Macromolecules **1998,** *31,* 4639−4641

Notes

Temperature Dependence of Dynamics in Solutions of Associating Random Copolymers

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Received October 30, 1997
Revised Manuscript Received April 27, 1998

Recently, we have investigated the association of styrene (S)−methyl methacrylate (MMA) random copolymers (S-*r*-MMA) in the selective solvent acetone (a thermodynamically good solvent for poly(methyl methacrylate) and a poor solvent for polystyrene) by static and dynamic light scattering methods.[1] It was found that 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 developed by Ngai and co-workers.[2−5] The driving force for the association process is the attractive interaction between the insoluble polystyrene segments.

In the present contribution we investigate the effect of temperature on cluster formation in semidilute solutions of S-*r*-MMA random copolymers in the selective solvent acetone.

Copolymer samples were prepared by radical polymerization of styrene and methyl methacrylate monomers in the desired initial compositions ranging from 10 to 50 vol % styrene. The polymerization was initiated thermally[6] 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 directly in the dust-free light-scattering cells by slow evaporation of acetone from a filtered dilute solution of initial concentration 0.02 g mL^{-1}. The final concentration was determined by weighing the resulting solutions.

Approximate molecular weights determined by the GPC method (THF, 25 °C) are shown in Table 1. The GPC column was calibrated with polystyrene standards.

Table 1. Molecular Characteristics of S-*r*-MMA Copolymers from GPC and the Activation Energy of Cluster Formation

code	composition[a]	$M_w/\times10^5$	M_w/M_n	$E_a/\times10^{21}$ J
sm1/9	10	16.5	3.5	2.6
sm2/8	20	9.1	3.3	3.4
sm3/7	30	5.9	3.1	2.4
sm4/6	40	4.9	2.8	4.7

[a] Volume percent styrene.

The dynamic behavior of the semidilute copolymer solutions in acetone was studied by the dynamic light scattering method 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, multitau autocorrelator covering approximately 10 decades in the delay time t. 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 β_s in accord with our previous results.[1] The exponent β_s is related to the width of the corresponding distributions of the relaxation times τ, and the smaller the value of β_s the broader is the distribution. Thus, two characteristic decay rates t_f and t_s (fast and slow) corresponding to the dynamics of cooperative and cluster diffusion mode, respectively, were evaluated. Since the q dependence of τ_s was found to be stronger than the usual q^2 dependence characteristic of diffusive modes, the slow diffusion coefficient cannot be introduced.[1] Instead, the quantity Γ_s/q^2, where Γ_s $(=1/\tau_s)$ is the decay rate of the slow mode measured at the scattering angle 90°, will be used throughout the paper. The relative contribution of the cluster mode to the total light-scattering intensity is characterized by the fraction $f_s = A_s/(A_f + A_s)$, where A_f and A_s are the scattering amplitudes of the fast and slow modes, respectively.

Semidilute solutions with the highest copolymer concentrations were selected for studying the effect of the temperature on the formation of copolymer clusters and on their dynamics. The particular concentrations used were $c = 0.1$ g mL^{-1} for the copolymer sm1/9, $c = 0.13$ g mL^{-1} for sm2/8, $c = 0.14$ g mL^{-1} for sm3/7, and $c = 0.13$ g mL^{-1} for sm4/6. These solutions have sufficiently well-developed clusters whose dynamics was clearly observable in dynamic light experiments at room temperature.[1] Only the temperature behavior of the long-time stretched exponential tail of the autocorrelation functions, which is related to the cluster dynamics (cluster mode), is discussed further.

Arrhenius plots of Γ_s/q^2 and f_s are shown in Figure 1a and b, respectively. This plot was selected because it provides a linear dependence of the measured quantities. In order to take into account the change of solvent viscosity with temperature, Γ_s/q^2 is multiplied by the factor η/T, where η is the solvent viscosity at the temperature T. The dynamics of cluster diffusion

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S0024-9297(97)01601-X CCC: $15.00

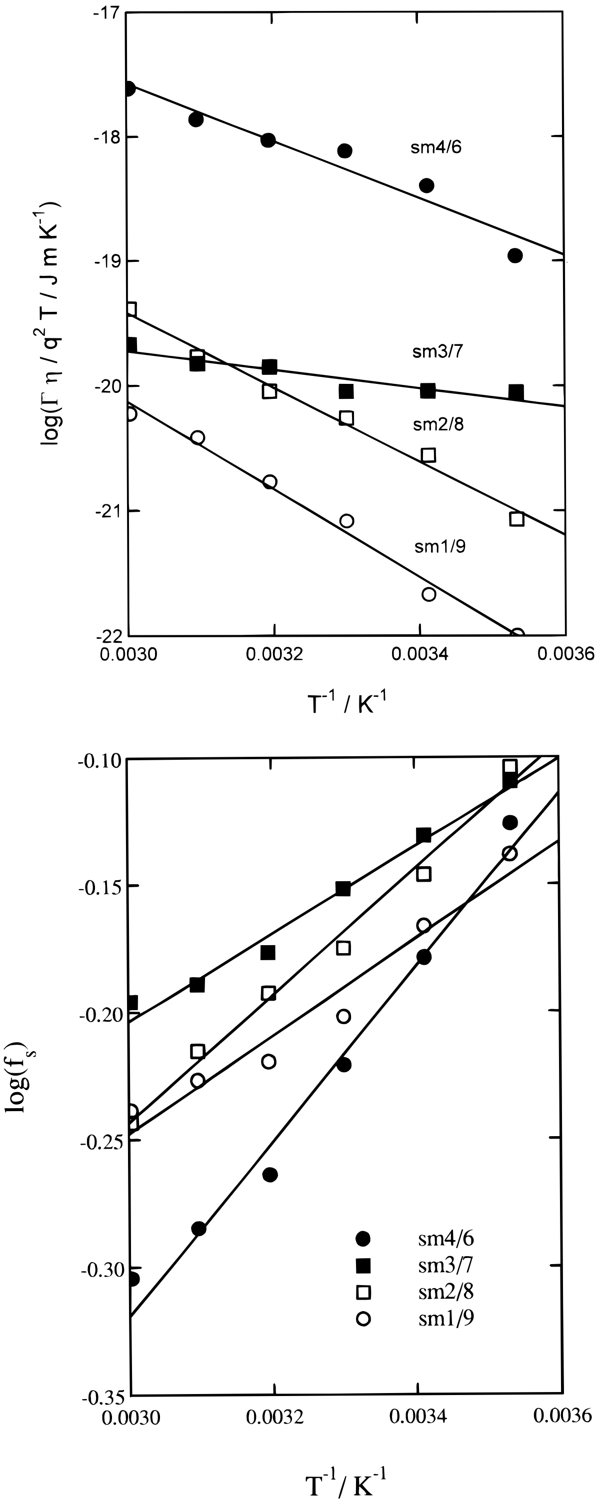

Figure 1. (a, top) Arrhenius plot of $\eta\Gamma_s/q^2T$ for the different copolymers, as indicated. The apparent diffusion coefficient Γ_s/q^2 is multiplied by the factor η/T, where η is the solvent viscosity at the temperature T, to correct for the temperature dependence of the solvent viscosity. (b, bottom) Arrhenius plot of the fraction of the scattered intensity due to the slow mode, f_s, for the different copolymers, as indicated.

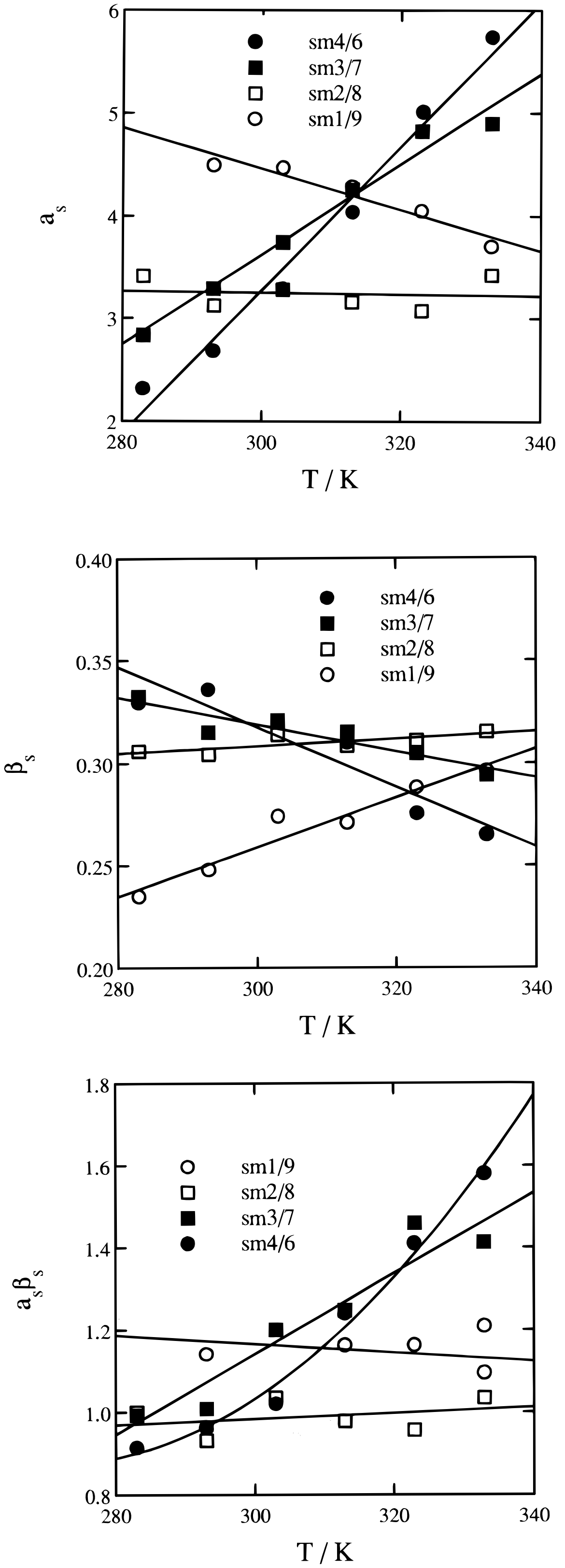

Figure 2. (a, top) Power law exponent a_s, in the relation $\Gamma_s \sim q^{a_s}$, for the slow mode as a function of temperature for the different copolymers, as indicated. (b, middle) Comparison of the temperature dependence of β_s for semidilute solutions of the different copolymers, as indicated. (c, bottom) Temperature dependence of the product $a_s\beta_s$ calculated using the data of parts a and b for the different copolymers, as indicated.

becomes faster with increasing temperature, and their relative contribution to the total scattered light decreases. Thus the effect of increasing temperature on the dynamics is opposite to the effect of increasing concentration.[1] The decrease of f_s is due to a decrease in the concentration and/or the size of the copolymer clusters. The increase of Γ_s/q^2T on heating can also be related to the decrease of cluster size and/or concentration and is also reflected in a decreased macroscopic viscosity.[7] Thus it is possible that the clusters disaggregate (i.e. “melt”) upon heating. Such a disaggregation is likely to occur because at higher temperatures acetone becomes a progressively better solvent for polystyrene. Moreover, the compatibility of MMA and PS segments increases with increasing temperature. The activation energy of cluster formation E_a evaluated from the slopes of f_s versus $1/T$ in Figure 1b is shown in Table 1 for the different copolymer samples.

The q dependence of Γ_s was found to be different from the usual q^2 dependence and may be expressed as $\Gamma_s \sim q^{a_s}$.[1] As shown in Figure 2a, a_s is greater than 2 for all the different copolymer solutions. However, the temperature dependence of a_s is different for the different samples; a_s increases with increasing temperature for sm3/7 and sm4/6 copolymers while it decreases with increasing temperature for sm1/9 and sm2/8 copolymers. These observations are in qualitative agreement with results of a number of studies on associating polymer systems[8] and both physical[9−12] and chemical gels,[7,13−16] where the q dependence of the slow mode in the pregel state is significantly stronger than that of the fast mode.

The experimental results in Figure 2b show that the exponent β_s is independent of q and decreases with increasing temperature for sm3/7 and sm4/6 copolymers while it increases for sm1/9 and sm2/8 copolymers (see Figure 2b).

According to the coupling model the exponent β_s is proportional to $(1 - n)$ and, therefore, the product $a_s\beta_s$ should be a constant, independent of temperature. The product $a_s\beta_s$ calculated using the data of Figure 2a and b is plotted as a function of concentration in Figure 2c. The experimental results show that $a_s\beta_s$ is approximately independent of temperature for the low-styrene-content copolymer solutions. In contrast, the results for sm3/4 and sm4/6 copolymers reveal a pronounced increase in this product, from values close to 1 at low temperatures to 1.5 at higher temperatures.

By examining the temperature dependence of all the quantities in Figure 2, we arrive at the conclusion that different coupling mechanisms must be operating for the copolymers with low and high content of polystyrene.

Acknowledgment. This work was funded by NSF U.S.−Czech Collaborative Research Grants (NSF INT-96 00679 and ME CR ES 044). R.B. acknowledges the support of the NSF Division of Materials Research (Grant NSF-DMR No. 9618467). C.K. acknowledges the financial support of the Alexander von Humboldt Foundation and the Grant Agency of the Academy of Sciences of the Czech Republic (No. A4050604). M.H. thanks the Deutsche Forschungsgemeinschaft (SFB 294) for financial support.

References and Notes

(1) Konak, C.; Helmstedt, M.; Bansil, R. *Macromolecules* **1997**, *30*, 4342.
(2) 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.
(3) Rendell, R. W.; Ngai, K. L.; McKenna, G. B. *Macromolecules* **1987**, *20*, 2250.
(4) Ngai, K. L.; Rajagopal, A. K.; Teitler, S. *J. Chem. Phys.* **1988**, *88*, 5086.
(5) Ngai, K. L. In *Structure and Dynamics of Strongly Interacting Colloids and Supramolecular Aggregates in Solution*; Chen, S. H., Huang, J. S., Tartaglia, P., Eds.; NATO ASI Series C; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. 369, p 221.
(6) Dvoranek, L.; Konak, C.; Neuhausel, T.; Machova, L.; Sorm, M. *Angew. Makromol. Chem.* **1992**, *194*, 149.
(7) Martin, J. E.; Wilcoxon, J. P. *Phys. Rev. Lett.* **1988**, *61*, 373.
(8) Nystrom, B.; Walderhaug, H.; Hansen, F. K. *J. Phys. Chem.* **1993**, *97*, 7743.
(9) Nystrom, B.; Lindman, B. *Macromolecules* **1995**, *28*, 967.
(10) Ren, S. Z.; Shi, W. F.; Zhang, W. B.; Sorensen, C. M. *Phys. Rev. A* **1992**, *45*, 2416.
(11) Ren, S. Z.; Sorensen, C. M. *Phys. Rev. Lett.* **1993**, *70*, 1727.
(12) Lang, P.; Burchard, W. *Macromolecules* **1991**, *24*, 814.
(13) Adam, M.; Delsanti, M.; Munch, J. P.; Durand, D. *Phys. Rev. Lett.* **1988**, *61*, 706.
(14) Martin, J. E.; Wilcoxon, J. P.; Odinek, J. *Phys. Rev. A* **1991**, *43*, 858.
(15) Fang, L.; Brown, W.; Konak, C. *Macromolecules* **1991**, *24*, 6839.
(16) 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.

MA971601M