Macromolecules **1989**, *22*, 3793–3798

(7) Rao, G. R.; Castiglioni, C.; Gussoni, M.; Zerbi, G.; Martuscelli, E. *Polymer* **1985**, *26*, 811.
(8) Martuscelli, E.; Silvestre, C.; Addonizio, M. L.; Amelino, L. *Makromol. Chem.* **1986**, *187*, 1557.
(9) Ito, H.; Russell, T. P.; Wignall, G. D. *Macromolecules* **1987**, *20*, 2213.
(10) Zhao, Y. Ph.D. Thesis, University of Paris VI, 1987.
(11) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 346.
(12) Eisenberg, A.; Navratil, M. *Macromolecules* **1973**, *6*, 604.
(13) Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic Press: New York, 1977.
(14) Jasse, B.; Koenig, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 799.
(15) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *2*, 123.
(16) Fitzgerald, W. E.; Nielsen, L. E. *Proc. R. Soc. (London)* **1964**, *A282*, 137.
(17) Zhao, Y.; Jasse, B.; Monnerie, L. *Makromol. Chem., Macromol. Symp.* **1986**, *5*, 87.
(18) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 954.
(19) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(20) Navratil, M.; Eisenberg, A. *Macromolecules* **1974**, *7*, 84.

Self-Diffusion and Tracer-Diffusion Coefficient and Viscosity of Concentrated Solutions of Linear Polystyrenes in Dibutyl Phthalate[†]

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ABSTRACT: The slow chain dynamics of linear macromolecules in the concentrated regime has been studied from measurements of the steady viscosity η and the self-diffusion coefficient D_s of seven polystyrene (PS) samples with weight-average molecular weight (M_w) from 43 900 to 2 890 000 in 40 wt % PS–dibutyl phthalate (DBP) solutions and also from measurements of the tracer-diffusion coefficient D_{tr} of 11 PS samples with probe molecular weight (M_N) from 2800 to 2 890 000 in 40 wt % DBP solutions of PSs with matrix molecular weight (M_P) varying from 43 900 to 8 420 000. The viscosity of the solutions was found to follow the well-established relation $\eta \propto M_w^{3.5\pm0.1}$ above $M_w = 102\,000$. The M dependence of D_s was approximately expressed by the power law $D_s \propto M_w^{-2.6\pm0.2}$ over the whole molecular weight range investigated. The product of D_s and η became approximately proportional to M in the highly entangled region, indicating that both viscosity and self-diffusion behavior can be related to the slowest chain motion with the same characteristic relaxation time τ_m. D_{tr} data in the unentangled 40 wt % DBP solution of PS with $M_P = 43\,900$ showed a gradual transition from the Rouse type of free-draining chain to the Einstein-Stokes type of impermeable sphere diffusion in the highest M_N end with increasing M_N. In entanglement networks with molecular weight between entanglements $M_e = 42\,300$ at $c = 40$ wt %, D_{tr} decreased with increase in M_P and assymptotically approached D_{tr}^{∞} independent of M_P for $M_P > 5M_N$. D_{tr}^{∞} was found to be proportional to M_N^{-1} in the range of $2800 \leq M_N \leq 10\,000$ and then to $M_N^{-2.5\pm0.1}$ for $43\,900 \leq M_N \leq 1\,260\,000$. The exponent 2.5 is appreciably larger than 2, either predicted by the reptation theory or observed for PS melts.

Introduction

Slow chain dynamics of a linear flexible polymer in solutions as well as in melts is greatly affected by the intermolecular interaction with surrounding polymer chains. Variables such as self- (or tracer-) diffusion coefficient D_s (or D_{tr}) and steady viscosity η are quantities suitable for a study on the topological interaction in extensively overlapped polymeric systems, that is, for a study of the entanglement effect.

Quite recently, we showed that D_s in melts as well as in concentrated solutions could be expressed by the product of two seperate contributions, f_2 and g_2, as is given in eq 1.[1,2] Here ζ is the segment friction constant, and C and

$$D_s = f_2(\zeta)g_2(C,M) \tag{1}$$

M are the concentration and molecular weight of the polymer, respectively. An analogous expression for viscosity is well established.[3]

$$\eta = f_1(\zeta)g_1(C,M) \tag{2}$$

$$\begin{aligned} g_1(C,M) &= CM & M &< M_c \\ &= (CM)^{3.5\pm0.2} & M &> M_c \end{aligned} \tag{3}$$

$f_i(\zeta)$ (i = 1, 2) represents a contribution from micro-Brownian motion of a segment, that is, local one in nature, being independent of the polymer molecular weight at high M. $f_1(\zeta)$ to η is a function simply proportional to ζ, while f_2 to D_s is inversely proportional to ζ as

$$f_2(\zeta) = k_BT/\zeta \tag{4}$$

Here k_B is the Boltzmann consant and T is the absolute temperature. The function g_i (i = 1, 2) represents the effect of the topological interaction with surrounding chains, and the dependence of g_1 on C and M is given by eq 3, which is verified for the viscosity of many polymer–solvent systems. On the other hand, the functional form of g_2 is presently in question. For example, M dependence of g_2 looks different between polymer melts and the semidilute regime.[4-14] That is, if the dependence of g_2 on M is expressed by the power law as $g_2 \propto M^{-\alpha}$, the exponent α ranges from 2 to 3 in the semidilute regime, while α is 2 in highly entangled polymer melts. It may be noted that the reptation theory predicts $\alpha = 2$ for entanglement networks independently of polymer concentration studied.[15]

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Table I
Characteristics of Polystyrene

sample	$M_w/10^4$	M_w/M_n	sample	$M_w/10^4$	M_w/M_n
A2500[a]	0.28	1.05	F40[a]	35.5	1.02
A5000[a]	0.61	1.04	F80[a]	77.5	1.01
F1[a]	1.03	1.02	F128[a]	126	1.05
F2[a]	1.67	1.02	F288[a]	289	1.09
F4[a]	4.39	1.01	F550[b]	548	1.15
F10[a]	10.2	1.02	F850[b]	842	1.17
F20[a]	18.6	1.07			

[a] Labeled with a photobleachable dye. [b] Used as matrix polymer.

Concerning self-diffusion and viscosity behavior of highly entangled systems, there seems to be consensous that both quantities should be related to the same slowest molecular motion of polymer chains. Therefore dependences of g_1 and g_2 on C and M must be in harmony with each other and should be consistently explained on the basis of the same physical concept. We should notice once again that 3.5 power dependence of η on M observed for entangled systems in melts as well as in the semidilte regime is in sharp contrast to the difference in the exponent α for D_s between the regimes. Graessley and his co-workers have observed a gradual transition from $\eta \propto M^{3.4}$ to $\eta \propto M^3$ for an extremely entangled polybutadiene melt to which $D_s \propto M^{-2}$ holds, though definite conclusion was not made owing to subtle experimental errors involved in their experiments.[30] In taking into account these complicated situations, we experimetalists may consider that it is worth making a systematic viscosity and diffusion study in the concentrated regime where reliable data are lacking.

In this study, we have chosen concentrated dibutyl phthalate solutions of polystyrene (PS) as test solutions and report results of forced Rayleigh scattering measurements on the solutions over a wide range of molecular weight of both the probe PS(M_N) and the matrix PS(M_P) and also results of viscosity measurements on homogeneous solutions with $M_N = M_P$. Molecular weight dependences of D_s, D_{tr}, and η are critically examined in comparison with those of PS melts and also theoretical predictions.

Experimental Section

Materials. Thirteen samples of narrow-distribution polystyrenes (PS, Toyo Soda) with different molecular weights were used in this study. Their sample codes, weight-average molecular weights M_w, and ratios M_w/M_n are listed in Table I. Eleven PS samples except the two highest molecular weight PSs, which were used as matrix polymer for tracer diffusion experiments, were labeled with a photobleachable dye of 2-nitro-4-carboxy-4′-(dimethylamino)stilbene following the labeling procedure described in earlier papers.[16,17] GPC combined with low-angle light-scattering measurements showed that there was no change in either molecular weight or molecular weight distribution of the polymers during the labeling procedure. Distilled dibutyl phthalate (DBP), a good solvent for PS, was used.

Test solutions with PS molecular weight less than that of the sample F80 were prepared by dissolving a weighed amount of dust-free labeled PS, unlabeled PS, and DBP in an excess amount of methylene dichloride, stirring for a couple of days to complete homogenous mixing, and subsequently evaporating methylene dichloride very slowly from the solutions. Solutions containing higher molecular weight PS samples were prepared by a freeze-drying procedure on molecularly mixed benzene solutions of weighed amount of polymers and the solvent for a week. Polymer concentration was determined by assuming that a very slight decrease in total weight of the PS–DBP solutions during the freeze-drying procedure was due to evaporation of DBP. Total polymer concentration C of all solutions was fixed at 40.6 ± 0.3 wt % and C of the labeled PS component in D_s and D_{tr} measurements was 5 and 1 wt %, respectively, unless stated explicitly in the Results.

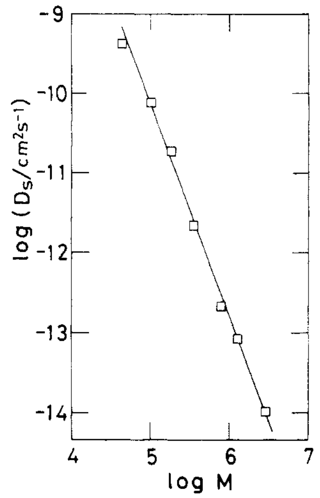

Figure 1. Self-diffusion coefficient D_s of 40 wt % PS–DBP solutions at T_r = 60 °C plotted against molecular weight M.

Methods. Forced Rayleigh scattering measurements were performed with an instrument recently constructed in our laboratory.[17] A sample was sandwiched between 15-mm diameter fused-silica optical windows, fixed into the cell, and annealed for mechanical equilibrium in an electric oven at 60 ± 3 °C for at least more than 2 weeks.[31] The cell holder was thermoregulated within ±0.05 °C by circulating ethylene glycol through an outer bath and an external thermostating bath. Monochromatic light of an Ar ion laser (λ = 488 nm) and of a He–Ne laser (λ = 633 nm) was used as a writing and reading beam, respectively. Acqusition and analysis of light intensity data $I_d(t)$ diffracted from the solutions were handled with a homemade processor. Measurements were made at 110 °C on solutions with both M_N and M_P higher than 775 000 and at 60 °C on other solutions.

Time profiles of $I_d(t)$ could be fitted by eq 5 with a single decay rate Γ_d to all solutions. Here A is amplitude; B_1 and B_2 are

$$I_d(t) = \{A \exp(-\Gamma_d t) + B_1\}^2 + B_2^2 \tag{5}$$

contributions from coherent and incoherent background optical field, respectively. Γ_d was estimated from a least-square fit to an accuracy of 10% at all temperatures. D_s (or D_{tr}) of the polymers in solutions was calculated as the slope in the linear plot of Γ_d against square of the wave vector q, which is related to the grating spacing d as $q = 2\pi/d$. Examples of such a plot are shown in an earlier paper.[2]

The steady viscosity η was measured by using a mechanical spectrometer (Rheometrics, RMS-800) at 60 ± 0.1 °C for five homogeneous solutions of PS samples from F4 to F80 and at 100 ± 0.1 °C for solutions of F128.

Diffusion and viscosity data obtained at temperatures different from 60 °C were all reduced to values at the reference temperature T_r = 60 °C by using the shift factor given by eq 6. Here $D_{s,r}$ and

$$\log (D_{s,r}T/D_sT_r) = \log (\eta/\eta_r) = -\frac{4.06(T-60)}{143 + (T-60)} \tag{6}$$

η_r are values at T_r. This equation was derived from temperature dependence of D_s and η of the 40 wt % DBP solution of F4 in a previous study.[2] By taking account of the 10% error involved in determination of the shift factor, we estimate that the diffusion coefficient and the viscosity were determined to an accuracy of 20 and 30%, respectively, when measurements were done at temperatures different from 60 °C.

Results

Self-Diffusion and Viscosity Behavior. Figure 1 shows the dependence of the self-diffusion coefficient D_s of PS in 40 wt % PS–DBP solutions on molecular weight in the range from 43 900 to 2 890 000. The molecular weight between entanglements M_e at the concentration of 40 wt % was estimated as 42 300 from an empirical relation M_eC = 18 000 g cm^{-3}.[18] Therefore the solution of the lowest

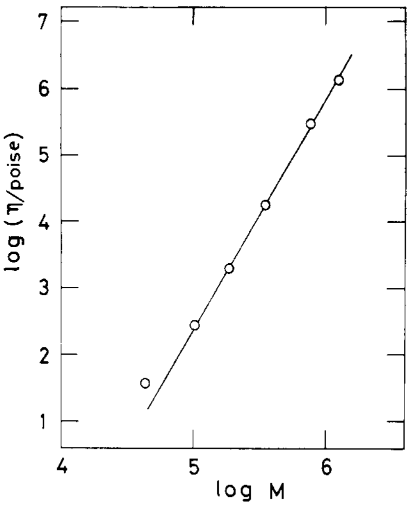

Figure 2. Steady viscosity η of 40 wt % PS–DBP solutions at T_r = 60 °C plotted against molecular weight M.

Table II
Values of D_s and η in 40 wt % PS–DBP Solutions at T_r = 60 °C

sample	$D_s/10^{-11}$ cm^2 s^{-1}	$\eta/10^3$ P	sample	$D_s/10^{-11}$ cm^2 s^{-1}	$\eta/10^3$ P
F4	41	0.036	F80	0.022[a]	300
F10	7.6	0.27	F128	0.0083[a]	1300
F20	1.8	1.9	F288	0.0010[a]	
F40	0.21	18			

[a] Calculated from D_s values of 2.78×10^{-12}, 1.07×10^{-12}, and 1.03×10^{-13} cm^2 s^{-1} at T = 110 °C for F80, F128, and F288 by using the shift factor eq 6 in the text, respectively. [b] Calculated from $\eta = 1.75 \times 10^5$ P at T = 100 °C by using the shift factor eq 6 in the text.

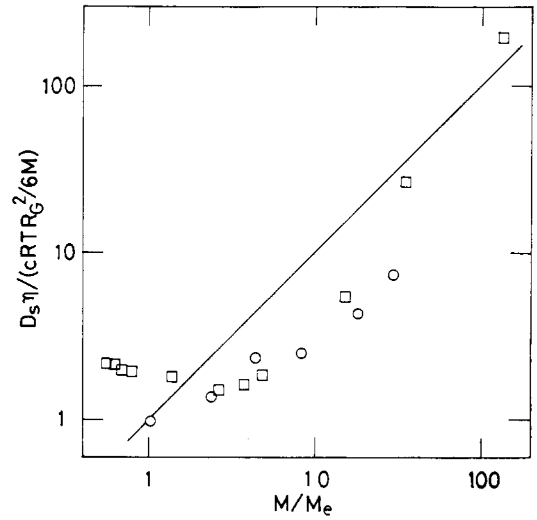

Figure 3. Product of the viscosity and the self-diffusion coefficient divided by the corresponding Rouse theoretical expression $CRTR_G^2/6M$ plotted against the number of entanglements per chain M/M_e: (○) 40 wt % PS–DBP solution; (□) polyethylene melt.

molecular weight PS(F4) is not entangled, but other solutions are entangled. If the dependence is represented by the power law, $D_s \propto M^{-\alpha}$, for D_s data of $M > 100\,000$, the straight line in the figure gives 2.6 ± 0.2 as the value of the exponent α. As is clear from the figure, D_s decreases with increasing molecular weight more steeply than the prediction of the reptation theory of $D_s \propto M^{-2}$ even at the highest M end. Here the value was obtained without any correction of molecular weight distribution of the samples used. If the polydispersity effect is taken into account following the treatment given in ref 14, the slope becomes a little bit steeper because the molecular weight distribution of the samples is broader with increasing molecular weight. However the molecular weight distribution is sufficiently narrow even for the sample F288 with the largest M_w/M_n ratio of 1.09, so that the effect of the polydispersity correction on the value of the exponent may be adsorbed into the experimental uncertainty of ±0.2. The uncertainty of ±0.2 originates, in fact, from that, at around M = 300 000, the molecular weight dependence looks strongest with α = 2.8, while the α value is about 2.4 at the highest M end.[32] If we wish defend the reptation model, such a gradual decrease in the exponent with increasing molecular weight might lead to supposition that the molecular weight range investigated by this study still belongs to the transition zone from the unentangled state to the extremely entangled state only in which the reptation model applies. However, the value of M/M_e studied in this work reaches about 70 for the solution of the highest molecular weight PS, and this value is beyond the maximum M/M_e value investigated for PS melts so far, to which the relation $D_s \propto M^{-2}$ is reported to hold. We will later define the highly entangled state on the basis of viscoelastic data and discuss the problem once again. It is also to be noted that in the original tube model, the tube is fixed in space during the characteristic diffusion time $\tau \simeq R_G^2/D_s$, where R_G is the radius of gyration of the diffusing chain. This condition may be satisfied when the tracer diffusion coefficient D_{tr} is measured in the entanglement network of the same polymers with molecular weights much higher than that of the diffusing polymer, as was done first by Kramer et al.[12] Results of tracer-diffusion experiments will be described in the next section.

Figure 2 shows molecular weight dependence of the steady viscosity in the range from 43 900 to 1 260 000.[19] Above M = 102 000, the data can be represented by a straight line with the slope of 3.5 ± 0.1, in good agreement with earlier investigations.[3] Table II lists values of D_s and η. As was stated in the Introduction, both D_s and η contain a parameter ζ whose magnitude is unknown. However, their product does not depend on ζ as is easily understood from the functional dependence of f_1 and f_2 on ζ in eq 1 and 2. Therefore $D_s\eta$ can be directly compared with theories without any adjustable parameter. In Figure 3, reduced values of $D_s\eta$ divided by the corresponding Rouse theoretical expression, $CRTR_G^2/6M$, are plotted against the number of entanglements per chain, M/M_e. Here R_G was calculated from an empirical R_G–M_w relationship at the Θ state under the assumption that the chain is in the unperturbed state in the concentrated regime.[21]

$$R_G^2 = 7.86 \times 10^{-18} M_w \qquad (7)$$

The solid line in the figure is eq 8 predicted from the tube model.[15]

$$D_s\eta/(CRTR_G^2/6M) = M/M_e \qquad (8)$$

Here R is the gas constant. Polyethylene data in the melt reported by Pearson et al.[14] are also shown for comparison. At the lowest molecular weight end, where chains are unentangled, the reduced value of the PS solution is very close to unity, indicating the applicability of the Rouse theory, especially for the sample F4. It gradually increases with increasing entanglement strength. Since we do not have a viscosity value of the highest molecular weight PS sample, it is not clear whether $D_s\eta$ becomes linearly proportional to M/M_e in the highly entangled state, in agreement with the prediction of the reptation theory. Even if the linear region might be attained, it appears that

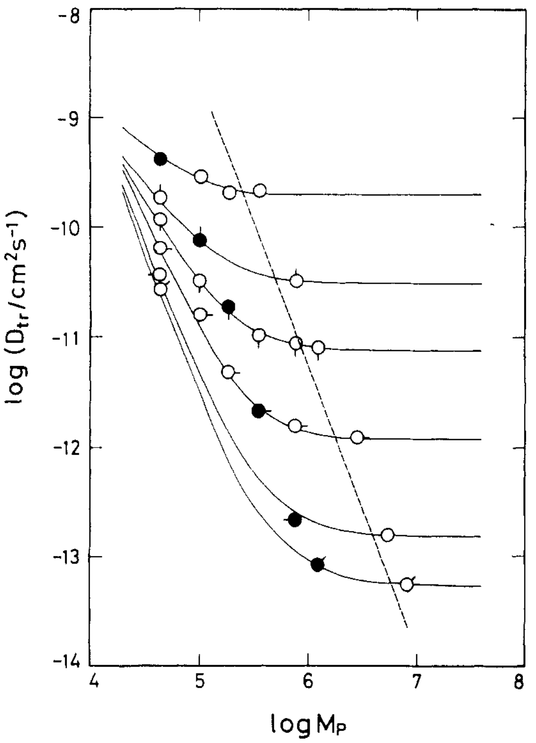

Figure 4. Dependence of diffusion coefficient on molecular weight of matrix polymer M_P in 40 wt % PS–DBP solutions. Molecular weight of the diffusing PS molecule, M_N: (○) 43 900; (ó) 102 000; (♀) 186 000; (○-) 355 000; (-○) 775 000; (σ) 1 260 000. (○) Tracer-diffusion coefficient D_{tr}; (●) self-diffusion coefficient D_s. The dashed line is obtained by connecting D_{tr} values expected at $M_P = 5M_N$.

the theory shown by the solid line in the figure would give values about four times larger than experimental ones. The discrepancy might be partly ascribed to that onset of the deviation of D_s from $D_s \propto M^{-1}$ begins at a molecular weight appreciably lower than M_c, at which η exhibits a sharp break for its molecular weight dependence from M^1 to $M^{3.5}$. Moreover, it should be remembered that the agreement of the M dependence of $D_s\eta$ between experiment and theory was brought by cancellation of the extra 0.5 power dependence of both D_s and η like $D_s \propto M^{-2.5}$ and $\eta \propto M^{3.5}$, not predicted by the original reptation theory. Polyethylene melt data appear to take, in the reduced form, about same values as the concentrated solution data in the range $1 < M/M_e < 10$ and then increase more steeply than the solution data, reflecting that D_s and η are proportional to M^{-2} and $M^{3.4}$, respectively, in the highly entangled region.

Tracer-Diffusion Behavior. The dependence of D_{tr} on molecular weight of matrix polymer chains, M_P, is shown for six PS samples with molecular weight M_N ranging from 43 900 to 1 260 000 in Figure 4, where smooth curves are empirically drawn to connect D_{tr} data for respective M_N. From the figure, each D_{tr} appears to take a value, D_{tr}^∞, independent of M_P for $M_P > 5M_N$, as was demonstrated by Yu et al.[7] and also Deschamps and Leger.[4b] These constant values may be considered as a value to be obtained for diffusion of respective chains through the entanglement network composed of polymers with infinite molecular weight. D_{tr} of four low molecular weight samples from 2800 to 16 700 was only measured in the 40 wt % entangled solution of F40 and assigned as D_{tr}^∞ because of $M_P/M_N > 20$. Numerical values of D_{tr} obtained for $M_P > 5M_N$ are given in Table III.

Figure 5 shows a logarithmic plot of D_{tr}^∞ against M_N at T_r = 60 °C, with D_s data that are replotted from Figure 1. The plot may be represented by two straight lines that intersect at a characteristic molecular weight M_D of 28 000 ± 2 000, which is a little smaller than M_e of the network, 42 300. The slope of 1 ± 0.2 below M_D agrees with the Rouse theory. When the characteristic mesh size of the entanglement network is much larger than the coil size of the diffusant, the topological interaction from the network may be negligible and the hydrodynamic interaction is strongly screened. Thus the chain behaves as the free-draining chain. Above M_D, on the other hand, the slope is −2.5 ± 0.1, which is again appreciably larger than the theoretical value of the reptating chain −2. From comparison of D_{tr}^∞ with D_s data, we may consider that the higher exponent value of −2.6 ± 0.2 for self-diffusion behavior is partly attributed to the dependence of D_s on the molecular weight of surrounding polymer chains. However, the effect becomes less significant for higher M or larger M/M_e, and D_s appears to approach asymptotically D_{tr}^∞ in the highly entangled state.

Figure 6 shows tracer-diffusion behavior in the 40 wt % unentangled solution of F4 with M_P = 43 900. Here the D_{tr} value of the highest molecular weight sample (F288) is that at infinite dilution of the diffusant derived from linear extrapolation of the data obtained at C = 1 and 0.6 wt %. Values of the next highest molecular weight sample (F128) obtained at C = 1 and 0.6 wt % agreed with each other within an experimental accuracy of 10%, thus their average is shown in the figure. The dashed line in Figure

Table III
Values of D_{tr} in 40 wt % PS–DBP Solutions at T_r = 60 °C

sample	D_{tr}/10^{-11} cm^2 s^{-1}	sample	D_{tr}/10^{-11} cm^2 s^{-1}
A2500 in F40	720	F80 in F550	0.016[a]
A5000 in F40	400	F128 in F850	0.0055[a]
F1 in F40	200	F10 in F4	18
F2 in F40	71	F20 in F4	12
F4 in F40	21	F40 in F4	6.3
F10 in F80	3.2	F80 in F4	3.6
F20 in F128	0.79	F128 in F4	2.6
F40 in F288	0.12	F288 in F4	1.6

[a] Calculated from D_{tr} values of 2.04 × 10^{-12} and 7.02 × 10^{-13} cm^2 s^{-1} at T = 110 °C for F80/F550 and F128/F850, respectively, by using the shift factor eq 6 in the text. [b] Estimated from linear extrapolation of the data, 1.07 × 10^{-11} cm^2 s^{-1} at C_{F288} = 1 wt % and 1.29 × 10^{-11} cm^2 s^{-1} at C_{F288} = 0.6 wt % to infinite dilution.

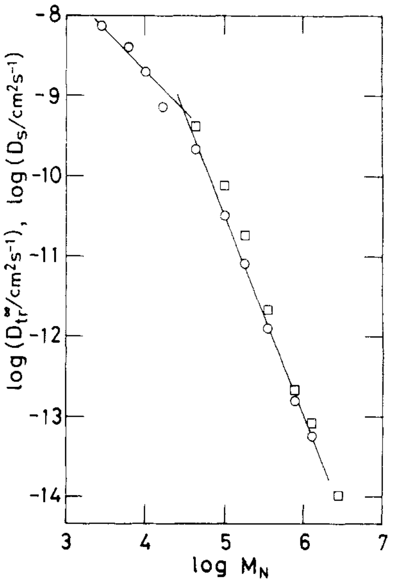

Figure 5. D_{tr} and D_s are plotted against molecular weight of the diffusant for comparison: (○) D_{tr}; (□) D_s.

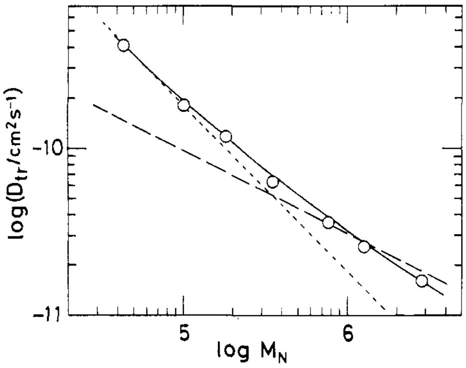

Figure 6. Tracer-diffusion behavior in the unentangled 40 wt % PS(F4)-DBP solution. The dashed line represents the free-draining chain behavior given by eq 9 and the long dashed line shows the nondraining behavior by eq 10. The solid curve is calculated by using eq 11 with $h^* = 0.07$.

6 represents diffusion behavior of the free-draining chain calculated from the following expression:

$$D_{tr} = \left(\frac{CRTR_G{}^2}{6\eta M_N}\right)_{M_N=43900} \frac{43900}{M_N} \tag{9}$$

by using $\eta = 36$ P as the viscosity of the host F4 solution and R_G from eq 7 for F4. As was stated in the previous section, the theory quantitatively predicts the D_s value of the sample F4, the point farthest left in the figure. Also, the D_{tr} value of the sample F10 with $M_N = 102\,000$ is still closely located on the dashed line. With further increase in molecular weight of the diffusant, D_{tr} data start to deviate upward from the Rouse theory. The coil size of the chain with the highest molecular weight is about eight times larger than that of the matrix PS. Such a difference in the coil size implies that the DBP solution of the matrix PS molecules may be effectively regarded as viscous liquid for diffusion of the very high molecular weight PS molecule. Then the chain may diffuse in the medium as a nondraining sphere to which the Einstein-Stokes relationship is applicable.

$$D_{tr} = k_B T/6\pi\eta R_H \tag{10}$$

The hydrodynamic radius R_H of the diffusing chain can be estimated from R_G in eq 7 and the asumption that the ratio R_G/R_H at $C = 40$ wt % is the same as the value of 1.30 obtained for unperturbed PS chain at infinite dilution.[22] Employing $\eta = 36$ P for calculation of D_{tr} by eq 10, we obtained the long dashed line in Figure 6. It appears that the line semiquantitatively reproduces the D_{tr} data of higher moleculr weight samples. This clearly indicates that even in the concentrated regime the intramolecular hydrodynamic interaction affects the translational diffusion behavior for high values of M_N/M_P.

The dependence of D_{tr} on M_N as a whole can be fitted with eq 11, which was successful in reproducing molecular weight dependence of the sedimentation coefficient of poly(methyl methacrylate) in a semidilute thiophenol solution of PS with the same molecular weight of 43 900.[23]

$$D_{tr} = \frac{k_B T}{N f_B}(1 + (8/3)2^{1/2}h^* N^{1/2}) \tag{11}$$

Here N ($\equiv M_N/M_P$) is the rescaled degree of polymerization of the diffusing chain, f_B is the friction coefficient of the matrix polymer F4 at $C = 40$ wt %, and h^* is the draining parameter. $h^* = 0$ corresponds to no hydrodynamic interaction and $h^* = 0.27$ to the dominant hydrodynamic interaction case.[24] The solid curve with $h^* = 0.07$ in the figure was found to give a best fit to the D_{tr} data.[25] Fitting of eq 11 to sedimentation data of PMMA in PS-thiophenol solutions gave $h^* = 0.27$ for $C = 16.8$ wt % and $h^* = 0.21$ for $C = 22.0$ wt %. Although the system studied is different from the present system, h^* appears to decrease with increasing polymer concentration. This may lead to the conjecture that the chain may behave as the free-draining chain in melts up to a very high ratio of M_N/M_P. On the other hand, Green and Kramer[12b] have shown from D_{tr} measurements of high molecular weight PSs with M_N from 55 000 to 915 000 in unentangled PS melts with $M_P = 20\,400$ that D_{tr} is proportional to $M^{-(0.5 \text{ to } 0.6)}$ over the whole range of M_N/M_P from 2.7 to 45, that is, the diffusant behaves as the nondraining chain. Their measurements were conducted at finite concentration of the diffusant. The effect of finite concentration is, however, supposed to give stronger dependence of D_{tr} on M_N. Thus the situation looks quite complicated.

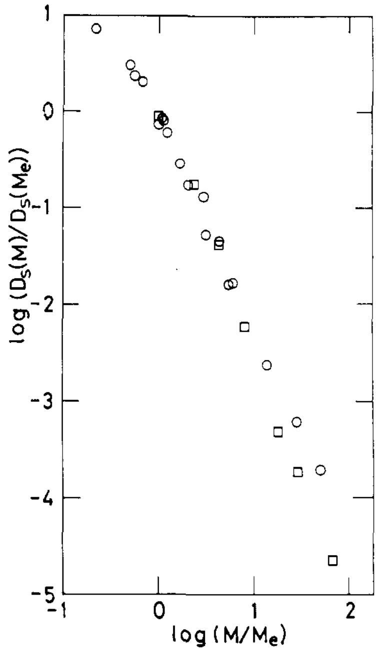

Figure 7. Self-diffusion behavior in solution compared in the reduced form with that in the melt: (○) melt data at $T = T_g + 125$ °C; (□) solution data at $T = 60$ °C and $C = 40$ wt %.

Discussion

Viscoelastic properties of neutral flexible polymers in solution as well as in the melt are systematically described in terms of two parameters, the segment friction constant ζ and the molecular weight between entanglements M_e, being characteristic of respective polymer species.[20] In order to examine applicability of the above scheme to self-diffusion behavior, we compare the solution data obtained in this study with melt data corrected to the iso-free-volume state.[26] For elimination of the factor $f_2(\zeta)$ from D_s, each $D_s(M)$ was divided by the corresponding value of D_s at $M = M_e$, $D_s(M_e)$. In the reduction, it was assumed that the effect of the screened hydrodynamic interaction, if it is present, is adsorbed into the effective segment friction constant, thus the reduced variable $D_s(M)/D_s(M_e)$ does not contain any contribution from the effect. $M_e = 18\,000$ was taken as the value in the melt.[27] Reduced quantities $D_s(M)/D_s(M_e)$ are ploted against the number of entanglements per chain M/M_e in Figure 7. In the range $1 < M/M_e < 10$, both sets of data are in excellent agreement with each other. It should be remarked that if both data were expressed by a single straight line, the slope is read as about -2.5. For $M/M_e > 10$, on the other hand, they do not agree, but the solution data give a stronger dependence on M/M_e than the melt data.

It is well-known that viscoelastic properties in the terminal zone can be characterized by the viscosity η and the steady-state compliance J_e.[20] The latter represents the elastic response of polymers due to entanglements and is quite sensitive to the shape and intensity of the relaxation spectrum at the longest relaxation time end. Experiments on various narrow-distribution polymers concerning the molecular weight dependence of J_e established that J_e does not become independent of M at around M_c but continuously increases in accordance with the Rouse theory up to M several times larger than M_c and then takes a constant value characteristic of each polymer species. If we may define the highly entangled state as the region where J_e is independent of M, roughly corresponding to the region above $M = 130000$ or $M/M_e = 8$ for PS, both the viscosity and the diffusion behavior are dominated by the slowest chain motion with the characteristic relaxation time τ_m. Then we expect a following proportionality relation will hold:

$$\eta \propto R_G^2/D_s \propto \tau_m \qquad (12)$$

Viscoelastic measurements on entangled polymer solutions showed that τ_m ($\equiv \eta J_e$) is proportional to $M^{3.5}$ at high M.[20] From the results of $\eta \propto M^{3.5}$ and $D_s \propto M^{-2.6}$ in Figures 1 and 2, and also $R_G^2 \propto M$, we may consider that the solution data approximately satisfy eq 12. On the other hand, the melt data do not satisfy eq 12 because of $D_s \propto M^{-2}$ in the highly entangled region.

The applicability of the relation $D_s \propto M^{-2}$ itself appears to have been confirmed for other polymer species such as hydrogeneated polybutadiene[9] and also polyethylene melt[14] in the highly entangled region. These results have strongly suggested the success of the reptation theory in melts, even though results of dynamic Monte Carlo simulations found no evidence for the well-defined tube required by the reptation model of polymer melt dynamics.[28] Quite recently Fixman[29] attempted to resolve the discrepancy in molecular weight dependence between D_s and η for polymer melts by taking into account the viscoelastic nature of the tube. Viscoelastic quantities of entangled systems such as η, J_e, and τ_m are known to exhibit the same molecular weight dependence in the concentrated regime and the melt. If the reptation theory and its modification were correct, then we might expect that the $D_s \propto M^{-2}$ relation also holds in the concentrated regime as it does in the melt. However, our results that D_s of highly entangled polymers in the concentrated regime is proportional to $M^{-\alpha}$, with an α value appreciably higher than 2, and also that the viscosity and the diffusion behavior in the highly entangled concentrated solutions are consistent with each other give serious doubt about the above conjecture. Reformulation of a theory that can systematically explain both the melt and the solution behavior on the basis of a new physical concept seems to be required. From an experimental point of view, we should make measurements on more concentrated solutions such as 60 and 80 wt % solutions to examine whether the dependence of D_s on molecular weight will assymptotically approach the melt behavior with increasing polymer concentration.

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References and Notes

(1) Nemoto, N.; Landry, M. R.; Noh, I.; Yu, H. *Polym. Commun.* **1984**, *25*, 141.
(2) Nemoto, N.; Kojima, T.; Inoue, T.; Kurata, M. *Polym. J.* **1988**, *20*, 875.
(3) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(4) (a) Leger, L.; Hervet, H.; Rondelez, F. *Macromolecules* **1981**, *14*, 1732. (b) Deschamps, H.; Leger, L. *Macromolecules* **1986**, *19*, 2760.
(5) Wesson, J. A.; Noh, I.; Kitano, T.; Yu, H. *Macromolecules* **1984**, *17*, 782.
(6) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1984**, *17*, 431.
(7) Kim, H.; Chang, T.; Yohanan, J. M.; Wang, L.; Yu, H. *Macromolecules* **1986**, *19*, 2737.
(8) (a) Klein, J. *Nature (London)* **1978**, *271*, 143. (b) Klein, J.; Briscoe, B. J. *Proc. R. Soc. London, Ser. A.* **1979**, *365*, 53.
(9) Bartles, C. R.; Christ, B.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2702.
(10) (a) Antonietti, M.; Countandin, J.; Grutter, R.; Sillescu, H. *Macromolecules* **1984**, *17*, 798. (b) Antonietti, M.; Countandin, J.; Sillescu, H. *Macromolecules* **1986**, *19*, 793.
(11) (a) Smith, B. A. Macromolecules **1982**, *15*, 469. (b) Smith, B. A.; Samulski, E. T.; Yu, L.-P.; Winnik, M. A. *Macromolecules* **1985**, *18*, 1901. (c) Smith, B. A.; Mumby, S. J.; Samulski, E. T.; Yu, L.-P. *Macromolecules* **1986**, *19*, 470.
(12) (a) Green, P. F.; Mills, P. J.; Palmstron, C. J.; Mayer, J. W.; Kramer, E. J. *Phys. Rev. Lett.* **1984**, *58*, 2145. (b) Green, P. F.; Kramer, E. J. *Macromolecules* **1986**, *19*, 1108.
(13) Fleisher, G. *Polym. Bull.* **1984**, *11*, 75.
(14) Pearson, D. S.; VerStrate, G.; von Meerwall, E.; Schilling, F. G. *Macromolecules* **1987**, *20*, 1133.
(15) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2*, **1978**, *74*, 1789.
(16) Inoue, T.; Nemoto, N.; Kojima, T.; Kurata, M. *J. Soc. Rheol. Jpn.* **1988**, *16*, 72 (in Japanese); *Polym. J.* **1988**, *20*, 869.
(17) Inoue, T. Ph. D. Thesis, Kyoto University, 1988 (in Japanese).
(18) Osaki, K.; Nishizawa, K.; Kurata, M. *Macromolecules* **1982**, *15*, 1068.
(19) We failed to obtain a reliable η value of the solution with the highest molecular weight of 2890000.
(20) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; John Wiley: New York, 1980.
(21) Fukuda, M.; Fukumoto, M.; Kato, Y.; Hashimoto, T. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 871.
(22) Tsunashima, Y.; Nemoto, N.; Kurata, M. *Macromolecules* **1983**, *16*, 1184.
(23) Nemoto, N.; Okada, S.; Inoue, T.; Kurata, M. *Macromolecules* **1988**, *21*, 1502.
(24) Akcasu, Z.; Benmouna, M.; Han, C. C. *Polymer* **1980**, *21*, 866.
(25) Details of the fitting procedure is described in ref 23.
(26) Watanabe, H.; Kotaka, T. *Macromolecules* **1987**, *20*, 530.
(27) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(28) Kolinski, A.; Skolnick, J.; Yaris, R. J. *J. Chem. Phys.* **1987**, *86*, 1567, 7164, 7174.
(29) Fixman, M. *J. Chem. Phys.* **1988**, *89*, 3892, 3912.
(30) Colby, R. H.; Fetters, L. J.; Graessley, W. W. *Macromolecules* **1987**, *20*, 2226.
(31) The characteristic time τ_m for mechanical equilibrium may be approximately estimated by the relation $\tau_m = \eta J_e$. The value for the 40 wt % DBP solution of the highest molecular weight sample F850 at 60 °C is about 1.6×10^4 s, which is much smaller than the annealing time of 2 weeks, $t = 1.2 \times 10^6$.
(32) The polydispersity effect is largest for the sample F288 with $M = 2890000$ and $M_w/M_n = 1.09$. D_s of the monodisperse PS sample with $M = 2890000$ is estimated to be smaller by 30% than the D_s value of F288. The exponent for D_s corrected for the polydispersity effect becomes close to −2.5 at the highest M end.