Evidence for Chain Length Dependent Local Ordering Surrounding Perylene Dissolved in Poly(ethylene glycol)

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ABSTRACT: Time-resolved fluorescence anisotropy measurements on dilute solutions of perylene dissolved in poly(ethylene glycol) (PEG) oligomers are carried out as a function of oligomer chain length and temperature. The perylene fluorescence anisotropy decay kinetics are best described by a double-exponential decay law. The temperature dependence of the perylene rotational reorientation dynamics in PEG is exponential activated; however, at the lower PEG chain lengths, the activation energies that describe the perylene rotational reorientation are significantly larger than the activation energy for PEG viscous flow. As the PEG molecular weight increases, the activation energies associated with the perylene rotational motions become equivalent to the activation energy for PEG viscous flow. The principal perylene rotational diffusion coefficients ($D_{\|}$ and $D_{\perp}$) are also a strong function of PEG chain length and temperature. The ratio of the principal diffusion coefficients ($D_{\|}/D_{\perp}$) shows that $D_{\perp}$ is hindered relative to $D_{\|}$ as the PEG chain length increases. These results are complementary to recent work from Goldie and Blanchard on the rotational reorientation dynamics of perylene dissolved in *n*-alkanols. On the basis of our data, we propose a chain length dependent ordering of the PEG oligomers around the perylene molecules that impedes $D_{\perp}$ to a greater extent compared to $D_{\|}$.

Introduction

Many researchers[1] use dielectric relaxation,[2−8] nuclear magnetic resonance spectroscopy,[9−11] electron spin resonance spectroscopy,[12] electronic absorbance,[13−20] second harmonic generation,[21−23] photobleaching,[24−27] and static[28−35] and/or time-resolved fluorescence[1,36−54] to study polymer systems. Time-resolved fluorescence is particularly well suited for investigating polymer dynamics because of its high time resolution.[1,39,41,54,55]

Information from the rotational reorientation dynamics of extrinsic or intrinsic luminescent probe molecules within polymers can yield reasonably detailed insights into probe/polymer dynamics, probe/polymer correlations, and probe/polymer interactions.[1,54,55] This approach is also attractive because the probe size (an adjustable) provides an intrinsic length scale to assess the aforementioned interactions. However, a detailed interpretation of a probe molecule's rotational reorientation dynamics relies on the assumption that the probe itself is simply a noninteracting or weakly interacting bystander within the polymer milieu. While this appears to be the case in most polymer/probe studies,[1,21−27,54] there are reports in which the probe molecule seems to dictate the observed dynamics and the activation energy associated with its own reorientational dynamics.[43,45,53] This disagreement between simple predictive theories and experimental data is sometimes manifest in the activation energy associated with a particular probe motion not being equivalent to the activation energy for polymer viscous flow, E_{η}. In some instances it also appears that luminescent probe molecules that normally behave as *isotropic* rotors when dissolved in ordinary liquids require that their rotational reorientation dynamics be interpreted with *anisotropic* rotor models in polymer systems.[43−45] We have set out to explore this issue in more detail by studying the rotational reorientation dynamics of a well-known *anisotropic* rotor when it is dissolved at low concentration within oligomers of varying chain length.

Perylene was chosen as the probe molecule because it has a high fluorescence quantum yield, its excitation and emission maxima are well separated from most polymer absorbance features, its fluorescence intensity decay kinetics are single exponential, and its excited-state fluorescence lifetime is not particularly solvent and/or temperature dependent.[56−58,62] In normal liquids, perylene behaves as a oblate ellipsoid (i.e., an anisotropic rotor),[56−62] and its decay of fluorescence anisotropy is well-described by two discrete rotational reorientation times. Given these facts, we have asked how the perylene rotational reorientation dynamics are affected when it is dissolved within a series of neat oligomer solutions as a function of oligomer chain length and sample temperature.

Poly(ethylene glycol) (PEG) was chosen as the oligomer because perylene is soluble in it, it does not absorb significantly in the mid-UV, it is molten at room temperature so solutions are easy to prepare, a large range of chain lengths are commercially available, and its termini can from hydrogen bonds. PEG is also used in ointments, pharmaceutical preparations, lubricants, solvents, cosmetics, and plasticizers and as a treatment for fecal impaction and severe constipation.[63−65]

Theory

When a fluorophore is excited with polarized light, its emission is also polarized.[55,58] However, fluorophore rotational reorientation leads to a time-dependent decay in the emission depolarization.[55,58] By measuring the decay of the fluorescence anisotropy, one can obtain information on the fluorophore's rotational reorientation

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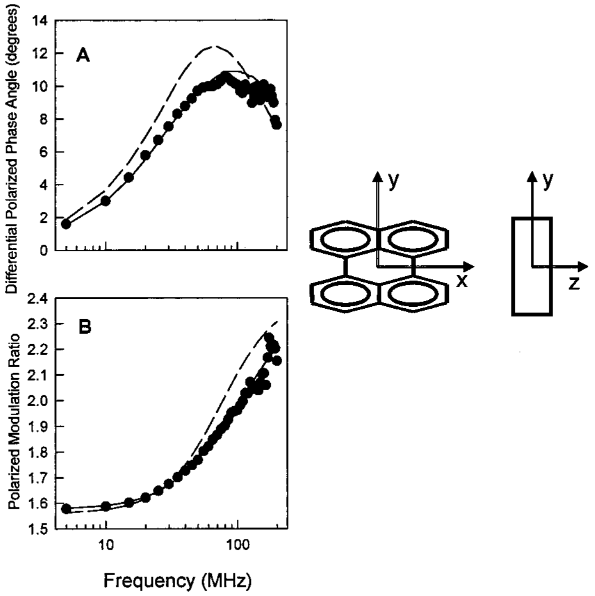

Figure 1. Frequency-domain fluorescence data (●) and fits for perylene dissolved in PEG (MW = 200 g/mol) at − 9 °C. (Panel A) Differential polarized phase angle. (Panel B) Polarized modulation ratio of the same sample. Fits to single- (- - -) and double-exponential (—) decay laws are shown. (Inset) The perylene structure and its in-plane, $D_{\parallel}$, and out-of-plane, $D_{\perp}$, rotational motions relative to a 3-D Cartesian coordinate system.

dynamics and the local microenvironment surrounding the fluorophore.[54,55,58]

For a general ellipsoid of revolution, the time-resolved fluorescence anisotropy decay, $r(t)$, is described by a triple-exponential decay law.[59−62,66,67] The perylene electronic transition moments lie within the ring plane, and it behaves as an oblate ellipsoid of revolution.[59−62,66,67] Thus, $r(t)$ is given by

$$r(t) = r_0\sum_{i=1}^{2}\beta_i \exp(-t/\phi_i) \tag{1}$$

where the β_i terms are simple trigonometric functions of the angles between the absorption and emission transition moments within the perylene molecular framework.[59,60,67] The β_i terms are independent of solvent, temperature, and viscosity, depending only on the excitation wavelength which affects the angular orientation between the transition moments.[59,60] The observed rotational correlation times, ϕ_i, are functions of the fluorophore principal diffusion coefficients (D). For perylene, these are given by

$$\phi_1 = (6D_{\perp})^{-1} \tag{2}$$

$$\phi_2 = (2D_{\perp} + 4D_{\parallel})^{-1} \tag{3}$$

In these expressions, $D_{\perp}$ denotes the perylene rotational diffusion coefficient about an axis (x or y in Figure 1) that is perpendicular to the molecular symmetry axis (z), and $D_{\parallel}$ represents perylene rotational diffusion about the symmetry axis (z in Figure 1). The magnitude of these diffusion coefficients depends on the solvent viscosity, temperature, the ellipsoid's dimension and shape, and the extent to which the solute−solvent interact with one another.[67,68]

In the current work, we perform multifrequency differential polarized phase and polarized modulation ratio experiments on perylene dissolved in four neat PEG oligomers to determine (1) the perylene fluorescence anisotropy decay kinetics (ϕ_1 and ϕ_2) and (2) the principal diffusion coefficients ($D_{\parallel}$ and $D_{\perp}$) as a function of PEG chain length and temperature. We use this information to determine how the activation energies for perylene rotational reorientation compare to the activation energy for PEG viscous flow and elucidate how the perylene principal rotational diffusion coefficients are influenced by the PEG chain length.

Experimental Section

PEG (molecular weights 200, 300, 400, and 600 g/mol) and perylene were purchased from Sigma and used as received. Ethanol (200 proof) was from Pharmco. All reagents were of the highest purity available, and they were used without further purification.

Perylene-Doped Polymer Sample Preparation. A 1 mM stock solution of perylene was prepared in 95% ethanol/water. To make the perylene/PEG samples, an appropriate amount of the perylene stock solution was pipetted into clean dry glass vials. The vials were then placed in a 100 °C oven for 1 h to ensure complete solvent evaporation. PEG was then added directly into each vial, and the samples were mixed for several weeks. The final perylene concentration in the PEG solution was 20 μM. There was no evidence of perylene aggregation.

Instrumentation. All time-resolved fluorescence measurements were made with a SLM AMINCO 48000 MHF frequency-domain fluorometer (Spectronic Instruments). The excitation source was the 363.8 nm line from a CW argon ion laser (Coherent model Innova 90-6). The perylene fluorescence was passed through an emission polarizer and a 420 nm long-pass filter. The Pockels cell modulator was driven at 5 MHz, and data were collected from 5 to 200 MHz at 5 MHz intervals.

The sample temperature was regulated (±0.1 °C) by using a Lauda RLS-6 circulating bath. The actual sample temperature was determined prior to each measurement by placing a calibrated solid-state thermocouple (Cole-Palmer) directly into the sample.

The PEG viscosities were measured by using a cone plate viscometer (Brookfield model DV-II). The viscometer sample temperature was regulated (±0.2 °C) with a Haake model F3 circulating bath.

All experiments were performed at least five times on discrete samples. Results are reported as the average and associated standard deviation of these individual experiments.

Results and Discussion

In a separate experiment we determined that the perylene excited-state fluorescence lifetime in PEG is independent of oligomer chain length and temperature ($\tau = 4.81 \pm 0.03$ ns).

Typical frequency-dependent differential polarized phase angle and polarized modulation ratio data for perylene dissolved in PEG 200 at −9 °C (●) are shown in Figure 1 along with the best fits of these data to isotropic (- - -) and anisotropic rotor models (—). The fit between the data and the anistropic rotor model results in a lower χ^2 value (1.10) relative to the isotropic rotor model ($\chi^2 = 66$).

To more accurately determine the perylene kinetic parameters, we performed simultaneous global analysis[69] on *all* our available perylene data files as a function of sample temperature and PEG chain length. Specifically, we set the perylene excited-state fluorescence lifetime and limiting anisotropy to values that we determined from separate experiments (4.81 ns and 0.34, respectively), β_1 was linked across all the data files

Table 1. Recovered Temperature-Dependent Rotational Reorientation Times (ϕ_i) and Principal Diffusion Coefficients (D_i, s^{-1}) for Perylene Dissolved in PEG[a,b]

T (°C)	ϕ_1 (ns)	ϕ_2 (ns)	$D_{\parallel} \times 10^{-8}$	$D_{\perp} \times 10^{-7}$
		PEG 200		
−9.0	10.6	1.67	1.42	1.57
−5.0	6.98	1.30	1.80	2.39
0.0	4.63	0.81	2.90	3.60
5.0	3.04	0.43	5.60	5.48
10	2.57	0.29	8.27	6.49
		PEG 400		
10.0	4.63	0.58	4.14	3.60
15.0	4.52	0.63	3.81	3.69
20.0	2.56	0.28	8.60	6.51
25.0	2.31	0.28	8.66	7.22
30.0	1.49	0.14	17.7	11.2
		PEG 300		
−5.0	10.1	1.36	1.76	1.65
0.0	5.73	0.84	2.83	2.91
5.0	4.05	0.81	2.90	4.12
10.0	3.31	0.34	7.08	5.04
15.0	2.08	0.35	6.70	8.01
20.0	1.96	0.14	18.0	8.50
		PEG 600		
20.0	24.5	2.61	0.928	0.680
30.0	15.8	1.72	1.40	1.05
40.0	10.2	1.09	2.21	1.63
50.0	6.58	0.69	3.51	2.53

[a] The imprecision in the ϕ results is ≤8%. [b] The imprecision in the D results is ≤12%.

Table 2. Temperature-Dependent PEG Viscosities (cP)[a]

temp (°C)	PEG 200	PEG 300	PEG 400	PEG 600
24.8	47.7 ± 0.1	70.6 ± 0.1	87.7 ± 0.2	ND
30.0	36.2 ± 0.1	50.4 ± 0.2	65.6 ± 0.2	95.4 ± 0.2
35.0	30.0 ± 0.1	41.1 ± 0.2	50.7 ± 0.1	75.3 ± 0.2
40.0	24.4 ± 0.1	33.7 ± 0.2	40.5 ± 0.1	60.7 ± 0.1
45.0	20.0 ± 0.1	27.5 ± 0.2	33.1 ± 0.1	48.1 ± 0.1
50.0	ND	ND	ND	39.4 ± 0.1

[a] ND = not determined.

Table 3. Recovered Experimental Activation Energies (kJ/mol)

	activation energies (kJ/mol)				
PEG MW	perylene ϕ_1	perylene ϕ_2	perylene $D_{\perp}$	perylene $D_{\parallel}$	PEG η
200	47.3 ± 4.0	59.8 ± 3.9	47.3 ± 4.0	60.4 ± 4.2	33.4 ± 1.0
300	42.9 ± 3.9	55.7 ± 8.2	42.8 ± 3.9	56.1 ± 8.8	35.9 ± 2.0
400	42.8 ± 6.6	52.6 ± 11.6	41.8 ± 6.6	53.0 ± 11.8	38.1 ± 1.0
600	34.5 ± 0.7	35.0 ± 1.3	34.4 ± 0.7	35.0 ± 1.4	36.1 ± 0.3

because the β_i terms change only with the excitation wavelength,[59,60] and we allowed ϕ_1 and ϕ_2 to float. The recovered global χ^2 was 1.08. Other models and linking strategies were also tested, but none yielded a statistically relevant improvement in χ^2. Table 1 reports the recovered perylene rotational reorientation times in the four PEG samples as a function of temperature.

A common strategy[1,21−27,43,45,53,54] that is used to interpret temperature-dependent probe molecule rotational reorientation dynamics within polymers relies on a comparison between the activation energy for rotation reorientation, $E_{a,r}$, and the activation energy for polymer viscous flow, $E_{a,\eta}$. Toward this end, we determined the viscosity (η) of each of our PEG samples as a function of temperature (Table 2). We then used the data in Tables 1 and 2 to compute the activation energy for polymer viscous flow and rotational reorientation by using the Arrhenius relationship. Table 3 reports all the associated activation parameters.

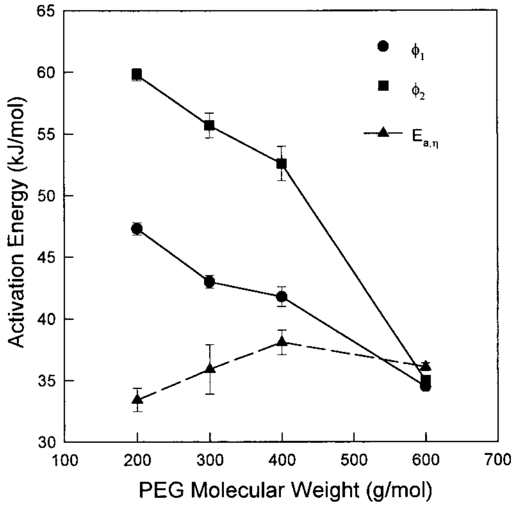

Figure 2. Comparison of the activation energies associated with the perylene rotational reorientation times ϕ_1 (●) and ϕ_2 (■) to the activation energy for PEG viscous flow (▲) as a function of PEG chain length. The lines between points are an aid for the eye.

Figure 2 illustrates the effects of PEG chain length/molecular weight on the $E_{a,r}$ associated with the perylene ϕ_1 (●) and ϕ_2 (■) and compares these values to the actual PEG $E_{a,\eta}$. Several aspects of these results merit additional discussion. First, although both perylene rotational reorientation events appear to be exponentially activated, the recovered $E_{a,r}$ values are, in the lower molecule weight PEG samples, substantially *greater* than $E_{a,\eta}$ (▲). Second, as the PEG oligomer chain length increases, the $E_{a,r}$ associated with each perylene reorientation event appears to converge to the actual PEG $E_{a,\eta}$. Third, the $E_{a,r}$ associated with ϕ_2 is substantially larger than the $E_{a,r}$ associated with ϕ_1 at the lower PEG chain lengths.

The observed rotational reorientation times (ϕ_1 and ϕ_2) are, of course, functions of the perylene principal diffusion coefficients $D_{\perp}$ and $D_{\parallel}$ (eqs 2 and 3). The temperature dependence of the recovered $D_{\perp}$ and $D_{\parallel}$ values (Table 1) is also exponentially activated, and the observed energetics appear very similar (results not shown) to the ϕ_1 and ϕ_2 results that we have presented in Figure 2. This is not particularly surprising because ϕ_1 and ϕ_2 are dominated by $D_{\perp}$ and $D_{\parallel}$, respectively. The key features of the $D_{\perp}$ and $D_{\parallel}$ results are as follows. First, the activation energy associated with in-plane rotational diffusion about the perylene z axis ($E_{a,\parallel}$) is substantially *larger* than the corresponding activation energy associated with out-of-plane rotational diffusion about the x or y axis ($E_{a,\perp}$) at the lower PEG chain lengths. For example, when perylene is dissolved in the shorter chain PEG oligomers, it is ~13 kJ/mol more energetically demanding for perylene to reorient around its z axis relative to its x and y axis. Second, at the lower PEG chain lengths, $E_{a,\parallel}$ and $E_{a,\perp}$ exceed $E_{a,\eta}$ by between 14 and 27 kJ/mol. Finally, as the PEG oligomer chain length increases, $E_{a,\parallel}$ and $E_{a,\perp}$ become less dissimilar, and they each converge to $E_{a,\eta}$. These results imply that the PEG chain length influences the energetics associated with the perylene in-plane and out-of plane dynamics differently.

Several authors have previously explored the notion of solvent ordering around anisotropic rotors and its influence on solute rotational reorientation dynamics.[70,71] For example, Sanders and Wirth,[70] in studies

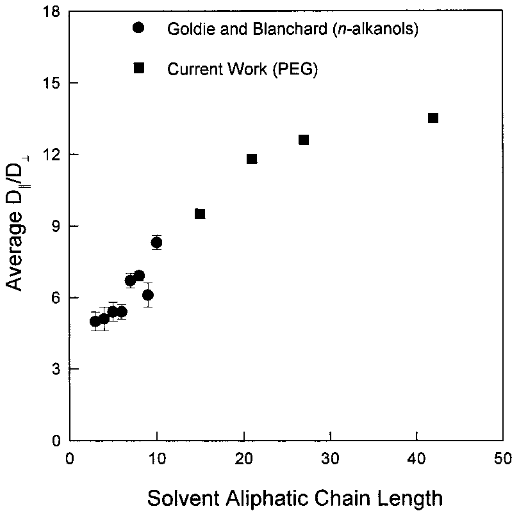

Figure 3. Effects of solvent chain length on the perylene $D_{\parallel}/D_{\perp}$ in liquid *n*-alkanols (●) and PEG (■).

Table 4. Reported Perylene $D_{\parallel}/D_{\perp}$ Values in Various Liquid Solvents

author(s), year	λ_{ex} (nm)	solvent(s)	$D_{\parallel}/D_{\perp}$
Zinsil, 1977	395	parafin	10 ± 2
Barkley et al., 1981	430	glycerol	10 ± 1
Lakowicz et al., 1985	442	propylene glycol	8.8
Christensen et al., 1986	257	glycerol/water	6.5 ± 0.3
Piston et al., 1989	442	glycerol	22 ± 10
		propylene glycol	12.8 ± 1.5
		both	11.8 ± 1.3
Brocklehurst and Young, 1995	430	methylcyclohexane	6.5
		squalane	12.7

of tetracence dissolved in ethylene glycol and *n*-dodecanol, reported that "solvation structure" can play a role in solute rotational reorientation dynamics. More recently, Goldie and Blanchard reported on the rotational reorientation dynamics of perylene dissolved in a series of *n*-alkanols.[71] The conclusion from this work is that there is a Langmiur-type "ordering" of the solvents surrounding perylene that is solvent chain length dependent.

To explore this solvent ordering issue in more detail, we have compared the recent results from Goldie and Blanchard (●)[71] on perylene dissolved in *n*-alkanols to the average perylene $D_{\parallel}/D_{\perp}$ that we have found in the PEG samples (■). The results are presented in Figure 3 as the experimental $D_{\parallel}/D_{\perp}$ vs "solvent" chain length. Table 4 collects the reported $D_{\parallel}/D_{\perp}$ values for perylene dissolved in several liquids.[57,59,60,62,66,72] The results presented in Table 4, especially those from Piston et al.[57] and Brocklehurst and Young,[72] and our new results for perylene dissolved in PEG argue for a solvent effect on the perylene $D_{\parallel}/D_{\perp}$. Our results are also in line with results reported by Sanders and Wirth[70] for tetracene dissolved in ethylene glycol and *n*-dodecanol where these authors found anomalously fast tetracene rotational reorientation in the molecular plane in ethylene glycol relative to *n*-dodecanol and attributed this result to differences in the local solvation environment.

Other work on perylene dissolved in 1,2-propanediol and perylene associated with 3-(dimethylamino)propyl chloride hydrochloride (DMPC) vesicles shows a similar increase in the $D_{\parallel}/D_{\perp}$ when one changed the "solvent" from 1,2-propanediol to DMPC vesicles.[73] van Zandvoort et al.[74] attributed this particular result to the planar perylene molecules distributing into an oriented population within a lipid bilayer such that the perylene molecules undergo a highly anisotropic motion with $D_{\parallel} \gg D_{\perp}$.[74] On the basis of our results and these previous offerings,[70-73] we propose that there is a similar type of oligomer ordering surrounding the individual perylene molecules when they are dissolved in PEG oligomers which gives rise to the increasing $D_{\parallel}/D_{\perp}$ ratio and differences in the energetics of the individual motions with increasing PEG/solvent chain length akin to the Langmiur ordering proposed by Goldie and Blanchard[71] and/or the ordering suggested by Sanders and Wirth.[70] This ordering appears to imped the perylene in-plane motion more relative to the out-of-plane motion in the shorter chain oligomers.

Conclusions

The perylene rotational reorientation dynamics when it is dissolved in neat PEG oligomers is well-described by a two-term rate law at all oligomer molecular weights and temperatures investigated. The perylene rotational events are exponentially activated over the temperature range studied. However, analysis of the actual perylene principal rotational diffusion coefficients demonstrates that the rotational diffusion around the perylene *z* axis (Figure 1) and around the *x* and *y* axis have different energetics, and they do not behave in the same way as the PEG chain length is changed. We suggest that these results arise from local differences in the perylene molecule's solvation in PEG that is modulated by the PEG and the PEG chain length. This interpretation is consistent with recent work by Goldie and Blanchard[71] on perylene dissolved in *n*-alkanols and work by Sanders and Wirth[70] on tetracene dissolved in ethylene glycol and *n*-dodecanol.

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