LETTER

Clustering of Poly(ethylene oxide) in Water Revisited

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ABSTRACT: The dynamic light scattering results presented in this letter demonstrate that the clustering of poly(ethylene oxide) (PEO) can be observed even in ultrapure, freshly double-distilled and filtered deionized water. It is confirmed that the filtration of solutions removes the clustering structure and that a steady-state amount of PEO in clusters is reformed in filtered solutions within 24 h. Adding a drop of chloroform to unfiltered aqueous solutions of PEO temporarily alters the clustering structure, but it prevents the clustering of PEO in filtered solutions. © 2002 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 41: 135–138, 2003

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There has been a large amount of research interest in the poly(ethylene oxide) (PEO)/water system. This interest is due to the great similarity of the basic interactions (hydrogen-bonding and hydrophobic interactions) involved in PEO/water and protein/water systems. The PEO/water system is a simple model system (synthetic analogue) for studying fundamental biomolecular interactions in which hydrogen-bonding and hydrophobic interactions play an important role, such as protein folding and stabilization. Among all the unique properties of PEO solutions, the clustering behavior of PEO in water is the most intriguing and has been extensively studied. The contradictions in the experimental literature[1–8] raise the question of whether the clustering of PEO in water is an intrinsic property of the basic interactions. Our research interests in the cluster formation of PEO in water have led us to a previous investigation[3] in which the authors concluded that the clustering of PEO in solution is due to impurities in the water used. The authors reached this conclusion after performing dynamic light scattering (DLS) measurements in which they added a drop of chloroform to the PEO/water solutions and then filtered the solutions (not just the water). For the verification of their conclusions, a series of systematic experiments were undertaken in which their procedures were followed closely, but the steps were broken down and investigated individually and carefully with the DLS technique.

PEO with a weight-average molecular weight (M_w) of 100,000 g/mol and a number-average molecular weight (M_n) of 96,000 g/mol was dissolved in freshly double-distilled deionized (DI) water (pH ~ 6.4) at a concentration of approximately 0.025 wt %. Solutions were allowed to reach equilibrium overnight under ambient conditions before the DLS measurements. For the verification of the filtration effect on PEO clusters in water, the same batch of the initial (unfiltered) solution at 0.025 wt % was filtered through a 0.1-μm filter directly into a 45-μL sample cell and measured immediately. The filtered solution in a sample cell was then well sealed and remeasured as a function of time (for 1 day, 4 days, etc.). A fresh and clean filter was used for each solution. Before use, all glassware and sample cells were cleaned in chromerge at 80 °C for 3 h to remove any organic residuals, thoroughly rinsed with DI water, and dried in an oven at 100 °C for 2 h. All the

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solutions studied were probed by DLS at 25.0 ± 0.1 °C. Each measurement was carefully carried out twice so that the reproducibility of the results was ensured. The DLS measurements were performed with a laser wavelength of 8324 Å and at a scattering angle of 90°. DLS is a powerful technique for directly measuring cluster populations in solutions. Monochromatic laser light scattered by a solution at a given angle is analyzed in terms of the autocorrelation function $g^{(2)}(t)$ obtained over a broad range of time t. Through a Laplace inversion, the obtained spectra can be transformed to yield a population distribution of hydrodynamic radii $N(R_h)$,[9,10] as illustrated in Figures 1–3, if we assume that the characteristic relaxation time represents the diffusion process.

The 0.025 wt % unfiltered solution (without chloroform) exhibits two peaks (modes), as shown in Figure 1(a). The first peak (peak 1), also known as the fast (or cooperative diffusion) mode, at approximately 0.01 μm corresponds to the random PEO coils, whereas the second one (peak 2), called the slow (or interdiffusion) mode, represents the clusters in solution.[10] The hydrodynamic radius R_h for random coils of PEO used in this work was calculated to be approximately 104 Å (1 Å = 10^{-4} μm) with the following equation:[5] $R_h = 0.145 M_w^{0.571}$. In contrast, the filtered solution, measured immediately after filtration [Fig. 1(b)], only shows the random coil peak (fast mode), indicating that filtration removes or destroys the clustering structure. However, a measurable amount of PEO clusters in the filtered solution was observed within 24 h [Fig. 1(c)]. If the area underneath the peaks reflects the corresponding amounts of coils or clusters in the solution, both the average size and the amount of clusters reformed in the filtered solution remained stable for up to 10 days under the experimental conditions. These observations are in good agreement with the results of Polverari and van de Ven.[7]

In addition, contrary experimental results from PEO in methanol solutions were reported by Zhou and Brown[4] and Kinugasa et al.,[6] probably because of solution filtration. Kinugasa et al. centrifuged and filtered the PEO solutions before the measurements and observed no clustering, whereas Zhou and Brown measured the solutions directly and obtained evidence of clustering. Both groups used the same PEO samples, as pointed out by the authors;[6] therefore, the history of the PEO materials used, proposed by Duval and Sarazin,[8] should not be responsible for the clustering behavior in this case.

A drop of chloroform was added to the same batch of the 0.025 wt % unfiltered solution to determine the corresponding effects on clusters of PEO in ultrapure water. Analytical-grade chloroform was filtered twice through a 0.22-μm solvent-resistant filter to remove all dust before use. The same batch of the 0.025 wt % unfiltered PEO solution with chloroform was then filtered directly into a sample cell and measured immediately. Both the unfiltered and filtered solutions with chloroform were measured as a function of time.

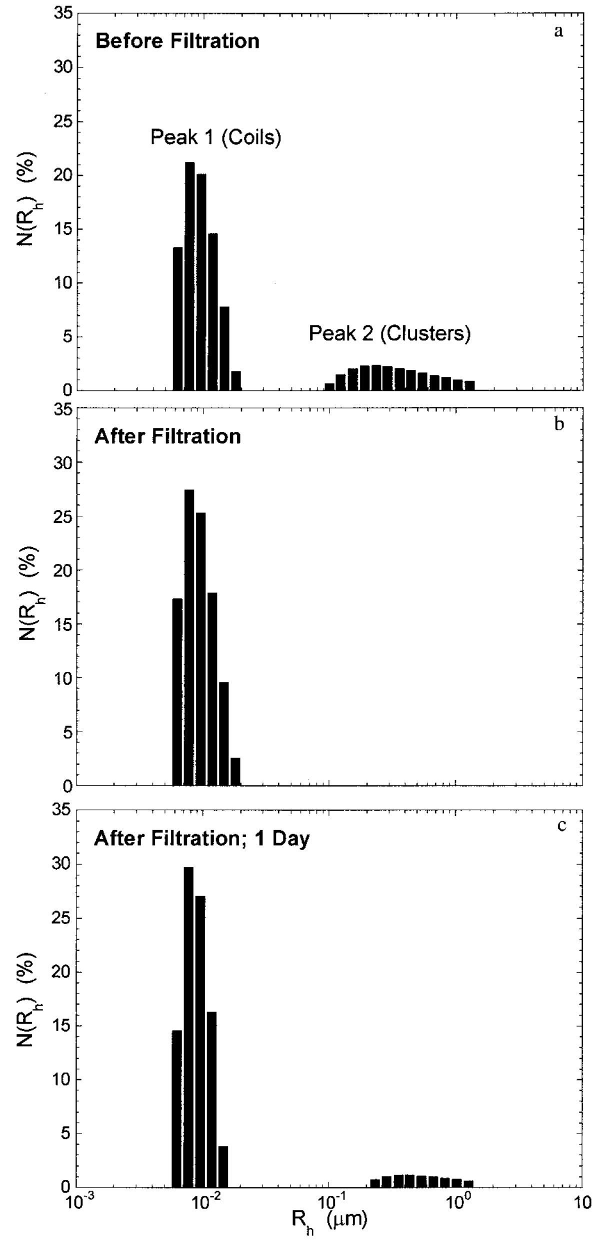

Figure 1. Histogram of $N(R_h)$ from the 0.025 wt % solution without chloroform measured with DLS: (a) before filtration, (b) immediately after filtration, and (c) 1 day after filtration.

Adding a drop of chloroform[3] to the unfiltered PEO solution affects the clustering structure, but it prevents the clustering in the filtered solution sample, as illustrated in Figures 2 and 3, respectively. Solutions without and with chloroform, filtered and measured immediately, possess only the first peak, corresponding to the random coils of PEO in solution, as demonstrated in Figures 1(b) and 2(c), respectively. Perhaps this resulted in the following erroneous conclusion:[3] "finding that within experimental uncertainties, the presence of chloroform did not affect our results." No evidence of clustering was observed in the filtered solution with chloroform within the experimental time performed, as shown in Figure 3. It is noted that switching the order of adding chloroform and filtration (i.e., filtering the original aqueous PEO solution first and then adding one droplet of chloroform) does not affect the results. Consequently, had the authors[3] waited for a certain time period before performing the measurements on the filtered solution with chloroform, no evidence of aggregation would also be expected. In the unfiltered solution with chloroform, the second peak (slow mode) was recovered within 24 h and remained stable for up to 4 days under the experimental conditions.

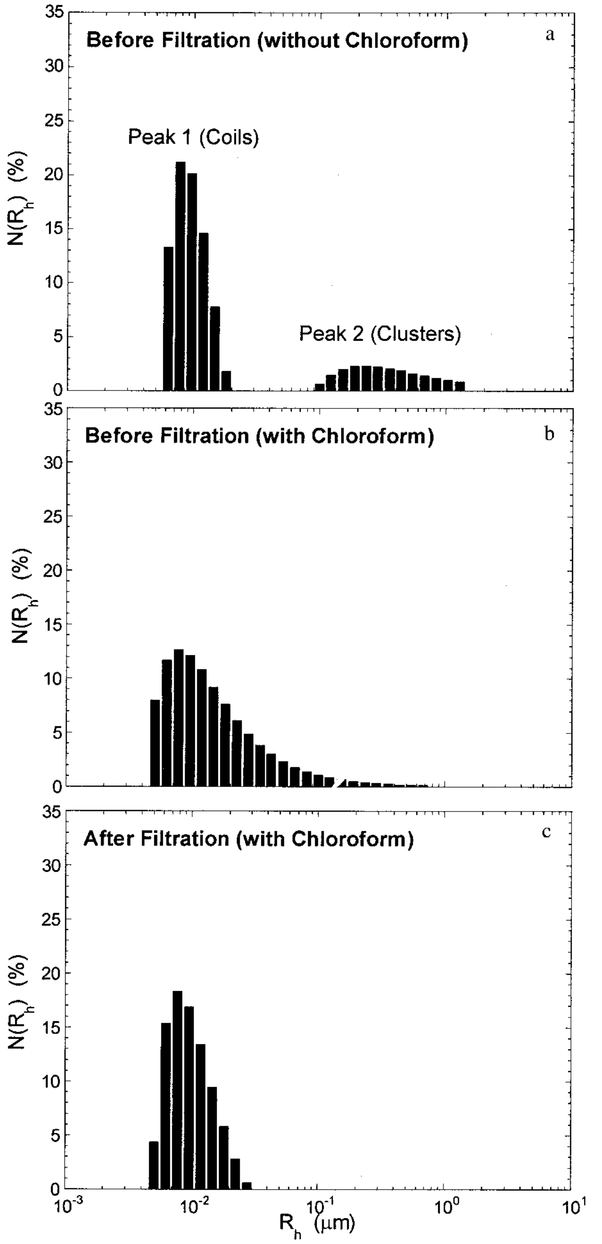

Figure 2. Histogram of $N(R_h)$ from the 0.025 wt % solution measured with DLS: (a) without chloroform and before filtration, (b) with chloroform and before filtration, and (c) with chloroform and immediately after filtration.

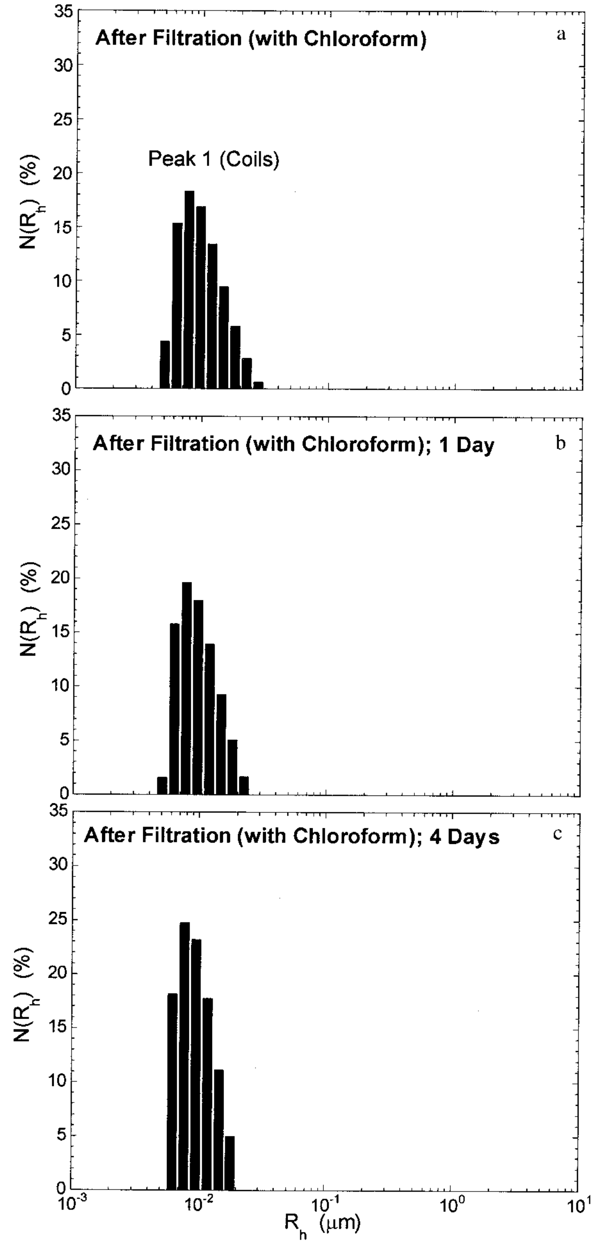

Figure 3. Histogram of $N(R_h)$ from the 0.025 wt % solution with chloroform measured with DLS: (a) immediately after filtration, (b) 1 day after filtration, and (c) 4 days after filtration.

Three major interactions occur in the PEO/water system: (1) repulsive hydrophobic interactions between

the CH_2 groups and the water molecules;[11] (2) attractive hydrogen bonding between PEO monomer groups mediated by water molecules,[12,13] that is, —CH_2CH_2O...HOH...OCH_2
CH_2—; and (3) van der Waals interactions. The weak van der Waals attractions contribute to the crystallization of PEO, which was not observed in any of our low-concentration PEO solutions with wide-angle X-ray scattering. This observation, plus their relatively weak strength, suggests that van der Waals attractions do not contribute to cluster formation in PEO. Another polymer system[14] exhibited small-angle neutron scattering (SANS) behavior similar to that of our PEO/water system,[13] namely, scattering from two different length scales corresponding to individual polymer coils and large clusters. Blends of polystyrene and poly(butyl methacrylate) were modified by the addition of specific hydroxyl (OH) groups to the backbone of polystyrene to introduce hydrogen-bonding interactions.[14] This polymer blend system does not contain any hydrophobic interactions (no water involved) or crystallinity; therefore, the dominant interactions arise from hydrogen bonding. The similarity of the two-length-scale SANS spectra for our PEO/water system and this blend system adds evidence to these DLS results that clustering is dominated by hydrogen bonding.

The DLS results presented in this article demonstrate that the clustering of PEO can be observed even in ultrapure, freshly double-distilled DI water. It is confirmed that the filtration of solutions removes the clustering structure and that a steady-state amount of PEO in the clusters is reformed in the filtered solution within 24 h.[7] Adding a drop of chloroform to unfiltered aqueous solutions of PEO temporarily alters the clustering structure, but it prevents the clustering of PEO in filtered solutions. It is clear that the solution filtering process and the addition of a drop of chloroform are steps that eliminate the PEO clusters in solution. Either of these steps is enough to remove the clusters. The same filtration effect on PEO clusters and the cluster reformation of PEO in filtered solutions were also observed in solutions of the same PEO material in filtered DI water (pH ~ 7.1) and DI water (pH ~ 7.0) by DLS. The DLS data suggest that if one waits long enough, the clusters reappear even in an ultrapure and dust-free solvent/solution system (without chloroform).

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