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# Small-Molecule Probe Diffusion in Polymer Solutions: Studies by Taylor Dispersion and Phosphorescence Quenching

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ABSTRACT: The most comprehensive study to date of the effects of size, shape, and flexibility on the translational diffusion of small probe molecules in polymer solutions has been completed by Taylor dispersion, which directly yields $D_{\text{probe}}$, and phosphorescence quenching, which yields $k_q$, the concentration dependence of which is identical to that of $D_{\text{probe}}$ for appropriate conditions. Diffusion of 16 probes ranging by a factor of 6 in molar volume was investigated using both Taylor dispersion in solutions of up to 400 g/L polystyrene in tetrahydrofuran and phosphorescence quenching in solutions of up to 700 g/L polystyrene in tetrahydrofuran, cyclohexane, and carbon tetrachloride. Results were compared quantitatively to modified Vrentas−Duda free volume theory for ternary solutions to obtain probe jumping unit sizes relative to the solvent, $\xi_{\text{probe,s}}$, which correlate with probe volume. With the exception of 3,4-hexanedione (a highly flexible and small probe), the PS concentration dependencies of $D_{\text{probe}}$ and $k_q$ were approximately equal to or greater than that of solvent ($0.9 \le \xi_{\text{probe,s}} \le 1.75$). The data fell into two types of behavior: when $\xi_{\text{probe,s}}$ was plotted against the ratio of probe to solvent molar volume, $\tilde{V}(0)_{\text{probe}}/\tilde{V}(0)_{\text{s}}$, the vast majority of data fell around a line of slope 0.13, while for two of the probes $\xi_{\text{probe,s}}$ fell near a line of slope unity. Literature data for five probes in several polymer−solvent systems could also be described by these two types of behavior. The former behavior indicates that for most probes the concentration dependence can be described by modified free volume theory, with the understanding that the critical hole free volume for a jump unit for these probes is but a fraction of the probe molar volume. The apparent dichotomy in the probe volume dependence of $\xi_{\text{probe,s}}$ raises the question of whether only two dependencies are possible or whether, by virtue of the probes selected, only these two distinct behaviors are observable. Small effects of flexibility and shape on $D_{\text{probe}}$ for probes with large aspect ratios were also observed and discussed in terms of anisotropic diffusion. A comparison of concentration dependence data with limited temperature dependence data from the literature shows a consistency based on the modified free volume picture. This, along with an understanding of the "bimodal" $\xi_{\text{probe,s}}$ data, indicates that the modified free volume theory for ternary systems forms a reasonably robust picture by which to interpret probe diffusion in polymer solutions.

## Introduction

The diffusion of small molecules in polymer solutions has been a subject of considerable study over several decades.[1−30] Knowledge of diffusion in polymer−solvent systems is of practical concern. For example, the solvent self-diffusion coefficient, $D_s$, is of interest in designing devolatilization equipment that removes residual toxic species such as monomers and solvents from polymer products.[6] The polymer−solvent binary mutual-diffusion coefficient, which may be related to $D_s$[7−9], is also important in polymerization kinetics since the rates of several steps of a free radical chain reaction may be controlled by the diffusion of species in a polymer−monomer or polymer−solvent−monomer mixture.[10−19] Many other applications require knowledge of small-molecule diffusion data, including controlled drug release,[20−22] the drying of coatings,[23] membrane permeation,[24,25] and polymer dissolution.[26]

Despite the importance of small-molecule diffusion in polymer systems, diffusion data are relatively limited,[27] in part because many techniques involved in diffusion measurements are time consuming or complex. Recently, there has been renewed interest in methods that allow for rapid and inexpensive measurement of diffusion coefficients in small-molecule and polymer solutions.[31−36] Furthermore, correlative[7,8,37] and predictive[27,38−41] theories have been developed that allow diffusion coefficients in polymer solutions to be estimated over a wide range of concentrations and temperatures. These theories have included models based on free volume,[7,8,37] modifications of the kinetic rate theories of Eyring[38,42,43] and Enskog,[5,40] tortuosity in a cubic lattice,[5,44] and simpler mixture models based on electric conductivity by Maxwell[45] and Fricke.[46]

In this study, a comprehensive investigation of the effects of size, shape, and flexibility on the translational diffusion of small molecule probes in polymer solutions has been undertaken. Sixteen probes with molar volumes ranging from about 70 to over 400 cm$^3$/mol have been studied in solutions up to 400−700 g/L in polymer content. To accomplish this study, two complementary and relatively little-employed techniques are used to obtain information on diffusion: Taylor dispersion[47−55] and phosphorescence quenching.[56,57]

Taylor dispersion is a rapid and relatively inexpensive technique based on the dispersion of a solute in a liquid undergoing laminar tube flow. The theory was first discussed by Taylor,[47,48] and later by Aris,[49] and was applied by Ouano,[50] who demonstrated that the solute diffusion coefficient in a two-component system can be determined from the mean, $\bar{t}$, and variance, $\sigma^2$, of the solute concentration profile as it exits the tube. The technique was further developed by Pratt and Wakeham[51] and Grushka and Kikta.[52] A number of restrictions and corrections to the analysis relating to sample injection, detector volume, tube uniformity, connecting volumes, and tube coiling can be applied, as reviewed by Alizadeh et al.[53] Recently, we extended the applicability of this technique so as to make measurements

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of tracer diffusion coefficients, $D_{\mathrm{probe}}$, of polymers and small molecules in more concentrated polymer solutions—in some cases in solutions of at least 400 g/L polymer concentration.[54] Values of $D_{\mathrm{probe}}$ as low as $3 \times 10^{-7}$ cm$^2$/s, the smallest value of $D_{\mathrm{probe}}$ measured by Taylor dispersion, were obtained in that study.

Phosphorescence quenching, a useful tool in obtaining information on diffusion-limited interactions in concentrated polymer solutions, is employed to determine the bimolecular quenching rate constant, $k_q$, associated with the reduction of phosphorescence intensity with the addition of quencher, as a function of polymer concentration. Previous studies[19,56,57] have shown that for interactions involving small molecules $k_q$ can be related to the self-diffusion coefficients of the chromophore, $D_c$, and quencher, $D_q$, through the modified Smoluchowski equation:[58]

$$k_q = 4\pi\rho R_T N_A(\mathrm{D}_c + D_q) \tag{1}$$

where $\rho$ is a steric factor taken to be 0.5, $R_T$ is the encounter radius between chromophore and quencher, and $N_A$ is Avogadro's number per millimole. Small molecule−polymer interactions have also been studied using phosphorescence quenching.[59] For interactions involving a small-molecule chromophore and a quencher-labeled polymer of sufficiently high molecular weight, $D_c$ is several orders of magnitude higher than $D_q$. Thus, $k_q \sim D_c = D_{\mathrm{probe}}$ for all polymer concentrations, and $\log(k_q/k_{qo}) = \log(D_{\mathrm{probe}}/D_{\mathrm{probe,o}})$. (The subscript o denotes zero polymer concentration.)

With the comprehensive range of diffusion data obtained from Taylor dispersion and phosphorescence quenching in this study, the Vrentas−Duda[7−9,27] free volume theory, modified by Ferguson and von Meerwall[60] to account for ternary probe diffusion as opposed to solvent self-diffusion, is critically tested. The theory is based on the pioneering work by Cohen and Turnbull,[61] which states 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 its original position." In a solvent−probe−polymer system, the dependence of probe diffusion, $D_{\mathrm{probe}}$, can be related to that of the solvent self-diffusion coefficient, $D_s$:[60]

$$\log\left(\frac{D_{\mathrm{probe}}}{D_{\mathrm{probe,o}}}\right) = \xi_{\mathrm{probe,s}} \log\left(\frac{D_s}{D_{\mathrm{so}}}\right) \tag{2}$$

with

$$\xi_{\mathrm{probe,s}} = \frac{\hat{V}^*_{\mathrm{probe}} M_{\mathrm{jprobe}}}{\hat{V}^*_s M_{\mathrm{js}}} \tag{3}$$

where $\xi_{\mathrm{probe,s}}$ has been interpreted as being the ratio of the "jumping unit size" of the probe to that of the solvent, provided that the weight fraction of probe, $\omega_{\mathrm{probe}}$, is negligible. $\hat{V}^*_{\mathrm{probe}}$ and $\hat{V}^*_s$ are the specific hole free volumes of probe and solvent required for a jump, respectively, and $M_{\mathrm{jprobe}}$ and $M_{\mathrm{js}}$ are the corresponding molecular weights of a jumping unit. For small and rigid solvents believed to diffuse as one unit, $M_{\mathrm{js}}$ is usually taken to equal the molecular weight of the solvent molecule, $M_s$. However, for flexible solvents, $M_{\mathrm{js}}$ may be less than $M_s$.[62,63]

Limited data are available on how $\xi_{\mathrm{probe,s}}$ varies with probe size and shape; as a result, eq 3 has gone largely untested. Yu and Torkelson[56] have shown by phosphorescence quenching that $\xi_{\mathrm{probe,s}}$ is approximately 1 for benzil and anthracene in polystyrene (PS)−toluene solutions. $\xi_{\mathrm{probe,s}}$ has also been found to equal 1 for hexafluorobenzene in PS−tetrahydrofuran (THF).[64] For larger probes, $\xi_{\mathrm{probe,s}}$ can exceed 1. For example, in PS−toluene solutions, Frick et al.[1,2] have reported that $\xi_{\mathrm{probe,s}}$ is about 1.77 for azobenzene and 4.92 for aberchrome 540. Interestingly, Huang et al.[65] measured $\xi_{\mathrm{probe,s}}$ to be about 1.70 for methyl red in PS−toluene, while Landry et al.[66] determined $\xi_{\mathrm{probe,s}}$ to be about 0.9 for methyl red in PS−THF solutions.[67]

Here, we critically evaluate the modified Vrentas−Duda theory, including eqs 2 and 3, through measurement of probe diffusion in PS−THF, PS−$CCl_4$ and PS−cyclohexane solutions. The probes and polymer−solvent systems were chosen to allow for comparison with other studies regarding translational diffusion and rotational dynamics of the same probes[66,68−70] or with solvent or other probe self-diffusion in the same system,[64,66,68,69,71−73] as well as to allow for examining the effects of probe size, shape, and flexibility. These choices also provide for comparison of the applicability of various techniques for measuring translational dynamics of small molecules in polymer solutions, making clear the utility of Taylor dispersion and phosphorescence quenching.

## Experimental Section

**Materials.** Platinum octaethylporphyrin (PtOEP) was obtained from Porphyrin Products, Inc. and used as received. Other probe molecules and spectrophotometric-grade solvents were obtained from Aldrich and used as received. Unless indicated otherwise, the matrix polymer used was atactic PS $\bar{M}_n = 3800$, $\bar{M}_w/\bar{M}_n = 1.05$), synthesized anionically under $N_2$ gas using *sec*-butyllithium as initiator in cyclohexane. The polymer molecular weight was chosen to be low so as to minimize the bulk solution viscosity, facilitating transport through the pump and tubing, and to maintain Newtonian flow for the Taylor dispersion measurements. Terminally anthracene-labeled polystyrene (85K PS-A, $\bar{M}_n = 85\,000$, $\bar{M}_w/\bar{M}_n = 1.05$) was prepared by adding 9-(chloromethyl)anthracene to living polystyryl monoanion prepared by anionic polymerization. Terminally benzil-labeled polystyrene (70K PS-B, $\bar{M}_n = 70\,000$, $\bar{M}_w/\bar{M}_n = 1.20$) was prepared by adding 1,1-diphenylethylene to living polystyryl monoanion, followed by addition of 4-bromomethylbenzil.[74] Polymers were purified by repeated dissolution in dichloromethane and precipitation in methanol and were dried in a vacuum oven for a week prior to use. $\bar{M}_n$ and $\bar{M}_w$ were determined by gel permeation chromatography. The fraction of labeled PS was determined by UV−visible absorbance spectroscopy. PS−THF solution viscosities were measured using Ubbelohde capillary viscometers.

**Taylor Dispersion Measurements.** The apparatus used for Taylor dispersion measurements has been described in detail previously.[54] The dispersion tube consisted of a stainless steel tube (Alltech 3000) of 30.5 m length and internal radius, $a$, of 0.405 ± 0.005 mm. For long dispersion times, and for experimental conditions in which $D$ is on the order of $10^{-6}$ cm$^2$/s, $D$ can be expressed as[75]

$$D = \frac{a^2\bar{t}}{48\sigma^2}\left[1 + \left(1 + \frac{4\sigma^2}{\bar{t}^2}\right)^{1/2}\right] \tag{4}$$

where $a$ is the radius of the dispersion tube and $\bar{t}$ is the mean and $\sigma^2$ is the variance of the solute concentration profile. For Taylor's condition ($\bar{t} \gg a^2/14.44D$) to be met, slow flows in long tubes and/or narrow-bore capillaries are required. The common method is to employ 0.5−1.0 mm i.d. tubing often used for high-pressure liquid chromatography, with a tube length of 10−50 m. Due to physical constraints, the tubing is usually wound into a coil or helix. As eq 4 was derived for straight tubes, and as tube curvature can create secondary flows, use of eq 4 is limited to conditions in which $Dn^2Sc < 20$. Otherwise, values of the measured diffusivity are erroneously high.[76] Here, the Dean number (Dn) is $\kappa^{-0.5}Re$, the Reynolds number (Re) is $2\bar{U}a\rho/\mu$, $\kappa$ is the ratio of the coil radius to the tube radius, $\bar{U}$ is the average velocity, $\rho$ is the solution density, $\mu$ is the solution viscosity, and the Schmidt (Sc) number is $\mu/(\rho D)$. At low flow rates, the effects of curvature on measurements of $D$ are minimal for most liquids. However, for probe diffusion in polymer solutions, the low $D$ value and high Sc number exacerbate the problem.

To minimize deleterious effects of tube curvature on diffusion measurements, the tube was kept uncoiled so as to follow the perimeter of a square, 58 $m^2$ lab space. Except for bends at the corners of the room (6 m length), the trajectory of the tube was primarily straight. The tube temperature was maintained by encasing it in $^3/_8$ in. i.d. polybutylene tubing, through which water at ±0.5 °C of the set temperature was flowing. The flow rate was set at 0.3 mL/min (Re of about 15 and a dispersion time of about 50 min). The injection volume was 20 $\mu$L, about 0.1% of the total volume of the tube. The probe concentration in the injected phase was 2 g/L; with use of a dilute probe concentration, $D$ can be defined as a tracer diffusion coefficient. For studies of ternary probe diffusion in polymer solutions, the mobile phase contained polymer and solvent while the injected phase contained polymer, solvent, and probe.

Chromatograms were measured by UV absorbance at a wavelength where probe absorbed and polymer did not. Detector data were fit by nonlinear regression to

$$Y = A + B \exp\left[-\frac{(t-\bar{t})^2}{2\sigma^2}\right] + \epsilon t \qquad (5)$$

where $Y$ is the detector response, and $A$, $B$, $\bar{t}$, $\sigma^2$, and $\epsilon$ are fitted parameters. Generally, baseline drift was negligible, and $\epsilon = 0$. Using the fitted values of $\bar{t}$ and $\sigma^2$, the diffusion coefficients were calculated from eq 4. $D$ values represent averages of 3–10 experimental trials, with reproducibility within 2%. By minimizing the effects of tube curvature, diffusion coefficients lower than $3 \times 10^{-7}$ $cm^2/s$ could be measured.[54]

**Phosphorescence Quenching Measurements.** The Stern–Volmer analysis of phosphorescence lifetime data, from which the values of $k_q$ were determined, has been described elsewhere in detail.[56] The phosphorescence lifetimes of benzil, benzil end-labeled polystyrene (PS-B), 1-bromonaphthalene, and platinum octaethylporphyrin (PtOEP) were measured by a PTI LS 100 fluorescence spectrophotometer using PTI phosphorescence lifetime software. Sample excitation was achieved by a xenon lamp pulse at a wavelength in the range of 300–425 nm, depending on the phosphorescence probe used, while the phosphorescence decay was observed at the wavelength of maximum emission. Excitation and emission wavelengths ($\lambda_{ex}$ and $\lambda_{em}$) for the various phosphorescence probes are as follows: benzil and PS-B, $\lambda_{ex} = 305$ nm, $\lambda_{em} = 560$ nm; 1-bromonaphthalene, $\lambda_{ex} = 305$ nm, $\lambda_{em} = 538$ nm; 3,4-hexanedione, $\lambda_{ex} = 425$ nm, $\lambda_{em} = 540$ nm; PtOEP, $\lambda_{ex} = 410$ nm, $\lambda_{em} = 644$ nm. After a defined delay time, the phosphorescence emission intensity was measured and integrated for a period of 10 $\mu$s. This delay time was varied from 10 to 500 $\mu$s to produce the phosphorescence emission decay. Emission decays were generally single-exponential and were well characterized by a lifetime, $\tau$, provided that the ratio of donor concentration to quencher concentration was at least 50. The quenching rate constant, $k_q$, was calculated by the Stern–Volmer equation:[58]

$$\frac{1}{\tau} = \frac{1}{\tau_o} + k_q[Q] \qquad (6)$$

where $\tau$ and $\tau_o$ are the phosphorescence lifetimes in the presence and absence of quencher, respectively. [Q] is the concentration of quencher (anthracene, 9,10-diphenylanthracene, PtOEP, or the anthracene moiety of PS-A). Generally, lifetimes were measured for five solutions with different quencher concentrations, and $k_q$ was determined by the method of least-squares.

Solutions contained $10^{-3}$–$10^{-4}$ M phosphorescent dye (e.g., $10^{-3}$ M benzil or $10^{-4}$ M benzil moiety in the solutions containing PS-B), and $10^{-6}$–$10^{-4}$ M quencher. This corresponded to 3–10 g/L labeled PS in addition to sufficient unlabeled PS to form the overall PS concentration; dilute solutions contained no unlabeled PS. Prior to measurement, samples were treated by seven freeze–pump–thaw cycles in order to remove oxygen; samples then remained for several hours at room temperature after which they were shaken to obtain a "relaxed" solution.

## Results and Discussion

**(A) Taylor Dispersion Results. Concentration Dependence.** Previously, we demonstrated[54] that Taylor dispersion was suitable for measuring the diffusion of anthracene, benzil, and methyl red in PS–THF solutions. Here, in order to investigate the effects of size, shape, and flexibility on probe diffusion, we chose to broaden greatly the scope of molecules tested. (See Table 1 and Figure 1.)

As is typically done in a Taylor dispersion experiment, the diffusion coefficient of the probe molecule is determined from a plot of the normalized UV absorbance detector output versus elution time. In Figure 2, the absorbance output is plotted for the diffusion measurements of anthracene, 9,10-diphenylanthracene, and rubrene in 0 and 400 g/L PS in THF at 25 °C. The profiles are Gaussian-shaped and are fit to eq 5 with a correlation coefficient of $r^2 > 0.999$. The figure demonstrates an inverse relationship between $D_{probe}$ and the variance $\sigma^2$ expected of Taylor dispersion. At 0 g/L concentration, $D_{probe}$ decreases with increasing size of the probe molecule. It is also apparent that for a given probe molecule we see a decrease in $D_{probe}$ with polymer concentration; Table 1 illustrates that, as the PS concentration increases from 0 to 400 g/L, the value of $D_{probe}$ for anthracene is reduced 82% from its value in pure THF ($1.58 \times 10^{-5}$ $cm^2/s$).[54] This demonstrates the sensitivity of Taylor dispersion to the range of diffusivities associated with probe diffusion in polymer solutions.

The most striking feature of Figure 2 is that the decrease in $D_{probe}$ with polymer concentration becomes more pronounced as the size of the probe molecule is increased. This is consistent with the intent of eqs 2 and 3 that the probe diffusion coefficient should decrease with polymer concentration more strongly as the "jumping unit" size is increased. Though forced Rayleigh scattering experiments[1] have indicated that $\xi_{probe,s}$ for aberchrome (4.92) is greater than that for the smaller probe azobenzene (1.77) in PS–toluene, no study has shown a systematic increase in $\xi_{probe,s}$ with probe size for a variety of probes in a single polymer–solvent system. In fact, some investigators[68,69] have maintained that translational diffusion coefficients of various probe molecules have identical polymer concentration dependencies despite differences in size.

To investigate the effects of probe molecular weight and molar volume on the polymer concentration dependence of the diffusion coefficient, $D_{probe}$ was measured for 14 solutes in PS–THF solutions of concentration as high as 400 g/L (45 wt %). (At high PS concentration, $D_{probe}$ could not be determined for some probes using the UV detector. The absorbance spectra of these probes overlap considerably with that of PS, making it impossible to distinguish between detection of probe and

**Table 1. Summary of Probe Diffusion Coefficients in PS−THF Solutions at 25 and 50 °C and Fitted Values of $\xi_{\mathrm{probe,s}}$**

| probe molecule | $\tilde{V}(T_b)$[a] (cm$^3$/mol) | $\tilde{V}(0)$[b] (cm$^3$/mol) | $D_o$(25 °C) ($10^{-5}$ cm$^2$/s) | $D_{\mathrm{probe}}/D_o$(25 °C)[c] |  |  |  | $\xi_{\mathrm{probe,s}}$ (25 °C) | $D_o$(50 °C) ($10^{-5}$ cm$^2$/s) | $D_{\mathrm{probe}}/D_o$(50 °C) |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | 100 g/L | 200 g/L | 300 g/L | 400 g/L |  |  | 100 g/L | 200 g/L | 300 g/L | 400 g/L |
| 1. biacetyl | 111 | 66 | 2.52 | 0.80 | 0.58 |  |  | $0.9_4$ | 3.15 | 0.82 | 0.56 |  |  |
| 2. aniline | 102 | 80 | 2.03 | 0.73 | 0.48 |  |  | $1.2_9$ | 2.50 | 0.69 | 0.47 |  |  |
| 3. styrene | 133 | 94 | 2.01 | 0.86 | 0.58 |  |  | $0.9_4$ | 2.52 | 0.86 | 0.54 |  |  |
| 4. 2,3-hexanedione | 163 | 93 | 1.90 | 0.90 |  |  |  | *d* | 2.67 | 0.78 |  |  |  |
| 5. naphthalene | 157 | 105 | 1.80 | 0.76 | 0.49 | 0.43 | 0.20 | $1.0_5$ | 2.33 | 0.81 | 0.54 | 0.43 |  |
| 6. anthracene | 214 | 136 | 1.58 | 0.79 | 0.54 | 0.41 | 0.18 | $1.0_9$ | 1.92 | 0.80 | 0.58 | 0.43 | 0.17 |
| 7. pyrene | 228 | 151 | 1.45 | 0.75 | 0.48 | 0.33 | 0.13 | $1.2_4$ | 1.90 | 0.69 | 0.50 | 0.37 | 0.15 |
| 8. benzil | 229 | 153 | 1.39 | 0.75 | 0.50 | 0.33 | 0.16 | $1.1_6$ | 1.68 | 0.81 | 0.53 | 0.40 | 0.16 |
| 9. benzoyl peroxide | 258 | 170 | 1.24 | 0.79 | 0.48 |  |  | $1.2_1$ | 1.69 | 0.74 |  |  |  |
| 10. methyl red | 315 | 204 | 1.22 | 0.72 | 0.46 | 0.32 | 0.13 | $1.2_6$ | 1.53 | 0.69 | 0.46 | 0.32 | 0.13 |
| 11. 9,10-diphenylanthracene | 391 | 250 | 1.05 | 0.69 | 0.41 | 0.33 | 0.11 | $1.3_5$ | 1.39 | 0.68 | 0.40 | 0.30 | 0.11 |
| 12. 9,10-bis(phenylethynyl)anthracene | 450 | 288 | 0.91 | 0.72 | 0.44 | 0.30 | 0.11 | $1.3_5$ | 1.23 | 0.68 | 0.41 | 0.29 | 0.11 |
| 13. decacyclene | 523 | 314 | 1.00 | 0.67 | 0.39 | 0.27 | 0.08 | $1.5_3$ | 1.32 | 0.70 | 0.40 | 0.24 |  |
| 14. rubrene | 605 | 436 | 0.77 | 0.72 | 0.39 | 0.23 | 0.06 | 1.67 | 1.03 | 0.70 | 0.39 | 0.25 | 0.08 |

[a] The probe volume at its boiling point, $\tilde{V}(T_b)$, is estimated by the method of Le Bas.[78] [b] The probe volume at 0 K, $\tilde{V}(0)$, estimated by the method of Sugden,[79] is used in eq 3 in the form of $\hat{V}^*_{\mathrm{probe}} = \tilde{V}(0)/M_{\mathrm{probe}}$. [c] Values of $D_o$ are taken from ref 54. (These values of $D_o$ are also given in ref 77.) [d] Value not determined due to measurements being limited to concentrations of 100 g/L.

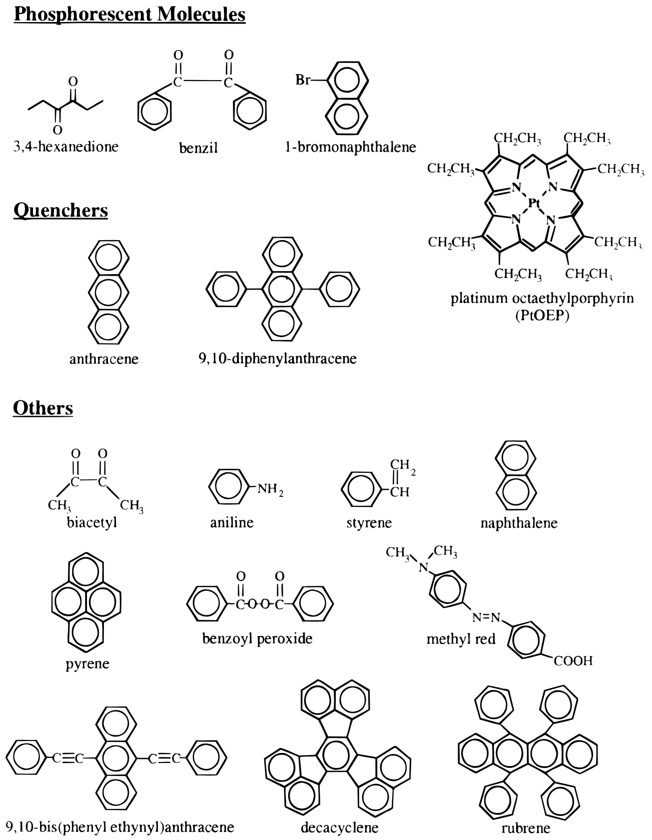

**Figure 1.** Chemical structures of small-molecule probes. Note that PtOEP is used as both a phosphorescent molecule and a quencher. Also, many of the molecules categorized as "others" can act as phosphorescence quenchers but were not used as such in this study.

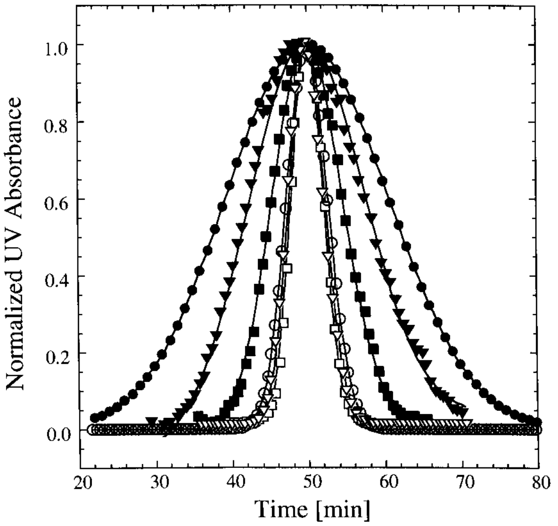

**Figure 2.** Normalized UV absorbance detector output for measuring diffusion coefficients of anthracene (□), 9,10-diphenylanthracene (▽), and rubrene (○) in tetrahydrofuran at 25 °C, and anthracene (■), 9,10-diphenylanthracene (▼), and rubrene (●) in solutions of 400 g/L PS in tetrahydrofuran at 25 °C. Solid curves represent fits to eq 5.

detection of small differences in PS concentration of the injected and mobile phases.) Table 1 lists values of $D_{\mathrm{probe}}$ normalized to their values at 0 PS concentration, $D_o$, at 25 and 50 °C. Values of $D_o$ are from refs 54 and 77. Also tabulated are molar volumes of the probes at their normal boiling point, $\tilde{V}(T_b)$, calculated from the atomic contribution method of Le Bas,[78] and the molar volumes of the probes at 0 K, $\tilde{V}(0)$, calculated by the

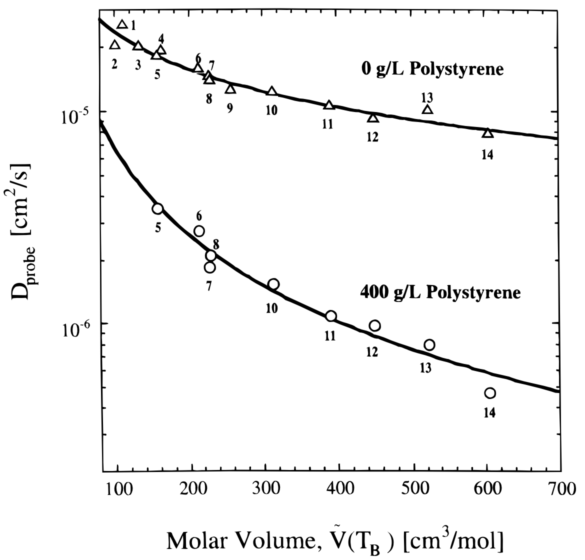

**Figure 3.** Diffusion coefficients of probe molecules at 25 °C in THF (△) and in solutions of 400 g/L PS in THF (○) as a function of estimated probe molar volume at its normal boiling point, $\tilde{V}(T_b)$. Also shown are best-fit lines through the data. Numbers identify the probes as listed in Table 1.

methods of Sugden.[79] It is customary to use $\tilde{V}(T_b)$ when characterizing solute diffusion in dilute solution[80] and $\tilde{V}(0)$ when applying free volume theory to diffusion in polymer solution.[27]

In Figure 3, values of $D_{probe}$ are plotted versus probe molar volume, $\tilde{V}(T_b)$, for the data at 25 °C and at concentrations of 0 and 400 g/L. At 0 g/L PS (neat THF), $D_{probe}$ can be fit reasonably well, with a correlation coefficient of $r^2 = 0.97$, to a scaling law of $\tilde{V}(T_b)^{-0.6}$. ($D_{probe}$ also scales well with $M_{probe}^{-0.6}$, where $M_{probe}$ is the probe molecular weight.) The scaling power of $-0.6$ is consistent with the Wilke–Chang correlation:[80]

$$D_{probe} = 7.4 \times 10^{-8} \frac{T(M_s\phi)^{0.5}}{\mu \tilde{V}^{0.6}} \tag{7}$$

where $T$ is temperature (K), $M_s$ is the molecular weight of the solvent, $\phi$ is a dimensionless association factor for the solvent which is taken to be 1.0 for THF, $\mu$ is the solvent viscosity (cP), and $\tilde{V}$ is the molar volume of the probe at its normal boiling temperature (cm³/mol), yielding $D_{probe}$ in units of cm²/s. This correlation has been found to work well with several solute–solvent systems.[78] The dependence of $D_{probe}$ on $M_{probe}$ in dilute solution is also consistent with the findings of von Meerwall et al.[81] that $D_{probe}$ for various plasticizer molecules in carbon tetrachloride scaled as $M_{probe}^{-0.7\pm0.05}$.

As the concentration of polymer in the solution increases, $D_{probe}$ decreases more strongly with probe molar volume and $M_{probe}$. At 400 g/L PS, $D_{probe}$ scales as $\tilde{V}(T_b)^{-1.4}$ and as $M_{probe}^{-1.4}$, with a correlation coefficient of $r^2 = 0.97$. It should be noted that the same scaling power is obtained if $\tilde{V}(0)$ is used instead of $\tilde{V}(T_b)$. Thus, it is evident that the Wilke–Chang correlation underestimates the dependence of $D_{probe}$ on molar volume in PS–THF solutions. It is not surprising that in polymer solutions $D_{probe}$ scales with $M_{probe}$ or $\tilde{V}(T_b)$ with a power greater than 1. Ehlich and Sillescu[82] found for various tracer dyes in bulk PS that $D_{probe} \sim M_{probe}^{-1.8}$, while von Meerwall et al.[81] found for various plasticizer molecules in their own neat melt that $D_{probe} \sim M_{probe}^{-2}$.

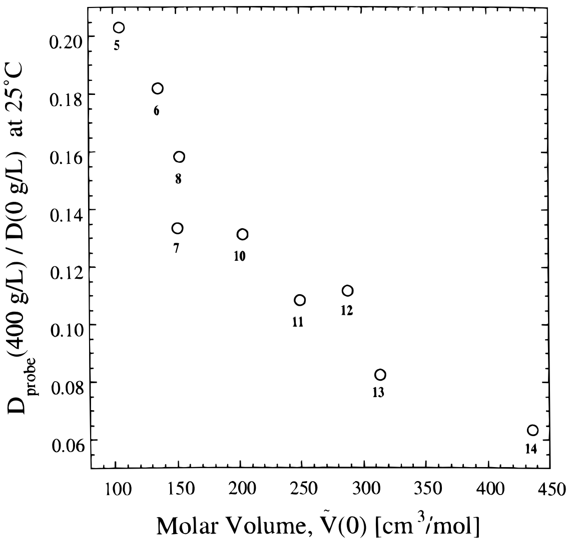

**Figure 4.** Diffusion coefficients of probe molecules at 25 °C in solutions of 400 g/L PS in THF divided by their values at zero polymer concentration (○) as a function of probe molar volume at 0 K, $\tilde{V}(0)$.

In Figure 4, probe diffusion coefficients at 400 g/L PS concentration, $D_{400}$, normalized by $D_o$, are plotted versus probe molar volume, $\tilde{V}(0)$. The methyl red diffusion data are in agreement with those of Landry et al.,[66] although the value of $D_o$ varies slightly from theirs. (Values of $D_o$ measured for other small molecules and polymers agree very well with literature values.[54]) The value of $D_{400}/D_o$ decreases almost 3-fold as $\tilde{V}(0)$ is increased by a factor of 4. The decrease in $D_{400}/D_o$ with molar volume indicates that the mobility of larger probes such as 9,10-diphenylanthracene, decacyclene, and rubrene is hindered by the presence of polymer much more than that of smaller probes such as naphthalene and anthracene.

To investigate further the dependence of ternary probe diffusion on PS solution concentration, values of $D_{probe}$ were also measured at 100, 200, and 300 g/L PS in THF at 25 and 50 °C. These data, together with the data at 400 g/L, are summarized in Table 1. Figure 5 shows the decrease with polymer concentration of the logarithm of $D_{probe}$ normalized to its value at zero polymer concentration, $D_o$, for naphthalene, anthracene, benzil, 9,10-diphenylanthracene, decacyclene, and rubrene. Also shown is the negative logarithm of the PS solution viscosity, $\eta$, at 25 °C, normalized by its value at zero polymer concentration, $\eta_o$. The PS sample $\bar{M}_n$ = 3800) used for viscosity characterization was similar to that used for Taylor dispersion. The concentration dependence of the inverse solution viscosity is stronger than that of $D_{probe}$ for any probe used here, thus showing that probe diffusion does not scale with inverse macroscopic viscosity; instead, microscopic viscosity or the local friction that a probe molecule experiences controls its diffusion. (If higher molecular weight PS had been used, the concentration dependence of inverse solution viscosity would have been steeper, while that of $D_{probe}$ would have been essentially unchanged.[64] Macroscopic viscosity increases rapidly with polymer concentration and molecular weight, while the microscopic friction coefficient of the probe, $\zeta_{probe}$, increases less strongly with polymer concentration and is essentially independent of polymer molecular weight.[83])

The concept of microscopic viscosity has been used before to describe the concentration dependence of solvent self-diffusion and probe diffusion of a small

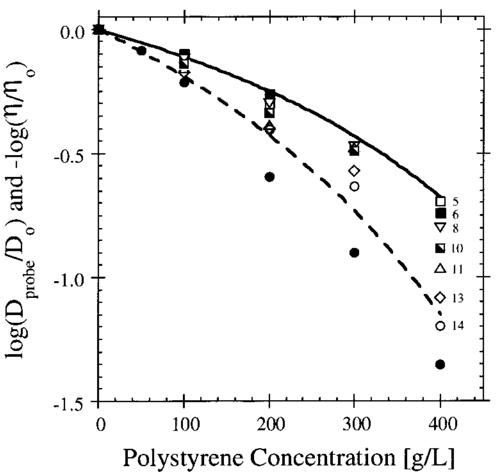

**Figure 5.** Logarithm of $D_{\mathrm{probe}}$ divided by its value at zero PS concentration as a function of PS concentration in THF at 25 °C for naphthalene (□), anthracene (■), benzil (▽), methyl red (◪), 9,10-diphenylanthracene (△), decacyclene (◇), and rubrene (○). Also plotted are the free-volume predictions of $\log(D_s/D_o)$ for the self-diffusion of THF (—) and $\xi_{\mathrm{probe,s}} \log(D_s/D_o)$ (---) for a probe having $\xi_{\mathrm{probe,s}} = 1.7$, and the concentration dependence of the inverse solution viscosity of PS–THF solutions at 25 °C (●). Numbers identify the probes as listed in Table 1.

number of molecules.[64,66,68] Comparison of the concentration dependence of probe diffusion for probes of varying size allows one to test how the friction coefficient, $\zeta_{\mathrm{probe}}$, of a small-molecule probe can be related to its molecular weight and/or molar volume and to the monomeric friction coefficient, $\zeta_o$, in that system. Free volume theory[7–9,37,84] has been successful in interpreting the concentration and temperature dependence of $\zeta_{\mathrm{probe}}$ for small-molecule diffusion.[85] Most notably, the generalized theory by Vrentas and Duda[84] has been successfully used with several polymer–solvent systems.

For a ternary solution consisting of solvent, probe, and polymer, the Vrentas–Duda free volume theory[7] predicts the following polymer concentration dependence of $\ln(D_s/D_{so})$:

$$\ln\left(\frac{D_s}{D_{so}}\right) = \left[-\frac{\gamma(\omega_s \hat{V}_s^* + \omega_{\mathrm{probe}}\xi_{\mathrm{s,probe}}\hat{V}_{\mathrm{probe}}^* + \omega_p \xi_{\mathrm{s,p}} \hat{V}_{\mathrm{probe}}^*)}{\hat{V}_{\mathrm{FH}}}\right] \quad (8)$$

where $\omega_i$ is the weight fraction of component $i$, $\hat{V}_{\mathrm{FH}}$ is the average hole free volume per gram of solution, $\gamma$ is an overlap factor, introduced because the same free volume is available to more than one molecule, and $\xi_{ij}$ is the ratio of jumping unit size of component $i$ to component $j$. (The subscripts "s", "probe", and "p" denote the solvent, small-molecule probe, and polymer components, respectively.) The specific hole free volume may be expressed as[9]

$$\hat{V}_{\mathrm{FH}} = \omega_s K_{1s}(T - T_{gs} + K_{2s}) + \omega_{\mathrm{probe}} K_{1\mathrm{probe}}(T - T_{g\mathrm{probe}} + K_{2\mathrm{probe}}) + \omega_p K_{1p}(T - T_{gp} + K_{2p}) \quad (9)$$

where $K_{1i}$ and $K_{2i}$ are free volume parameters for component $i$, and $T_{gi}$ is its glass transition temperature. Probe diffusion coefficients are then modeled by use of eqs 2, 3, 8, and 9.

The Vrentas–Duda free volume theory prediction of the normalized solvent (THF) self-diffusion coefficient, $\log(D_s/D_{so})$, is plotted in Figure 5 as a comparison with the probe diffusion data. Free volume parameters for PS–THF have been taken from ref 27 and are listed in Table 2. After calculating $D_s/D_{so}$ from eq 8, the probe diffusion data are fit by regression analysis to eq 2 to calculate $\xi_{\mathrm{probe,s}}$. For the probes considered in Figure 4, the smallest probe, naphthalene, has $\xi_{\mathrm{probe,s}} = 1.0_5$, while the largest probe, rubrene, has $\xi_{\mathrm{probe,s}} = 1.6_7$. As shown in Figure 5, 1.7 $\log(D_s/D_{so})$ appears to fit the rubrene diffusion data satisfactorily, indicating that eq 3 in combination with eq 8 can adequately model the concentration dependence of probe diffusion for large, rigid probes. Diffusion data at 25 °C for the other probes are treated in the same manner in order to generate the values of $\xi_{\mathrm{probe,s}}$ listed in Table 1. The values of $\xi_{\mathrm{probe,s}}$ for anthracene ($1.0_9$) and benzil ($1.1_6$) support the polymer concentration dependence of phosphorescence quenching rate data by Torkelson and coworkers,[54,58] where $\xi_{\mathrm{probe,s}}$ was found to be approximately 1 for the benzil–anthracene system in PS–toluene and PS–cyclohexane systems. Furthermore, $\xi_{\mathrm{probe,s}}$ correlates with the size of the probes.

**Table 2. Vrentas–Duda Model Parameters**

| parameter | PS–THF[a] | PS–CCl$_4$[b] | PS–cyclohexane[c] |
|---|---|---|---|
| $\hat{V}_s^*$ (cm$^3$/g) | 0.899 | 0.469 | 0.930 |
| $\hat{V}_p^*$ (cm$^3$/g) | 0.850 | 0.850 | 0.850 |
| $\tilde{V}(0)_s$ (cm$^3$/mol) | 65 | 72 | 78 |
| $K_{1s}/\gamma \times 10^4$ (cm$^3$ g$^{-1}$ K$^{-1}$) | 7.53 | 4.31 | 7.00 |
| $K_{1p}/\gamma \times 10^4$ (cm$^3$ g$^{-1}$ K$^{-1}$) | 5.82 | 5.82 | 5.82 |
| $K_{2s} - T_{gs}$ (K) | 10.45 | −38.00 | −32.07 |
| $K_{2p} - T_{gp}$ (K) | −327 | −327 | −327 |
| $\xi_{\mathrm{s,p}}$ | 0.466 | 0.519 | 0.563 |

[a] Parameters for the PS–tetrahydrofuran system were taken from ref 27. Slightly different $K_{1s}$ and $K_{2s}$ parameters for PS–THF appear in ref 103, but do not appear to affect $D_s$ appreciably. [b] Parameters for the PS–CCl$_4$ system were taken from ref 27. [c] Parameters for the PS–cyclohexane system were taken from ref 56.

By using eq 3, which relates $\xi_{\mathrm{probe,s}}$ with the molecular weight of a probe jumping unit, $M_{\mathrm{jprobe}}$, it is possible to assess what fraction of a probe's molecular volume or molecular weight may participate in the jumping process. In Figure 6, $\xi_{\mathrm{probe,s}}$ is plotted versus the ratio of probe to solvent molar volumes, $\tilde{V}(0)_{\mathrm{probe}}/\tilde{V}(0)_s$. Under the circumstance in which both the probe and solvent molecules "jump" as whole units, i.e., where $\tilde{V}(0)_{\mathrm{probe}}$ and $\tilde{V}(0)_s$ are equal to $\hat{V}_{\mathrm{probe}}^* M_{\mathrm{probe}}$ and $\hat{V}_s^* M_s$, respectively, then $\xi_{\mathrm{probe,s}} = \tilde{V}(0)_{\mathrm{probe}}/\tilde{V}(0)_s$. One of the probe molecules, aniline, apparently follows this behavior, indicated by the solid line in Figure 6. Of the probe molecules that possess no or very limited flexibility/bond rotation possibilities, aniline is closest in size and shape to that of the solvent, THF, and this similarity may be the origin of this effect. This relationship may not require that probe and solvent molecules jump as whole units but simply that both have the same fraction of their volume or molecular weight involved in the diffusive process.

Ignoring the aniline data point, all of the other data fit approximately to a line of slope 0.13, represented by the dashed line in Figure 6. This demonstrates that, even if THF executed jumps as a whole single unit, for probe molecules larger than THF a critical hole free volume that is only a fraction of the probe molecular volume is necessary for diffusion to occur. If THF executes a jump requiring that only a fraction of its volume move into space previously unoccupied by itself, then increasingly smaller fractions of probe volume are required for diffusion as probe volume increases. An

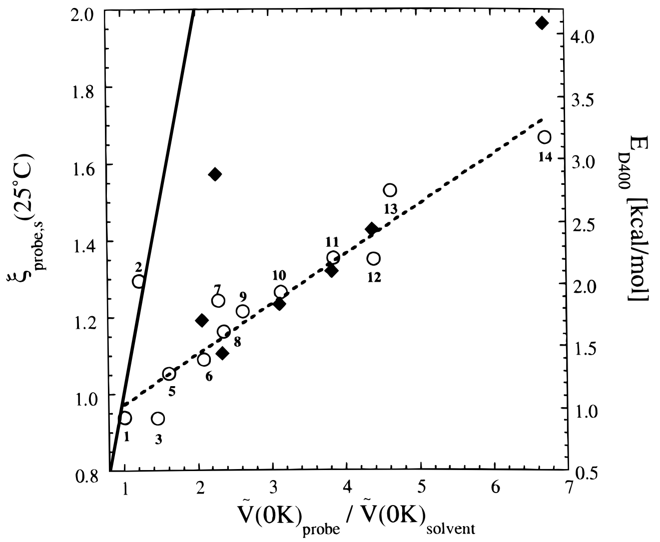

**Figure 6.** Free volume parameter $\xi_{probe,s}$ at 25 °C (○) and apparent activation energy for diffusion, $E_D$, in solutions of 400 g/L PS in THF (◆) as a function of the ratio of molar volumes at 0 K for various probe molecules to that for the solvent THF. Also plotted is a line (—) with slope of 1.0, indicating probes presumably diffusing as single units, and a line (- - -) with slope of 0.13, indicating probes with a segmental jumping unit molecular weight of approximately one-seventh to one-eighth that of the total probe molecular weight.

alternative picture is that the diffusion of the probe through the polymer–solvent continuum is dictated by the friction across an effective hydrodynamic diameter or "frontal diameter" [81] that is a fraction of the average diameter calculated from a sphere of volume equal to that of the probe.

Simple visual inspection of the probe molecule structures given in Figure 1 provides an explanation for the muted effects of probe volume as increasingly larger probes are employed. For the case of absolutely rigid probe molecules with no bond rotational freedom (naphthalene, anthracene, pyrene, and decacyclene), it is clear that these highly anisometric molecules will have preferred diffusional configurations. For example, anthracene is 30% larger in volume than naphthalene; however, $\xi_{probe,s}$ values are only 4% different for these two molecules (1.0$_5$ for naphthalene vs 1.0$_9$ for anthracene). The nearly identical $\xi_{probe,s}$ values are likely due to the fact that naphthalene and anthracene have the same "width" but differ only in aspect ratio, meaning that they can have almost the same requirements for the critical hole free volume. This requires that the most favored mode of diffusion involves a longitudinal motion along the long axis of the molecule, such as that illustrated in the top of Figure 7. The net motion is small, and in both cases most of the molecular volume will diffuse into space already occupied by the molecule; thus, almost no additional critical hole free volume is required for a diffusive motion of anthracene as compared to that of naphthalene. Similarly, while decacyclene has more than double the volume of pyrene, decacyclene requires only a quarter more critical hole free volume due to the highly anisotropic nature of the preferred diffusive motions. Visual inspection also reveals that rubrene requires only marginally more free volume for diffusion than decacyclene, resulting in only a 9% difference in $\xi_{probe,s}$, even though the two molecules differ in volume by nearly 40%.

Shape effects are also evident in a comparison of $\xi_{probe,s}$ and $\tilde{V}(0)_{probe}/\tilde{V}(0)_s$ values for 9,10-diphenylanthracene (DPA) and 9,10-bis(phenyl ethynyl)anthracene (BPEA). Although BPEA is 15% larger in volume than DPA, the two probes have identical $\xi_{probe,s}$ values, associated with the fact that, if the probes diffused preferentially in the direction indicated in the bottom of Figure 7, they would have nearly the same critical hole free volume requirements (the diffusive resistance is dominated by the drag past the anthryl group). A comparison of $\xi_{probe,s}$ and $\tilde{V}(0)_{probe}/\tilde{V}(0)_s$ for pyrene and methyl red also reveals the important role of shape. While methyl red occupies one-third more volume than pyrene, the high aspect ratio of methyl red results in nearly identical $\xi_{probe,s}$ parameters.

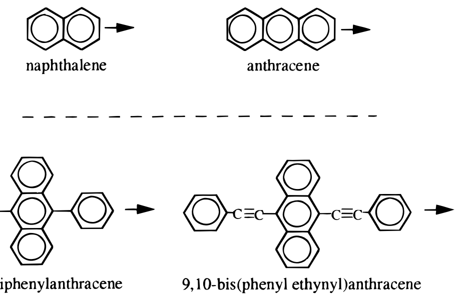

**Figure 7.** (Top) For anisometric molecules such as naphthalene and anthracene, the diffusive motion is favored along the long axis of the molecule. Therefore, the critical hole free volume necessary for molecular diffusion is just a fraction of the molecular volume. (Bottom) 9,10-Diphenylanthracene and 9,10-bis(phenylethynyl)anthracene require nearly the same critical hole free volume in order to diffuse in the direction indicated by the arrow, since the resistance to diffusion is dominated by the drag past the anthryl group. Thus, the polymer concentration dependence of $D_{probe}$ (and $\xi_{probe,s}$) for both molecules is nearly identical.

Finally, the role of flexibility is evident through comparisons of pyrene with benzil and with benzoyl peroxide. While pyrene and benzil have essentially the same volume, benzil diffusion has a significantly lower polymer concentration dependence because of its higher degree of flexibility. Benzoyl peroxide is larger than pyrene but exhibits a smaller concentration dependence of its diffusion coefficient (and thereby a smaller $\xi_{probe,s}$ parameter), also due to flexibility effects.

The importance of shape (molecular anisometry) and flexibility in dictating diffusion behavior of trace solvent in bulk polymer has been noted by Arnould and Laurence[62] and Mauritz and Storey[86,87]; likewise, von Meerwall et al.[81] noted these effects at 10–60 wt % solvent (plasticizer) content. Vrentas et al.[63] recently modified the Vrentas–Duda free volume theory to include solvent size effects which consider molecular asymmetry. However, there has been no previous study of these effects for the ranges of ternary probe and polymer concentration (0–400 g/L) considered here using Taylor dispersion.

**Temperature Dependence.** Effects of probe size and geometry on small-molecule probe diffusion can also be studied by measuring the temperature dependence of diffusion in ternary systems. For this purpose, data were collected at 50 °C for comparison with the data at 25 °C. Activation energies for diffusion, $E_D$, were obtained from Arrhenius plots of $\ln(D_{probe})$ versus $1/T$, in accord with the following:

$$E_D = RT^2\left(\frac{\partial \ln (D_{probe}/D_{probe,o})}{\partial T}\right)_{P,\omega_{probe},\omega_p} \qquad (10)$$

Due to the experimental uncertainties of $D_{probe}$ and use of only two temperatures for calculation of $E_D$, the temperature dependence data are subject to much greater uncertainty than the concentration dependence data. In dilute solution, within experimental error, there is no significant trend of $E_D$ with probe size for diffusion of the probes listed in Table 1. Activation energies are about 2 kcal/mol. The value of 1.8 kcal/mol for methyl red compares favorably with the value of 2.6 kcal/mol obtained by Landry et al.[66]

Inspection of the data in Table 1 reveals that the polymer concentration dependence of $D_{\mathrm{probe}}$ at 50 °C is slightly less than that at 25 °C. This trend is consistent with the Vrentas–Duda theory.

Furthermore, in general, $E_D$ increases with polymer concentration;[88] $E_D$ at 400 g/L PS concentration exceeds $E_D$ in THF for five of the seven probes studied at 25 and 50 °C. A similar trend is seen in the methyl red data of Landry et al.;[66] however, they reported a stronger increase, with $E_D$ increasing from 2.6 kcal/mol in dilute solution to 5.5 kcal/mol at 0.4 weight fraction polymer.

Values of $E_D$ at 400 g/L PS concentration increase with probe molecule size as shown in Figure 6. With the notable exception of pyrene, for which $E_D$ is greater than for all other probes except rubrene, $E_D$ correlates with $\tilde{V}(0)_{\mathrm{probe}}/\tilde{V}(0)_{\mathrm{s}}$ in a manner similar to $\xi_{\mathrm{probe,s}}$. This apparent relationship can be understood in terms of free volume theory for ternary solutions. By combining eqs 2, 3, 8, and 9, and setting $\omega_{\mathrm{probe}} = 0$, the concentration dependence of $D_{\mathrm{probe}}$ in a probe–polymer–solvent system in which the probe is present only in trace amounts is given by

$$\ln\left(\frac{D_{\mathrm{probe}}}{D_{\mathrm{probe,o}}}\right) = \left[-\frac{\gamma(\omega_{\mathrm{s}}\xi_{\mathrm{probe,s}}\hat{V}_{\mathrm{s}}^{*} + \omega_{\mathrm{p}}\xi_{\mathrm{probe,p}}\hat{V}_{\mathrm{p}}^{*})}{\omega_{\mathrm{s}}K_{1\mathrm{s}}(T - T_{\mathrm{gs}} + K_{2\mathrm{s}}) + \omega_{\mathrm{p}}K_{1\mathrm{p}}(T - T_{\mathrm{gp}} + K_{2\mathrm{p}})}\right] \tag{11}$$

Inserting this into the definition of $E_D$ in eq 10, the resulting equation for $E_D$ is obtained:

$$E_{\mathrm{D}} = RT^2\xi_{\mathrm{probe,s}} \times \frac{\gamma(\omega_{\mathrm{s}}\hat{V}_{\mathrm{s}}^{*} + \omega_{\mathrm{p}}\xi_{\mathrm{s,p}}\hat{V}_{\mathrm{p}}^{*})(K_{1\mathrm{s}}\omega_{\mathrm{s}} + K_{1\mathrm{p}}\omega_{\mathrm{p}})}{[\omega_{\mathrm{s}}K_{1\mathrm{s}}(T - T_{\mathrm{gs}} + K_{2\mathrm{s}}) + \omega_{\mathrm{p}}K_{1\mathrm{p}}(T - T_{\mathrm{gp}} + K_{2\mathrm{p}})]^2} \tag{12}$$

where $\xi_{\mathrm{s,p}}$ is the ratio of jumping unit size of solvent to polymer and can be related to $\xi_{\mathrm{probe,s}}$ by[65]

$$\xi_{\mathrm{probe,s}} = \xi_{\mathrm{probe,p}}/\xi_{\mathrm{s,p}} \tag{13}$$

From eq 12, it is clear that $E_D$ is related to $\xi_{\mathrm{probe,s}}$ and therefore the size of the probe molecule. Furthermore, eq 12 describes how $E_D$ increases with polymer concentration.

In the limit as $\omega_{\mathrm{p}} \to 0$, i.e., probe in solvent, eq 12 reduces to

$$E_{\mathrm{D}} = RT^2\xi_{\mathrm{probe,s}}\frac{\gamma\hat{V}_{\mathrm{s}}^{*}/K_{1\mathrm{s}}}{(K_{2\mathrm{s}} + T - T_{\mathrm{gs}})^2} \tag{14}$$

Thus, in dilute solutions, $\xi_{\mathrm{probe,s}}$ is most important in describing how $E_D$ depends on probe size, while in more concentrated solutions, $\xi_{\mathrm{probe,p}}$ becomes most important. The dependence of $E_D$ on polymer concentration and $\xi_{\mathrm{probe,s}}$ is shown in Figure 8a. Also plotted are the data from Landry et al.[66] for the concentration dependence of $E_D$ for methyl red diffusion in PS–THF and the apparent activation energy of viscosity, $E_A$, based on measurements of PS–THF solution viscosity at 25, 40, and 55 °C. Very good agreement is found between the values of $E_D$ predicted from eq 12 using $\xi_{\mathrm{probe,s}} = 1.25$ and the experimental data for methyl red in PS–THF. This value of $\xi_{\mathrm{probe,s}}$ compares surprisingly well with the value of 1.26 obtained using Taylor dispersion for methyl red diffusion in PS-THF. This suggests that eq 12 could be used to test the probe size dependence of $\xi_{\mathrm{probe,s}}$ in polymer solutions and thereby critically test the modified Vrentas–Duda theory, provided that the temperature dependence of $D_{\mathrm{probe}}$ is carefully measured. This is further supported by Figure 8b, which compares data from Lodge et al.[2] for the concentration dependence of $E_D$ for methyl red diffusion in poly(vinyl acetate) (PVAc)–toluene to the data for the same probe in PS–THF.[66] Although there is some scatter in the data for the PVAc–toluene system, the data fall in the range of $1 \leq \xi_{\mathrm{probe,s}} \leq 1.35$ and may also be reasonably fit by

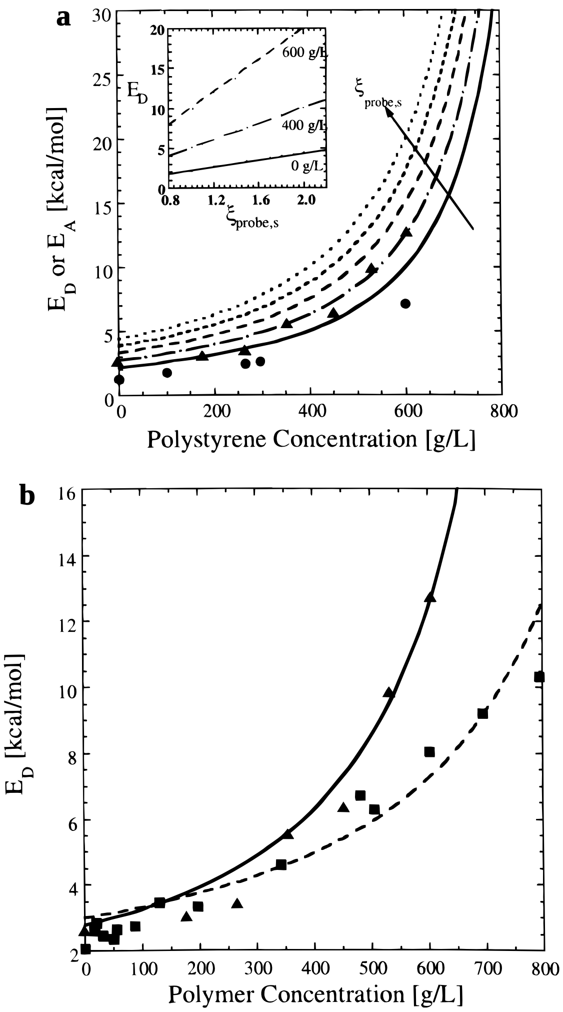

**Figure 8.** (a) Main: Activation energy for diffusion, $E_D$, as a function of polymer concentration for the PS–THF system as predicted by eq 12 for values of $\xi_{\mathrm{probe,s}}$ equal to 1.0 (—), 1.25 (—•—), 1.50 (— —), 1.75 (- - -), and 2.0 (•••). Also plotted are values of $E_D$ (▲) for methyl red diffusion in PS–THF from Landry et al.,[66] showing $\xi_{\mathrm{probe,s}}$ to be about 1.25 for that system and values of $E_A$ (●) for the viscosity of PS–THF solutions. Inset: Dependence of $E_D$ on $\xi_{\mathrm{probe,s}}$ for concentrations of 0 (—), 400 (— —), and 600 g/L (- - -) of polystyrene in THF as predicted by eq 12. (b) Activation energies, $E_D$, as a function of polymer concentration for diffusion of methyl red in PS–THF[66] (▲) and in PVAc–toluene[2] (■). The lines correspond to activation energies predicted by eq 12 for diffusion in PS–THF (—) and PVAc–toluene (- - -) using a value of $\xi_{\mathrm{probe,s}} = 1.25$.

$\xi_{\mathrm{probe,s}} = 1.25$. (From these results, it is clear that data must be taken at many concentrations, as done by Landry et al.[66] and Lodge et al.,[2] for such a test to be accurate and precise.)

In the limit as $\omega_{\mathrm{p}} \rightarrow 1$, i.e., probe dispersed within bulk polymer film, eq 12 reduces to

$$E_{\mathrm{D}} = RT^2\xi_{\mathrm{probe,p}}\frac{\gamma \hat{V}_{\mathrm{p}}^{*}/K_{1\mathrm{p}}}{(K_{2\mathrm{p}} + T - T_{\mathrm{gs}})^2} \qquad (15)$$

The form of this equation is similar to one defined[62,89] for solvent diffusion in polymer–solvent systems (with $\xi_{\mathrm{probe,p}}$ replaced by $\xi_{\mathrm{s,p}}$). Equation 15 suggests that $E_{\mathrm{D}}$ should increase without bound with the size of the probe molecule. In practice, $E_{\mathrm{D}}$ may reach some limiting value independent of probe size; in particular, in bulk rubbery polymer it has been suggested by Ehlich and Sillescu[82] that the temperature dependence of probe diffusion should not exceed the temperature dependence of the polymer cooperative segmental mobility or α-relaxation, i.e., $\xi_{\mathrm{probe,p}}$ must be $\leq 1$ (in terms of eq 15). With this picture, diffusion of probe molecules larger than a polymeric jumping unit will be controlled by polymer segmental motion. Additional support of this point has been given in fluorescence nonradiative energy transfer studies[90–92] of translational diffusion of seven probes of various size, shape, and flexibility in methacrylate-based polymers, as well as in other studies.[93–95] (The limit essentially asserts that probes whose motion can couple fully with the α-relaxation will have $\xi_{\mathrm{probe,p}} = 1$.) By using a ceiling value of $\xi_{\mathrm{probe,p}} = 1$, eq 13, and a value of $\xi_{\mathrm{s,p}} = 0.466$ from Table 2, a maximum value of $\xi_{\mathrm{probe,s}}$ for probe diffusion in PS–THF solutions would be 2.14. It is noteworthy that the data for all probes employed here and in other PS–THF–probe studies[64,66,68,69] are consistent with this limit.

**(B) Phosphorescence Quenching Results.** An alternative method for investigating $\xi_{\mathrm{probe,s}}$ is to measure phosphorescence quenching rate constants for small molecule–polymer interactions. These interactions are controlled by small-molecule diffusion and provide a means for probing the translational mobility of small molecules in polymer solutions. The small molecule can be either a phosphorescent molecule (if polymer is used as the quencher) or a quencher molecule (if polymer is the phosphorescent molecule).

Phosphorescence quenching has an advantage over Taylor dispersion for investigating the polymer concentration dependence of probe diffusion. As employed here, Taylor dispersion is limited by the macroscopic viscosity of the polymer solution (~10–15 cP), requiring the use of matrix polymer of sufficiently low molecular weight and concentration; phosphorescence quenching does not have this limitation. For example, small molecule–polymer interactions were studied by Gebert et al.[59] using MW 101 000 PS in the range of 0–700 g/L in toluene. The drawback of quenching is that probe molecules are generally limited to chromophores. However, with judicious selection, a range of probe molecules varying in size and shape can be studied.

Only a small number of organic chromophores exhibit room-temperature phosphorescence in fluid solution with sufficiently high quantum yield and long lifetime (>30 μs) to be useful, employing simple experimental equipment, as phosphorescence quenching probes. Among these are benzil,[56,57,59,74,96] biacetyl,[19] and other aliphatic diketones[97] such as 3,4-hexanedione,[98] porphyrins such as platinum octaethyl porphyrin (PtOEP),[99,100] and halogenated naphthalenes.[101] A much broader selection of molecules exists for the quencher. Generally, molecules having triplet levels below those of the phosphorescent molecules listed above will quench phosphorescence at diffusion-controlled rates, including anthracene derivatives, for example.

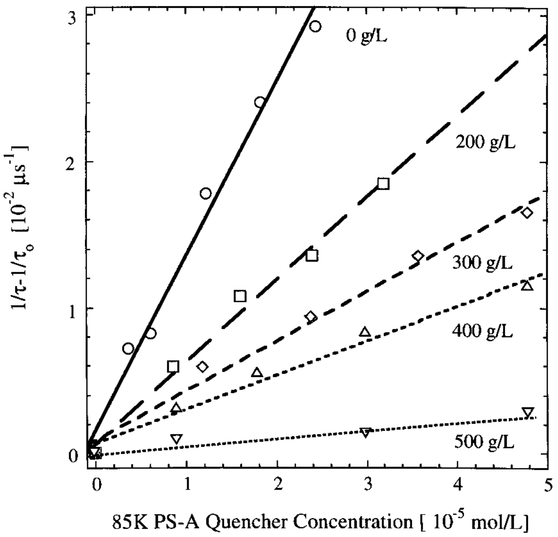

**Figure 9.** Stern–Volmer plot showing the inverse phosphorescence lifetime of platinum octaethylporphyrin as a function of 85K PS-A quencher concentration in PS–THF solutions. The data sets are for polystyrene concentrations of 0 (○), 200 (□), 300 (◇), 400 (△), and 500 g/L (▽). Diffusion-controlled quenching rate constants, $k_{\mathrm{q}}$'s, which are obtained from the slope of each line, decrease with increasing polystyrene concentration.

A Stern–Volmer plot for quenching of PtOEP phosphorescence by MW 85 000 PS-A in PS–THF solutions is shown in Figure 9 for several concentrations of matrix PS (MW 3800). The phosphorescence lifetime of PtOEP, $\tau_{\mathrm{o}}$, is about 90 μs in neat THF and decreases slightly upon addition of PS. Values of $k_{\mathrm{q}}$ are obtained from the slope of each line as described by eq 6. Immediately apparent is the pronounced decrease in $k_{\mathrm{q}}$ with increasing polymer concentration. $k_{\mathrm{qo}}$ is $1.2 \times 10^9$ M$^{-1}$ s$^{-1}$ in dilute THF and drops to $1.4 \times 10^8$ M$^{-1}$ s$^{-1}$ at 400 g/L PS concentration.

The decrease in $\log(k_{\mathrm{q}}/k_{\mathrm{qo}})$ with PS concentration for the PtOEP/85K PS-A system is shown in Figure 10. Also shown are values of $\log(k_{\mathrm{q}}/k_{\mathrm{qo}})$ for the quenching of 3,4-hexanedione and l-bromonaphthalene by 85K PS-A. While PtOEP and l-bromonaphthalene have large phosphorescence lifetimes in THF ($\tau_{\mathrm{o}} \approx 90$ μs in both cases), $\tau_{\mathrm{o}}$ for 3,4-hexanedione at 25 °C was only 25 μs, resulting in increased experimental uncertainty. However, upon lowering the temperature to 10 °C, $\tau_{\mathrm{o}}$ increased to 45 μs, and $k_{\mathrm{q}}$ was obtained with more accuracy. It is also notable that the measurements are sensitive to the slight decrease in concentration dependence resulting from the lowered temperature. In dilute THF, $k_{\mathrm{qo}}$ is $6.0 \times 10^9$ M$^{-1}$ s$^{-1}$ for the 3,4-hexanedione/85K PS-A interaction and $3.8 \times 10^9$ M$^{-1}$ s$^{-1}$ for the l-bromonaphthalene/85K PS-A interaction. Unfortunately, $\tau_{\mathrm{o}}$ values for benzil and PS-B in THF were too low to be used accurately.

As shown in Figure 10, the concentration dependence for PtOEP in the 3800 MW PS–THF system is more similar to the dependence of the inverse macroscopic viscosity than that for smaller probes. Had a larger probe been used with a $\xi_{\mathrm{probe,s}}$ parameter of 2.2 (close to the postulated maximum $\xi_{\mathrm{probe,s}}$ value of 2.14 described in the previous section), then the concentration

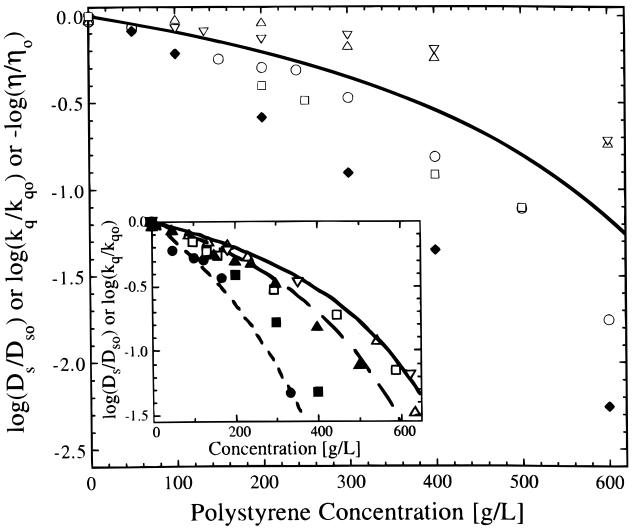

**Figure 10.** Comparison of log($k_q/k_{qo}$) in PS−THF solutions for phosphorescence quenching interactions between 85K PS-A and 3,4-hexanedione at 10 (▽) and 25 °C (△), 1-bromonaphthalene at 25 °C (□), and PtOEP at 25 °C (○). Also plotted are the free volume prediction of log($D_s/D_o$) for the solvent self-diffusion of THF (—) and the concentration dependence of the solution viscosity of PS−THF solutions at 25 °C (◆). Inset: Comparison of log($k_q/k_{qo}$) for phosphorescence quenching interactions between PtOEP and 85K PS-A in PS−THF (▲) and PS−cyclohexane solutions (■) and for interactions between benzil and anthracene in PS−$CCl_4$ solutions (●) with Vrentas−Duda free volume theory predictions of log($D_s/D_{so}$) for THF (—), for cyclohexane (— —), and for $CCl_4$ (- - -). Also plotted are values of solvent self-diffusion coefficients for THF from refs 68 (▽) and 103 (△) and for cyclohexane from ref 104 (□). The concentration dependences of $k_q$ and solvent self-diffusion coefficients depend strongly on the polymer−solvent system. Also, $k_q$'s for quenching of PtOEP phosphorescence in PS−solvent systems show a stronger concentration dependence than the self-diffusion coefficients of the corresponding solvents.

dependence of the probe mobility would have been identical to that of the inverse macroscopic viscosity. For exceedingly large probes, it is expected that the concentration dependence would be no greater than that for the inverse macroscopic viscosity and would become independent of probe size. Thus, the concentration dependence of the inverse macroscopic viscosity may serve as an upper limit on the concentration dependence of $D_{probe}$. It is unclear whether $\xi_{probe,s}$ for very large probes would increase as the concentration dependence of macroscopic viscosity increases with polymer molecular weight or would remain at the postulated maximum $\xi_{probe,s}$ value of 2.14.

It is expected that $\xi_{probe,s}$ would depend upon polymer molecular weight in cases in which the concentration dependence of $D_{probe}$ is limited by macroscopic viscosity (for exceedingly large probes of size comparable to a polymer jumping unit or in solutions containing very short polymer chains). To test whether $\xi_{probe,s}$ for PtOEP was limited by the use of low molecular weight PS (3800 MW in the Taylor dispersion studies), PtOEP/85K PS-A interactions were measured in 300 g/L PS−THF solutions as a function of matrix polymer molecular weight. Values of $k_q$ (units of $10^8$ $M^{-1}$ $s^{-1}$) were 3.4 ± 0.4, 3.3 ± 0.3, and 2.8 ± 0.8 for molecular weights of 3800, 101 000, and 650 000, respectively. The data are independent of matrix molecular weight, suggesting that PtOEP is not large enough to observe limiting behavior of $\xi_{probe,s}$ in these solutions ($\xi_{probe,s} < 2.2$ for PtOEP) and that the PS molecular weight used in the Taylor dispersion studies is sufficient for investigation of high molecular weight polymer behavior. These results are consistent with the molecular weight independence of $k_q$ for phosphorescence quenching between the smaller probes of anthracene and benzil.[56] Diffusion or phosphorescence quenching of exceedingly large probes, much larger than PtOEP (e.g., PS microspheres[102]), in polymer solutions warrants investigation. Studies of PtOEP in lower molecular weight polymer solutions, with the concentration dependence of solution viscosity closer to that of $D_{probe}$, may also be of interest.

Solvent can affect significantly the concentration dependence of probe diffusion and quenching rate constants in polymer solutions. In the inset of Figure 10, log($D_s/D_{so}$) is plotted for the self-diffusion of THF, cyclohexane, and $CCl_4$, in respective order of increasing concentration dependence. Though differences between log($D_s/D_{so}$) for THF and cyclohexane are small, differences between THF and $CCl_4$ can be quite large. For example, at 400 g/L polymer concentration, $D_s/D_{so}$ is 0.02 in $CCl_4$, while $D_s/D_{so}$ is 0.28 in THF. The differences in concentration dependence are reflected in the free volume parameters listed in Table 3. Also plotted in Figure 10 are values of solvent self-diffusion coefficients for THF from refs 68 and 103, and for cyclohexane from ref 104. To our knowledge, self-diffusion coefficients of $CCl_4$ in PS solutions have not been reported. The filled symbols in Figure 10 represent phosphorescence quenching data. Plotted are values of log($k_q/k_{qo}$) for PtOEP/85K PS-A interactions in THF and cyclohexane and benzil−anthracene interactions in $CCl_4$. The concentration dependencies of $k_q$ for PtOEP/85K PS-A interactions in cyclohexane and THF are much stronger than those for solvent self-diffusion. However, $\xi_{probe,s}$ for PtOEP is slightly higher in cyclohexane (1.7) than in THF (1.5). This is interesting, given that $\tilde{V}(0)_s$ for cyclohexane is 78 $cm^3$/mol and $\tilde{V}(0)_s$ for THF is 65 $cm^3$/mol. Based on the definition of $\xi_{probe,s}$ it is expected that $\xi_{probe,s}$ would be higher for THF than for cyclohexane. The observed differences in $\xi_{probe,s}$ in cyclohexane and THF may be due to effects of solvent not addressed by the free volume theory. Finally, values of log($k_q/k_{qo}$) for benzil−anthracene interactions in $CCl_4$ show that $\xi_{probe,s} \approx 1.0$ for these probes.

Interactions between phosphorescent polymer (PS-B) and small-molecule quenchers were also studied, as small molecules more often quench phosphorescence than phosphoresce. These interactions were studied in cyclohexane rather than THF due to the higher lifetime of PS-B in that solvent. Results from interactions involving quenching of benzil, PtOEP, and PS-B are shown in Figure 11, along with the Vrentas−Duda theory prediction of cyclohexane self-diffusion. For both 70K PS-B/anthracene and benzil/85K PS-A interactions, the concentration dependence is similar to that for cyclohexane self-diffusion. Thus, $\xi_{probe,s}$ is about 1 for both systems. The concentration dependence for 70K PS-B/DPA interactions is slightly higher, with $\xi_{probe,s}$ equal to $1.3_6$. This is consistent with the value of $1.3_5$ for DPA diffusion in PS−THF measured using Taylor dispersion. Finally, interactions involving PtOEP as either a phosphorophore or a quencher were studied. Because of the location of the triplet energy levels of benzil, PtOEP, and anthracene, the phosphorescence of benzil (or PS-B) is quenched by PtOEP, and PtOEP phosphorescence is quenched by anthracene (or PS-A). As shown in Figure 11, the concentration dependencies of 70K PS-B/PtOEP ($\xi_{probe,s} = 1.7_0$) and PtOEP/85K PS-A ($\xi_{probe,s} = 1.7_5$) interactions are nearly identical.

**Table 3. Values of $k_{qo}$ and $\xi_{probe,s}$ for Phosphorescence Quenching Interactions in PS Solutions**

| system | solvent | $\tilde{V}(0)^a$ (cm$^3$/mol) | $k_{qo}$ ($10^9$ M$^{-1}$ s$^{-1}$) | $\xi_{probe,s}$ |
|---|---|---|---|---|
| benzil/anthracene | $CCl_4$ | 153/136 | 2.7 | $0.9_7$ |
| benzil/85K PS-A | cyclohexane | 153 | 2.5 | $0.9_0$ |
| 70K PS-B/anthracene | cyclohexane | 136 | 4.2 | $1.0_5$ |
| 70K PS-B/9,10-diphenylanthracene | cyclohexane | 250 | 1.7 | $1.3_6$ |
| 70K PS-B/PtOEP | cyclohexane | $446^b$ | 0.9 | $1.7_0$ |
| PtOEP/85K PS-A | cyclohexane | $446^b$ | 1.2 | $1.7_5$ |
| 3,4-hexanedione/85K PS-A | THF | 93 | 6.0 | $0.6_5$ |
| PtOEP/85K PS-A | THF | $446^b$ | 1.2 | $1.5_0$ |
| 1-bromonaphthalene/85K PS-A | THF | 121 | 3.8 | $1.6_5$ |

[a] Values of $\tilde{V}(0)$ are tabulated for the small molecule of each small molecule/polymer interaction. [b] This value is a conservative estimate of $\tilde{V}(0)$ for PtOEP. The atomic contribution of Pt was not included in calculation of the overall molar volume, as its value was not tabulated by Sugden and Biltz (cited in ref 79).

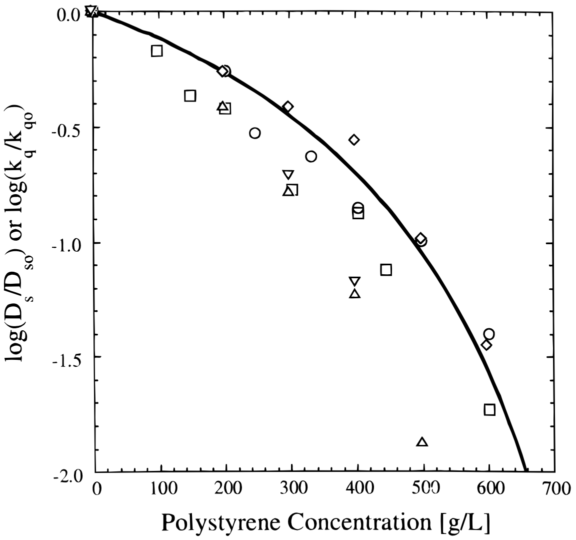

**Figure 11.** Comparison of $\log(k_q/k_{qo})$ for phosphorescence quenching interactions between 70K PS-B and anthracene (○), 9,10-diphenylanthracene (□), and PtOEP (▽) in PS–cyclohexane solutions. Also plotted are values of $\log(k_q/k_{qo})$ for interactions between 85K PS-A and benzil (◇), and PtOEP (△). The solid curve (—) represents the free volume prediction[56] of the concentration dependence of cyclohexane self-diffusion.

This shows that the diffusion-controlled nature of these interactions is independent of whether the probe is an energy transfer donor or acceptor (quencher).

Values of $k_{qo}$ and $\xi_{probe,s}$ obtained from the various phosphorescence quenching studies are listed in Table 3. Values of $\xi_{probe,s}$ for the PtOEP system in PS–THF (1 .$5_0$) and in PS–cyclohexane ($1.7_5$ and $1.7_0$) compare favorably with that for the diffusion of rubrene in PS–THF ($1.6_7$), consistent with the similarity of the molar volumes of the probes (446 and 436 cm$^3$/mol, respectively). The value of $\xi_{probe,s}$ for l-bromonaphthalene ($1.6_5$) is much higher than that for naphthalene ($1.0_5$), despite their small difference in molar volume (121 and 105 cm$^3$/mol, respectively). This difference in $\xi_{probe,s}$ illustrates further the importance of probe shape; in the case of l-bromonaphthalene, the steric hindrance of the bromine group greatly increases $\xi_{probe,s}$. As with aniline in PS–THF, the PS concentration dependence of diffusion of 1-bromonaphthalene in PS–THF reflects the whole volume of the probe relative to that of THF, as evidenced by the value of $\xi_{probe,s}$ falling on the line of unity slope in Figure 12. For the smallest phosphorescent molecule investigated, 3,4-hexanedione, the value of $\xi_{probe,s}$ ($0.6_5$) is surprisingly small. One would expect 3,4-hexanedione and biacetyl, as well, to have low values of $\xi_{probe,s}$ due to the small and flexible nature of their aliphatic structures. However, in free volume theory, a value of $\xi_{probe,s}$ below 1.0 is unusual. It is unclear what this implies in terms of the original free volume model by Cohen and Turnbull.[105] It may be that 3,4-hexanedione can move segmentally within the vacancy provided by the diffusive "jump" of a THF molecule more easily than THF itself. Studies of diffusion of small, flexible probes in polymer solutions containing large solvent molecules are warranted.

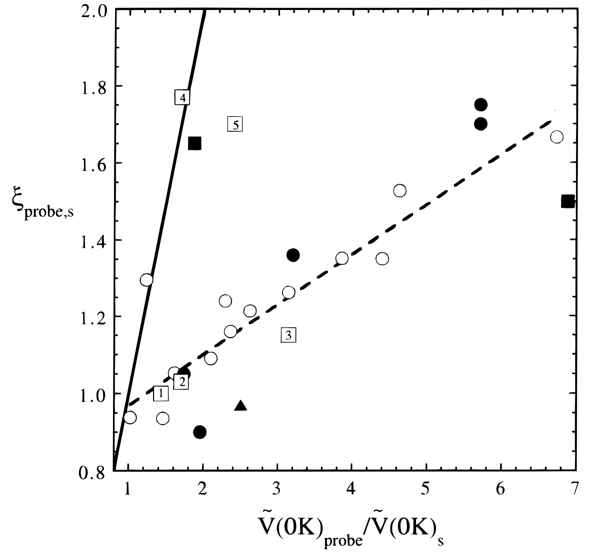

**Figure 12.** Free volume parameter $\xi_{probe,s}$ as a function of the ratio of molar volumes at 0 K for various probe molecules to that for the solvent. Taylor dispersion measurements: diffusion in PS–THF of probes listed in Table 1 (○). Phosphorescence quenching measurements: interactions in PS–THF (■), interactions in PS–cyclohexane (●), and interactions in PS–$CCl_4$ (▲). Other probe diffusion data from the literature (□): 1, hexafluorobenzene in PS–THF;[64] 2, azobenzene in PVAc–toluene;[65] 3, $\xi_{probe,s}$ for methyl red in PS–THF obtained by refitting[67] the data by Landry et al.;[66] 4, azobenzene in PS–toluene;[1] and 5, methyl red in PS–toluene.[65] Also plotted are lines with slopes of 1.0 (—) and 0.13 (- - -). See text for explanation. $\xi_{probe,s}$ for the 3,4-hexanedione/85K PS-A interaction in PS–THF is omitted from the figure due to its low value ($0.6_5$).

**(C) Comparison of Data from Taylor Dispersion with Data from Phosphorescence Quenching and Other Studies.** Figure 12 summarizes $\xi_{probe,s}$ as a function of $\tilde{V}(0)_{probe}/\tilde{V}(0)_s$ for all probes investigated here with the exception of 3,4-hexanedione, omitted due to its anomalously low $\xi_{probe,s}$ value. Interestingly, for the 15 probes represented, the data split between two types of behavior, the vast majority fitting approximately on a line of slope 0.13, and two data points, those for aniline and 1-bromonaphthalene, falling on a line with unity slope. (For biacetyl with $\tilde{V}(0)_{probe}/\tilde{V}(0)_s$ nearly 1.00, $\xi_{probe,s}$ can fit acceptably on either line.)

The data for aniline and l-bromonaphthalene illustrate the importance of probe shape on diffusion. In both cases, a sizable, approximately spherical unit ($-NH_3$ or $-Br$) is attached to the side of an aromatic ring. That aniline and l-bromonaphthalene have much stronger polymer concentration dependencies of diffusion, reflecting approximately their total molar volume, than naphthalene and anthracene indicates that attachment of such a unit to the side of an aromatic ring may result in an increased resistance to diffusion, reflecting the size of the whole molecule (see eq 3). In contrast, upon addition of a second or third aromatic ring to an aromatic ring, the possibility of anisotropic diffusion minimizes additional steric contributions to diffusional resistance.

The other probes whose data fall approximately on the line with a slope of 0.13 have shapes which apparently allow for only a fraction of the probe volume to contribute to diffusional resistance, and that contribution grows by about one-eighth to one-seventh of the increase in probe molar volume. That is, for a rigid probe molecule equal in molecular volume to that of the solvent, $\xi_{\mathrm{probe,s}} \approx 1.00$, while for a probe molecule double the molecular volume of solvent, $\xi_{\mathrm{probe,s}} \approx 1.13$, meaning that only 13% of the increase in molecular volume contributes to increased diffusional resistance. As discussed earlier, flexibility and aspect ratio effects can modify these effects to some extent; e.g., pyrene and benzil have virtually the same molar volumes, but pyrene, due to its lower aspect ratio and structural rigidity, has a slightly higher $\xi_{\mathrm{probe,s}}$ value. However, these modifications are small, except possibly in cases of extreme flexibility in very small probes, such as 3,4-hexanedione, for which $\xi_{\mathrm{probe,s}}$ is considerably below 1.

Also included in Figure 12 are literature data, represented by numbers enclosed by open squares, from several polymer−solvent systems, including PS−toluene, PVAc−toluene, and PS−THF. The literature data also seem to split between the two types of behavior describing the data obtained by Taylor dispersion and phosphorescence quenching. In particular, data points 1, 2, and 3, representing hexafluorobenzene in PS−THF,[64] azobenzene in PVAc−toluene[2,65] (ref 2 lists $\xi_{\mathrm{probe,s}} = 0.99$, while ref 65 lists $\xi_{\mathrm{probe,s}} = 1.03$; we use the result from ref 2 as it is the later reference by the same authors), and methyl red in PS−THF (obtained by refitting[67] the data by Landry et al.[66]), respectively, fall near the line with slope 0.13. In contrast, data points 4 and 5, representing azobenzene in PS−toluene[1,106] and methyl red in PS−toluene,[65] lie close to the line of slope unity. (A literature value for methyl red in PVAc−toluene[2,65,107] was not included due to uncertainty regarding the appropriate value of $\xi_{\mathrm{probe,s}}$; see ref 108.)

Data points 1, 2, and 3 are easily resolved with the data obtained by Taylor dispersion and phosphorescence quenching. Hexafluorobenzene (1) in PS−THF[64] would be expected to present a resistance to diffusion no greater than that of naphthalene and anthracene, and given its $\xi_{\mathrm{probe,s}}$ value of 1 and $\tilde{V}(0)_{\mathrm{probe}}/\tilde{V}(0)_{\mathrm{s}}$ value of 1.4, it fits the data set following the line with slope 0.13. Based on the high aspect ratios, it is also possible to resolve the data for azobenzene (2) in PVAc−toluene[2,65] and methyl red (3) in PS−THF[66,67] approximately following the line with slope 0.13.

However, it is more difficult to resolve the data for azobenzene (4) in PS−toluene[1] and methyl red (5) in PS−toluene[65] which fall near the line with slope unity. For methyl red, data obtained here and in an earlier study[66] (reanalyzed here[67]) show that, in PS−THF, $\xi_{\mathrm{probe,s}}$ does not reflect the ratio of probe molar volume relative to that of solvent. In contrast, according to ref 65, methyl red in PS−toluene yields $\xi_{\mathrm{probe,s}} = 1.70 \pm 0.09$, much higher than reported in the PS−THF systems. It is not clear why methyl red should exhibit a much larger PS concentration dependence of its diffusion relative to toluene than to THF. However, lesser, albeit resolvable, solvent effects on $\xi_{\mathrm{probe,s}}$ were also observed in the present study for PtOEP diffusion in PS−THF and PS−cyclohexane systems. Thus, further solvent studies are warranted to address this issue, given that such effects are not considered by free volume theory.

Azobenzene diffusion apparently shows a much greater PS concentration dependence in toluene than in THF, the cause of which is also unclear. Further clouding the issue is that for azobenzene in PVAc−toluene $\xi_{\mathrm{probe,s}} = 0.99$[2] while in PS−toluene $\xi_{\mathrm{probe,s}} = 1.77$.[1] According to the modified free volume theory, $\xi_{\mathrm{probe,s}}$ should be a function of the probe and solvent but not of the polymer (see eq 3). However, the results of Lodge and coworkers[1,2] apparently show a huge effect of polymer. Also confusing is the result they report[1] for aberchrome 540 in PS−toluene solutions. Forced Rayleigh scattering (FRS) data yield $\xi_{\mathrm{probe,s}} = 4.92$. (Given this anomalously high $\xi_{\mathrm{probe,s}}$ value, it was not included in Figure 12.) However, as aberchrome 540 has a molar volume $\tilde{V}(0)_{\mathrm{probe}}$ only 2.3 times as large as that of toluene, $\xi_{\mathrm{probe,s}}$ would not be expected to exceed 2.3 for this system. Thus, it is difficult to resolve this result with any physical picture. A value of $\xi_{\mathrm{probe,s}} = 4.92$ suggests that a critical hole free volume equaling more than twice the size of an aberchrome 540 molecule needs to be open before it can diffuse. Frick et al. have stated that the large volume required for aberchrome diffusion is “in conflict with the physical picture underlying the original Cohen and Turnbull theory, and consequently the Vrentas−Duda model”.[1] They conclude that the aberchrome data as well as the unequal $\xi_{\mathrm{probe,s}}$ values for azobenzene in PVAc and PS solutions in toluene “indicate a failure in one of the fundamental assumptions of free volume theory, namely that diffusion of a molecule can be characterized by a single, constant size parameter” [1] and that “it is entirely reasonable to assume that (the free volume picture) fails for a diffusant as bulky and semirigid as (aberchrome 540).” [1]

However, the latter conclusion may be incorrect, given that aberchrome 540 is not much larger than methyl red and that vastly larger and more rigid probes were used here, e.g., PtOEP, rubrene, and decacyclene, whose diffusion behavior can be explained by modified free volume theory. The extreme difference in $\xi_{\mathrm{probe,s}}$ for azobenzene in PVAc−toluene[2] and PS−toluene[1] does call into question the assumptions of free volume theory. However, as $\xi_{\mathrm{probe,s}}$ values obtained via FRS for *all* probes (aberchrome 540, azobenzene, and methyl red) studied in PS−toluene[1,2,65] seem anomalously high, it would be important to measure $\xi_{\mathrm{probe,s}}$ in PS−toluene via other methods. (With FRS,[1,2,65] the mean of the diffusion coefficients of two isomers of differing shape and polarity is reported; with Taylor dispersion or phosphorescence quenching, such issues do not arise.) Only then will it be possible to determine with confidence the general applicability or failure of the modified free volume theory[7,9,60] or whether there is something symptomatic of toluene relative to THF to cause these results.

It is interesting to note that, with the exception of the anomalous result for aberchrome 540,[1] all $\xi_{\text{probe,s}}$ data from the present and other studies have values below the proposed ceiling value of $\xi_{\text{probe,s}} = 2.14$, based on the argument that $\xi_{\text{probe,s}}$ can be related (by eq 13) to $\xi_{\text{probe,p}}$ and $\xi_{\text{s,p}}$, where $\xi_{\text{s,p}} = 0.466$ for PS–THF solutions and $\xi_{\text{probe,p}}$ is expected to be less than 1. (See the discussion in section A.) Further study investigating a variety of probe–solvent–polymer systems is warranted in order to test the ceiling value hypothesis and to determine whether the $\xi_{\text{probe,s}}$ values were below the ceiling value only as a result of the probes coincidentally chosen for this study.

Finally, when a limited number of probes in PS–THF solutions were considered in another study,[68,69] in particular anthracene, DPA, BPEA, and methyl red, it was concluded via measurements of $D_{\text{probe}}$ for methyl red and of rotational correlation times for the other three probes that the concentration dependencies of the translational diffusion of methyl red and the rotational dynamics of the other probes were the same. An unproven hypothesis in that study was that for a single probe the concentration dependencies of rotational and translational diffusion are identical. Given their results, that would imply that translational diffusion was deemed to be independent of probe size or shape for the four probes, a condition in conflict with the basic tenets of free volume theory and with the results of the present study. From Taylor dispersion measurements, we find that the polymer concentration dependencies of DPA and BPEA translational diffusion at 0–400 g/L PS concentration are equivalent, i.e., $\xi_{\text{probe,s}} = 1.3_5$, and furthermore that they coincide with the concentration dependencies of the rotational dynamics reported in refs 68 and 69, thus providing credence to their hypothesis.[68,69] However, the equivalence of anthracene translational diffusion to that of the other probes, implied in ref 68, is in conflict with the results presented here. For example, at 400 g/L PS concentration, $D_{\text{probe}}/D_{\text{o}}$ for anthracene is about 63% higher than those for DPA and BPEA, and for anthracene $\xi_{\text{probe,s}} = 1.0_9$. Consequently, the results of the present study are consistent with the hypothesis in ref 68 that rotational and translational dynamics of DPA and BPEA in polymer solutions have the same PS concentration dependence but conflict with the conclusion in ref 68 that the microscopic friction coefficient has identical PS concentration dependencies for anthracene, DPA, and BPEA.

## Summary

The most comprehensive study to date of the effects of size, shape, and flexibility on the translational diffusion of small probe molecules in polymer solutions has been completed by Taylor dispersion, which directly yields $D_{\text{probe}}$, and phosphorescence quenching, which yields $k_q$, the concentration dependence of which is identical to that of $D_{\text{probe}}$ for appropriate conditions. As applied here, Taylor dispersion is attractive in its simplicity, requiring only that probes absorb light in a wavelength range where there is little absorbance by polymer or solvent, thereby easily accommodating tests of probe size and shape effects, and allowing for studies in THF solutions with up to 400g/L PS when employing low molecular weight PS. Although limited to a smaller number of probes serving as chromophores or quenchers, phosphorescence quenching allows investigation of a broader range of polymer concentrations and molecular weights.

Data for the PS concentration dependencies of $D_{\text{probe}}$ for 16 probes ranging by a factor of 6 in molar volume were compared to the modified Vrentas–Duda theory[7,9,60] for ternary solutions to obtain the free volume parameter $\xi_{\text{probe,s}}$ for each probe. With the exception of one highly flexible, small probe molecule, 3,4-hexanedione, with a much weaker PS concentration dependence of diffusion than that of the solvent THF, i.e., $\xi_{\text{probe,s}} = 0.6_5$, the results for all probes yielded PS concentration dependencies of $D_{\text{probe}}$ approximately equal to or greater than that of solvent, i.e., for our studies, $0.9 \le \xi_{\text{probe,s}}$. Furthermore, for all probes the PS concentration dependencies of $D_{\text{probe}}$ fell well below both the concentration dependence of inverse macroscopic viscosity and a limiting value of $\xi_{\text{probe,s}} = 2.14$, predicted based on the hypothesis that $\xi_{\text{probe,p}}$ is expected to be less than 1, i.e., for our studies, $\xi_{\text{probe,s}} \le 1.75$. The data fell into two types of behavior: when $\xi_{\text{probe,s}}$ was plotted against $\tilde{V}(0)_{\text{probe}}/\tilde{V}(0)_{\text{s}}$, the vast majority of data fell around a line of slope 0.13, while for two of the probes $\xi_{\text{probe,s}}$ fell on a line of slope unity. The former behavior indicates that for most probes the PS concentration dependence of $D_{\text{probe}}$ can be described by the modified free volume theory[7,9,60] with the understanding that the critical hole free volume for a jump unit for these probes is but a fraction of the probe molar volume and grows slowly with probe molar volume. This may be understood on the basis of shape effects for these probes, which allow for only a fraction of the probe volume to execute a jump into space previously unoccupied by the probe, with the rest of the probe volume moving into space previously occupied by the probe. Probe aspect ratio and flexibility effects were observed, but they were typically small. The latter diffusion behavior with the much stronger PS concentration dependence indicates that aniline and 1-bromonaphthalene have critical hole free volumes for a jump unit which, in comparison to solvent, are in proportion to their volumes; i.e., if solvent has a critical hole free volume for a jump unit equivalent to its volume, then so do the probes. The apparent dichotomy in the probe volume dependence of $\xi_{\text{probe,s}}$ raises the question of whether, as deigned by nature, only two dependencies are possible or whether, by virtue of the probes selected, only these two distinct behaviors are observable. We speculate that the latter is closer to the truth, but studies on more probes, including those that are highly nonplanar or form a homologous series, will be needed in order to answer this question.

A comparison of concentration dependence data with limited temperature dependence data from the literature[2,66] shows a consistency based on the modified free volume picture. This, along with an understanding of the "bimodal" $\xi_{\text{probe,s}}$ data based on a logical interpretation of the modified free volume theory,[7,9,60] indicates that the modified free volume theory for ternary systems, although probably not the last word on the subject, forms an apparently robust picture by which to interpret probe diffusion in polymer solutions. While questions remain about the ability of free volume theory to explain a limited set of data in the literature,[1,2,65] it is possible that diffusion should be measured in these systems via other approaches besides forced Rayleigh scattering before concluding whether there is inconsistency with the free volume picture or whether a change in solvent (from THF to toluene) is enough to cause very dramatic changes in sensitivity of $D_{\text{probe}}$ to polymer concentration. Such studies along with further investigations of effects of solvent and of extremely flexible, small probe molecules such as 3,4-hexanedione, whose very small $\xi_{\mathrm{probe,s}}$ value cannot be resolved by free volume theory (the current free volume picture does not account for flexibility effects), will be needed to understand better the limits of application of the reasonably robust modified free volume theory.

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Based on these hydrodynamic considerations, one might expect a transition in diffusivity near the polymer overlap concentration that no free volume theory could adequately describe. We do not observe such a disparity between Vrentas−Duda theory and our data, although additional measurements below 100 g/L polymer concentration would need to be made in order to reach a more definitive conclusion. Furthermore, comparisons of Fujita free volume theory to the data should be re-evaluated in consideration of recent improvements to the theory (Fujita, H. *Macromolecules* **1993**, *26*, 643).

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