(C_8–C_{14}) based on the least-squares method. In the present study, hydrophobic interaction among bound surfactants was monitored through the conformational change of polypeptide chains as a result of their interaction with surfactants. A slight difference in the interaction can be largely amplified by the cooperative nature of conformational change of the polypeptide. Hence observed nonlinear dependence most likely originates from the present sensitively detecting device, which makes use of characteristic property of the β-structure.

A nonlinear dependence of the hydrocarbon chain length of surfactants has been found in their binding to polyacrylate and its copolymers.[10] Attractive interaction, as monitored in terms of conductivity of salt-free solutions, decreased with decreasing chain length down to C_6, which was attributed to the decrease in the hydrophobic interaction. However, attractive interaction increased as the chain length further decreased from C_6, leading to a break around C_6. The increase was attributed to the enhancement of electric attraction due to the decrease of counterion size.[10] The trend after the break was opposite to that found in the present study. The different behavior found on short chain lengths between the two studies most likely arises from different properties employed to monitor the polyion–counterion interaction. Electrostatic interaction affects the conductivity but it alone cannot induce the β-structure, as shown in the study on dodecyltrimethylammonium counterions. Consequently, observed nonlinearity represents different things. In the present study, it represents nonlinear dependence of the hydrophobic interaction on the hydrocarbon chain length, while in the other case it occurs as a result of superposition of two interactions.

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Registry No. PGA (homopolymer), 25513-46-6; PGA (SRU), 24991-23-9; poly[Cys(CH_2COOH)] (homopolymer), 29433-95-2; poly[Cys(CH_2COOH)] (SRU), 31851-29-3; decylammonium chloride, 143-09-9; hexylammonium chloride, 142-81-4; octylammonium chloride, 142-95-0; dodecylammonium chloride, 929-73-7; tetradecylammonium chloride, 1838-04-6.

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Probe Molecule Diffusion in Polymer Solutions

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ABSTRACT: Translational diffusion coefficients of probe molecules have been examined as functions of polymer concentration and temperature in polystyrene and polyisoprene solutions in tetrahydrofuran (THF). The probes were azo dyes, methyl red and methyl yellow. Concentration range examined for polystyrene solution was 0–68.2 wt % while that for polyisoprene solution was for the entire range, pure solvent to pure bulk polymer. The transient optical grating technique of forced Rayleigh scattering was used to determine the diffusion coefficients. Two free volume theories, Fujita and Vrentas–Duda, were compared relative to their predictions of the concentration dependence of the probe diffusion coefficient under isothermal conditions. Both theories provide reasonable agreement with the experiment for the polyisoprene–THF system over the entire concentration range, whereas agreement is less satisfactory with the polystyrene–THF even over a narrower concentration range. In addition, temperature and concentration dependences were simultaneously examined by combining the Vrentas–Duda model with the Williams–Landel–Ferry theory.

It has long been established that one may learn about local segmental motions of polymer molecules from the study of small molecule diffusion in solutions, particularly at high polymer concentrations or in the undiluted state.[1,2] In the vast literature of small molecule diffusion in polymer systems,[1,3-12] much attention is directed toward the comparison of the frictional resistance of probe or diluent molecules undergoing translational diffusion to the resistance of segmental motion of the host polymer molecules. It is this segmental resistance which is often considered in the formulation of molecular and phenomenological theories of chain dynamics; it is often characterized by a friction coefficient ζ_0 of a monomer unit.[2] In particular, a free volume theory by Fujita[1] has been demonstrated to be rather successful in the interpretation of the concentration dependence[1,3-7] and the temperature dependence[1,3,7-9] of ζ_0 via small molecule diffusion. The free volume concept has been used to interpret the temperature dependence of steady-shear viscosity of polymeric systems via the temperature shift factor a_T; from this theory one is able to derive the Williams–Landel–Ferry (WLF) equation[13] which has proven to be widely applicable for numerous viscoelastic quantities.[2] However, it appears less clear whether the Fujita free volume theory should be applicable to the region of low polymer concentration.[1]

A more generalized approach to the free volume concept of small molecule and segmental motion has been developed by Vrentas and Duda.[14,15] In the Vrentas–Duda extension, several restrictive assumptions implicit in the Fujita treatment have been removed,[14] allowing for a possibility to extract the collisional dynamics information

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Table I
Summary of Methyl Red Diffusion Coefficients in Polystyrene–Tetrahydrofuran Solutions

polymer wt fractn[b] w_2, g/g	diffusion coeff $10^7 D_d$, cm^2/s					activatn energy, E_D, kcal/mol
	5 °C	15 °C	25 °C	35 °C	45 °C	
0	114 ± 8	140 ± 7	160 ± 6	184 ± 11	208 ± 9	2.6 ± 0.4
0.20	60.3 ± 3.3	74.3 ± 3.6	91.1 ± 7.9			3.0 ± 0.6
0.30	45.0 ± 2.0	56.0 ± 6.6	66.1 ± 8.4	71.1 ± 7.6	94.2 ± 10	3.4 ± 0.5
0.40	16.0 ± 1.2	24.0 ± 2.9	34.4 ± 1.8	43.9 ± 3.5	56.8 ± 3.9	5.5 ± 0.8
0.51	5.16 ± 0.25 4.98 ± 0.89	7.81 ± 0.34 6.88 ± 0.54	11.1 ± 0.5 10.4 ± 1.3	14.9 ± 1.4	21.6 ± 1.7	6.3 ± 0.4
0.60	1.04 ± 0.07	1.69 ± 0.21	3.18 ± 0.16	5.94 ± 0.33	9.51 ± 0.75 8.43 ± 0.56	9.8 ± 1.0
0.682	0.16 ± 0.01	0.32 ± 0.02	0.73 ± 0.04	1.46 ± 0.04	2.80 ± 0.12	12.7 ± 0.8
0.30[a]	40.6 ± 1.7	53.0 ± 4.2	65.7 ± 3.0	67.0 ± 4.1	95.0 ± 16	3.4 ± 0.5

[a] Molecular weight = 4.11×10^5 g/mol. [b] Molecular weight = 5.1×10^4 g/mol.

as well as the free volume parameters from the diffusion behavior of small molecules. Success of the Vrentas–Duda method has been seen experimentally,[6–22] for solvent and probe molecule diffusion in polymer solutions over the full polymer concentration range, i.e., from pure solvent to pure polymer.

In the following, probe molecule diffusion coefficients in polystyrene–tetrahydrofuran (THF) and polyisoprene–THF solutions are obtained by the transient grating technique of forced Rayleigh scattering (FRS), and they are analyzed in terms of the Fujita and Vrentas–Duda free volume theories. The purpose will be to compare the two approaches. At the same time, some insight into the dynamics of segmental motion in polymer solutions is gained.

Experimental Section

Materials. The probe molecules used for the diffusion measurements in the polymer–THF solutions were derivatives of azobenzene. For the polystyrene (PS) solutions, methyl red, (2-[*p*-(dimethylamino)phenylazo]benzoic acid (Aldrich), was used. Methyl yellow, [*p*-(dimethylamino)azo]benzene (Aldrich), and methyl red were used for polyisoprene (PI)–THF solutions. Each dye photoisomerizes via their diazo linkage, undergoing a change between the trans and cis configurations.[23]

The polystyrene was obtained from Pressure Chemical Co. (Pittsburgh, PA) and was used as received. The molecular weights used were 411 000 and 51 000 g/mol, with a majority of the solutions composed of the latter. The polyisoprene samples (M = 25 300 and 16 700; $M_w/M_n \leq 1.10$) were prepared anionically in this laboratory, and the synthetic route has been given elsewhere.[24] The solvent for both polymers was tetrahydrofuran (Aldrich, Gold Label); it was used as received after filtering through 0.2-μm pore Teflon filters.

The solutions were prepared gravimetrically by adding a THF–dye solution to the polymer samples. The THF–dye solutions were very dilute in terms of the total dye concentration: 1.6×10^{-4} g/mL for methyl red and 1.0×10^{-4} g/mL for methyl yellow. These values are quoted before addition to the polymer samples. The final concentrations of the dyes are estimated as about 0.1 mM. The independence of the dye diffusion coefficient vs dye concentration was confirmed, and one example is reported in the Results and Discussion.

Forced Rayleigh Scattering Measurements. The two optical configurations used for the FRS experiments have been described previously.[25–27] Temperature control was accomplished by enclosing the sample cells (modified 1 mm or 2 mm path length spectrophotometer cells) between two specially designed copper blocks and then circulating water in channels drilled throughout the blocks.[28] Collection of the diffraction signals, data acquisition, and analysis were performed as described by Wesson et al.[26]

Results and Discussion

1. Methyl Red in Polystyrene–THF Solutions. As is customary with the FRS technique, the diffusion coefficients D_d of the dye molecules were determined from a plot of the relaxation time τ of a diffraction signal vs the square of the transient grating spacing d^2, where $D_d = d^2/(4\pi^2\tau)$. In Figure 1 is displayed the τ vs d^2 results for methyl red diffusion at a polymer weight fraction w_2 of 0.51 at five different temperatures. The increasing slopes with decreasing temperature T indicate the progressive decrease of the diffusion coefficient D_d. The values for D_d for all of the PS–THF solutions are collected in Table I. The diffusion coefficients are calculated from the slopes of linear least-squares fits of data similar to those presented in Figure 1, and the uncertainties in D_d are the 95% confidence limits of the slope determination with use of the Student's t-distribution.

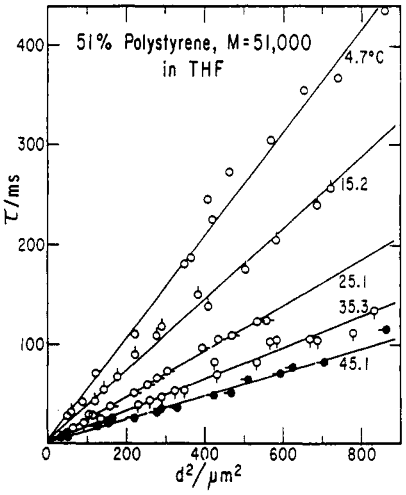

Figure 1. Plot of the transient optical grating decay constant τ against the square of the grating spacing d^2 for methyl red diffusion in 51% polystyrene in THF. The data sets for temperatures of 4.7 (○), 15.2 (ȯ), 25.1 (○), 35.3 (ọ), and 45 °C (●). The values of D_d are inversely proportional to the slope of each line; $D_d = (4\pi^2 \times \text{slope})^{-1}$.

The methyl red diffusion coefficients were determined for the temperatures 5, 15, 25, 35, and 45 °C. The results are displayed by an Arrhenius plot shown in Figure 2. Aside from the apparent Arrhenius behavior, the discussion of which is deferred to later, there are two important details that should be pointed out. All of the D_d values are recorded for solutions prepared from 51 000 g/mol polystyrene, with the exception of the 30% (wt %) series, in which both 51 000 g/mol (open circles, Figure 2) and 411 000 g/mol (filled circles) are given. The half-filled circles indicate that the data points overlap. The independence of the dye diffusion coefficients with respect to the polymer molecular weight is not totally unexpected, notwithstanding the enormous difference in the solution viscosities.[33] The second point of interest in Figure 2 is the one circled at T = 25 °C and w_2 = 0.30. There are actually two data points represented here for the M =

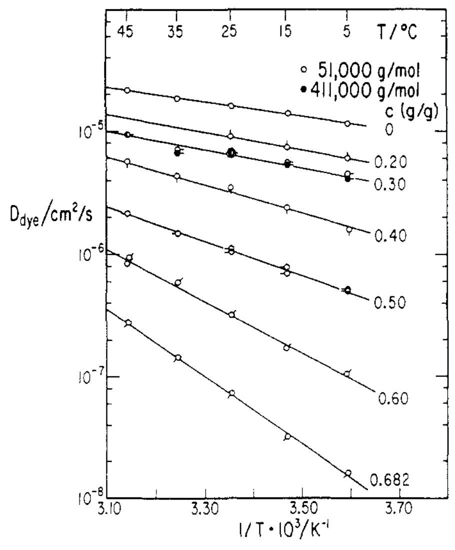

Figure 2. Arrhenius plot of $\ln D_d$ versus $1/T$ for methyl red diffusion for the PS–THF system with PS molecular weight 51 000 g/mol (○) and 411 000 (●). The concentrations are listed on the right-hand column in weight fraction w_2. The diffusion coefficients and resulting activation energies for this figure are given Table I.

51 000 g/mol PS–THF solution, each of which is for a separate dye concentration (1×10^{-4} and 5×10^{-4} g/mL). The independence may be taken as evidence that we are indeed measuring the diffusion coefficient in the limit of infinite dilution of the dye.

The linear dependence of $\ln D_d$ against reciprocal temperature $1/T$ in Figure 2 indicates an Arrhenius behavior, whereby an "activation energy" for diffusion, E_D, can be determined

$$D = A \exp(-E_D/RT) \qquad (1)$$

The values for E_D so obtained are listed in Table I. Others have observed the similar Arrhenius behavior: benzene and cyclohexane self-diffusion studied by Kosfeld and Goffloo;[7,29] ethyl benzene and toluene diffusion in PS solutions measured by Maklokov;[30] and by Moore and Ferry[4] for the diffusion of cetane in polyisobutylene solutions. If WLF behavior is expected, such a plot should not be linear for a wide enough temperature range. However, if the temperature range is narrow, the data may appear to fall on a straight line exhibiting an apparent Arrhenius behavior. It may be also argued that for the majority of the concentrations examined here, the temperatures are above $T_g(w_2)$ + 100 °C [$T_g(w_2)$ is the glass transition temperature for the solution at w_2], which is the approximate upper limit for one to expect WLF behavior.[2] Recently Huang et al.[22] have demonstrated that the WLF equation does indeed describe the temperature dependence of probe molecule diffusion in PS/toluene and PVAc/toluene solutions. More concentrated solutions are examined in the Huang study; hence the measurements fall within the T_g + 100 °C range necessary for WLF behavior.

We now turn to the data analysis for the concentration dependence according to the Fujita free volume theory. Equations 2 and 3 describe the diffusion coefficient D_1 of a diluent molecule at a particular solvent volume fraction ϕ_1 as[1,2]

$$\ln\left[\frac{D_1(T,\phi_1)}{D_1(T,0)}\right] = \frac{B_d\beta(T)\phi_1}{[f^2(T,0) + \beta(T)f(T,0)\phi_1]} \qquad (2)$$

$$f(T,\phi_1) = f_2(T,0) + \beta(T)\phi_1 \qquad (3a)$$

$$\beta(T) = f_1(T,0) - f_2(T,0) \qquad (3b)$$

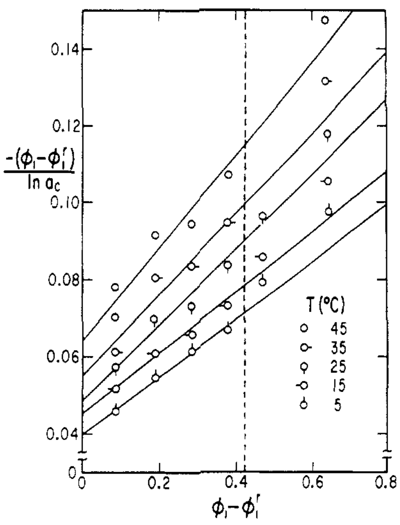

Figure 3. Plot of $-(\phi_1 - \phi_1^r)/\ln a_c$ against $\phi_1 - \phi_1^r$ at several temperatures for methyl red diffusion in the polystyrene–THF system. The reference solvent volume fraction ϕ_1^r corresponds to w_2 = 0.682 g/g. The solid lines are drawn to fit the data points with more weights given to smaller values of $\phi_1 - \phi_1^r$ (to the left side of the vertical dashed line where the Fujita free volume treatment (eq 4) is expected to be valid. The free volume parameters $f(T,\phi_1^r)$ and $\beta(T)$ obtained from the slopes and intercepts of each line are listed in Table II.

where f_1 and f_2 are the fractional free volumes of solvent and polymer, respectively, $D_1(T,0)$ is the diffusion coefficient of the diluent in the limit of vanishing solvent concentration (reference concentration), and B_d is a free volume parameter that is usually taken as unity as a first-order approximation. Comparison of eq 2 and 3 with experimental results cannot be made unless the free volume parameters have been previously determined. Upon rearrangement of eq 2 and redefining the reference concentration as ϕ_1^r, two linear equations result which have the forms[1,2]

$$-\frac{1}{\ln a_c} = \frac{f(T,\phi_1^r)}{B_d} + \frac{f^2(T,\phi_1^r)}{B_d\beta(T)}\,\frac{1}{(\phi_1 - \phi_1^r)} \qquad (4)$$

$$-\frac{(\phi_1 - \phi_1^r)}{\ln a_c} = \frac{f^2(T,\phi_1^r)}{B_d\beta(T)} + \frac{f(T,\phi_1^r)}{B_d}(\phi_1 - \phi_1^r) \qquad (5)$$

The ratio $D_1(T,\phi_1^r)/D_1(T,\phi_1)$ has been known as the concentration shift factor a_c.

If the free volume theory is successful in accounting for the concentration dependence of probe molecule diffusion as well as diluent diffusion, then plotting the methyl red data for the PS–THF solutions as suggested by eq 4 and 5 allows the parameters $f(T,\phi_1^r)$ and $\beta(T)$ to be determined, provided that B_d is assumed to be a known constant, e.g., unity, as is commonly done.[2] The plot according to eq 5, $-(\phi_1 - \phi_1^r)/\ln a_c$ against $\phi_1 - \phi_1^r$, is displayed in Figure 3 for all temperatures, whereas the linear relationship of $-(\ln a_c)^{-1}$ vs $(\phi_1 - \phi_1^r)^{-1}$ according to eq 4 is not shown. The volume fractions of solvent ϕ_1 were calculated from the polymer weight fractions by using the densities of THF[31] and polystyrene,[32,37] assuming additivity of the volumes. The reference weight fraction of polymer w_2^r = 0.682; hence that of solvent w_1^r = 0.318, which translates into ϕ_1^r = 0.359 at 5 °C and 0.364 at 45 °C. As seen from Figure 3, the data seem to be reasonably represented by eq 5, with the exception of the two highest solvent concentrations (w_1 = 1.0 and 0.8; i.e., at $\phi_1 - \phi_1^r$ = 0.64 and 0.47). Since Fujita[1] has expressed reservations for high diluent concentrations, these points are not used in the subsequent analyses. A similar behavior is seen for data plotted by using eq 4. The

Table II
Free Volume Parameters from the Fujita Theory for Methyl Red Diffusion in Polystyrene–Tetrahydrofuran Solutions[a]

temp, °C	$f(T, \phi_1^r)$		$\beta(T)$	
	eq 5	eq 4	eq 5	eq 4
45	0.120 ± 0.015	0.120 ± 0.020	0.225 ± 0.060	0.220 ± 0.055
35	0.105 ± 0.010	0.105 ± 0.010	0.200 ± 0.075	0.200 ± 0.055
25	0.100 ± 0.005	0.100 ± 0.005	0.195 ± 0.020	0.190 ± 0.035
15	0.080 ± 0.005	0.085 ± 0.005	0.135 ± 0.030	0.165 ± 0.040
5	0.075 ± 0.005	0.075 ± 0.005	0.135 ± 0.035	0.150 ± 0.030

[a] These parameters were calculated assuming $B_d = 1$, eq 4 and 5.

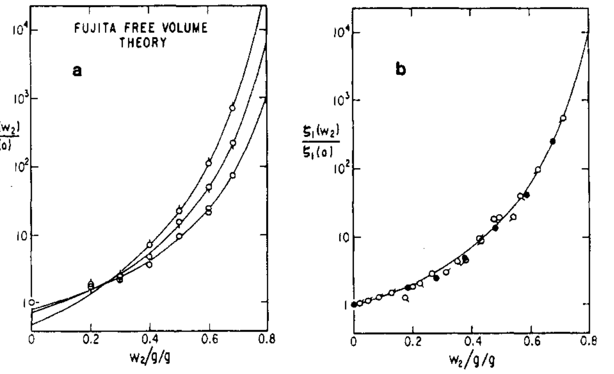

Figure 4. (a) Concentration dependence of the methyl red friction coefficient ζ_d for three temperatures (same symbols as given in Figure 3). The solid curves represent the best fits to the data using the Fujita free volume parameters listed in Table II. (b) A comparison of the friction coefficients (interpolated to T = 30 °C) for dye molecule (filled circles) and another probe, C_6F_6 (the open circles with pips, von Meerwall, Amis and Ferry;[33] data measured T = 30 °C). The solid curve is the free volume theory fit of the C_6F_6 data in PS–THF.

Table III
Summary of Methyl Red and Methyl Yellow Diffusion Coefficients in Polyisoprene–Tetrahydrofuran Solutions

polymer[c] wt fractn w_2, g/g	diffusion coeff $10^7 D_d$, cm^2/s	
	25 °C	45 °C
MR[a]		
0	160 ± 6	208 ± 9
0.158	105 ± 14	130 ± 21
0.251	83.9 ± 4.0	116 ± 8
0.493	32.3 ± 3.3	42.4 ± 5.6
0.62	19.4 ± 1.1	25.3 ± 1.4
0.75	6.25 ± 0.19	12.9 ± 1.0
0.796	4.71 ± 0.42	9.86 ± 0.74
1.0	0.49 (estimate)[d]	1.46 (estimate)[d]
MY[b]		
0	176 ± 9	236 ± 13
0.249	97.1 ± 7.1	
0.605	23.0 ± 5.0	30 ± 4
1.00[e]	0.56 ± 0.04	1.68 ± 0.52

[a] Methyl red diffusion data. [b] Methyl yellow diffusion data. [c] Polyisoprene molecular weight M = 2.53 × 10^4 g/mol. [d] Estimated from MY diffusion coefficients, with D_{MY}/D_{MR} = 1.15 (see text). [e] Polyisoprene molecular weight M = 1.67 × 10^4 g/mol.

free volume parameters $f(T,\phi_1^r)$ and $\beta(T)$ have been obtained from the slopes and intercepts of the plots in Figure 3 (eq 5) as well as from eq 4 and are listed in Table II; B_d has been assumed to be unity throughout. Uncertainties are estimated by analyzing the data according to a linear least-squares routine, and they represent a 95% confidence interval.

Whether these values are reasonable or not will be taken up shortly. For the moment, we proceed to compare the above results with those obtained by another method in the same polymer solution. In an NMR experiment by von Meerwall, Amis, and Ferry,[33] the diffusion coefficients of the solvent, THF, and another probe molecule, C_6F_6, were determined for polystyrene–THF solutions over an identical concentration range. In order to facilitate the comparison, the dye diffusion data are plotted as ln $[\zeta_d(w_2)/\zeta_d(0)]$ against w_2 and shown in Figure 4a for the three temperatures 5, 25, and 45 °C; $\zeta_d(w_2) = kT/D_d(w_2)$ is the dye friction coefficient at polymer weight fraction w_2. Since the data are plotted for $\zeta_d(w_2)/\zeta_d(0)$, the solid curves in the figure are calculated for $a_c[\zeta_d(w_2^r)/\zeta_d(0)]$, with a_c determined according to eq 2 and 3.

The C_6F_6 diffusion data of von Meerwall et al.[33] at T = 30 °C are plotted in a similar fashion in Figure 4b and represented by the open circles. The pips designate solutions composed of different PS molecular weights and are the same as those used in the cited reference.[33] The solid curve in this figure was calculated, from Fujita's free volume theory with the C_6F_6 diffusion data. Also plotted for direct comparison in Figure 4b are data points (filled circles) for the dye friction coefficient ratios, interpolated to 30 °C. Both parts a and b of Figure 4 indicate that the two-parameter description of the concentration dependence according to the free volume theory for the dye diffusion data by FRS or the C_6F_6 diffusion data by NMR in PS–THF solutions are both reasonably adequate. There is a subtle difference, however, between the solid curve in Figure 4b and the dye diffusion data (filled circles). The curve overestimates $\zeta_d(w_2)/\zeta_d(0)$ in the range between $w_2 \simeq 0.20$ and 0.40. A possible explanation for this discrepancy is that perhaps B_d (eq 4 or eq 5) is not identically equal to unity for both methyl red and C_6F_6 diffusion; it is related to the minimum void size necessary for the displacement of the diffusing species (single molecule or several polymer monomer units, for example). Another, more general, reason may be that the implicit assumptions used for the derivation of Fujita's free volume theory are not completely correct.[14,15] Its applicability at low polymer concentrations has been already questioned experimentally.[1,9,33]

Nevertheless, it appears that Fujita's free volume theory with its two parameters, $f(\phi_1^r)$ and β, is reasonable in fitting the diffusion data in the polystyrene–THF system, and the discrepancy between the values of β determined from methyl red and C_6F_6 diffusion appears to be of no significance.

2. Methyl Red and Methyl Yellow Diffusion in Polyisoprene–THF Solutions. In Table III are tabulated the methyl red and methyl yellow diffusion coefficients for the polyisoprene–THF solutions. The methyl red diffusion measurements were carried out to high polyisoprene concentrations but not to the bulk state. The reason for not quoting the D_d value at the bulk state is that an anomalous feature was observed for the diffraction signals which could not be traced to a simple cause, therefore rendering it impossible to extract a reliable diffusion coefficient. (Explanations for this anomaly have recently been put forth.[34]) However, with methyl yellow in bulk polyisoprene, the diffraction signals were normal. Since there was a possibility that the diffusion coefficients

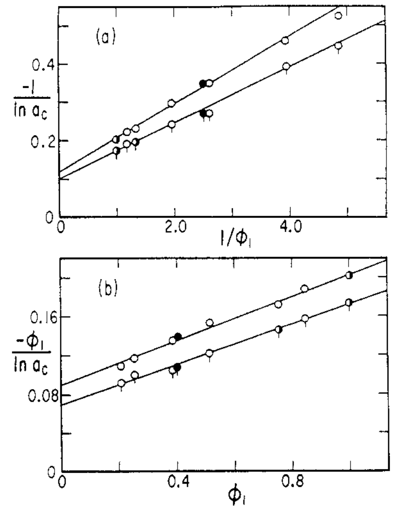

Figure 5. (a) Plot of $-1/\ln a_c$ vs $1/\phi_1$ for methyl red (○) and methyl yellow (●) diffusion in polystyrene–THF according to eq 4. (b) Plot of $-\phi_1/\ln a_c$ vs ϕ_1 for the same system. This figure is analogous to Figure 3, with $\phi_1^r = 0$. The free volume parameters determined from these plots are listed in the text (eq 6 and 7). The two data sets in each figure are for $T = 25$ °C (no pip) and 45 °C (pips down). The half-filled points indicate that both the MR and MY data overlap.

of methyl red (MR) and methyl yellow (MY) were not identical for a given polymer concentration, measurements were carried out for MY at a few overlapping concentrations. Finding that the ratio of D_{MY}/D_{MR} remains constant ($\sim$1.15), the D_{MR} value in bulk polyisoprene was estimated from this ratio and the corresponding D_{MY} value.

Because the dye diffusion measurements were performed over a complete polymer concentration range, these data are subjected to the test of Fujita's free volume theory in order to examine possible departure. Parts a and b of Figure 5 represent tests of the free volume theory, as given by eq 4 and 5, respectively. For these plots, the reference volume fraction is taken to be the bulk polymer, that is, $\phi_1^r = 0$. Thus the quantity $\phi_1 - \phi_1^r$ in eq 4 and 5 is replaced by ϕ_1. Unlike in the polystyrene–THF system, these plots show excellent fits over the *entire* concentration range. The open circles represent methyl red data, the filled ones are for methyl yellow, and the half-filled circles indicate where the two overlap. From the slope and intercept of each plot, the free volume parameters $f(T,0)$ and $\beta(T)$ are determined. From Figure 5a, we have

$$\begin{aligned} f(25\ ^\circ\text{C},0) = f_2(25\ ^\circ\text{C}) &= 0.100 \pm 0.005 \\ f_1(25\ ^\circ\text{C}) &= 0.235 \pm 0.020 \\ \beta(25\ ^\circ\text{C}) &= 0.135 \pm 0.015 \\ f(45\ ^\circ\text{C},0) = f_2(45\ ^\circ\text{C}) &= 0.115 \pm 0.005 \\ f_1(45\ ^\circ\text{C}) &= 0.270 \pm 0.025 \\ \beta(45\ ^\circ\text{C}) &= 0.155 \pm 0.020 \end{aligned} \tag{6}$$

The values of $f_1(T)$ have been determined according to

$$\beta(\text{T}) = f_1(T) - f_2(T,0)$$

from eq 3a. Likewise, the plots in Figure 5b give rise to

$$\begin{aligned} f_2(25\ ^\circ\text{C}) &= 0.105 \pm 0.005 \\ f_1(25\ ^\circ\text{C}) &= 0.255 \pm 0.015 \\ \beta(25\ ^\circ\text{C}) &= 0.150 \pm 0.015 \\ f_2(45\ ^\circ\text{C}) &= 0.110 \pm 0.005 \\ f_1(45\ ^\circ\text{C}) &= 0.240 \pm 0.020 \\ \beta(45\ ^\circ\text{C}) &= 0.130 \pm 0.015 \end{aligned} \tag{7}$$

To calculate f_{2g}, the fractional free volume for polyisoprene at its T_g, we use[2]

$$f_{2g} = f_2 + \alpha_2(T - T_g) \tag{8}$$

with $T_g = 200$ K and $\alpha_2 = 4.8 \times 10^{-4}$ K^{-1} (for Hevea rubber[2]). From the dye diffusion measurements, our results give $f_{2g} = 0.055$, which is about a factor of 2 greater than the value of 0.026 for f_{2g}/B reported by Ferry.[2] The 100% deviation may arise from the difference between Hevea rubber and synthetic polyisoprene free volume thermal expansion coefficients. A difference is seen in the next section.

3. Comparison with the Free Volume Theory of Vrentas and Duda. In a pair of publications by Vrentas and Duda,[14,15] a reexamination of the free volume theory was presented which resulted in a more generalized relationship between small molecule diffusion and the free volume in a solution. The purpose here of using the Vrentas–Duda extension is not only to examine its ability to interpret the dye diffusion behavior vis-à-vis that of the simpler and more approximate Fujita free volume treatment but also to extract dynamical information about the polymer system.

For a binary solution (polymer and solvent only) at a given T, the concentration dependence of the solvent diffusion coefficient D_1 at solvent weight fraction w_1 may be written as[14,16]

$$\ln\left[\frac{D_1(T,w_1)}{D_1(T,0)}\right] = g\frac{\hat{V}_1^*}{\hat{V}_2^\circ}w_1\left[\frac{(M_1/M_j)\Gamma_1 - f_2}{f_2^2 + f_2w_1(\Gamma_1 - f_2)}\right] \tag{9}$$

where M_1 and M_j are the molecular weight of the solvent and polymer segment undergoing a translation or "jump", respectively, $f_i = \hat{V}_{FHi}/\hat{V}_i^\circ$ ($i = 1, 2$; solvent, polymer), and $\Gamma_1 = (\hat{V}_1^\circ/\hat{V}_2^\circ)f_1$. The parameter $\hat{V}_i^\circ$ is the specific occupied volume of component i, $\hat{V}_1^*$ is the specific critical hole free volume required for translation of a solvent molecule, and g is an overlap factor. Lastly, $\hat{V}_{FHi}$ is the specific hole free volume of component i.

Examination of eq 9 reveals that information regarding the mass ratio of solvent and polymer jumping unit and the specific volume ratio of solvent and polymer are important for the determination of a solvent diffusion coefficient. However, for probe molecule diffusion experiments, such as the case here where we examine dye diffusion, we have essentially a ternary system (dye, solvent, and polymer). Equation 9 can be rederived for a ternary system to yield[16]

$$\ln\left[\frac{D_i(T,w_{\text{dil}})}{D_i(T,0)}\right] = g\frac{\hat{V}_i^*}{\hat{V}_2^\circ}\left[\frac{(M_i/M_j)\Gamma_{\text{dil}} - \sigma f_2}{f_2^2 + f_2w_{\text{dil}}(\Gamma_{\text{dil}} - f_2)}\right] \tag{10}$$

where subscript i is either 1 (solvent) or d (dye) and

$$\begin{aligned} \Gamma_{\text{dil}} &= (\hat{V}_1^\circ f_1 w_1 + \hat{V}_d^\circ f_d w_d)/\hat{V}_2^\circ w_{\text{dil}} \\ \sigma &= (M_i/w_{\text{dil}})(w_1/M_1 + w_d/M_d) \\ w_{\text{dil}} &= w_1 + w_d \end{aligned} \tag{11}$$

Since $w_d \simeq 0$ for our experiments, eq 10 may be reduced to give[20]

$$\ln\left[\frac{D_d(T,w_1)}{D_d(T,0)}\right] = \frac{\hat{V}_d^* M_d}{\hat{V}_1^* M_1}\ln\left[\frac{D_1(T,w_1)}{D_1(T,0)}\right] \tag{12}$$

It is evident from eq 9 and 12 that from our dye diffusion measurements we may obtain information about free volume parameters and mass ratios for the polymer–solvent binary system.

In addition to the concentration dependence on diffusion, the Vrentas–Duda theory can be extended to en-

Table IV
Estimated and Fitted Parameters for the Vrentas–Duda Free Volume Theory for Methyl Red Diffusion in Polystyrene–Tetrahydrofuran Solutions

estimated			fitted[b]		
parameter	value	eq	parameter	value	eq
$(\hat{V}_d{}^*/\hat{V}_1{}^*)(\mathrm{M_d/M_1})$	0.9	12	B_d	0.55	13
V_i^0	$1/\rho_i$	9, 18, 19	$D_1(T_{gs}, \phi_1{}^r)$[a]	2×10^{-13} cm^2/s	13
k	0.01	16	M_1/M_j	1.4	9
α_1	1.14×10^{-3} K^{-1}	13, 15, 16	T_{gl}	−130 °C	13, 16
α_2	3.5×10^{-4} K^{-1}	13, 15, 16			
T_{g2}	94 °C	13, 16			
f_{g1}	0.025	13, 14			
f_{g2}	0.033	13, 14			
$\phi_1{}^r$	0.36	13			

[a] T_{gs} in this table signifies T_g for the solution at $\phi_1{}^r = 0.36$. [b] Uncertainty in fitted parameters estimated at 15–20%.

compass the temperature dependence as well. The temperature dependence of density and viscosity data for pure solvent and pure polymer may be used to evaluate the free volume contributions of each. For example, the parameters that are obtained from the temperature dependence of the polymer viscosity data are simply related to WLF constants for the polymer; a similar situation prevails with the solvent viscosity data.[15,21,35] It is important to note, however, that the Vrentas–Duda theory is better applicable when appropriate viscosity data are in the vicinity of the temperatures used in the diffusion experiments.[21] Since our polystyrene–THF solutions are well below T_g for the polymer, it is obvious that we cannot use the suggested temperature analysis scheme. We therefore adopt a procedure similar to one which was shown to fit adequately the solvent diffusion data of von Meerwall and Van Antwerp.[18] This analysis scheme combines the Vrentas–Duda equations for the concentration dependence, i.e., eq 9 and 12, with the one given below which is essentially WLF in format, recast such that it employs the glass transition temperature of the solution, T_{gs}

$$\ln\left[\frac{D_1(T,\phi_1)T_{gs}}{D_1(T_{gs},\phi_1)T}\right] = \frac{[B_d/f_2(T_{gs},\phi_1)][T - T_{gs}]}{[f_s(T_{gs},\phi_1)/\alpha_s] + (T - T_{gs})} \qquad (13)$$

where $f_s(T_{gs},\phi_1)$ is the fractional free volume of the solution at volume fraction ϕ_1 and at T_{gs} and is determined from

$$f_s = f_1\phi_1 + f_2(1 - \phi_1) \qquad (14)$$

Similarly, α_s is for the solution and is assumed to be related to α_1 and α_2, the thermal expansion coefficients for the fractional free volume of solvent and polymer, respectively, by[18]

$$\alpha_s = \alpha_2 + (\alpha_1 - \alpha_2)\phi_1 \qquad (15)$$

(We note that eq 13 differs from eq 8 of ref 18 by a factor of T_{gs}/T on the left-hand side, which is necessary for the temperature corrections of D_1 at their respective temperatures.)

As the final step before proceeding to the dye diffusion analysis, we list an empirical expression for T_{gs} of a polymer solution as a function of volume fraction and T_g of each component, originally supplied by Braun and Kovacs[36]

$$T_{gs}(\phi_1) = \frac{\phi_1\alpha_1T_{g1} + (1 - \phi_1)\alpha_2T_{g2} + k\phi_1(1 - \phi_1)}{\phi_1\alpha_1 + (1 - \phi_1)\alpha_2} \qquad (16)$$

Although this equation was determined for a polystyrene–toluene solution, it is assumed to be valid for PS–THF solutions as well.

We now proceed to the evaluation of as many parameters as possible before the actual data fitting; they are listed in Table IV under the heading "estimated". Upon examination of eq 12, it is evident that the dye diffusion coefficient is related to that of the diluent, which is the quantity predicted by the Vrentas–Duda theory, eq 9, by a factor of $(\hat{V}_d{}^*M_d)/(\hat{V}_1M_1) = 0.9$. Since this value is determined from experimental data as opposed to an empirical formula, it will be used in the remaining analysis.

Next we need the temperature dependences of the specific volumes $\hat{V}_i{}^o$ in eq 9, which may be determined from density data; that is

$$\hat{V}_i{}^o = 1/\rho_i \qquad (17)$$

The temperature dependences of both the solvent and polymer densities have been reported in the literature. For THF,[31] we have

$$\rho_1(T) = 0.8892 + 0.001\,01(293 - T)\ (\mathrm{g/cm^3}) \qquad (18)$$

and for polystyrene,[32] the density is

$$\rho_2(T) = 1/(0.767 + 5.5 \times 10^{-4}\ T + 643 \times 10^{-4}\ T/M)\ (\mathrm{g/cm^3}) \qquad (19)$$

Turning to eq 16, the constant k accounts for the slight interaction between the free volumes of each component upon mixing and is assumed to be equal to 0.01. The remaining parameters in eq 16 are as follows: $\alpha_1 = 1.14 \times 10^{-3}$ K^{-1},[31] $\alpha_2 = 3.5 \times 10^{-4}$ K^{-1},[36] and $T_{g2} = 94$ °C.[36,37] T_{gl} will be determined from the best fit of the methyl red diffusion data to the Vrentas–Duda equations. (As a parenthetical remark, T_g for a diffusant 1,3-dimethyladamantane in polybutadiene solutions is obtained in the same manner.[18]) The temperature dependence for the remaining parameters, the fractional free volumes of THF and polystyrene, f_1 and f_2, respectively, are obtained by rearranging eq 8, with $f_{g1} = 0.025$ and $f_{g2} = 0.033$.[2] The expansion coefficients α_1 and α_2 necessary for eq 8 are taken to be the same as those used for evaluating T_{gs} (eq 16).

There remain four quantities that are unspecified: B_d and $D_1(T_{gs},\phi_1)$ of eq 13, T_{gl} from eq 16, and M_1/M_j of eq 9. A value for B_d was obtained by taking the ratio of the dye diffusion coefficients at 5 and 45 °C, with $\phi_1 = 0.360$ ($w_1 = 0.318$), the highest polymer concentration, using eq 13. Upon evaluation of B_d, any experimentally determined value of $D_d(T,0.36)$ could be reinserted to calculate $D_d(T_{gs},0.36)$. Next, M_1/M_j is obtained as follows. It is deduced from D_d at the concentration extremes (i.e., $w_1 = 1.0$ and $w_1 = 0.318$) at 5 °C. It is noted that in determining M_1/M_j from eq 13, $g\hat{V}_1{}^*/\hat{V}_2{}^o = B_d$[16,17] and the relationship between dye and solvent diffusion coefficients (eq 12) is used. The final step is to introduce into eq 16 estimates for T_{gl}, the glass transition temperature for THF, until the experimental value of $D_d(45\ °\mathrm{C}, w_1 = 1)$ was reproduced. Having thus determined the four parameters by fitting the

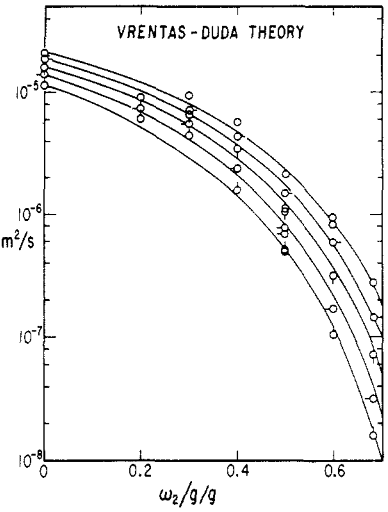

Figure 6. Plot of ln D_d against polymer weight fraction w_2 for methyl red in polystyrene–THF at five different temperatures. The symbols in the figure are the same as for Figure 3. The solid curves represent the best fit of the data and to the Vrentas–Duda free volume theory, accounting for both c and T dependences.

data, we claim that they cannot be classified as arbitrarily adjustable. Table IV lists the final results for the fitted parameters as well as the initially estimated quantities. Because we did not proceed with multivariate fitting, at best we estimate the uncertainties to be about 15–20%.

We now present the concentration dependence results. In Figure 6 is plotted the experimentally determined methyl red diffusion coefficients D_d against the polymer weight fraction w_2 for the polystyrene–THF solutions. The solid curves in Figure 6 are the result of the fitting procedure described above. Despite some serious assumptions introduced, the Vrentas–Duda theory provides a fair representation of the diffusion data for the entire concentration range. It may be argued that with so many parameters, one should have no trouble with curve fitting. On the other hand, if each parameter is examined for what it represents physically, the theory has a sound physical basis. For example, T_{g1} (for THF) was determined as −130 °C, which can be compared to the value for toluene, reported to be between −167 and −159 °C.[38,39] The value of $B_d = 0.55$ is also acceptable, but it does change the Fujita free volume parameters in Table II. The ratio $M_1/M_j = 1.4$ may be interpreted that roughly it takes two THF molecules to replace a translating monomer of polystyrene in the oversimplified picture of diffusion.

It appears that the Vrentas–Duda extension of the free volume theory will "fit" the dye diffusion data, although the quality of the fit over a simpler treatment of Fujita appears to have not improved substantially. In previous reports by von Meerwall and co-workers,[16,18] the Vrentas–Duda treatment was shown to give a notable improvement over the Fujita free volume theory. In the aforementioned citations, all of the polymers were above their glass transition temperatures under the experimental conditions reported, and we note that the Vrentas–Duda theory was derived for the regime above T_g of all components. Thus, there is reason to suspect that the value of the thermal expansion coefficient for polystyrene, α_2, and the corresponding expression relating it to the polymer fraction free volume (eq 8) are not applicable for temperatures below T_{g2}. There is also the question of how many parameters one can use before the theory becomes too burdensome to be of significant use.

The dye diffusion data in polyisoprene solutions should provide a better test if we are to ascribe lack of improvement to T_g effects for the PS solutions. The T_g of polyisoprene is reported as −68 °C,[40] well below the temperatures used here. Evaluation of the theoretical expressions was as stated before for the case of polystyrene–THF solutions with the exception listed below. The reference concentration in eq 13 was taken as the pure polymer; since only two temperatures are reported, it was not necessary to use eq 16. The value $\hat{V}_d{}^*M_d/\hat{V}_1{}^*M_1 = 0.9$ is the same as before because this quantity only considers the dye/solvent system. The fractional free volume of pure polyisoprene at T_{g2} was taken as 0.026.[2]

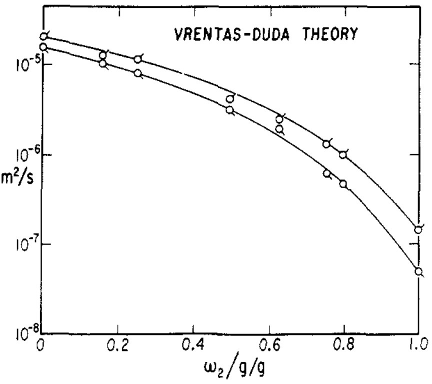

Figure 7. Plot of ln D_d against w_2 for methyl red diffusion in polyisoprene–THF system. The solid curves represent the best fit of the data to the Vrentas–Duda free volume theory. The symbols are for T = 45 °C (ơ) and T = 25 °C (ọ).

Table V
Fitted Parameters for the Vrentas–Duda Free Volume Theory for Dye Diffusion in Polyisoprene–Tetrahydrofuran Solutions[a]

$D_1(-68\ °C,1)$,[b] cm^2/s	B_d	M_1/M_j	α_2, K^{-1}
1.44×10^{-16}	0.73	1.16	6.6×10^{-4}

[a] Uncertainties are estimated at 15–20%. [b] Dye diffusion coefficient in bulk polyisoprene at T_{g2} = −68 °C, determined from data fitting.

The result of the curve-fitting procedure is presented in Figure 7. Values of the fitted parameters are collected in Table V. There is an additional entry in the table, α_2, which is not listed as a fitted variable in Table IV. Originally, the first attempt to use $\alpha_2 = 4.8 \times 10^{-4}\ K^{-1}$,[2] which is the expansion coefficient for natural rubber, produced a much more linear concentration dependence with respect to w_2 than the solid curve in Figure 7. In order to arrive at the solid curve to duplicate the concavity of the experimental data, α_2 was gradually changed to $6.6 \times 10^{-4}\ K^{-1}$ to give rise to the fit trend. T_{g1} for THF also had to be changed from −130 (determined by fitting the PS–THF results) to −145 °C to produce the final curves. The ratio $M_1/M_j = 1.16$ is approximately equal to the ratio of solvent and monomer unit molecular weights 1.06; we are tempted to interpret this as an indication that the polymer jumping unit is no more than a single monomer unit, or at least roughly equal masses of the two species may be involved.

Summary

Despite some serious assumptions invoked in choosing the various Vrentas–Duda free volume parameters and the misgivings one might have concerning the number of these parameters, it appears that the model has a substantial merit in imparting insight into the dynamics of a polymer system by examining small molecule diffusion. However, the quality of data fits vis-à-vis the Fujita free volume method is somewhat inconclusive from our experiments. Both theories seem to account for the *concentration* dependences of dye diffusion in polyisoprene–THF solutions with moderate success, yet marginally hold for the polystyrene–THF solutions.

Finally, we were unable to test the Vrentas–Dudas model against that of Fujita with respect to the *temperature* dependence of probe molecule diffusion. However, the models of Vrentas and Duda and of Fujita have used expressions which can be related to the WLF method; therefore we examined the temperature dependence with the WLF format. Parenthetically we should add that the simpler Fujita free volume theory coupled with the WLF equation was shown to suffice[24] in accounting for the temperature dependence of polymer self-diffusion coefficients through the monomer friction coefficient ζ_0.

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Registry No. PS, 9003-53-6; PI, 9003-31-0; methyl red, 493-52-7; methyl yellow, 60-11-7.

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On the Cross-Linking Mechanism of Benzophenone-Containing Polyimides

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ABSTRACT: A group of fully imidized polyimides containing benzophenone as well as alkyl-substituted biphenylmethane in the main chain were prepared. In these materials cross-links are formed on exposure to UV radiation through hydrogen abstraction by triplet benzophenone from the alkyl groups acting as hydrogen donors and subsequent coupling of the radicals so formed. The involvement of radicals in the process is supported by the ESR spectra of the films under irradiation. The quantum yield of cross-linking is $\phi = 0.027$, and less than half of the benzophenone units in the solid are reactive. Even at the reactive sites the reaction probability is a mere 3%. The low quantum efficiency in the solid state of a reaction which in solution proceeds with high yield is attributed to a specific energy dissipation process, which operates at the reactive site in the solid state, namely, reversible hydrogen exchange between benzophenone and the hydrogen donor.

The increasing importance of polyimides in the manufacture of integrated circuits has motivated numerous investigations on the development of photoimageable polyimides. The objective here is to produce polymers that can be exposed and processed like a photoresist but which are sufficiently stable, thermally and mechanically, to be