weight polydispersity. These two contributions are not equal; the diffusive mechanism of exchange of polymer chains of different composition dominates the slow mode. The slow diffusion coefficient is practically identical to D_h. The arguments for the above statement are as follows:

(a) Slow dynamic mode has not been observed in semidilute solutions of polydisperse homopolymers prepared by the same thermal radical polymerization; e.g., polystyrene/toluene,[38] polybutylmethacrylate/dioxane.[39] GPC analysis of the polystyrene sample used in ref 38 gave $M_w/M_n = 3.3$ which is in the upper limit of statistical copolymers used (Table 1).

(b) The composition of the copolymer sm5/5 is close to the azeotropic composition of the S-MMA system displaying negligible compositional (chemical) polydispersity.[31] Therefore, the sm5/5 sample should have a low compositional polydispersity. In spite of the high molecular weight polydispersity $A_s/A_f \sim 0$.

(c) Small decrease of M_w/M_n with increasing content of styrene in copolymers (see Table 1) cannot explain the observation that the slow diffusive process is hardly observed in sm4/6 and sm5/5 solutions.

By assuming that the slow mode is identified with composition polydispersity mode, a variation of A_s/A_f at a fixed value of Φ should be governed by variations of n_c, N, and κ_o (according to eqs 1a and 2a $A_s/A_f \approx I_h/I_c$). In order to eliminate the effect of copolymer parameters n_c and N, the ratio $A_s(n_c^2 - n_s^2)^2/A_f\, N$ *is* given in Table 2 for each sample. In the case of small κ_o ($2\chi N\kappa_o\Phi^{1.59} \ll 1$), the above ratio can be interpreted as a measure of the composition polydispersity. An independent estimate of the composition polydispersity is a serious experimental problem.[31] Nevertheless, it is possible to calculate the variance in the copolymer chemical composition for random copolymers using the monomer reactivity ratios.[31,40,41] The maximum attainable value of the composition polydispersity for styrene-methyl methacrylate system was found 2 × 10^{-3} for initial composition 21.5 vol % of styrene at conversion 0.9.[42] The composition polydispersity decreases to zero on approaching the PMMA homopolymer or copolymer with the azeotropic composition which for this particular system is in the vicinity of 50 vol % of styrene.[31] Thus, the variations of the ratio $A_s(n_c^2 - n_s^2)^2/A_f\, N$ (Table 2) with the copolymer composition qualitatively agree with the above predictions and also support the above interpretation of the slow mode. Although, the condition $2\chi N\kappa_o\Phi^{1.59} \ll 1$ is not realized for samples sm1/9 and sm2/8 (cf. the discussion further), this fact does not change the qualitative conclusions derived above.

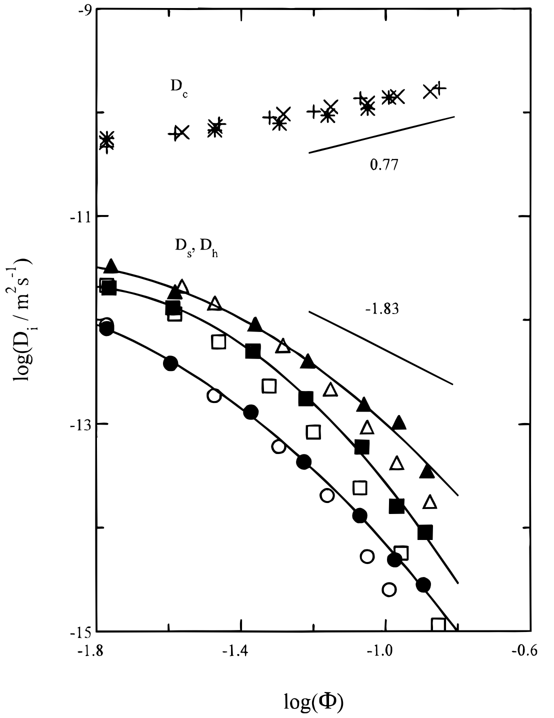

Figure 5. Concentration dependence of the cooperative diffusion (+, ×, *), interdiffusion (○, □, △) and self-diffusion (●, ■, ▲): (●, ○, *) sm1/9, (■, □, +) sm2/8, (▲, △, ×) sm3/7. The slopes +0.77 and −1.83 are the predictions for the cooperative diffusion and self-diffusion in the semidilute regime, respectively. The solid lines through the D_s results are not indications of any fit.

It can be seen from the results in Table 2 that the heterogeneity mode is easily detectable in solutions of copolymer samples sm1/9, sm2/8 and sm3/7. Therefore, detailed measurement of concentration dependence of dynamic and static properties were only conducted with these three samples. Both $(I_h)^{-1}$ and A_f/A_s were found to be only slightly q-dependent (Figure 4b). Figure 5 shows the variation of diffusion coefficients D_c, D_h, and D_s obtained by DLS and PFG-NMR with the polymer volume fraction at 25 °C. The cooperative diffusion coefficient, D_c, increases for all measured samples with increasing Φ approaching the power law dependence with an exponent 0.77 as expected.[7,8] On the contrary, both translational diffusion coefficients D_h and D_s are decreasing functions of Φ.[19,24,27] In qualitative agreement with the theoretical prediction given in eq 2b, D_h

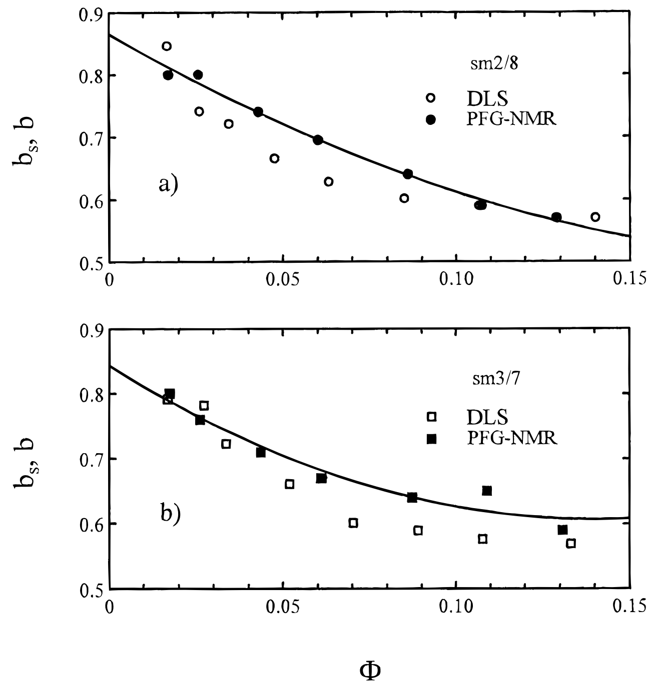

Figure 6. The b_s and b exponents dependence on the concentration Φ of sm2/8 (a) and sm3/7 (b) obtained from DLS and PFG-NMR experiments, respectively.

is systematically smaller than corresponding D_s. The concentration dependence of D_s obtained from PFG-NMR is similar to those found for semidilute and concentrated solutions of block copolymers[19,24] but they exceed the power law of $\Phi^{-1.83}$ predicted for the entanglement regime in good solvent at high concentrations.

The values of b_s and b obtained from DLS and PFG-NMR experiments, respectively, are shown for samples sm2/8 and sm3/7 in Figure 6, parts a and b. The results from both methods agree very well. The DLS results are systematically smaller, particularly at low concentrations. Inspection of Figure 6 reveals that both b_s and b decrease with increasing concentration. This effect probably reflects a crossover from the free Stokes–Einstein diffusion of polymer chains at low concentrations to reptation behavior at high concentrations. The polydispersity in molecular weight results in a distribution of diffusion coefficients which becomes broader with increasing concentration since the Stokes–Einstein-type scaling ($D_s \sim M^{-0.6}$) valid for the case of low concentrations changes into the reptation scaling ($D_s \sim M^{-2}$).

The theory of "composition polydispersity" elaborated for monodisperse diblock copolymers[17] cannot be directly applied to polydisperse statistical copolymers. Nevertheless, we use this theory to initially analyze the experimental results. In view of this, one should not necessarily anticipate quantitative agreement between the experiments and the above predictions (eqs 2a and 2b). In order to evaluate the effect of thermodynamic interactions on the mutual diffusion coefficient, D_h, expressed by eq 2b (the term in parentheses) and on the component of scattered light, I_p, described in eq 2a, the ratios and Φ/I_h and D_h/D_s were plotted as a function of $\Phi^{1.59}$ in Figure 7, parts a and b, respectively.[24] The values of Φ/I_h were normalized to unity in the zero concentration limit. Both quantities are expected to be virtually independent of the concentration if the term $2\chi N\kappa_o \ll 1$. Figures 7, parts a and b shows that both quantities exhibit concentration dependency for all samples and decrease with increasing Φ. Accordingly, the term $2\chi N\kappa_o$ should not be negligible. According to eqs 2, both D_h/D_s and Φ/I_h should vary linearly with $\Phi^{1.59}$ which is only found for Φ/I_h (Figure 7a). In the case of D_h/D_s (Figure 7b), the dependence on $\Phi^{1.59}$ is nonlinear showing only a qualitative similarity with the Φ/I_h plot. Such an inconsistency is probably related to the analysis of the DLS results at low copolymer concentrations. An overlap between the cooperative and mutual diffusion processes at low concentrations imposes limitation on the separation of these processes by the fitting procedure. Any quantitative comparison of the results obtained by two different methods is generally a difficult problem. Therefore, only Φ/I_h data were used to evaluate $2\chi N\kappa_o$ values which are shown in Table 2 for samples sm1/9, sm2/8, and sm3/7. The related κ_o values (Table 2) were estimated using $\chi = 0.15$ published for polystyrene and poly(methyl methacrylate) mixtures.[43] The composition polydispersity can be estimated from DLS experiments in an independent way using the fast to slow amplitudes ratio, A_f/A_s. Combining eqs 1a and 2a, the prediction for A_f/A_s is

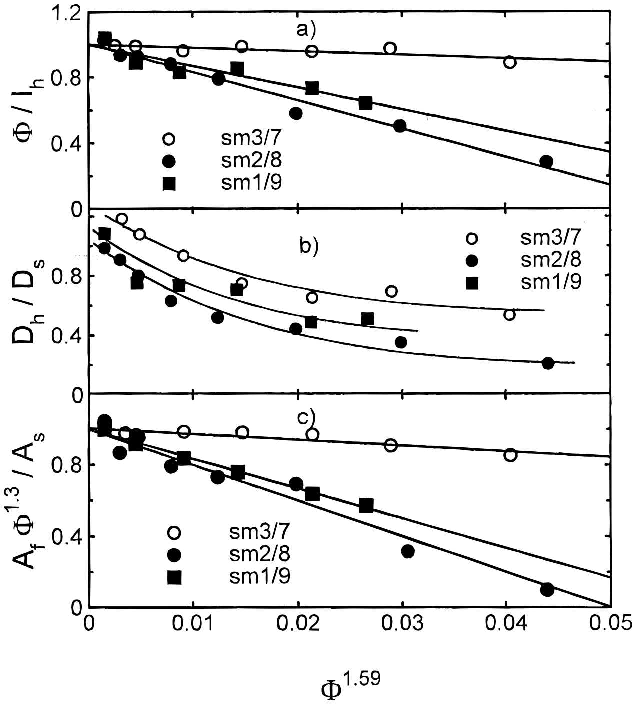

Figure 7. The plot of Φ/I_p (a), D_h/D_s (b) and $A_f\Phi^{1.3}/A_s$ (c) vs copolymer volume concentration $\Phi^{1.59}$. The solid lines represent linear least-square fits in the a and c, and there are no indications of any fit in b.

$$A_f N\Phi^{1.3}/[A_s\,(n_c^{\,2} - n_s^{\,2})^2] \propto 1 - 2\chi N\kappa_o\,\Phi^{1.59} \quad (11)$$

The ratio $A_f\,\Phi^{1.3}/A_s$ is plotted as a function of $\Phi^{1.59}$ for three copolymers in Figure 7c. The data were again normalized to unity in the zero concentration limit. Inspection of Figure 7c reveals that $A_f\,\Phi^{1.3}/A_s$ is linear function of $\Phi^{1.59}$. The derived slopes $2\chi N\kappa_o$ and κ_o values are listed in Table 2. The values of κ_o obtained from DLS experiments are higher than the respective values found from the static light scattering measurements. The maximum attainable value of composition polydispersity for styrene–methyl methacrylate system computed from the monomer reactivity ratios is 2×10^{-3} for the 21.5 vol % initial composition of styrene at 0.9

conversion.[42] This value is smaller than the corresponding values of κ_o (Table 2) for the sample sm2/8 (20 vol % of styrene). The discrepancy probably arises from the theory which is not fully applicable to statistical copolymers. Altogether, the κ_o values in Table 2 are comparable with those for block copolymers but smaller than the respective values found for mixtures of two asymmetric diblocks.[24]

Conclusions

The light scattering from semidilute solutions of styrene–methyl methacrylate random copolymers in the neutral good solvent, benzene, was examined. Two dynamic modes were observed at higher values of Φ. Measurements of self-diffusion by PFG-NMR were also conducted. The results were interpreted in terms of the theory developed by Semenov[17] for diblock copolymers. The main conclusions are as follows:

(1) A cooperative diffusion mode, characterized by the diffusion coefficient D_c, was consistently observed in all samples. D_c increases with increasing Φ approaching the power-law dependence with an exponent +0.77 in agreement with the theory and experiments carried out on homopolymer solutions.

(2) The slow mode typically observed in semidilute solutions of copolymer samples with lower styrene volume fraction (10, 20 and 30 vol %) was found to be dominated by the so called "heterogeneity" mode. This mode is present due to compositional heterogeneity in the copolymer chains and it reflects mutual diffusion. The value of the diffusion coefficient characteristic for this process, D_h, agreed with the self-diffusion coefficient, D_s, determined by PFG-NMR. The two diffusion coefficients, D_h and D_s, were decreasing functions of Φ. The concentration effects on D_s were exceeded the power law of $\Phi^{-1.83}$ predicted for the entanglement regime in good solvent at high concentrations.

(3) The effect of the thermodynamic forces was observed as concentration dependent quantities D_h/D_s, $A_f\,\Phi^{1.3}/A_s$, and Φ/I_h. The quantities Φ/I_h and $A_f\,\Phi^{1.3}/A_s$, and their dependence on concentration were used to evaluate the composition polydispersity of the statistical copolymers under study. These results were compared with a computed variance of the chemical composition for statistical S-*s*-MMA copolymers and with similar results obtained on semidilute solutions of block copolymers.

In conclusion, it should be pointed out that a combination of SLS and DLS experiments on semidilute solutions of statistical copolymers in solvents which are approximately isorefractive with one of the copolymers ($n_c - n_s \sim 0$) provides a new analytical tool for the evaluation of compositional polydispersity of high-molecular-weight copolymer samples with strong chemical heterogeneity. A new theory of "composition polydispersity" mode for solutions of polydisperse statistical copolymers is needed for the quantitative analysis of data.

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