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# Slow-Mode Diffusion in Semidilute Solutions Examined by Dynamic Light Scattering

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ABSTRACT: A slow relaxation, which is 1–2 orders of magnitude slower than that corresponding to self-diffusion, has been investigated in semidilute polymer solutions by dynamic light scattering. The slow relaxation is considered to reflect the translational diffusion of intermolecularly entangled coils in this concentration regime. Five fractions of narrow-distribution poly(ethylene oxide) ($M = 4 \times 10^4$ to $6.6 \times 10^5$) were used in aqueous solution. Measurements were made at $\theta = 90°$ of diffusion coefficients and the amplitudes of the fast and slow components, resolvable using a suitable choice of sampling times with cumulant analysis, as a function of concentration and temperature. The molar mass/concentration regime covers the transition region where the slow relaxation is initially observed up to conditions where it is a dominant feature of the autocorrelation function. The amplitude of the slow mode increased with increasing concentration and the relative amplitude (slow/fast) was found to slowly decrease with increasing temperature. Further measurements were made on semidilute solutions of polystyrene ($M = 1.1 \times 10^5$) in the $\Theta$ system cyclopentane (20.4 °C); only a single-exponential relaxation could be detected in the concentration interval investigated (≤17% (w/w)).

## Introduction

There has been growing interest in competing "fast" and "slow" modes of relaxation observed in dynamic light scattering measurements, which are a striking feature of the dynamics of semidilute solutions of monodisperse polymers.[1-9] These modes are detected experimentally by the departure of the photocount autocorrelation function from the single-exponential characteristic of dilute solutions; there is, for example, a pronounced increase of the variance of the average decay rate with increasing concentration. Chu and Nose[1] made the first detailed description of the different modes and used a histogram method to analyze the autocorrelation function and establish the existence of two modes in the system polystyrene/*trans*-decalin. In a subsequent contribution[2] they approximated the experimental curves with a squared sum of two exponentials. Mathiez et al.[3] and Nishio and Wada[4] used a similar approach. There has, however, been substantial disagreement between authors regarding the source of the slow relaxation. Chu and Nose[2] concluded that in the semidilute region, the slower mode (here, $\bar{\Gamma}_s$ is the line width of the slow mode and $\bar{\Gamma} = \bar{D}\cdot\mathbf{q}^2$, where $\mathbf{q}$ is the scattering vector: $\mathbf{q} = (4\pi n/\lambda)\sin(\theta/2)$) is related to translation of the entangled polymer, including a finite lifetime of the network (disentanglement) and which at infinite dilution would correspond to translational diffusion of the coil itself. The faster mode ($\bar{\Gamma}_f$) corresponds to local internal motions and pseudogel motions. It was noted that $\bar{\Gamma}_s$ decreases with increasing concentration, while $\bar{\Gamma}_f$ increases. The data thus involve a resolvable composite of fast and slow components but their separation was found to be difficult. The whole picture is complicated by the necessity of defining the dynamical regime (in the $\mathbf{q}\cdot R_G$–$C/C^*$ plane) in which the measurements in question have been made[13]—a feature that is frequently neglected ($R_G$ is the radius of gyration and $C^*$ is the concentration of incipient overlap). A recent review of these concepts as applied to diffusion (and sedimentation) has been given by Nyström and Roots.[10]

Mathiez et al.[3] described measurements on semidilute solutions of poly-A and polystyrene and examined the roles of concentration, molar mass, and solvent quality on observable fast and slow modes and their interrelationship. They attributed the slow mode to transient knots which diminish in number as time elapses after preparation of a solution. Nishio and Wada[4] considered a slow relaxation in polystyrene in 2-butanone to represent diffusion of the "whole polymer" which becomes slower as the concentration and solution viscosity increase.

More recently, workers have[8,9] used a judicious choice of sampling times to obtain a more complete separation of fast and slow relaxations and make an identification of a slow component with the self-diffusion coefficient ($D^*$). The latter identification was tenuous, however, since it rested primarily on the negative concentration dependence, which had not been expected in a good solvent, but it was not validated by a comparison with experimental $D^*$ values.

Brown et al.[11] subsequently made dynamic light scattering and pulsed field gradient NMR measurements on several narrow-distribution fractions of poly(ethylene oxide) in semidilute aqueous solutions. Comparison of the apparent diffusion coefficients derived from the slow relaxation with self-diffusion coefficients showed that the former are between one and two orders of magnitude slower than self-diffusion but have a qualitatively similar concentration dependence within the semidilute region.

The present paper comprises a more detailed extension of the earlier report.[11] It describes measurements on PEO fractions in aqueous solution, at various concentrations and

Table I

| type | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ | $[\eta]/(\mathrm{dL\ g^{-1}})$ |
|---|---|---|---|
| SE-5 | 40 000 | 1.03 | 0.639 |
| SE-8 | 73 000 | 1.02 | 0.930 |
| SE-15 | 148 000 | 1.04 | 1.51 |
| SE-30 | 278 000 | 1.05 | 2.35 |
| SE-70 | 661 000 | 1.10 | 4.18 |

temperatures, and also on polystyrene in a Θ solvent, cyclopentane (20.4 °C). The poly(ethylene oxide)/water system is particularly suitable for studying the slow relaxation since it manifests itself at much lower concentrations than with, for example, polystyrene in a good solvent such as benzene.[12] The molar mass of the samples and experimental conditions were chosen so that measurements were in practically all cases confined to the $\mathbf{q}{\cdot}R_g < 1$ and $C/C^* > 1$ sector[13] and are thus largely uncomplicated by internal motions of the polymer coil.

## Experimental Section

**Materials and Methods. Polymers.** Narrow-distribution poly(ethylene oxide) (PEO) fractions were obtained from Toya Soda Ltd., Tokyo, Japan (Table I). Polystyrene ($M = 1.1 \times 10^6$, $\bar{M}_w/\bar{M}_n < 1.06$) was obtained from Pressure Chemical Co., Pittsburgh, Pa.

**Solvents and Solutions.** Deuterium oxide (99.8% D) was obtained from Norsk Hydro, Rjukan, Norway. Measurements on PEO were made in $D_2O/H_2O$ (50:50) since this was the preferred solvent for pulsed field gradient NMR and sedimentation measurements[11,14] previously performed on these fractions.

Measurements on polystyrene were made in cyclopentane obtained from Merck (puriss). All solutions were prepared by weighing and corrections made for moisture content of the poly(ethylene oxide) samples.

**Dynamic Light Scattering and Data Treatment.** The experimental arrangement has been described previously[15] and the main features only are summarized here.

The light source was a Coherent Radiation, Model CR-4, argon ion laser containing a quartz etalon frequency stabilizer in the cavity to ensure single-mode operation at 488 nm. The detector system comprised an ITT FW 130 photomultiplier, the output of which was digitized by a Nuclear Enterprises amplifier/discriminator system. A Langley-Ford 128-channel autocorrelator was used to generate the full autocorrelation function of the scattered intensity. All experiments were performed in the homodyne mode. The correlator was interfaced to a Luxor ABC computer, programed to calculate the normalized full photon counting time correlation function, and the data were stored on floppy disks. The measurements were made at $\theta = 90°$ and 25 °C except where otherwise specified. The solutions were continuously and slowly filtered through a 0.22-μm Millipore filter in a closed-circuit flow-cell assembly and finally transferred to rectangular quartz measurement cuvettes. Aqueous solutions of polymers frequently pose special problems in light scattering due to the formation of aggregates or the presence of dust. The absence of dust or aggregates in the present systems was checked by measurement of the angular dependence of the scattering intensity. After the usual angle correction, an angular-independent photoncount was obtained.

The full photon counting time autocorrelation function was analyzed by the method of cumulants.[16] Thus $\ln/g^{(2)}(\tau) - 1/$ vs. $\tau$ was fitted with appropriate weighting in a linear regression program to a second-order equation. The first coefficient equals $-2\bar{\Gamma}$ and the second $\mu_2$, where $\bar{\Gamma}$ is the average decay rate ($\bar{\Gamma} = \bar{D}{\cdot}\mathbf{q}^2$) and its variance is $\mu_2/\bar{\Gamma}^2$. Here, with $\mathbf{q}{\cdot}R_G < 1$, $\bar{D}$ should correspond to the center of mass translational diffusion coefficient.

The intensity correlation function was in most cases clearly the sum of two exponential functions, where the Γ values were in the ratio of approximately 100:1. It was thus necessary to make two experiments on each solution using sampling times differing by a factor ≥100. The sampling time was chosen so that the 120 channels covered 2–4 relaxation times in the observed exponential process. In the short sampling time experiment the "experimental" base line was used; the correlator also allows the last 8 channels to be delayed so that the last channel corresponds to a delay time of 256 channels. In the long sampling time experiment the extended base line was used. With the slow process it was necessary to discard the data for the shortest correlation times; thus the first ten points were rejected. From the intercepts of the cumulant treatment, the amplitudes of the fast and slow components could be estimated. These are designated $A_f$ and $A_s$.

## Results and Discussion

**Concentration Dependence of Diffusion.** The primary data are summarized in Table II. Autocorrelation functions for short (0.5 μs) and long (50 μs) sampling times for a semidilute solution of PEO ($M = 0.73 \times 10^5$) are shown in Figure 1. (The sampling times usually differed by a factor of 100, but this depended on the system; its

Table II
Diffusion Coefficients and Relative Amplitudes for the Fast and Slow Relaxations in Poly(ethylene oxide) Aqueous Solutions at 25 °C

|  | $C/(\mathrm{kg\ m^{-3}})$ | $C/C^{*a}$ | fast $D \times 10^{11}/$ $(\mathrm{m^2\ s^{-1}})$ | slow $D \times 10^{11}/$ $(\mathrm{m^2\ s^{-1}})$ | $A_s/A_f$ |
|---|---|---|---|---|---|
| PEO 40 ($M = 4.0 \times 10^4$), $q{\cdot}R_G = 0.22$ | 14.0 | 0.9 | 3.73 | 11.5 | 0.1 |
|  | 20.6 | 1.3 | 4.05 | 9.3 | 0.1 |
|  | 34.7 | 2.2 | 5.28 | 5.8 | 0.1 |
| PEO 73 ($M = 7.3 \times 10^4$), $q{\cdot}R_G = 0.30$ | 4.8 | 0.4 | 2.09 | 25.9 | 0.3 |
|  | 10.2 | 0.9 | 2.46 | 16.0 | 0.3 |
|  | 18.9 | 1.8 | 2.48 | 6.3 | 2.3 |
|  | 36.5 | 3.4 | 3.30 | 2.6 | 4.0 |
|  | 53.0 | 4.9 | 4.31 | 1.2 | 4.0 |
| PEO 150 ($M = 1.48 \times 10^5$), $q{\cdot}R_G = 0.45$ | 3.2 | 0.5 | 1.66 |  |  |
|  | 6.0 | 0.9 | 1.78 | 11.2 | 0.2 |
|  | 10.5 | 1.6 | 2.26 | 6.2 | 1.0 |
|  | 19.9 | 3.0 | 2.52 | 2.4 | 1.5 |
|  | 25.6 | 3.9 | 2.63 | 1.7 | 4.0 |
|  | 36.5 | 5.5 | 2.70 | 1.2 | 9.0 |
| PEO 280 ($M = 2.78 \times 10^5$), $q{\cdot}R_G = 0.64$ | 10.6 | 2.5 | 1.72 | 6.5 | 0.4 |
|  | 19.0 | 4.5 | 2.47 | 1.4 | 0.6 |
|  | 36.8 | 8.6 | 3.03 | 0.3 | 4.0 |
| PEO 660 ($M = 6.61 \times 10^5$), $q{\cdot}R_G \sim 1.0$ | 3.6 | 1.5 | 1.07 | 8.3 | 0.1 |
|  | 5.5 | 2.3 | 1.30 | 3.3 | 0.7 |
|  | 9.0 | 3.8 | 1.21 | 1.4 | 4.5 |
|  | 18.3 | 7.6 | 1.75 | $2.9 \times 10^{-14}$ | 19.0 |
|  | 37.4 | 15.6 | 2.55 | $3.7 \times 10^{-15}$ | — |

[a] $C^* = [\eta]^{-1}$.[21,22]

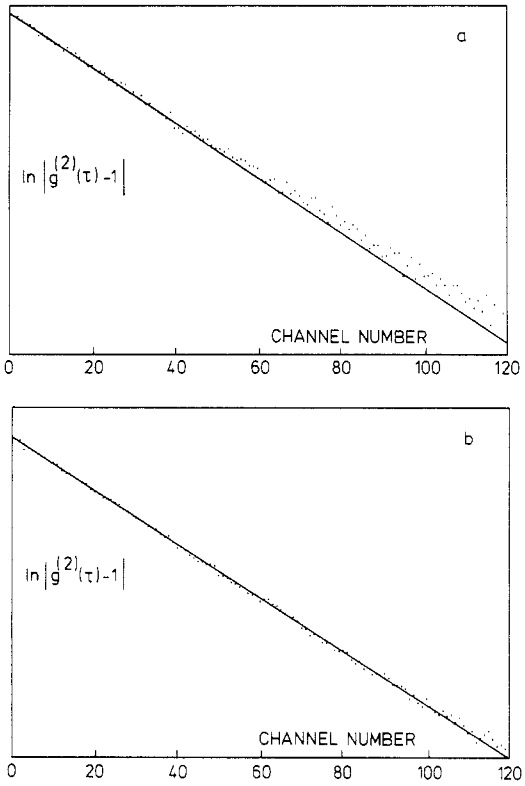

**Figure 1.** Plots of normalized autocorrelation function in semilogarithmic form for PEO 73 at a concentration of 36.5 kg $m^{-3}$ using the method of cumulants:[16] (a) 0.5 $\mu$s per channel; (b) 50 $\mu$s per channel. The relative amplitude is $A_s/A_f \sim 5$.

selection was governed by the consideration that the 120 channels of the autocorrelator should cover between 2 and 4 relaxation times in the exponential decay under consideration. The data in Figure 1 are typical of the fractions of lower molar mass at the higher concentrations. Although a simple exponential was usually a reasonable approximation for the slow relaxation, it is not suggested that the latter always reflects a single relaxing entity. In many cases, particularly at the low concentrations, the scatter as well as the more difficult separation of the fast and slow processes allows only a good estimate of the relaxation frequency. With increasing molar mass it again becomes increasingly difficult to separate the fast and slow modes. Measurements were repeated at $\theta = 68°$ and 112° and, within experimental error, the same diffusion coefficient was found for the corresponding fast (and slow) modes independent of angle.

The results for poly(ethylene oxide) systems are shown in Figure 2, together with earlier data[14] for these fractions for self-diffusion obtained with Fourier transform pulsed field gradient NMR and dynamic light scattering. At infinite dilution the fast-mode data coincide with the extrapolation from the self-diffusion data, as expected. It may be noted that PFG-NMR self-diffusion inherently monitors purely geometric displacements of individual molecules during a time typically of the order 10–2000 ms (here 240 ms). For the higher molar masses ($M_{PEO}$ 2.8 × $10^5$ and 6.6 × $10^5$) the fast mode shows a pronounced curvature in plots of $D$ vs. $C$. This tendency was noted and discussed by Patterson and co-workers.[17] For these fractions the relationship $D_f \sim C^{0.47}$ is applicable, in comparison with a predicted scaling exponent of 0.75 for the cooperative diffusion coefficient; see also ref 10. Preliminary measurements show, however, that $D_{fast}$ is considerably lower than values of $D_{CGD}$ obtained using the concentration gradient technique, which is known to yield coefficients corresponding to center of mass diffusion. Several possibilities exist for this divergence, which will

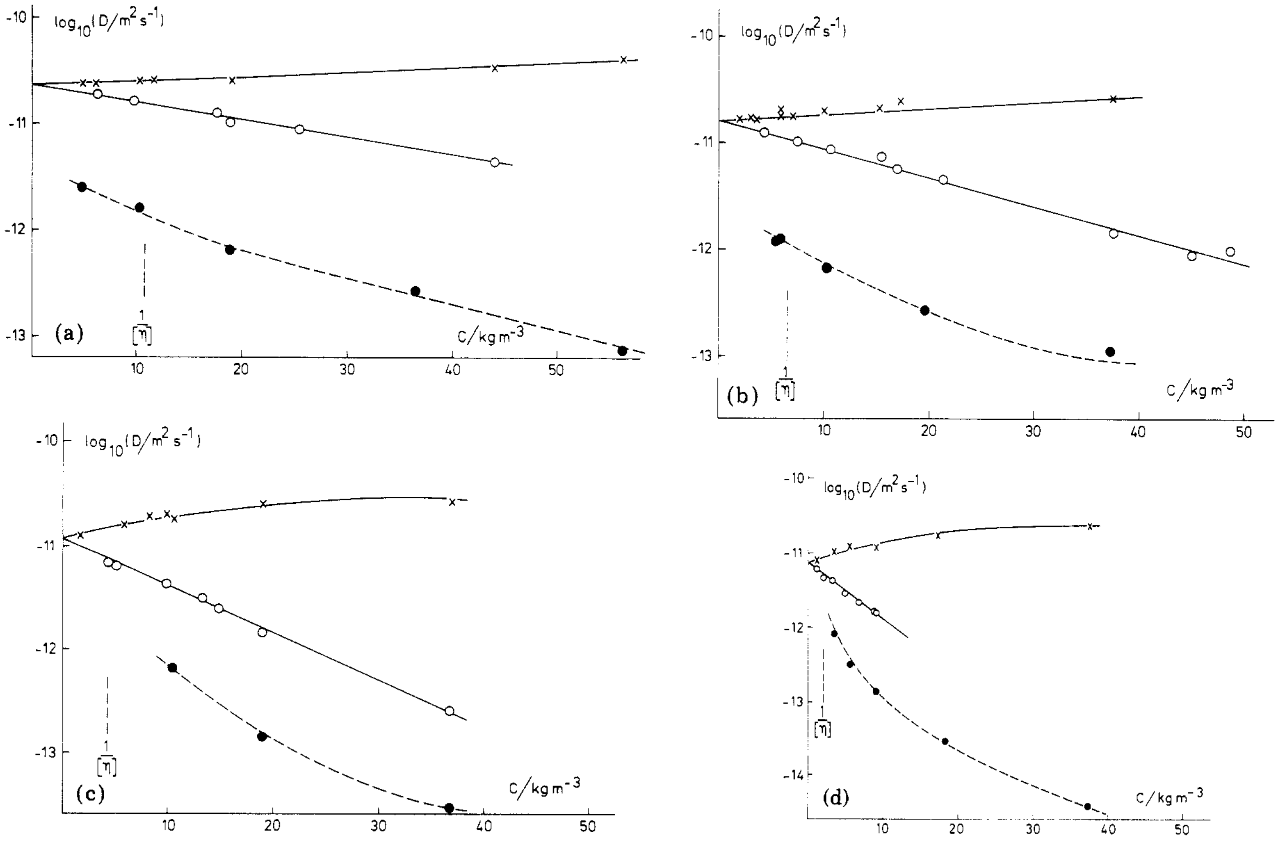

**Figure 2.** Semilogarithmic plots of $D$ vs. $C$ for PEO fractions in aqueous solution: (a) 73 000; (b) 148 000; (c) 278 000; (d) 661000. Fast-mode QELS (×); slow-mode QELS (●); pulsed field gradient NMR (○). Values of $C^* = [\eta]^{-1}$ are shown; this parameter has frequently been used[31] for the concentration of first overlap.

be discussed in a forthcoming contribution.

As noted previously,[11,14] a simple exponential decay of the self-diffusion coefficient $D^*$ is observed with increasing concentration at all values of $M$; the concentration dependence also increases with increasing $M$, which strikes one as being intuitively reasonable. These data are thus internally consistent in that when normalized and plotted as log $(D^*/D_0)$ vs. $C/C^*$, they yield a common plot[12] with a limiting slope of −1.25. This behavior differs qualitatively from, and is difficult to reconcile with, that observed by Lĝer et al.,[19] where the molecular weight dependence is found to be independent of concentration in the semidilute region and to yield $D \sim M^{-2.05}$. The molar mass of the present samples is, however, probably too low to allow a test of scaling laws.

There are comparatively few self-diffusion data in the literature to either contradict or confirm the scaling result $D^* \sim C^{-1.75}$. Most of these data reveal a disturbing curvature in the log $D^*$ vs. log $C$ plots; see, for example, ref 18–20.

The bimodal autocorrelation function appears first as a feature of the semidilute region. The slow mode has a strong negative concentration dependence which approximately parallels the experimental self-diffusion data and this suggests a reptative mechanism above $C^*$. It may be noted that the log $D$ vs. log $C$ plots are linear but that the slope increases with increasing molar mass. Thus the following relationships apply: $D_{\text{slow}} \sim C^{-1.3}$ for $M = 1.5 \times 10^5$ and $D_{\text{slow}} \sim C^{-2.0}$ for $M = 6.61 \times 10^5$.

Table II includes values of the relative intensity amplitude $A_s/A_f$. The values are necessarily imprecise due to the extrapolation procedure. $A_s/A_f$ is dependent on the measurement angle as has been noted by Yu et al.[6] This ratio decreases linearly with increasing angle from 1.7 (68°) to 0.4 (112°) for PEO 150 at $C = 19.9$ kg m$^{-3}$. There does not seem to be any clear relationship between the amplitude of the slow component and $C^*$ (here $\doteq [\eta]^{-1}$). If the slow relaxation denotes reptative transport, then the results indicate that significant entanglement[22] takes place below $C^*$, although it is usually assumed[23] that entanglement occurs at substantially higher concentrations than $C^*$. The latter conclusion may be valid for less extended coils than those of PEO. Measurements were also made on a fraction of the branched polysaccharide dextran ($M = 7 \times 10^4$) in water. Only a single relaxation could be detected up to a reduced concentration of $C/C^* = 6$, showing that chain geometry is an important factor promoting entanglement and/or that such compact coils do not diffuse readily by a reptative mechanism. Similarly, only a single relaxation mode is noted for polystyrene in cyclopentane at the $\Theta$ temperature; see below.

Measurements of the relative amplitude ratio were made at frequent intervals over a period of 6 weeks for PEO 150 at $C = 10.5$ kg m$^{-3}$. This ratio was found to be strictly constant, in contrast with the finding of Mathiez et al.[3] and suggests the presence of dust or aggregates in their solutions.

Measurements on a low molecular weight fraction of PEO ($M = 2.5 \times 10^4$) showed a striking dependence of the scattering intensity on measurement angle, indicating the presence of aggregates. This fraction was therefore excluded from the investigation. However, similar evidence for aggregate formation was not found in solutions of PEO with $M \geq 4 \times 10^4$, and this suggests that very short chains of PEO can preferentially associate into larger structures. Polik and Burchard,[24] using static light scattering, also observed that aggregates are formed and this tendency increased with increasing temperature, the measurements being made on a PEO fraction of $M = 2 \times 10^4$. (It may also be noted here that preliminary measurements on a low molecular weight dextran fraction ($M = 10^4$) also show the presence of aggregates whereas these effects were not found with fractions of higher molar mass. The aggregates could, however, be eliminated by heating the solutions at above 60 °C overnight.)

The influence of "annealing" a solution of PEO was examined. A solution of PEO 150 ($C = 10.5$ kg m$^{-3}$) was held at 65 °C for 1 week; the relative intensity, $A_s/A_f$, and relaxation time of the slow component were found to be unchanged after this treatment.

**Dependence of the Slow Relaxation on Molar Mass.** For the sample of the lowest molar mass ($M = 4 \times 10^4$), only a small proportion of the slow relaxation was observed (~10% at the highest concentration).

The data in Figure 2 show that the magnitude of the concentration dependence of the slow mode increases with molar mass as the friction per unit volume increases. As mentioned above, the concentration dependence approximately parallels the self-diffusion data at the higher concentrations, a fact that stimulated the earlier workers[8,9] to erroneously identify the slow relaxation with self-diffusion. Amis and Han[9] also find the slow component to be strongly dependent on molar mass. Their estimation of a molar mass dependence of $M^{-2}$ in a log $D$ vs. log $M$ plot is less than convincing, nonetheless, since the $D$ values were arbitrarily taken at a concentration of 50 g/L and it would appear from their data that the concentration dependence of $D$ differs for the various fractions used. Moreover, since the slow relaxation does not correspond to self-diffusion, it is not self-evident that an $M^{-2}$ dependence should be observed. The present data at the highest concentration (37 kg m$^{-3}$) are shown in Figure 3b. The curvature is consistent with the observation that the concentration dependence (log $D$ vs. $C$) increases with increasing $M$. The four highest points in Figure 3b are, however, approximately in agreement with a slope of −2. The self-diffusion data exhibit similar curvature. (The molar mass dependence for the extrapolated fast-mode data, which at infinite dilution coincide with the intercepts from the self-diffusion data, is shown in Figure 3a and corresponds to a relationship of the form $D_f \sim M^{-0.58}$.)

**Temperature Dependence (PEO/H$_2$O System).** These data are shown in Table III and Figure 4. The following observations may be made:

(a) The apparent activation energy increases with increasing concentration for the slow mode ($E_D \sim 24$ kJ mol$^{-1}$ at 10.5 kg m$^{-3}$; $E_D \sim 38$ kJ mol$^{-1}$ at 25.6 kg m$^{-3}$). On the other hand, the corresponding quantity for the fast mode is independent of concentration ($E_D \sim 15$ kJ mol$^{-1}$) and this value approximates the activation energy for viscous flow of water itself. The latter behavior typifies diffusion in dilute solutions and is a condition[13] for the semidilute region. The slow-mode data indicate that friction ceases to be dominated by the solvent when entanglement is involved. These data may be compared with those for a self-entangled system i.e., polystyrene in cyclopentane under $\Theta$ conditions (see below).

(b) The intensity amplitude ratio $A_s/A_f$ is found to decrease with increasing temperature. This effect does not have the characteristics of a melting-out process but, as discussed by Chu and Nose,[2] derives from the change in the radius of gyration with temperature and a corresponding displacement in the $\mathbf{q}\cdot R_G$ vs. $C/C^*$ plane. With increasing temperature one moves further into the pseudogel domain and the slower motions of entangled coils receive less emphasis.

Table III
Temperature Dependence for Diffusion and Relative Amplitudes for Fast and Slow Relaxations in Poly(ethylene oxide) Aqueous Solutions

| | $T$/°C | fast $D \times 10^{11}$/ (m$^2$ s$^{-1}$) | slow $D \times 10^{13}$/ (m$^2$ s$^{-1}$) | $A_s/A_f$ |
|---|---|---|---|---|
| PEO 150 ($M = 1.48 \times 10^5$), $C = 10.5$ kg m$^{-3}$ | 15 | 1.73 | 8.0 | 1 |
| | 25 | 2.08 | 10.7 | 1 |
| | 34 | 2.47 | 13.1 | 0.7 |
| | 43 | 2.88 | 21.7 | 0.7 |
| PEO 150 ($M = 1.48 \times 10^5$), $C = 25.6$ kg m$^{-3}$ | 25.0 | 2.63 | 1.7 | 4 |
| | 30.3 | 2.72 | 1.94 | 4 |
| | 35.4 | 3.08 | 2.56 | 3.5 |
| | 40.5 | 3.25 | 3.10 | 3 |
| | 45.5 | 3.49 | 3.96 | 2 |

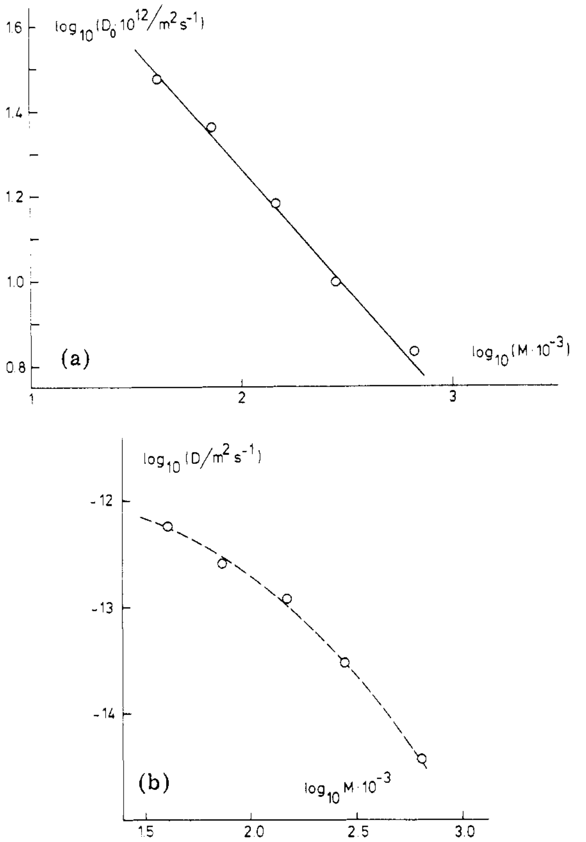

**Figure 3.** (a) Dependence of the extrapolated fast-mode diffusion coefficient on molar mass; the slope is given by the exponent in $D_0 \sim M^{-0.58}$. (b) Log–log plot of $D_{\text{slow}}$ vs. molar mass for poly(ethylene oxides) in aqueous solution. The data are taken at a concentration of 37 kg m$^{-3}$.

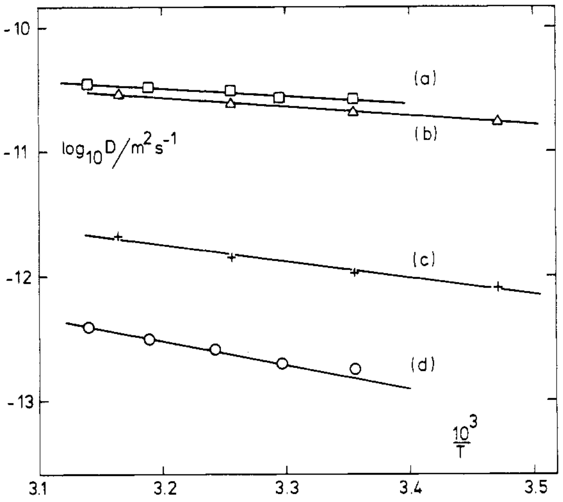

**Figure 4.** Temperature dependence of the fast- and slow-mode components for PEO 150/water: (a) $C = 10.5$ kg m$^{-3}$, $E_D = 15$ kJ mol$^{-1}$; (b) $C = 25.6$ kg m$^{-3}$; $E_D = 15$ kJ mol$^{-1}$ (where (a) and (b) refer to the fast mode); (c) $C = 10.5$ kg m$^{-3}$, $E_D = 24$ kJ mol$^{-1}$ ($C/C^* = 1.6$); (d) $C = 25.6$ kg m$^{-3}$, $E_D = 38$ kJ mol$^{-1}$ ($C/C^* = 3.9$). The activation energy of viscous flow for water is $\sim E_A = 15$ kJ mol$^{-1}$.

Table IV
Diffusion Coefficients for Polystyrene ($M = 1.1 \times 10^5$) in Cyclopentane as a Function of Temperature and Concentration

| $T$/°C | conc/% (w/w) | $D \times 10^{11}$/ (m$^2$ s$^{-1}$) |
|---|---|---|
| 20.4 °C (Θ conditions), $C^* = 3.1\%$ (w/w) | 0.55 | 5.91 |
| | 1.34 | 5.43 |
| | 2.67 | 4.61 |
| | 5.95 | 3.90 |
| | 11.9 | 3.20 |
| | 16.9 | 3.11 |
| 24.8 | 5.95 | 4.54 |
| | 11.9 | 3.82 |
| | 16.9 | 3.69 |
| 29.0 | 5.95 | 5.27 |
| | 11.9 | 4.49 |
| | 16.9 | 4.40 |
| 34.0 | 5.95 | 6.13 |
| | 11.9 | 5.02 |
| | 16.9 | 5.54 |

**Polystyrene ($M = 1.1 \times 10^5$) in Cyclopentane (20.4 °C).** These data are summarized in Table IV. Only single-exponential relaxation could be detected in cyclopentane up to a concentration of 17% (w/w). A negative and nonlinear concentration dependence was observed for the diffusion coefficient as is expected when the thermodynamic contribution is negligible under Θ conditions; see Figure 5 and also ref 25. This concentration dependence has the same overall character as that for the polystyrene/*trans*-decalin system described by Nose and Chu.[1,2] At even higher concentrations an upward curvature deriving from the pseudogel is to be expected. Nose and Chu,[1] however, describe bimodal relaxation behavior in *trans*-decalin, which arises from the presence of an additional *faster* mode of motion distinct from the hydrodynamic mode. Munch et al.[28] using a higher molecular weight polystyrene sample ($M = 5.7 \times 10^5$) also observe an increasingly nonexponential autocorrelation function in cyclopentane at the Θ temperature.

Data from Figure 5 are presented in the form of Arrhenius plots in Figure 6. At 25 °C the apparent activation energy has the values $E_D = 26$ kJ mol$^{-1}$ (5.9%) and $E_D = 34$ kJ mol$^{-1}$ (16.9%), which may be compared with the figure $E_A = 8.7$ kJ mol$^{-1}$ obtained from a similar plot of the inverse solvent viscosity (Figure 6a). Thus $E_D$ varies significantly with concentration in a Θ solvent in the sem-

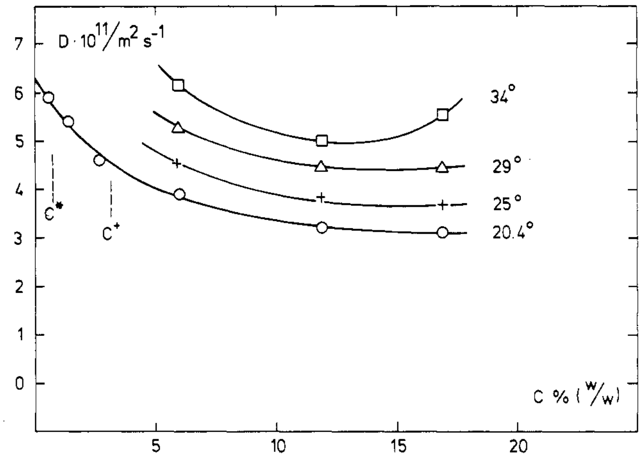

**Figure 5.** Concentration dependence of mutual diffusion for polystyrene ($M = 1.1 \times 10^5$) in cyclopentane at various temperatures. No slow-mode relaxation could be detected in this concentration interval; $C^* = [\eta]^{-1}$; $C^+ = M/N_A R_G{}^3$.

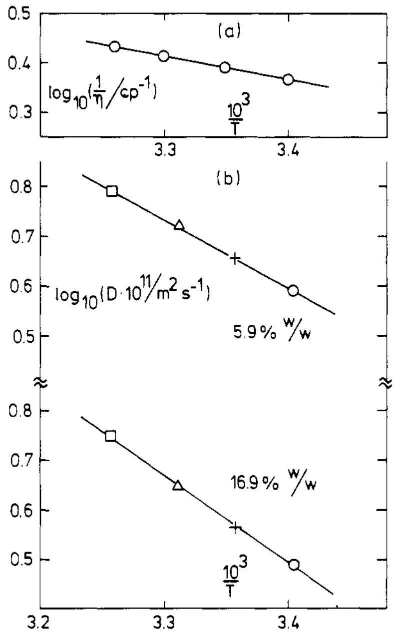

**Figure 6.** Arrhenius plots for polystyrene ($M = 1.1 \times 10^5$) in cyclopentane at the concentrations shown. The slopes at 25 °C correspond (b) to $E_D = 26$ kJ mol$^{-1}$ (5.9%) and $E_D = 34$ kJ mol$^{-1}$ (16.9%); the activation energy of viscous flow for cyclopentane is $E_A = 8.7$ kJ mol$^{-1}$ (a).

idilute region. Pronounced concentration dependence of the apparent activation energy has been noted before.[25-27] A low degree of interchain entanglement appears to be characteristic of compact coils dominated by intramolecular interactions; this is self-evident and is in substantial agreement with the conclusions of Brochard and de Gennes[29] that in a Θ solvent there are many "self-knots" and that the self-knots of a single coil do not disentangle easily. Reihanian and Jamieson[5] also conclude that only the usual hydrodynamic mode will be observable at all accessible wave vectors.

**Sodium Poly(styrenesulfonate)/0.1 M NaCl.** Data for sodium poly(styrenesulfonate) ($M = 3.5 \times 10^5$)/0.1 M NaCl are shown in Table V. One expects that entanglement will be inhibited by electrostatic repulsive forces and also influenced by chain stiffness, and this finds support in the low values of $A_s/A_f$. The constancy of the latter with change in temperature, which differs from the situation for poly(ethylene oxide) in water, is noted. Subsequent to submission of this paper, a detailed study of this system by Koene et al.[33,34] appeared.

Table V
**Diffusion Coefficients and Relative Amplitudes for the Fast and Slow Relaxations in Polystyrenesulfonate ($M = 3.4 \times 10^5$) Solutions in 0.1 M NaCl at Various Temperatures**

| $T$/°C | $C$/ (kg m$^{-3}$) | fast $D \times 10^{11}$/ (m$^2$ s$^{-1}$) | slow $D \times 10^{13}$/ (m$^2$ s$^{-1}$) | $A_s/A_f$ |
|---|---|---|---|---|
| 12 | 13.1 | 1.05 | 3.1 | 0.3 |
| 15 | 13.1 | 1.20 | 4.1 | 0.3 |
| 20 | 13.1 | 1.65 | 8.2 | 0.3 |
| 25 | 13.1 | 2.7 | 11.7 | 0.3 |

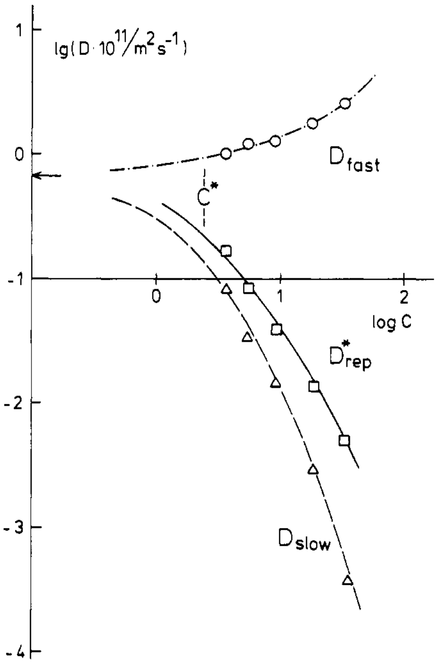

**Figure 7.** Logarithmic plot of $D_{fast}$ and $D_{slow}$ vs. concentration. The data are those for PEO 660. Approximate values for the limiting slopes are 0.6 and −2. Values for $D^*_{rep}$ according to the equations of de Gennes[13] are inserted (□).

## Conclusions

There is some confusion in the literature concerning the source of the slow relaxations with a frequency of the order 10 s$^{-1}$. This ambiguity derives from the superposition of two or more modes which may be observed in semidilute polymer solutions and our limited ability to successfully resolve the autocorrelation function into more than two components with present techniques. The present paper is primarily concerned with the crossover region above overlap ($C^* = 1/[\eta]$), which is experimentally accessible without undue loss of precision. There is a sharp increase in the amplitude of the slow relaxation with increasing concentration. The concentration dependence of the slow relaxation increases with molar mass and is found to parallel that for the self-diffusion ($D^*$) data in the semidilute region. This may suggest a reptative mechanism for transport as proposed by de Gennes[13] and which is the most readily visualized form of translation in the pseudogel. $D^*_{rep}$ has been calculated using the de Gennes equations for self-diffusion for PEO 660. As shown in Figure 7, $D^*_{rep}$ has a similar concentration dependence to $D_{slow}$.

It is concluded here that the slow relaxation observed in semidilute solutions of PEO, and which is about an order of magnitude lower than the experimentally determined self-diffusion coefficient at a given concentration, describes the relaxation of entangled structures on a wavelength scale greater than the entanglement separation. The slow relaxation manifests itself at a concentration which appears to be related to the chain geometry. Thus, slow relaxations are observed in the PEO/$H_2O$ system at a concentration lower by an order of magnitude than that for polystyrene in benzene.[12] There is good evidence[30] for binding of water molecules to the PEO chain in the ratio 2:1. Such hydrogen-bonding interactions with the chain are undoubtedly a factor determining the relatively high chain extension. PEO has, for example, a much greater intrinsic viscosity than polystyrene in good solvents; furthermore, the ratio ($R_G^2/M$) is reported[32] to be 10 times larger than for polystyrene in toluene. However, the relationships between concentration, chain extension, polymer–solvent interaction and geometric entanglement still require elucidation. The present measurements only provide support for the view that these quantities are of central importance. It is noted that a model for the coupling between internal modes and anisotropic translational diffusion in congested solutions has been put forward by Lee et al.,[35] who describe dynamic light scattering measurements on DNA.

**Registry No.** Poly(ethylene oxide), 25322-68-3; polystyrene, 9003-53-6.

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# ESR Investigation of Molecular Motion in Thermotropic Liquid Crystalline Polyesters Containing Nitroxide Spin Probes

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ABSTRACT: Two aromatic–aliphatic polyesters $-CO(p\text{-}C_6H_4)_3COO(CH_2CH_2O)_n-$, abbreviated TO11 and TO29 for $n = 4$ and $n = 10$, respectively, which form liquid crystalline phases, were investigated. The ESR spectra of these polyesters doped with various nitroxide radicals were recorded at 108–413 K and were given a preliminary interpretation with a model of isotropic rotational reorientation. Such an analysis argues for a glass transition temperature $T_{g_L}$ at 223–263 K with a second $T_{g_U}$ at 293–333 K. A more careful analysis of the spectra by using a model of anisotropic rotational reorientation showed that below the crystal ↔ mesophase transition (i.e., the melting point) the axis $z'$ of the rotational diffusion tensor describing this rotational reorientation was an axis perpendicular to that of the N–O bond and that, depending on the length of the "ether" sequence, the rotational reorientation about this axis is 2–7 times faster than about the remaining two axes. The observed changes in the ESR spectra of probes as they pass through the crystal ↔ mesophase transition are explained in terms of a change in the anisotropic rotation of probes.

## Introduction

There is now a considerable body of literature dealing with thermotropic liquid crystalline polymers that melt to give fluid anisotropic phases whose textures and properties appear similar to those observed with low molecular weight liquid crystals. So far, most of the work has focused on the search for newer and newer polymers and the study of their structures as liquid crystalline phases.[1] By contrast, only a few attempts have been made to give a detailed explanation of the relaxation processes in these materials.[2-5] Since the detection and evaluation of polymer motions may aid in correlating polymer structure with observed mechanical properties, it seems of interest to

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