Properties of PEO in Dilute Solution under Stirring

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ABSTRACT: The degradation of two high molecular weight PEOs ($M_W = 3.3 \times 10^4$ and 3.3×10^6 Da) by stirring using a magnet is studied by static and dynamic light scattering at room temperature in dilute solution in several good solvents. Besides the "parent polymer", three species are formed under stirring: a soluble species having smaller hydrodynamic radius than the original polymer, soluble aggregates of larger dimensions, and insoluble aggregates of several microns. The formation of these species depends on the nature of the solvent and the stirring speed. The low dimension species are generated in allyl alcohol and in methanol/hydroquinone solutions where, in a turbulent flow, the large molecular chains are broken and could form radicals which are deactivated. The formation of the soluble aggregates is the result of the association of several molecules under the effect of orientation in the flow of the monomer units that belong to different molecular chains. These entities are stabilized by dipolar interactions. The subsequent addition of sodium chloride breaks these associations, and well-solvated polymer units are recovered. The insoluble aggregates are preferentially formed in solvents that have intermediate and low values of the dielectric constant ($\epsilon \cong 7-40$) such as dimethylformamide, acetonitrile, methanol, or methyl acetate. Indeed, in these solvents the formation of living macroradicals in the flow by breaking of the large macromolecular chains could be at the origin of the formation of insoluble reticulated gels.

Introduction

Poly(ethylene oxide) (PEO) is available in a wide range of molecular weights and has many interesting properties. For example, it is soluble in water and in a number of organic solvents. That is the reason why this polymer is used in a wide range of applications.[1,3] However, PEO can be easily degraded by oxidative attack, and this degradation can be accelerated in the presence of heavy metal ions, oxidizing agents, strong acids, and radiations. From this point of view great care must be taken when handling this polymer, and probably this reactivity against external factors is at the origin of a lot of contradictory results that have been set out in the literature. Thus, many uncertainties remain concerning its tendency to form soluble aggregates in solution in such solvents as dioxane,[4,5] water,[4,6−11] methanol,[4,5,6,8,11] and dimethylformamide[4,12] (DMF). Recently,[13,14] we have shown that the formation of soluble aggregates in aqueous solutions for small molecular weight sample ($M_W = 6500$ Da) depends on the method of preparation of the solutions and that, once they are formed, these aggregates are difficult to crumble. Therefore, we arrived at the conclusion that the presence of aggregates in the PEO solutions should be due to the history of the polymer.

In this contribution we report some observations obtained on two high molecular weight PEOs in dilute solution. We especially investigate the structure of the PEO solutions submitted to a turbulent flow produced by stirring with a magnet at room temperature. First, we emphasize the preparation and the optical clarification of the solutions for this step which is a very tricky stage and could be at the origin of many artifacts. Next we investigate the behavior of two PEO samples of large molecular weight submitted to a stirring. Aqueous and methanolic solutions are studied by static (SLS) and quasi-elastic (QELS) light scattering measurements. Afterward, we clarify the way PEO reacts to a turbulent flow in allyl alcohol and in methanol/hydroquinone solutions which are known as stabilizers. The stability of the solutions is tested with respect to the temperature, to the time, and to the addition of sodium chloride. Finally, we study the behavior of PEO subjected to the influence of the stirring by a magnet in various solvents quoted by decreasing value of their dielectric constant: water, dimethylformamide (DMF), acetonitrile, methanol, methyl acetate, and dioxane.

Experimental Section

Materials. The PEO samples used in this study are commercial samples from Hoechst (Hoechst-Frankfurt, Germany; PEO35) and Aldrich (Aldrich Chemical Co., PEO3500). The distribution function of the molecular weight of these samples is measured by gel permeation chromatography in 3 times distilled water (0.1 N $NaNO_3$). The weight-average molecular weight M_w, the second virial coefficient A_2, the radius of gyration R_G, and the hydrodynamical radius R_H are measured by SLS and QELS in methanol, 3 times distilled water, and methyl acetate for the PEO35 sample and in methanol for the PEO3500 sample. The results are given in Table 1. These values are in agreement with the values calculated from the empirical power laws of Devanand et al.[11] and Kinugasa et al.[15] in methanol ($A_2 = 1.79 \times 10^{-3}$ cm^3 mol g^{-2}, $R_H = 5.6$ nm for PEO35; $A_2 = 4.92 \times 10^{-4}$ cm^3 mol g^{-2}, $R_G = 135$ nm, $R_H = 68.2$ nm for PEO3500). Furthermore, the experimental value of $R_H/R_G = 0.532$ for PEO3500 in methanol is close to the theoretical value of 0.538 for polymers in good solvent as calculated by Akcasu and Benmouna[16] using the fully swollen Gaussian chain model.

All the solvents are spectroscopic purity grade products and used without further purification. Fresh 3 times distilled water is used for the preparation of the aqueous solutions.

Solution Preparation. In the first step of the preparation all the solutions are heated at 55 °C without stirring. To ensure a homogeneous aggregate-free medium, it is verified at this moment by QELS that the polymer is well dissolved (monomodal distribution of the dimensions of the solvated species). Afterward, during the stage of stirring, it is necessary to use a magnet wrapped with glass instead of Teflon. Indeed, using Teflon can lead to the formation of associated complexes due to the porosity of this material and to the diffusion of iron salts in the PEO solutions through the Teflon wrapping. Moreover, careful optical clarification of the solutions is very important

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Table 1. Properties of Polymer Samples

sample	solvent	M_w (Da)	A_2 (cm^3 mol g^{-2})	R_G (nm)	R_H (nm)	polydispersity index
PEO35		36 000[a]				1.05[a]
	methanol[b]	33 000	1.26×10^{-3}		5.5	
	3× distilled water[b]	36 000	2.03×10^{-3}		6.1	
	methyl acetate[b]	37 000	1.02×10^{-3}		5.6	
PEO3500		3 700 000[a]				1.26[a]
	methanol[b]	3 300 000	5.0×10^{-4}	147.4	78.4	

[a] Measured by gel permeation chromatography in 3× distilled water (0.1 N $NaNO_3$). [b] Measured by SLS and QELS.

for the light scattering measurements; otherwise, side effects may occur. For example, we have shown that, in the case of solutions containing aggregates, it was possible to eliminate these aggregates by centrifugation.[14] Therefore, in the study of the ability of PEO in solution to aggregate under external factors (nature of the solvent, temperature, shear stress, metallic ions, etc.), one should not use this technique in order to get optically cleared PEO solutions. The filtration alone should be used. Nevertheless, it has been reported in the literature that filtration of the solutions could induce crystallization.[6] At the beginning of the study we show that the nature of the filters may have a very significant influence on the quality of the prepared solutions.

We emphasize the fact that the stage of preparation and treatment of the PEO solutions is crucial, and in order to verify the validity and the reproducibility of the results, some of the experiments have been done again. This is the case for the test of the different kinds of filters, the experiments on the stirring of the PEO in methanol and in water, and the study of the effects of addition of NaCl in the solutions showing the presence of the solubles aggregates. Identical results have been obtained in these experiments, and the reproducibility is a guarantee against artifacts.

Light Scattering Measurements. SLS measurements are performed at $T = 25$ °C on a FICA50 (SOFICA, France) photometer. A vertically polarized light ($\lambda_0 = 633$ nm) of a He–Ne laser is used as incident beam. The intensity of the scattered light is measured at scattering angles from $\theta = 22.5°$ to 150° in order to control the stability of the solutions and the reproducibility of the results.

QELS measurements are made at 25 °C in the homodyne mode using a photon correlation spectrometer described in full detail elsewhere.[17] A Spectra Physics 2020-2W argon ion laser ($\lambda_0 = 514.5$ nm) acts as the coherent light source. An ALV5000 autocorrelator (ALV, Langen, Germany) is used to measure the correlation functions of the scattered intensity. The normalized autocorrelation functions $g^{(2)}(\tau)$ of the intensity of the light scattered by the particles are measured at a scattering angle $\theta = 30°$ and are analyzed using the CONTIN software[18] following

$$g^{(2)}(q,\tau) = g^{(2)}(q,0)\int \exp(-\tau/\tau_r)\, G(\tau_r)\, d\tau_r \qquad (1)$$

where q is the scattering vector, τ is the time, and $G(\tau_r)$ is the distribution function of the relaxation time τ_r. The apparent hydrodynamic radius R_H of the particles in solution is calculated through the Stokes–Einstein relationship:[19]

$$R_H = 2q^2 \frac{k_B T}{6\pi\eta_0} \tau_r \qquad (2)$$

where k_B is the Boltzmann constant, T the absolute temperature, and η_0 the viscosity of the solvent.

Results and Discussion

Clarification of the PEO Solutions As mentioned above, the clarification of the samples is an essential stage in the study of the PEO solutions by light scattering. All the samples used in this work are filtered in order to remove dust. The nature of the filter can play a major influence upon the behavior of the PEO. Thus, we have tested four kinds of filters. The pore rating (0.45 μm) and the surface area of filtration (3.9 cm^2) of these filters are identical, but their shape and the nature of the membrane and the holder are different. The tested filters are the following: Rotilabo hydrophobic (Roth-Sochiel Sarl; Lauterbourg, France); membrane: PTFE; holder: PE. Dynagard (Interchim Co.; Clermont-Ferrand, France); membrane: poly(propylene) (PP). Millex HA (Millipore Co.; Molsheim, France); membrane: cellulose ester; holder: poly(vinyl chloride) (PVC). Millex LCR hydrophilic (Millipore Co.; Molsheim, France); membrane: poly(tetrafluoroethylene) (PTFE); holder: poly(ethylene) (PE).

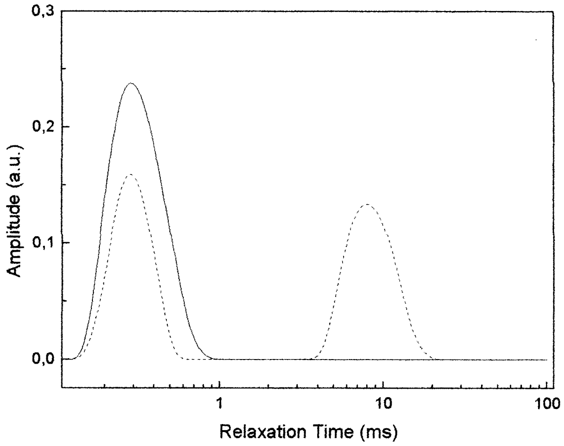

Figure 1. Distribution function of the relaxation time of the correlation function of the intensity of the light scattered at $\theta = 30°$ by PEO35 in aqueous solution ($C = 5.32 \times 10^{-3}$ g cm^{-3}) as obtained by the CONTIN analysis: solid line, solution filtered on Millex PTFE/PE/hydrophilic filter; dashed line, solution filtered on Millex HA cellulose ester/PVC filter.

The Dynagard filter is cone-shaped whereas the others are disk-shaped. The filtration of nonaqueous specific solutions containing aggregates on the PTFE/PE/hydrophobe filters induces a loss of 50% of the scattered intensity whereas there is a loss of 40% with the Dynagard filters. Moreover, this loss of the scattered intensity is accompanied by a decrease (40%) of the size of the larger scattering species as measured by QELS. Although the surface area of filtration is the same as for the PTFE/PE filters, the progress of the solutions in these cone-shaped filters is longer than in the disk-shaped filters, and a great part of the aggregates is adsorbed on the filter.

The distribution function of the relaxation time as obtained by QELS measurement is shown in Figure 1 for a PEO35 aqueous solution that is filtered on a PTFE/PE/hydrophilic and cellulose ester/PVC filters. It clearly appears that the filtration on the cellulose ester filter induces the formation of aggregates of large size. Furthermore, the intensity of the light scattered by this solution at an angle of 30° is twice the intensity of the light scattered by the solution filtered on the PTFE

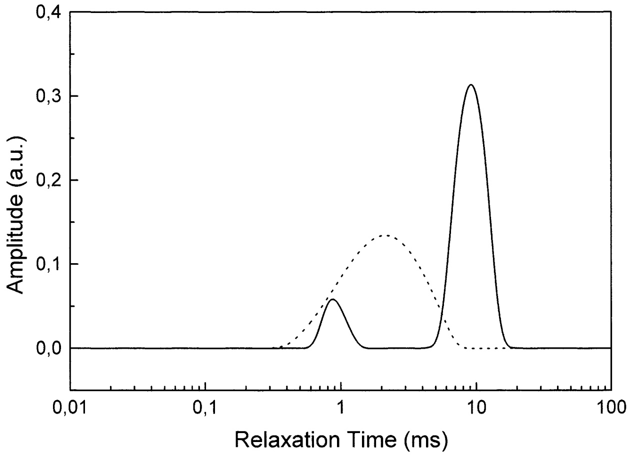

Figure 2. Distribution function of the relaxation time of the correlation function of the intensity of the light scattered at $\theta = 30°$ by PEO3500 in methanol solution ($C = 8.03 \times 10^{-3}$ g cm^{-3}) as obtained by the CONTIN analysis: dashed line, before stirring; solid line, after stirring (2 h at 120 rpm).

filter. This phenomenon of aggregation of the PEO molecules under filtration has already been described in the literature.[6]

Among these filters only the PTFE/PE/hydrophilic filters give satisfactory results. This is particularly confirmed by the fact that the characteristics of the sample determined by light scattering where the solutions are optically cleared using this type of filter are the same as the characteristics measured by GPC (see Table 1). However, one must take care of the adsorption of matter on the filter. Thus, a second filtration on a hydrophilic PTFE filter that has already been used leads to a decrease of 10% of the light scattered by the solution. A small amount of polymer can be adsorbed, and in order to avoid this phenomenon of adsorption, each filter is used only once.

Influence of a Turbulent Flow upon the Behavior of PEO in Dilute Solution. A solution of PEO3500 in methanol ($C = 8.03 \times 10^{-4}$ g cm^{-3}) is prepared by dissolution as described above over a period of 2 days. The distribution function $G(\tau_r)$ of the PEO3500 measured by QELS is shown in Figure 2. This distribution is monomodal ($R_H = 53.8$ nm) and rather broad in agreement with the high value of the polydispersity index of the sample (see Table 1). Afterward, the same solution is stirred for 2 h at low speed (120 rpm) using a magnet. The solution becomes turbid and remains turbid after subsequent heating at 55°C (3 h). The filtration of this solution into a scattering cell leads to a clear filtrate. The distribution function $G(\tau_r)$ measured by QELS is bimodal (see Figure 2). The apparent R_H value of the larger species (253 nm) is 5 times higher than in the first measurement before stirring, and the distribution function is fairly narrow. Moreover, the scatterred intensity decreases by a factor of 15%. Upon the influence of the turbulent flow produced by the magnet, a small part of the polymer turns into insoluble species that remains on the filter. Another part aggregates and forms soluble species of large dimensions.

To compare the action of a turbulent flow to the action of ultrasounds, a solution of PEO3500 in methanol ($C = 1.7 \times 10^{-4}$ g cm^{-3}) is submitted to the degradation by ultrasounds. Before sonication, the distribution function of the hydrodynamic radius $G(R_H)$ of the PEO3500 measured by QELS is monomodal ($R_H = 783$ Å). After 20 min of sonication the solution remains clear, but $G(R_H)$ is bimodal ($R_{H1} = 125$ Å and $R_{H2} = 1353$ Å). These values indicate that there is a break of one part of the large macromolecular chains associated with the aggregation of the other part. The common point between the two experiments is the formation of soluble aggregates in the solution. This comparison must be considered as qualitative because, from a quantitative point of view, one should know the amount of energy involved in the two kinds of experiments. In the current work we only want to report the fact that the aggregation of the PEO molecules occurs not only in a turbulent flow.

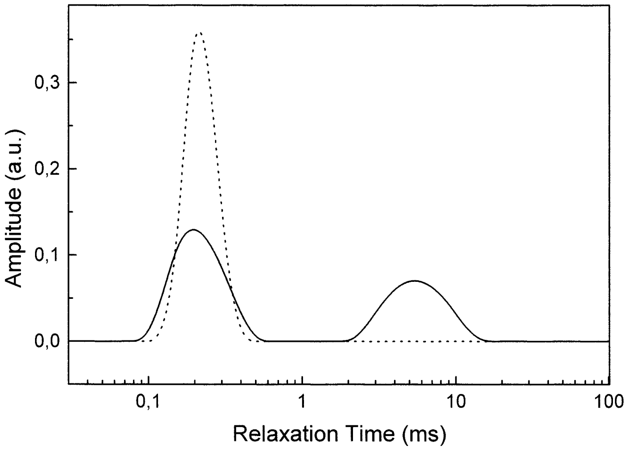

Figure 3. Distribution function of the relaxation time of the correlation function of the intensity of the light scattered at $\theta = 30°$ by PEO35 in aqueous solution ($C = 2.01 \times 10^{-2}$ g cm^{-3}) as obtained by the CONTIN analysis: dashed line, before stirring; solid line, after stirring (72 h at 900 rpm).

An almost similar observation is made on an aqueous solution of the PEO35 sample that has a much smaller molecular weight. However, in this case the phenomenon of aggregation appears in a solution that is submitted to a higher stirring speed (900 rpm) and for a longer time. Figure 3 shows the distribution functions of the relaxation time of the correlation functions measured by QELS before and after stirring at high speed at room temperature over a period of 72 h. If, at the beginning of the experiment, the distribution of the PEO is monomodal ($R_H = 3.8$ nm), it becomes bimodal ($R_{H1} = 3.9$ nm; $R_{H2} = 94.5$ nm) after stirring. The small entity is identical to the well-dissolved nonassociated polymer. The large entity corresponds to the aggregation of several molecules. Contrary to the case of PEO3500, no turbidity appears in the solution, and the scattered intensity increases by a factor of 40% at $\theta = 30°$ at the end of the experiment. This is the result of the formation of large soluble aggregates without loss of matter.

Insoluble Aggregates Previously, we have seen that insoluble aggregates are formed in a stirred methanolic solution of PEO of large molecular weight. The observation of this turbid solution in cross-polar optical microscopy shows the presence of oblong particles which are several microns in length and slightly birefringent. The chemical mechanism of the formation of these insoluble aggregates could involve the fact that the experiment is performed under air atmosphere (influence of the oxygen). However, the same observations are made in a solution under an argon atmosphere. In the absence of other chemical reagent one could refer to reactions between macroradicals of PEO formed by the breaking of large macromolecular chains in the turbulent flow

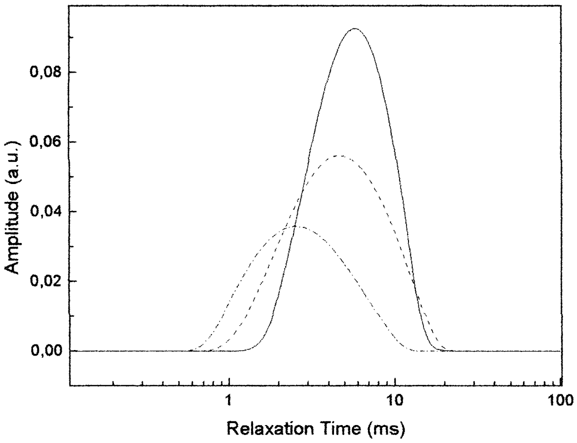

Figure 4. Distribution function of the relaxation time of the correlation function of the intensity of the light scattered at $\theta = 30°$ by PEO3500 in allyl alcohol ($C = 2.3 \times 10^{-4}$ g cm^{-3}) as obtained by the CONTIN analysis: solid line, before stirring; dashed line, after stirring (24 h at 120 rpm); dash–dotted line, after stirring (24 h at 120 rpm + 14 h at 900 rpm).

created by the stirring rod. Unfortunately, we were unable to detect directly the presence of macroradicals by EPR (electron paramagnetic resonance). This could be due to the lifetime of these radicals which could be too much short.

However, an indirect proof of the veracity of this hypothesis is to show that, in a solvent where the radicals are trapped before recombination, no insoluble aggregates are formed by stirring. In this intention a solution of PEO3500 ($C = 2.3 \times 10^{-4}$ g cm^{-3}) in allyl alcohol is subjected to a turbulent flow using a magnet in rotation at different speeds in the course of the time. It is well-known that allyl alcohol is a stabilizer for PEO in solution.[1] The results of this experiment are shown in Figure 4. At the beginning of the experiment the distribution of τ_r or R_H (see eq 2) is centered at the value corresponding to 77.1 nm. After 1 day of stirring at low speed the same solution shows a larger distribution centered at 64.2 nm. A decrease of the scattered intensity at $\theta = 30°$ is observed (8%). Fourteen hours later at the maximum stirring speed the intensity has once more decreased (20%) as well as the mean value of R_H (37.2 nm). One can also note that the width of the distribution function of τ_r has increased (see Figure 4). Moreover, the solution remains clear, and no aggregation (soluble or insoluble aggregates) occurs in this solvent. The decrease of the dimension of the PEO molecules could be interpretated as a break of the polymer chains under the effect of the stress induced by the flow. This break could generate macroradicals which are trapped by the double bond of the allyl alcohol molecule, leading to small chains that coexist with the large chains of the parent molecules. In other solvents, these macroradicals should be able to react with each other following a process that involves radicals at the origin of the formation of insoluble reticulated gels as observed for example in the system PEO3500/methanol.

To corroborate this assertion, the behavior of the PEO3500 ($C = 8.1 \times 10^{-4}$ g cm^{-3})/methanol/hydroquinone (0.36 M) solution submitted to the stirring by a magnet is studied by SLS. Hydroquinone is well-known to react with the living radicals. No formation of precipitate can be observed in this case even after 10 days of stirring at 600 rpm. Meanwhile, the average molecular weight of the PEO has decreased significantly from 3.3×10^6 to 2.5×10^6 Da. One can arrive to the conclusion that, in a medium where the living radicals are deactivated by reaction with small molecules (allyl alcohol, hydroquinone), low dimension species are formed when a PEO is submitted to a turbulent flow. These species correspond to the break of the polymer chains. Moreover, one cannot observe any formation of insoluble species in this type of medium.

Soluble Aggregates. In the first experiment described in this study on the PEO35/water system we have seen that soluble aggregates can be generated after stirring of the solution. To investigate thoroughly the properties of this soluble species, we recover the sample (now named A11) by evaporation of water, solubilization in dimethyl sulfoxide (DMSO), and precipitation in ether. It is verified that the same treatment on a nonassociated well-dissolved PEO35 sample has no specific influence upon the subsequent behavior in solution (monomodal distribution of the relaxation time).

We investigate the time course of SLS and QELS from the A11 solutions for a long period of time at room temperature (1 week for the aqueous solutions and 4 weeks for the solutions in methanol). Furthermore, we test the stability of these solutions with respect to the temperature (4–5 h at 70 °C). The observed angular depencies of the scattered light and the distribution functions $G(\tau_r)$ of the relaxation time τ_r are the same as the initial ones for all these solutions. These findings suggest that the distribution of PEO molecules in these solvents is quite stable.

Some authors have attributed the ability of PEO in solution to aggregate to the fact that these aggregates are stabilized by hydrogen bonds or, in the case of aqueous solutions, by hydrophobic interactions.[7] It is well-known that urea has the property to break the hydrogen bond (denaturation of the DNA helical molecule). However, we do not observe any modification on the distribution function $G(\tau_r)$ for A11 in 1.8 M urea aqueous solutions. Two relaxation modes, as described in Figure 3, still exist in the presence of urea, showing that the stabilization of the soluble aggregates should not be caused by the hydrogen bond.

On the other side, we prepare an aqueous solution of A11 ($C = 1 \times 10^{-3}$ g cm^{-3}) and separated this solution into three parts. The first sample is used as a reference whereas in the other two samples we add sodium chloride (NaCl: 5.5×10^{-3} and 1.6×10^{-2} M). The distribution functions $G(\tau_r)$ measured on these three A11 (PEO35) aqueous solutions are shown in Figure 5. As expected, the solution without NaCl shows a bimodal distribution ($R_{H1} = 6.0$ nm; $R_{H2} = 89.4$ nm). Furthermore, the relative area under the peak which corresponds to the scattering by the large species represents 34% of the total area, and the dissymmetry factor I_D (ratio between the integrated scattered intensity at $\theta = 45°$ and $\theta = 135°$) has a value of 1.09. Two species are still observed in the 5.5×10^{-3} M NaCl aqueous solution. Their hydrodynamic radii ($R_{H1} = 5.7$ nm; $R_{H2} = 88.5$ nm) are equal to the R_H values measured in the aqueous solution without salt. However, the relative area under the peak which corresponds to the large species has decreased to 27%. Finally, there is only one species in the 1.6×10^{-2} M NaCl aqueous solution. The R_H value (5.8 nm) of this species is equal to the R_H value of the PEO35 sample at the same concentration in an aqueous solution that has not been stirred. One should

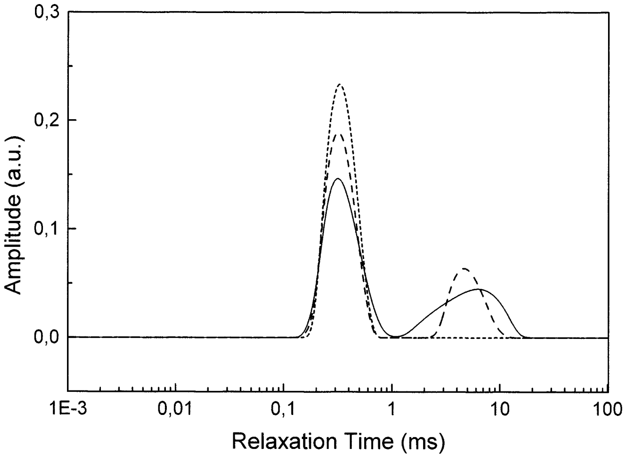

Figure 5. Distribution function of the relaxation time of the correlation function of the intensity of the light scattered at $\theta = 30°$ by A11 (modified PEO35) in aqueous solution ($C = 1.0 \times 10^{-3}$ g cm^{-3}) as obtained by the CONTIN analysis: solid line, without NaCl; dashed line, 5.5×10^{-3} M NaCl; dotted line, 1.6×10^{-2} M NaCl.

note that the concentration of the aggregates decreases with the addition of increasing quantities of salt, but their dimensions do not change in agreement with the model of closed association.[20] From this experiment it comes out that the soluble aggregates are destroyed by the addition of a small amount of NaCl. The same observation is made for All in methanol and for PEO3500 in water and methanol. This result indicates that the formation of soluble and stable aggregates should be due to dipolar interactions between segments of different adjoining chains rather extended along the streamline of flow in the solution under stirring. Then one can infer that the dielectric properties of the solvents could be one of the parameters that act upon the behavior of the PEO chains in solution under the influence of a turbulent flow. Finally, it should be noted that a solution of PEO3500 in methanol/NaCl remains clear after stirring. This is observed in the same conditions of stirring where, in the absence of salt, insoluble aggregates of PEO are formed. NaCl has a stabilizer effect under stirring.

The full characterization of the PEO solutions involving the determination of the molecular weight and the concentration of the soluble aggregates is currently in progress. This study will show the influence of the time and the intensity of the stress applied on the polymer solution. It will also show the influence of the concentration and the molecular weight of the PEO sample.

Influence of the Nature of the Solvent. To study the influence of the nature of the solvent on the behavior of PEO3500 in solution and under stirring, we subject a dilute solution ($C = 2.2 \times 10^{-4}$ g cm^{-3}) of this sample in various solvents to the same processing, namely the stirring for 2 h at low speed. Then SLS and QELS measurements are performed. It is verified that, before stirring, the correlation functions of the intensities of the light scattered by all these solutions, as measured by QELS, are monomodals. The results that come out from SLS and QELS measurements before and after stirring are given in Table 2 where the solvents are classified following the order of the value of their dielectric constant, beginning with water ($\epsilon = 78$) and ending with dioxane ($\epsilon = 2.2$). At first sight no general rule can be drawn from these results. However, it appears that all the solutions become turbid after stirring except for aqueous and dioxane solutions. As mentioned previously for the PEO solutions in methanol, the turbidity of the solutions observed after stirring in DMF, acetonitrile, and methyl acetate is due to the formation of reticulated gels following a process that could involve radicals initiated by the breaking of the chains. Taking account of the relatively high polydispersity of the PEO3500 chains, it seems that this breaking off concerns selectively the larger chains in the first place since the appearance of turbidity in these solvents goes with a small decrease of R_H and I_D.

Table 2. Characteristics of Dilute Solutions ($C = 2.2 \times 10^{-4}$ g cm^{-3}) of PEO3500 in Various Solvents after Stirring for 2 h at Low Speed[a]

solvent	appearance	R_H (nm)	I_D
water	clear	68–70	2.1–2.0
DMF	slightly turbid	59–52	1.3–1.2
acetonitrile	slightly turbid	53–49	1.7–1.2
methanol	turbid, soluble aggregates	54–86	2.0–2.3
methyl acetate	turbid	76–71	2.2–2.1
dioxane	clear	39–38	1.2–1.2

[a] The hydrodynamic radius R_H and the dissymmetry factor I_D are measured by light scattering before (first value) and after (second value) stirring.

The behavior of PEO3500 in methanol is somewhat different since the QELS measurements show the presence of soluble species of large dimension (86 nm instead of 54 nm before stirring) comparable to the soluble aggregates observed in PEO35 aqueous solutions but obtained at higher stirring speed for a longer time.

In dioxane solution the PEO chains are less expanded ($R_H = 39$ nm) than in the other solvents ($R_H > 50$ nm) which must be imputed without doubt to the quality of this solvent with respect to PEO. The aligning of the dipoles should be achieved at a higher stirring speed. In the same conditions as those which are set for the other solvents, the dioxane solution undergoes no modification after stirring.

The case of the PEO aqueous solution is special. The macromolecular chains are as well expanded ($R_H = 68$ nm) in water as in methyl acetate ($R_H = 76$ nm). Nevertheless, in the same conditions the aqueous solution remains insensitive to the stirring effects. This can be explained by the fact that, contrary to the situation in methyl acetate where the dielectric constant is very low ($\epsilon = 6.7$), the dipolar interactions between adjacent chains in water ($\epsilon = 78$) should be very weak. Moreover, one should take into account that the PEO molecules have a specific conformation in water.[21]

To conclude, it should be noted that probably there is not only one factor that governs the behavior of the PEO chains in solution under stirring. However, considering Table 2 and the discussion above, three main criteria (the quality of the solvent, its dielectric properties, and the nature of the polymer–solvent interactions) should most probably be considered in order to avoid aggregation or precipitation in the PEO solutions. It must be recalled that the previous results are obtained under specific conditions of stirring. Under other conditions, for example at higher stirring speed for a longer time, one should observe different behavior as is the case in aqueous solutions of PEO35 (see Figure 3 at high stirring speed for 72 h). The conclusions that are drawn in this last study on the nature of the solvent are only valid in the case of the comparative analysis, which is resumed in Table 2.

Conclusion

Following a careful study of the different artifacts that come on top of the clarification of the PEO in dilute solutions, we have investigated the behavior of this polymer in a turbulent flow created by the stirring through a magnet. Using SLS and QELS, we have identified four different species that can exist after this processing. In solvents such as allyl alcohol and methanol/hydroquinone which deactivate the radicals, the break of the macromolecular chains in the flow leads to the formation of shorter chains than the parent polymer. In solvents where the macroradicals have a longer lifetime, insoluble aggregates corresponding to reticulated gels are formed. These aggregates that could result from reaction involving radicals are very stable with respect to the temperature and other solvents. In solvents such as water or methanol one can observe the presence of soluble aggregates which are stabilized by dipolar interactions between segments pertaining to adjacent macromolecular chains oriented along the streamline of flow in the solution under stirring. These entities are dissolved by addition of a small amount of salt. The addition of salt in the solution before stirring prevents aggregation and stabilizes the solution. To avoid at the maximum the aggregation or precipitation of PEO in solution under stirring, it should be better to use solvents characterized by high dielectric constant or solvents in which the polymer chains are somewhat collapsed.

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