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Relationship between Chain Length and the Concentration Dependence of Polymer and Oligomer Self-Diffusion in Solution

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ABSTRACT: A complex relationship between chain length and the concentration dependence of polymer self-diffusion, $D_p(c)/D_p(0)$, is revealed from analysis of polystyrene (PS) and oligostyrene self-diffusion in solution. Pulsed-field-gradient NMR measurements of PS self-diffusion in styrene and toluene were compared with literature results for PS self-diffusion in benzene, tetrahydrafuran, toluene, and carbon tetrachloride. An empirical relationship was used to correlate $D_p(c)/D_p(0)$ to the concentration dependence of solvent self-diffusion, $D_s(c)/D_s(0)$: $D_p(c)/D_p(0) = [D_s(c)/D_s(0)]^{\beta}$ where β quantifies the relationship between chain length and the concentration dependence of D_p. (This power law, with a chain-length-independent β, may be justified from Vrentas−Duda free volume theory.) Accounting for differences in the free volume contribution of the solvent species, β values obtained in the five solvents can be normalized to a single solvent, styrene, revealing universality in the relationship between chain length and the concentration dependence of PS self-diffusion in solution. A strong dependence of β on chain length was observed for oligomers, increasing from 1.0 for styrene (1-unit chain) to ~2.3 for a 20-unit chain. For unentangled PS, β is nearly chain-length-independent, ranging from 2.5 to 3.4 for chain lengths of ~55 to ~1000 units. For longer chains, there is a sharp rise in β with increasing chain length, consistent with entanglement effects. The β values for PS correspond with those from analysis of limited poly(methyl methacrylate) self-diffusion data, supporting the notion that polymers with similar glass transitions and critical chain lengths for entanglement should exhibit similar impact of chain length on the concentration dependence of D_p in solution.

Introduction

For a given polymer/solvent system, it is well-known that polymer self-diffusion in solution depends on temperature, polymer concentration, and chain length.[1−4] For unentangled solutions, the polymer self-diffusion coefficient is inversely related to the direct frictional drag experienced by the chain segments. The overall frictional drag is expressed as a product of chain length (number of units per chain) and a monomeric friction coefficient.[5] As noted by Tirrell,[1] the monomeric friction coefficient is a strong function of concentration due to the dependence of free volume on concentration. Tirrell[1] also noted that for bulk polymer the monomeric friction coefficient is a function of chain length at low chain lengths and is independent of chain length above a critical value. A related impact of chain length on the concentration dependence of polymer and oligomer self-diffusion may be expected in polymer solutions, although little experimental study has been focused on this issue. An investigation of this chain-length dependence in polystyrene (PS) solutions is the subject of the present study.

The analysis employed in this study takes advantage of earlier work on the concentration dependence of ternary probe diffusion in polymer solutions[6,7] as well as on fits[8,9] of data on the concentration dependence of poly(methyl methacrylate) (PMMA) self-diffusion in toluene solutions. It was observed that quantitative fits of the polymer concentration dependence of probe diffusion could be obtained using the following equation:

$$D_{\mathrm{probe}}(c)/D_{\mathrm{probe}}(0) = [D_s(c)/D_s(0)]^{\xi_{\mathrm{probe,s}}} \tag{1}$$

where D_{probe} (D_s) is the probe (solvent) self-diffusion coefficient at a polymer concentration, c. Equation 1 is a modification of Vrentas−Duda free volume theory[10−13] by Ferguson and von Meerwall,[14] who accounted for differences in the "jumping unit size" of the probe and solvent. This theory is based on work by Cohen and Turnbull[15] that stated that molecular diffusion occurs if "there is a fluctuation in density which opens up a hole within a cage large enough to permit a considerable displacement of the molecule contained by it. Such a displacement gives rise to diffusive motion only if another molecule jumps into the hole before the first can return to the original position." In this modification, $\xi_{\mathrm{probe,s}}$ is the ratio of the jumping unit volume of the small-molecule probe to that of the solvent. For small, rigid molecules believed to diffuse as one unit, the jumping unit volume is often taken to be molecular volume. However, for many small-molecule probes, $\xi_{\mathrm{probe,s}}$ scales with a factor of ~$^1/_8$ of molecular volume, indicating that, in this picture of diffusion, jumping unit sizes may be substantially smaller than molecular volume.[6,7]

With regard to the concentration dependence of PMMA self-diffusion in toluene solutions, O'Neil et al.[8,9] fit limited data by Faldi et al.[16] to a form similar to that of eq 1:

$$D_p(c)/D_p(0) = [D_s(c)/D_s(0)]^{\beta} \tag{2}$$

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where D_p denotes the polymer self-diffusion coefficient and the value of the exponent β denotes the strength of the concentration dependence of polymer self-diffusion relative to that of solvent self-diffusion.[17] O'Neil et al.[8,9] found that β values of 3.0−3.5 provided reasonable fits to data for unentangled PMMA self-diffusion relative to toluene self-diffusion while a β value of 9.5−10.0 provided a good fit to data for 330K PMMA in toluene, supposedly an entangled polymer solution. O'Neil et al. did not ascribe fundamental meaning[18] to β but instead used β as an empirical parameter expressing the strength of the concentration dependence of self-diffusion of polymer to that of solvent. By extension, they obtained the polymer concentration dependence of an averaged termination rate parameter and used this to model autoacceleration in methyl methacrylate free radical polymerization. (The termination rate is controlled by polymer radical self-diffusion and thus is proportional to the sum of the self-diffusion coefficients of the polymer/oligomer radicals involved in termination.) They also noted that the β value could be assumed to take on values of 1.0 and higher, with values for oligomer diffusion between those of monomer diffusion ($\beta = 1.0$) and unentangled polymer diffusion ($\beta \sim 3.0$−3.5), and supported this with analysis of data on PS oligomer self-diffusion in benzene by Piton et al.[19]

With few exceptions,[19−23] little study has focused on the impact of chain length on the concentration dependence of polymer and oligomer self-diffusion in unentangled polymer solutions. This may be due to several reasons. First, with the exception of PS and polyethylene, nearly monodisperse standards of polymers *and* oligomers either do not exist or are very expensive. Second, many polymers such as PS and PMMA present difficulties in obtaining well-homogenized samples at high concentration in solution,[6,24−29] making sample preparation problematic, particularly in comparison to studies of polymer self-diffusion in the melt state. Finally, the relevance of the reptation picture to self-diffusion has more commonly been the focus of research[2,30−34] investigating self-diffusion and related dynamics in polymer solutions, with unentangled polymer and oligomer solutions receiving less attention as a result.

However, significant reasons remain for developing a comprehensive picture of the impact of chain length on the concentration dependence of polymer and oligomer self-diffusion in solution. Beyond obtaining an understanding of how chain length affects the frictional drag of a polymer or oligomer in solution, there is also the need to obtain data for undertaking a critical study of short−long termination[35−41] and its relationship to the strength of autoacceleration (also called the gel effect or the Trommsdorff effect[8,9,42−50]) in free radical polymerization. The concept of short−long termination indicates that the average termination rate parameter, k_t, is controlled by diffusion of the shortest radical species present in significant number, meaning that termination is generally controlled by a radical considerably shorter than one-half the chain length of the dead polymer being synthesized. Support is accumulating for short−long termination, including the fact that lower β values are needed to fit conversion−time data with a reduction in the molecular weight (MW) of PMMA produced by free radical polymerization.[8,9,50]

Using both results obtained in this study via pulsed field gradient (PFG)-NMR and data from the literature,[19,23,51−53] the present study investigates the impact of chain length on the concentration dependence of unentangled polymer and oligomer self-diffusion on PS solutions near room temperature. This study reveals a complex relationship between chain length and the concentration dependence of polymer and oligomer self-diffusion in polymer solutions. Using Vrentas−Duda free volume theory[10−13] in order to normalize data from several solvent systems to a single solvent, styrene, good agreement is obtained among the normalized data. A strong chain-length dependence of the value of β is seen for oligomeric PS, with a transition to a chain-length-independent or nearly chain-length-independent value of β occurring at 20−55 repeat units. At much higher chain lengths, $> \sim 1000$ repeat units, the impact of entanglements is evident even in solutions supposedly too dilute to be entangled, with β values increasing strongly with increasing chain length. Generalization of these results to other polymers is also discussed.

Experimental Section

Binary PS/solvent samples were prepared by adding PS and solvent into 5 mm NMR tubes. Narrow MW distribution PS standards with peak MWs of 1300 g/mol (1.3K), 5800 g/mol (5.8K), 13 000 g/mol (13.0K), 16 700 g/mol (16.7K), and 152 000 g/mol (152K) and with $M_w/M_n < 1.07$ were used as received. All PS samples were from Pressure Chemical, except for the 16.7K sample (Toyo Soda). For one set of experiments, 165 500 g/mol deuterated PS (Polymer Source, Inc.) was used as background polymer. Styrene and HPLC-grade toluene were used as received (Sigma-Aldrich). To minimize autopolymerization as the samples homogenized (from 1 to 14 days depending on polymer MW and concentration),[24] PS/styrene samples containing inhibitor were refrigerated at 4 °C.

Polymer and solvent self-diffusion coefficients were measured by PFG-NMR using an Inova 400 NMR spectrometer with a proton frequency of 400 MHz and a static magnetic field strength of 9.4 T. (A L700 Highland PFG magnet driver can deliver up to 20 A to the probe and create magnetic field gradients up to 10.6 T/m.) Self-diffusion coefficients were measured using a modified version of the Stejskal−Tanner PSGE pulse sequence.[54] The gradient pulse strength was calibrated by measuring water diffusion at 25 °C and comparing with the literature value of 2.30×10^{-5} cm^2/s.[55] The calibration was verified by measuring the diffusion coefficient of methanol or toluene. Diffusion measurements were taken using at least 10 steps in the strength of the applied gradient while maintaining all delay times in the pulse sequence constant. The self-diffusion coefficient was calculated from the slope of a linear plot of the natural logarithm of peak intensity as a function the square of the applied gradient. In the case of neat styrene, four separable chemical shift peaks exhibited the same attenuation of intensity with increasing gradient; therefore, taking integral measurements of the peak areas allowed for four independent measurements of the styrene diffusion coefficient, determined to be 1.91×10^{-5} cm^2/s at 25 °C. Since PS/solvent samples have some overlapping chemical shift peaks, only nonoverlapping peaks were used to measure the solvent diffusion coefficient. For slowly diffusing polymer species, the magnitudes of the applied gradient were set sufficiently high in order to make negligible the chemical shift peaks from the solvent. Each experiment was maintained at 25 °C by passing controlled-temperature air through the NMR probe.

Results and Discussion

A. Diffusion in PS/Styrene Solutions. To employ eq 2 in evaluating the impact of chain length on the concentration dependence of polymer self-diffusion in PS/styrene solutions, it is necessary to have information regarding the concentration dependence of styrene self-diffusion in PS/styrene solutions. Although diffusion

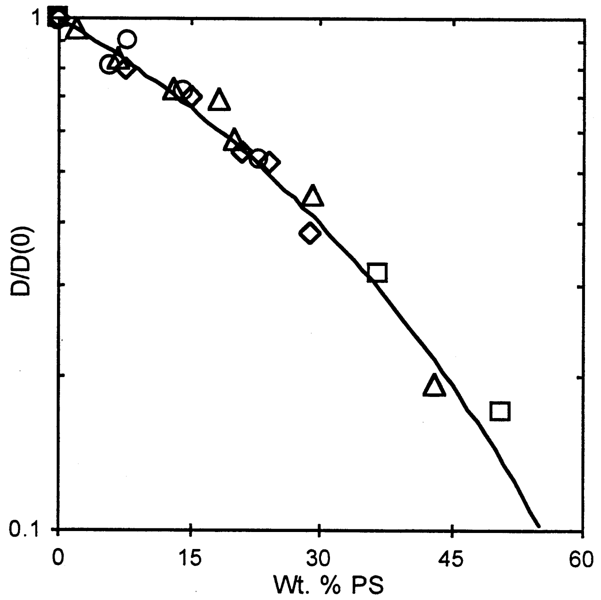

Figure 1. Styrene diffusion in PS/styrene solutions containing 1.3K PS (○), 5.8K PS (□), 16.7K PS (◇), or 152K PS (△) measured at 25 °C. The solid line indicates the Vrentas−Duda free volume fit of styrene diffusion in PS with $\xi_{s,p} = 0.78$.

Table 1. Polystyrene and Styrene Self-Diffusion Coefficients Measured by PFG-NMR at 25 °C

solution	wt %	D_s (cm^2/s)	D_p (cm^2/s)
1.3K PS/styrene	0.0	1.89E−5[a]	
	0.0	1.92E−5	
	5.8	1.54E−5	3.77E−6
	7.8	1.73E−5	3.99E−6
	14	1.38E−5	1.82E−6
	23	1.01E−5	1.36E−6
	3.7		3.68E−6
	8.9		3.47E−6
	18		1.88E−6
	23		1.13E−6
5.8K PS/styrene	0.0	1.91E−5	
	37	6.10E−6	
	51	3.45E−6	
	8.7		1.55E−6
	9.0		1.48E−6
	11		1.29E−6
	11		1.18E−6
	19		6.01E−7
	27		3.25E−7
	36		1.78E−7
13K PS/styrene	8.9		5.40E−7
	11		4.16E−7
	15		3.12E−7
	18		2.50E−7
	25		1.45E−7
16.7K PS/styrene	0.0	1.91E−5	
	7.7	1.52E−5	3.86E−7
	15	1.19E−5	2.70E−7
	21	9.33E−6	1.38E−7
	24	8.88E−6	1.23E−7
	29	6.51E−6	6.62E−8
152K PS/styrene	2.0	1.82E−5	1.74E−7
	6.8	1.60E−5	6.87E−8
	13	1.24E−5	3.70E−8
	18	1.18E−5	8.71E−9
	29	7.66E−6	1.47E−9
	43	3.29E−6	
1.3K PS/165K dPS/styrene	5.8		3.19E−6
	10		2.33E−6
	10		2.12E−6
	11		2.22E−6
	12		1.93E−6
	17		1.56E−6
	19		1.28E−6
5.8kPS/toluene	2.5		2.43E−6
	2.7		2.88E−6
	6.6		2.13E−6
	14		1.20E−6
	16		1.05E−6
	20		8.57E−7
	25		6.68E−7
16.7kPS/toluene	1.3		3.17E−6
	6.9		1.30E−6
	20		5.03E−7
	29		3.13E−7

[a] Read as 1.89×10^{-5}.

coefficients for various solvent species in PS have been reported in the literature, there is almost no information on the polymer concentration dependence of styrene diffusion in PS/styrene solutions. Previous investigations,[56−58] motivated by interest in human exposure to styrene from PS food packaging, measured diffusion of trace styrene in bulk PS via inverse gas chromatography or a reaction−diffusion cell. In contrast, the present study obtained data on the concentration dependence of styrene self-diffusion for samples ranging from 0 to 51 wt % PS, covering the range of polymer concentration over which PS self-diffusion coefficients were measured.

The concentration dependence of styrene diffusion in PS/styrene solutions is shown in Figure 1. (See Table 1 for $D_s(c)$ values.) Within error, all styrene self-diffusion data exhibit the same polymer concentration dependence independent of PS MW down to 1.3K. For PS systems investigated in this study with MW ranging from 1.3K to 152K, differences in chain-end free volume are apparently too small to affect the concentration dependence of styrene diffusion. However, at some MW less than 1.3K, the added free volume contribution of chain ends must reduce the concentration dependence of styrene diffusion. (Considering styrene as an imperfect model of a one-repeat-unit oligomer of PS, for the hypothetical system where styrene diffusion is measured in a styrene/one-repeat-unit length PS solution, i.e., styrene, the self-diffusion coefficient must by definition be independent of the concentration of one-repeat-unit length PS.)

Vrentas−Duda free volume theory[10−13] provides the following expression for D_s:

$$\frac{D_s}{D_{01}} = \exp\left[\frac{-\gamma(\omega_1\hat{V}_1{}^* + \omega_2\xi_{s,p}\hat{V}_2{}^*)}{\hat{V}_{FH}}\right] \tag{3}$$

where D_{01} is the solvent self-diffusion coefficient in the absence of polymer, γ is an overlap factor that accounts for the same free volume being available to more than one jumping unit, ω_1 (ω_2) is the weight fraction of solvent (polymer), and $V_1{}^*$ ($V_2{}^*$) is the critical hole free volume for a solvent (polymer) diffusive jump to take place. In the Vrentas−Duda free volume theory, $\xi_{s,p}$ is the molar size ratio of a solvent jumping unit to a polymer jumping unit. Since diffusion was measured below the polymer glass transition temperature, T_g, eq 4 was used to calculate the total hole free volume of the system, V_{FH}, using specific volume data[59] for PS from the literature:

$$\frac{\hat{V}_{FH}}{\gamma} = \omega_1\frac{K_{11}}{\gamma_1}(K_{21} - T_{g1} + T) + \omega_2\frac{\hat{V}_2^0(T_{g2})}{\gamma_2}\left[f_{H2}^G - \int_T^{T_{g2}}(\alpha_2 - \alpha_{c2})\,dT'\right] \tag{4}$$

where K_{11} and K_{21} are solvent free volume parameters

Table 2. Vrentas−Duda Solvent Free Volume Parameters Used To Describe the Concentration Dependence of Solvent Self-Diffusion with Eq 1[a]

parameter	styrene	benzene	THF	CCl_4	toluene
M_1 (g/mol)	104.15	78.11	72.11	153.82	92.14
V_1* (cm^3/g)	0.846	0.901	0.899	0.469	0.917
K_{11}/g_1 (cm^3/(g K))	8.01×10^{-4}	1.07×10^{-3}	7.53×10^{-4}	4.31×10^{-4}	1.45×10^{-3}
$K_{21} - T_{g1}$ (K)	−41.19	−73.79	10.45	−38.00	−86.32
$\xi_{s,p}$	0.782	0.869	0.840	0.626	0.852

[a] All solvent Vrentas−Duda free volume parameters except $\xi_{s,p}$, which is fit to experimental data, are either from ref 9 for styrene or from ref 13 for all other solvents. Vrentas−Duda free volume parameters for PS: $V_2^0(T_{g2}) = 0.972$ cm^3/g (calculated from data in ref 59), $V_2^* = 0.850$ cm^3/g (from ref 13). For toluene diffusion in PMMA, the Vrentas−Duda free volume parameters listed in the above table for toluene diffusion in PS were used with the exception of $\xi_{s,p}$. An $\xi_{s,p}$ value of 1.07 was used for toluene diffusion in PMMA. Vrentas−Duda free volume parameters for PMMA: $V_2^0(T_{g2}) = 0.855$ cm^3/g (calculated from data in ref 94), $V_2^* = 0.788$ cm^3/g (from ref 13).

and T_{g1} (T_{g2}) is the glass transition temperature of the solvent (polymer). $V_2^0(T_{g2})$ is the specific equilibrium volume of the pure polymer at T_g, while f_{H2}^G is the fractional hole free volume of the polymer at T_g. The parameter α_2 is the thermal expansion coefficient of the equilibrium liquid polymer while α_{c2} is the thermal expansion coefficient for the sum of the specific occupied volume and the specific interstitial free volume of the polymer. The difference between the two thermal expansion coefficients describes the temperature dependence of the polymer hole free volume. This approach for addressing the issue of the solution temperature being below the polymer T_g was proposed by Vrentas.[60] The solid curve in Figure 1 is the fit of eq 3 to the experimentally determined D_s values, where all parameters except for $\xi_{s,p}$ were obtained from free volume theory predictions for styrene/PS. (See Table 2.) To achieve the fitted concentration dependence of styrene diffusion indicated in Figure 1, the $\xi_{s,p}$ parameter was adjusted to a value of 0.78, allowing for eq 3 to best describe the data. This is outside the range of predicted values of 0.61−0.68 calculated using procedures and constants in the free volume literature.[13,61,62]

For many measurements of the styrene self-diffusion coefficient, a corresponding measurement of the PS self-diffusion coefficient was also made, as no literature data were found for the concentration dependence of PS self-diffusion in PS/styrene solutions. Figure 2 shows the polymer concentration dependence for the self-diffusion of various MW PS samples in PS/styrene solutions. (See Table 1 for $D_p(c)$ values.) The three intermediate MW samples, 5.8K, 13K, and 16.7K, exhibit the same dependence. This indicates that the critical chain length necessary to achieve a concentration dependence of PS self-diffusion in styrene solution that is independent of chain length or nearly so is less than ~55 units, the chain length of 5.8K PS. The concentration dependence of unentangled PS diffusion is quantified using eq 2, which relates the concentration dependence of polymer diffusion to that of styrene diffusion. The three samples exhibit a concentration dependence of diffusion that is best described by a β exponent of 2.6.

In contrast, the 1.3K PS exhibits a weaker concentration dependence of self-diffusion, described by a β exponent of 1.9−2.3. Since the PFG-NMR samples used for the initial study of 1.3K PS diffusion only contained 1300 g/mol PS, there was concern that the polymer concentration dependence measured for this system might be reduced relative to the case where high-MW background polymer was used, in conjunction with 1.3K MW PS probe, to make the polymer solutions. (Although the styrene diffusion data in Figure 1 exhibit a concentration dependence that is independent of the background PS MW down to 1.3K, one might expect that the additional chain-end free volume present for the 1.3K PS system could alter the observed concentration dependence of PS diffusion since polymer self-diffusion is more dependent on free volume.) Thus, 1.3K PS self-diffusion was also measured in solutions containing styrene and 165 500 g/mol deuterated PS (dPS). This dPS was added to provide a high-MW background polymer in solution; its deuterated nature caused it to be “invisible” during ^{1}H PFG-NMR measurement. Figure 2 shows that the concentration dependence of 1.3K PS diffusion with the high-MW dPS is similar to that obtained in solutions in which all of the PS was 1.3K; thus, for diffusion studies 1.3K is a sufficient MW for background PS. With this issue resolved, the weaker concentration dependence of 1.3K PS self-diffusion relative to that of 5.8K PS diffusion indicates that the critical MW at which the concentration dependence of unentangled PS self-diffusion becomes (nearly) chain-length-independent is greater than 1.3K (13 repeat units).

The 152K PS exhibits a much stronger concentration dependence of self-diffusion than the other PS samples, yielding a β value of 5.7, suggesting that entanglements are affecting the concentration dependence of PS diffusion. Using a standard relationship[63] to predict the onset of entanglements in solution ($\rho M_{c,bulk} \approx c^{**} M_{c,soln}$) and recognizing that the critical MW needed for a bulk PS sample to exhibit entanglement effects, $M_{c,bulk}$, is ~31K,[64] 152K PS/styrene solutions are not expected to be entangled at concentrations below 20 wt % polymer. However, the 152K PS/styrene results reveal a much stronger concentration dependence of D_p than in the lower MW PS solutions, even at concentrations well below the classical, theoretical limit for entanglements.

One might expect this 152K PS/styrene system to exhibit a transition from a weaker concentration dependence at low concentration, as exhibited by the lower MW samples, to a stronger concentration dependence as the polymer in solution becomes entangled with increasing polymer concentration. The transition from unentangled to entangled polymer self-diffusion behavior in solution with increasing polymer concentration is not well understood, and as noted by Lodge et al.,[2] it is difficult to predict. A possible explanation of the strong concentration dependence exhibited by the lower polymer concentration samples in the 152K PS/styrene system is that transient entanglement couplings reduce the rate of diffusion for this system. The transient entanglement mechanism was proposed to describe the separation of DNA using capillary electrophoresis with dilute polymer solutions.[65] In the transient entanglement-coupling model, the DNA mobility is reduced because a charged DNA molecule drags uncharged polymer though the dilute polymer solution inside the

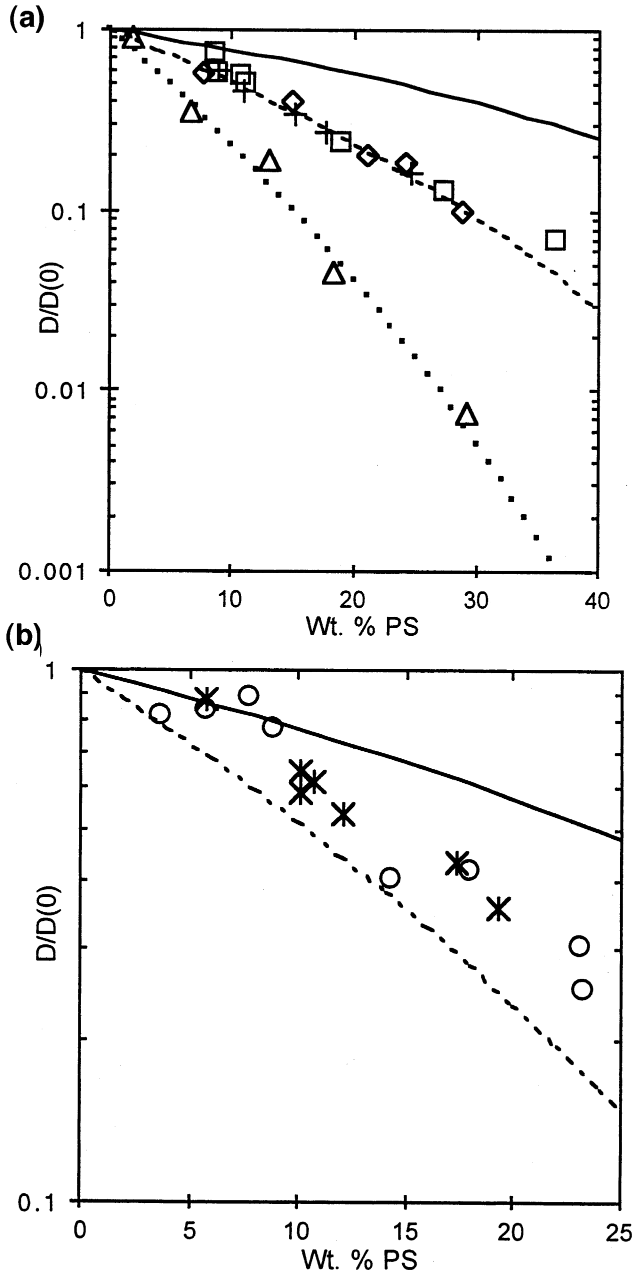

Figure 2. PS diffusion in PS/styrene solutions measured at 25 °C. (a) Diffusion of 5.8K PS (□), of 13K PS (+), of 16.7K PS (◇), and of 152K PS (△). The solid line indicates the Vrentas–Duda free volume fit of styrene diffusion in PS/styrene solutions. The dashed line indicates the power-law fit of low-molecular-weight PS diffusion with $\beta \approx 2.6$. The dotted line indicates the power-law fit of 152K PS diffusion with $\beta \approx 5.7$. (b) 1.3K PS diffusion in 1.3K PS/styrene solutions (○) and in 1.3K PS/165.5K dPS/styrene solutions (∗) measured at 25 °C via PFG-NMR. The solid line indicates the Vrentas–Duda free volume fit of styrene diffusion in PS/styrene solutions. The dashed line indicates the power-law fit of low-molecular-weight PS diffusion with $\beta \approx 2.6$. For the samples containing 165.5K dPS, the wt % of 1.3K PS in the solution varies, but on average the solutions contains approximately 6 wt % of 1.3K PS.

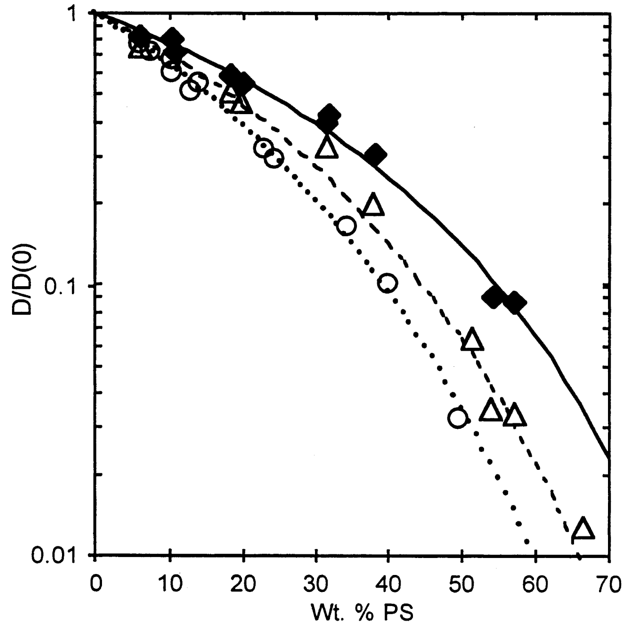

Figure 3. Diffusion in the PS/benzene system at 25 °C: benzene diffusion (◆) and PS dimer (△) and PS pentamer (○) diffusion in PS/benzene solutions reported by Piton et al.[19] The solid line indicates the Vrentas–Duda free volume fit of benzene diffusion in PS/benzene solutions with $\xi_{s,p} = 0.87$. The dashed line indicates the power-law fit of PS dimer diffusion with $\beta \approx 1.3$. The dotted line indicates the power-law fit of PS pentamer diffusion with $\beta \approx 1.7$.

electrophoresis capillary. Extending this picture to describe the mobility of PS chains in solution, the reduction in the rate of diffusion for the 152K PS at concentrations below 20 wt % may be rationalized by the presence of temporary polymer chain entanglements formed in solution. Other literature data show effects similar to those observed in the PS/styrene solutions examined here. Data for PMMA self-diffusion in toluene[16] indicate a similar strong concentration dependence for samples too dilute to be entangled. These results, along with comparisons of PMMA diffusion and PS diffusion, are discussed in part E.

B. Diffusion in Other PS/Solvent Systems. Literature data related to the concentration dependences of PS and oligostyrene self-diffusion in various solvents are available.[19,23,51–53,66–76] A subset of these data was used in the analysis of the polymer concentration dependence of D_p.[77] In some cases, incomplete information was given on experimental conditions, e.g., temperature. In other cases, data were taken over a too narrow concentration range, too few points were taken for analysis to be done with confidence, or the fits relied heavily on the accuracy of a single point. In yet other cases, studies focused on diffusion behavior in entangled PS solutions, using very high-MW PS samples that are not the subject of the present study. While literature data were available on PS self-diffusion in cyclohexane solutions, the absence of cyclohexane self-diffusion data in such solutions prevented the direct method of analysis undertaken in the present study. Finally, while literature data are also available on PS self-diffusion in ternary solutions with poly(vinyl methyl ether), which is miscible with PS, and *o*-fluorotoluene[77–81] or toluene,[82] they were not included in the present analysis which focuses on binary solutions.

Given below is analysis of the concentration dependences of D_p for various chain lengths of PS in four solvents. Most data are from the literature although PFG-NMR measurements of D_p of PS in toluene solutions were made and analyzed as part of the current study.

B.1. Diffusion in PS/Benzene Solutions. Literature data for PS dimer and pentamer diffusion and for benzene diffusion in PS/benzene solutions are given in Figure 3. The oligostyrene and benzene self-diffusion data by Piton et al.,[19] measured at 25 °C, demonstrate that the concentration dependence of D_p for oligostyrene is strongly chain-length-dependent.

To compare concentration dependences, the approach used to analyze diffusion in the PS/styrene system was applied here. Vrentas–Duda free volume theory was used with the standard free volume parameters for PS and benzene (Table 2) to describe the concentration dependence of the benzene diffusion data shown in Figure 3. The PS concentration dependence of benzene diffusion was fit with eq 3 by adjusting $\xi_{s,p}$ to a value of 0.87, much higher than the value of 0.48 obtained by Zielinski and Duda[13] using predictive methods rather than analysis of diffusion data. The relative concentration dependence of PS oligomer diffusion was determined by adjusting the value of β in eq 2 to 1.4 and 1.7 to best describe dimer and pentamer diffusion, respectively. The β values quantify the dramatic change in concentration dependence of self-diffusion as molecular size increases from benzene to a two-unit chain and to a five-unit chain. These β values are slightly larger than those reported by O'Neil and Torkelson,[8] who analyzed the same oligostyrene diffusion data, which is due to differences in handling the polymer contribution to the hole free volume. In the current study, the effect of the solution temperature being below the polymer T_g was addressed by use of eq 4; this effect was not considered in ref 8.

In addition to the benzene diffusion data by Piton et al.[19] analyzed here, Kosfeld et al.[83,84] reported data for the PS concentration dependence of benzene diffusion. In the current study, the decision was made to employ the benzene self-diffusion data by Piton et al. as the basis for analyzing the oligomer diffusion data since the same group measured both solvent and oligomer data. Thus, any systematic error would be expected to cancel after comparing the concentration dependences of solvent and oligomer diffusion. However, it should be noted that the benzene diffusion data from Kosfeld and Zumkley[84] exhibit a slightly weaker concentration dependence than the Piton[19] data. The greater concentration dependence of the Piton benzene diffusion data requires a slightly larger $\xi_{s,p}$ parameter for fitting the data to eq 3 and yields smaller β parameters when analyzing the dimer and pentamer diffusion data with eq 2. Piton et al.[19] note that the concentration dependence of their benzene data agrees with diffusion results interpolated to 25 °C from data reported in the earlier study of benzene diffusion in PS by Kosfeld and Goffloo.[83] The Kosfeld and Zumkley data[84] were not analyzed by Piton et al.[19] nor was a comparison to earlier results by Kosfeld and Goffloo[83] for benzene diffusion made by Kosfeld and Zumkley.[84]

B.2. Diffusion in PS/Tetrahydrofuran Solutions. Data by Wesson et al.[51] for 46K and 105K PS self-diffusion in tetrahydrofuran (THF) were analyzed. Figure 4 shows that the data sets, measured at room temperature ($T \approx 22$ °C), yield the same concentration dependence of D_p for samples ranging from ~10 wt % PS to ~45 wt % PS, indicating that both samples are exhibiting the long chain limit to the concentration dependence of unentangled PS diffusion in THF.

The concentration dependence of THF self-diffusion measured at 25 °C by Gisser et al.[85] is also illustrated in Figure 4 along with the free volume fit using the standard free volume parameters listed for PS and THF in Table 2. The fit of the PS concentration dependence of THF self-diffusion to eq 3 yielded a value of $\xi_{s,p} = 0.84$. Analysis via eq 2 of the concentration dependence of both sets of PS self-diffusion data relative to that of THF yielded a β value of 3.2. Analysis of other data (not shown in Figure 4) by Wesson et al.[51] of 36K PS and 130K PS self-diffusion in THF solutions yielded β values of 2.7 and 4.2, respectively. The increase in β value for the 130K PS sample relative to the other samples may be due to entanglement effects.

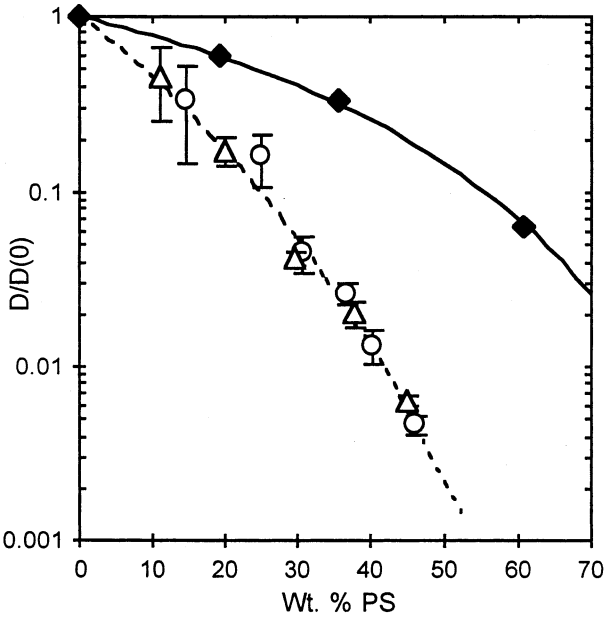

Figure 4. Diffusion in the PS/THF system near 25 °C: THF diffusion (◆) in PS/THF solutions measured at 25 °C by Gisser et al.;[85] 46K PS diffusion (△) and 105K PS diffusion (○) in PS/THF solutions data measured at 22 °C by Wesson et al.[51] The solid line indicates the Vrentas–Duda free volume fit of THF diffusion in PS/THF solutions at 25 °C with $\xi_{s,p} = 0.84$. The dashed line indicates the power-law fit of PS diffusion with $\beta \approx 3.2$.

B.3. Diffusion in PS/Toluene Solutions. Figure 5 compares data obtained in the current study of 5.8K PS and 16.7K PS self-diffusion in toluene to data from Fleischer[53,86] of 125K PS self-diffusion in toluene. Also shown are data by Pickup and Blum[87] for toluene self-diffusion in PS/toluene solutions measured at 25 °C. The concentration dependence of the toluene self-diffusion data is fit by eq 3 using the standard free volume parameters listed in Table 2 for toluene and PS, yielding a value of $\xi_{s,p}$ of 0.85. The concentration dependence of the 5.8K PS and 16.7K PS is best fit with a β value of 2.6 (see Table 1 for $D_p(c)$ values), while the 125K PS data are best fit with a β value of 4.8. The higher β value in the 125K PS sample suggests that it is subject to entanglement effects, similar to the 152K PS/styrene and 130K PS/THF systems.

It should be noted that, besides the data by Pickup and Blum[87] for the self-diffusion of toluene in PS solutions at 25 °C, other measurements of the PS concentration dependence of toluene self-diffusion at 25 °C have been reported by Piton et al.[19] and Waggoner et al.[88] The data set by Pickup and Blum[87] was used as it is the most complete. However, all three sets of toluene self-diffusion data exhibit PS concentration dependences that are in close agreement.

B.4. Diffusion in PS/Carbon Tetrachloride Solutions. Data by Pinder[23] of oligostyrene self-diffusion in carbon tetrachloride (CCl_4) at 30 °C were analyzed to

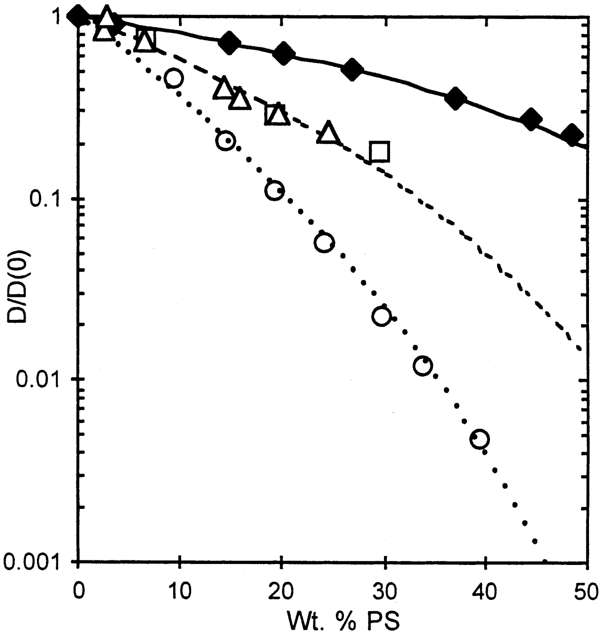

Figure 5. Diffusion in the PS/toluene system near 25 °C: toluene diffusion (◆) in PS/toluene solutions data measured at 25 °C by Pickup and Blum;[87] 5.8K PS diffusion (△) and 16.7K PS diffusion (□) measured at 25 °C in PS/toluene solutions; 125K PS diffusion measured at 22 °C (○) in PS/toluene solutions, reported by Fleischer.[53] The solid line indicates the Vrentas−Duda free volume fit of toluene diffusion in PS at 25 °C with $\xi_{s,p} = 0.85$. The dashed line indicates the power-law fit of 5.8K PS and 16.7K PS diffusion with $\beta \approx 2.6$. The dotted line indicates the power-law fit of 125K PS diffusion with $\beta \approx 4.8$.

investigate the MW at which the chain-length dependence of the concentration dependence of D_p reaches its asymptotic limit. Pinder studied ternary solutions of PS oligomer, CCl_4, and deuterated polystyrene, the latter used as background polymer. The polymer concentration dependences of 0.58K, 1.20K, and 2.47K PS diffusion shown in Figure 6a are different. Thus, the asymptotic concentration dependence of unentangled PS self-diffusion is achieved for PS chains larger than 1.20K MW (12 repeat units).

Also shown in Figure 6a is the expectation for the PS concentration dependence for CCl_4 diffusion in PS/CCl_4 solutions at 30 °C. This prediction is made using eq 3 with a $\xi_{s,p} = 0.63$. This $\xi_{s,p}$ value for CCl_4 diffusion in PS/CCl_4 solutions was calculated using data for styrene probe diffusion in dPS/CCl_4/styrene solutions from Pinder[23] and shown in Figure 6b. The concentration dependence of styrene probe diffusion was fit using eq 5 by adjusting the value of $\xi_{\rm probe,s}$ (probe = styrene and s = CCl_4) and using the standard free volume parameters in Table 2.

$$\frac{D_{\rm probe}(c)}{D_{\rm probe}(0)} = \exp\left[-\frac{\gamma(\omega_{\rm s}\xi_{\rm probe,s}\hat{V}_{\rm s}^* + \omega_{\rm p}\xi_{\rm probe,p}\hat{V}_{\rm p}^*)}{\hat{V}_{\rm FH}}\right] \quad (5)$$

Since $\xi_{\rm probe,p}$ describes the jumping unit size ratio of styrene to PS, the value of $\xi_{s,p}$ obtained from fitting data in Figure 1 for styrene diffusion in the styrene/PS system ($\xi_{s,p} = 0.78$) was used for $\xi_{\rm probe,p}$ in eq 5. The value for $\xi_{\rm probe,s}$ (1.25) from the fit to data in Figure 6b agrees with the value of the jumping unit size ratio of styrene to CCl_4 (1.22) predicted from standard free volume parameters in Table 1. The value of $\xi_{s,p}$ (s = CCl_4 and p = PS) was in turn determined by eq 6:

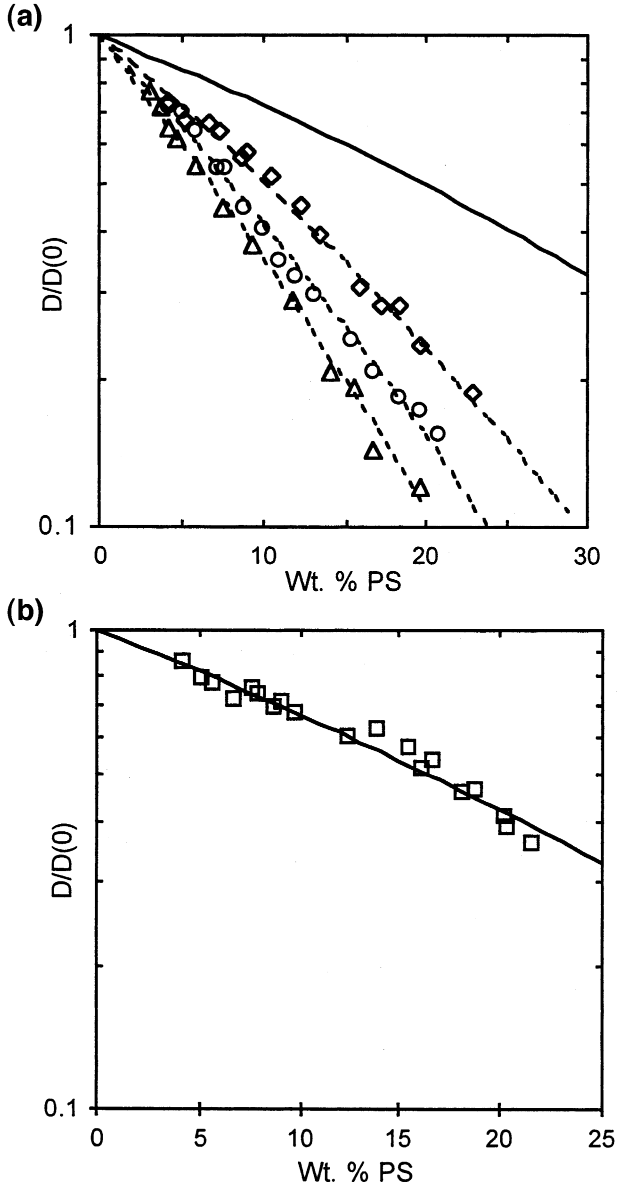

Figure 6. Diffusion in PS/carbon tetrachloride solutions measured at 30 °C reported by Pinder.[23] (a) Diffusion of PS of molecular weight 580 g/mol (◇), 1200 g/mol (○), and 2470 g/mol (△). The dashed lines indicate power-law fits of 580 g/mol, 1200 g/mol, and 2470 g/mol PS diffusion in CCl_4 with $\beta \approx 2.1$, with $\beta \approx 2.7$, and with $\beta \approx 3.2$, respectively. The solid line indicates the Vrentas−Duda free volume prediction of CCl_4 diffusion in PS/CCl_4 solutions with $\xi_{s,p} = 0.63$. (b) Styrene probe diffusion in PS-d_8/CCl_4/styrene solutions measured at 30 °C (□) used to calculate $\xi_{s,p}$ value. The solid line indicates Vrentas−Duda-based free volume prediction for styrene probe diffusion in CCl_4/PS solutions with $\xi_{\rm styrene,CCl_4} = 1.25$.

$$\xi_{\rm CCl_4,PS} = \xi_{\rm styrene,PS}/\xi_{\rm styrene,CCl_4} \quad (6)$$

where $\xi_{\rm styrene,PS} = 0.78$ and $\xi_{\rm styrene,CCl_4} = 1.25$. This ratio yielded the value of 0.63 for $\xi_{\rm CCl_4,PS}$.

Once the PS concentration dependence of CCl_4 self-diffusion was determined, the PS oligomer self-diffusion data in Figure 6a were analyzed yielding β values of 2.1, 2.7, and 3.2 for 0.58K, 1.20K, and 2.47K PS, respectively. Analysis of data by Callaghan and Pinder[52] for 2.00K and 233K PS self-diffusion in CCl_4 yielded β values of 2.8 and 9.3, respectively. The 2.00K PS result agrees with the data in Figure 6 and suggests that the

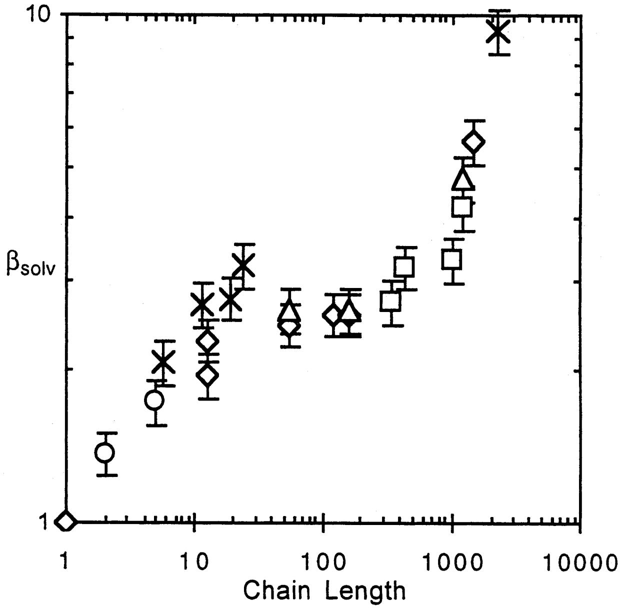

Figure 7. Comparison of the relative concentration dependence of PS diffusion measured near room temperature. Results shown for PS diffusion in styrene (◇), benzene (○), THF (□), CCl_4 (∗), and toluene (△). Error bars represent 10% relative error estimated for fitting concentration dependence of diffusion data with β parameter.

MW at which the concentration dependence of unentangled PS self-diffusion becomes independent or nearly so of MW exceeds 2.00K (19 repeat units). The high β value for 233K PS may be ascribed to entanglement effects.

C. Normalization of PS Self-Diffusion Coefficients to a Single System. Figure 7 summarizes the PS chain-length dependence of the β exponents for the various PS−solvent systems. Most β values follow the same chain-length dependence. While some may find this sufficient to indicate universality of the impact of chain length on the concentration dependence of PS self-diffusion, it must be noted that somewhat higher β values at a given chain length are obtained for PS/CCl_4 solutions. Related results have been observed in the concentration dependence of probe self-diffusion in PS/CCl_4 solutions relative to PS solutions made with other solvents, e.g., toluene.[89] This section elaborates on this difference and provides a method to normalize data to a single solvent system in order to facilitate comparison of PS self-diffusion data.

The increased relative concentration dependence of PS self-diffusion in CCl_4 relative to other solvents may be rationalized by considering differences in the $\xi_{s,p}$ values for various PS−solvent systems: $\xi_{s,p} = 0.63$ for CCl_4 while $\xi_{s,p}$ ranges from 0.78 to 0.87 for other solvents. In the Vrentas−Duda free volume theory,[10−13] $\xi_{s,p}$ is the ratio of the size of a solvent jumping unit to the size of a polymer jumping unit. Vrentas−Duda theory also results in a relationship between the concentration dependences of polymer self-diffusion and solvent self-diffusion of the type given by eq 2 but with β taking the form $1/\xi_{s,p}$; i.e., Vrentas−Duda free volume theory indicates that the concentration dependence of D_p is proportional to the concentration dependence of D_s raised to a power quantified by the ratio of the polymer jumping unit size to the solvent jumping unit size. In fact, the values of β obtained in this study of unentangled, nonoligomeric PS self-diffusion are a factor of 2.0−2.7 greater than the reciprocal of the values of $\xi_{s,p}$ obtained from fits to solvent diffusion data. Further discussion on this difference is given in section D.

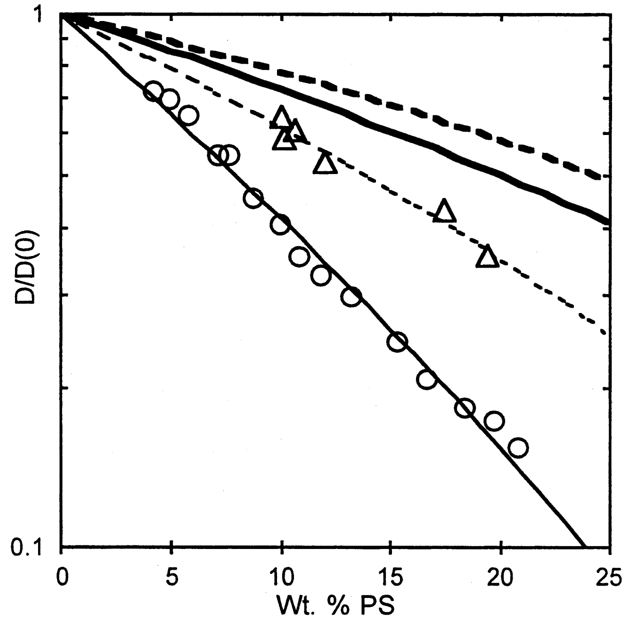

Figure 8. Comparison of the concentration dependence of PS diffusion in PS/styrene and PS/CCl_4 solutions: 1.3K PS diffusion in PS/styrene solutions measured at 25 °C (△); 1.2K PS diffusion in PS/CCl_4 solutions measured by Pinder[23] at 30 °C (○). The thick dashed line indicates the Vrentas−Duda free volume fit of styrene diffusion in PS/styrene solutions, while the thick solid line indicates the Vrentas−Duda free volume prediction of CCl_4 diffusion in PS/CCl_4 solutions. The thin dashed line indicates the power-law fit of 1.3K PS diffusion in PS/styrene solutions with $\beta_{sty} \approx 1.9$. The thin solid line indicates the power-law fit of 1.2K PS diffusion in PS/CCl_4 solutions with $\beta_{CCl_4} \approx 2.7$.

Equation 6 indicates that it is possible to shift β values between solvent systems, e.g., solvent A and solvent B, by employing a factor of $\xi_{A,B}$. This suggests that the ratio of β exponents for PS/solvent B to PS/solvent A may be given by the following:

$$\beta_B/\beta_A = \xi_{A,B} = \xi_{A,p}/\xi_{B,p} \tag{7}$$

The following example illustrates how the relative concentration dependence of solvent diffusion can be scaled from one solvent to another. Figure 8 shows data for 1.3K PS self-diffusion in styrene obtained here and for 1.2K PS diffusion in CCl_4 measured by Pinder.[23] Also indicated are the concentration dependences of styrene and CCl_4 self-diffusion. Figure 8 indicates that the self-diffusion of 1.2K PS in CCl_4 has a stronger relative concentration dependence as compared to the 1.3K PS diffusion in styrene. The difference in relative concentration dependence is not expected on the basis of the similar polymer chain lengths but instead is the result of the measurements being made in different solvents. To compare these results by normalizing to a single solvent system, the relative concentration dependence of one set of data must be translated into the other solvent. The β value measured for self-diffusion of 1.2K PS in CCl_4, β_{CCl_4}, may be translated into the styrene reference system to give the appropriate value of β_{sty}:

$$\beta_{sty} = \beta_{CCl_4}\xi_{CCl_4,sty} = \beta_{CCl_4}\xi_{CCl_4,PS}/\xi_{sty,PS} = (2.7)(0.63)/0.78 = 2.1_8 \tag{8}$$

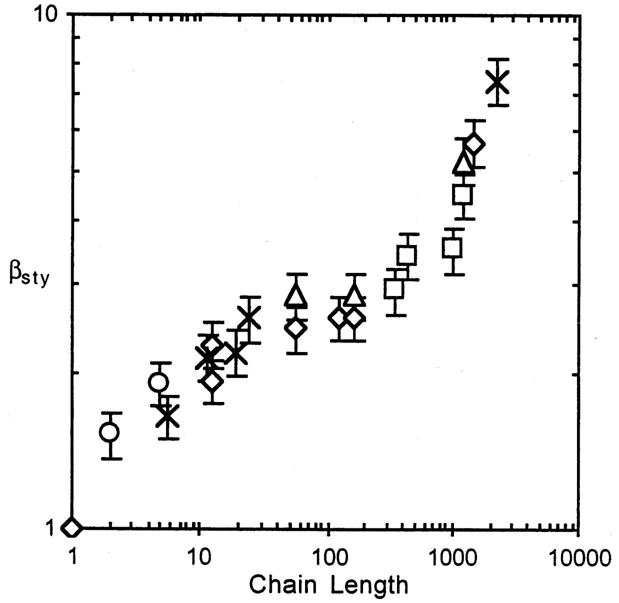

Figure 9. Comparison of the adjusted relative concentration dependence of PS diffusion measured near room temperature. All β values shown as if measured in styrene. Results shown for PS diffusion in styrene (◇), in benzene (○), in THF (□), in CCl_4 (*), and in toluene (△). Error bars represent 10% relative error estimated for fitting concentration dependence of diffusion data with β parameter.

The resulting β_{sty} value for 1.2K PS diffusion obtained by translating the result from CCl_4 solution to styrene solution is close to the β_{sty} value (1.9) for 1.3K PS self-diffusion in styrene.

To compare diffusion data among solvent systems, eq 7 was used to translate β_{solv} values to the styrene system, β_{sty}. Styrene was chosen as the reference because the largest fraction of PS diffusion data analyzed for this study was measured in styrene solutions. In addition, the choice of styrene as the reference was motivated by the desire to apply the results from this study to a critical investigation[41] of short−long termination[35−40] and its relationship to the strength of autoacceleration during free radical polymerization, in which radical chains terminate in a diffusion-controlled manner in polymer/monomer solutions.

Figure 9 summarizes the relative concentration dependence of all PS diffusion data after the data were translated into the styrene reference system. (Values for β_{solv} and β_{sty}, given in Figures 7 and 9, respectively, are also listed in Table 3.) Figure 9 shows that all of the relative concentration dependence results exhibit the same complex chain-length dependence. For short chain lengths (1 to ~20 repeat units), β has a strong chain-length dependence, while for medium chain lengths (~55−1000 repeat units), β is nearly chain-length-independent with values between 2.5 and 3.4. When chain length exceeds 1000−1200 units, as in the case of the 152K PS/styrene system as well as with other PS self-diffusion data,[51,52] β increases dramatically with chain length due to entanglement effects. Such an increase in the poly(vinyl methyl ether) concentration dependence of PS self-diffusion with increasing PS chain length was also observed by Wheeler et al.[79] for PS probe of 179K MW and greater in their ternary solution study.

The relative concentration dependence results given in Figure 9 show that a transition between the chain-length-dependent and the chain-length-independent regimes occurs between ~20 and ~55 repeat units. That is, the chain length at which the concentration dependence of unentangled PS diffusion becomes nearly chain-length-independent lies within this range. This range agrees with measurements by Horinaka et al.[90] for the chain-length dependence of chain-end relaxation times for PS in solution. In that study, the mean relaxation time of end-labeled PS chains in benzene at 20 °C was measured as a function of PS chain length via fluorescence depolarization. The mean relaxation time exhibited a strong chain-length dependence below a critical chain length, while above the critical chain length the relaxation time became chain-length-independent, with the critical chain length being ~20 units. Their description of how chain length affects local polymer motion is the same as the theoretical picture that may be used to describe the asymptotic chain-length dependence of the concentration dependence of polymer self-diffusion. In both pictures, asymptotic behavior occurs above a critical chain length because the addition of an extra subunit does not affect the concentration dependence of chain mobility.

D. β Being Larger Than $1/\xi_{s,p}$. In all cases β values, either for systems measured here by PFG-NMR or for literature data analyzed via eq 2, exceed the values of $1/\xi_{s,p}$, where $\xi_{s,p}$ is obtained by fitting the PS concentration dependence of experimentally determined solvent self-diffusion data. Assuming the absolute validity of all assumptions in the Vrentas−Duda free volume theory, $1/\xi_{s,p}$ is equal to $\xi_{p,s}$ which should be identical to the value of β determined in this study. We postulate that the discrepancy in the values of β and $1/\xi_{s,p}$ may be related to differences in segmental mobility and polymer self-diffusion. The polymer concentration dependence of polymer segmental mobility in solution is weaker than that of D_p and instead appears to be closer to that of solvent self-diffusion.[8,91] This difference in concentration dependence has not received significant attention in the literature but suggests that there are substantial differences in the effective frictional drag opposing polymer segmental mobility and polymer self-diffusion. In the context of the Vrentas−Duda free volume theory,[10−13] this means that the jump unit size for polymer self-diffusion is significantly greater than that of segmental mobility.

In a concentrated solution or gel, all that is required for diffusion of solvent is segmental mobility of the polymer, not polymer self-diffusion. Hence, the $\xi_{s,p}$ value obtained from fits to the polymer concentration dependence of solvent self-diffusion may reflect something close to the ratio of jump unit size of solvent to that of polymer segmental mobility. In contrast, fits to data of the concentration dependence of D_p should reflect the ratio of jump unit sizes for polymer self-diffusion to solvent self-diffusion. Further study of this issue is warranted.

An alternate explanation of the difference in β and $1/\xi_{s,p}$ is that the Vrentas−Duda free volume theory is incorrect. While this study is not designed to test that proposition, studies[6,7] of probe diffusion in polymer solutions found Vrentas−Duda free volume theory to be quantitatively robust. An exception to this was that for many rigid probes $\xi_{probe,s}$ scaled with a factor of $^1/_8$ of the molecular volume, i.e., jump unit size was smaller than molecular volume; Vrentas−Duda free volume theory assumes that jump unit size is the molecular volume for small, rigid probes.

Table 3. Relative Concentration Dependence of PS Self-Diffusion Fit to Experimental and Literature Data and Translated into Styrene Reference System Using Eq 7

PS mol wt (g/mol)	chain length (repeat units)	solvent	temp (°C)	β_{solv}	β_{sty}	reference for diffusion data
104.15	1	styrene	25	1.0	1.0	this study
208	2	benzene	25	1.4	1.5	19
500	5	benzene	25	1.7	1.9	19
580	6	CCl_4	30	2.1	1.7	23
1200	12	CCl_4	30	2.7	2.2	23
1300	13	styrene	25	1.9	1.9	this study
1306	13	styrene	25	2.3	2.3	this study
2000	19	CCl_4	28	2.8	2.2	52
2470	24	CCl_4	30	3.2	2.6	23
5780	56	styrene	25	2.5	2.5	this study
5780	56	toluene	25	2.6	2.9	this study
13000	125	styrene	25	2.6	2.6	this study
16700	160	styrene	25	2.6	2.6	this study
16700	160	toluene	25	2.6	2.9	this study
36000	346	THF	22	2.7	2.9	51
46000	442	THF	22	3.2	3.4	51
105000	1010	THF	22	3.2	3.4	51
125000	1200	toluene	22	4.8	5.2	53
130000	1250	THF	22	4.2	4.5	51
152000	1460	styrene	25	5.7	5.7	this study
233000	2240	CCl_4	28	9.3	7.4	52

E. Comparison to Other Polymer Systems. The relationship between chain length and the concentration dependence of polymer self-diffusion in solution may be a function of various characteristics of the polymer, including T_g and $M_{c,\mathrm{bulk}}$. For example, PS and PMMA have similar T_g's and almost identical values of $M_{c,\mathrm{bulk}}$ (~31K in the case of PS and ~32K in the case of PMMA,[64] which translate to critical chain lengths for entanglements in bulk of 300−320 for the two polymers). This suggests that PS and PMMA systems would exhibit similar impact of chain length on the concentration dependence of D_p. In contrast, there are major differences in the values of T_g and $M_{c,\mathrm{bulk}}$ for PS and polyethylene, suggesting that these systems may exhibit very different relationships between chain length and concentration dependence of D_p.

Support for these expectations is found by comparing the PS self-diffusion data with data for PMMA self-diffusion reported by Faldi et al.[16] and data for polyethylene-based self-diffusion reported by von Meerwall et al.[20,21] The relative concentration dependence of the PMMA self-diffusion data in toluene[16] was analyzed by the same method used for the concentration dependence of PS diffusion. Figure 10 shows the concentration dependence of PMMA diffusion in toluene measured at 20 °C along with power law fits of the concentration dependence of PMMA diffusion using eq 3. As literature data for toluene self-diffusion in PMMA solutions are not available, the concentration dependence of toluene diffusion in PMMA was predicted via eq 1 with free volume parameters listed in Table 2. Figure 10 indicates that the concentration dependence of unentangled 9K PMMA diffusion in a 330K PMMA matrix is best fit by $\beta \approx 4.0$ while unentangled 330K PMMA diffusion in a 9K PMMA matrix is best described by $\beta \approx 3.4$. For entangled 330K PMMA diffusion in a 330K matrix, a higher β value ($\beta \approx 10.7$) is needed to fit the concentration dependence of diffusion. (These β values are slightly larger than those reported in ref 8 for the analysis of the same data. This due to differences in how the polymer contribution to the hole free volume was handled. In the current study, the effect of the solution temperature being below the polymer T_g was addressed with eq 4; this was not done in ref 8.)

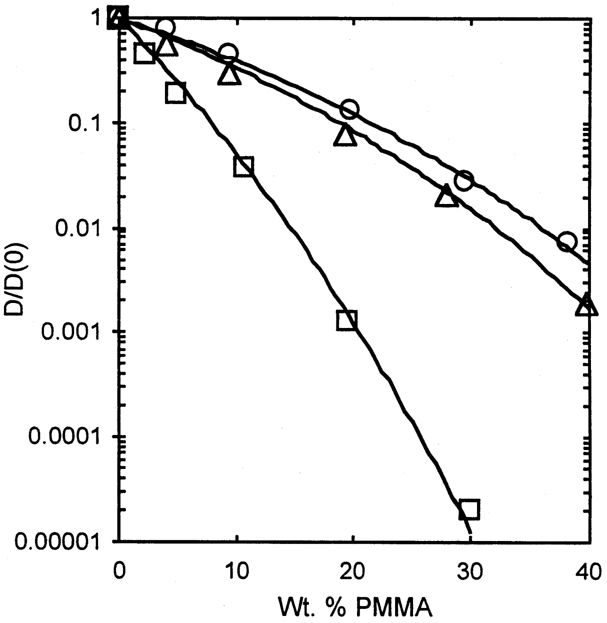

Figure 10. Diffusion of PMMA in PMMA/toluene solutions at 20 °C reported by Faldi et al.[16] Forced Rayleigh scattering results for 9K PMMA diffusion in a 330K PMMA matrix (△), 330K diffusion in a 9K matrix (○), and 330K diffusion in a 330K matrix (□). Power-law fits with $\beta \approx 4.0$ for 9K diffusion in a 330K matrix (△), with $\beta \approx 3.4$ for 330K diffusion in a 9K matrix (○), and with $\beta \approx 10.7$ for 330K diffusion in a 330K matrix (□) indicated.

Also noteworthy in Figure 10 is the difference in the strength of the concentration dependence of 330K PMMA at low concentration in the 330K PMMA matrix relative to the 9K matrix. Below ~10 wt % PMMA, the 330K PMMA matrix system is expected to be unentangled while at all concentrations the 9K PMMA matrix system should be unentangled. This suggests that similar concentration dependences for 330K PMMA self-diffusion should be observed in the two matrix systems at concentrations of ~10 wt % and below. However, as with the 152K PS self-diffusion data in Figure 1, the concentration dependence of 330K PMMA self-diffusion in the 330K PMMA matrix system exhibits a stronger concentration dependence consistent with

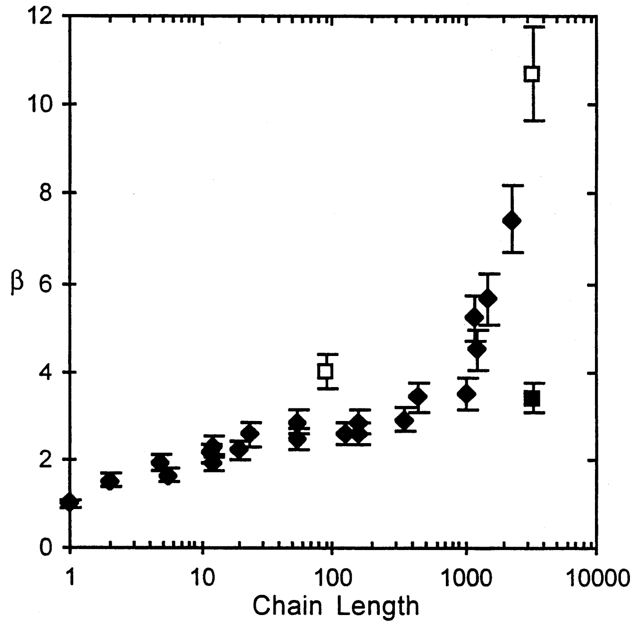

Figure 11. Comparison of the relative concentration dependence of PS diffusion (◆) and PMMA diffusion (□, ■). Open squares represent PMMA diffusion in 330K PMMA matrix, while closed square represents PMMA diffusion in unentangled 9K PMMA matrix. All PS β values shown as if measured in styrene, while the relative concentration dependence of PMMA diffusion compared to the predicted concentration dependence of toluene diffusion. Error bars represent 10% relative error estimated for fitting concentration dependence of diffusion data with β parameter.

entanglement effects even for samples that, by classical arguments, are too dilute to be entangled. In contrast, the 330K PMMA self-diffusion in the 9K PMMA matrix solution exhibits a weaker concentration dependence expected for a system lacking entanglements. This provides further support of the postulate described in section A that transient entanglement coupling in high-MW polymer solutions that are too dilute to be considered entangled may yield an enhanced concentration dependence of polymer self-diffusion. Similar effects of enhanced concentration dependence of high-MW PS self-diffusion at solution concentrations too dilute to be considered entangled are observed upon inspection of PS self-diffusion data in refs 51 and 52.

Figure 11 compares the chain-length dependence of β values for PMMA self-diffusion in toluene with β values for PS self-diffusion normalized to styrene solvent.[92] Figure 11 indicates significant similarity between the limited PMMA and PS results. The β value for the self-diffusion of 330K PMMA in the 9K unentangled PMMA matrix extends the trend of a nearly chain-length-independent β value for nonoligomeric, unentangled PS solutions. The β value for the self-diffusion of 330K PMMA in the 330K PMMA matrix extends the trend of a strongly chain-length-dependent β value seen in the high-MW PS solutions exhibiting entangled behavior. The relative concentration dependence of the self-diffusion of the 9K PMMA probe in 330K PMMA matrix/toluene solutions is somewhat greater than the relative concentration dependence of similar chain-length PS. (This is true regardless of whether the PS self-diffusion is measured in styrene or toluene solutions.) This may be due to experimental uncertainty or the need to estimate the PMMA concentration dependence of toluene self-diffusion with predictive Vrentas−Duda free volume theory. (The data by Faldi et al.[16] show a slightly greater concentration dependence of PMMA self-diffusion in the 9K PMMA probe/330K PMMA system than in the 330K PMMA probe/9K PMMA system, which cannot be rationalized.) Also, there is evidence that, in the bulk, rubbery state, the monomeric friction coefficient of PMMA exceeds that of PS,[64,93] which suggests that the concentration dependence of PMMA self-diffusion in solution could be somewhat greater than that of PS self-diffusion. Nevertheless, the correspondence in the PMMA and PS results is consistent with the notion that polymers with similar T_g's and critical chain lengths for entanglement behavior in bulk should exhibit similar relationships between chain length and the concentration dependence of polymer self-diffusion in solution.

In contrast, PS and polyethylene (PE) systems exhibit dissimilarity regarding the impact of chain length and the concentration dependence of polymer self-diffusion in solution. Much of that dissimilarity in entangled polymer solutions is related to the difference in the critical chain length for entanglement behavior in bulk, ∼62 repeat units in PE[21] vs ∼300 repeat units in PS.[64] However, research by von Meerwall et al.[21] on self-diffusion *n*-hexacontane (a 30-repeat-unit analogue of PE) in *n*-dodecane (a 6-repeat-unit analogue of PE) and vice versa reveals that the concentration dependence of self-diffusion can be modeled, at least semiquantitatively, by use of density−chain length information, accounting quantitatively for effects of chain-end free volume. This means that, except for chain-end free volume effects, there is no inherent difference in frictional drag per repeat unit experienced by oligoethylene chains of 6 and 30 repeat units. This is in contrast to the strong effects of chain length observed here in oligostyrene solutions and in the work by Horinaka et al.[90] that investigated the chain-length dependence of chain-end relaxation times for PS in solution. The possible causes for this difference, including the impact of the difference in T_g values of the two polymers, warrant greater study.

Conclusions

Experimental measurements and literature data of PS, oligostyrene, and solvent self-diffusion in solution have revealed the impact of chain length on the polymer concentration dependence of polymer self-diffusion. A method of analysis has been developed that allows for comparison of the relative concentration dependence of PS and oligostyrene self-diffusion measured in different solvents, using a correlation that can be justified by Vrentas−Duda free volume theory. Normalization of data from five solvent systems to a single solvent system resulted in a universal, complex relationship between PS chain length and the concentration dependence of PS self-diffusion in solution. For oligomeric chains (1 to ∼20 units), the concentration dependence is strongly chain-length-dependent, while for longer, unentangled, PS chains (∼55 to ∼1000 units), the concentration dependence is approximately independent of chain length. Thus, the transition from a chain-length-dependent monomeric friction coefficient to a nearly chain-length-independent monomeric friction coefficient occurs between ∼20 and ∼55 repeat units. This critical chain length agrees with the chain length at which the rate of segmental reorientation of PS chain ends becomes independent of chain length.[90] For PS chains longer than ∼1000 units, the concentration dependence of polymer diffusion increases with chain length, consistent with entanglement effects. Diffusion data for PS chains longer than 1000 units show that a stronger concentration dependence of diffusion is observed even for samples too dilute to be considered entangled, suggesting that transient entanglement coupling may play a role in slowing the polymer self-diffusion in high-MW, dilute polymer solutions.

The impact of chain length on the concentration dependence of PS self-diffusion in solution is in reasonable agreement with limited data for PMMA self-diffusion in solution. This correspondence may be expected since PS and PMMA have similar critical entanglement MW's and T_g's, and it allows for the application of results from this study to the investigation of autoacceleration in free-radical polymerization of methyl methacrylate, including a critical study[41] of the role of short−long termination in the severity of autoacceleration behavior.

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