Apparent Aggregation Behavior of Poly(ethylene oxide) in Water as a Result of the Presence of an Impurity[†]

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ABSTRACT: Poly(ethylene oxide) does not aggregate in dilute water solutions. The slow-mode behavior frequently observed by dynamic light scattering from poly(ethylene oxide) solutions in water already below and around the coil overlap concentration, often interpreted as the onset of semidilute behavior and/or clustering, is shown to be a result of the presence of an impurity. The impurity may be conveniently described as microdroplets or compact microparticles, sterically stabilized by the presence of poly(ethylene oxide) macromolecules, formed from a hydrophobic organic substance sparingly soluble or insoluble in water and increasingly soluble in methanol and collected within samples at the ppm level during their whole history. A solid phase extraction mechanism governs the successful removal of the impurity from poly(ethylene oxide)–water solutions when hydrophobic filters are used.

Introduction

Aqueous solutions of poly(ethylene oxide) (PEO) exhibit anomalous interactions in several respects;[1–4] in particular, their aggregation has been a matter of concern in dynamic light scattering (DLS) studies of this polymer.[5–8] The PEO/water system was suggested[8] as especially suitable for studying the DLS slow relaxation mode observed in semidilute solutions since it manifests at much lower concentrations than in the case of other polymers dissolved in organic solvents. Recently, it has been shown[2,9] that PEO does not necessarily aggregate in water, and there is no reason to believe that aggregation is an inherent property of the PEO/water system.

Commercial narrow molecular weight standard PEO samples usually used in the studies mentioned above are common calibrants of size exclusion chromatography (SEC) columns applied to the distribution analysis of water-soluble polymers. SEC should, in principle, be capable of resolving the presence of large particles (stable aggregates) in these standards, but no such experiments have been reported so far. The natural explanation is found in the extreme sensitivity of the DLS technique to large particles[10] as compared to refractometric SEC detection; the mass concentration of large particles, if present, might be too low to be detected by differential refractometry but clearly detectable by the DLS technique. The recently applied combination of SEC and DLS experiments allowed in such a case the separation and detection of extremely low particle contamination of dextrans.[11]

The aim of this paper is to find an alternative explanation of DLS slow-mode observations in dilute aqueous PEO solutions other than equilibrium intermolecular aggregation (clustering[7]) since the possible absence of PEO aggregation in this system was already pointed out.[9]

Experimental Section

Materials. Narrow PEO standards with nominal M_w = 150 000, M_w = 250 000 (Polymer Laboratories, Shropshire, UK), and M_w = 250 000 (TOSOH Corp., Tokyo, Japan) and technical grade PEO with M_w = 20 000 (Fluka AG, Buchs, Switzerland) were used. Millex-AA and GS filters (0.8 and 0.22 μm, mixed cellulose ester membrane), a Millex-FG filter (0.2 μm, PTFE membrane) (Millipore, Bedford, MA), and inorganic aluminum based Anotop (0.02 μm) and Anotop Plus (0.1 μm) membrane filters (Anotec Separations, Banbury, UK) served for sample filtrations. All filters were 25 mm in diameter. Analytical reagent grade NaCl and methanol were obtained from Lachema (Brno, Czech Republic). Water from a Millipore Milli-Q$_{\mathrm{PLUS}}$$^{\mathrm{UF}}$ ultrapure water purification unit was used.

DLS Experiments. An Inova-series 4 W argon ion laser (Coherent Laser Division, Palo Alto, CA) tuned to 514.5 nm was focused onto a precision scattering 10 × 10 mm cell (Hellma, Mullheim Baden, Germany). Time fluctuations in light scattering were detected at $\Theta = 90°$ using a commercially available Brookhaven photomultiplier tube and a 128-channel BI-8000 digital correlator (Brookhaven Instruments, Holtsville, NY). The correlator was set to 64 channels and to the linear mode in all experiments. The Brookhaven particle size distribution software package contains five of the most common analytical procedures;[12] the Brookhaven CONTIN Version 3.0 and cumulant fit procedures were used here. All solutions were prepared by weighing and filtered through selected filters directly into the scattering cells.

Micropreparative SEC Experiments. The equipment consisted of a VCR 40 HPLC pump (Academy Development Works, Prague, Czech Republic), a Model 7125 injection valve (Rheodyne, Cotati, CA) with a 100 μL loop, and an R-401 differential refractometer (Waters, Milford, MA) connected through a Black Star (Huntingdon, UK) 2308 A/D converter to an IBM-compatible computer. Two stainless steel columns in series (250 × 8 mm i.d.) from Tessek (Prague, Czech Republic) were packed with diol-modified LiChrospher 300 and 1000 packing (Merck Darmstadt, Germany). Methanol/10 mM NaCl in water = 1/1 (v/v) served as the mobile phase, and a 2% solution of the PEO sample in the mobile phase was injected. Details of this procedure were described elsewhere.[11]

Results and Discussion

The autocorrelation function obtained for the PEO sample having M_w = 150 000 (Polymer Laboratories) dissolved in water and filtered through the 0.22 μm GS

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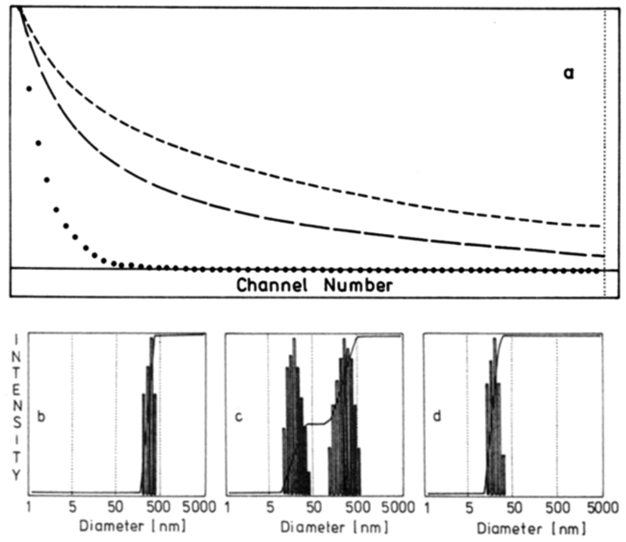

Figure 1. Autocorrelation functions (a) and corresponding CONTIN plots (b–d) obtained for a PEO (M_w = 150 000, Polymer Laboratories) solution in water (c = 0.12%, w/w) after filtration through 0.8 (- - -, b), 0.22 (— — —, c), and 0.02 μm (···, d) filters at identical settings of the DLS experiments (duration 1×10^9 μs, delay time 20 μs; see text).

filter is shown (long dashed) in Figure 1a. The corresponding CONTIN analysis of this curve has clearly revealed (Figure 1c) two modes; the second peak was assumed to emerge from a partly filterable impurity. When the same solution was filtered through a filter having a larger pore size (0.8 μm AA), the autocorrelation function obtained at a correlator setting identical to that in the previous case changed to the short dashed curve in Figure 1a. The corresponding CONTIN analysis (Figure 1b) of this curve did not separate the polymer peak from the impurity peak at all and confirmed partial removal of the impurity by the 0.22 μm filter where the PEO peak was correctly found. Fortunately, this sample could be filtered by the Anotop 0.02 μm filter, and the resulting autocorrelation function (dotted curve, Figure 1a) was obtained at the same correlator setting as in previous experiments. The CONTIN analysis then correctly proved the presence of the dissolved PEO only, with hydrodynamic diameter d_h = 26 nm (Figure 1d); i.e., the complete removal of the impurity was confirmed. The simple comparison of primary autocorrelation functions in the exact correlator mode (the maximum of the curve is always shown at the top of the display) at constant delay time was used throughout this paper since it nicely visualizes the effect of filtrations. In cases when the autocorrelation function decayed too quickly and had many channel values at the baseline, an optimum delay time for the CONTIN analysis was selected in the next experiment. To check the short-time interval stability of these effects, all three solutions were measured 3 days later and practically identical behavior as displayed in Figure 1 was obtained again. Finally, to check the long-time stability of the PEO solution after the impurity removal, the PEO solution filtered by the 0.02 μm filter was stored 17 months in a well-sealed DLS cell at 4 °C and measured again. The autocorrelation curves obtained for a fresh solution and for the same solution after this period of time were indistinguishable from the dotted curve in Figure 1a; corresponding CONTIN plots obtained for 17 month old and fresh solutions were also identical to that displayed in Figure 1d within the error of the CONTIN procedure, proving unambiguously a full long-time stability of properly filtered PEO solution. Hence, if the slow mode is eliminated by filtration and does not reappear over the period of 17 months, the physical state corresponding to it is not a reversible, equilibrium state on the time scales appropriate to electrostatic, steric, and hydrodynamic forces that govern most solution dynamics.

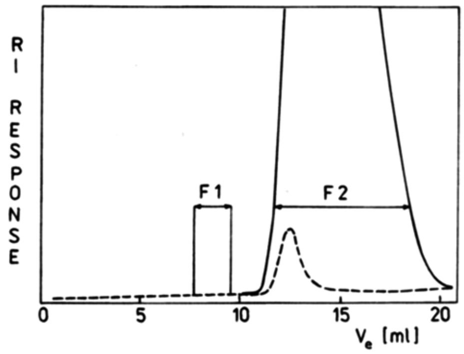

Figure 2. Micropreparative SEC separation of PEO (M_w = 150 000, Polymer Laboratories) in methanol/10 mM NaCl in water (1:1, v/v) after injection of 100 μL of a 2% solution in the mobile phase (—) and comparable analytical chromatogram (- - -) after injection of 5 μL of the solution. Intervals where the excluded volume (F1) and main (F2) PEO fractions are collected are indicated by the arrows.

The dimensionless DLS polydispersity factor[12] $\mu_2/\bar{\Gamma}^2$ (normalized second cumulant) obtained from cumulant analysis has been shown[9] to be less than 0.1 in the case of narrow PEO samples in water if aggregates and/or impurities are properly removed. In our case, the cumulant analysis of the data obtained from solution filtered through the 0.02 μm filter gave $\mu_2/\bar{\Gamma}^2 = 0.05$. When this analysis was applied to the data related to the 0.22 and 0.8 μm filtrations, the values of $\mu_2/\bar{\Gamma}^2$ were 0.44 and 0.55, respectively. These values compare well with polydispersity factors between 0.3 and 0.46 observed by Layec and Layec-Raphalen[13] and interpreted as the evidence of equilibrium aggregation. Our experiments indicate the presence of a stable impurity completely removable only by a 0.02 μm filter.

Micropreparative SEC was recently used[11] for the separation and subsequent DLS characterization of a very low amount (not detectable by mass proportional RI detection) of foreign particles contained in commercial dextran samples. The column set used in the dextran experiment was found[14] to be suitable also for SEC of PEO if methanol/0.01 M NaCl in water = 1/1 (v/v) was used as the mobile phase. The impurity having a particle size as indicated in Figure 1b,c should elute at the exclusion limit of the column set used (F1, Figure 2) and should be well separated from the main polymer peak. The SEC elution profiles of an analytical (small volume) injection (dashed curve) and micropreparative (large volume) injection (full curve) of the PEO sample used in previous filtration experiments are shown in Figure 2. The elution volume intervals where the PEO and excluded fractions were collected are indicated by arrows and denoted as F2 and F1, respectively. The autocorrelation functions of the injected PEO solution in the mobile phase diluted to 0.1% and filtered by a 0.8 μm AA filter (dashed curve) and of the collected PEO fraction F2 (dotted curve) are shown in Figure 3a. Together with the CONTIN plots corresponding to the injected solution (Figure 3b) and fraction F2 (Figure 3c), these results confirmed complete removal of the impurity from the injected PEO solution. Surprisingly, the excluded fraction F1 did not contain

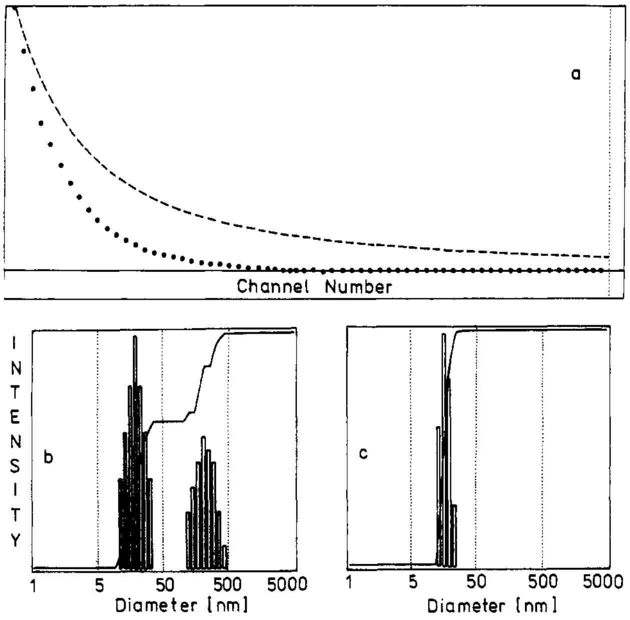

Figure 3. Autocorrelation functions (a) and related CONTIN plots (b,c) obtained for a PEO solution (diluted to 0.1% by the mobile phase and filtered with a 0.8 μm filter) before SEC injection (- - -, b) and for the F2 main PEO fraction (⋯, c) at identical settings of the DLS experiments.

any large particles; its DLS behavior was fully identical to that of the mobile phase itself. The only possible conclusion is that the impurity was adsorbed on the column packing used, taking into consideration the fact that size of the impurity is not large enough to assume its mechanical filtration by the column itself. As PEO exhibits correct SEC behavior in the mobile phase used, this is direct evidence that the impurity is not PEO. The diol-hydrophilized silica column packing used here is known to interact weakly also by hydrophobic interaction; hence, this is the most natural explanation of the impurity retention. Being hydrophobic, the impurity should be sparingly soluble (or insoluble) in water but might be more soluble in the methanol-containing mobile phase. This is a proper explanation of the observed difference between autocorrelation functions (short dashed curves) obtained for the PEO solution in water (Figure 1a) and in the mobile phase (Figure 3a) when both solutions were filtered with the same 0.8 μm AA filter. Accordingly, the comparison of the related CONTIN plots (Figures 1b and 3b) clearly shows a less pronounced impurity peak in the case of PEO solution in the mobile phase, the relative intensity of the impurity (compared to PEO) being lower than that obtained after filtration of the PEO–water solution through a 0.22 μm GS filter (Figure 1c).

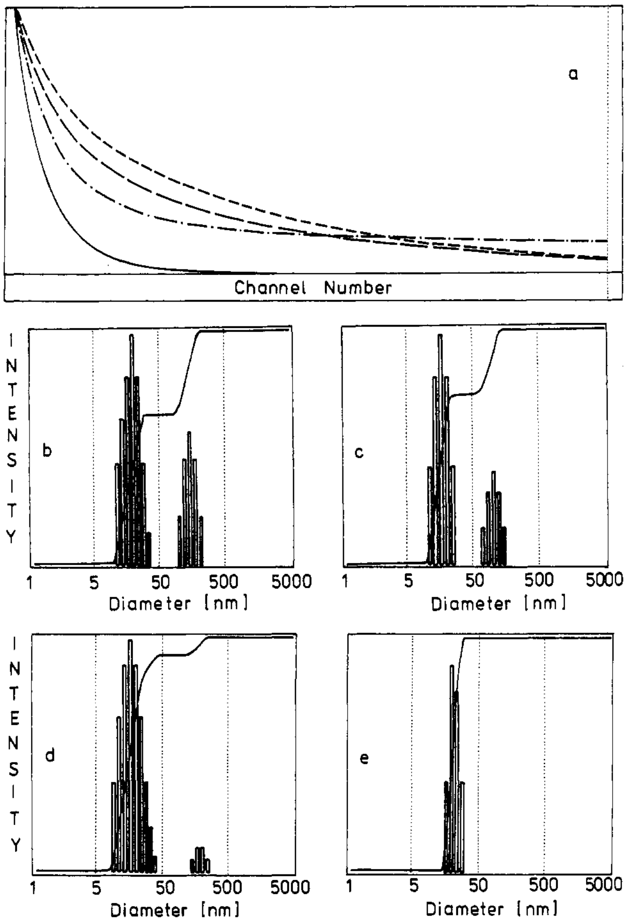

Figure 4. Autocorrelation functions (a) and corresponding CONTIN plots (b–e) obtained from a PEO (M_w = 250 000, Polymer Laboratories) solution in water (0.11%, w/w) after filtration through 0.8 (- - -, b), 0.22 (— — —, c), 0.1 (–·–, d), and 0.2 μm (—, e) hydrophobic filters at identical settings of the DLS experiments (duration 1 × 10^9 μs, delay time 20 μs).

A similar “sieve analysis” of another Polymer Laboratories PEO sample with a higher molecular weight (M_w = 250 000) dissolved in water was performed, and the results are summarized in Figure 4. Due to the larger coil size of this sample, instead of the 0.02 μm filter, a 0.1 μm Anotop filter was used. The autocorrelation curves in Figure 4a corresponding to 0.8 μm (short dashed) and 0.22 μm (long dashed) filtrations exhibit a behavior similar to that of the same filtrations of the sample with M_w = 150 000 (Figure 1a). The impurity is less pronounced (Figure 4b,c) as compared to Figure 1b,c also due to the higher scattering power of the dissolved polymer at the same concentration. The 0.1 μm filter failed to completely remove the impurity (Figure 4a, dash and dotted curve; CONTIN plot, Figure 4d). As the chromatographic experiment indicated hydrophobic adsorption of the impurity to the column packing, the 0.2 μm hydrophobic (PTFE) filter was applied, expecting the adsorption of the impurity (due to hydrophobic interaction) also on the PTFE filter membrane. The corresponding autocorrelation curve (full curve, Figure 4a) and related CONTIN plot (Figure 4e) confirmed this assumption. Let us note that this hydrophobic filter must be properly wetted by methanol, before the water solution is applied, to guarantee a complete wetting of the membrane surface necessary for correct filtration.

In fact, the hydrophobic filter operates here as a solid-phase membrane extraction device, and all the well-known experience with the solid-phase extraction technique common in HPLC sample preparation and clean up applies. The break-through volume of the impurity was determined using the same PEO solution (0.11%, w/w) described in Figure 4 by successive filtrations of 3 mL portions into the DLS cell. The filtrates were successively checked by DLS, and the slow mode appeared when 27 mL of the solution passed through the filter. The surface of the filter membrane is not very large due to its physical dimensions and rather large pore size; hence, its adsorption capacity must be quite low, confirming only a low content of the impurity in the sample. The relative scattering amplitude of the sample described in Figure 4 and filtered by the 0.8 μm filter had dropped to 0.26 of its value after 0.2 μm FG filtration. The scattering intensity in a DLS experiment is proportional to $K_iC_iM_iP_{\theta,i}$, where K_i is an optical constant, c_i is the particle concentration, M_i is its molecular weight, and P_θ is a particle scattering factor[9] different from unity when the particles size is larger than $^1/_{20}$ of the wavelength of the light used. Three unknowns—K_{IMP}, C_{IMP}, and M_{IMP}—would thus be needed to calculate the total scattering intensity in our case unless some simplifying assumptions concerning the structure of the impurity particles are used. Assuming the same (or at least very similar) coil behavior of the impurity as PEO, e.g., a larger particle formed from several PEO chains coupled together by quite a few hydrophobic low molecular weight entities, the scattering properties ($K_{PEO} \sim K_{IMP}$) of such a cluster should be very similar to PEO itself and the ratio of relative scattering amplitudes is obtained as

$$I_{PEO}/I_{IMP} = (c - c_{IMP})M_{PEO}/c_{IMP}M_{IMP}P_{\theta,IMP} = 0.35 \quad (1)$$

In such a case, the relation between the hydrodynamic radius of PEO, R_h (in angstroms), and its molecular weight[2]

$$R_h = 0.145M_w^{\,0.571} \quad (2)$$

may be used to estimate the impurity molecular weight. Using its size at the maximum of the impurity peak in Figure 4b, d_h = 173 nm, the value $M_w = 4.1 \times 10^6$ is obtained. Taking $P_{\theta,IMP} = 0.64$ from ref 15, the value $c_{IMP} = 0.02_3\%$ is found from eq 1. This is certainly an unrealistic amount to be adsorbed on the tiny filter membrane in the solid-phase adsorption experiment; hence, the assumed form of the impurity seems impossible. On the other hand, a molecular weight multiplication factor of 2.4×10^3 follows from Strazielle's results[16] if the particles have the same size but their conformation in the solution changes from a PEO coil to a hard sphere having a density of solid PEO. Then, the concentration of a hard sphere impurity would drop (eq 1) to $1.2 \times 10^{-5}\%$. Alhough this is a crude estimate, the result means that contamination by a compact spherical impurity (e.g., liquid microdroplets) at the ppm level is quite realistic as this is just what could be expected to be adsorbed by the filter membrane.

The comparison of the DLS behavior of the PEO sample in water (Figure 1) and in a methanol–water mixture (Figure 3) indicated a possibly increased solubility of the impurity when methanol was added. To prove this, a solution of the PEO sample (M_w = 250 000, Polymer Laboratories) in pure methanol was prepared and filtered through a 0.1 μm Anotop filter, which was shown to remove the impurity only partly in water (Figure 4). The CONTIN plot obtained in this case (Figure 5b) as well as the value of $\mu_2/\bar{\Gamma}^2 = 0.08$ proved the complete absence of any slow mode due to the impurity. Kinugasa et al.[17] have conclusively shown the absence of PEO aggregation in methanolic dilute solutions, contrary to ref 18, and pointed out that heating of the methanolic solution might be essential to obtain aggregate-free solutions. The same behavior was observed during this study; by cooling the solution in a refrigerator, PEO crystallized in the DLS cell and heating to 40 °C was necessary to obtain single-mode DLS data, although the solutions were visually transparent already at temperatures around 23 °C. Most probably, a sufficient number of crystalline nuclei can exist in equilibrium with dissolved polymer at this temperature after the dissolution of macroscopic crystals, similarly to the case of PEO solutions in dimethylformamide.[19] The methanolic PEO solution free of any slow mode was mixed 1:1 with 0.02 μm filtered water, and the resulting mixture was filtered through a 0.8 μm filter into the DLS cell. The CONTIN plot in Figure 5c as well as the value $\mu_2/\bar{\Gamma}^2 = 0.3$ confirmed that the impurity was precipitated by the water addition. The extent of the change of primary DLS data is visualized in Figure 5a by dash and dotted (methanol) and dashed (methanol/water) curves.

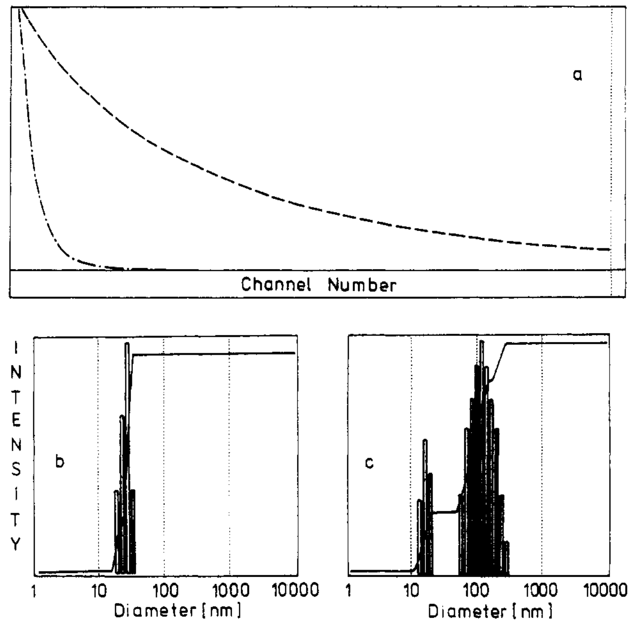

Figure 5. Autocorrelation functions (a) and related CONTIN plots (b,c) obtained for a PEO (M_w = 250 000, Polymer Laboratories) solution (0.24%, w/w) filtered with a 0.1 μm pore size (—·—, b) and for this methanolic PEO solution diluted by water (1:1, v/v) and filtered through a 0.8 μm filter (- - -, c) at identical settings of the DLS experiments.

Having access to an impurity-free PEO solution obtained after solid-phase membrane adsorption, a "slow-mode synthesis" was tried in the next experiment. A heptane/water emulsion was prepared by intensive shaking and was left to stand 1 h to separate two layers. The water layer still containing microdroplets of heptane was then mixed with impurity-free PEO solution 1:1 by volume, and the solution was filtered with a 0.8 μm filter and measured by DLS. The resulting autocorrelation function (Figure 6a, dashed curve) and the related CONTIN plot (Figure 6b) compare favorably with the same experiments after the same filtration of PEO–water solution (Figure 4a,b). Using a filter size of 0.22 μm, the heptane-formed "slow mode" decreased (Figure 6a, long dashed curve; Figure 6c) and disappeared completely after filtration through a 0.2 μm hydrophobic filter (Figure 6a, full curve; Figure 6d); i.e., the behavior of the original PEO solution in water was completely recovered. During the next few days, a slow decrease in the relative scattering amplitude of the impurity was observed, similar to the results of ref 13.

The most probable description of the impurity that can be given from the experiments described is that microdroplets or compact microparticles, formed from hydrophobic and sparingly soluble low molecular weight organics and collected within the PEO sample during its whole history, are sterically stabilized[20] by the presence of PEO molecules.

Most previous work dealing with PEO slow-mode studies,[1,6–8,13,18] where it was assumed that the slow mode gave evidence of semidilute scaling behavior[5] at

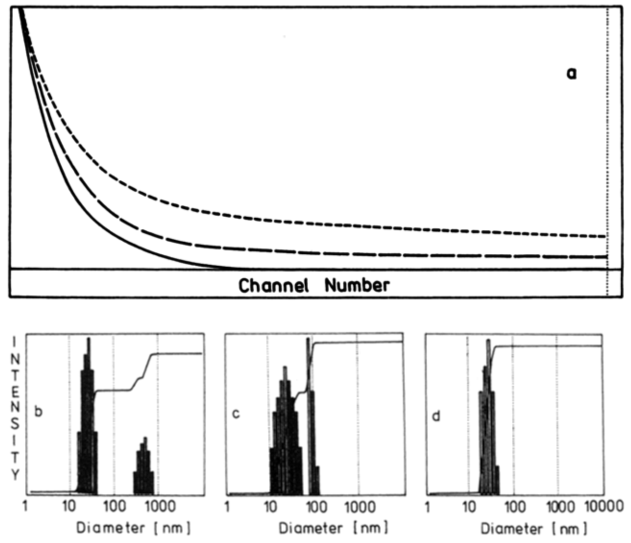

Figure 6. Autocorrelation functions (a) and corresponding CONTIN plots (b–d) obtained after mixing (1:1, v/v) a PEO ($M_w = 250\,000$, Polymer Laboratories) solution in water (free of slow mode) with a water emulsion of heptane (see text) and filtration by 0.8 (- - -, b), 0.22 (— — —, c), and 0.2 μm hydrophobic (—, d) filters at identical settings of the DLS experiments.

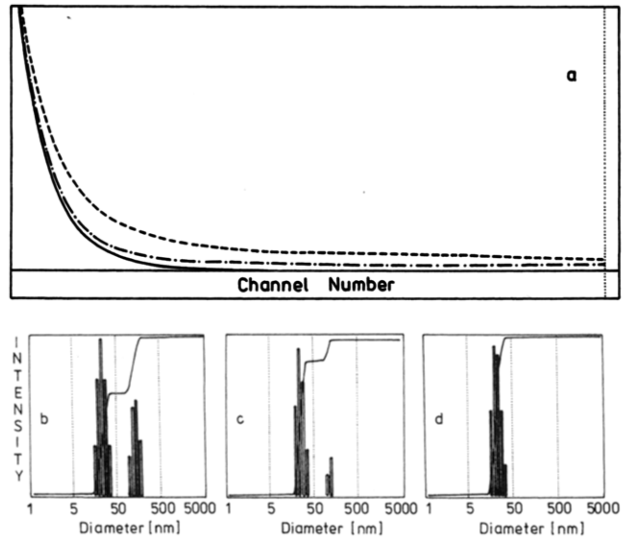

Figure 7. Autocorrelation functions (a) and related CONTIN plots (b–d) obtained for a PEO ($M_w = 250\,000$, TOSOH) solution in water (0.11%, w/w) after filtration through 0.8 (- - -, b), 0.1 (—·—, c), and 0.2 μm hydrophobic (—, d) filters at identical settings of the DLS experiments.

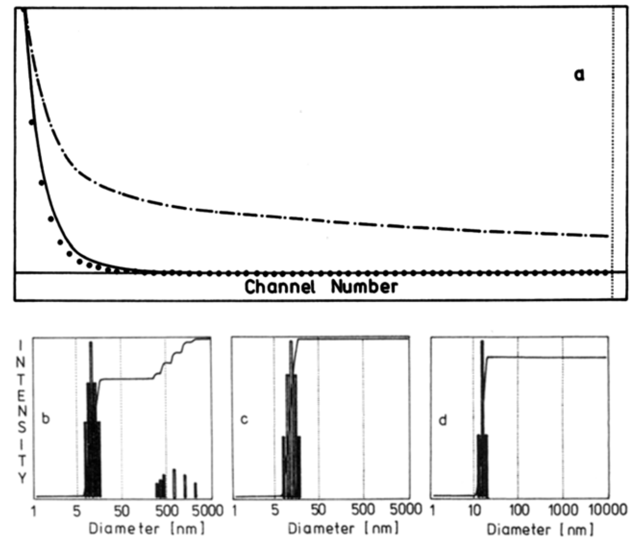

Figure 8. Autocorrelation functions (a) and corresponding CONTIN plots (b–d) obtained for a PEO ($M_w = 250\,000$, TOSOH) solution in water (0.92%, w/w) after filtration by 0.1 (—·—, b) and 0.2 μm hydrophobic (—, c) filters and for a PEO ($M_w = 150\,000$, Polymer Laboratories) solution in water (0.98%, w/w) filtered through a 0.02 μm (···, d) filter at identical settings of the DLS experiments.

much lower concentrations than that observed with polymers in organic solvents,[6] were performed with TSK narrow PEO samples (currently marketed by TOSOH). A "sieve analysis" analogous to that in Figure 4 (Polymer Laboratories sample) was, therefore, made with a solution of the TSK product with both the $M_w = 250\,000$ and the solution concentration the same as those of the Polymer Laboratories sample (Figure 7). Almost no difference between the results after 0.8 μm filtration (dashed decay curve, Figure 7a; CONTIN plot, Figure 7b) and 0.22 μm filtration (not shown) was observed. The incomplete removal of the slow mode by the 0.1 μm filter remained (dash and dotted curve, Figure 7a; CONTIN plot, Figure 7c) and complete disappearance of the impurity was again seen from the autocorrelation function (full curve, Figure 7a) as well as from the related CONTIN plot (Figure 7d) after use of a 0.2 μm hydrophobic filter. In fact, the only difference between the Polymer Laboratories and TSK samples is seen to be a lower relative content of the impurity in the latter one. Since the 0.2 μm hydrophobic filter was capable of removing the impurity from 27 mL of a 0.11% solution of the Polymer Laboratories sample and TSK PEO contained less of the impurity, the correct removal of the impurity from a sufficient volume (3 mL) of its 0.93% solution could be assumed. The autocorelation function in Figure 8a (dash and dotted) and the CONTIN plot in Figure 8b illustrate the effect of the presence of the impurity after 0.1 μm filtration. Using the 0.2 μm hydrophobic filter, a single-mode exponential decay curve (full curve, Figure 8a), substantially different from the previous one, and the corresponding CONTIN plot (Figure 8c) proved the absence of any slow mode. The same behavior was observed when the Polymer Laboratories sample ($M_w = 150\,000$, $c = 0.98\%$) was filtered through a 0.02 μm Anotop membrane (Figure 8a, dotted curve; CONTIN plot, Figure 8d), indicating the possibility of removal of a slow mode by mechanical filtration if a sufficiently small filter pore size is used. The values[8] of c/c^*, where c is the concentration of the measured solution and $c^* = [\eta]^{-1}$, $[\eta]$ being the intrinsic viscosity of a given PEO sample, are obtained for $M_w = 250\,000$ and $M_w = 150\,000$ as 1.68 and 1.38, respectively. These experiments thus confirm the absence of any slow mode in the PEO solutions in water even above c^*, contrary to the previous investigations.[6–8] It may be concluded that, although the previous experimental observations of bimodal DLS decay curves and of features of both modes (q^2 and temperature dependence, total scattered intensity and its angular dependence, etc.) in studies of PEO in water[1,6–8,13,16,18] were real, the presence of the impurity was misinterpreted as evidence for the onset of semidilute behavior[5–8] and/or clustering[7,13] of PEO coils. The conclusion that a PEO semidilute behavior manifests itself at much lower concentrations[8] than with polymers in organic solvents is also highly questioned and requires reconsideration. Also the observed temperature dependence of the slow mode and/or apparent aggregation[4,8] might be explained when

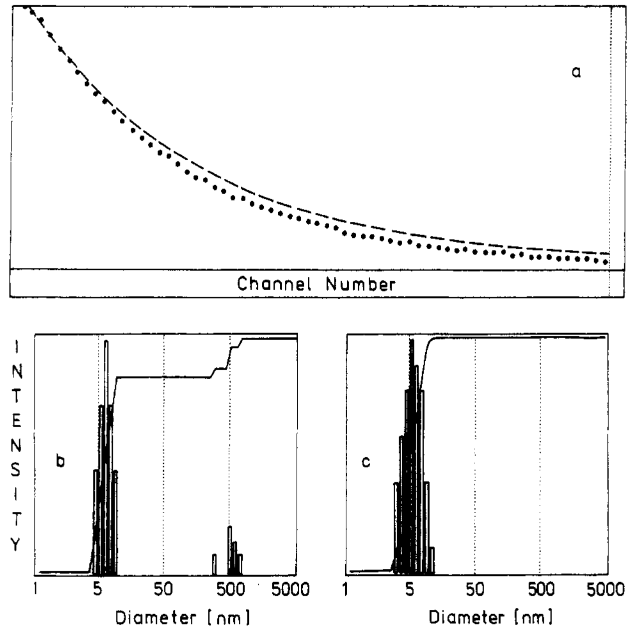

Figure 9. Autocorrelation functions (a) and related CONTIN plots (b,c) obtained for a PEO (M_w = 20 000, Fluka) solution in water (1%, w/w) after filtration by 0.8 (- - -, b) and 0.02 μm (···, c) filters at identical settings of the DLS experiments (duration 1 × 10^9 μs, delay time 1 μs).

the temperature effect on the steric stabilization[20] of the impurity is accounted for.

A commercial grade PEO sample (M_w = 20 000) should substantially differ concerning the technology used for its preparation from narrow PEO standards. The autocorrelation functions obtained for a 1% solution of this sample after filtration by 0.02 μm (dotted curve) and 0.8 μm (dashed curve) filters are compared in Figure 9a, and relevant CONTIN plots are in parts c and b of Figure 9, respectively. The amount of filterable impurity might be sufficient to cause the behavior observed by Polik and Burchard[4] on a similar PEO sample. On the other hand, the fraction of the filterable matter is substantially lower than in the case of standard PEO samples. This indicates that the origin of the impurity in PEO standards should be traced in the technological process of their preparation; this question is left to the suppliers to answer. A similar contamination of other water-soluble polymer samples might also explain some other observations of slow modes in their water solutions below and around the coil overlap concentration. A possible impact of the presence of such an impurity on the ordinary–extraordinary transition observed in salt-free polyelectrolyte solutions is currently being investigated.

Conclusions

PEO solutions in water do not aggregate below and around the overlap concentration c^*. The frequently observed slow mode originates in these solutions from the presence of a hydrophobic impurity sparingly soluble or insoluble in water but increasingly soluble in methanol. This explains why methanolic solutions of PEO, if properly dissolved, do not exhibit slow-mode behavior. Most probably, the impurity may be described as microdroplets or compact microparticles formed from some hydrophobic organic substance, collected within the sample during its whole history at the ppm level, and sterically stabilized in solution by the presence of PEO macromolecules. The solid-phase extraction mechanism governs the successful removal of the impurity by hydrophobic filters. Mechanical filtration by inert filters removes the impurity only in the cases when a very small filter size (0.02 μm) may be used. Most interpretations of the PEO slow mode as evidence of semidilute behavior and/or clustering require reconsideration.

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