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Diffusion Measurements of Poly(methyl methacrylate) in Semidilute Solutions of Polystyrene in Thiophenol with an Analytical Ultracentrifuge. Dynamics of Polymer–Polymer–Solvent Ternary Systems. 3

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In a previous paper,[1] referred to as part 2 hereafter, we studied the diffusion and the sedimentation behavior of poly(methyl methacrylate) (PMMA) in mixtures of polystyrene (PS) and thiophenol (TPh) over wide ranges of both concentration and molecular weight of PS by using the dynamic light scattering (DLS) and the sedimentation velocity (SV) techniques. In the study, we compared the reduced quantity D/D_0 with the corresponding reduced quantity s/s_0. Here D_0 and s_0 are values of D and s in pure thiophenol extrapolated to infinite dilution. The two reduced quantities should be identical if the same friction coefficient f were effective for both diffusion and sedimentation even in the semidilute regime where polymer dynamics are greatly affected by the intermolecular interaction between polymer chains. It was found that (1) as far as molecular weight of PS, M_{PS}, was lower than that of PMMA, M_{PMMA}, the ratios were in good agreement with each other within experimental uncertainties; (2) when M_{PS} was higher than M_{PMMA}, D/D_0 was smaller than s/s_0 by more than 30% at higher c_{PS}. Taking into account that time and spatial scales of DLS (ms and μm) and SV measurements (min and mm) are different for more than 3 orders of magnitude, we attributed the observed difference between D/D_0 and s/s_0 to the cause that the frictional force experienced by a PMMA molecule in the PS solutions depended on the relaxation time characteristic of the surrounding medium.[2,3] In order to examine this conjecture, we have attempted one classical diffusion measurement on the same solutions, of which time and spatial scales are comparable with those of SV measurements. Only preliminary results were reported in part 2. Here we report results of a more systematic study.

Polymer samples of PMMA and PS used are the same as those used in part 2; $M_{PMMA} = 343000$, and $M_{PS} = 43900$, 775000 and 8420000, respectively. Polymer solutions were prepared by exactly the same way as described in part 2. The concentrations of polymer in solutions were determined by weighing.

Diffusion experiments were performed at 25 ± 0.05 °C by making use of an analytical ultracentrifuge (Beckmann Spinco Model E). Since the principle of the technique is described in detail in texts,[4] experimental procedures are here mentioned only briefly. The synthetic boundary method, which uses a cell with double sectors connected with a capillary, has been adopted. One sector is filled with a solution of PS in TPh as a solvent and the other is half-filled with a ternary solution of PMMA and PS in TPh with exactly the same c_{PS} as that of the solvent. Under a small centrifugal force, the solvent in the former sector flows into the latter sector through the capillary and a sharp synthetic boundary is formed. The spreading of the synthetic boundary with time due to the diffusion of PMMA has been detected by using the schlieren optics. D has been estimated from eq 1, where A and H are an

$$(A/H)^2 = 4\pi Dt(1-z) \tag{1}$$

area and a peak height of the schlieren pattern at time t, and z is a factor that corrects the sharpening effect of the pattern due to the concentration dependence of s.

$$z = 2r_0\omega^2 k_S c_0 s(0)(H/A)t \tag{2}$$

Here r_0 is a distance from the center of rotation to the meniscus, k_s is the concentration coefficient of s, ω is the angular frequency of rotation, and $s(0)$ is the value of s at infinite dilution of PMMA. Since eq 1 holds only for $z \leq 0.16$, ω was made as low as possible to keep z smaller than 0.08.

The reliability of the method has been tested by comparing D data of dilute PMMA solutions in TPh with those obtained by DLS.[5] By fitting the data to eq 3,

$$D = D_0(1 + k_D c_{PMMA}) \tag{3}$$

we obtained $D_0 = 1.30 \times 10^{-7}$ cm^2 s^{-1} and $k_D = 46$ cm^3 g^{-1}. By comparing these values with $D_0 = 1.32 \times 10^{-7}$ cm^2 s^{-1} and $k_D = 63.8$ cm^3 g^{-1} obtained from DLS measurements, we may say that agreement is excellent for D_0 but less satisfactory for k_D. Thus the macroscopic method we adopted for diffusion measurements tends to give a D value smaller than true one at finite c_{PMMA}. The difference is however only 5% at the highest concentration of $c_{PMMA} = 0.2\%$ measured and is about 2% at $c_{PMMA} = 0.1\%$, at which most D data were obtained. According to Kawahara, an experimental accuracy of the method is at best 5%. Therefore the differences at finite c_{PMMA} still remain within an experimental error of 5%. This indicates that D can be accurately determined with this classical method as long as experiments are carefully performed.

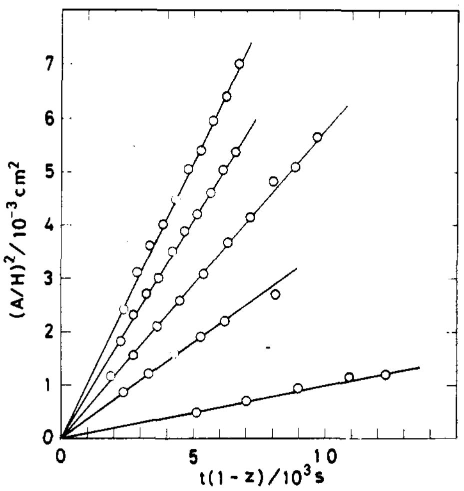

Figure 1. Data analysis for the diffusion behavior of PMMA in solutions of PS ($M_{PS} = 43900$, F4 series) with eq 1. From the top, $c_{PS} = 1.01$, 3.01, 5.00, 9.99, and 16.8%.

Figure 1 illustrates data analysis with eq 1 on PMMA in a series of solutions of PS with $M_{PS} = 43900$ from the dilute to the semidilute regime. The plots are well represented by solid straight lines and the slope provides an estimate of D to an accuracy of about 10%.[6] D thus obtained has been reduced to $(D/D_0)_{AU}$ by using the value of D in pure thiophenol, $D_0 = 1.30 \times 10^{-7}$. In Figure 2 the present data of $(D/D_0)_{AU}$ are compared with earlier data

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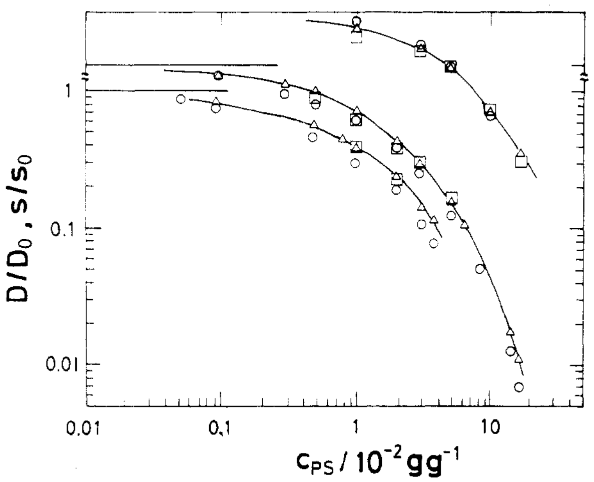

Figure 2. Comparison of $(D/D_0)_{AU}$ measured by using an analytical ultracentrifuge with earlier D/D_0 and s/s_0 data.[1] Symbols are (□) $(D/D_0)_{AU}$ with an ultracentrifuge; (○) $(D/D_0)_{DLS}$ with DLS; (△) s/s_0 with an ultracentrifuge. M of PS for each curve is, from the top, 43 900, 775 000 and 8 420 000, respectively.

of $(D/D_0)_{DLS}$ and s/s_0 that were obtained by DLS and SV methods, respectively. In solutions of PS with M_{PS} = 43 900, three reduced quantities agree with one other except those in the 1% PS solution. This supports our view that as long as the molecular weight of the polymer constituting the medium is much smaller than the molecular weight of the diffusive component the medium simply acts as the viscous fluid for the Brownian motion of the particle, and thus the friction coefficient of a PMMA molecule does not depend on the time and the spatial scales of the methods of measurements.

On solutions of PS with M_{PS} = 775 000 (F80 series) and M_{PS} = 8 420 000 (F850 series) higher than M_{PMMA}, all measurements of $(D/D_0)_{AU}$ have been made in the semidilute regime of PS. The critical overlapping concentration c_{PS}* is 0.5 and 0.1% for F80 and F850 series, respectively, as estimated from $c_{PS}^* = 1/[\eta]\rho$.[1] When the present data of $(D/D_0)_{AU}$ are compared with the s/s_0 data, they look to agree with each other within an uncertainty of 15%, being about equal to the sum of experimental uncertainties for the two quantities. The agreement conforms to our expectation that as long as the time and spatial scales of the diffusion and sedimentation measurements are similar in magnitude, the same friction coefficient is applicable to both the transport processes of PMMA in the semidilute regime. It has been found in part 2 that $(D/D_0)_{DLS}$ obtained by using the dynamic light scattering technique is always smaller than s/s_0 in the semidilute solutions of PS with $M_{PS} > M_{PMMA}$ and the difference amounts to about 50% in the PS solution with M_{PS} = 775 000 at the highest concentration of 16.2% measured. It is seen from Figure 2 that $(D/D_0)_{AU}$ is larger, beyond the experimental uncertainty, than $(D/D_0)_{DLS}$ at $c_{PS} \geq 3\%$ for F80 series and also at $c_{PS} \geq 1\%$ for F850 series. Since products of c_{PS} and M_{PS} of these solutions are close to or larger than the critical entanglement molecular weight M_c = 31 000 defined as a break in the η-M_w relationship of the PS melt,[7] we may expect the formation of a stable entanglement network with very long relaxation times in these solutions. This network then may give rise to varying D as the time and spatial scale of the measurements are varied. It appears that at $c_{PS} \leq 2\%$ for F80 series, $(D/D_0)_{AU}$ takes a value intermediate between $(D/D_0)_{DLS}$ and s/s_0. In this concentration region the entanglement network is not yet formed and concentration fluctuation of PS occurs in a large scale. At present it seems quite difficult to make a clear-cut interpretation on the observed difference between $(D/D_0)_{DLS}$ and s/s_0 in this concentration region. In conclusion, this work gives a support to the idea proposed by Marqusee and Deutch that the frequency-dependent friction coefficient is applicable for the transport of a polymer molecule in the entangled polymer network.

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Note Added in Proof. When this note was submitted for publication, one of the reviewers kindly pointed out that the correct expression of the ratio s/s_0 for the three-component system should read as

$$s/s_0 = (f_0/f)(\partial\rho/\partial c_{PMMA})/(\partial\rho/\partial c_{PMMA})_{c_{PS}=0} = (f_0/f)(\partial\rho/\partial c_{PMMA})/(1 - \bar{v}\rho)$$

This equation indicates that s/s_0 reflects the dependence of f on M_{PS} and c_{PS} only after the dependence of the buoyancy term on M_{PS} and c_{PS} is properly corrected. We have measured $(\partial\rho/\partial c_{PMMA})$ by using a mechanical oscillator in three media such as pure TPh, 5% PS (F80, M_{PS} = 775 000)–TPh, and 1% PS (F850, M_{PS} = 8 420 000)–TPh and obtained values of 0.120 ± 0.002, 0.118 ± 0.004 and 0.113 ± 0.002 for the respective solvents. Though the data are limited, $(\partial\rho/\partial c_{PMMA})$ appears to take a value in PS solutions slightly smaller than that in pure TPh. Thus, if s/s_0 is corrected for this effect as $(s/s_0)_{corr}$, the difference between $(s/s_0)_{corr}$ and (D/D_0) (by DLS) observed for the solutions with high M_{PS} at higher c_{PS} will become larger. It may be concluded that, at least, the effect of the $(\partial\rho/\partial c_{PMMA})$ term cannot explain the disagreement between s/s_0 and D/D_0 reported in part 2 of this series.

Registry No. PMMA, 9011-14-7; PS, 9003-53-6; TPh, 108-98-5.

References and Notes

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