

Polymer Communication

Identification of the formation of aggregates in PEO solutions

M. Duval*, D. Sarazin

Institut Charles Sadron (CNRS-ULP), 6 rue Boussingault, 67083 Strasbourg Cedex, France

Received 11 June 1999; received in revised form 25 August 1999; accepted 13 September 1999

Abstract

The properties of poly(ethylene oxide) PEO chains (molecular weight M_w : 6500) have been examined in dilute solutions in methanol using static (SLS) and dynamic (DLS) light scattering. The ability of PEO chains to aggregate depends on the history of the sample. Thus two relaxation times have been observed in the correlation functions of the intensity of the light scattered by PEO in methanol when the sample was previously dissolved in hot water ($t \geq 60^\circ\text{C}$). The fast mode is attributed to the well-solvated monomolecular species and the slow mode is because of the formation of aggregates that are generated by hydrophobic interactions. These aggregates are well defined, relatively monodisperse and very stable. No aggregation is observed for PEO in methanol when the sample has been previously dissolved in a lot of solvents such as water ($t = 30^\circ\text{C}$), chloroform, dioxane, dimethylsulfoxide (DMSO), dimethylformamide (DMF) or acetonitrile. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene oxide); Dilute solution; Aggregation conditions

1. Introduction

For about 30 years, poly(ethylene oxide) (PEO) in solution has been the subject of many studies involving a lot of laboratories and a lot of techniques. These studies have led to somewhat contradictory results concerning the ability of PEO to be perfectly soluble in dispersed species in some solvents or to form aggregates in these same solvents. For example one of the first work by Elias et al. [1] on the couple PEO/water shows that PEO is completely soluble in aqueous solution. This result was confirmed recently by Devanand et al. [2,3] and Kinugasa et al. [4,5]. However, the formation of aggregates on the same system has been reported in many other studies [6–11]. Strazielle [12] has shown, by light scattering measurements on samples of various molecular weights, that the ability of PEO to form aggregates in aqueous solutions depends on the molecular weight of the sample and on the method of preparation of the solutions. The same contradictory results have been obtained for PEO in methanol that has been found to be partially associated [13] or well solvated [1–5,7,14]. Even when the results tend to ascertain the presence of aggregates, the factors that control their formation are not well identified. Thus, at low molecular weight, one can expect that crystallisation or aggregation occur under certain condition [12].

Many hypothesis have been expressed to explain the formation of aggregates including the presence of impurities, the formation of hydrogen bonds [15], the formation of complex entities associated with the presence of residual water molecules and with hydrophobic interactions [6,16].

The purpose of this study is to clarify the situation with regard to the formation of aggregates in the solutions of PEO. In order to do that, a PEO sample has been submitted to different manipulations. It is shown that the aggregation is dependent on the history of the samples. It depends especially on the fact that one of the manipulations is the dissolution of the sample in water in a given range of temperature.

In this way the many contradictory results which are reported in the literature can be attributed to two different causes. Firstly the authors do not always know what exactly is the history of the samples they use. Secondly the techniques of investigation have not the same sensibility with regard to the formation of large particles. For example it is well known that the light scattering technique is much more sensitive to the presence of a small amount of large species than the viscosity.

2. Experimental

2.1. Samples, solvents and solution preparation

2.1.1. Sample E0

The sample, which is used as reference, is a commercial

* Corresponding author. Fax: +33-03-88-41-40-99.
E-mail address: duval@ics.u-strasbg.fr (M. Duval)

Table 1

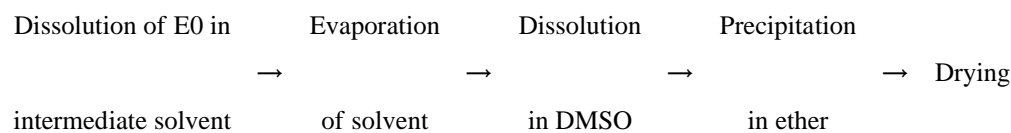
Laser light scattering results in methanol at 25°C. Intermediate solvent: solvent in which E0 has been dissolved before obtaining samples E1 → E8. R_{Hf} : hydrodynamic radius of the dispersed molecular species. R_{Hs} : hydrodynamic radius of the large aggregates

Samples	Intermediate solvent	M_w (g mol ⁻¹)	$A_2 \times 10^3$ (cm ³ .mol.g ⁻²)	R_{Hf} (Å)	R_{Hs} (Å)
E1	Water 30°C	6600	2.06	23	–
E2	Water 60°C	10 900	0.53	23	779
E3	Water 89°C	13 900	0.46	23	689
E4	Methanol	6000	2.32	22	–
E5	Chloroform	5900	1.86	23	–
E6	Dioxane	6200	1.99	23	–
E7	DMF	7000	2.34	23	–
E8	Acetonitrile	6700	2.22	23	–

sample PEO-6000 from Hoechst (Frankfurt, Germany). It is named E0 in the remainder of the paper. Gel Permeation Chromatography (GPC) in 3 × distilled water (0.1 N NaCl) gave a polydispersity of 1.04 (number-average molecular weight: $M_n = 6850$; weight-average molecular weight: $M_w = 7100$) while Static light scattering (SLS) in methanol gave a value of $M_w = 6500$ that agrees with the GPC value.

2.1.2. Samples E1 → E8

In order to characterise the influence of the history of the sample on the behaviour in solution, E0 has been submitted to different manipulations that are shown in the following diagram:



The final products are named E1 → E8 and they all have the same history except that they were dissolved in different intermediate solvents that are given in column 2 of Table 1. The last steps of the procedure for the preparation of samples have been adopted because DMSO, which is a good solvent for PEO, is also miscible with ether, which is a precipitant of this polymer.

- All solvents were spectroscopic purity grade products and used without further purification. Deionized water was used for the intermediate stage of dilution.
- For each sample (E0 → E8) a set of five concentrations ranging approximately from 0.6 to 3.2% in methanol was prepared by heating ($t \cong 40^\circ\text{C}$) and stirring over a period of 12 h. The solutions were directly filtered through 0.45 μm DynaGard filters (Spectrum Microgon, USA) in the light scattering cells for optical clarification. Aqueous solutions were filtered through 0.5 μm Millex LCR (Millipore, France) filters.

2.2. Static light scattering

SLS measurements were performed at $t = 25^\circ\text{C}$ on a FICA50 (SOFICA, France) photometer. A vertically polarised light of $\lambda_0 = 633$ nm wavelength from a He–Ne laser was used as an incident beam. The intensity of the scattered light was measured at scattering angles from $\theta = 22.5$ to 150° . The refractive index increment values were taken as 0.15 cm³ g⁻¹ in methanol and 0.13 cm³ g⁻¹ in water [12]. The Zimm plot method was used to determine the osmotic virial coefficient A_2 and the molecular weight M_w using the equation:

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{M_w} + 2A_2c \quad (1)$$

where c is the polymer concentration and ΔR_θ is the excess Rayleigh ratio.

2.3. Dynamic light scattering

Quasi-elastic light scattering experiments were performed at 25°C in the homodyne mode using a photon correlation spectrometer described in full detail elsewhere [17]. The correlation functions of the scattered intensity defined on 192 channels were obtained by using the ALV-3000 (ALV-Langen, FRG) autocorrelator in its multi- τ mode. In this mode the correlation functions cover seven decades in delay times going from $\tau = 1$ μs to 63 s. The normalised autocorrelation functions $g^{(2)}(\tau)$ of the scattered intensity were measured at a scattering angle $\theta = 20^\circ$ and were analysed using the CONTIN software [18] following the classical expression:

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

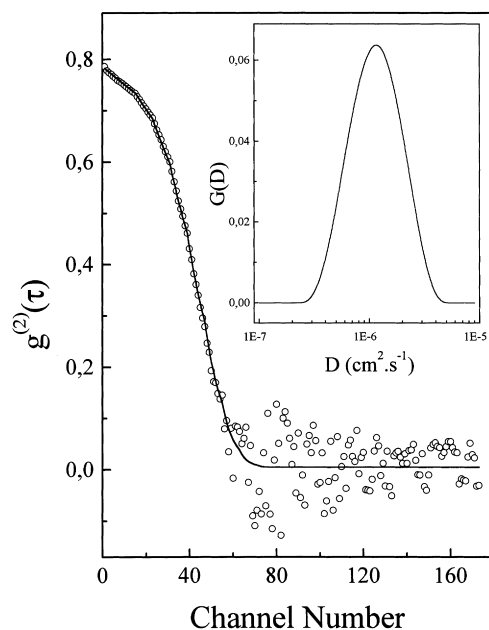


Fig. 1. Plot of the normalised autocorrelation function for E0 in water at a concentration of $2.59 \times 10^{-2} \text{ g cm}^{-3}$ (temperature $t = 25^\circ\text{C}$, scattering angle $\theta = 20^\circ$). Solid line: Fitted curve. Inset: Distribution function of the diffusion coefficient given by CONTIN analysis.

where q is the scattering wave vector and $G(D)$ is the distribution function of the translational diffusion coefficient D of the scattering particles. In a dilute solution the diffusion coefficient varies with concentration as:

$$D = D_0(1 + k_D c) \quad (3)$$

The extrapolated value D_0 of D at $c = 0$ is related to the

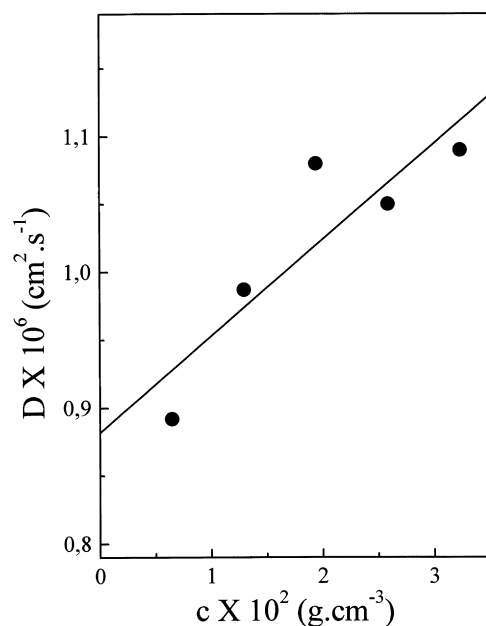


Fig. 2. Plot of the diffusion coefficient as a function of the E0 concentration in water at 25°C . The solid line corresponds to the linear fit through the experimental points.

hydrodynamic radius R_H through the Stokes–Einstein relation for a sphere [19]:

$$R_H = \frac{k_B T}{6\pi\eta_0 D_0} \quad (4)$$

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

3. Results and discussion

3.1. Direct measurements on E0 in water, water 0.1 N NaCl and methanol

At the outset SLS and dynamic light scattering (DLS) measurements were carried out on E0 dissolved in water, water 0.1 N NaCl and methanol. The inverse of the scattered intensities varies linearly with the square of the scattering wave vector showing no downwards curvature characteristic of the presence of large molecular species (aggregates) beside small ones. A typical correlation function and the distribution function of the diffusion coefficient is shown in Fig. 1. In these three solvents only one mode of relaxation is observed. The variation of the diffusion coefficient as a function of the concentration is shown in Fig. 2. The hydrodynamic radius R_H is calculated from a linear fit of this variation according to Eqs. (3) and (4). The static and dynamical parameters calculated for these systems are given Table 2. One can note that it is much more difficult to prepare very clean aqueous solutions than methanol solutions. For example the noise in the experimental correlation functions and accordingly the width of the distribution functions of the diffusion coefficients is larger in water than in methanol. In that way the M_w and R_H values are slightly higher for aqueous solutions than for methanol solutions. Further the addition of a small amount of salt that, in the case of charged polymers, should induce large effects has no influence on the M_w and R_H values of E0 in aqueous solution as expected for neutral polymers. The value of the molecular weight of E0 agrees with the value determined by GPC. The values of A_2 in the three solvents show that these solvents have quite the same quality of solvation. Further the A_2 and R_H values are in good agreement with the experimental power laws [3]:

$$A_2 = 1.84 \times 10^{-2} M_w^{-0.20} \quad (\text{cm}^3 \text{ mol g}^{-2}) \quad (5)$$

$$R_H = 0.145 M_w^{0.571} \quad (\text{\AA}) \quad (6)$$

obtained in water at 30°C ($A_2 = 3.1 \times 10^{-3} \text{ cm}^3 \text{ mol g}^{-2}$ for $M_w = 7400$ and $R_H = 22 \text{ \AA}$ for $M_w = 6500$). We emphasise the fact that the value $R_H = 22 \text{ \AA}$, measured in methanol (see Table 2), corresponds to the dimension for the non-aggregated mono-molecular PEO species. These first experiments show that the results agree with some of the previous studies [1–3,14] but are in contradiction to the

Table 2
Laser light scattering results on sample E0 at 25°C

Solvent	M_w (g mol ⁻¹)	$A_2 \times 10^3$ (cm ³ mol g ⁻²)	R_H (Å)
Water	7400	2.96	28
Water 0.1 N NaCl	6900	3.27	29
Methanol	6500	2.36	22

results of other experiments [6–13] as no aggregates are observed in either aqueous or methanol solutions.

3.2. Measurements on samples E1 → E8 in methanol

3.2.1. Characteristic of the solutions

All these samples were obtained by dissolution in DMSO and precipitation by ether at the latest stage of their preparation. The static ($M_w = 6300$ g mol⁻¹, $A_2 = 2.14 \times 10^{-3}$ cm³ mol g⁻²) and dynamical ($R_H = 22$ Å) parameters in methanol of a sample E0 that had previously been dissolved in DMSO and precipitated by ether are close to the values given in Table 2 for E0 in methanol. Thus, this mode of preparation has no influence on the behaviour of the polymer in solution. The experiments in methanol are very reproducible.

The static and dynamical parameters obtained by SLS and DLS on samples E1 → E8 in methanol are given in Table 1. One mode of relaxation is observed for all solutions except for those containing samples E2 and E3. The values of the molecular weight ($M_w \cong 6500$ g mol⁻¹), the second

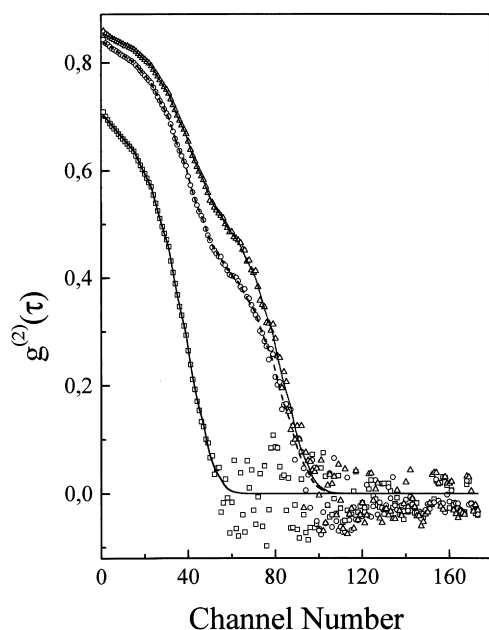


Fig. 3. Plot of the normalised autocorrelation function for E1 (\square , $c = 2.50 \times 10^{-2}$ g cm⁻³), E2 (\circ , $c = 2.50 \times 10^{-2}$ g cm⁻³) and E3 (\triangle , $c = 2.45 \times 10^{-2}$ g cm⁻³) in methanol at $\theta = 20^\circ$ and $t = 25^\circ\text{C}$. The lines are fitted curves given by CONTIN analysis.

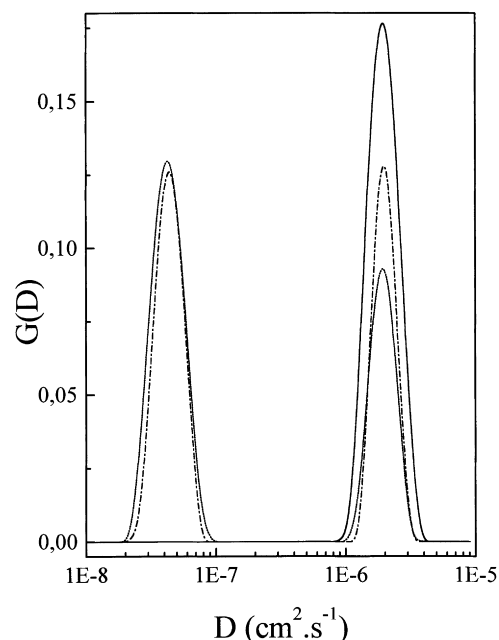


Fig. 4. Plot of the distribution function of the diffusion coefficient for E1 ($—$, $c = 2.50 \times 10^{-2}$ g cm⁻³), E2 ($- - -$, $c = 2.50 \times 10^{-2}$ g cm⁻³) and E3 (\dots , $c = 2.45 \times 10^{-2}$ g cm⁻³) in methanol at $\theta = 20^\circ$ and $t = 25^\circ\text{C}$.

virial coefficient ($A_2 \cong 2.2 \times 10^{-3}$ cm³ mol g⁻²) and the hydrodynamic radius ($R_{Hf} = 23$ Å) agree with the values measured in the E0/methanol system shown in Table 2.

The normalised autocorrelation functions for E1, E2 and E3 at quite the same concentration ($c \cong 2.5 \times 10^{-2}$ g cm⁻³) and at the same scattering angle ($\theta = 20^\circ$) are given in Fig. 3. The experimental results concerning samples E2 and E3 show a deviation with respect to monoexponential behaviour. This is corroborated by the CONTIN analysis which is illustrated in Fig. 4 and which shows a bimodal distribution. This bimodal distribution of PEO molecules has already been observed for aqueous [9–10] and methanol [13] solutions of PEO samples with higher molecular weight. However the relative amplitude of the slow mode is found to be constant ($\cong 54\%$ for E2 and $\cong 62\%$ for E3) as a function of the polymer concentration in the range of concentration and at the scattering wave vector investigated in this study. Nevertheless, as in Ref. [13], the diffusion coefficient associated with the fast mode increases when the polymer concentration increases (Fig. 5a) whereas the diffusion coefficient of the slow mode decreases when the polymer concentration increases (Fig. 5b). The hydrodynamic radius of the species associated with the fast mode is 23 Å whereas it is 779 and 689 Å for the species associated with the slow mode observed in samples E2 and E3, respectively. The fast mode can be attributed unambiguously to the diffusion of well-solvated monomolecular species present in samples E0, E1 and E4–E8. The slow mode is generated by large species due to aggregation that occurs when the sample E0 has been exposed to hot water.

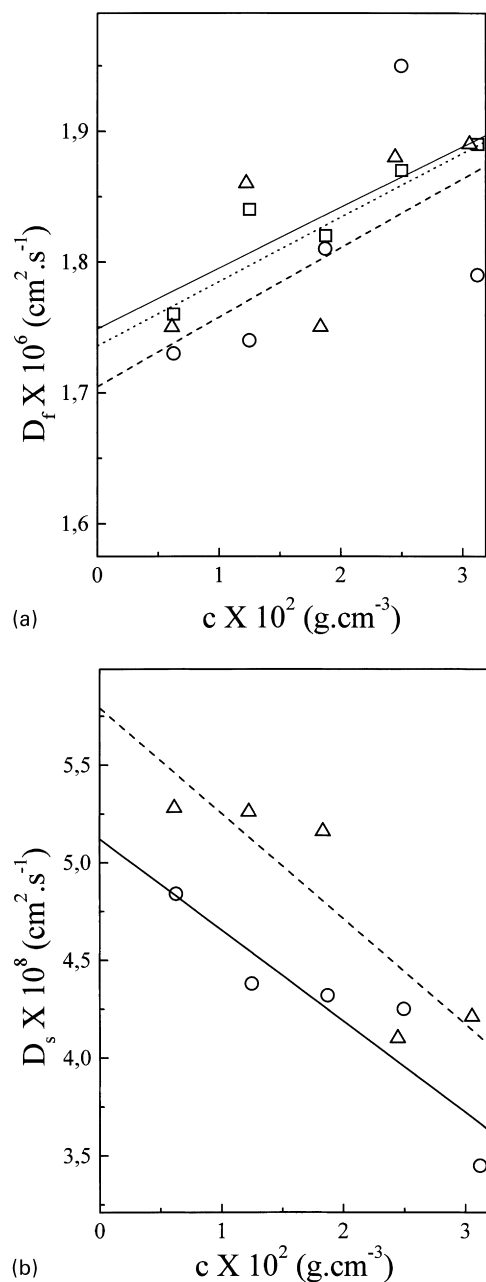


Fig. 5. (a) Plot of the fast diffusion coefficient as a function of the polymer concentration in methanol at 25°C. The lines correspond to the linear fit through the experimental points. Samples E1 (\square , —), E2 (\circ , - - -) and E3 (Δ ,). (b) Plot of the slow diffusion coefficient as a function of the polymer concentration in methanol at 25°C. The lines correspond to the linear fit through the experimental points. Samples E2 (\circ , —) and E3 (Δ , - - -).

3.2.2. Characteristic of the aggregates

The aggregates are well defined entities with a relatively low polydispersity ascertained by the width of the slow peak in Fig. 4. They are stable and remain even after further dissolution of samples E2 and E3 in other solvents. For example the aggregates are still present when E2 is dissolved in tetrahydrofuran (THF) or DMF. In agreement with other findings [6] their dimensions are found to decrease with increasing temperature.

An example of the Zimm representation of the SLS measurements for sample E3 is shown in Fig. 6 where no downward curvature typical of the presence of aggregates can be observed. It can be explained by the low concentration of this kind of scattering species. Nevertheless the extrapolation of the data to zero scattering angle and zero concentration leads to apparent molecular weights higher than 6500 g mol^{-1} and to apparent second virial coefficient lower than for the other samples where no aggregation occurs.

To characterise the aggregates by their molecular weight and concentration, a light scattering measurement was carried out on an aqueous solution of E2 with the light scattering apparatus coupled to a gel permeation chromatograph. The chromatogram shows a peak corresponding to $M_w = 7200$ as for the sample E0 in water (see Table 2). A very small peak appearing at low elution volume (high molecular weight) shows that the concentration of aggregates is very low.

The only real experimental value accessible from the experiment is the hydrodynamic radius of the aggregates. Assuming that these aggregates approximate compact spheres with radius R_H , leads to an estimate of very high molecular weight ($\cong 10^9 \text{ g mol}^{-1}$), given the density of PEO. From the equation

$$M_w^{\text{app}} = (1 - x)M_w^u + xM_w^a \quad (7)$$

where M_w^{app} is the experimental value obtained by SLS and M_w^u and M_w^a are the weight-average molecular weight of the non-associated and aggregated species, respectively, one can calculate the weight fraction x of the aggregates which turns out in this case to be very small ($\cong 10^{-4}\%$).

On the contrary, assuming that the physical properties of the clusters of PEO are similar to PEO itself, one can use the empirical law of the variation of the hydrodynamic radius as a function of the molecular weight obtained by Devanand and Selser for PEO in methanol [2]. The solutions of E2 and E3 are then found to contain 0.1% of aggregates with a molecular weight of about $4 \times 10^6 \text{ g mol}^{-1}$. These two types of estimation should provide upper and lower limits of the molecular weight and of the weight fraction of the aggregates present in the E2 and E3 samples.

We have shown that treating the dispersed E0 sample with hot water leads to the formation of clusters that are not broken by further dissolution in other solvents such as THF, DMF, DMSO and methanol. It is the combination of the solvent (water) and the temperature that produces the clusters. For example, no aggregation occurred when the samples E6, E7 and E8 were prepared by heating the solution at 60°C with dioxane, DMF or acetonitrile used as intermediate solvent. PEO is known to exhibit both upper (103°C) and lower (−9°C) critical solution temperature phenomena in water. Further it has a Flory critical point (θ temperature) of 102°C [6]. The possibility that hydrogen bonds between PEO and water allow water molecules to remain linked to the polymer throughout the history of the

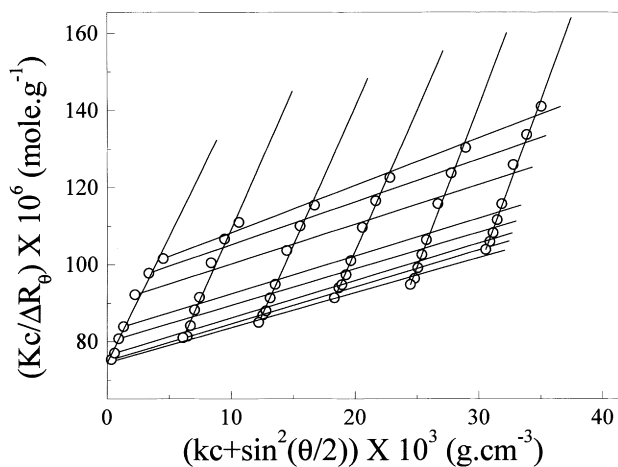


Fig. 6. Zimm plot of E3 sample in methanol at 25°C.

sample is contraindicated by the inability of solvents such as DMSO and methanol to brake up these clusters although they accept hydrogen bonds. The mechanism of formation of the aggregates in water presumably arises by the system approaching a θ point as the temperature increases and hydrophobic interactions then becoming dominant, as suggested by Polik and Burchard [6]. It should be noted that no aggregation occurs after the sample E0 is dissolved in water at 60 or 89°C and held for eight hours at room temperature before evaporation of water under vacuum at 90°C. Decreasing the temperature increases the quality of the solvent and the aggregates formed at high temperature are dissolved at lower temperature. However, if they are preserved by removing the water as soon as they are formed, as for samples E2 and E3, they are stable and cannot be easily broken even after renewed dissolution in water at room temperature or in other very good solvents. At this stage the process of formation or disaggregation of the clusters is no longer reversible. Finally it must be emphasised the fact that the slow mode of relaxation observed in this study has nothing to do with the crystallisation of PEO that has been detected under some conditions that are not fulfilled for samples E1–E8 and that will be described elsewhere. Indeed this phenomena of crystallisation induces the appearance of characteristic brightening spots in the laser beam leading to very large fluctuations of the scattered light which is not observed in this study.

4. Conclusion

We are able to reproduce faithfully the formation of

aggregates in the PEO solutions which is connected with some peculiar situations that are investigated in this study. It is the association of the temperature effect ($t > 30^\circ\text{C}$) and the nature of the solvent (water) which is the main factor governing this formation. Once they are created these clusters are difficult to brake and are still present when the sample is dissolved in very good solvent of the polymer. The many contradictions that appear in the literature dealing with the behaviour of PEO in solution are probably due to this phenomenon. The samples used by some authors have certainly been subjected to conditions under which clusters are known to form, as described above. The molecular weight of the aggregates is very high whereas their concentration is very low. However it seems obvious that subsequent dissolution in hot water of samples E2 and E3 should increase either the molecular weight or the concentration of the aggregates. This should bring upward curvatures in the Zimm plot given by the PEO solutions as observed by others authors [6,11,12,14]. The cluster formation originates from hydrophobic interactions that take place at high temperature in the vicinity of the θ point in aqueous solution. Further specific studies in order to characterise more precisely the aggregates and to find the way to brake them for regeneration of the samples are currently under investigation.

References

- [1] Elias HG, Lys H. *Makromol Chem* 1966;92:1–24.
- [2] Devanand K, Selser JC. *Nature* 1990;343:739–741.
- [3] Devanand K, Selser JC. *Macromolecules* 1991;24:5943–5947.
- [4] Kinugasa S, Nakahara H, Fudagawa N, Koga Y. *Macromolecules* 1994;27:6889–6892.
- [5] Kinugasa S, Nakahara H, Kawahara JI, Koga Y, Takaya H. *J Polym Sci, Polym Phys Ed* 1996;34:583–586.
- [6] Polik WF, Burchard W. *Macromolecules* 1983;16:978–982.
- [7] Layec Y, Layec-Raphalen MN. *J Phys Lett (Paris)* 1983;44:L121–L128.
- [8] Brown W, Stilbs P, Johnsen RM. *J Polym Sci, Polym Phys Ed* 1983;21:1029–1039.
- [9] Brown W. *Macromolecules* 1984;17:66–72.
- [10] Brown W. *Polymer* 1985;26:1647–1650.
- [11] Kambe Y, Honda C. *Polym Commun* 1984;25:154–157.
- [12] Strazielle C. *Makromol Chem* 1968;119:50–63.
- [13] Zhou P, Brown W. *Macromolecules* 1990;23:1131–1139.
- [14] Carpenter DK, Santiago G, Hunt AH. *J Polym Sci, Polym Symp* 1974;44:75–92.
- [15] Afifi-Effat AM, Hay JN. *J Polym Sci, Polym Lett* 1971;9:651–655.
- [16] Porsch B, Sundelöf LO. *Macromolecules* 1995;28:7165–7170.
- [17] Duval M, Coles HJ. *Rev Phys Appl* 1980;15:1399–1408.
- [18] Provencher SW. *Makromol Chem* 1979;180:201–209.
- [19] Yamakawa H. *Modern theory of polymer solutions*, New York: Harper and Row, 1971 p. 280.