Dynamics in Solutions of Associating Statistical Copolymers

Čestmír Koňák,[†] Martin Helmstedt,[‡] and Rama Bansil*[,§]

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic, Fakultät für Physik und Geowissenschaften, Univerität Leipzig, Linnéstrasse 5, D-04103 Leipzig, Germany, and Department of Physics, Boston University, 590 Commonwealth Avenue, Boston, Massachusetts 02215

Received November 6, 1996; Revised Manuscript Received May 21, 1997[⊗]

ABSTRACT: The association of styrene−methyl methacrylate statistical copolymers in the selective solvent acetone (a thermodynamically good solvent for poly(methyl methacrylate and bad for polystyrene) was examined by static and dynamic light scattering methods. In dilute solutions, the dynamics was dominated by a single fast mode, whereas in semidilute solutions two modes were generally seen, with fast and slow mean relaxation times. The fast dynamic mode was related to the cooperative diffusion mode. The slow mode was associated with dynamics of polymeric clusters formed by the random association process. Experimental results were interpreted in terms of the coupling model of partly penetrating polydispersed clusters formed by random association of copolymers.

Introduction

Macromolecules bearing active groups or parts possessing attractive interactions in common solvents can form supramolecular clusters by random association of macromolecules.[1] Thus, the random association of macromolecules has been observed, e.g., in solutions of ionomers in low polarity solvents[2−5] and in solutions of multiblock copolymers in selective solvents.[6] In the former case the counterions are undissociated in low polarity solvents forming ion pairs (dipoles) with ions of the polymer chains. Attractive forces (electric dipole−dipole interactions) among the ion pairs result in inter- and intramolecular dipole association (multiplet formation).[7,8] This leads to multichain aggregation and eventually gelation at higher ionomer concentrations. In the latter case, the insoluble blocks of multiblock copolymer form multiplet-like insoluble domains bridged by soluble blocks.[6] Formation of polydispersed clusters takes place at lower copolymer concentrations, while gel formation is favored at higher concentrations. The network-forming process can be understood in terms of the growth of randomly multiconnected clusters starting from individual macromolecules, which are linked together by insoluble domains (multiplets). These associations are, in some sense, an intermediate between the transient polymer entanglements found in semidilute solutions of flexible homopolymers and permanent covalent cross-links of gels.

Hydrophobically associating water-soluble polymers or "associative thickeners" are another class of complex disordered systems, that associate by a random association process.[9−19] These polymers are hydrophobically modified, water-soluble, statistical copolymers generally composed of both water-soluble and water-insoluble components. The driving force for the association process is the attractive interaction between the hydrophobic segments. Hydrophobic interactions induce association of macromolecules forming supramolecular clusters, and at sufficiently high concentrations a network composed of interpenetrating clusters is created.[18,19] Extrapolating from these results, we suggest that such random association should exist even in solutions of statistical copolymers in selective nonaqueous solvents.

Table 1. Molecular Characteristics of S-*s*-MMA Copolymers from GPC

code	composition vol % styrene	$M_w \times 10^{-6}$	M_w/M_n
sm1/9	10	1.65	3.5
sm2/8	20	0.91	3.3
sm3/7	30	0.59	3.1
sm4/6	40	0.49	2.8
sm5/5	50	0.43	2.7

In order to test this idea, dilute and semidilute solutions of styrene (S)−methyl methacrylate (MMA) statistical copolymers (S-*s*-MMA) in acetone were studied by static and dynamic light scattering methods. Acetone is a thermodynamically good solvent for poly(methyl methacrylate) (PMMA) and a nonsolvent for polystyrene (PS). The dynamical behavior of these solutions was interpreted in terms of the coupling model developed by Ngai and co-workers.[20−23]

Experimental Section

Sample Preparation. Both monomers, styrene and methyl methacrylate, were purified by removing the inhibitor and mixed together to obtain desired initial composition, from 10 to 50 vol % of styrene. The reaction mixtures were filtered through PTFE membrane filters with a pore diameter of 0.2 μm into glass ampules, freed from oxygen by three freeze−thaw cycles, and sealed in a vacuum. The polymerization was initiated thermally[24] by heating 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 acetone were prepared from filtered dilute solutions with copolymer concentration $c = 0.02$ g mL^{-1} directly in the dust-free light scattering cells by slow evaporation of acetone. The concentrations of the solutions were determined by weighing the resulting solutions.

Approximate molecular weights determined by the GPC method (in tetrahydrofuran, THF, solutions at 25 °C) are shown in Table 1. All samples used in this study showed a single broad M_w distribution. The column was calibrated with polystyrene standards.

Static Light Scattering (SLS). Static light scattering measurements were performed with a light scattering goniometer equipped with He−Ne and Ar ion lasers (vertically

---

[†] Academy of Sciences of the Czech Republic.

[‡] Universität Leipzig.

[§] Boston University.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

S0024-9297(96)01646-4 CCC: $14.00

Table 2. Molecular Characteristics of S-*s*-MMA copolymers in Acetone(Light Scattering Data)

code	dn/dc	$M_w \times 10^{-6}$	$A_2 \times 10^4$, mL g^{-2} mol	R_g, nm	R_h, nm	$c^* \times 10^3$, g mL^{-1}
sm1/9	0.134	1.7	1.9	76	34.5	1.5
sm2/8	0.143	0.93	1.37	41	26	5.4
sm3/7	0.151	0.65	0.86	34	21.5	7.1
sm4/6	0.160	0.54	0.33	28	20	9.8
sm5/5	0.168				15	

polarized, wavelength $\lambda_o = 632.8$ and 514.5 nm, respectively) in the angular range $\theta = 30-150°$. The SLS data from dilute solutions of copolymers were analyzed by the usual Zimm plot procedure. The processed SLS data for semidilute solutions are represented as

$$Kc/\Delta R(0) = (K^*/D)\,(\mathrm{d}n/\mathrm{d}c)^2 c I_b/(I_s \sin(\theta))_{\theta\to 0} \qquad (1)$$

where K and D are the usual optical constants, $K^* = K/(\mathrm{d}n/\mathrm{d}c)^2$, $\Delta\ R(0)$ is the excess Rayleigh ratio, dn/dc is the refractive index increment, c is the copolymer concentration in g mL^{-1}, θ is the scattering angle, I_b is the scattered intensity of benzene at $\theta = 90°$ and I_s is the excess scattered intensity at θ. Refractive index increments of copolymer solutions in acetone, (dn/dc), measured with a Brice-Phoenix differential refractometer, are given in Table 2.

Dynamic Light Scattering (DLS). Polarized DLS measurements were made in the angular range $\theta = 30-140°$ using a light scattering apparatus equipped with an Ar-ion laser (514.5 nm) and an ALV 5000, multibit, multi-τ autocorrelator covering approximately 10 decades in delay time, t. The normalized intensity autocorrelation functions

$$g^2(t) = [G^2(t) - B]/[G^2(0) - B] \qquad (2)$$

are used for demonstration of DLS results and for analysis; B is the baseline. The electric field autocorrelation functions, $g^1(t) = (g^2(t))^{0.5}$ were fitted to the sum of an exponential and a stretched exponential function with exponent b_s:

$$g^1(t) = A_c\, exp(-[t/\tau_c]) + A_s \exp(-[t/\tau_s]^{b_s}), \qquad (3)$$

Here τ_i (i = s or c) are the characteristic decay times; A_i are the relative scattering amplitudes. The exponent b_s is related to the width of the corresponding distributions of the relaxation times τ; the smaller the value of b_s the broader is the distribution.

The apparent diffusion coefficients, D_i, were calculated from

$$D_i = 1/\tau^o{}_i \boldsymbol{q}^2, \qquad (4)$$

where $\boldsymbol{q}$ is the scattering vector and $\tau^o{}_i$ is the zero angle limit of τ_i..

Results and Discussion

(a) Static Light Scattering. The statistical copolymers were soluble at room temperature in a selective solvent acetone (good for PMMA and bad for PS) up to styrene content of 40 vol %. The copolymer sm5/5 with 50 vol % of S was only partly soluble at very low concentrations. Values of the weight-average-molar mass, M_w, the second virial coefficient, A_2, and the radius of gyration, R_g, evaluated by the Zimm plot procedure from light scattering measurements in acetone solutions are given in Table 2. It is well-known that heterogeneity in chemical composition of statistical copolymers may cause a systematic error in the macromolecular characteristics of copolymers evaluated from SLS measurements.[25] According to ref 25, the measured value of M_w is a function of the parameter $(\nu_A - \nu_B)/\nu$ where ν_A and ν_B denote the refractive index increments of the pure A and B homopolymers and ν denotes that of the copolymer. As a consequence the SLS measurement depends on the solvent used. Thus the data in Table 2 are only apparent M_w values for the given solvent acetone. Since the refractive index increment of the copolymers in acetone is high the error in M_w can be considered low. Table 1 and 2 show that apparent M_w values obtained from GPC (in THF solutions) and light scattering experiments (in acetone solutions) are very similar. This implies that the statistical copolymers are molecularly dissolved at low concentrations. The second virial coefficient, A_2, evaluated from acetone solutions decreases with increasing content of S in the copolymer and is very small for the copolymer sm4/6, revealing decreasing solubility of copolymers in acetone. The crossover concentration estimated for acetone solutions using $c^* \approx 3M_w/4\pi(R_g)^3 N_A$ are also given in Table 2.

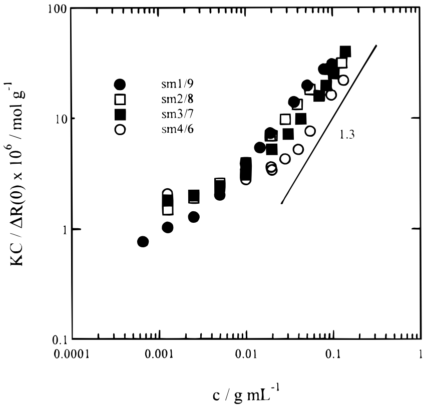

Figure 1. Concentration dependence of $Kc/\Delta R(0)$ in the semidilute regime. The line with slope 1.3 is the prediction for concentration fluctuations relaxing via the cooperative diffusion process.

A log−log plot of $Kc/\Delta R(0)$ *vs* copolymer concentration c is shown in Figure 1. The concentration dependence of $Kc/\Delta R(0)$ at low concentrations is controlled by the second virial coefficient. However, at higher concentrations in the semidilute regime, $Kc/\Delta R(0)$ increases faster and can be approximated by a power law, $Kc/\Delta R(0) \approx c^x$. The exponent x decreases with decreasing S/M ratio from $x \approx 1.3$ for the copolymer sm4/6 to $x \approx 1$ for the copolymer sm1/9. In semidilute homopolymer solutions, the contribution of the excess scattered intensity arising from concentration fluctuations relaxing via a cooperative diffusion process, A_c, decreases with increasing concentration[26,27]

$$A_c \propto (n_p{}^2 - n_s{}^2)^2 c^{-0.3} \qquad (5)$$

where n_p and n_s are the refractive indices of the polymer and the solvent, respectively. Combining eqs 1 and 5, we expect an exponent of 1.3 in the plot used in Figure 1. The smaller values of x observed in semidilute solutions of statistic copolymers with lower S/M ratios probably reflect the additional contribution to the total excess scattered intensity due to concentration fluctuations associated with dynamics of polymer clusters formed by the random association process.

(b) Dynamic Light Scattering. The random association of S-*s*-MMA copolymers is also manifested in dynamic light experiments. This is demonstrated in Figure 2a where the normalized autocorrelation functions $g^2(t)$ are shown for several concentrations of the copolymer sm3/7. A long-time tail, which is practically negligible at low concentrations, becomes stronger with

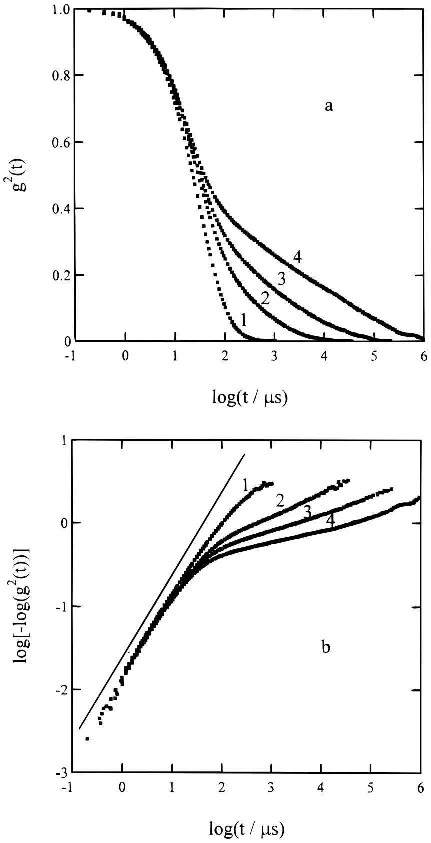

Figure 2. (a) Normalized intensity autocorrelation functions, $g^2(t)$, at $\theta = 90°$, for semidilute solutions of copolymers with the styrene volume fraction of 30 vol % at different concentrations: 1, 0.02 g mL^{-1}; 2, 0.07 g mL^{-1}; 3, 0.10 g mL^{-1}; 4, 0.14 g mL^{-1}. (b) Data of part a, plotted as the double logarithm of the autocorrelation function *vs* logarithm of delay time. The line of slope 1 corresponds to a normalized single exponential autocorrelation function.

increasing copolymer concentration. Double logarithm of $g^2(t)$ functions from Figure 2a are plotted against the logarithm of delay time *t* in Figure 2b. This type of plot yields straight lines for functions which can be represented by a stretched exponential. The autocorrelation functions show a fast initial single exponential decay (the slope ≈ 1 in the plot) followed by a long-time tail, which can be described quite well by straight lines with slopes smaller than 1 for all concentrations. Therefore, the long-time behavior of the correlation functions can be described by a stretched exponential function with an exponent $b_s \leq 1$ and the fast behavior by a single exponential function with $b_f \approx 1$. Therefore, the autocorrelation functions were fitted to eq 3.

The initial, fast single exponential decay (τ_c) may be assumed to correspond to the cooperative motions of the polymer matrix since it has a relaxation frequency similar to that of the cooperative mode in solutions of linear homopolymers. The long-time tail can be related to two dynamic processes: (1) the dynamics of the partly penetrating polydispersed clusters formed by random association of copolymers and (2) the dynamics of concentration fluctuations due to the composition polydispersity of copolymers, which is often called the "heterogeneity" mode.[31−33] The dynamic behavior due to the first process should be similar to that observed in gelling systems in the pregel state; e.g., Adam et al.[28] and Martin et al.[29,30] According to our previous results[34] the "heterogeneity" mode can be only observed in solvents which are approximately isorefractive with one of the copolymers (e.g. benzene). The refractive index increments of the copolymers in acetone are high and, therefore, the relative contribution of the "heterogeneity" mode should be weak and overlapped with the cluster dynamics. Thus, the former dynamic process dominates at longer decay times.

The log of decay rates of the fast cooperative mode, Γ_c ($=1/\tau_c$), and slow mode, Γ_s ($=1/\tau_s$), obtained by fitting of experimental correlation functions to the sum of the single exponential and stretched exponential functions (eq 3) are plotted as a function of log(q) for the different copolymers at approximately the same concentrations in Figure 3a. Since the fast dynamic mode was found to be proportional to q^2 for all the statistical copolymers, the fast cooperative diffusion coefficient, D_c, could be evaluated from the fast characteristic decay times (τ_c) at low scattering angles. The q dependence of Γ_s was found to be different from the usual q^2 dependence and may be expressed as $\Gamma_s \sim q^{a_s}$ (c.f., Figure 3a). As shown in Figure 3b, a_s obtained for the different copolymers is greater than 2 and increases with increasing concentration, implying that all the copolymers are characterized by a gradually stronger q dependence of Γ_s, as the concentration increases. The most pronounced deviation from q^2 dependence of Γ_s was found for the copolymers sm1/9, sm2/8 and sm3/7. In the case of sm4/6, a_s is only slightly higher then 2. These observations are in agreement with results of a number of studies on associating polymer systems,[18] and both physical[19,35−37] and chemical gels,[28−30,38,39] where q dependence of the slow mode is significantly stronger than that of the fast mode. Such a behavior of the slow mode can be qualitatively explained by the theory of Ngai and co-workers,[20−23] dealing with the problem of how the relaxation of a specific cluster is "slowed down" due to the coupling to complex surroundings. This coupling model predicts that $a_s = a_c/(1 - n)$, where the coupling parameter n ($0 < n < 1$) is a measure of the coupling strength of the dynamic mode to its surroundings and a_c is the exponent for the corresponding fast mode.

The exponent b_s, which was found to be independent of q, decreases with increasing concentration (see Figure 3c) and is generally lower for copolymers sm1/9 and sm2/8 than for sm3/7 and sm4/6. According to the coupling model the quantity $(1 - n)$ is proportional to exponent b_s and, therefore, the product $a_s b_s$ should be a constant independent of c. In order to verify this result, the product $a_s b_s$ calculated using the data of Figure 3b,c is plotted as a function of concentration in Figure 3d. The experimental results show that $a_s b_s$ is not satisfactorily independent of concentration, instead, it shows a systematic decrease from values close to 2 at low concentrations down to 1 at higher concentrations.

In stretched exponential autocorrelation functions a decrease of b_s reflects an increase of polydispersity of the distribution of characteristic relaxation times with increasing concentration and, probably, can be related to growing coupling effects appearing in complex systems.[18,19,39,40] The behavior of b_s is analogous to that in gelling systems on approaching the gel point.[29,30] Thus, the copolymer concentration in randomly associating systems plays the role of the cross-linking probability in cross-linking systems.

Because of the stronger q dependence of Γ_s the slow cluster diffusion coefficient cannot be introduced. Therefore, the quantity Γ_s/q^2 measured at the scattering angle of 90° will be discussed further. The concentra-

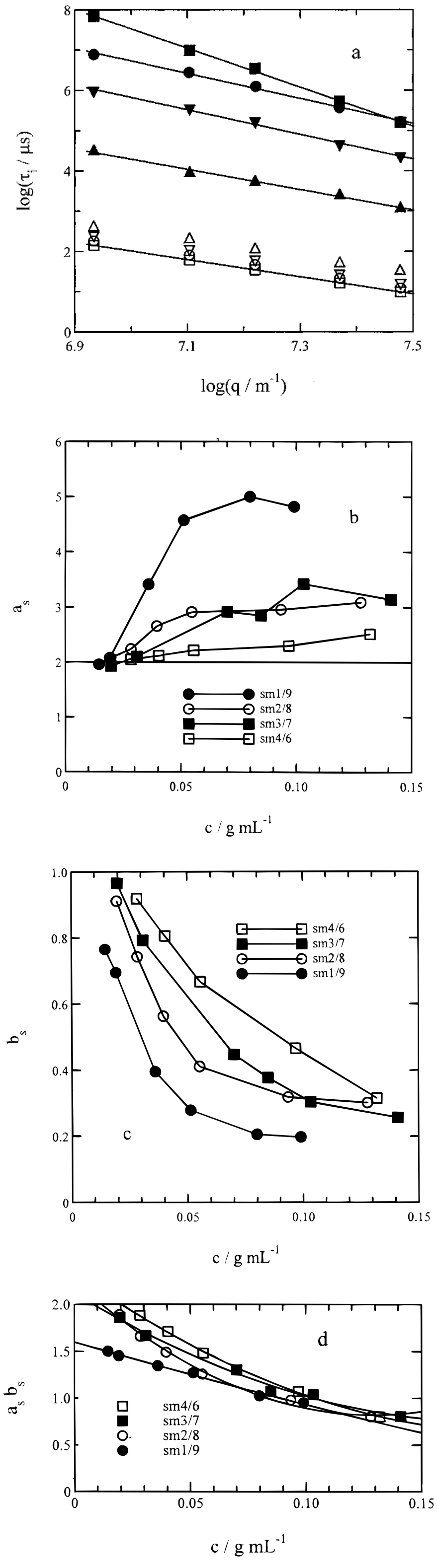

Figure 3. (a) q dependence of the fast, τ_c (open points), and slow, τ_s (solid points), decay times for semidilute copolymer solutions: (■, □) sm1/9, $c = 0.1$ g mL^{-1}; (●, ○) sm2/8, $c = 0.13$ g mL^{-1}, (▼, ▽) sm3/7, $c = 0.14$ g mL^{-1}; (▲, △) sm4/6, $c = 0.13$ g mL^{-1}. (b) Power law exponent, a_s, in the relation $\Gamma_s \sim q^{a_s}$, for the slow mode, as a function of concentration for the different copolymers as indicated. (c) Comparison of the concentration dependence of b_s for semidilute solutions of the different copolymers as indicated. (d) Concentration dependence of $a_s b_s$ products calculated using the data of Figure 3b and 3c for the different copolymers as indicated.

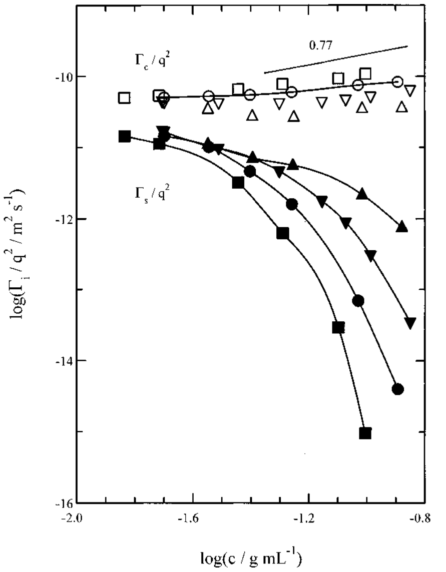

Figure 4. Concentration dependence of the cooperative diffusion, D_c ($=\Gamma_c/q^2$) and $\Gamma_s(90°)/q^2$: (■, □) sm1/9; (●, ○) sm2/8; (▼, ▽) sm3/7; (▲, △) sm4/6. The slope of 0.77 is the prediction for the cooperative diffusion in the semidilute regime. The solid lines through the data are to guide the eye.

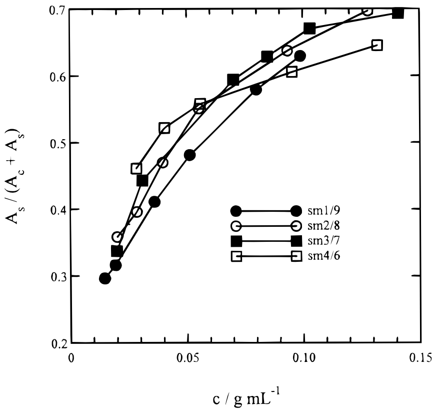

Figure 5. Concentration dependence of the relative scattering amplitude of the slow mode, $A_s/(A_s + A_c)$, at the scattering angle $\theta = 90°$ for semidilute solutions of copolymers, as indicated.

tion dependence of Γ_s/q^2 and Γ_c/q^2 ($\equiv D_c$) are shown in Figure 4. As expected,[26,27] the cooperative diffusion coefficient, D_c, increases with increasing c for all the samples. The figure shows a weak power-law dependence, with an exponent somewhat smaller than the predicted value of 0.77. On the other hand, Γ_s/q^2 is a very strongly decreasing function of c. This slowing down of the decay rate of the slow mode with increasing concentration can be rationalized in the framework of the coupling model as a result of increasing coupling between the clusters. It is plausible that the impact of dynamical constraints should increase with concentration due to enhanced cluster interpenetration.

The relative amplitude $A_s/(A_s + A_c)$ of the slow mode measured at the scattering angle $\theta = 90°$ is plotted as a function of concentration in Figure 5. It can be seen that the relative contribution of the slow mode increases with increasing concentration. This increase is partly due to the increase in the concentration of copolymer clusters and partly due to the overall concentration dependent decrease in the excess scattered intensity, A_c of the cooperative diffusion mode (see eq 5). Furthermore, the slow mode becomes more dominant with decreasing scattering angle; this effect is much stronger at higher concentrations. This trend can be related to the stronger excess scattering intensity at small angles in semidilute solutions of large clusters.

Conclusions

We have examined the association behavior in semidilute solutions of styrene−methyl methacrylate statistical copolymers in the selective solvent, acetone, using dynamic and static light scattering. Two dynamic modes were seen at higher copolymer concentrations. The main conclusions are as follows.

(1) A cooperative diffusion mode was always observed, with the cooperative diffusion constant D_c increasing with increasing copolymer concentration and approaching the power-law dependence with an exponent of +0.77, in agreement with theory and measurements on homopolymer solutions.

(2) A slow mode was clearly seen in semidilute solutions of copolymer samples with styrene volume fractions of 10, 20, 30, and 40 vol %. This mode is due to the dynamics of the partly penetrating polydispersed clusters formed by random association of copolymers and their dynamic behavior is similar to that observed in gelling systems in the pregel state

(3) The q dependence of Γ_s was found to be stronger than the usual q^2 dependence and may be expressed as $\Gamma_s \sim q^{a_s}$. The higher the concentration the greater is the deviation from $a_s = 2$. The most pronounced deviation was found for the copolymers sm1/9, sm2/8, and sm3/7. In the case of sm4/6, a_s was only slightly larger than 2. Such a behavior of the slow mode can be qualitatively explained by the coupling model of Ngai and co-workers, which predicts that the relaxation of a specific cluster is “slowed down” due to the coupling to its complex environment.

In conclusion, we note that random association of S-*s*-MMA copolymers in a selective solvent, acetone, is effective at higher concentrations. This was confirmed by both the static and dynamic light scattering experiments.

Acknowledgment. This work was funded by the U.S.−Czechoslovak Science and Technology Program (No. 93003) and a NSF U.S.−Czech Collaborative Research Grant (NSF INT-96 00679, ME ES 044). R.B. acknowledges the support of NSF-Division of Materials Research (NSF-DMR No. 9618467). C.K. acknowledges the financial support of the Alexander von Humboldt Foundation. M.H. thanks the Deutsche Forschungsgemeinschaft (SFB 294) for financial support.

References and Notes

(1) Burchard W. *TRIP* **1993**, *1*, 192.

(2) Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098.

(3) Utracki, L. A., Weiss R. A., Eds. *Multiphase Polymers: Blends and Ionomers*, ASC Symposium Series 395; American Chemical Society: Washington, DC, 1989.

(4) Lantman, C. W.; MacKnight, W. J.; Lundberg, R. D. In *Comprehensive Polymer Science*, Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, England, 1989; Vol 2, Chapter 25.

(5) Pedley, A. M.; Higgins, J. S.; Pfeiffer, D. G.; Burchard, W. *Macromolecules* **1990**, *23*, 1434.

(6) Nyrkova, I. A; Khokhlov, A. R.; Doi, M. *Macromolecules* **1993**, *26*, 3601.

(7) Eisenberg, A. *Macromolecules* **1970**, *3*, 147.

(8) MacKnight, W. J.; Earnest, T. R., Jr. *J. Polym. Sci., Macromol. Rev.* **1982**, *16*, 41.

(9) McCormick, C. L.; Bock, J.; Schulz, D. N. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1989; Vol. 17, p 730.

(10) Glass, J. E. Ed. *Polymers in Aqueous Media: Performance through Association*, Advances in Chemistry, 223; American Chemical Society: Washington, DC, 1989.

(11) Jenkins, R. D.; Silebi, C. A.; El-Aasser, M. S. *Polym. Mater. Sci. Eng.* **1989**, *61*, 629.

(12) Wang, Y.; Winnik, M. A. *Langmuir* **1990**, *6*, 1437.

(13) Seery, T. A. P.; Yassini, M.; Hogen-Esch, T. E.; Amis, E. J. *Macromolecules* **1992**, *25*, 4784.

(14) Ringsdorf, H.; Simon, J.; Winnik, F. M. *Macromolecules* **1992**, *25*, 5353.

(15) Ulbrich, K.; Konak, C.; Tuzar, Z.; Kopecek, J. *Makromol. Chem.* **1987**, *188*, 1261.

(16) Konak, C.; Kopeckova, P.; Kopecek, J. *Macromolecules* **1992**, *25*, 5451.

(17) Gu, Z.-W.; Omelyanenko, V.; Kopeckova, P.; Kopecek, J.; Konak, C. *Macromolecules* **1995**, *28*, 8375.

(18) Nystrom, B.; Walderhaug, H.; Hansen, F. K. *J. Phys. Chem.* **1993**, *97*, 7743.

(19) Nystrom, B.; Lindman, B. *Macromolecules* **1995**, *28*, 967.

(20) Rendell, R. W.; Ngai, K. L. In *Relaxations in Complex Systems*; Ngai, K. L., Wright, G. B., Eds.; Office of Naval Research: Washington, DC, 1985.

(21) Ngai, K. L.; Rendell, R. W.; Rajagopal, A. K.; Teitler, S. *Ann. N.Y. Acad. Sci.* **1985**, *484*, 150.

(22) Rendell, R. W.; Ngai, K. L.; McKenna, G. B. *Macromolecules* **1987**, *20*, 2250.

(23) Ngai, K. L.; Rajagopal, A. K.; Teitler, S. *J. Chem. Phys.* **1988**, *88*, 5086.

(24) Dvoranek, L.; Konak, C.; Neuhausel, T.; Machova, L.; Sorm, M. *Angew. Makromol. Chem.* **1992**, *194*, 149.

(25) Bushuk, W.; Benoit, H. *Can. J. Chem.* **1958**, *36*, 1616.

(26) de Gennes, P. G. *Scaling Concept in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(27) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford Science Publishers: Oxford, U.K., 1986.

(28) Adam, M.; Delsanti, M.; Munch, J. P.; Durand, D. *Phys. Rev. Lett.* **1988**, *61*, 706.

(29) Martin, J. E.; Wilcoxon, J. P. *Phys Rev Lett.* **1988**, *61*, 373.

(30) Martin, J. E.; Wilcoxon, J. P.; Odinek, J. *Phys. Rev. A* **1991**, *43*, 858.

(31) Anastasiadis, S. H.; Fytas, G.; Vogt, S.; Fischer, E. W. *Phys. Rev. Lett.* **1993**, *70*, 2415.

(32) Jian T.; Anastasiadis, S. H.; Semenov, A. N.; Fytas, G.; Adachi, K.; Kotaka, T. *Macromolecules* **1994**, *27*, 4762.

(33) Balsara, N. P.; Stepanek, P.; Lodge, T. P.; Tirrell, M. *Macromolecules* **1991**, *24*, 6227.

(34) Konak, C.; Fleischer, G. *Macromolecules*, in press.

(35) Ren, S. Z.; Shi, W. F.; Zhang, W. B.; Sorensen, C. M. *Phys. Rev. A* **1992**, *45*, 2416.

(36) Ren, S. Z.; Sorennsen, C. M.; *Phys. Rev. Lett.* **1993**, *70*, 1727.

(37) Lang, P.; Burchard, W. *Macromolecules* **1991**, *24*, 814.

(38) Fang, L.; Brown, W.; Konak, C. *Macromolecules* **1991**, *24*, 6839.

(39) Delsanti, M.; Munch, J. P.; Adam, M.; Durand, D. In *Relaxation in Complex Systems and Related Topics*; Campbell, I. A., Giovannella, C., Eds.; Plenum Press: New York, 1990.

(40) Chen, S. H.; Sheu, E. Y.; Huang, J. S. In *Dynamics of Disordered Materials*; Richter, D., Dianoux, A. J., Petry, W., Teixeira, J., Eds.; Springer-Verlag: Berlin, 1989.

MA9616468