NOTES

Internal Motion of Polystyrene Single Chains in Semidilute Solutions of Poly(methyl methacrylate)/Benzene as Measured by Quasi-Elastic Light Scattering

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Extensive efforts with various kinds of experimental techniques have been made to measure the self-diffusion coefficient of a single chain in highly entangled polymer solution.^{1–8} On the contrary, only a few experimental studies have been reported on the internal motions of entangled chains.^{6,9–11} In a previous paper,⁶ we have studied the internal motions, as well as the translational diffusion, of single polystyrene (PS) chains being weakly entangled with matrix semidilute solutions of poly(methyl methacrylate) (PMMA) and benzene by means of the optical labeling technique of light scattering. In the range of wave number $K > R_g^{-1}$, where R_g is the radius of gyration, a strong K -dependence of the line width was observed in consistence with stronger molecular-weight dependence of the translational diffusion coefficient compared with those in pure benzene. In a following study,⁷ the translational diffusion of single PS chains highly entangled with matrix networks was investigated. This note is concerned with the internal motion of highly-entangled chains to complete a series of these studies.

Extensive measurements⁷ of the translational diffusion coefficient for various combinations of molecular weight of PS (M_N) (dif-

fusant) and PMMA (M_P) (matrix polymer) and the concentration of PMMA allowed us to establish a diffusion map representing dominant types of diffusion in a scaled M_N – M_P space, which is illustrated in Figure 1. The scaled factors $M_{\xi N}$ and $M_{\xi P}$ in Figure 1 are the molecular weight of a blob, a chain unit within the static correlation length, for PS and PMMA respectively. Crossover from Stokes–Einstein (S-E) type diffusion to reptation was found. The S-E type diffusion was realized in case of single long-chain diffusion in the semidilute matrices of short chains, whereas the reptational diffusion was dominant for relatively short chains in highly-entangled semidilute solutions of long chains.

It is easy to presume that this crossover behavior observed in translational motion may appear in the internal motion of entangled chains, as pointed out by Martin.¹¹

The purpose of this work is to investigate the consistent crossover behavior in the internal motion of single PS chains in highly entangled semidilute solution of PMMA and benzene. Molecular weights of PS and PMMA and PMMA concentrations chosen here are illustrated on the $M_N/M_{\xi N}$ – $M_P/M_{\xi P}$ map of Figure 1, which cover the S-E type and reptational diffusion regions.

Figure 1. Diffusion map in the M_N/M_{EP} - M_P/M_{EP} space. Solid circle (o) at the end of the boundary line separating the S-E type (S-E) and the reptative (rep) diffusion regions indicates the onset of the entanglements determined from diffusion behavior. Various symbols represent the samples chosen for this work: the symbols ($\square$, $\bullet$, $\circ$, $\blacktriangle$) are for PS of $M_N = 8.4 \times 10^6$ in the PMMA solution of $M_P = 4.05 \times 10^6$ at matrix concentrations $C = 0.9116 \times 10^{-2} \text{ g cm}^{-3}$ ($\square$), $1.292 \times 10^{-2} \text{ g cm}^{-3}$ ($\bullet$), $1.860 \times 10^{-2} \text{ g cm}^{-3}$ ($\circ$), and $2.723 \times 10^{-2} \text{ g cm}^{-3}$ ($\blacktriangle$); the symbols ($\blacksquare$, $\triangle$, $\blacktriangle$) are for PS of $M_N = 3.84 \times 10^6$ ($\blacksquare$), 5.5×10^6 ($\triangle$), and 8.42×10^6 ($\blacktriangle$) in the PMMA solution of $M_P = 4.05 \times 10^6$ and $C = 0.036 \text{ g cm}^{-3}$; and the symbol ($\circ$) represents PS of $M_N = 4.2 \times 10^5$ in the matrix solution of $M_P = 1.93 \times 10^6$ and $C = 0.037 \text{ g cm}^{-3}$.

EXPERIMENTAL

Poly(methyl methacrylate)s (PMMA) prepared by radical polymerization followed by fractionation had weight-average molecular weight $\bar{M}_w = 1.93 \times 10^6$ and 4.05×10^6 with polydispersity index $\bar{M}_w/\bar{M}_n = 1.04$ and 1.06 , respectively. Narrow-distribution polystyrene (PS) samples (Toyo Soda Co.) had nominal $\bar{M}_w$ ranging from 4.2×10^5 to 8.4×10^6 . The concentration C of PMMA ranged from $0.911 \times 10^{-2} \text{ g cm}^{-3}$ to $3.73 \times 10^{-2} \text{ g cm}^{-3}$.

Details of solution preparation and the light-scattering spectrometer have been described elsewhere.^{6,7,12}

The autocorrelation function $G^{(2)}(\tau)$ of the intensity of scattered light was measured at various scattering angles θ by a Kowa digital correlator Z216 and a Malvern Dual Function Digital Correlator K7027, using an argon ion laser (operating at wavelength $\lambda_0 = 488 \text{ nm}$)

and a He-Ne laser ($\lambda_0 = 633 \text{ nm}$). The measured $G^{(2)}$ has the form of

$$G^{(2)}(\tau) = A(1 + \beta |g^{(1)}(\tau)|^2)$$

where $g^{(1)}(\tau)$ is the normalized correlation function of the scattered electric field, A is the background, and β an unknown parameter in the data-fitting procedure.

Average line width $\bar{\Gamma}$ was computed from the $g^{(1)}(\tau)$ by the method of cumulants.¹³ The wave number K was calculated by the definition $K = (4\pi n/\lambda_0) \sin(\theta/2)$ with λ_0 being the wavelength of light in vacuum and n the refractive index of the solution.⁷

RESULTS AND DISCUSSION

Figure 2 represents K -dependence of $\bar{\Gamma}$, in which are shown double logarithmic plots of $\bar{\Gamma}/K^2$ against K for the PS of $M_N = 8.42 \times 10^6$ in the PMMA solutions of $M_P = 4.05 \times 10^6$ with different matrix concentrations, and those for different molecular-weight PS's in the PMMA solution of $M_P = 4.05 \times 10^6$ with $C = 0.036 \text{ g cm}^{-3}$. Here, the same symbols as Figure 1 are used. With increase in matrix concentration, the K -dependence of $\bar{\Gamma}/K^2$ at higher angles becomes stronger to have the power of more than unity. (See upper four data and one of the lower data ($\blacktriangle$).) The values of $\bar{\Gamma}/K^2$ for different $\bar{M}_w$'s of PS appear to merge in a single curve, *i.e.*, to become independent of $\bar{M}_w$, at higher angles, which results in the stronger K -dependence for higher $\bar{M}_w$'s.

Type of the translational diffusion of polymer chains is reflected on the internal motion, *i.e.*, on the K -dependence of $\bar{\Gamma}$ at $R_g K > 1$, and scaling arguments logically lead to the speculation that there must be a change in K -dependence at a threshold wave-number K_c corresponding to the crossover of S-E type/reptation, as Martin¹¹ has proposed. The K_c is given by the reciprocal of a characteristic length λ representing the critical dimension of the largest chain that can make reptative diffusion:¹⁴ if $R_g > \lambda$, the S-E type diffusion is

Figure 2. Angular dependence of $\bar{F}/K^2$ for PS single chains in PMMA/benzene semidilute solutions. Upper data ($\square, \bullet, \circ, \circ$) and one of the lower data ($\blacktriangle$) are for PS of $M_N = 8.4 \times 10^6$ in the PMMA solution of $M_P = 4.05 \times 10^6$ at different matrix concentrations. Lower data ($\blacksquare, \triangle, \blacktriangle$) are for PS of different molecular weights in the PMMA solution of $M_P = 4.05 \times 10^6$ and $C = 0.036 \text{ g cm}^{-3}$. Symbols are the same as those in Figure 1.

dominant, while if $R_g < \lambda$, the reptational motion is dominant, in translational diffusion of a whole chain. In case of $\lambda > \xi$ (the static correlation length), the K -dependence of $\bar{F}$ is predicted for each case as follows.

For $R_g/\lambda < 1$,

$$\begin{aligned} K < R_g^{-1} & \quad \bar{F}/K^2 \sim K^0 \\ R_g^{-1} < K < \xi^{-1} & \quad \bar{F}/K^2 \sim K^4 \\ \xi^{-1} < K & \quad \bar{F}/K^2 \sim K^1 \end{aligned} \quad (1)$$

If $R_g/\lambda > 1$,¹¹

$$\begin{aligned} K < R_g^{-1} & \quad \bar{F}/K^2 \sim K^0 \\ R_g^{-1} < K < \lambda^{-1} & \quad \bar{F}/K^2 \sim K^1 \\ & \quad \text{(the second Zimm)} \\ \lambda^{-1} < K < \xi^{-1} & \quad \bar{F}/K^2 \sim K^4 \\ \xi^{-1} < K & \quad \bar{F}/K^2 \sim K^1 \end{aligned} \quad (2)$$

Figure 3. Double-logarithmic plots of $\bar{F}/K^2 D$ vs. KR_g for various combinations of molecular weights and concentrations of PMMA. Symbols are the same as those in Figure 1. Dashed line represents the result for PS in pure benzene.⁶

It is worth noting that, in the second Zimm regime, $\bar{F}$ is represented as $\bar{F} \sim T/\eta_p K^3$, where η_p is the viscosity of the matrix solution, while in the first Zimm regime ($\xi^{-1} < K$), $\bar{F} \sim T/\eta_s K^3$ with the solvent viscosity η_s . Thus, for a S-E type diffusion chain, the second Zimm regime appears in the internal motion ($R_g K > 1$) at $K\lambda < 1$, in other words, as long as the length scale of observation is longer than λ , the chain motion is of the Zimm type for $R_g > \lambda$, while a reptative chain ($R_g < \lambda$) has no second Zimm regime.

To examine the above prediction, in Figure 3 are plotted the values of $\bar{F}/K^2 D$ against KR_g with the same symbols as in Figure 1, where D is the translational diffusion coefficient obtained in the previous study.⁷ The dashed line indicates the data of PS/benzene binary solution obtained in a previous study.⁶ Comparing Figure 1 and Figure 3, one finds that the points assigned to the S-E type diffusion in Figure 1 make a single master curve in Figure 3, which is almost superposed on that of the binary system (the dashed line) in the range of $\log(KR_g) < 0.5$. This finding suggests that single chains of S-E type translational diffusion have the wide second Zimm regime, namely, hydrodynamic interaction is effective in this case. It should be noted here, however, that the hydrodynamic interaction

Figure 4. Profiles of the time correlation function $|g^{(1)}(\tau)|$. $\circ$, at $KR_g = 2.95$ for the sample indicated by $\bullet$ in Figure 1 ($M_N = 8.4 \times 10^6$; $M_P = 4.05 \times 10^6$; $C = 0.0129 \text{ g cm}^{-3}$); Δ , at $KR_g = 2.56$ for the sample indicated by $\blacksquare$ in Figure 1 ($M_N = 3.84 \times 10^6$, $M_P = 4.05 \times 10^6$; $C = 0.036 \text{ g cm}^{-3}$); $\blacksquare$, at $KR_g = 3.34$ for PS of $M_N = 3.84 \times 10^6$ in pure benzene. Bars (—) indicate one decade.

may not be so simple as in pure benzene, or that the Zimm-like behavior might be only apparent, in view of the finding that the ratio of hydrodynamic radius R_h to R_g for PS in PMMA/benzene semidilute solutions is around a half of that for PS in pure benzene.⁷

On the other hand, the points in Figure 3 that correspond to those which locate close to or inside of the reptation region in Figure 1 tend to deviate upwards from the master curve. This deviation suggests no existence of the second Zimm regime and a stronger K -dependence which are expected for the reptative chains ($R_g < \lambda$), although the power of K -dependence of $\bar{F}/K^2$ does not reach the theoretical value for reptative motion yet.

The crossover behavior consistently observed in translational diffusion and internal motion was also found in the profile of time-correlation function at $KR_g > 1$. In Figure 4 are shown double logarithmic plots of the correlation functions for two representative samples measured at $\log(R_g K) \approx 0.5$: one (a) is a

sample that has the $\bar{F}/K^2$ -value on the master curve in Figure 3, and the other (b) has the $\bar{F}/K^2$ -value deviating from the master curve. The correlation function (a) indicated by ($\circ$) is superposed on that of PS in pure benzene ($\blacksquare$) in arbitrary scale, while the profile of correlation function (b) (Δ) differs from that in benzene: the chain motion assigned to the S-E type exhibits not only the same K -dependence of $\bar{F}/K^2$ but also the same profile of the correlation function at $KR_g > 1$ as those of the PS/benzene binary solution, whereas the correlation function of the sample showing more reptative motion decays in a different manner from that of the PS in pure benzene.

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14. The explicit expression of λ is given as

$$\lambda = M_p^{1/(1-\nu)} \phi^{\nu/(3\nu-1)(1-\nu)}$$

in terms of the quantities defined in the previous paper of ref 7, which can be derived from the crossover condition.