Aggregative Behavior of Poly(ethylene oxide) in Water and Methanol

Shinichi Kinugasa,* Hisae Nakahara, Noriko Fudagawa, and Yoshinori Koga

National Institute of Materials and Chemical Research, Higashi 1-1, Tsukuba 305, Japan

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ABSTRACT: Static and dynamic light scattering were measured for monodisperse poly(ethylene oxide) (PEO) in water and methanol at 25 °C. PEOs of three different molecular weights ranging from nominal $M_w = 2.6 \times 10^4$ to 9.96×10^5 were used. For all of these molecular weights, angular dependence of Zimm plots showed no downturn at low angles not only in water but also in methanol, indicating no large aggregates of PEO in both solvents. Furthermore, apparent weight-average molecular weight $M_{w,app}$, radius of gyration $R_{G,app}$, and hydrodynamic radius $R_{H,app}$ did not change over 3 weeks. This observation indicates that molecularly dispersed PEO is stable and aggregate-free property is inherent in these solvents.

Introduction

Since Elias and Lys' experiments,[1] many authors have studied the aggregation of poly(ethylene oxide) (PEO) in water[2–4] and in some organic solvents.[5–8] It has been reported that PEO aggregates in various solvents. For example, it has been reported that particularly low-molecular-weight PEO has a pronounced tendency to aggregate in water.[2,9] In addition to aqueous solution, aggregation of PEO in methanol is another interesting problem because until recently conflicting evidence has been given in the literature. Elias outlined the aggregation problem on the basis of his and Strazielle's results of static light scattering (SLS) measurements.[10] Recently, Zhow and Brown reported that PEO molecules aggregate in methanol:[8] they observed a significant downturn in angular distribution of inverse excess Rayleigh ratio $Kc/\Delta R_\theta$ at low angles.

However, recent light scattering experiments by Devanand and Selser have given evidence for no aggregation of high-molecular-weight PEO molecules in water.[11,12] They have also insisted that it is important to take proper care in the preparation of PEO aqueous solutions. Furthermore, dynamic light scattering (DLS) experiments by these authors have given evidence that PEO does not necessarily aggregate in methanol nor in water.[11]

In this study, our attention is focused mainly on the question of whether the PEO aggregation in water and methanol is an inherent property or not. To investigate the PEO aggregation, we have used techniques of SLS because the curvature of angular dependence of scattered light at low angles is very sensitive to aggregation in solution. We have also explored the time dependence of angular variation of SLS and the photon correlation function of DLS at constant temperature over a long period of time in order to check the stability of PEO in both solvents.

Experimental Section

Sample Preparation. We used three monodisperse and well-characterized PEO samples. These samples were purchased from the Tosoh Co., Japan. The characteristics of the PEO samples are listed in Table 1. Prior to solution preparation, the PEO samples were dried under vacuum over 1 or 2 days at room temperature.

Table 1. Characteristics of PEOs

type	$M_w \times 10^{-5}$ [a]	$M_w \times 10^{-5}$ [b]	M_w/M_n [b]
SE2	0.22	0.26	1.20
SE30	3.1	3.4	1.05
SE150	9.92	9.96	1.05

[a] Measured values by SLS from PEO in water. [b] Values provided by the manufacturer.

For the preparation of aqueous PEO solutions, two kinds of water were prepared. One (water-I) was prepared by doubly distilling with glassware commonly used for the preparation of dust-free water. The other (water-II) was obtained from special purification equipment (Model-S, Organo Co., Japan): water was purified by a process of deionization coupled with filtration. The pH, resistivity, and concentration of Fe of the two waters are presented in Table 2, respectively. Here, the concentration of Fe in the waters was determined by metal furnace atomic absorption spectrometry.[13]

Table 2. Characteristics of Two Kinds of Water

type	pH	resistivity (MΩ·cm)	Fe (mM)
water-I	6.2	0.70	1.0×10^{-5}
water-II	6.4	15.1	5.4×10^{-7}

Spectral grade methanol (Dojindo Lab. Co., Japan) was used as the solvent: it was refluxed over Mg to remove water and then distilled. Spectral grade benzene (Dojindo Lab. Co., Japan), which was used for optical calibration, was refluxed over calcium hydride (CaH_2) and then distilled. All solutions were prepared gravimetrically, and their polymer mass concentrations c (g·mL^{-1}) were calculated from their weight fractions. In this calculation, we used the density of methanol $\rho_0 = 0.7866$ g·mL^{-1} at 25 °C. All solutions, including the aqueous solutions, were stirred first at 50 °C for about 1 h and then shaken in shielded tubes continuously for about 2 days at 26 ± 1 °C.

For optical clarification, all the sample solutions were centrifuged at 30 °C in a Beckman Model L8-M ultracentrifuge. Centrifugal acceleration is 160 000g for the aqueous solutions and 63 000g for the methanolic solutions, respectively. Further, the centrifuged solutions were filtered slowly and directly into light scattering cells through two 0.2-μm (nominal pore size) PTFE filters (Advantec Toyo Co., Japan).

Static Light Scattering. SLS measurements were carried out with a commercial photometer DLS-700 (Otsuka Electronics Co., Japan). Vertically polarized light of $\lambda_0 = 633$ nm wavelength from a 5-mW He–Ne laser was used as an incident beam. Intensities of scattered light were measured at scattering angles $\theta = 20$–130° in increments of 5°. All measurements were performed at 25.0 ± 0.1 °C. To avoid precipitation by cooling, all solutions were kept at 25 ± 1 °C in a dark room throughout the experiment except when light scattering measurements were made. Other details of the measurement conditions were described in our previous papers.[14]

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* To whom correspondence should be addressed.

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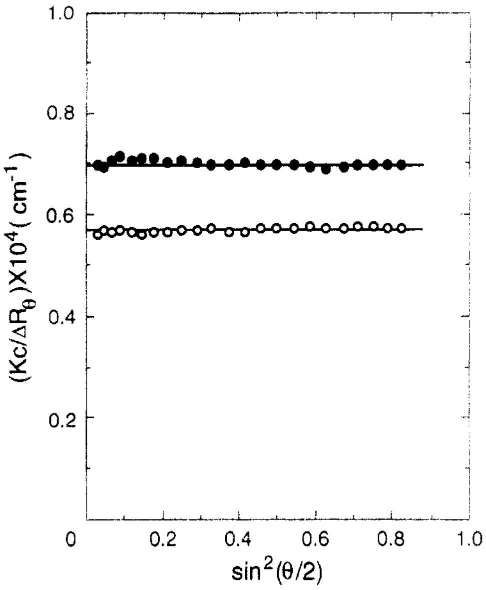

Figure 1. Angular distribution of the excess Rayleigh ratio ΔR_θ for PEO SE2 solutions at 25 °C: (○) in water (c = 4.34 mg/mL); (●) in methanol (c = 4.12 mg/mL).

Rayleigh ratio R_θ of the scattered light was calculated on the basis of the Rayleigh ratio $R_B = 11.84 \times 10^{-6}$ cm^{-1} of pure benzene at the wavelength λ_0 = 633 nm. Specific refractive index increment dn/dc of PEO (PEG20000; Fulka) in methanol at 25 °C was measured at λ_0 = 633 nm using a Brice KMX-16 differential refractometer (Chromatix Inc.). The measured value of dn/dc is 0.142 mL·g^{-1}. For the value of dn/dc of PEO in water at 25 °C, we used 0.134 mL·g^{-1}.[2] Scattered intensity data were analyzed in terms of the Zimm plot method: the excess Rayleigh ratio ΔR_θ was plotted against $\sin^2(\theta/2)$ or the magnitude of the scattering vector q

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{M_{\mathrm{w,app}}}\left(1 + \frac{R_{\mathrm{G,app}}^{\;2}}{3}q^2\right) \quad \left(q = \frac{4\pi n_0}{\lambda_0}\sin\frac{\theta}{2}\right) \qquad (1)$$

where n_0 is the refractive index of the solvents and K is the optical constant given as $K = 4\pi^2 n_0^{\,2}(\mathrm{d}n/\mathrm{d}c)^2/(\lambda_0^{\,4}N_A)$ with Avogadro's number N_A. Here, $M_{\mathrm{w,app}}$ and $R_{\mathrm{G,app}}$ are defined as the apparent molecular weight and radius of gyration, respectively.

Dynamic Light Scattering. DLS measurements were performed for the SE150 sample in both water and methanol at 25 °C with the same apparatus as the SLS measurements. The normalized autocorrelation function $g^{(2)}(t)$ of the scattered intensity was measured at a scattering angle θ = 20°, corresponding to the small-qR_G region where contributions of internal coil motions to $g^{(2)}(t)$ can be neglected. Using the homodyne method, the following equation is derived:[15]

$$\ln|g^{(2)}(t) - 1| = \mathrm{const} - \Gamma t + (\mu_2/2)t^2 + ...$$

where Γ and μ_2 are the first and second cumulants, respectively. An apparent hydrodynamic radius of the PEO coil $R_{\mathrm{H,app}}$ was obtained from the Stokes–Einstein relationship, $R_{\mathrm{H,app}} = k_BT/6\pi\eta_0 D_{\mathrm{app}}$ where k_B is Boltzmann's constant, T is the absolute temperature, and η_0 is the solvent viscosity, respectively. Here, the apparent diffusion coefficient D_{app} was derived from the first cumulant Γ by the equation $D_{\mathrm{app}} = \Gamma/q^2$.

Results and Discussion

Aggregation in aqueous solution of low-molecular-weight PEO is still uncertain. In fact, from the angular dependence of scattered light, it has been shown that low-molecular-weight PEO ($M_w = 2 \times 10^4$) has a pronounced tendency to aggregate in water.[2,9]

First, we explored aggregation of low-molecular-weight PEO in water and methanol. Figure 1 shows the angular dependence of excess scattered light from the low-molecular-weight PEO SE2 in water (deionized water-II), i.e., $Kc/\Delta R_\theta$ is plotted against $\sin^2(\theta/2)$. As the figure shows, no striking downturn at low angles is observed, indicating that the PEO molecules disperse molecularly and practically no aggregate exists in water. This is in contrast to the earlier results reported by Polik and Burchard.[2] The difference between our result and theirs might come from end-group effects because the effects become greater as the polymer chain becomes shorter. Unfortunately, we cannot discuss the effects anymore because we do not know the details on the synthesis routes for the respective low-molecular-weight PEO samples.

Solution preparation may possibly be the reason for the difference in the angular dependences of $Kc/\Delta R_\theta$. As described in the Experimental Section, we heated the solution up to 50 °C before optical clarification. This heating process might dissolve residues of PEO crystals which could be present around room temperature.[6] Furthermore, optical clarification, especially filtration, is an important factor in the solution preparation, though it is usually difficult to remove dust or aggregates from aqueous solution. As a matter of fact, we found from experience that rapid filtration frequently gives an apparent downturn at low angles.

In addition to the aqueous solution, the angular dependence of $Kc/\Delta R_\theta$ for PEO in methanol is similar to that of the aqueous solution as Figure 1 shows: similarly no downturn is observed at low angles. This indicates that low-molecular-weight PEO does not aggregate in methanol nor in water within the scattering angles θ = 20–130°. In this case, heating of the solution in the solution preparation may be important to obtain the aggregate-free methanolic solution. In the literature, there is an example showing that curvature of the angular dependence of $Kc/\Delta R_\theta$ greatly decreases by heating solutions.[5] PEO crystallizes near 19 °C in methanol, and therefore microscopic and stable crystalline nuclei could exist even in dilute solutions of PEO around room temperature.[3,6]

For high-molecular-weight PEO aqueous solutions, Devanand and Selser have recently given evidence that PEO does not necessarily aggregate in water:[11,12] they have obtained good Zimm plots with no downturn at low angles. To obtain such aggregate-free aqueous solutions, they have taken special care in preparing solutions. The water used in their experiments was highly purified, and their sample solutions were carefully treated to avoid oxidation effects. As Table 2 shows, water-II, which may correspond to the highly purified water described above, is purer than water-I corresponding to those commonly used in SLS experiments. We checked the concentration of iron for both waters because the degradation of the PEO chain is catalyzed by Fe^{3+} ions in an oxygen atmosphere.[16] However, Table 2 shows that the concentration of iron is extremely less than that which induces the degradation for both waters.

Figure 2 shows a typical Zimm plot of SE150 in water. A good Zimm plot has been obtained, and the observed molecular weight $M_w = 9.92 \times 10^5$, in good agreement with the manufacturer's value $M_w = 9.96 \times 10^5$ determined by low-angle light scattering. There exists no downturn at low angles in accordance with Devanand and Selser's results.[12] This is so with respect to the PEO of SE30 and SE2 in water. The good agreement of M_w indicates that filtration and ultracentrifugation cause neither degradation nor precipitation.

In these measurements, water-I was used instead of water-II and no special care was taken in preparing the aqueous solutions without preheating. On the contrary,

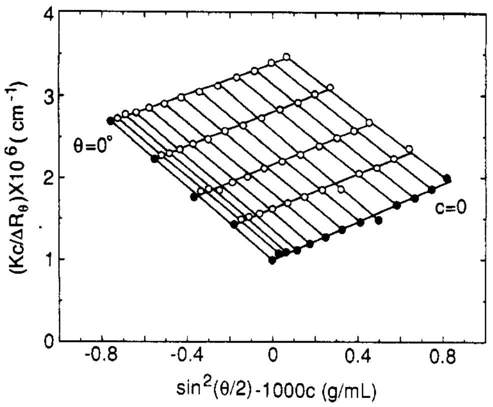

Figure 2. Typical Zimm plot of PEO SE150 in water at 25 °C.

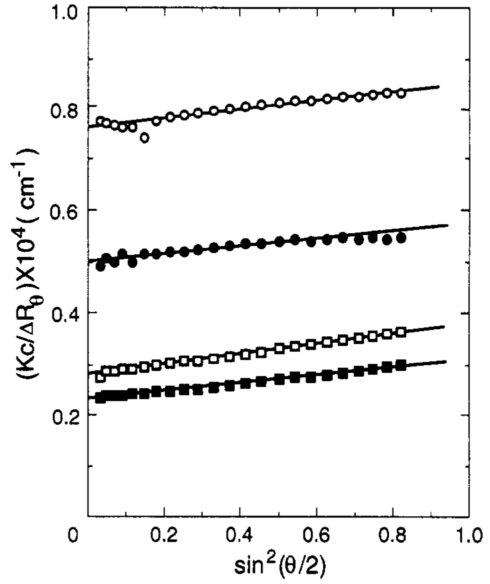

Figure 3. Angular distribution of the excess Rayleigh ratio ΔR_θ of PEO solutions at 25 °C: (○) PEO SE30 in water (c = 1.58 mg/mL); (●) in methanol (c = 0.939 mg/mL); (□) PEO SE150 in water (c = 0.775 mg/mL); (■) in methanol (c = 0.805 mg/mL).

Devanand and Selser insisted that highly purified water, water-II in our experiments, should be used to obtain aggregate-free solutions.[12] Nevertheless, we obtained good Zimm plots for all the PEO samples. This indicates that the special care in the preparation of the PEO aqueous solution is not necessarily essential to obtaining the good Zimm plots. Instead, we have found that it is important to clarify the solutions carefully rather than to take the special care in the solution preparation described by Devanand and Selser.[11,12] The important thing in the solution preparation is that sample solutions and solvents should be filtered more slowly and carefully into light scattering cells because dust or aggregates cannot be removed completely.

In Figure 3, plots of $Kc/\Delta R_\theta$ against $\sin^2(\theta/2)$ are shown for dilute solutions of the SE30 and SE150 samples in both solvents. Contrary to the results by Zhou and Brown,[8] there exists neither downward curvature nor significant downturn at low angles. To the best of our knowledge, this is the first time that linear plots of $Kc/\Delta R_\theta$ against $\sin^2(\theta/2)$ for PEO in methanol are obtained. This linear angular dependence indicates that high-molecular-weight PEO does not necessarily aggregate in methanol nor in water. At the present time we cannot explain clearly why there exists the discrepancy of scattering behavior between our results and those by Zhou and Brown.[8] However, at least the end-group effect is not the reason for the discrepancy because both of the high-molecular-weight PEO samples we used and those used by Zhou and Brown are from the same source or have the same chemical structure, including end groups.

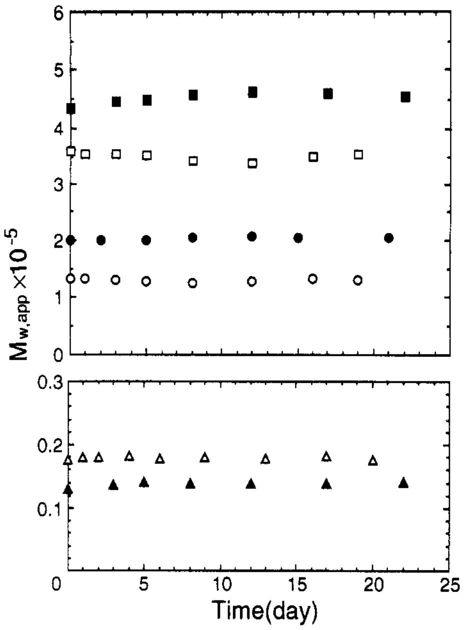

Figure 4. Time dependence of the apparent weight-average molecular weight $M_{w,app}$ for PEO solutions at 25 °C: (△) PEO SE2 in water (c = 4.34 mg/mL); (▲) in methanol (c = 4.12 mg/mL). Other symbols are the same as in Figure 3.

In these cases, we also found from experience that careful optical clarification of the solution is quite essential to obtaining aggregate-free solution as well as in the case of the aqueous solution of the low-molecular-weight PEO. Furthermore, heating of the methanolic solutions in the solution preparation might be essential to aggregate-free solutions.

It is very important to investigate the time course of SLS from the PEO solutions for a long period of time because optical clarification may affect inherent solution properties. As a matter of fact, it has been reported in the literature that filtration of the solution induces crystallization for high-molecular-weight PEO.[10] It has also been suggested that PEO suffers degradation through filtration or dialysis.[17] Further, optical clarification might remove aggregates erroneously which exist in the solution by nature. The aging process of PEO dissolved in solution is another problem in considering its solution properties. For example, aggregates of PEO in water are shown to be unstable and time-dependent:[3] initial aggregates of PEO dissociate gradually with time over a long period of time.

We have repeatedly measured the angular dependence of ΔR_θ of PEOs in dilute aqueous and methanolic solutions over a period of about 3 weeks. For all the molecular weights of PEOs, the observed angular dependences were essentially the same as the initial ones such as shown in Figures 1 and 3. The angular distribution of $Kc/\Delta R_\theta$ against $\sin^2(\theta/2)$ for each measurement could be fitted well by eq 1. The fit of each scattering data to eq 1 gives the values of the apparent $M_{w,app}$ and $R_{G,app}$. Figure 4 shows the variation of the apparent molecular weight $M_{w,app}$ as a function of time observed for PEOs in both solvents over 3 weeks. For all the PEO samples, we found that within experimental error $M_{w,app}$ does not change over the period of time.

In addition, the time dependence of the apparent radius of gyration $R_{G,app}$ is shown in Figure 5. Although the data points are somewhat scattered, $R_{G,app}$, as well as $M_{w,app}$, does not vary with time. These findings suggest that the

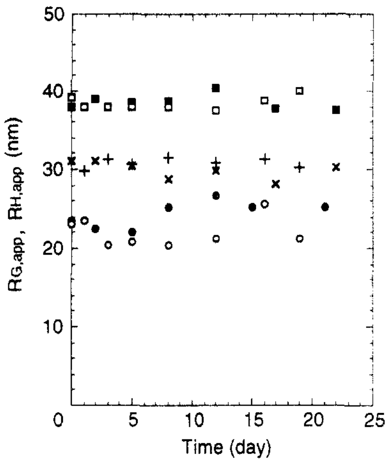

Figure 5. Time dependence of the apparent radius of gyration $R_{G,app}$ and hydrodynamic radius $R_{H,app}$ for PEO solutions at 25 °C. $R_{H,app}$: (+) PEO SE150 in water (c = 0.775 mg/mL); (×) in methanol (c = 0.805 mg/mL). Other symbols are for $R_{G,app}$ and have the same meanings as in Figure 3.

distribution of PEO molecules in these solvents is quite stable and does hardly vary with time for a long period of 3 weeks.

Our results of the apparent hydrodynamic radius $R_{H,app}$ also gave evidence for aggregate-free solution properties for both solvents. Figure 5 shows $R_{H,app}$ of SE150 as a function of time, where $R_{H,app}$, as well as $R_{G,app}$, is independent of time. The observed values of $R_{H,app}$ for the aqueous solution are consistent with those evaluated from the experimental concentration dependence of the diffusion coefficient D_{app} corresponding to molecularly dispersed PEO.[11] In addition to $R_{H,app}$, another important factor is a polydispersity factor μ_2/Γ^2, the normalized second cumulant, which is a measure for the width of distribution of particle sizes in solution.[18] Larger values of the factor indicate wider distributions of particle sizes or presence of aggregates. In our experiments, the values of μ_2/Γ^2 remained usually less than 0.15 for both solvents. They are comparable with the value 0.1 obtained by Devanand and Selser.[11] According to these authors, the small values also indicate that PEO does not form aggregates. On the other hand, the corresponding values of polydispersity factors presented by Layec and Layec-Raphalen range from 0.3 to 0.46, much higher than our values.[3]

Conclusions

In conclusion, using light scattering methods, we have shown that PEO does not aggregate not only in water but also in methanol at 25 °C within our results. For high-molecular-weight PEOs, our result is fully consistent with the recent results by Devanand and Selser.[11,12] Furthermore, we have also shown that molecularly dispersed PEO is quite stable in these solvents over a long period of time. To obtain aggregate-free PEO solutions of water and methanol, we found that preheating and careful optical clarification of the solutions are quite important: incomplete operations in solution preparation easily give anomalous light scattering erroneously attributable to "aggregates" both in water and in methanol. Our success in the preparation of unaggregated PEO dilute solutions could pave the way for a basic study of the solution properties of PEO in methanol. The study of dilute solution properties such as the radius of gyration as a function of PEO molecular weight in methanol is currently taking place.

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