Self Diffusion of Polymers in the Concentrated Regime I. Temperature Dependence of the Self Diffusion Coefficient and the Steady Viscosity of Polystyrene in Dibutyl Phthalate

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ABSTRACT: The role of the segment friction coefficient in slow chain dynamics in concentrated polymer solutions was studied from temperature dependence of the self diffusion coefficient D_s and the steady viscosity η. Concentrated solutions of two polystyrene samples (code F4; $\bar{M}_w = 43900$ and F40; $\bar{M}_w = 355000$) in dibutyl phthalate with concentration of 40 and 50 wt% were used as test samples. Solutions of their blend containing 1 wt% of labeled F40 were also studied at total concentration of 40 wt%. For unentangled PS (F4) solutions, temperature dependence of D_s and η at each concentration was found to be in good agreement with each other and the functional form was well described in terms of the free volume theory. The function with the same values of the free volume parameters at each concentration is also applicable for description of T dependence of D_s of entangled PS (F40) solutions and also of D_s of F40 in the blend solution. The same segment friction coefficient was concluded to be operative in mass and momentum transports in concentrated solutions irrespective of the entanglement coupling.
    KEY WORDS   Self Diffusion Coefficient / Steady Viscosity / Concentrated Solution / Polystyrene / Temperature Dependence / Free Volume Theory / Forced Rayleigh Scattering /

In recent publications,[1,2] we postulated that the self diffusion coefficient D_s of flexible polymers in the semidilute regime as well as in melts can be given by the product of two contributions as eq 1,

$$D_s = f_2(\zeta)g_2(c, M) \qquad (1)$$

Here $f_2(\zeta)$ represents contribution from micro Brownian motion of a segment and is a simple function of the segment friction coefficient ζ, *i.e.*, $f_2 \propto T/\zeta$. The ζ is supposed, from its definition, to be independent of molecular weight of the polymer and to be a function of concentration c and temperature T. $g_2(c, M)$ represents the effect of the topological interac-

tion with surrounding polymer chains and depends on M and c in a very complicated manner.[3-14] Results on temperature dependence of D_s of a polyisoprene melt support eq 1.[1] In the semidilute regime, data analysis on D_s of polystyrene in tetrahydrofuran[2] and also recent reports on the translational friction coefficient of poly(methyl methacrylate) in polystyrene solutions[15] have shown that their behavior can be successfully interpreted by the same idea on which eq 1 is based. Thus a similar study on the concentrated regime seems to be all that remains for establishing the validity of eq 1 over the whole concentration range from the semidilute regime to

pure melt. By fully specifying dependences of $g_2(c, M)$ on the c and M, we may get deeper insight on the effects of the topological interaction on slow chain dynamics in condensed systems, which is still under extensive study.

In this paper, we report the results of forced Rayleigh scattering measurements on concentrated solutions of two polystyrene samples and their binary blends in dibutyl phthalate at $c = 40$ and $50 \, wt\%$ over a wide range of temperature. We also report results of steady viscosity measurements on solutions of the low molecular weight PS. Solutions of the higher molecular weight PS form entanglement networks at these concentrations, but those of the lower molecular weight PS are not entangled. Their temperature dependences are critically

compared with one other and are analyzed on the basis of the free volume concept.

EXPERIMENTAL

Materials

Two narrow distribution polystyrene samples (code F4; $\bar{M}_w = 43900$ and F40; $\bar{M}_w = 355000$) were labeled with a photobleachable dye of 2-nitro-4-carboxy-4'-dimethylaminostilbene by following the labelling procedure described in an earlier report.[16] Concentrated solutions of the labeled homopolymers and their binary blend in dibutyl phthalate (DBP) were prepared for two different concentrations of 40 and $50 \, wt\%$ by exactly the same procedure as described earlier.[17] The solu-
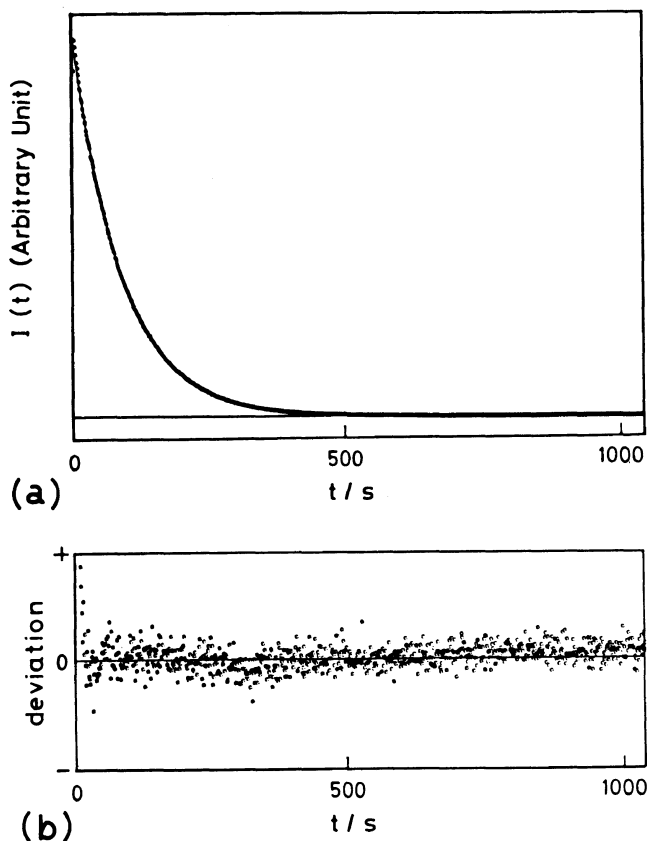
Figure 1. (a) Decay of diffracted light intensity of I_d due to self diffusion of labeled PS with $\bar{M}_w = 43900$ in DBP at $T = 60°C$. Polymer concentration is $40 \, wt\%$ and the grating spacing is $8 \, \mu m$. The solid curve is a least-square fit with eq 2. (b) Normal residuals obtained from the fit in the upper figure.

tion of the blend contained 1 wt% of the labeled higher molecular weight PS(F40) and 39% of the unlabeled lower molecular weight PS(F4).

Methods

Forced Rayleigh scattering measurements were performed with an instrument recently constructed at our laboratory.[16] Diffracted light intensity I_d at the Bragg angle from the solutions was measured as a function of time over a temperature range from 25 to 120°C under temperature control of $\pm 0.1°C$. A typical example of raw data is shown in Figure 1. The time profile of I_d could be fitted by eq 2 with a single decay rate Γ_d to all data.

$$I_d = \{A \exp(-\Gamma_d t) + B\}^2 + C^2 \qquad (2)$$

Here A is amplitude, B and C are contributions from coherent and incoherent background optical field, respectively. The Γ_d was estimated from a least-square fit to an accuracy of 10% at all temperatures. The self diffusion coefficient D_s 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

Figure 2. Plot of the decay rate Γ_d against square of the wave vector q obtained for the 40 wt% solution of F4 in DBP at three temperatures of 1, 70°; 2, 40°; and 3, 25°C.

d as $q = 2\pi/d$.

$$D_s = \Gamma_d/q^2 \qquad (3)$$

Good linearity, as is shown in Figure 2, assures that D_s was determined to an accuracy of 10%.

The steady viscosity $\eta(\dot{\gamma})$ of solutions of the lower molecular weight PS(F4) has been measured as a function of the shear rate $\dot{\gamma}$ with a cone and plate type of viscometer. Details of the viscometer and experimental procedure are described elsewhere.[18] The zero shear rate value η was determined to an accuracy of 10%.
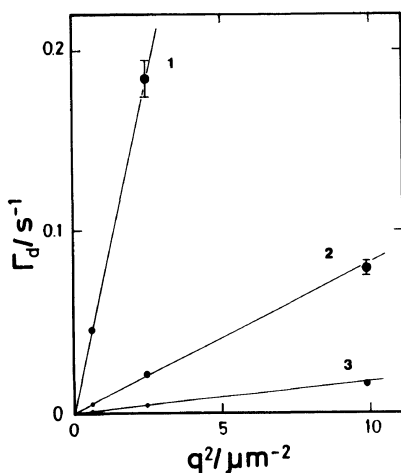
RESULTS AND DISCUSSION

Temperature Dependence of D_s and η of Unentangled PS–DBP Solutions

In Figure 3, D_s and η of the lower molecular weight PS(F4)–DBP solutions at $c = 40$ and 50 wt% are semilogarithmically plotted against the reciprocal of temperature T^{-1}. The solutions are not entangled at these concentrations, if the extent of entanglement coupling is estimated by the relation, $M_e c = 1.8 \times 10^4$ $(g\,cm^{-3})$,[19] where M_e is the molecular weight between entanglements. It is evident from the figure that T dependence of either D_s or η can not be represented with the Arrehnius type of equation. The behavior, which is convex to the abscissa for D_s and concave for η, may be interpreted in terms of the free volume theory as will be shown later.

It is well known that dependences of η on c, M, and T can be discussed with eq 4 in analogy with eq 1 for D_s.[20]

$$\eta = f_1(\zeta) g_1(c, M) \qquad (4)$$

Here $f_1(\zeta)$ is a function of c and T, and is supposed to be proportional to ζ, i.e., $f_1(\zeta) \propto T/f_2(\zeta)$. $g_1(c, M)$ is a function which expresses the effect of the topological interaction on η. If g_1 and g_2 are independent of T to PS solutions as is postulated here, then T/D_s should have the same temperature dependence as η does at fixed c and M. In Figure 4, reduced quantities $D_{s,r} T/D_s T_r$ and η/η_r are compared.
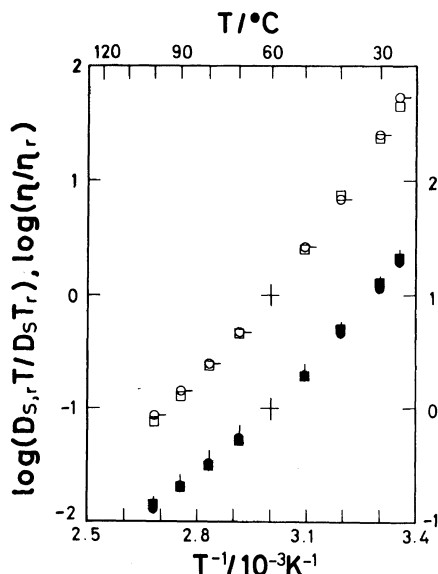
(a)

(b)
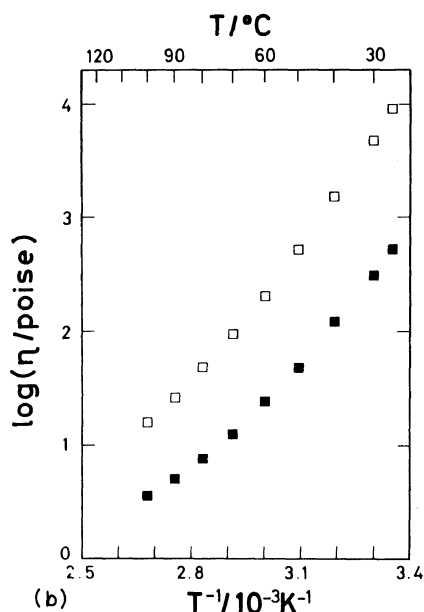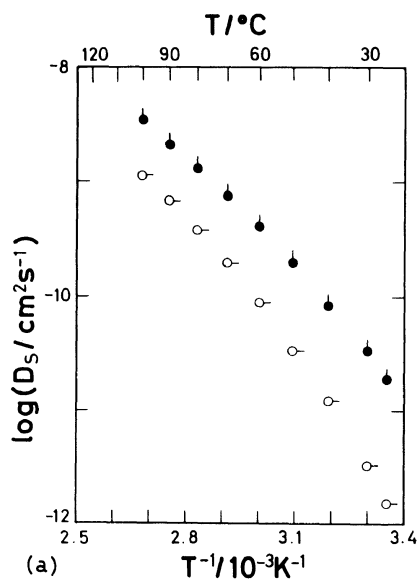
Figure 3. Temperature dependence of the self diffusion coefficient D_s and the steady viscosity η of F4 solutions. (a) Plot of D_s vs. T^{-1}. Concentration is (●), 40 and (○-), 50 wt%. (b) Plot of η vs. T^{-1}. Concentration is (■), 40 and (□), 50 wt%.

Here 60°C is chosen as a reference temperature T_r, and $D_{s,r}$ and η_r are corresponding values at T_r. Agreement looks excellent for

Figure 4. Comparison of temperature dependence between $D_{s,r}T/D_sT_r$ and η/η_r calculated from the data in Figure 3. The reference temperature T_r is 60°C. Symbols are (●) and (■) for D_s and η at $c=40$ wt% and (○-) and (□) for D_s and η at $c=50$ wt%, respectively.

the reduced data at each concentration. Thus, we can conclude that separation of local and global motions by f and g as is given by eq 1 and 4 is valid for D_s and η, and that the same segment friction coefficient ζ may be used to mass and momentum transports at least in unentangled solutions.
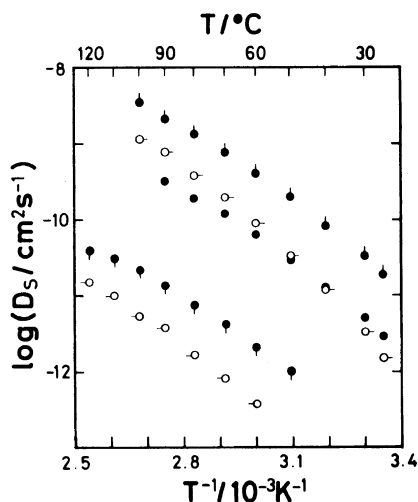
Effect of Entanglement Coupling on Temperature Dependence of D_s

The higher molecular weight PS sample (F40; $\bar{M}_w=355000$) forms an entanglement network at $c=40$ and 50 wt%. Thus, comparison of D_s data of these solutions with those of the unentangled PS(F4) solutions in the previous section is quite suitable for examination of the effect of entanglement coupling on T dependence of D_s. In addition, we studied T dependence of the tracer diffusion coefficient of F40 ($c=1$ wt%) in the F4 solution ($c=39$ wt%). Values of D_s obtained are tabulated with D_s and η values of the F4 solutions in Table I. Figure 5 gives a semilogarithmic plot

Table I. Self diffusion coefficient D_s and η of PS in DBP

Sample code	$T/^\circ C$	$D_s \times 10^{11}/$ cm^2 s^{-1}	$\dfrac{D_{s,r}T}{D_s T_r}$	η/poise	$\eta \times \eta_r$
F4 40%	25	1.87	19.6	532	21.6
	30	3.30	11.3	315	12.8
	40	8.39	4.59	123	5.00
	50	20.0	1.99	48.0	1.95
	60	41.0	1	24.6	1
	70	76.4	0.553	12.8	0.520
	80	131	0.332	7.75	0.315
	90	212	0.221	5.10	0.207
	100	347	0.132	3.60	0.146
F40 in F4 40%	25	0.292	19.3		
	30	0.513	11.2		
	40	1.27	4.66		
	50	2.92	2.09		
	60	6.30	1.00		
	70	11.4	0.569		
	80	19.4	0.344		
	90	32.4	0.212		
F40 40%	50	0.102	2.04		
	60	0.214	1.00		
	70	0.419	0.526		
	80	0.755	0.300		
	90	1.34	0.174		
	100	2.17	0.110		
	110	3.07	0.0802		
	120	3.90	0.0648		
F4 50%	25	0.152	52.7	9140	44.4
	30	0.327	24.9	4780	23.2
	40	1.22	6.90	1530	7.43
	50	3.31	2.62	527	2.56
	60	8.95	1	206	1
	70	19.7	0.468	94.0	0.456
	80	38.2	0.248	48.7	0.236
	90	68.9	0.142	26.2	0.127
	100	114	0.0879	16.0	0.0777
F40 50%	60	0.0382	1.00		
	70	0.0837	0.470		
	80	0.164	0.247		
	90	0.386	0.108		
	100	0.536	0.0798		
	110	0.981	0.0448		
	120	1.51	0.0299		

Figure 5. Semilogarithmic plot of D_s vs. T^{-1}. Symbols are: ($\bullet$), F4, 40%; ($\bullet$), F40, 40%; ($\bullet$), F40 in F4, 40%; ($\bigcirc$-), F4, 50%; and (-$\bigcirc$), F40, 50 wt%.
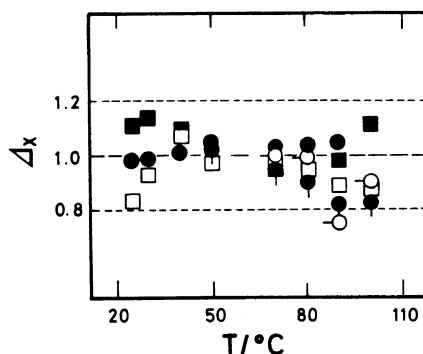
Figure 6. Temperature dependence of D_s and η was critically examined by plotting a ratio $\varDelta_x$, defined by eq 5, against T. Symbols are the same as in Figures 3 and 5.

of D_s vs. T^{-1}. The most pronounced feature in the figure is that D_s decreased drastically with the increase in both c and M at constant T. If the dependence of D_s on M at constant c and T were boldly expressed by the power law of $D_s \propto M^{-\beta}$, the exponent β would become 2.5

and 2.6 at $c = 40$ and 50 wt%, respectively. Such a strong M dependence in the transition region from the unentangled to entangled state is consistent with the self diffusion behavior of the same PS molecule in melts around $M/M_e \simeq 1$ where the value β has been found to be close to 2.5.[21,22] On the other hand, decrease in D_s with increasing c may be mainly related to increase in local friction. More detailed studies on dependences of D_s on c and M will be reported in forthcoming papers.

In spite of the strong dependence of D_s on c

and M, relative changes in D_s values with varying temperature look almost the same for two homopolymer solutions and one blend solution with the same total concentration. For a quantitative comparison, a reduced quantity $a_x = [D_{s,r}T/D_sT_r]_x$ was first calculated from D_s data in Figure 5 by taking the reference temperature T_r as 60°C. Here the suffix x denotes the F40 or F4 solutions, or the blend solution. Then a ratio Δ_x, defined by eq 5, has been calculated and is plotted against T in Figure 6.

$$\Delta_x = a_x/a_{F4} \qquad (5)$$

In the figure, we also show Δ_x of η of the F4 solutions estimated by the same procedure. The $\Delta_x = 1$ in the ordinate means that the temperature dependence of D_s or η of the solution denoted by the suffix x is identical with that of D_s of the F4 solution at the corresponding concentration. If there is a 10% difference between $a_x(T)$ and $a_{F4}(T)$, it results in $\Delta_x = 1.1$ or 0.9. All Δ_x values are located in the range from 0.8 to 1.2 except only one Δ_x value for D_s of the 50% F40 solution at 90°C. In consideration of an experimental accuracy of 10% for both quantities of D_s and η, agreement seems satisfactory. Thus the temperature dependence of D_s is unaffected by the presence of entanglement coupling. The above results may be regarded as strong support of the applicability of eq 1 to D_s over a wide concentration range from the semidilute region to pure polymer melts.

Analysis of the Data in Terms of the Free Volume Theory

It was pointed out in a previous section that T dependence of D_s and η (Figures 3 and 5) did not obey the simple Arrehnius type of equation. We here apply the free volume theory for interpretation of the data, because the theory has been demonstrated to be quite successful for explaining the T dependence of viscoelastic properties of polymeric materials in concentrated solutions and in bulk.[23] If D_s and η can

be expressed by the product of the local friction factor f and the global structure factor g as given by eq 1 and 4, reduced quantities such as $D_{s,r}T/D_sT_r$ and η/η_r are equal to a ratio of the segment friction coefficient ζ at T and T_r. Their temperature dependences may be expressed in terms of the WLF type of equation,

$$\log(D_{s,r}T/D_sT_r) = \log(\eta/\eta_r)$$
$$= \log(\zeta(T)/\zeta(T_r))$$
$$= -\frac{C_1^r(T-T_r)}{C_2^r+(T-T_r)} \qquad (6)$$

Here C_1^r and C_2^r are constants and related to the free volume parameters, the fractional free volume, f_r, and the thermal expansion coefficient of the free volume, α_f, by eq 7.

$$C_1^r = B/2.303f_r, \qquad C_2^r = f_r/\alpha_f \qquad (7)$$

where B is a constant of an order of unity. Equation 6 implies that a plot of $(T-T_r)/\log(\zeta(T)/\zeta(T_r))$ against $T-T_r$ should give a
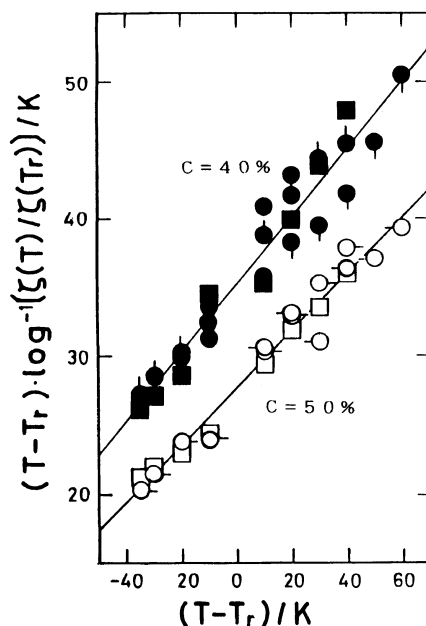
Figure 7. Applicability of WLF equation to temperature dependence of D_s and η in Figures 3 and 5 was tested. Symbols are the same as in Figures 3 and 5. Solid lines are the best fit from eq 6.

Table II. Free volume parameters

$\dfrac{c}{\text{wt}\%}$	C_1^{r}	$\dfrac{C_2^{\text{r}}}{\text{K}}$	f_{r}	$\dfrac{\alpha_{\text{f}}}{10^{-4}\,\text{K}^{-1}}$
40	4.06	143.	0.107	7.49
50	4.84	134.	0.0898	6.71

straight line. When the D_s and η data are plotted in such a manner, we obtain a straight line at each c, as is shown in Figure 7, from which C_1^{r} and C_2^{r} are easily evaluated. The α_{f} and f_{r} were calculated from eq 7 by putting $B = 1$, and are listed with values of C_1^{r} and C_2^{r} in Table II. The thermal expansion cofficient of DBP and PS above T_{g} is 8.6×10^{-4} and 6.5×10^{-4} K^{-1}, respectively.[24] The α_{f} values of the two PS–DBP solutions in Table II are intermediate between them. The glass transition temperature T_{g} of the solutions was roughly estimated from DSC measurements as $-55°$ for $c = 40\,\text{wt}\%$ and $-38°\text{C}$ for $50\,\text{wt}\%$, respectively. Assuming linear dependence of f on T, the fractional free volume at T_{g} was calculated as 0.021 and 0.024 for the solutions with $c = 40$ and $50\,\text{wt}\%$, respectively. The values are in reasonable agreement with the accepted value of $f_{\text{g}} = 0.025 \pm 0.003$.[23]

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