Diffusion of poly(ethylene oxide) in semidilute aqueous solution: Dynamic light scattering and gradient diffusion

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Gradient diffusion measurements and dynamic light scattering data are presented for semidilute aqueous solutions of narrow distribution (molecular weight M: 2.5×10^4–1.2×10^6) poly(ethylene oxide) fractions. Resolution of the time correlation function using bimodal analysis gave: (a) a fast mode, identical within experimental error to the classical gradient diffusion values; (b) a slow mode, interpreted as reflecting the translational motions of clusters of entangled chains. The results are similar to those found for other aqueous polymer systems, probably reflecting the ease with which association occurs between extended, polar, chains.

(Keywords: semidilute; polymer; solutions; diffusion; light scattering)

INTRODUCTION

Aqueous solutions of poly(ethylene oxide) (PEO) exhibit anomalous behaviour in several respects. Recent papers[1–6] suggest that globular aggregates and/or microgels exist in solutions of the low molecular weight ($M<25\times10^3$) polymers, while higher molecular weights exhibit[7,8] behaviour more characteristic of other synthetic polymers in a good solvent. For example, $D_0\sim M^{-0.58}$ which is in good agreement with the theoretical exponent. The tendency to associate exists in other solvents: measurements using dynamic light scattering in dioxane and chloroform[9] show extensive aggregation exponent as demonstrated by the very low diffusion coefficients while, on the other hand, solutions in methanol[5] contain the molecularly dispersed polymer. A recent paper[1] described the properties of a very slow relaxational mode in aqueous PEO solutions. The present paper describes classical gradient diffusion measurements on semidilute solutions of the same fractions and a comparison is made of these data with those from dynamic light scattering in which the component modes have been isolated using an alternative procedure to that previously reported.

EXPERIMENTAL

Polymers

Narrow distribution poly(ethylene oxide) fractions were obtained from Toya Soda Ltd., Tokyo, Japan:

Type	$M\times10^3$	$[\eta]$ (dl g^{-1})	M_w/M_n
SE-2	25	0.412	1.14
SE-15	148	1.51	1.04
SE-30	278	2.35	1.05
SE-70	661	4.18	1.10
SE-150	1200	6.50	1.12

Solutions

Solutions were prepared by weighing. Dust-free solutions in the concentration range 0.4–4% (w/w) were prepared using a closed-circuit filtration unit. The lower molecular weights were filtered through 0.22 μm millipore filters and the $M=1.2\times10^6$ sample through a 0.45 μm filter. The solution was bled off into 10 mm precision-bore n.m.r. tubes and weighed. A series of dilutions were prepared by similarly treating solvent and weighing appropriate quantities into each tube.

Dynamic light scattering

The experimental arrangement has been described recently[1]. Measurements were made in the homodyne mode over the angular region 30°–60°.$(qR_G\,0.5$–$1)$ with the n.m.r. tubes immersed in a large diameter bath of index-matching liquid (decalin). Incident radiation at 488 nm was provided by a Coherent Super-Graphite 4-W argon-ion laser containing a quartz etalon frequency stabilizer in the cavity to ensure single-mode operation.

The correlation function was treated interactively on the same microcomputer (Luxor ABC 800) as employed for data collection and reduction. The programs were written in FORTH for rapidity and compactness.

Classical gradient diffusion

Gradient diffusion measurements were made using a shearing-type cell for free-diffusion, equipped with a schlieren optical system. The half-width at the inflection point (Δx) was measured and $(\Delta x)^2$ plotted *versus* time. The mutual diffusion coefficient was evaluated from the slope according to:

$$(\Delta x)^2=2D_m t$$

The starting-time correction was always approximately equal to zero, otherwise the experiment was rejected. The boundary was always made between two solutions differing in concentration by about 1%, which was sufficient for accurate determination of boundary width. The diffusion coefficients then correspond to the average value, $\bar{C}$, across the boundary.

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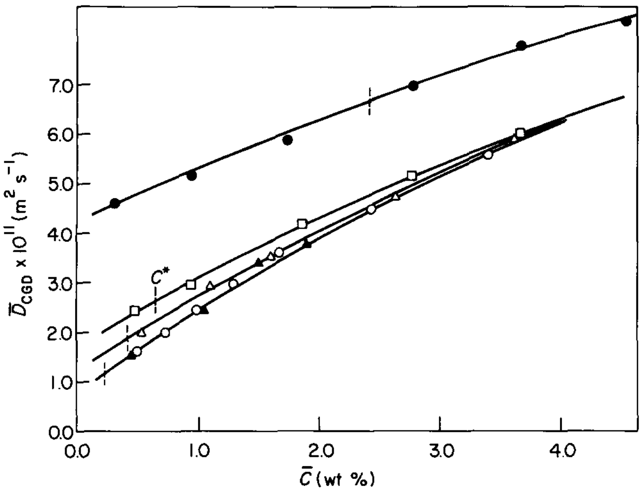

Figure 1 Results of gradient diffusion measurements for poly(ethylene oxide) fractions in aqueous solution (25°C): (●) $M=2.5\times10^4$; (□) $M=1.48\times10^5$; (△) $M=2.78\times10^5$; (○) $M=6.61\times10^5$; (▲) $M=1.2\times10^6$)

RESULTS AND DISCUSSION

Gradient diffusion measurements ($\bar{D}_{CGD}$) for a series of PEO fractions in water solution are shown in *Figure 1* for the semidilute concentration range.

The results show the behaviour expected in the semidilute region, i.e. where D is approximately independent of molecular weight for the fraction with the exception of the very low fraction $M=2.5\times10^4$. A log–log plot for the data of one of the fractions ($M=6.6\times10^5$) is shown in *Figure 2* and corresponds to the relationship:

$$D_{CGD} \sim C^{0.65}$$

This is similar to that found for PEO by Kambe and Honda[4] (exponent $\gamma=0.707$) who evaluated D-values from dynamic light scattering data using the method of cumulants and Nyström *et al.*[8] (exponent $\gamma=0.60$) using the gradient technique as here.

Figure 3 shows data from dynamic light scattering measurements on a fraction with $M=1.2\times10^6$. Such measurements can provide a much deeper insight into the dynamic behaviour than gradient measurements as was shown in a previous communication[1] dealing with the slow relaxation characterizing PEO/water solutions. Thus, the time correlation function for semidilute solutions may potentially be resolved into fast and slow components which differ greatly in relaxation frequency (by at least a factor of 10^2). These have an opposite signs for the concentration dependence as is shown in curves (A) and (C) in *Figure 3*. Moreover, the relative contributions to the total scattering intensity vary strongly with concentration, the slow mode becoming dominant in intensity with increasing concentration. The large separation in relaxation frequencies was utilized in the earlier evaluation[1] by performing the runs at short and long sampling times; the time correlation function for each data set could then be approximated by a single exponential in each case. Thus, on fitting the data registered using a short sampling time, the baseline was allowed to float under the assumption that the initial value of the slow decay is constant over several relaxation times of the fast decay. Secondly it was assumed that contributions of the fast decay to the time correlation function for data collected with a long sampling time can be neglected if the first 10 channels are, for example, omitted. This procedure has been used extensively, primarily by Amis and coworkers[10–12] on polystyrene solutions in good and poor solvents.

The present data were treated by an alternative procedure. The runs were initially screened using the cumulants method—any runs showing an unusual intensity pattern or exhibiting a deviation of delayed channels from the calculated baseline were rejected. Subsequently the data were fitted to a range of functions of discrete multiexponentials:

(a) 3-parameters (single exponential plus floating baseline);
(b) 4-parameters (two exponentials);
(c) 5-parameters (two exponentials plus baseline term);
(d) 6-parameters (3-exponentials).

The choice of the most appropriate fit was made partly on the basis of the Q-function:

$$Q=1-\frac{\sum_{i=1}^{n-1}\varepsilon_i\varepsilon_{i+1}/(n-1)}{\sum_{i=1}^{n}\varepsilon_i\varepsilon_i/n} \qquad (1)$$

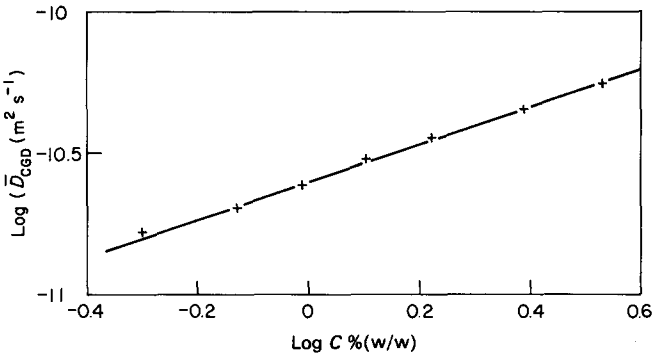

Figure 2 Log–log plot of gradient diffusion data for PEO fraction ($M=6.61\times10^5$) in aqueous solution. The relationship $D\sim C^{0.65}$ applies to these data

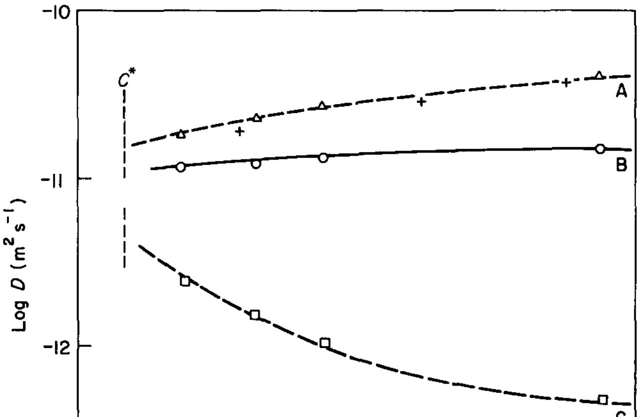

Figure 3 Data from dynamic light scattering on PEO fraction $M=1.2\times10^6$. The results of bimodal analysis give a fast mode (△) and a slow mode (□). The cumulant analysis gives the intermediate line (○). Data from gradient diffusion are included (+)

If there is no grouping of the residuals, ε, Q will approximate unity. In the present case Q-values >0.95 were found using (b). Also the bimodal fit gave the lowest minimum of the reduced sum of squares of residuals to the fit, χ^2. The general level of the precision of the data correspond to a variance of 2×10^{-7} (i.e. a standard deviation of the error of $\simeq 4\times10^{-4}$). An extensive series of simulations has earlier been made to establish both the reliability and limitations of the present fitting procedures (see refs. 15 and 16).

The best fit was consistently obtained using a bimodal expression, utilizing data accumulated with an intermediate value of the sampling time to encompass both relaxations:

$$g^{(2)}_{(\tau)} - 1 = \beta[A_s\exp(-\Gamma_s\tau) + A_f\exp(-\Gamma_f\tau)]^2 \quad (2)$$

which expresses the normalized second-order correlation function in terms of two relaxation rates. This model is validated by the possibility of isolating the slow component as a single exponential using a sufficiently long sampling time. β is an instrumental parameter, here approximately 0.7. Our model does not include an adjustable baseline. From experiments in this and previous investigations, no basis was found for using other than the statistical baseline if the solutions are rigorously prepared to be dust- and particle-free.

An example of the data obtained using bimodal analysis is shown in *Figure 3* (curves (A) and (C)); the points obtained using the cumulant fit and corresponding to the weighted average of fast and slow modes are shown in curve (B).

Comparing the data obtained with the bimodal model with those evaluated for the same fraction using selected window times as previously described[1] shows that, whereas the slow decay is identical in both cases, the value of the fast decay measured using a short sampling time is some 50% too low. This shows that the assumption of the constancy of the initial value of the slow decay is not justified and the procedure with the floating baseline not reliable. Examination of the earlier published data of Amis *et al.*[12] suggests that this effect may be present in their fast mode as evaluated. The latter was found to have a concentration dependence for the exponent in $D_c \sim C^\gamma$ much lower (<0.5) than predicted for the cooperative mode in the hydrodynamic regime with a *theta* system (1.0). More significantly, the fast mode was observed to be molecular weight dependent. If the fast mode has been incompletely separated from the slow (which was shown to have a strong dependence on molecular weight: $D_s \sim M^{-2}$) then this observation may be understood. An additional complication has also been introduced in several of the earlier publications[10,11] through a probably unwarranted assumption that the fast decay is detected by heterodyne scattering and the slow by homodyne scattering. These results serve to stress the pitfalls in the use of dynamic light scattering for testing scaling theories, since more than one mode of relaxation is invariably represented at semidilute concentration.

Kambe and Honda[4] have used the cumulant method to evaluate their data. This is clearly an adequate procedure only if the distribution is unimodal. The cumulant data will otherwise simply provide a weighted average over the contributions from the participating modes.

We note that the data from the classical gradient measurements are approximately identical to the fast mode evaluated using bimodal analysis. This is not necessarily expected. A recent paper[15] described the resolution of the correlation function into fast (pseudogel) and slow (translational motions) for semidilute solution of polystyrene in solvents of various quality. In these systems $\bar{D}_{\mathrm{CGD}}$ was found to be intermediate in value between fast and slow modes. The relative position of $\bar{D}_{\mathrm{CGD}}$ will, however, reflect the weighting of the modes which actively contribute to the decay of the macroscopic concentration gradient in the particular system.

Only if the correlation function may be approximated by a single exponential (for example, for dilute solutions and for values of the scattering vector q such that $qR_G \ll 1$, where R_G is the radius of gyration) will the diffusion coefficient evaluated in dynamic light scattering unequivocally equal that obtained using the classical gradient method. The use of the latter data to test scaling relationships in the semidilute region[17] will also, in general, be questionable, as previously noted[15]. As an example of a system in which the unimodal relaxation behaviour is the case we give data for a dextran fraction ($M=7\times10^4$) in aqueous solution in *Figure 4*. The time correlation function can be adequately represented by a single exponential function over the entire concentration range studied (up to $6C^*$). The gradient diffusion results are shown to coincide within experimental error with the QELS data. There is a profound difference between the data for this polymer and a PEO fraction of the same molecular weight for which the time correlation function is clearly bimodal. This suggests that the chain extension/flexibility is an important factor in the formation of entangled structures as postulated below.

The nature of the strongly concentration-dependent slow mode for PEO ((C) in *Figure 3*) has been discussed in a prior communication[1]. It was concluded there that it represents the diffusion of entangled coils—an interpretation which is consistent with the observation that D_s is lower by at least a factor of 10 than D^* for the polymer (where D^* is the self-diffusion coefficient evaluated using pulsed-field-gradient n.m.r.) and also the strong nonlinear concentration dependence of D_s. Reference may be given to a recent paper by Hwang and Cohen[14] who discuss the various diffusion coefficients. These workers find (for the system poly(n-butyl methacrylate) in MEK) essentially similar results to those here and interpret the fast mode as the pseudogel component and the slow as representing diffusive transport as postulated by de Gennes[22,23] implying that it refers to motions of a single coil. We note, however, that Eisele and Burchard[3] find analogous results to those depicted in *Figure 3* (for the

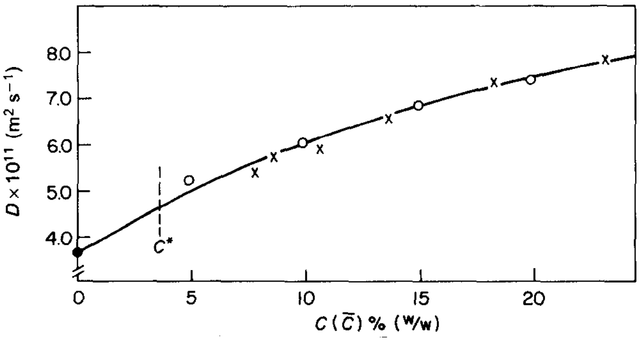

Figure 4 Concentration dependence of diffusion coefficients for dextran ($M=7\times10^4$) in aqueous solution: (○) gradient diffusion; (×) QELS data using cumulants evaluation)

system poly(vinyl pyrrolidone)/H_2O) and they observe, significantly, that the apparent radius of gyration of the scattering entities increases strongly with concentration. This suggests that D_s corresponds to the diffusion of clusters of chains. There is reason to believe that this interpretation applies to the data of Amis *et al.*[10-12]. A recent note by Chang and Yu[13] compares the slow mode with self-diffusion coefficients evaluated using forced Rayleigh scattering (FRS) and they concur in the finding that the slow mode is an order of magnitude lower than the polymer self-diffusion coefficients for the single coil.

Layec and Layec-Raphalen[5] have made dynamic light scattering measurements on dilute solutions of PEO in both water and in methanol. They found that D increased over a period of 2 months in aqueous solution indicating a break up of aggregates. In methanol (a poor solvent) the PEO is molecularly dispersed. We note that these workers did not stir or filter their solutions, or otherwise treat them. Their limiting value of D_0 after a period of two months is approximately equal to the value found here for the same fraction using the filtration procedure described in the Experimental section.

CONCLUSIONS

The complexity of the time correlation function for semidilute solutions owing to contributions from different relaxational modes is well-established. However, the origin of the participating modes varies between systems. In aqueous solution a very slow relaxation appears as a common feature and is found at comparatively low concentrations. One may cite the results on solutions of DNA[18,24] poly(ethylene oxide)[1], hydroxethyl cellulose[19], poly(vinyl pyrrolidone)[3]. The slow relaxation is probably related to the ease with which polar chains, being comparatively extended, form entangled structures and which then diffuse as entities. This interpretation of the slow mode as deriving from the motions of local gels is consistent with the observation that D_{slow} is much lower than self-diffusion of the individual coil.

In very high M.wt. polystyrene systems, where the chains are considerably more flexible, the origin of the fast and slow modes is quite different. Here one invariably observes[15,20] components having relaxation times of similar magnitude and which are cooperative in nature, apparently reflecting the heterogeneity of the transient gel structure over a wide interval of concentration. In a good solvent, the slower mode exhibits a positive concentration dependence in contrast to the behaviour shown in *Figure 3*.

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