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Asymptotic Behavior and Long-Range Interactions in Aqueous Solutions of Poly(ethylene oxide)

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ABSTRACT: Static and dynamic light scattering measurements of single-chain behavior reveal that, even for the readily accessible molecular weight range 10^5–10^6, poly(ethylene oxide) (PEO) in water at 30 °C exhibits asymptotic good solvent behavior both for the equilibrium parameters A_2 and R_g as well as for the dynamic parameters R_h and k_D. Moreover, it is shown that PEO coils are larger and PEO coil–coil interactions stronger than those found for typical polymer coils in organic solvents. It is concluded that the unusually large size and long range of PEO coil–coil interactions in water are due to the unusual ability of water molecules to "pack" into and swell coils along with a general structuring of water in the PEO/H_2O system, respectively. It is further noted that while observed k_D values are typical of those expected in a good solvent, these values cannot be rationalized in terms of theories that treat coil–coil interactions in good solvent solely in terms of "equivalent hard-sphere" interactions.

Introduction

Poly(ethylene oxide) (PEO) is a unique member of the polyepoxides, with the general formula $[(CH_2)_nO]_x$, in that it is soluble in both organic and aqueous solvents.[1] Its properties have made it a polymer of considerable commercial and fundamental importance[2–5] as evidenced by the extensive literature that exists regarding this polymer, especially in aqueous solution. In terms of basic understanding, a recent study[6] has shown for instance that physical bond formation between polymer segments and solvent can be a major cause for the existence of both an upper as well as a lower critical solution temperature in aqueous solutions of PEO. One example of its industrial importance is its ability to reduce friction between surfaces.[7,8] This ability has been shown to be linked to the tendency of PEO to aggregate in aqueous solution.[9,10] In an earlier paper,[11] it was shown that it is possible to study PEO single-chain behavior in solutions without aggregates and that this tendency to aggregate in water is highly dependent on the purity of the water. Thus aggregates form very easily and uncontrollably if the proper care is not taken in the preparation of these solutions.

Along with light scattering, PEO in water has been studied by a number of other techniques.[12–17] The amphiphilic character of PEO opens the possibility for particularly interesting site-specific interactions along the PEO chain. Thus, for example, the question of the packing of water molecules at ether linkages in the PEO/water system has been examined.[13] There has also been a hypothesis that PEO, which is known to be helical in the solid state,[15] retains some of its helicity even in dilute aqueous solution. The extent of the influence, if any, of these local properties on the results of light scattering studies, which are characterized by certain global, universal properties as evidenced in such chain parameters as the radius of gyration, the hydrodynamic radius, and the second virial coefficient, is therefore worth examining.

In this study, certain of these questions have been addressed. The nature of the solvent with respect to PEO has been examined, and it is shown unambiguously by consideration of the power law exponents obtained that water is certainly a good solvent at 30 °C. In view of the fact that PEO in water has both an upper and lower critical solution temperature of −9 and +103 °C, respectively,[18] good solvent behavior at this intermediate temperature is to be expected. One of the most interesting results that emerged from this study concerns the fact that, unlike other flexible, linear polymers in a good solvent where one obtains asymptotic good solvent behavior only in the limit of extremely high molecular weights, PEO in water at 30 °C already exhibits such behavior even for molecular weights as low as 80 000. In this study, both static and dynamic light scattering measurements have been performed to elucidate this interesting behavior for aqueous PEO solutions in the dilute regime.

Experimental Section

1. Sample Preparation. In our measurements we have used seven well-characterized poly(ethylene oxide) samples. All of the samples used, except one, were obtained from the Toyo Soda Co.[19] One of the samples whose molecular weight was determined to be 838 000 was purchased from the Pressure Chemical Co., Pittsburgh, PA. The preparation of aqueous PEO solutions for study using light scattering requires great care and patience. This is especially so with respect to aqueous PEO solutions because, in addition to its propensity to aggregate, the PEO in water is known to degrade with time.[20] All stock solutions were prepared gravimetrically. The water used in the preparation of the solutions was obtained first from a reverse osmosis/deionization/filtration unit, which was then fed into a special polishing unit just before use. Here the water is further deionized, and residual trace organic impurities are removed. Finally, the water is degassed through gentle heating. The pH of this water was typically about 5.5. The resistivity of the water, monitored at the polishing unit, was typically about 12 MΩ·cm. Solutions were isolated in an oven for about 2 days at 30 °C to equilibrate and to avoid prolonged exposure to sunlight that might have caused polymer degradation. They were occasionally gently stirred using a magnetic stirrer, and in cases where the waiting period for experimental measurement exceeded 2 days, a drop of chloroform was added to solutions to prevent bacterial growth and PEO degradation. In addition, air above sample solutions was replaced by triply filtered freon to avoid oxidation effects. As was shown earlier,[11] chloroform addition did not affect light scattering measurements. Final dilution solutions were filtered directly into light scattering cells using Schleicher and Schuell Nylon 66 filters.

2. Static Intensity Measurements. Elastic light scattering is a standard technique to extract information about the size and structure as well as equilibrium polymer–polymer coil interactions of flexible, linear polymer chains in a dilute solution.[21,24–26] The Zimm plot method was used to determine the radius of gyration

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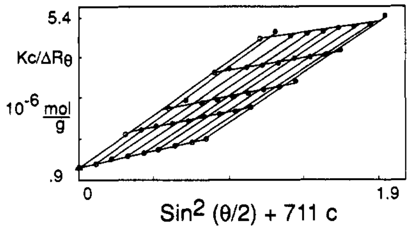

Figure 1. Typical Zimm plot. The molecular weight of this sample was determined to be 8.38 × 10^5.

Table I

$M_w \times 10^{-5}$	M_w/M_n	$A_2 \times 10^3$ (±17%), mL·mol/g²	R_G (±5%), Å
0.86	1.02		
1.60	1.07		
2.52	1.04	1.56	304
5.70	1.10	1.21	508
5.94	1.04	1.33	483
8.38	1.20	1.10	594
8.60	1.17	1.26	615
9.96	1.05	1.22	698

R_g, the osmotic second virial coefficient A_2, and the molecular weight M_w using the equation

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{M_w}\left(1 + \frac{q^2 R_g^{\,2}}{3}\right) + 2A_2 c \qquad (1)$$

where ΔR_θ is the excess Rayleigh ratio and q the magnitude of the scattering wavevector. For vertically polarized incident light the optical constant K is given as $K = 4\pi^2 n^2 (dn/dc)^2/\lambda_0^4 N_a$ where n is the refractive index of the solvent, λ_0 the vacuum wavelength of incident light, and N_a Avogadro's number. The refractive index increment, dn/dc, for PEO in water at 30 °C was measured to be 0.135 mL/mg at 6328 Å using a temperature-controlled differential refractometer.[22]

All light scattering measurements were made by using the Brookhaven Instruments light scattering photometer.[27] The experimental arrangement and the Zimm plot software from Brookhaven Instruments were tested by using a thoroughly characterized poly(α-methylstyrene) (PαMS) sample in toluene.[28] The values of all the equilibrium parameters agreed to within 5%. Figure 1 shows a typical Zimm plot. The intercept from the zero-concentration and zero-angle lines agreed in all cases to within 1%. Zimm plot M_w results were in excellent agreement (typically within 2%) with the vendor's values obtained using low-angle laser light scattering. The other two parameters obtained from the Zimm plot, namely, the radius of gyration and the second virial coefficient, are summarized in Table I. They were fit to log-log plots against molecular weight (Figures 2 and 3). The following relation was established by using a direct power law fit of R_g to M_w:

$$R_g = 0.215 M_w^{\,0.583\pm0.031}\ \text{Å} \qquad (2)$$

The corresponding relation for A_2 was found to be (Figure 3)

$$A_2 = 1.84 \times 10^{-2} M_w^{\,-0.20\pm0.06}\ \text{mL·mol/g}^2 \qquad (3)$$

3. Dynamic Measurements When effects of intramolecular interference are negligible, the dynamic structure factor[23] for polymer coils in dilute solution may be written as $S(q,t) \cong \exp(-q^2 Dt)$ where D is the mutual diffusion coefficient for a monodisperse system. By extrapolation of the mutual diffusion coefficient $D(c)$ measured at various concentrations to zero concentration one obtains the self-diffusion coefficient of the isolated polymer, D_0. Experimentally, $D(c)$ was determined from measured values by using the method of cumulants[29] in which the normalized first-order electric field correlation function $|g^1(t)|$ is expanded in powers of the delay time t as

$$\ln|g^1(t)| = -\bar{\Gamma}_1 t + \mu_2 t^2/2 + \ldots \qquad (4)$$

The normalized measured intensity autocorrelation function, $g^2(t)$, can then be related to $g^1(t)$ as

$$b^{1/2}|g^1(t)| = [g^2(t) - 1]^{1/2} \qquad (5)$$

where b is an optical coherence factor. The measured intensity correlation function $G^2(t)$ is divided by the base line B to obtain $g^2(t)$. Experimentally, B was determined as an average of six channels delayed 1024 sample times beyond the last correlator channel. The z-average mutual diffusion coefficient, $\bar{D}$, is obtained from the first cumulant $\bar{\Gamma}_1$ from the relation

$$\bar{\Gamma}_1 = \bar{D} q^2 \qquad (6)$$

The normalized second cumulant, $\mu_2/\bar{\Gamma}_1^{\,2}$, or the "polydispersity factor" is then a measure of the width of the distribution of particle sizes in solution.

All measurements were made in the small-qR_g region to avoid contributions to the measured intensity autocorrelation function $G^2(t)$ of internal coil motions. The light source was an argon ion laser, using a wavelength of 514.5 nm. By using an achromat as the front focusing lens, we could switch between the He-Ne and the argon lasers to make static/dynamic measurements of the same sample. The alignment of the instrument was checked before each measurement using $I \sin\theta$ measurement,[27,30] and typical angular accuracies, over the angular range 30–150°, were on the order of 0.05°. PEO solutions were clean and well-behaved: Differences between the calculated and measured base lines were usually less than 0.01%, and polydispersity factors were typically less than 0.1. Measurements were done at a scattering angle of 45° for most samples. Typically eight intensity autocorrelation functions, $G^2(t)$, were obtained at each polymer concentration. The uncertainties in D_0 and R_h (Table II) therefore reflect experimental uncertainties.

For each molecular weight, the diffusion coefficients were plotted as a function of polymer concentration. All of the plots

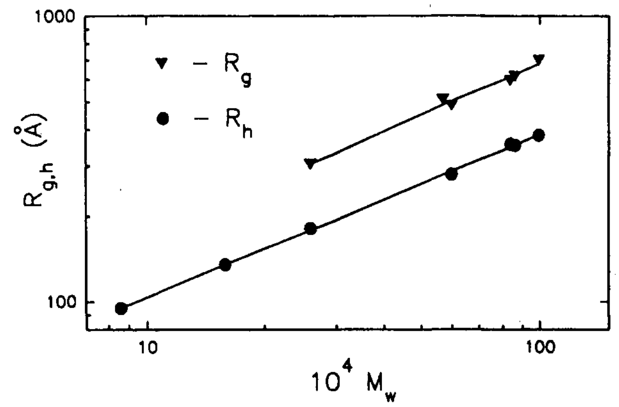

Figure 2. log-log plot of the PEO radius of gyration and the hydrodynamic radius versus molecular weight.

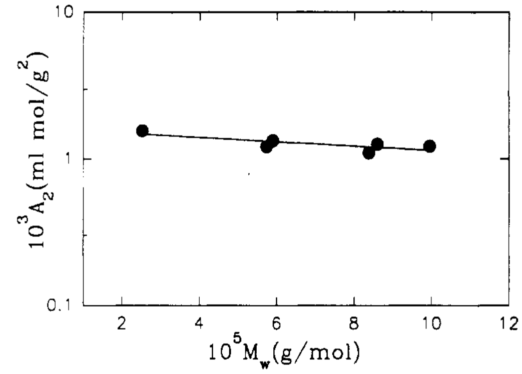

Figure 3. Dependence of the PEO second virial coefficient on M_w shown as a log-log plot. The exponent of $-1/5$ for A_2 agrees well with the asymptotic approximation for good solvents.

Table II

$M_w \times 10^{-5}$	$D_0 \times 10^7$ (±1%), cm^2/s	R_h (±1%), Å	$k_D{}^c$ (±5%), cm^3/g
0.86	2.91	95	21
1.60	2.06	135	80
2.52	1.60	181	110
5.94	1.00	279	142
8.38	0.78	355	248
8.60	0.79	352	283
9.96	0.73	381	276

are linear, and all were well fit via linear least squares to obtain D_0. Measurements were made at four different scattering angles for the highest molecular weight sample, to ensure that the only contribution to the correlation function was from the polymer center of mass mode. D_0 was then fit directly to a power law in M_w, and this fit is displayed in the log–log plot in Figure 4. The hydrodynamic radius of the coil was obtained from the Stokes–Einstein relationship, $R_h = k_BT/6\pi\eta_0 D_0$ where k_BT is the Boltzmann constant times the absolute temperature and η_0 the solvent viscosity. A log–log plot of the hydrodynamic radius against molecular weight is presented alongside the R_g data in Figure 2. The molecular weight dependence of R_h was obtained by fitting R_h directly to a power law in M_w, as for D_0. The following relation was found:

$$R_h = 0.145 M_w{}^{0.571\pm0.009}\ \text{Å} \tag{7}$$

Discussion

By any measure, the aqueous PEO solutions studied here exhibit asymptotic good solvent behavior. To the best of our knowledge, this is the first time that the molecular weight dependence of the radius of gyration has been investigated for aqueous solutions of PEO. This may be at least partly due to the difficulty associated with obtaining aggregate-free solutions and good Zimm plots for PEO in an aqueous medium. The exponent $\nu_g = 0.583 \pm 0.031$ is in good agreement both with asymptotic values from the Flory prediction[31] of $^3/_5$ and with the renormalization group calculation value of 0.588.[32] The exponent ν_h corresponding to the exponent for the hydrodynamic radius is also close to the theoretically predicted value.[33] The difference between ν_g and ν_h has been attributed by Weill and des Cloizeaux[33] to the fact that the hydrodynamic radius does not reach its asymptotic value as fast as the radius of gyration, while Wang et al.[34] have ascribed this difference to the interplay of excluded-volume effects and hydrodynamic interactions. Note, however, that the difference found here is smaller than is typically seen in other good solvent systems.[35,36] The prefactors in the scaling relations are specific to solvent–polymer interactions for the system used. This is observed in the variation of the values of the prefactor in different good solvent systems (see ref 37, e.g.). These prefactors reflect the unusually large size of PEO in good solvent compared to PαMS in toluene for the same molecular weight range, for example. Nevertheless, the exponents obtained from the power laws reflect universal asymptotic behavior.

Besides the results reported here, the relation between the second virial coefficient and molecular weight has been obtained earlier for the PEO/water system at 25 °C using low-angle light scattering measurements.[38] The discrepancy in the value of the exponents in the relation between A_2 and M_w compared to the present results as well as the smaller magnitudes of the earlier A_2 values is presumably due to the presence of a small population of aggregates in their solutions. While the value of the exponent in the earlier work is larger than predicted for an "asymptotically" good solvent system, the value obtained from our experiments is in good agreement with that predicted both from earlier work[26] and later independently by de Gennes.[39] To the best of our knowledge, no other random-coil polymer–good solvent system exhibits such unusually large values of A_2.

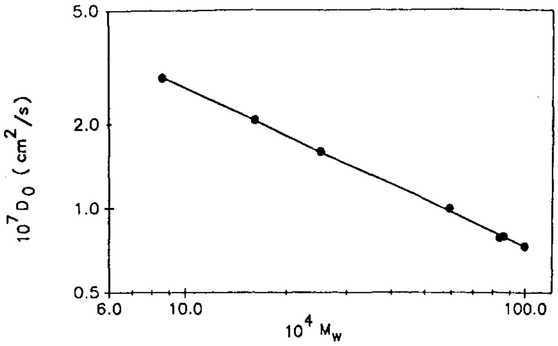

Figure 4. log–log plot of the dependence of PEO D_0 versus polymer M_w values.

Another measure of the solution behavior of PEO is Ψ,[26] the interpenetration function,[37,40] defined as

$$\Psi = \frac{1}{4\pi^{3/2}} \frac{A_2 M^2}{N_a R_g{}^3} \tag{8}$$

For the results presented here, the average value of Ψ is 0.282 ± 0.02. This value is in good agreement with a value predicted earlier by Stockmayer for the asymptotic good solvent limit of Ψ, viz., 0.27.[40] Experimentally, Berry[41] and Norisuye[42] et al. have investigated the dependence of Ψ with the expansion factor for polystyrene and polychloroprene systems in various solvents, and their asymptotic values for Ψ are 0.280 and 0.315, respectively. In addition, Cotton[43] has computed Ψ values for three good solvent systems and has found values to average around 0.245. Again, the results of the present study are consistent with asymptotic, good solvent behavior.

Another parameter that provides information about the nature of the solvent–polymer interaction is the ratio $\rho = R_g/R_h$. Treatments based on the assumption of a Gaussian chain predict values of ρ of about 1.5.[44,45] In the good solvent limit, however, where coils are highly swollen due to the effects of excluded volume, r_{ij}, the spatial distance between segments i and j, may be represented by the distribution function[46]

$$W(r,n) = C_n r^l \exp[-(r/\sigma_n)^t] \quad (n \equiv |i-j|, r \equiv r_{ij}) \tag{9}$$

with critical indices $t = 2.40$ and $l = 2.80$. C_n is a normalization constant and σ_n the scaling factor. This gives $\rho = 1.596$. Benmouna and Akcasu[47] used Ptitsyn's pseudo-Gaussian (blob model) of $W(r,n)$ and obtained a value of $\rho = 1.860$ for highly swollen chains with $\nu_g = {}^3/_5$. Our mean value of $\rho = 1.73$ is therefore in reasonable agreement with theoretical predictions for swollen coils.

Data from dynamic light scattering further corroborates the asymptotic good solvent nature of the PEO/water system. Thus, measured values of $k_D{}^c$ in the virial expansion for the concentration dependence of the diffusion coefficient

$$D(c) = D_0(1 + k_D{}^c c) \tag{10}$$

are close to those expected for good solvents (Table II). Conversion of $k_D{}^c$ to volume fraction units[26] yields values of $k_D{}^\Phi$ of about 2.0 (Figure 5) in agreement with values predicted for good solvent systems.[43]

Comparison of certain of these experimental results with theoretical predictions is complicated because of the anomalously large magnitudes of the PEO/H_2O A_2 values. For example, predictions for $k_D{}^\Phi$ cast in terms of its

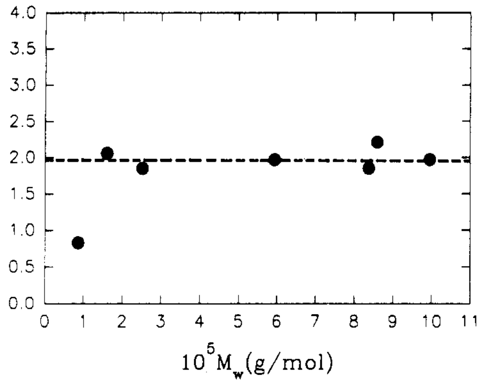

Figure 5. Interaction parameter k_D^Φ plotted against molecular weight, illustrating good solvent behavior. The average value of k_D^Φ is 1.97, where the first point corresponding to the lowest molecular weight is excluded. The dashed line at k_D^Φ = 1.97 shows the independence of k_D^Φ on molecular weight.

dependence on the ratio $X = \bar{S}/R_h$ are much too large in comparison to the actual, measured values of k_D^Φ obtained here. $\bar{S}$ is the coil "equivalent" hard-sphere radius obtained from the equilibrium second virial coefficient: $A_2 = 16\pi N_a \bar{S}^3/3M^2$. In terms of coil–coil interactions, $\bar{S}$ is meaningful as long as coil–coil interactions can be treated as interactions corresponding to those of hard spheres of radius $\bar{S}$. The details of the dependence of k_D^Φ on X then vary from treatment to treatment. For coils in good solvent, Yamakawa[26] predicts $k_D^\Phi = 3.2X^3 - 1$ while the prediction of Akcasu and Benmouna[47] is $k_D^\Phi = 2X^2(4X - 3)$, as examples. Both of these treatments generally agree with observed values of $K_D^\Phi \cong 2$, when $X \cong 1$ (see refs 37 and 48 and references therein, for example). Here, while k_D^Φ, as for other linear, flexible polymers in good organic solvents, $X = 1.28$, and, consequently, the calculated value of k_D^Φ is much too large in comparison to the measured value using either of the above cited, generally successful theoretical treatments. A longer ranged interaction, originating ultimately from localized polymer segment–solvent interactions, is observed. Recalling that[26]

$$k_D{}^c = 2A_2M - k_f{}^c - \bar{v} \qquad (11)$$

in concentration units with $\bar{v}$ the polymer partial specific volume in solution, it is seen that the friction coefficient virial coefficient, k_f^c, for PEO in water must be correspondingly large for measured k_D^Φ to have values of about 2.

A way of interpreting this situation is to assume that water molecules are "packed" so efficiently in the coil's interior that they swell the polymer to a size substantially larger than would normally be possible in a solution where such solvent packing and structuring is not possible. There is also evidence for local chain helicity from experimental measurements.[15] Also, the packing of water molecules at the ether linkages along the chain is greatly facilitated by the fact that PEO is an unusually flexible polymer. In fact, of all the linear, flexible polymer chains studied, PEO is reported to have the lowest characteristic ratio of 4.0.[49] This may be compared, for example, to the value of $C_\infty \cong 10$, for a "standard" linear, flexible polymer such as polystyrene. Coil expansion factors,[26] α_s, calculated from the known radii of gyration and unperturbed dimension[50] varied from 1.91 for the molecular weight of 2.52 × 10^5 to a maximum value of 2.2 for the highest molecular weight used, 9.96 × 10^5. For comparable α_s values, polystyrene in benzene[51] molecular weights ranged from 8.7 × 10^6 to 57 × 10^6, further corroborating the shift to lower molecular weights of PEO/water asymptotic behavior when compared to other polymer/good solvent systems. This helps to explain the large values obtained for the hydrodynamic radii and the radii of gyration as compared to values of the size of the coils for comparable molecular weights in other polymer/good solvent systems (see ref 37, e.g.). It is interesting to note that, in studies of polyacrylamide, another linear, flexible water-soluble polymer[52] in which power law relations were investigated, A_2 values were in fact comparable with those obtained for "typical" chains in organic good solvents. Taken altogether, then, the evidence suggests that the unusually large A_2 values obtained in this study are in fact a result of a particularly strong, perhaps even unique interation between PEO and water.

Intrinsic viscosity measurements of PEO/water solutions made in our laboratory[53] are consistent with those from static and dynamic light scattering measurements reported here. The exponent in the power law relation between intrinsic viscosity and molecular weight was found to be 0.795 and is thus that expected for a good solvent and is also in reasonable agreement with earlier measurements.[19,54,55] In addition, shear viscosities of polymer solutions exhibit a distinct quadratic dependence on polymer concentration in dilute solution, reinforcing the contention that PEO–PEO interactions in water are unusually strong.

Conclusions

In conclusion, we have shown that aqueous solutions of PEO for readily accessible molecular weights have certain extraordinary properties. The exponents obtained from power law relations of both static and dynamic single-chain parameters are representative of asymptotically good solvents. Further, the local structure of the solvent and site-specific interactions between the solvent and the polymer chain are shown not to affect power law exponents, as expected. The actual values of the second virial coefficient, the radius of gyration, and the hydrodynamic radius are much larger than is typically found for linear, flexible polymers in good solvents. Theoretical treatments assuming hard-sphere behavior to represent interactions between polymer coils in good solvent in equilibrium are found to be inadequate to account for the observed long-ranged interactions.

Further work to assess the nature of these unusual long-range interactions is in progress. Specifically, the ability of certain inorganic salts to "unpack" water molecules from within the PEO coil and the consequent implications for such size parameters as the hydrodynamic radius are being investigated.

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