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# Draining and Long-Ranged Interactions in the Poly(ethylene oxide)/Water Good Solvent System

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ABSTRACT: Viscometry results, in conjunction with earlier light scattering data, revealed anomalously large values of the parameters $\Pi = MA_2/[\eta]$ and $k_s/[\eta]$ for dilute solutions of high molecular weight poly(ethylene oxide) (PEO) in water at 30 °C. Taken together with unusually large values of $\rho = R_G/R_H$ and $X = \bar{S}/R_H$ for this system, it is concluded that these results may be partly explained by PEO coil draining, but, as suggested in the light scattering study, unusually strong and long-ranged PEO coil–coil interactions in solution were also responsible.

## Introduction

Aside from their considerable practical uses,[1-5] aqueous solutions of poly(ethylene oxide) (PEO) continue to be extensively studied, both theoretically[6] and experimentally[7] because such studies reveal new and interesting features of polymer behavior in solution. In particular, a recent light scattering investigation[8] of the PEO/$H_2O$ system for good solvent conditions indicates that PEO–PEO interactions in dilute solution are unusually strong, perhaps even anomalous in character, when compared to the behavior of other linear, flexible polymers in good solvent—behavior noted earlier in at least one experimental study of this system.[9]

Viscometry affords a powerful and relatively straightforward means of studying polymer behavior in solution. Specifically, extraction of the polymer intrinsic viscosity $[\eta]$ from the concentration dependence of measured shear viscosities, especially in conjunction with other solution parameters such as the friction virial coefficient $k_S$ and the solution second virial coefficient $A_2$, provides important information about this behavior. For these reasons, a number of viscometry studies of dilute solutions of PEO in water have been carried out and the results reported in the literature.[4,9-15] In the present work, the results of viscometry measurements, along with earlier light scattering measurements, are used to further investigate and characterize PEO behavior in dilute solution for good solvent conditions.

## Experimental Section

Viscosity measurements were made on seven well-characterized, narrow molecular weight distribution PEO samples ranging in molecular weight from 86 000 to 996 000 (Table I). Sample 5 was obtained from Pressure Chemical Co.[16] while the other samples were obtained from Toyo Soda Co.[17] Light scattering Zimm plot analyses confirmed the molecular weights reported by the vendor for samples 3, 4, 6, and 7 while that of sample 5 was found to be somewhat lower than the reported value.[8] The effectively monodisperse character of all seven samples ($M_W/M_N$ values reported in ref 8 are those reported by the vendor based on size exclusion chromatography measurements) was confirmed by photon correlation spectroscopy (PCS) measurements.[18] $M_W$ values for samples 1 and 2 were not confirmed by Zimm plot analyses but were assumed accurate based on the accuracies of the reported values for the other samples and because they gave results consistent with the other samples both from viscosity measurements of the present work and for measurements from earlier static and dynamic light scattering work.[8,18]

**Table I**
**PEO/$H_2O$, 30 °C Results**

| sample | $10^{-5}M_w$ | $[\eta]$ (mL/mg) | $k'$ | $\Pi$ | $k_S/[\eta]$ |
|---|---|---|---|---|---|
| 1 | 0.86 | 0.0861 | 0.681 | | |
| 2 | 1.60 | 0.141 | 0.446 | | |
| 3 | 2.52 | 0.227 | 0.225 | 1.73 | 2.98 |
| 4 | 5.94 | 0.397 | 0.217 | 1.99 | 3.62 |
| 5 | 8.38 | 0.529 | 0.295 | 1.74 | 3.49 |
| 6 | 8.60 | 0.540 | 0.293 | 2.01 | 4.01 |
| 7 | 9.96 | 0.633 | 0.265 | 1.92 | 3.84 |

PEO/$H_2O$ dilute solution shear viscosity measurements were made at 30 °C using a falling-needle viscometer (FNV). Details of the features and operation of the FNV are presented in ref 19. The FNV sat on a dedicated air table to avoid problems in measurement arising from mechanical vibrations. The temperature of polymer solutions in the FNV was controlled by circulating water from a temperature-controlled bath via insulated tubing through the water-jacketed FNV. The temperature stability and accuracy for solutions in this setup were reckoned to be 0.05 and 0.01 °C, respectively.

To improve the accuracy, reproducibility, and throughput of measured shear viscosities in the range 0.50–5.0 cP, the FNV was fitted with a specially designed needle dropping device. The modified FNV apparatus was then checked by measuring the viscosity, $\eta_0$, of neat, purified and degassed water (see below) at 30 °C. For seven replicate measurements, a mean value of $\eta_0$ = 0.784 cP with a root-mean-squared deviation of 0.009 cP (1.1%) was obtained. This value is within 1.7% of the reference value provided in ref 20, for example.

Stock PEO solutions for each molecular weight were prepared gravimetrically, and solutions of lower concentration were made from stock solutions by dilution. PEO samples were kept in a freezer between −15 and −20 °C under triply filtered Freon.

As emphasized in earlier light scattering investigations of aqueous PEO solutions,[8,18] water purity is essential for measuring PEO single-chain behavior in dilute aqueous solutions. Accordingly, house water used in these measurements was first purified by filtration, softening, and deionization and organic impurities were removed by passage through granulated and activated charcoal, all followed by reverse osmosis. This water was then further purified in the laboratory by filtration, deionization, passage through granulated and activated charcoal, and ultrafiltration using a point-of-use water "polishing" unit.[21] This water was then degassed by gentle heating. While the nominal resistivity of the polished water in the polishing unit was measured to be 12–18 MΩ-cm, after brief exposure to ambient air, the resistivity decreased to 2–4 MΩ-cm. Correspondingly, the pH of the water was about 5.5. For measurement, PEO solutions were then directly filtered into the FNV sample tube using 0.45-μm-rated pore size hydrophilic Nylon 66 disposable filters.[22]

While awaiting measurements, solutions were kept in sealed flasks in the dark under triply filtered Freon. To avoid bacterial degradation, a drop of spectrophotometric grade chloroform was added to each flask, and problems associated with mechanical

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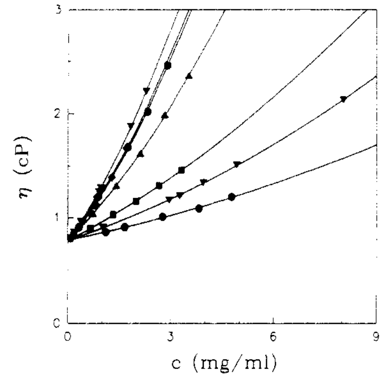

**Figure 1.** PEO/$H_2O$ dilute solution shear viscosity concentration dependences for seven PEO samples ranging in molecular weight from 86 000 (●) to 996 000 (▽).

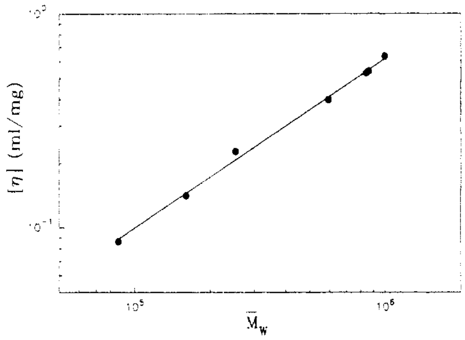

**Figure 2.** log–log presentation of the PEO intrinsic viscosity molecular weight dependence for seven high molecular weight PEO samples used to study the PEO/$H_2O$ good solvent system.

degradation[12] were circumvented by gentle handling, especially during PEO dissolution when gentle swirling, rocking, and periodic flask inversion were employed.

## Results and Discussion

This section is organized into two parts. In the first part, the more direct results of the present work, namely, the PEO intrinsic viscosities, the associated Huggins' coefficients, and the Mark–Houwink–Sakurada (MHS) parameters, are presented and discussed. In the second part, PEO intracoil behavior and the relationship between intracoil hydrodynamic interactions and excluded volume along with PEO–PEO interactions are discussed.

The viscosity measurement results of the present study are summarized in the seven plots of PEO solution shear viscosity, $\eta$, versus PEO concentration, $c$, presented in Figure 1. PEO–PEO interactions are clearly evident in the distinct upward curvature of these plots, behavior which, for a given polymer concentration, becomes increasingly stronger as PEO molecular weight increases. These plots were least-squares fit to a second-degree polynomial in $c$ and interpreted in terms of the virial expansion for $\eta(c)$:[23]

$$\eta(c) = \eta_0(1 + [\eta]c + k'[\eta]^2c^2) \tag{1}$$

with $\eta_0$ the viscosity of neat water, $[\eta]$ the PEO intrinsic viscosity, and $k'$ the Huggins' coefficient. PEO $[\eta]$ and $k'$ values are presented in Table I.

It was gratifying to see that $\eta(c)$ intercept values (Figure 1) for all seven PEO samples were very consistent, having a mean value within 0.8% of that for the seven replicate measurements of neat, purified water described earlier.

The molecular weight ($M_W$) dependence of $[\eta]$ is power law (Figure 2), and from the MHS relation[23]

$$[\eta] = KM^a \tag{2}$$

A direct power-law fit to the data yields $K = (1.10 \pm 0.48) \times 10^{-5}$ and $a = 0.791 \pm 0.032$ with $[\eta]$ expressed in mL/mg.

The Huggins' coefficients, except for the two lowest molecular weight samples, are quite consistent with a mean value of $k' = 0.26$. While this value is typical for linear, flexible polymers in good solvents,[14,15,23] it is nevertheless noteworthy because the corresponding PEO $[\eta]$ values are not at all typical (see below). The unusually high $k'$ values for samples 1 and 2 are presumably artifactual, arising from fit difficulties in assessing the coefficient of the $c^2$ terms in eq 1 due to the relatively weak curvature in the $\eta(c)$ versus $c$ data for these samples (Figure 1).

The value $a = 0.79$ reflects extensive coil swelling due to excluded volume effects and provides further support for the conclusion presented earlier[8] that the PEO/$H_2O$ good solvent system exhibits asymptotic good solvent behavior already in the molecular weight range $10^5$–$10^6$. These values for $K$ and $a$ for the PEO/$H_2O$ good solvent system are also in accord with earlier, experimentally determined values for the same system[4,9–12] for high molecular weight PEO, though the exponent, $a$, has been found to have a lower value for lower molecular weight PEO.[15]

The unusual degree of swelling for PEO coils in water as a good solvent is also apparent in that PEO intrinsic viscosity values are consistently larger than those for other linear, flexible polymers in good solvents. A rough comparison between PEO and certain of these other polymers for samples with comparable molecular weights illustrates the point: PEO $[\eta]$ values are about threefold larger than those for poly($\alpha$-methylstyrene) (P$\alpha$MS) in benzene[24] or toluene,[25] about fourfold larger than those for poly(methyl methacrylate) in benzene,[26] and about twice as large as those observed for polystyrene in benzene.[27] This extensive swelling was also observed as unusually large coil gyration and hydrodynamic radii ($R_G$ and $R_H$) for PEO.[8] For example, $R_G$ and $R_H$ values for a representative molecular weight of 500 000 were 452 and 260 Å for PEO in water at 30 °C[8] while the corresponding values for P$\alpha$MS in toluene at 25 °C were 301[28] and 195 Å.[29] Aside from "static" contributions to this enhanced coil size, such as relatively dense solvent packing within the PEO coil, the unusual chain flexibility PEO possesses with its corresponding local segmental mobility contributes to the overall increase in $R_H$, though this effect is relatively small (ref 30 and references therein).

A comparison between these viscometry study results and the earlier light scattering results[8] supports the oft-cited proportionality[23,31]

$$[\eta] \propto R_G^2R_H/M \tag{3}$$

since from the light scattering study

$$R_G^2R_H/M \sim M^{0.74\pm0.06} \tag{4}$$

with an exponent which is in reasonable agreement with the MHS value of $a = 0.79 \pm 0.03$ of the present study, considering the magnitudes of the associated uncertainties.

Intracoil and intercoil behavior in solution are inextricably interrelated, and oftentimes a suitably chosen measure of coil size, or some combination of such measures, is especially helpful in understanding the relationship between the two types of behavior. Moreover, the relationship between excluded volume effects and intrapolymer hydrodynamic interactions, or "draining", in polymers is of great interest. This relationship has been studied extensively by Douglas and co-workers,[32–36] and the results of their work provide a basis for better understanding some aspects of the unusual PEO behavior.

For example, from the intrinsic viscosity, it is possible to define a coil volume as[37]

$$V_\eta = M[\eta]/N_A \tag{5}$$

with $N_A$ the Avogadro constant. As for $[\eta]$ values, PEO $V_\eta$ values are thus 2–4 times larger than those for typical linear, flexible polymers in good solvent. In addition, a coil volume $V_{A_2}$ may be employed[37]

$$V_{A_2} = M^2A_2/N_A = 16\Pi\bar{S}^3/3 \tag{6}$$

with $\bar{S}$ the corresponding coil "effective hard-sphere radius".[23] Then the ratio $V_{A_2}/V_\eta$ is the well-known dimensionless parameter $\Pi$ used to assess coil excluded volume effects and the interplay between coil draining and excluded volume effects.[23,33,37]

$$\Pi = V_{A_2}/V_\eta = MA_2/[\eta] \tag{7}$$

For PEO samples 3–7, a mean value of $\Pi = 1.88$ was found (Table I), a value distinctly larger than the range $\Pi = 1.0$–$1.2$ generally observed for linear, flexible polymers in good solvent[23] and larger than the value of 1.10 predicted, at least, for nondraining coils.[32] By comparison, five P$\alpha$MS samples in toluene at 25 °C having a range of molecular weights comparable to these PEO samples are quite consistent with a mean value of $\Pi = 1.01$.[26,29]

It might be argued that unlike the PEO/H$_2$O good solvent system, other good solvent systems, such as P$\alpha$MS/toluene, had not achieved asymptotic good solvent behavior. To resolve this issue, the behavior of six very high molecular weight ($M_W = (8.8$–$57) \times 10^6$) samples of linear polystyrene in benzene at 25 °C was examined. Light scattering $A_2$ values for these samples were reported by Miyaki et al.,[38] and the intrinsic viscosities of the same samples under the same conditions were reported by Einaga et al.[39] For both studies, asymptotic behavior was observed: $A_2 \sim M^{-0.2}$ for the four highest molecular weight samples, while $[\eta] \sim M^{0.75}$ for all six samples. $\Pi$ values for these six samples were very consistent with a mean value of $\Pi = 1.20$, a value somewhat higher than the most current theoretical value of 1.10[32] (nondraining version) and among the higher results of other experimental studies. Despite asymptotic behavior, these polystyrene results were still in clear disagreement with the larger value of $\Pi = 1.88$ of the PEO/H$_2$O good solvent system.

Extensive excluded volume swelling in PEO resulted in unusually large $A_2$ values[18]—3–6 times larger than those for the P$\alpha$MS/toluene system[29]—while corresponding $[\eta]$ values, though still distinctly larger, were only 2–4 times as large[26] (see above). Thus PEO $\Pi$ values (eq 7) were about a factor of 1.5 larger than those for typical linear, flexible polymers of comparable molecular weight in good solvent for which $V_{A_2}$ and $V_\eta$ increased together more proportionately. $\Pi$ values of 1.2 observed for the very high molecular weight polystyrene coils in benzene were also a factor of roughly 1.5 smaller than the value of $\Pi = 1.88$ observed for PEO.

Large PEO $\Pi$ values may be at least partly explained by coil draining.[33,34] While extensive excluded volume swelling produced unusually larger $A_2$ values, draining, particularly through the outer portions of PEO coils, resulted in relatively small hydrodynamic radii, and this relatively smaller component of $[\eta]$ (eq 3) helped produce large $\Pi$ values. This explanation may also be used to rationalize what may be considered large values of the ratio $\rho = R_G/R_H = 1.73$ found for the PEO/H$_2$O good solvent system.[32]

The view that draining helped produce large PEO $\Pi$ and $\rho$ values is supported by considering PEO values for the coil interpenetration function, $\psi$, defined by the relation[23]

$$\psi = A_2M^2/4\pi^{3/2}N_AR_G{}^3 \tag{8}$$

The value of $\psi = 0.28$ for PEO[8] is not unusually large and is in fact a typical good solvent value.[23,32] Why then are $\Pi$ and $\rho$ uncommonly large while $\psi$ is not? To help answer this question, $\psi$ may be rewritten in terms of another ratio of volumes using

$$V_{R_G} = 4\pi R_G{}^3/3 \tag{9}$$

so that

$$\psi = 0.188V_{A_2}/V_{R_G} \tag{10}$$

Significantly, both of these volumes are strictly "static" parameters that characterize equilibrium coil size and behavior in solution. $V_{A_2}$ and $V_{R_G}$ do not reflect coil hydrodynamic behavior and are therefore presumably uninfluenced by draining. Though both increased markedly as a result of excluded volume swelling, they did so proportionately. By contrast, both $\Pi$ and $\rho$ reflect the increasing influence of draining with increasing excluded volume swelling since both depend on $R_H$: $\Pi, \rho \sim 1/R_H$ ($[\eta] \sim R_H$).

Another dimensionless ratio of unusually large magnitude for this PEO system is $k_S/[\eta]$, with $k_S$ the friction factor, $f(c)$, virial coefficient[23]

$$f(c) = f_0(1 + k_Sc + ...) \tag{11}$$

PEO $k_S$ values in the present study were calculated from measured values of $A_2$[8] and measured diffusion constant, $D(c)$, virial coefficients $k_D$[8] using the relation

$$k_S = 2A_2M - k_D - \bar{v} \tag{12}$$

For these high molecular weight PEO samples, the polymer partial specific volume in solution, $\bar{v}$, was negligible in eq 12.

For linear, flexible polymers in good solvent, measured $k_S/[\eta]$ ratios are generally about 1.6, in accord with theory.[23] PEO $k_S/[\eta]$ values are much larger, having a mean value of 3.6 (Table I). These PEO values were compared once again with another polymer system exhibiting asymptotic good solvent behavior. Five very high molecular weight ($M_W = (7.5$–$40) \times 10^6$) polystyrene samples in toluene at 20 °C had a mean $k_S/[\eta]$ value of 1.65. The polystyrene intrinsic viscosity results were reported by Meyerhoff and Appelt,[40] while the $k_S$ values for the same samples under the same conditions, determined directly from polymer sedimentation coefficient concentration dependences, were reported by Appelt and Meyerhoff.[41]

It is seen that neither $k_S$ (eq 12) nor $[\eta]$ (eq 3) is a "pure" parameter. Both contain static and dynamic terms. Nevertheless, the PEO $k_S/[\eta]$ ratio is anomalously large, apparently due to the combined effects of $A_2$ in $k_S$ and $R_H$ in $[\eta]$. Again, draining can help explain these unusually large PEO $k_S/[\eta]$ results.

Given the magnitudes of PEO $\Pi$, $\rho$, and $k_S/[\eta]$ values in comparison with "normal" values, it seems unlikely that draining alone is responsible for these anomalies. This view is supported by the results of a recent light scattering study of internal motions in very large polystyrene coils in good and $\Theta$ solvents.[30] For this polystyrene in toluene at 30 °C, an asymptotic good solvent system, the scattering wavevector dependence of the collective decay constant describing coil internal relaxations was consistent with increased draining for the coil swollen by excluded volume effects. This measurement, which "looked" directly at coil internal motions, was quite sensitive to solvent quality and to draining effects. Nevertheless, $\Pi = 1.2$ (only) for this system. Apparently, the difference between this measured value and the value of $\Pi = 1.10$ calculated for nondraining coils[32] is both real and significant, though $\Pi$ is a less sensitive measure of draining than the wavevector dependence of the collective decay constant studied in ref 30. The fact that the measured value of $\Pi = 1.2$ in the asymptotic polystyrene/toluene good solvent system is only about 10% greater than the predicted nondraining value while that for the asymptotic PEO/$H_2O$ good solvent system, $\Pi = 1.88$, is approximately 70% larger is noteworthy. Since both $A_2$ and $[\eta]$ are relatively larger in the PEO/$H_2O$ system, unusually larger $A_2$ is seen to be responsible for this behavior (eq 7). The comparison between the two systems and the implication of $A_2$ for the PEO/$H_2O$ system indicate that, along with draining, unusually strong PEO–PEO interactions in solution were also responsible for large PEO/$H_2O$ $\Pi$ values. Furthermore, for impenetrable hard spheres in solution, $\Pi = 1.6$,[23] a result which incorporates the assumption that the range of interpolymer forces is negligibly small compared to the dimensions of the polymer molecules. The result $\Pi = 1.88$ suggests, then, that PEO–PEO interactions were relatively long-ranged as well as relatively strong.

Measured PEO $k_D$ values were "typical" with a value of $k_D{}^\phi \approx 2$ (volume fraction units). Consequently, unusually large $A_2$ values meant unusually large $k_S$ values (eq 12). Such large $A_2$ and $k_S$ values suggest that PEO coil–coil interactions in solution were unusually strong. For typical linear, flexible polymers in good solvent, coil–coil interactions may be taken as due to interactions between hard spheres having radii something like $R_G$, $R_H$, or $\bar{S}$.[23,42,43] In such cases, $R_H$ and $\bar{S}$ are approximately equal so that $\bar{S}/R_H \approx 1$ and $k_D{}^\phi \approx 2$. An example of this behavior is provided by the PαMS/toluene system,[29] for which a semiempirical relationship between $k_D{}^\phi$ and $\bar{S}/R_H$ obtained:

$$k_D{}^\phi = 4.8X^3 - 2.0 \tag{13}$$

with $X = \bar{S}/R_H$. This relationship described the data especially well for a solvent quality range from Θ to good solvent, i.e., for $0 \leq X \lesssim 1$. Interestingly, eq 13 also provided a reasonable fit to data below the Θ temperature, i.e., for $-1 \leq X \lesssim 0$.

Substituting the PEO value of $X = 1.28$—again an unusually large value that is the ratio of a pure static parameter to a pure dynamic parameter—into eq 13 a value of $k_D{}^\phi = 8.1$ is obtained, a value in clear disagreement with the measured values of $k_D{}^\phi \approx 2$ and clearly off the $k_D{}^\phi$ versus $X$ PαMS "map" illustrated in ref 29. By comparison, $k_D{}^\phi$ values calculated from eq 13 are, on the average, only 19% below $k_D{}^\phi$ values for the five very high molecular weight polystyrene samples in toluene at 20 °C studied by Appelt and Meyerhoff.[41] These results support the earlier contention that PEO–PEO interactions in water are unusually long-ranged as well as unusually strong.

## Conclusions

Anomalously high values for the ratios $\Pi = MA_2/[\eta]$, $\rho = R_G/R_H$, $k_S/[\eta]$, and $X = \bar{S}/R_H$ for the PEO/$H_2O$ good solvent system may be partly explained by enhanced draining in coils extensively swollen by the effect of excluded volume.[35,44] Comparisons with other polymer/good solvent systems indicate that, in addition to draining, unusually strong and unusually long-ranged PEO coil–coil interactions are also responsible for these anomalously high values.

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**Registry No.** PEO, 25322-68-3; $H_2O$, 7732-18-5.