Macromolecules 1985, *18*, 2516–2522

Dynamics of Polymer–Polymer–Solvent Ternary Systems. 2. Diffusion and Sedimentation of Poly(methyl methacrylate) in Semidilute Solutions of Polystyrene in Thiophenol

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Received March 4, 1985

ABSTRACT: The diffusion coefficient D and the sedimentation coefficient s of poly(methyl methacrylate) (PMMA, M_w = 343 000) in thiophenol (TPh) solutions of polystyrene (PS) have been studied as functions of PS concentration, c_{PS} (0.051–16.8 × 10^{-2} g g^{-1}), and molecular weight, M_{PS} (43 900–8 420 000), by using dynamic light scattering and analytical ultracentrifuge, respectively. The concentration of PMMA has been fixed at a low value of 0.1% so that D and s can be related, to a good approximation, to the transport of a single PMMA chain in semidilute solutions of PS. It has been found that the reduced quantity D/D_0 is in agreement with s/s_0 in solutions of PS with lower molecular weights of 43 900 and 186 000. Here D_0 and s_0 are the values of D and s for PMMA in pure thiophenol extrapolated to infinite dilution. In the solutions of PS with higher molecular weights of 775 000 and 8 420 000, however, D/D_0 has been found to be less than the corresponding s/s_0 by about 20–30%. These results have been interpreted as showing that the frictional force experienced by a PMMA molecule in the solutions depends on the relaxation time characteristic of the surrounding medium. The dependence of D/D_0 and s/s_0 on c_{PS} in the semidilute solutions of PS with high molecular weights could be well represented by the form of $\exp(-Ac^{\delta})$, which has been predicted by Ogston et al. for the diffusion of spherical particles in cross-linked gel networks. The exponent δ was found as 0.55 ± 0.05 and 0.67 ± 0.05 for the diffusion and the sedimentation data in the highest M_{PS} solutions, respectively. The difference in δ suggests again that there is a clear distinction between diffusion and sedimentation in the transport mechanism of the polymer chain.

Introduction

The friction coefficient f is a fundamental quantity in the transport process of polymer molecules in solutions. At infinite dilution where individual polymer molecules move independently of each other, f has a clear physical meaning and is directly related to the size and shape of the molecule; for example, the Stokes law $f = 6\pi\eta_s R$ is applicable to a spherical particle. Here R is the radius of the particle and η_s is the solvent viscosity. For an estimate of f, diffusion and sedimentation measurements are known as useful methods. Two transport coefficients, the translational diffusion coefficient D_0 and the sedimentation coefficient s_0, at infinite dilution can be expressed in terms of the *same* friction coefficient f. The combination of D_0 and s_0 then gives a well-known relationship that makes it possible to estimate the molecular weight of the polymer:[1]

$$M = \frac{s_0 RT}{D_0\,(1 - \bar{v}\rho_s)} \qquad (1)$$

Here $\bar{v}$ is the specific volume of the polymer in the solution, and ρ_s is the density of the solvent.

At finite concentration, f becomes dependent on concentration in quite a complicated manner due to the direct interaction as well as the hydrodynamic interaction between molecules.[2,3] Although the same friction coefficient has long been assumed to be operative in both diffusion and sedimentation even in the semidilute regime where polymer chains overlap extensively, recent experimental works[4–7] on binary polymer solutions raised a question concerning the identity of three frictional coefficients, f^*, f_s, and f_m. They are defined in eq 2–4, which can be obtained with three different techniques. Here, the sedimentation coefficient s has been measured by an analytical ultracentrifuge, the self-diffusion coefficient D_s by pulsed gradient NMR, and the mutual diffusion coefficient D_m by either the classical gradient diffusion technique or dynamic light scattering (DLS). ρ is the density of the solution, and μ and c are the chemical potential and the concentration (g/cm^3) of the solute, respectively. It has been shown that (1) f_m is equal to f^* within experimental error if the molecular weight distribution of the polymer is sufficiently narrow, but (2) f_m is not equal to f_s. The latter result seems compatible with the theoretical argument by Marqusee and Deutch that the fluctuating force due to the relative motion of the macromolecules gives rise to a significant contribution to the concentration dependence of f. The effect of the direct interaction on f leads further to the supposition that in general f is frequency dependent; that is, values of f may depend on both the time and the spatial scale on which the measurements of f are made.[2,26]

$$s = (M/N_a f^*)(1 - \bar{v}\rho) \qquad (2)$$

$$D_s = \frac{RT}{N_a f_s} \qquad (3)$$

$$D_m = \frac{c}{N_a f_m}\left(\frac{\partial \mu}{\partial c}\right)_{T,P} \qquad (4)$$

In a previous report,[8] hereafter referred to as part 1, we showed that (1) polystyrene (PS) and thiophenol (TPh) were not only isorefractive but also isopycnic and (2) s and D of poly(methyl methacrylate) (PMMA) in semidilute TPh solutions of PS were measurable fairly accurately at low PMMA concentration by the conventional sedimentation velocity experiments and dynamic light scattering, respectively. The use of this ternary system thus gives a unique opportunity for comparison of concentration dependence of two friction coefficients that are related to the sedimentation coefficient and the diffusion coefficient of a single PMMA chain.

Since the time and the spatial scale of the sedimentation experiments (min and mm) are much larger than those of the DLS (ms and μm), such a study is expected to give an additional insight on the frictional force experienced by the polymer molecule in the condensed state. This is the first objective of this paper.

The second purpose of the present study is concerned with the transport mechanism of a flexible polymer molecule in the semidilute regime. The diffusion of spherical

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particles in gels has been treated by Ogston et al.[9] The theory is based on the stochastic model of diffusion migration. The presence of the gel network has been considered to impede the diffusive motion of the particle in two ways; i.e., (1) diffusion effectively occurs only when the particle jumps from a position in one mesh of the network to another mesh and (2) the jumping frequency effective for the diffusion is decreased due to the collision of the particle with the network fiber. The final expression for the concentration dependence of D may be written in the form of eq 5 with $\delta = {}^1/_2$. Here A is a constant

$$D/D_0 = \exp(-Ac^{\delta}) \qquad (5)$$

determined by the radius R of the diffusing particle. The exponent ${}^1/_2$ agrees with their experimental data and also with an experimental finding of Laurent et al.[10] on the diffusion and the sedimentation of compact particles in aqueous solutions of hyaluronic acid. Langevin and Rondelez[11] have recently shown that s of spherical particles in aqueous solutions of poly(ethylene oxide) decreases with polymer concentration in the same form as eq 5 but with a slightly different value of the exponent $\delta = 0.62$. They have suggested that $\delta = 0.62$ is in harmony with the current idea that in the semidilute regime the polymer solution is characterized by the correlation length ξ which is dependent only on concentration as $\xi \propto c^{-\nu}$ and that the solution can be viewed as a transient network of mesh size ξ. Lin and Phillies[12] have reported $\delta \cong {}^2/_3$ for the diffusion of polystyrene latex particles in aqueous solutions of poly(acrylic acid). This value is very close to values of ν reported for polymer–good solvent systems in the semidilute regime.[13] Hydrodynamic properties of a flexible polymer molecule are, in many cases, successfully explained by modeling it as an impenetrable sphere of the hydrodynamic radius R_H. For $R_H < \xi$, eq 5 may be still applicable even if the diffusant is a flexible polymer. For $R_H > \xi$, however, there is no justification for the validity of eq 5, and other diffusion mechanisms such as reptation might be responsible above the critical overlapping concentration c.* This reptation model[14] predicts the power-law depdendence of the self-diffusion coefficient on c in the entangled region. This type of dependence is in contrast to that of the exponential type. Under the present circumstances where no reliable data are present for the test of the models, it seems worthwhile to make diffusion measurements over a wide range of concentration of a matrix component by using a well-characterized polymer–polymer–solvent ternary system such as PMMA–PS–thiophenol.

Experimental Section

Materials. Poly(methyl methacrylate) (Scientific Polymer Products) was purified by dissolving it in benzene and precipitating in methanol. The freeze-dried polymer was used as the sample. Molecular weight of the sample was determined as 343 000 from $[\eta] = 130$ cm^3 g^{-1} in chloroform at 30 °C by the use of the $[\eta]$–M_w relationship reported by Meyerhoff and Schultz.[15] GPC measurements on the sample gave $M_{GPC} = 342\,000$ and $M_w/M_n = 1.1$. Four narrow-distribution molecular weight polystyrene samples ($M_w = 43\,900$ (sample code F4), 186 000 (F20), 775 000 (F80), and 8 420 000 (F850, $M_w/M_n = 1.17$), Toyo Soda) were used as a matrix component of the polymer–polymer–solvent ternary solution without further purification. Reagent-grade thiophenol (TPh, Nakarai Co.) was distilled under nitrogen atmosphere at 48 °C and 7 mmHg. The distilled solvent was sealed in test tubes under nitrogen atmosphere until it was used for preparation of solutions. Specific densitites of the polymers in TPh and the density of the solvent were measured with a mechanical oscillator (Shibayama, Model SS-D-200) and are listed in Table I. The table also gives values of refractive index $n^{25}{}_D$. $n^{25}{}_D$ of thiophenol was measured with a Pulfrich refractometer.

Table I
Specific Densities of the Polymers, Density of the Solvent, and Their Refractive Indices

	ρ or $1/\bar{v}$, g cm^{-3}	$n^{25}{}_D$
polystyrene (PS)	1.0776	1.59–1.60[a]
poly(methyl methacrylate) (PMMA)	1.169	1.4947[a]
thiophenol (TPh)	1.0728	1.5871[b]

[a] Lindemann, M. K. "Polymer Handbook", 2nd ed.; Brandrup, J.; Immergut, E. H., Eds.; Wiley: New York, 1975; Chapter V. [b] $n^{20}{}_D = 1.5897$ ("Organic Solvents", 2nd ed.; Weissberger, A.; Proskaver, E. S.; Riddick, J. A.; Toops, E. E., Jr., Eds.; Interscience: New York, 1955.)

Table II
M of PS and PMMA, Range of c_{PS}, and c_{PS}* Values

sample	$M_w \times 10^{-4}$	c_{PS}/ $(10^{-2}$ g g$^{-1})$	c_{PS}*/ $(10^{-2}$ g g$^{-1})$ $(=1/[\eta]\rho)$[a]
PS F4	4.39	1–16	3.59
F20	18.6	0.3–10	1.31
F80	77.5	0.1–16	0.482
F850	842	0.05–4	0.0907
PMMA	34.2		

[a] $[\eta] = 1.46 \times 10^{-2} \times M^{0.70}$; cm^3 g^{-1} for PS in thiophenol at 25 °C.

Ternary solutions were prepared by dissolving the polymers in the optically clean thiophenol. A series of solutions with constant PMMA concentration of 1×10^{-3} g/g and varying PS concentration were prepared for each molecular weight of PS. They are designated as F4, F20, F80, and F850 series following the code name of PS. Each solution of F4 and F20 series was made optically clean by filtering with a Millipore filter (nominal pore size, 0.5 μm). Filtration with a Millipore filter (nominal pore size, 1 μm) was also applied to solutions of F80 series with $c_{PS} \leq 0.05$ (g/g) and of F850 series with $c_{PS} \leq 0.02$. Solutions of F80 series with $c_{PS} > 0.05$ and those of F850 series with $c_{PS} > 0.02$ were prepared by slowly evaporating thiophenol in a dust-free box from respective 5% and 2% solutions. Concentrations of solutions were determined by weighing. Concentration ranges investigated for respective series were chosen so as to cover both the dilute and the semidilute regime and are given in Table II. Critical overlapping concentration c_{PS}* was calculated as $c_{PS}^* = 1/[\eta]\rho$ and is also shown in the table. We used a $[\eta]$–M_w relation of PS in thiophenol for the calculation

$$[\eta] = 1.46 \times 10^{-2} M_w^{0.70\pm0.01} \qquad (6)$$

which has been reported in part 1.

Since polystyrene and poly(methyl methacrylate) are incompatible with each other, phase separation may occur at higher concentration. In the present study, however, no symptoms of phase separation were observable over the whole range of c_{PS} and M_{PS} investigated.

Methods. The dynamic light-scattering instrument used has been described earlier.[16] A single-frequency 488 nm line of an argon ion laser (Spectra Physics, Model 165-03) with an output power of 300 mW was used as a light source. The vertical component of the scattered light from a solution in a sample cell (NMR tube with outer diameter of 12 mm) was detected by photomultipliers (Hamamatsu Photonics) attached at five fixed scattering angles θ, i.e., 30°, 60°, 90°, 120° and 150°. The homodyne autocorrelation function $A(\tau)$ was measured at 25 ± 0.02 °C by using either a time interval correlator with 512 channels (Union Giken Co.) or a shift register correlator with 72 channels (Malvern).

Sedimentation veloctity experiments were made at 25 ± 0.05 °C by using an analytical ultracentrifuge (Beckman Spinco Model E). The rotor speed was 59 780 rpm.

Results

Diffusion Behavior. The intensity autocorrelation function $A(\tau)$ of the scattered light from the ternary so-

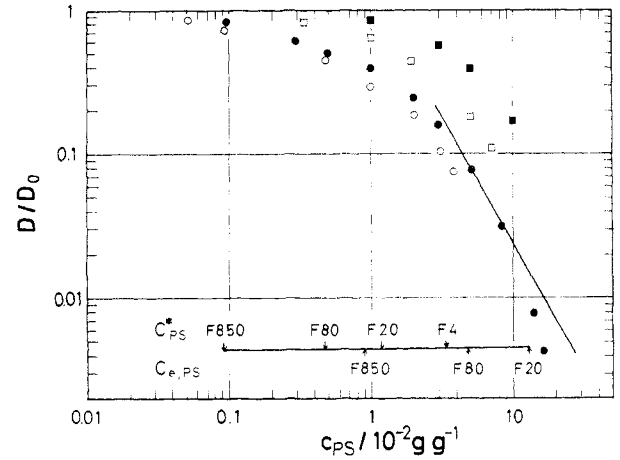

Figure 1. Reduced diffusion coefficients D/D_0 of PMMA in solutions of PS are plotted against PS concentration c_{PS}. Symbols are (■) F4 series; (□) F20 series; (●) F80 series; and (○) F850 series. PMMA concentration is 0.001 g/g. Critical overlapping concentration c_{PS}* and critical concentration for onset of entanglement $c_{e,PS}$ are shown in the inset for respective series. The straight line with the slope of −1.75 illustrates the power-law dependence of D on c_{PS} predicted by the scaling theory.

lutions has shown the presence of the distribution of the decay rate Γ. Assuming the Γ distribution is a bimodal type, we have analyzed the data by using the five-parameter equation

$$A(\tau) = (1 + \delta) + \{a_1 \exp(-\Gamma_1\tau) + a_2 \exp(-\Gamma_2\tau)\}^2 \quad (7)$$

where $\Gamma_1 < \Gamma_2$. The deviation of the base line from unity, δ, is kept less than 0.003 in the analysis. The histogram method[17] has been applied on a couple of data sets as an alternative procedure for data analysis. The analysis has not only confirmed the bimodal nature of the Γ distribution but also given good agreement between Γ_1 values obtained by the two methods.

Some data[18] have been found to be fitted with the single exponential type of decay curve (variance ≤ 0.05). The Γ obtained from those data has been identified as Γ_1. As has been discussed in part 1, the slow mode may be considered to represent the translational diffusion motion of a PMMA chain in PS–TPh solutions, and the fast mode with small amplitude factor $a_2(a_2/(a_1 + a_2) \leq 0.3)$ may be identified as the local motion of a PMMA chain excited by the cooperative motion of surrounding PS chains. The diffusion coefficient D of each solution has been estimated from the plot of Γ_1 against the scattering vector q. They were reduced by using the value of the translational diffusion coefficient D_0 of PMMA at infinite dilution in pure TPh. D/D_0 listed in Table III are logarithmically plotted against c_{PS} in Figure 1. At the bottom of the figure two critical concentrations, c_{PS}* and $c_{e,PS}$, are shown by arrows for each series of solutions. The latter $c_{e,PS}$ represents the concentration above which the entanglement effect becomes dominant. It has been calculated from eq 9(b) in ref 19 by assuming that thiophenol is as good a solvent for PS as aroclor. D/D_0 decreases monotonically with increasing c_{PS} and shows no sharp break near c_{PS}*. The decrease in D/D_0 begins at lower c_{PS} for higher PS molecular weight; i.e., D/D_0 takes, when compared at the same c_{PS}, smaller values with increasing M_{PS}. According to the scaling theory,[14] the D data for different molecular weight samples may be synthesized in the semidilute regime to one universal curve which is only a function of c/c*. As is clear from the figure, this is not the case. We have also found that an attempt to obtain a master curve by simply shifting the data along the horizontal axis is unsuccessful.

Table III
Sedimentation Coefficient s and Diffusion Coefficient D of PMMA in PS-TPh Solutions and Their Reduced Quantities s/s_0 and D/D_0[a]

	concn, g/100 g		$s \times 10^{13}$,		$D \times 10^7$	
series	PS	PMMA	s^{-1}	s/s_0	cm^2 s^{-1}	D/D_0
F4	0.995	0.0985	1.22	0.75	1.129	0.85
	2.99	0.105	0.883	0.54	0.754	0.57
	4.98	0.105	0.637	0.39	0.514	0.39
	5.09	0.174	0.603	0.37	0.510	0.39
	5.09	0.241	0.577	0.36	0.503	0.38
	5.09	0.338	0.528	0.33	0.506	0.38
	9.97	0.0996	0.299	0.19	0.238	0.17
	16.83	0.0832	0.145	0.089		
F20	0.341	0.105	1.27	0.78	1.11	0.94
	0.995	0.0928	1.00	0.62	0.852	0.64
	1.92	0.102	0.735	0.45	0.596	0.45
	4.99	0.0970	0.304	0.19	0.238	0.18
	7.10	0.0959	0.196	0.12	0.144	0.11
	9.18	0.0911	0.126	0.077		
F80	0.0956	0.100	1.38	0.85	1.11	0.84
	0.295	0.0981	1.19	0.73	0.811	0.61
	0.495	0.0995	1.04	0.64	0.673	0.51
	1.00	0.0999	0.756	0.47	0.523	0.40
	2.01	0.0988	0.448	0.28	0.323	0.24
	3.00	0.115	0.304	0.19	0.209	0.16
	5.16	0.103	0.160	0.098	0.103	0.078
	4.95	0.124			0.126[b]	0.095[b]
	6.40	0.100	0.108	0.066		
	8.27	0.0827			0.0420	0.032
	13.9	0.924	0.0177	0.011	0.0103	0.0078
	16.2	0.924	0.0113	0.0070	0.00561	0.0043
F850	0.0514	0.0993	1.43	0.88	1.14	0.86
	0.0926	0.0804	1.38	0.85	0.961	0.73
	0.478	0.0992	0.914	0.56	0.601	0.45
	0.795	0.0920	0.716	0.44	0.438	0.33
	0.998	0.0997	0.622	0.38	0.385	0.29
	1.01	0.204			0.377	0.29
	0.998	0.215	0.591	0.36	0.356	0.27
	0.997	0.318	0.580	0.36	0.332	0.25
	1.01	0.104			0.502[b]	0.38[b]
	2.03	0.0995	0.379	0.23	0.243	0.18
	3.11	0.103	0.227	0.14	0.136	0.10
	3.80	0.0952	0.183	0.11	0.0981	0.074
F40	1.01	0.101	0.832	0.51	0.621	0.47
F550	0.990	0.100	0.645	0.40	0.427	0.32

[a] $s_0 = 1.63 \times 10^{-13}$ s^{-1}, $D_0 = 1.32 \times 10^{-7}$ cm^2 s^{-1} from ref 8. [b] From diffusion measurements under small centrifugal force field with the synthetic boundary method.

The scaling theory with the reptation model predicts the power-law dependence of the self-diffusion coefficient D_s on polymer concentration in the semidilute regime. The D data in the present study may be identified as D_s because of the low PMMA concentration adopted, 0.001 g/g.[20] It can be also shown that the hydrodynamic screening length ξ_H of PS chains in TPh becomes smaller above c_{PS} = 0.01 than the hydrodynamic radius R_H of the PMMA molecule used as a probe. These considerations may provide the comparison of the D data with the theory. By comparing the straight line of the slope −1.75 drawn in the figure with the data of F80 series which have covered the largest concentration range, we can conclude that the power-law dependence is observed only in a very restricted region even if such a region exists. As was pointed out in a previous paper,[21] the concentration dependence of D must be corrected for the concentration effect on the monomeric friction coefficient for the rigorous test of the theory. This correction factor is, however, small in the concentration range investigated so that the correction would not change the above conclusion.

Recently Phillies[22] has measured the diffusion coefficient of spherical particles in solvents of high viscosity. He has shown that D^{-1} is linearly proportional to η_s/T even for

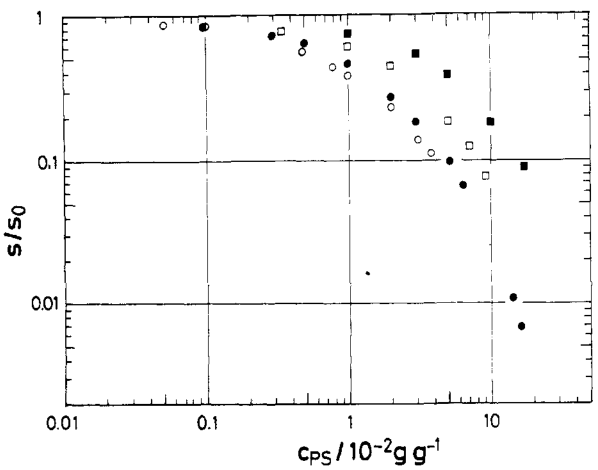

Figure 2. Reduced sedimentation coefficients s/s_0 of PMMA in solutions of PS are plotted against c_{PS}. Symbols are the same as in Figure 1.

$\eta_s \geq 100$ cP; i.e., the Stokes–Einstein equation is quite successful for describing the diffusion behavior of macroparticles in viscous solution as far as the solvent is composed of low molecular weight substances. When the size of the solvent becomes comparable with or larger than that of the particle, however, the decrease in D may not be explained by the increase in the macroscopic viscosity of the solution. We have measured the steady-state viscosity η_0 of two solutions with about the same value of $D/D_0 \cong 0.1$. Here one solution belongs to F4 series and the other to F850 series. We have found that η_0 values of the two solutions are different by more than 2 orders of magnitude. This suggests that the macroscopic viscosity cannot be directly related to the diffusion behavior of a flexible chain through the transient gellike network of other flexible chains, but that the solvent viscosity is mainly responsible for the micro-Brownian motion of the fundamental unit (or the segment) in the semidilute regime, as is proposed by the scaling theory.

Sedimentation Behavior. Sedimentation velocity experiments have been made mostly on the same solutions as used for DLS measurements. A single peak due to the sedimentation of PMMA molecules has been observed in the photographs of the sedimentation pattern. Therefore s has been estimated by the standard procedure to an accuracy of 5%. Both the pressure effect and the concentration effect were found to be negligible. By using the value of s at infinite dilution in pure TPh, $s_0 = 1.63 \times 10^{-13}$ s^{-1}, we show the logarithmic plot of the reduced quantity s/s_0 against c_{PS} in Figure 2. At first glance, the behavior appears very similar to the diffusion behavior shown in Figure 1; s/s_0 decreases monotonically with increasing c_{PS} and is dependent on M_{PS}. One noticeable difference between s and D is that for the s data a master curve can be obtained within experimental error from the horizontal shift of the data of each series with different M_{PS}. The shift factor is, however, not proportional to c_{PS}*. Thus the master curve is not an universal function of c_{PS}/c_{PS}*.

Discussion

Comparison of D/D_0 and s/s_0. It has been described in the introduction that if the same friction coefficient is operative in both diffusion and sedimentation, D/D_0 and s/s_0 should agree with each other. Figure 3 shows this comparison. For solutions of F4 and F20 series in which the molecular weight of PMMA is larger than that of PS, the two quantities appear to agree with each other, although D/D_0 has slightly stronger dependence on c_{PS}. In contrast, more systematic disagreement has been found for F80 and F850 series in which M_{PS} is much larger than M_{PMMA}. s/s_0 is always larger than D/D_0, and the difference amounts to more than 30% for the data at the highest c_{PS}. The 30% difference is, of course, quite small as compared with the decrease of 2 orders of magnitude in D/D_0 and s/s_0 with increasing c_{PS} but seems to be beyond unavoidable experimental uncertainty in the procedure taken for determination of D and s. We have reexamined our measurements concerning a few possible experimental artifacts that might rise to the 30% difference. They are (1) D and s are not values at infinite dilution of c_{PMMA} but at finite c_{PMMA} of 0.001. Therefore, D measured with the DLS technique is not the translational diffusion coefficient of a single PMMA molecule in a strict sense, but is the mutual diffusion coefficient that contains the contribution from the thermodynamic force $(\partial\mu/\partial c)$, whereas s is not influenced by this force. (2) The effect dust particles and nonuniformity of the solutions may have on DLS. (3) The apparent sedimentation velocity of PMMA is increased by the sedimentation of PS. Possibility 1 has been examined by studying the dependence of D and s on c_{PMMA} for two solutions, one of F4 series with $c_{PS} = 0.05$ and one of F850 series with $c_{PS} = 0.01$. The results are shown in Figure 4. Both D and s of the two solutions are linearly dependent on c_{PMMA} in the range of 0.001–0.004 investigated, and all slopes are negative and small. For the solution of F850 series the ratio of D at infinite dilution, $D(0)$, to $D(0.001)$ at $c_{PMMA} = 0.001$ is 1.07, and the corresponding ratio $s(0)/s(0.001)$ is 1.04. For the solution of F4 series, $D(0)/D(0.001)$ and $s(0)/s(0.001)$ are 1.01 and 1.07, respectively. The use of $D(0)$ and $s(0)$ instead of corresponding values at $c_{PMMA} = 0.001$ would vary the difference between s/s_0 and D/D_0 by about ±5%. Such a small correction alone cannot explain the 30% difference observed for solutions with high PS molecular weights at high c_{PS}. This may eliminate possibility 1. (2) Dust particles contaminated in solution surely affect the base line of $A(\tau)$. Because of their slow decay rates the apparent diffusion coefficient may be more or less decreased. Either formation of aggregates or inhomogeneity of PS networks would also contribute to the decrease in D. Nevertheless, the careful filtration procedure we adopted and the reproducibility of the data have confirmed that such effects need not be taken into account. (3) The sedimentation of PS in thiophenol could not be observed because they are isorefractive. We have prepared a 1% solution of PS with $M = 8\,420\,000$ in a mixture of chlorobenzene and benzene whose mixing ratio is adjusted so as to have the density

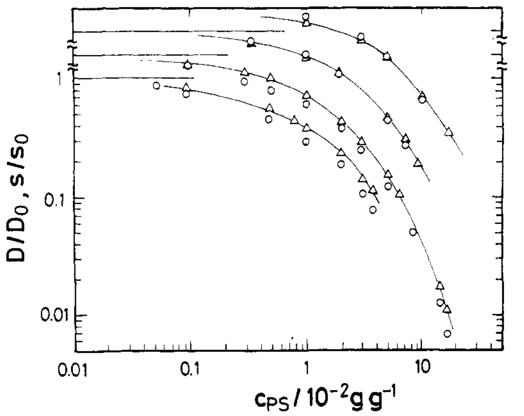

Figure 3. Comparison of D/D_0 and s/s_0. For clarity of the figure, the data of each series are shifted arbitrarily along the ordinate axis. From the top, F4, F20, F80, and F850 series. Symbols are (○) D/D_0 and (△) s/s_0.

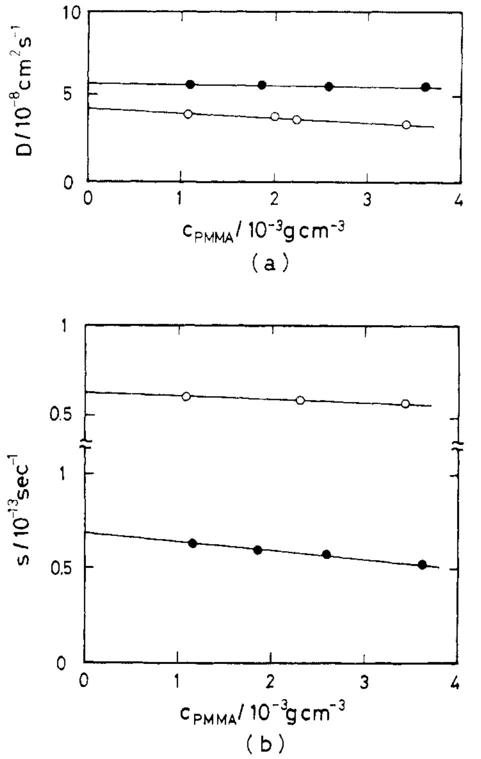

Figure 4. Dependences of D and s on PMMA concentration at constant c_{PS} are shown for two samples: (a) the diffusion coefficient; (b) the sedimentation coefficient. Symbols are (●) M_{PS} = 43 900 and c_{PS} = 0.05 (g/g) and (○) M_{PS} = 8 420 000 and c_{PS} = 0.01.

the same as that of thiophenol. Sedimentation of the polymer has not been detected for this solution with the schlieren method. These reexaminations strongly suggest that the difference between D/D_0 and s/s_0 of PMMA in semidilute solutions of high molecular weight polystyrenes is real.

The dinstinction between the diffusion and the sedimentation behavior may be also apparent in dependences of D/D_0 and s/s_0 on PS molecular weight. For this purpose we have made additional measurements of D and s of PMMA in a 1% solution of PS with M_{PS} = 422 000 and also in a 1% solution of PS with M_w = 5 530 000. Figure 5 shows the dependences on M_{PS} at c_{PS} = 0.01. Both quantities decrease with increasing M_{PS} and do not seem to approach asymptotic values in the range of molecular weight investigated. Two curves made from simple connection of the respective data points intersect around $M_{PS} \cong 270 000$. It is interesting that c_{PS} = 0.01 corresponds to the critical overlapping concentration c^* for PS with M_{PS} = 270 000 in TPh. For $M_{PS} \geq 400 000$ D/D_0 is smaller than s/s_0, and the difference between both quantities increases with increasing M_{PS}. For $M_{PS} \leq 200 000$ D/D_0 looks larger than s/s_0, but, in view of experimental uncertainties involved in D and s, we do not discuss this difference in the low M_{PS} region further.

It has been stated earlier that the time and the spatial scale over which DLS and sedimentation velocity measurements are made are quite different from each other. In 30 min, which is a typical time interval for taking photographs of the sedimentation pattern, numerous conformational rearrangements of PS molecules surrounding a PMMA molecule are allowed. In the sedimentation measurements, therefore, details of the transient network structure of PS at respective time t need not be considered. The force experienced by the sedimenting PMMA molecule can be taken as the random force. In contrast, the maximum delay time τ_m in the diffusion measurements by DLS is less than 1 s at longest, and the distance traveled by the PMMA molecule within τ_m is a few times as long as the inverse of scattering vactor q. For such a short time behavior, we now must take into account the relative magnitude of the longest relaxation time τ_1 of PS chains for their conformational rearrangements to τ_m. When $\tau_1 \ll \tau_m$, the same argument as was used in the sedimentation may be still applicable for the diffusion case. When $\tau_1 \gg \tau_m$, however, PS molecules do not change the positions of their center of gravity during the characteristic time ($=1/\Gamma$) of the translational diffusion of PMMA. As a result, time and spatial correlations between PS and PMMA are enhanced and might retard the diffusion motion of PMMA. From this point of view it seems worthwhile to notice the result of Laurent et al.[10] that D/D_0 obtained by the classical free-diffusion technique is in excellent agreement with s/s_0. We have measured D of PMMA in two solutions of PS in TPh with a technique that makes use of an analytical ultracentrifuge.[23] The two solutions tested are a 5% solution with M_{PS} = 775 000 and a 1% solution with M_{PS} = 8 420 000. The synthetic boundary method which uses a double sector cell has been adopted, and the spreading of the synthetic boundary with time due to the diffusion of PMMA under small centrifugal force has been detected by using the schlieren optics. It has been shown that this method can give D to an accuracy of 10% under careful experiments. As the results given in Table III show, D/D_0 obtained with this macroscopic method agrees with s/s_0 and is significantly larger than D/D_0 obtained by DLS for both solutions. This type of experiment will, we believe, be very illuminative for clear understanding of the very complicated transport process of a flexible polymer in semidilute solutions of flexible polymers. The results of more systematic study will be reported in the near future.

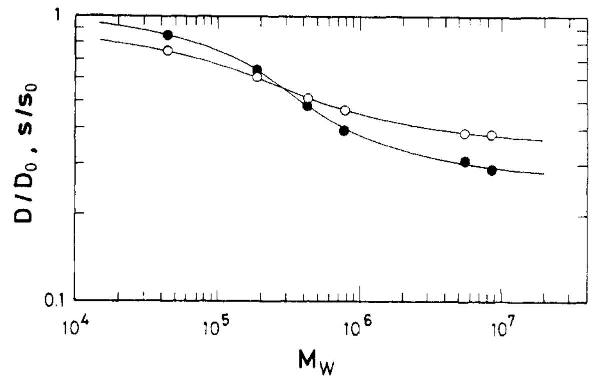

Figure 5. Dependence of D/D_0 and s/s_0 on PS molecular weight at c_{PS} = 0.01. Symbols are (○) s/s_0 and (●) D/D_0. The solid curve is drawn empirically by simple connection of data points.

Functional Form of the Concentration Dependences of D and s in the Semidilute Regime. Since semidilute solutions of flexible polymers can be regarded as the transient network of mesh size ξ_H, it is interesting to examine whether eq 5 is a suitable form as an expression of the concentration dependence of D and s in the semidilute regime. The data of F80 and F850 series obtained in the semidilute regime are replotted in Figures 6 and 7 by taking the natural logarithm of either D_0/D or s_0/s as ordinate and c_{PS} as abscissa. It should be noted that in this type of plot experimental errors of several percent are magnified when D_0/D (or s_0/s) values are close to unity, as is shown by the bars in the figures. When this fact is taken into account, the data of each series may be well described by a straight line. This indicates that eq 5 is

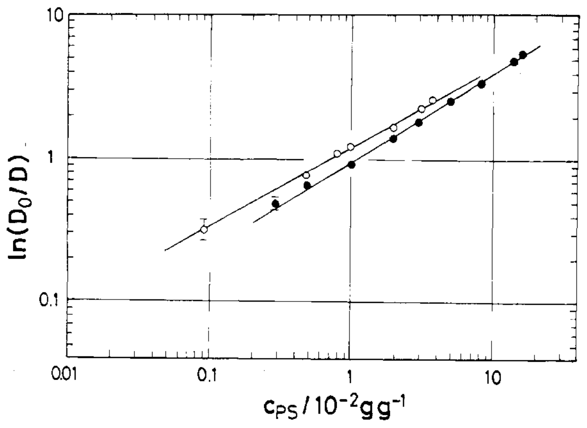

Figure 6. Applicability of eq 5 is tested for the diffusion data by the logarithmic plot of ln D_0/D against c_{PS}. Symbols are (●) F80 series and (○), F850 series. $\delta = 0.61 \pm 0.05$ for F80 series and 0.55 ± 0.05 for F850 series.

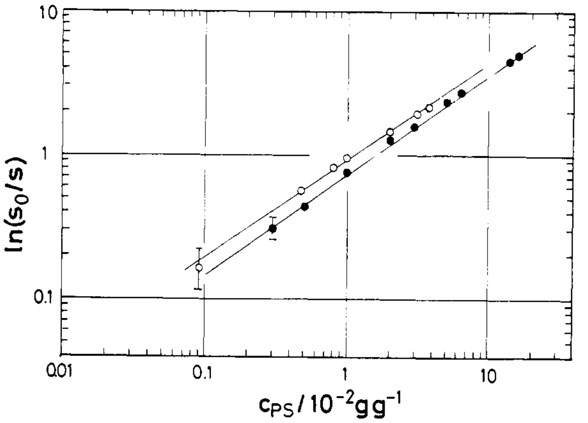

Figure 7. Applicability of eq 5 is tested for the sedimentation data by the logarithmic plot of ln s_0/s against c_{PS}. Symbols are same as in Figure 6. $\delta = 0.71 \pm 0.05$ for F80 series and 0.67 ± 0.05 for F850 series.

a useful form, and the exponent δ is easily read as the slope of each straight line. The factor A, which should be related to the size of the diffusant, has been found to be 15 ± 2 and 20 ± 3 independent of M_{PS} for D and s, respectively. δ tends to decrease slightly with increasing M_{PS} for both quantities, but a fitting error of ± 0.05 makes this trend ambiguous.

δ has been estimated as 0.55 ± 0.05 for the diffusion data of F850 series with the highest M_{PS}. This value is a little larger than the theoretical value of $\delta = 0.5$ predicted by Ogston et al.[9] $\delta = 0.5$ has been also deduced by Cukier[24] from the first-order calculation on the concentration dependence of the friction coefficient of spherical particles in semidilute polymer solutions. There remains a possibility that δ might asymptotically approach the theoretical value for PS solutions with very high molecular weight if the small dependence of δ on M_{PS} were true. The important point is that the exponentially decaying function, eq 5, may well represent the concentration dependence of the diffusion coefficient of PMMA over a c_{PS} range of nearly 2 orders of magnitude. This is in contrast to the failure of the power law predicted by the scaling theory in this region. Lin and Phillies[12] have found $\delta = {}^2/_3$ for the diffusion data of PS latex particles ($R = 0.02$–$1.5\ \mu$m) in aqueous solutions of poly(acrylic acid) ($M_w = 300\,000$) by using the DLS technique. The value is appreciably larger than $\delta = 0.55$. This difference may be attributed to the molecular weight of poly(acrylic acid) not being sufficiently high to form the network structure with long relaxation time. The fitting of the data of F20 series with $M_{PS} = 186\,000$ to eq 5, indeed, has given $\delta = 0.83 \pm 0.05$, which is larger than $\delta = {}^2/_3$. Thus the dependence of δ on M_{PS} may account for the difference in δ between their and our results. In this connection it should be noted that the linear dependence in ln D with increasing concentration has been reported for the self-diffusion data of low molecular weight dextran in water[5a] and also of short-chain polystyrene.[25] $\delta = 1.0 \pm 0.1$ has been obtained for the data of F4 series with $M_{PS} = 43\,000$. Equation 5 with $\delta = 1$ seems to be a limiting law applicable for the diffusion of polymer particles in solutions of low molecular weight polymers that do not exhibit strong intermolecular interaction such as the entanglement effect.

We have obtained $\delta = 0.71 \pm 0.05$ and 0.67 ± 0.05 for the sedimentation data in Figure 7. The small molecular weight dependence is again absorbed into a fitting error of ± 0.05. $\delta = 0.67$ for F850 series with the highest PS molecular weight is slightly larger than $\delta = 0.62$ reported for the sedimentation of spherical particles in aqueous solutions of poly(ethylene oxide) and much larger than $\delta = 0.5$ for the sedimentation data of compact particles in hyaluronic acid.[9,10] It is not clear whether the disagreement should be related to the flexibility of the diffusing molecule or to complicated electrostatic interaction in polyelectrolyte systems. $\delta = 0.67$ is very close to the exponent ν appearing in the empirical relation, $\xi_H \propto (c/c^*)^{-\nu}$. But this does not mean that s/s_0 can be written as $s/s_0 \propto \exp(-A'\xi_H)$ because shift factors obtained from construction of a master curve for the sedimentation data are not proportional to c^*_{PS}.

In conclusion, the difference in δ values between the D and the s data suggests again that the diffusion behavior of PMMA is quite distinct from the sedimentation behavior in semidilute solutions of high molecular weight PS.

Acknowledgment. We are greatly indebted to Prof. H. Fujita and Dr. T. Norisuye of Osaka University and to Prof. T. Nose of Tokyo Institute of Technology for valuable discussions. We also thank S. Okada for his help in sedimentation velocity experiments. We are grateful to Prof. K. Nakanishi and M. Denda of Kyoto University for their advice in specific-density measurements. This work was supported by Grants-in-Aid for Scientific Research (58 550 591, 59 470 090).

Registry No. PMMA (homopolymer), 9011-14-7; PS (homopolymer), 9003-53-6; thiophenol, 108-98-5.

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Center of Diffusion of Flexible Macromolecules

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Received January 9, 1985

ABSTRACT: We analyze the translational diffusion of an isolated flexible macromolecule by starting on a microscopic level that includes all degrees of freedom and allows for coupling between translational, rotational, and internal motions. Every flexible macromolecule is found to have a unique center of diffusion, which is that point of the body undergoing the slowest average Brownian displacements. The configurationally dependent location of this point is determined from a second-order partial differential equation involving the internal degrees of freedom. A perturbation treatment reduces the diffusion equation governing all the body's degrees of freedom to the ordinary diffusion equation governing the translational motions of some equivalent point particle with diffusion coefficient D_t. By identification, the average microscopic motions of the center of diffusion are shown to characterize the diffusive motions of the body over large distances. We consider several bounds to the macroscopic translational diffusion coefficient D_t that might eliminate the need to explicitly determine the center of diffusion. As an example, a frictionless centrally hinged rod is considered by using bead model methods in order to provide a realistic treatment that includes hydrodynamic interactions between rod halves. For the 20-bead case considered, D_t increases less than 7% from a straight rigid rod and is estimated to at least 1% by bounds that include a simple rigid-body approximation.

Introduction

Brenner[1–4] first considered the effects of rotational–translational coupling on the diffusion coefficients that govern the random microscopic displacements of rigid bodies with irregular shapes. He showed that every rigid body has a unique center of diffusion where the 3 × 3 matrix describing the coupling is symmetric. Like the center of mass in inertial mechanics, this is the natural point to use when evaluating diffusive behavior. Even so, the description of diffusive behavior remains more complicated than inertial mechanics since rotations and translations generally cannot be uncoupled.

Brenner's work has been recently reexamined and extended by several groups interested in modeling complicated biological macromolecules at low Reynold's numbers.[5–15] In particular, it has now been rigorously established that the diffusional motions of a rigid body over macroscopic distances are the same as the average microscopic motions of its center of diffusion.[11] Since Brenner had derived a simple algebraic expression for the location of the center of diffusion, the needed macroscopic translational diffusion coefficient, denoted D_t, can be determined exactly within these models.

The situation is not as satisfactory regarding the proper determination of D_t for flexible macromolecules in which translational motions are coupled to additional internal modes.[8,15–17] Although methods exist for determining the instantaneous diffusion coefficients of a flexible body with some particular configuration (see, for example, ref 18–21), no relation has been established between the microscopic displacements that these coefficients directly govern and the body's translational diffusion over large distances.

In this paper, we show that an isolated flexible body does indeed have a unique center of diffusion whose average microscopic motions characterize its macroscopic motions. We first examine the positional dependence of the diffusion coefficients governing the translational displacements of a point in the body. From a minimization condition, an analytic expression is found for the location of a center of diffusion. In order to rigorously prove that the resulting point does characterize macroscopic motions, we turn to perturbation theory. In the limit of motion over distances large compared to body size, the diffusion equation governing all the body's degrees of freedom reduces to the usual diffusion equation governing the translational motions of a point particle with diffusion coefficient D_t. By identification, D_t is the translational diffusion coefficient governing the average displacements of the center of diffusion. As an example, we consider several cases of a centrally hinged rod that bends either freely within a variable limited range or under the influence of a restoring potential. In each case, the center of diffusion is determined and D_t is found to depend little on the type or degree of flexibility. Several approximations that eliminate the need to explicitly determine the location of the center of diffusion are shown to give excellent bounded estimates of D_t.

An assumption underlying the following analysis is that all configurations are dynamically interchangeable on an appropriate macroscopic time scale, so that a particle can indeed be described by one D_t. Generalizations to include noninterchanging configurations (untieable knots, etc.) will

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