Monitoring of Cluster Formation and Elimination in PEO Solutions

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ABSTRACT: It has been shown in a recent work that the formation of aggregates in dilute PEO solutions depends on the history of the samples. In the current study it is confirmed by static and quasi-elastic light scattering measurements that, as soon as a PEO of small molecular weight ($M = 6500$) has been dissolved in water at high temperature (89 °C), subsequent dissolution of this sample in methanol reveals the presence of aggregates. The dimensions and the concentration of these aggregates depend on the time the sample has stayed in water. They are very stable and cannot be destroyed later on by dissolution in water or water 0.2 N HCl at room temperature or by heating under vacuum at high temperature (160 °C). However, they can be separated by centrifugation of PEO solutions in methanol. The sample recovered from the top of the centrifuged part is free from aggregates, but subsequent dissolution of this sample in hot water regenerates new aggregates. These observations lead to the conclusion that the formation of aggregates in the PEO solutions is due to hydrophobic interactions.

Introduction

Aggregative behavior of poly(ethylene oxide) (PEO) in various aqueous and organic solvents has been the subject of a lot of works. For example, many static and quasi-elastic light scattering experiments suggested that PEO molecules aggregate in solvents such as acetonitrile, dioxane, benzene, carbon tetrachloride,[2] chloroform,[3] water,[4−7] or methanol.[8] However, other light scattering experiments have given evidence for no aggregation of PEO molecules in water,[2,9,10] methanol,[2,3,5,9,10] dioxane,[3] or dimethylformamide.[11] In 1968, Strazielle[12] has shown that the ability of PEO to form aggregates depends on the molecular weight of the sample and on the method of preparation of the solutions.

In a recent study[1] on PEO of low molecular weight ($M = 6500$) in methanol, we arrived at the conclusion that the presence of clusters in dilute solution mainly depends on the history of the sample. We have defined a protocol to prepare solutions containing two kinds of species: on one hand a large amount of small particles (radius $R = 22$ Å) corresponding to well-solvated PEO molecules and on the other hand a small amount of large particles ($R \cong 700$ Å) formed by clusters of PEO molecules. It has been shown that it is the dissolution of PEO in water at high temperature ($t \geq 60$ °C) which is responsible for the formation of large entities that are very stable and cannot disappear by further dissolution in other usual organic solvents for PEO. It explains the discrepancy between the observations made on the behavior in solution in the previous works[2−12] where the authors had no control over the history of the samples they have used.

Several hypotheses have been given to explain the formation of clusters in PEO solutions including the presence of impurities, the formation of hydrogen bonds,[13] the formation of complex entities due to the presence of residual water molecules, and hydrophobic interactions.[4,14] In the current study the reproducibility of the formation of clusters in PEO samples is tested through characteristics such as their dimension and their concentration in dilute methanol solution. Some ways to eliminate these aggregates are explored: effect of a new dissolution of the sample in water at room temperature, in water 0.2 N HCl, heating at high temperature under vacuum, centrifugation of solutions in methanol. The possibility to regenerate new aggregates following the protocol defined previously is investigated on the sample where the aggregates have been removed. These experiments are done with the purpose to specify the nature of the interactions that contribute to the formation of the aggregates in the PEO samples.

Experimental Section

Materials. The sample E0 used in this study is a commercial sample named PEO-6000 (Hoechst-Frankfurt, Germany). This sample has a low polydispersity of 1.04 measured by gel permeation chromatography in 3× distilled water 0.1 N NaCl. The weight-average molecular weight of E0 measured by static light scattering in methanol[1] is $M_W = 6500$.

Specific processing of E0 is used to prepare samples E1 and E2. Indeed E0 is dissolved in water at 89 °C over a period of 1 h. Then the water is evaporated at this temperature under vacuum. The dried sample is dissolved in dimethyl sulfoxide (DMSO, 1 h at 50 °C), precipitated in ether, and dried. It has been shown[1] that this processing induces the formation of aggregates even in dilute solution when, later on, the samples are dissolved in common solvents of PEO. E3 is prepared in the same manner as E1 and E2 except that, after the dissolution in water at 89 °C and before evaporation of water, the aqueous solution is allowed to come back to room temperature over a period of 12 h.

Another set of three samples E4 to E6 is prepared from E0 following the process used for E1 and E2 except that E0 is allowed to stay 1 h in water at 89 °C for E4 and 2 and 3 h for E5 and E6, respectively. These samples are prepared in order to test the influence of the duration the primary product stays in water at 89 °C on the concentration and the dimensions of the aggregates.

To break the aggregates formed in solution, samples E1 and E2 are submitted to subsequent processes which are explained in the experimental part of this work.

All the solvents are spectroscopic purity grade products and used without further purification. Deionized water is used in the intermediate stage of the preparation of the samples.

The static light scattering (SLS) and quasi-elastic light scattering (QELS) measurements are made in methanol at 25 °C. The solutions are stirred at room temperature over a period of 12 h and then directly filtered through 0.45 μm Dynagard

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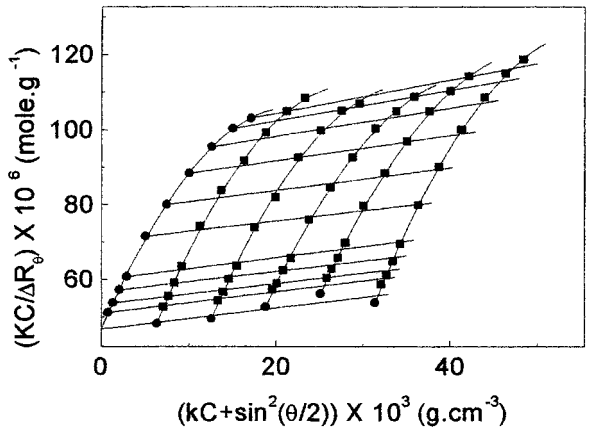

Figure 1. Zimm plot for sample E4 in methanol at 25 °C.

filters (Spectrum Microgon, USA) in the light scattering cells for optical clarification.

Static Light Scattering Measurements. SLS measurements are performed at t = 25 °C on a FICA50 (SOFICA, France) photometer. A vertically polarized light of λ_0 = 633 nm wavelength from a He−Ne laser is used as an incident beam. The intensity of the scattered light is measured at scattering angles from θ = 22.5° to 150°. The refractive index increment values is taken as 0.15 cm^3 g^{-1} for POE in methanol. The data are processed following Zimm.[15] The values of the weight-average molecular weight (M_W), the osmotic virial coefficient (A_2), and the radius of gyration (R_G) of the samples under investigation are calculated from the intercepts at the ordinate of the extrapolated double-reciprocal plots and from the slopes 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 c is the polymer concentration, ΔR_θ is the excess Rayleigh ratio, and q is the scattering wave vector. Figure 1 shows a typical example of the Zimm plot for sample E4. As the figure shows, there is a downturn in $Kc/\Delta R_\theta$, indicating the presence of large aggregates in the methanol solutions.

Quasi-Elastic Light Scattering Measurements. QELS measurements are made at 25 °C in the homodyne mode using a photon correlation spectrometer described in full detail elsewhere.[16] The correlation functions of the scattered intensity are obtained by using the ALV5000 autocorrelator (ALV, Langen, FRG). The normalized autocorrelation functions $g^{(2)}(\tau)$ of the scattered intensities are measured at a scattering angle θ = 20° where the contrast between the solutions and the solvent is maximum. This improves the accuracy of the measurements. Nevertheless, it has been verified in the θ range 20°−80° that the relaxation times of the slow and fast modes which are observed on the most concentrated solution of E1 are linearly $\sin^2 \theta/2$ dependent as expected for diffusive motions. These correlation functions are analyzed using the CONTIN software:[17]

$$g^{(2)}(q,\tau) = g^{(2)}(q,0)\int \exp(-2Dq^2\tau)\, G(D)\, \mathrm{d}D \qquad (2)$$

where $G(D)$ is the distribution function of the translational diffusion coefficient D of the scattering particles. The hydrodynamic radius R_H of the particles in solution is calculated through the Stokes−Einstein relationship:[18]

$$R_H = \frac{k_B T}{6\pi\eta_0 D_0} \qquad (3)$$

where k_B is the Boltzmann constant, T the absolute temperature, η_0 the viscosity of the solvent, and D_0 the diffusion coefficient of the particles extrapolated to zero concentration through

$$D = D_0(1 + k_D c) \qquad (4)$$

where k_D is the dynamical virial coefficient[17] related to the interactions between the chains in solution.

Results and Discussion

In the first study[1] on the PEO dilute solutions we have shown that the most significant parameters leading to the formation of aggregates are the nature of the solvent used (water) and the temperature at which the polymer is dissolved. If the polymer is dissolved in water at 30 °C, no aggregation occurs, but at $T \geq 60$ °C aggregates are formed in the samples which are still present when the polymer is later dissolved whatever the solvent may be. This aggregation leads to the presence of two relaxation times in the correlation functions of the light scattered by the PEO solutions. The diffusion coefficient of the fast mode (nonassociated species) increases when the polymer concentration decreases (see for example Figure 5a of ref 1) whereas the diffusion coefficient of the slow mode (aggregates) decreases when the polymer concentration increases (see for example Figure 5b of ref 1).

In the current study, in a first step, we check the influence of the duration the PEO stays in water at 89 °C on the concentration and the dimension of the aggregates when after recovery of the dried sample as described in the Experimental Section, it is later dissolved in methanol. In a second step we try to eliminate the clusters using several processing such as new dissolution in water and in water 0.2 N HCl or heating under vacuum or by centrifugation and decantation of the aggregates.

Influence of the Duration the PEO Stays in Water at 89 °C. In Figure 2a are represented the correlation functions of the light scattered by samples E1 and E2 in methanol at $c = 3.2 \times 10^{-2}$ g cm^{-3}. The two samples have been prepared independently using exactly the same processing. These correlation functions show two relaxation times as it appears in the distribution function $G(D)$ of the diffusion coefficients of Figure 2b calculated by CONTIN analysis[17] of the curves of Figure 2a. The experiment confirms that, following a dissolution in water at 89 °C, aggregates are generated in PEO samples. Moreover, it shows that there is a reproducibility of the phenomenon since the curves on Figures 2 are quasi-equivalent leading to diffusion coefficients of 3.80×10^{-8} and 3.07×10^{-8} cm^2 s^{-1} and having a contribution to the scattered intensity of 55% and 61% for the aggregated species of samples E1 and E2, respectively. In the same Figure 2 the correlation function and the diffusion coefficient distribution function for the sample E3 in methanol are represented. For this sample it is recalled that, just after dissolution in water at 89 °C and before evaporation of water, the aqueous solution has been allowed to come back to room temperature for 12 h. The correlation function given by E3 in methanol is monomodal, showing that no clusters are formed in this case. Furthermore, SLS and QELS measurements on five concentrations of this sample in methanol extrapolated to zero concentration give M_W = 6700 and R_H = 22 Å identical to the values obtained on E0. During the preparation of E3 it is obvious that clusters are formed in the first stage of the dissolution of E0 in water at 89 °C. However, letting the aqueous solution to cool at room temperature before evaporation of water allows the dissolution of these clusters. As

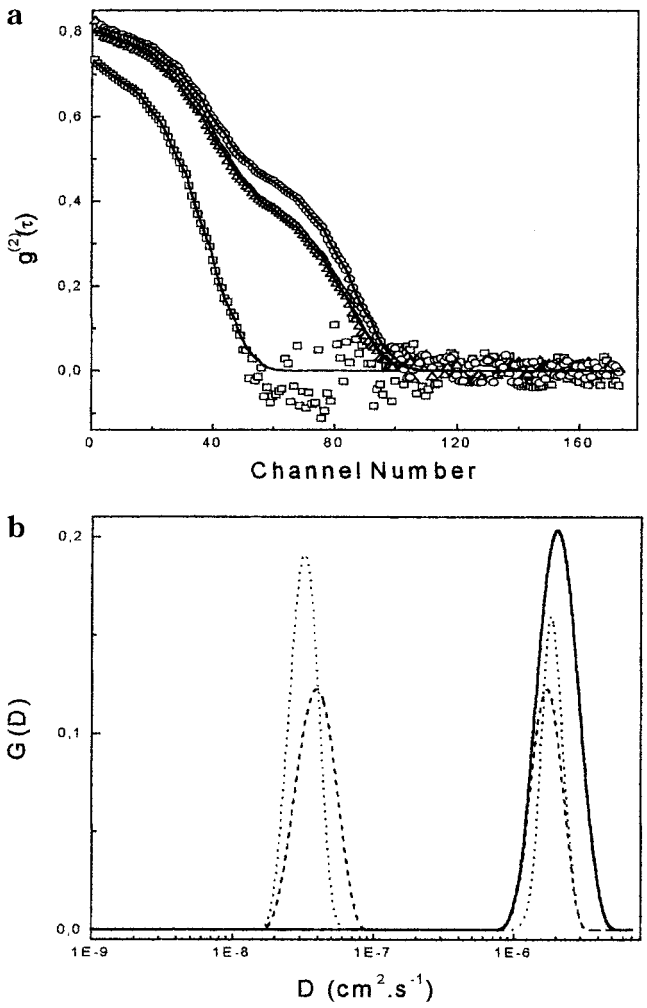

Figure 2. (a) Normalized autocorrelation functions of the scattered intensities for samples E1 (△), E2 (○), and E3 (□) in methanol (scattering angle, $\theta = 20°$; concentration, $c = 3.2 \times 10^{-2}$ g cm^{-3}; temperature, $T = 25$ °C). Solid line: fitted curve obtained by CONTIN analysis.[17] (b) Distribution function of the diffusion coefficients for samples E1 (- - -), E2 (• • •), and E3 (—) in methanol.

shown in the first study,[1] the step of dissolution in water and the processing used are essential for the formation of aggregates in PEO samples.

Samples E4, E5, and E6 have been prepared following the processing used for E1, i.e., dissolution of E0 in water at 89 °C for 1, 2, and 3 h, respectively. Then the aqueous solutions are dried, and the samples are dissolved in DMSO and precipitated in ether. The methanol solutions of these samples are studied by SLS and QELS. The results are shown in Table 1. The correlation functions of the light scattered by these solutions are bimodal, and the static parameters calculated from eq 1 are apparent values. It comes out from Table 1 that the longer the sample E0 stays in water at 89 °C, the less is the value of the apparent molecular weight of the PEO. The apparent radius of gyration and the hydrodynamic radius of the aggregates decrease for samples E4 to E6 while the hydrodynamic radius of the nonassociated species remains constant and equal to the hydrodynamic radius of E0 ($R_H = 22$ Å). Meanwhile, the last column of Table 1 shows that the contribution of the aggregates to the scattered intensities decreases from 68% to 45% for E4 to E6. These numbers are calculated from the area of the peaks given by the CONTIN analysis[17] of the correlation functions of the

Table 1. Characteristics of Samples E4, E5, and E6 in Methanol at 25 °C Measured by SLS and QELS[a]

sample	M_W	$A_2 \times 10^4$ (cm^3 g^{-1} mol^{-1})	R_G (Å)	R_{H1} (Å)	R_{H2} (Å)	w (%)
E4	24 000	8.70	860	866	24	68
E5	15 500	5.67	883	998	25	62
E6	10 100	5.93	600	758	22	45

[a] The weight-average molecular weight (M_W), the second virial coefficient (A_2), and the radius of gyration (R_G) are apparent values. R_{H1} and R_{H2} are the hydrodynamic radius of the aggregated and dispersed species, respectively. w (%) is the percentage of the light scattered by the aggregated species as calculated from the distribution function of the diffusion coefficient obtained by CONTIN analysis[17] of the correlation functions of the scattered intensities.

light scattered by the solutions. The results point out that the longer the sample E0 stays in water at 89 °C, the lower is the rate of aggregates in the sample which means the better is its dissolution. This is not surprising since it is known that the water is a Θ solvent at 102 °C for PEO.[4] In a logical way the nearest from the Θ temperature the solutions are, the longer it takes for the samples to be dissolved. For example, it has been shown[1] that no aggregates are formed when the samples have stayed 1 h at 30 °C in water. What is specific to the case of the PEO is the fact that as soon as aggregates are generated and isolated by drying (E3 is free from aggregates), they are very stable, hard to eliminate, and still remain after dissolution in methanol or other good solvents for PEO.

Attempt To Eliminate the Aggregates in the PEO Solutions. The best way to try to break down the clusters in a dried sample of PEO seems to dissolve the sample in water at room temperature. To do that, sample E1 is dissolved in water at room temperature under stirring for 3 days. The water is then evaporated, and sample E1a is recovered by dissolution in DMSO, precipitation in ether, and drying. Sample E1b is prepared using the same processing except that sample E1 is dissolved in water for 13 days. The distribution functions of the diffusion coefficients for the samples E1, E1a, and E1b in methanol at $c = 3.2 \times 10^{-2}$ g cm^{-3} obtained from QELS measurements are given in Figure 3a. These distributions are bimodal, and this shows that the clusters are not broken down by further dissolution in water. Moreover, the dimensions of the clusters are not modified by the new dissolution in water and do not depend on the time the samples stay in aqueous solution.

Bortel and Kochanowski[19] have studied the behavior of several PEO of high molecular weight in water 0.1 N HCl. They have always got correct Zimm diagrams by SLS showing no curvature. They have emphasized that without HCl this would not be the case. Polik and Burchard[4] have argued that the addition of a strong electrolyte induces a change in the order of the water structure and breaks down the hydrophobic interaction responsible for the formation of the clusters. The sample E1c has been prepared using the same processing as E1a, but instead of water, E1 has been dissolved in water 0.2 N HCl at room temperature under stirring over a period of 3 days. The distribution functions of the diffusion coefficients for the samples E1a and E1c in methanol are represented in Figure 3b. From this experiment it comes out that the dissolution in water 0.2 N HCl has no specific effect on the dimensions and the concentration of the aggregates for the curves are superimposed.

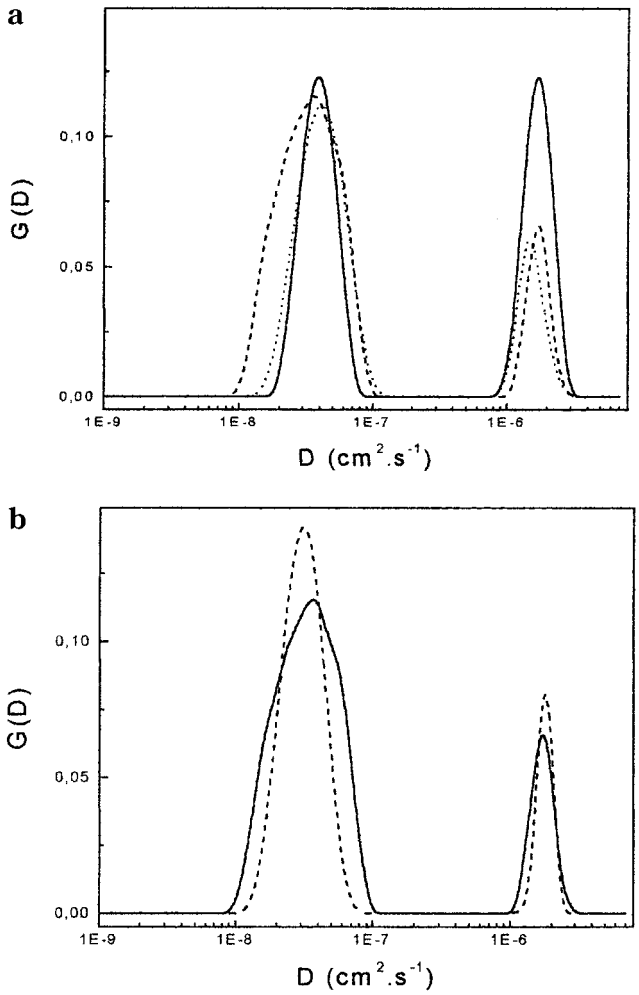

Figure 3. (a) Distribution function of the diffusion coefficients for samples E1 (—), E1a (- - -), and E1b (· · ·) in methanol. (b) Distribution function of the diffusion coefficients for samples E1a (—) and E1c (- - -) in methanol.

It has been mentioned that it is the presence of residual water molecules that contributes to the formation of the clusters in the PEO samples. To test the potential participation of water molecules, the sample E1 is heated at 160 °C under vacuum for 24 h (sample E1d) and 48 h (sample E1e). The curves in Figure 4 show the distribution functions of the diffusion coefficients for the samples E1, E1d, and E1e in methanol at $c = 3.2 \times 10^{-2}$ g cm^{-3}. The hydrodynamic radii of the clusters for these samples calculated by using the eq 3 are 1050, 1220, and 1090 Å, respectively. Meanwhile, the hydrodynamic radii of the nonaggregated species remain constant (22 Å). From this experiment it may be deduced that no modification of the dimensions of the aggregates is observed after heating. Either the samples are free from water molecules or a more drastic treatment is necessary. Anyway, the heating of the samples does not allow to dissolve the clusters.

The different methods used in this study in order to break down the aggregates formed in the PEO samples have failed. However, in a final attempt to regenerate samples free from clusters we have try to isolate these clusters by centrifugation. The correlation function of the light scattered by the methanol solution ($c = 3.2 \times 10^{-2}$ g cm^{-3}) of the sample E2 is shown in Figure 5a. The equivalent distribution function of the diffusion coefficient is given in Figure 5b. These figures show a bimodal distribution where the clusters and the non-

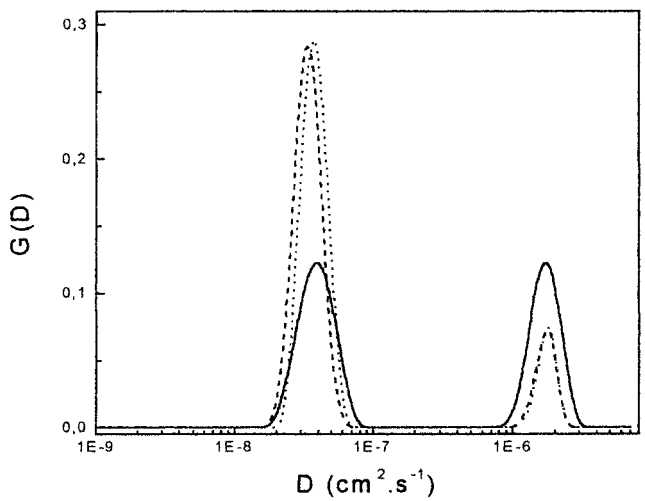

Figure 4. Distribution function of the diffusion coefficients for samples E1 (—), E1d (- - -), and E1e (· · ·) in methanol.

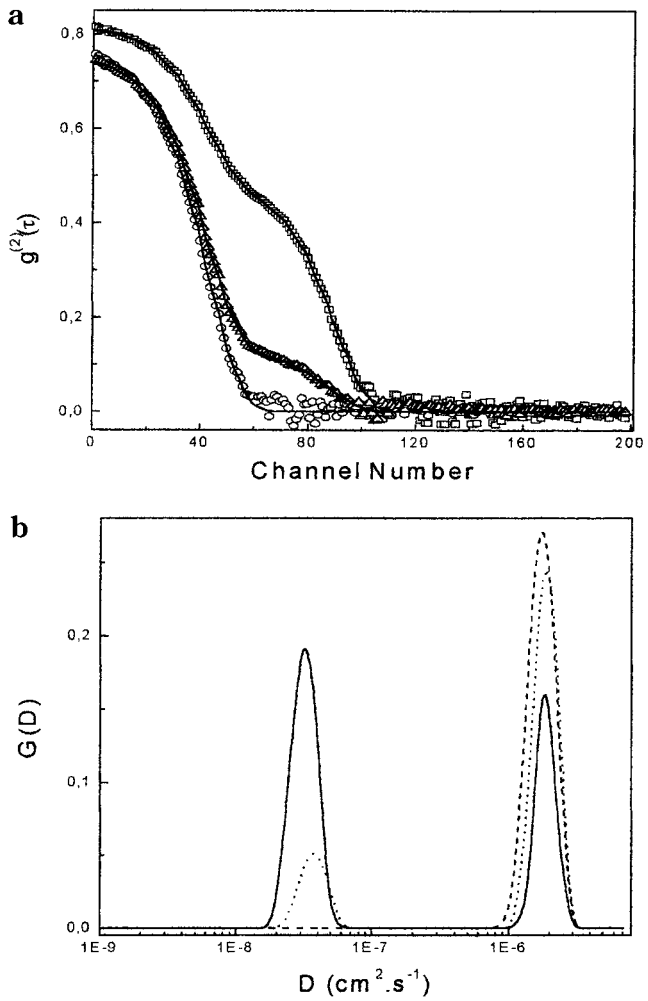

Figure 5. (a) Normalized autocorrelation functions of the scattered intensities for samples E2 (□), E2c (△), and E2s (○) in methanol (scattering angle, $\theta = 20°$; concentration, $c = 3.2 \times 10^{-2}$ g cm^{-3}; temperature, $T = 25$ °C). Solid line: fitted curve obtained by CONTIN analysis.[17] (b) Distribution function of the diffusion coefficients for samples E2 (—), E2c (· · ·), and E2s (- - -) in methanol.

aggregated species have a radius of gyration of 1300 and 22 Å, respectively. A solution of E2 in methanol is centrifuged at 25 000 rpm (4 h). The floating part of the solution (reference E2s) is pipeted in a scattering cell.

The correlation function and the distribution function of the diffusion coefficient for E2s in methanol as measured by QELS are shown in Figure 5. The distribution function is monomodal ($R_H = 23$ Å). On the other hand, the QELS measurement made on the bottom of the centrifuged cell (reference E2c in Figure 5) shows two relaxation modes ($R_H = 1260$ Å and $R_H = 22$ Å). Thus, it is possible to separate the aggregated species of a PEO sample by centrifugation of the solutions.

One can think that the PEO samples contain chemical impurities or that, according to the method of synthesis used, a small number of chains are ended with specific reactive chemical species. The presence of these impurities could induce the formation of the aggregates.[4] To test this hypothesis, we have submitted the floating part (E2s free from clusters) of the E2 sample to a new processing. The methanol has been evaporated, and E2s has been dissolved in DMSO and precipitated in ether. The dry sample is named E2s1. A part of E2s1 is submitted to the same processing leading to the formation of aggregates (dissolution in water at 89 °C for 1 h, drying at 89 °C, dissolution in DMSO, precipitation in ether, drying under vacuum). This sample is named E2s2. The correlation functions of the scattered light and the distribution functions of the diffusion coefficients of samples E2s1 and E2s2 in methanol ($c = 3.2 \times 10^{-2}$ g cm^{-3}) measured by QELS are given on Figure 6a,b. These figures show that E2s1 as E2s is still free from clusters. However, the distribution function of Figure 6b for the sample E2s2 is bimodal. This means that E2s2 contains aggregates ($R_H = 966$ Å). Thus, new clusters have been generated by the dissolution of E2s1 in water at 89 °C. Yet E2s1 is a fraction of E2 where the aggregates have been removed and therefore should be free from chemical impurities. This experiment confirms that it is not the presence of impurities that induces the formation of clusters in the PEO samples but rather the dissolution in water at high temperature in the vicinity of the Θ point as suggested in the first study.[1]

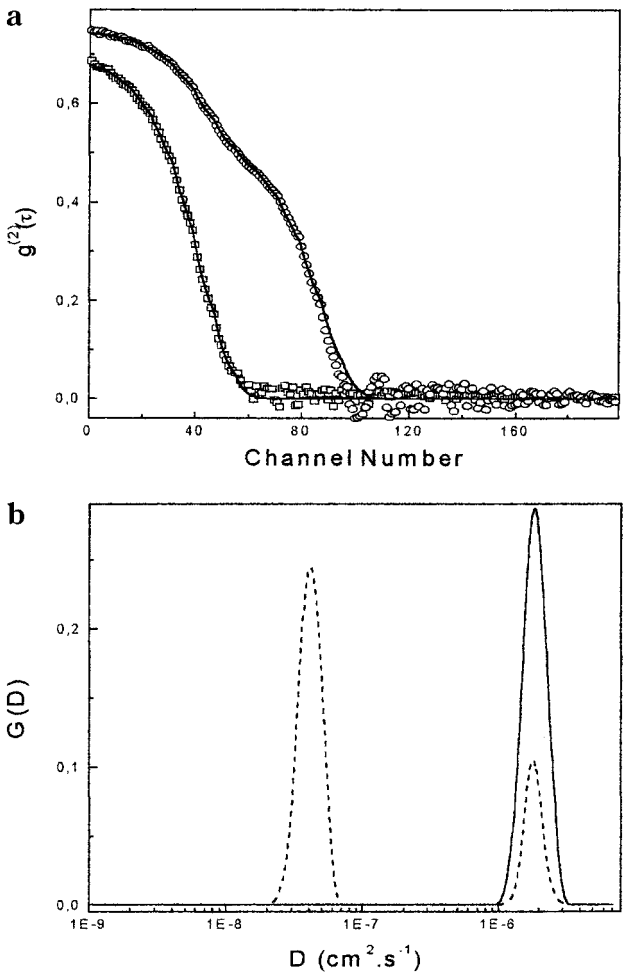

Figure 6. (a) Normalized autocorrelation functions of the scattered intensities for samples E2s1 (□) and E2s2 (○) in methanol (scattering angle, $\theta = 20°$; concentration, $c = 3.2 \times 10^{-2}$ g cm^{-3}; temperature, $T = 25$ °C). Solid line: fitted curve obtained by CONTIN analysis.[17] (b) Distribution function of the diffusion coefficients for samples E2s1 (—) and E2s2 (- - -) in methanol.

Conclusion

The conditions for producing clusters in PEO solutions have been tested. Whenever PEO is dissolved in water at high temperature (89 °C) and the water is evaporated at this temperature, large aggregates are formed when the sample is dissolved later in methanol. The dimensions and the concentration of the aggregates depend on the duration the samples stay in the water. If, before evaporation of water, the aqueous solution is cooled to room temperature, no aggregates are formed.

As soon as they are formed, these aggregates are very stable and relatively monodisperse. They cannot be broken down by further dissolution of the sample in water or water 0.2 N HCl at room temperature even under stirring over a period of several days. Furthermore, they are very stable with respect to the temperature and the heating at 160 °C under vacuum has no effect. These observations show that the interactions responsible of the formation of the clusters should not be due to residual water molecules or to hydrogen bonds as sometimes explained.[13,14]

The aggregates can be removed by centrifugation of a methanol solution and separation of the upper part of the solution. After the recovery of the sample free from clusters a second treatment in water at high temperature generates new aggregates. This result induces that it is not the presence of impurities or the peculiar chains ending with specific chemical groups that leads to the formation of the aggregates.

The closeness[4] of the upper critical solution temperature ($T_c = 103$ °C) and the Flory critical point ($\theta = 102$ °C) is very specific to aqueous PEO solutions. The aggregates that are formed in water at 89 °C not so far from T_c and θ should be due to hydrophobic interactions. Are these aggregates incompletely dissolved polymer or are they well-defined structures strengthened by specific interactions? Further experiments involving samples of higher molecular weight are currently performed and should bring some new clarification concerning this point. It is noteworthy that these entities are very stable and cannot be dissolved using the various processing investigated in this study. They can only be isolated by centrifugation of the solutions. The remarkable stability of the aggregates of PEO that is underlined in the current work is without doubt the source of the discrepancies between the results of the various studies involving the PEO solutions. Indeed, the authors of these studies had not always the control over the history of the samples they have used.

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