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Notes

Aggregation of Polystyrene–Poly(methyl methacrylate) Diblock Copolymers in Toluene

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Introduction

Recently, several studies of the dynamic properties of semidilute solutions of diblock copolymers in good solvent for both the blocks have been reported.[1-3] In addition to the modes corresponding to the macromolecular dynamics, modes due to aggregate or micelle formation were observed. The origin of these aggregates is not well understood.

In this note we present a dynamic light scattering (DLS) study of dilute and semidilute solutions of polystyrene (PS)–poly(methyl methacrylate) (PMMA) diblock copolymer in toluene, and give a plausible mechanism for aggregate formation.

Experimental Section

The poly(styrene-*b*-(methyl methacrylate)) diblock copolymer was prepared by a two-step anionic copolymerization, initiated with *n*-butyllithium in THF[4] at a temperature of −40 °C. Prior to the addition of MMA, living polystyrene was stabilized with lithium *tert*-butoxide[5] as described in ref 6. The product was characterized by GPC with a column filled by a mixture of Styragel (79911 GP-109 MIX, H-P) having a separation efficiency in a range of molecular weights of 10^3–10^6, with IR and UV (254 nm) detection. Mass- and number-average molar mass values of the whole copolymer were determined to be 80 000 and 50 000 g·mol^{-1}, respectively. The diblock copolymer was almost symmetrical in block composition, having 0.494 mole fraction of styrene units.

The copolymer samples were dissolved in toluene at room temperature, and the solutions were filtered through 0.2-μm (Milipore) filters into dust-free light scattering cells. The polymer concentrations were c = 0.5, 1, 2, 3, and 4 × 10^{-2} g·cm^{-3}. The overlap concentration $c^* \simeq 2.8 \times 10^{-2}$ g·cm^{-3} was calculated according to the space filling formula[7] using the radius of gyration estimated by interpolation of experimental data for the PS/toluene system.[1] Dynamic light scattering measurements were performed with a standard multiangle Brookhaven Instruments spectrometer with an argon ion laser and BI2030 (Brookhaven Instruments) multi-τ autocorrelator operating with 4 simultaneous sampling times covering approximately 4.5 decades in delay time. The samples were thermostated in a refractive index matching liquid (toluene). The multi-sampling-time autocorrelation functions were analyzed by the inverse Laplace transform using the CONTIN method[8] in order to obtain a distribution of decay times, $A(\tau)$.

Results and Discussion

The decay time distributions, $A(\tau)$, for autocorrelation functions measured at the scattering angle θ = 45° are shown in Figure 1 for several polymer concentrations in the vicinity of c^*. In all cases, the decay time distribution functions consist of two well-separated bands peaked at short and long decay times, τ_f and τ_s, respectively. Both of these dynamic processes correspond to diffusive motion because τ_f^{-1} and τ_s^{-1} were both linearly dependent on K^2 (K is the length of the scattering vector). Hence, it was possible to calculate the corresponding diffusion coefficients, D_f $(=1/2K^2\tau_f)$ and D_s $(=1/2K^2\tau_s)$. The concentration dependences of D_f and D_s and the ratio of the corresponding scattering amplitudes, A_s/A_f, are summarized in Table I. The fast diffusion coefficient D_f decreases with decreasing concentration, while the diffusion coefficient D_s and the ratio A_s/A_f are practically independent of concentration with the exception of only the lowest concentration, where both the quantities are smaller than at higher concentrations. This finding is in contradiction with the results in ref 1, where the slow mode was observed

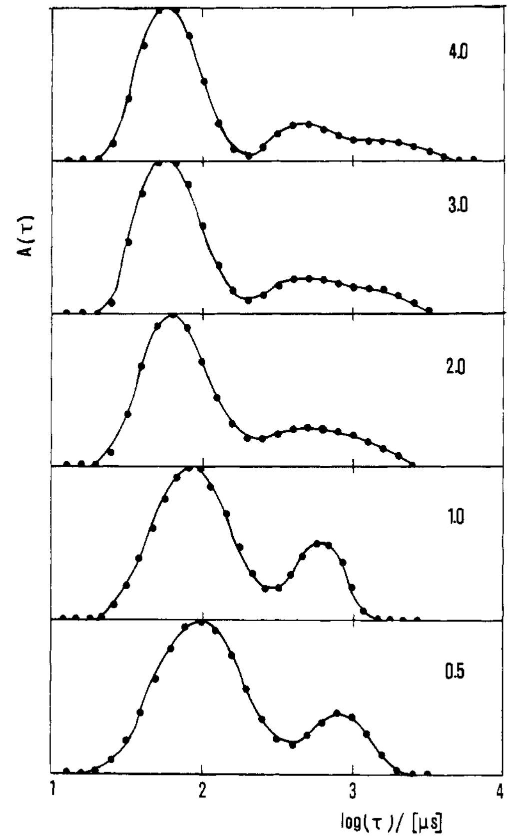

Figure 1. Distribution function $A(\tau)$ of decay time τ of correlation functions from block copolymer solutions (scattering angle Θ = 45°). Numbers on the right side of the figure represent the respective concentrations (10^{-2} g·cm^{-3}).

Table I. Concentration Dependence of D_f and D_s and Ratio of the Corresponding Scattering Amplitudes, A_s/A_f

$c \times 10^2$ (g·cm^{-3})	$D_f \times 10^{11}$ (m^2·s^{-1})	$D_s \times 10^{12}$ (m^2·s^{-1})	A_s/A_f
0.5	3.09	3.21	0.245
1.0	3.40	4.38	0.321
2.0	4.06	4.28	0.304
3.0	4.63	4.29	0.344
4.0	4.65	4.17	0.337

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at high concentrations only ($c^* < c < 8c^*$). Moreover, they found a strong concentration dependence of D_s. The existence of two diffusion coefficients in dilute solutions ($c < c^*$) is generally attributed to the existence of at least two types of well-defined particles with different hydrodynamic sizes or polydispersity. The ratio of D_f/D_s is about an order of magnitude which is much too large to be accounted for the polydispersity of the polymer used in this work ($M_w/M_n = 1.6$). The hydrodynamic radii $R_{Hf} = 12.6$ nm and $R_{Hs} = 107$ nm were calculated from the Stokes–Einstein relation using the zero angle and zero concentration limits of D_f and D_s, respectively.

According to results on PS/toluene solutions,[9] the fast mode should correspond to the cooperative diffusion mode of the copolymer solutions. The slow mode could come from traces of aggregates/associates of the copolymer molecules. The structural mode, which is characteristic of the motion of one block of the copolymer with respect to another,[10] for the PS–PMMA copolymer is too fast to be observed on the time scale used.

What is the driving force of the aggregate formation? Since toluene is a nonselective solvent for PS–PMMA copolymers, which is an equally good solvent for both the blocks,[12] the aggregation cannot be due to the solvent–polymer interactions. A straightforward explanation would be that the incompatibility of PS and PMMA blocks could initiate an aggregation of blocks of the same chemical composition. However, solutions of PS and atactic PMMA mixtures of similar concentrations and molecular mass did not show any phase separation under these conditions,[11,12] suggesting that incompatibility alone is not responsible for aggregation in this copolymer. An alternative explanation can be deduced from the stereoregularity of PMMA blocks. It is well known[13] that syndiotactic (s-PMMA) and/or isotactic PMMA (i-PMMA) macromolecules crystallize in toluene solutions, forming aggregates. PMMA blocks of PS–PMMA block copolymers prepared by anionic polymerization always contain a portion of stereoregular sequences depending on preparation conditions[14] which could account for the aggregation. Using NMR spectroscopy, we found 60% s-PMMA, 17.7% i-PMMA, and 22.3% heterotactic PMMA in the PMMA blocks of the copolymer under study.

Since the formation of stereocomplexes, i.e., aggregates of stereoregular polymers, is strongly influenced by the solvent and temperature, we also performed DLS measurements in different solvents and at different temperatures. (1) The formation of such complexes in stereoregular PMMA is enhanced in toluene, suppressed in benzene, and absent in chloroform (for details, see ref 13). Since the aggregate formation of PMMA macromolecules is suppressed in chloroform solutions,[13] DLS measurements on semidilute solutions ($c = 4 \times 10^{-2}$ g·cm^{-3}) of the PS–PMMA block copolymer in chloroform were performed. Only one mode corresponding to the cooperative diffusion motion was observed; no trace of any aggregates was found. (2) The aggregates of PMMA disassociate (melt) at higher temperatures;[13,15,16] therefore, DLS measurements were made at several temperatures. The temperature dependence of $D_f\eta/T$ and $D_s\eta/T$ and values of the ratio of the corresponding scattering amplitudes A_s/A_f for $\theta = 45°$ are summarized in Table II. D_f and D_s values were multiplied by the factor η/T to eliminate the effect of solvent viscosity and temperature changes. From Table II and Figure 2, where A_s/A_f is plotted as a function of temperature, T, it can be seen that the aggregates melt between 60 and 70 °C and almost disappear above 70 °C. The hydrodynamic size of aggregates is practically independent of temperature below the melting temperature. This is in agreement with the behavior of stereocomplex aggregates of some mixtures of s-PMMA and i-PMMA in toluene[13] and acetonitrile.[17,18] We therefore suggest that the stereoregularity of PMMA chains in the PS–PMMA diblock copolymers could be responsible for the aggregates detected by the DLS measurements. The aggregates probably have a micellar structure with the core formed by a stereocomplex aggregate of s-PMMA and i-PMMA sequences of PMMA blocks and with the shell formed by PS. A similar mechanism probably accounts for aggregation in PS–isoprene block copolymer solutions.[3,19] The isoprene blocks can also crystallize at room temperature.[20] The crystallization process can further be enhanced due to the incompatibility of the blocks. In the case of atactic PMMA the incompatibility of the chemically different blocks of a copolymer would be the primary driving force for aggregation. Thus, the aggregation observed in ref 1 at higher concentrations is, probably, due to phase separation. This also would account for the strong concentration dependence seen in ref 1 which is characteristic of a phase separation process whereas the aggregate formation in the stereoregular copolymers studied here is independent of concentration.

Table II. Temperature Dependence of $D_f\eta/T$ and $D_s\eta/T$ and the Ratio of the Corresponding Scattering Amplitudes, A_s/A_f

temp (°C)	$D_f\eta/T \times 10^{17}$ [a] (Pa·m^2·T^{-1})	$D_s\eta/T \times 10^{18}$ [a] (Pa·m^2·T^{-1})	A_s/A_f [a,b]
25	7.58	7.99	0.30
40	7.13	6.40	0.35
50	7.91	7.73	0.41
60	9.02	8.27	0.39
70	11.1	6.64	0.12

[a] $c = 0.02$ g·cm^{-3}. [b] $\theta = 45°$.

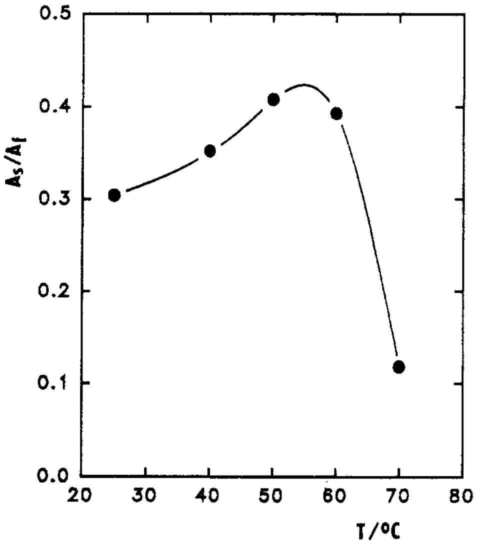

Figure 2. Temperature dependence of A_s/A_f ($c = 2 \times 10^{-2}$ g·cm^{-3}, $\theta = 45°$).

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References and Notes

(1) Haida, H.; Lingelser, J. P.; Gallot, Y.; Duval, M. *Makromol. Chem.* **1991**, *24*, 2701.
(2) Borsali, R.; Fischer, E. W.; Benmouna, M. *Phys. Rev. A* **1991**, *43*, 5732.

(3) Koňák, C.; Podešva, J. *Macromolecules* **1991**, *24*, 6502.
(4) Fetters, L. J.; Young, R. N. In *Anionic Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrat, J. E., Ed.; ACS Symposium Series 166; American Chemical Society: Washington, DC, 1981; p 95.
(5) Vlček, P. Manuscript in preparation.
(6) Vlček, P.; Lochmann, L.; Otoupalová, J. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 163.
(7) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: London, 1979.
(8) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.
(9) Duval, M.; Haida, H.; Lingelser, J. P.; Gallot, Y. *Macromolecules* **1991**, *24*, 6867.
(10) Benmouna, M.; Benoit, H.; Borsali, R.; Duval, M. *Macromolecules* **1987**, *20*, 2620.
(11) Borsali, R.; Duval, M.; Benoit, H.; Benmouna, M. *Macromolecules* **1987**, *20*, 1112.
(12) Koňák, C.; Tuzar, Z.; Jakeš, J. *Polymer* **1990**, *31*, 1866.
(13) Spěváček, J.; Schneider, B. *Adv. Colloid Interface Sci.* **1987**, *27*, 81.
(14) Braun, D.; Herner, H.; Johnsen, U.; Kern, W. *Makromol. Chem.* **1962**, *51*, 15.
(15) Spěváček, J.; Schneider, B. *Makromol. Chem.* **1974**, *175*, 2939.
(16) Spěváček, J.; Schneider, B.; Bohdanecký, M.; Sikora, A. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1623.
(17) Spěváček, J.; Fernandez-Pierola, J. *Makromol. Chem.* **1987**, *188*, 861.
(18) Spěváček, J. *Makromol. Chem., Makromol. Symp.* **1990**, *39*, 71.
(19) Balsara, N.; Štěpánek, P.; Lodge, T. P.; Tirell, M. *Macromolecules* **1991**, *24*, 6227.
(20) Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Interscience Publishers: New York, 1966.