Macromol. Symp. ***146****, 171–177 (1999)*

Influence of salts on hydrophobically end-capped polyethylene oxides in aqueous solution

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Summary: The influence of four different salts (NaCl, KBr, $CaCl_2$ and $MgCl_2$) on the associative behaviour of poly(ethylene oxide) (POE with M=32000g/mol) hydrophobically end-capped with hexadecyl groups in aqueous solutions was investigated. Phase diagrams were obtained, structural properties were established by small angle neutron scattering (SANS) measurements and studies on the viscoelastic properties of the solutions were performed by low-shear viscosity and dynamic stress experiments. The influence of the four salts is compared as well as the difference of the interactions obtained with and without salts.

Introduction: Aqueous solutions of poly(ethylene oxide) (PEO) use to separate into a polymer poor and a polymer rich phase upon heating(1). When temperature is increasing, the quality of the solvent is decreased for PEO. This phenomenon is characterized by a binodal demixing curve which minimum is called lower critical solution temperature (LCST). Similarly, it is well known that the addition of salts into water has an analogue effect(2). Depending on the nature of the salt, the shift of the demixing curve toward smaller temperatures is more or less important.

Hydrophobically end-capped poly(ethylene oxides) have attracted widespread interest in recent years(3-6). They are of great use in many fields: oil-recovering, colloidal stabilisation, paint thickening, gels in cosmetic. Previous studies(3-6) have showed that end-capped PEO with two hydrophobic tails are capable of "flower-like" association in aqueous solution. This kind of micelles consists in a compact hydrophobic core (the hydrophobic tails) surrounded by the long water-soluble chains of PEO that form loops. A critical micellar concentration can be determined, and it has been shown that as soon as flowers are formed, even at concentration as low as 1%, a liquid order appears in the solutions(5,6). The scale of this order increases with the average hydrophobicity of the polymer on the one hand, with the concentration on the other hand. The behaviour of such solutions is due to the competition between a repulsive interaction of the large coronas of PEO in good solvent (osmotic effect)

CCC 1022-1360/99/$ 17.50+.50/0

and an attractive potential due to the hydrophobic tails that induces bridging between the microdomains. According to Semenov and *al.*⁽⁷⁾ theoretical study, above the overlap concentration of the flowers, the structure and viscoelastic behaviour of these systems are more dominated by the strong repulsive potential than by a bridging phenomenon. Low shear viscosity measurements tend to confirm these predictions. Moreover, the introduction of hydrophobic tails fixed at the extremities of the PEO chains decreases the LCST in pure water. Nevertheless, quite different shapes of the demixing curves are obtained (see below). This depression of the LCST is more closely related to the bridging phenomena than to the molecular weight.

By decreasing the quality of the solvent for associative PEO, one can expect a decrease of repulsive effects between the PEO coronas, an enhancement of the bridging and some consequences on the viscoelastic properties. Consequently, in order to clearly understand the respective contributions of bridging and osmotic effects in these systems, it is interesting to systematically study one polymer either increasing the temperature of the water or introducing salts into water. Because of the evaporation of the aqueous solutions at high temperature, the latter solution appears more judicious.

This paper aims to study the associative properties of modified PEO when the quality of the solvent for PEO chains is modified by the introduction into water of these salts: NaCl, KBr, $CaCl_2$, $MgCl_2$. The associative polymer used is a poly(ethylene oxide) with two paraffinic end-groups of 16 carbon atoms with a urethane rotule. It is denoted C16N32. Solutions of this polymer are homogeneous in pure water at room temperature up to the crystallization concentration of the PEO. For these polymer solutions, phase diagrams are obtained, structural and viscoelastic properties are established with small angle neutron scattering (SANS), low-shear viscosity and dynamic stress experiments.

Material: The associative polymer C16N32 was synthesized and purified according to a method described elsewhere⁽⁶⁾. The molecular weight, the polydispersity index M_w/M_n and the fonctionalization rate f were determined by U.V., static light scattering and NMR measurements. The molecular weight of the PEO precursor was M_w=32000g/mol with $M_w/M_n \approx 1.02$ and f was found to be close to 100%. NaCl (Aldrich 99+% purity), KBr (Prolabo, 98.5% purity) and MgCl2 (Aldrich, 98% purity) were dried several hours at 90° C before use, $CaCl_2$ (Prolabo, min 94% purity) was used without further purification.

All the solutions were prepared with water 3 times distilled on quartz. Depending on their concentrations, the solutions were stirred between 24 hours and several days before use.

Methods: *Phase diagram*: the phase diagrams of C16N32 with or without salt were obtained by simple visual observation of clouding while the temperature was increased for concentrations of polymers ranging from 0.1% to 10%. The concentration of salt was 3M. The solutions were heated in a thermostated oven.

Small angle neutron scattering experiments (SANS): SANS experiments on the different solutions were performed on the PACE instrument at Léon Brilloin Laboratory (LLB) (Saclay, France). The range of scattering vector covered was $0.006Å^{-1}<q<0.2Å^{-1}$. All the experiments were performed at 20°C and D_2O was used instead of H_20 as solvent.

Viscosity: A low shear Couette flow-type rheometer, Contraves LS30, working in a shear rate range from 0.02 to 100 s^{-1} was used to measure the viscosity of the solutions. The measurements were performed at 25 °C.

Rheological measurements: The viscoelastic properties of the solutions were investigated through dynamic spectroscopy experiments. On a Rheometrics dynamic stress rheometer operating with a Couette cell, a sinusoidal stress ($\tau=\tau_0\cos(\omega t)$) was imposed to the solution, and the storage and loss modulii ($G'(\omega)$ and $G''(\omega)$) were recorded. For each pulsation ω ranging from 10^{-3} rad/s and 100 rad/s, the maximum amplitude τ_0 was chosen small enough to have a linear variation between applied stress and measured strain. In order to limit evaporation of water the rheological experiments were performed at 5°C.

Results: *Phase diagram*: Figure 1 shows the binodal demixing curves of PEO 32000 and C16N35 solutions with and without salt for polymer concentrations ranging from 0 to 20 g/ml. It has been divided into four graphs, one for each salt, in order to allow an easier comparison of the influence of the different salts on the unmodified PEO and on the associative one. First, one can observe a systematic reduction of the solubility of unmodified POE 32000 for all the salts, the demixing curves being shifted toward lower temperatures. Without salt the LCST of POE 32000 is about equal to 105°C, while its value is around 90°C for 3M $CaCl_2$ and $MgCl_2$ solutions and around 80°C and 55°C for 3M KBr and NaCl respectively. For the associative polymer, as expected, hydrophobic tails of C16N32 highly decrease the solubility of the polymer: the LCST of C16N32 without salt is about equal to 62°C. Moreover, the shape of the demixing

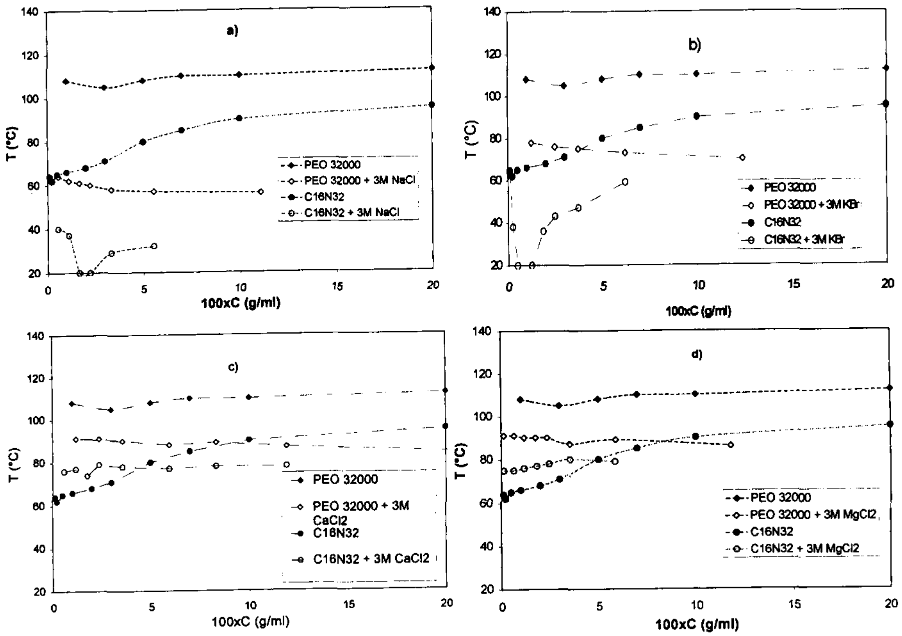

Fig. 1: cloud point temperatures versus concentration of POE 32000 and C16N32 in pure water and in 3M salted solutions (a) NaCl, (b) KBr, (c) $CaCl_2$, (d) $MgCl_2$.

curves is quite different from that of the precursor. At low concentrations, the temperature of the binodal curve sharply decreases when the concentration increases. After the LCST is reached, the temperature of the demixing curve increases with C16N32 concentration, quite sharply in a first step, then more gently. This effect is much more pronounced with KBr and NaCl solutions (monovalent cations) than with $CaCl_2$ and $MgCl_2$ ones (divalent cations). Indeed, at room temperature, for concentrations ranging from 0.5 g/ml to 1.25 g/ml and from 0.1 g/ml to 2.2 g/ml, KBr respectively NaCl solution shows two different phases. The influence of the divalent cations Ca^{2+} and Mg^{2+} are also of a great interest. For small concentrations, the binodal curve is below that of POEM in pure water. In other words $CaCl_2$ and $MgCl_2$ increase in a first step the hydration of the associated polymer.

SANS: For concentrations c of polymer ranging between 1.5% and 25%, solutions of C16N32 in pure water and in presence of KBr and $CaCl_2$ (3M) were systematically studied by SANS. At concentration as low as 1.5%, a shoulder is observed. At c= 3% a well-defined diffraction peak is observed. This peak is shifted toward high value of q when c increases. This peak proves the existence of a local organisation into the solution. We can consider than the characteristic distance d between the ordered scattering objects is given by $d=2\pi/q_{max}$. Figure 2 shows the evolution of this distance with c for C16N32 in pure water

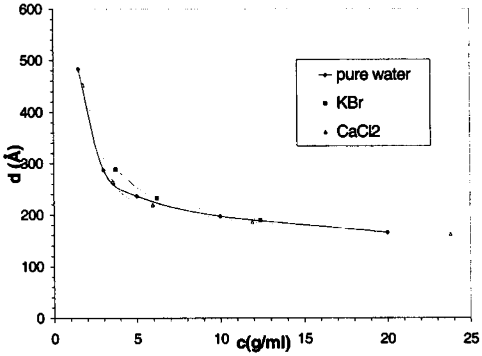

Fig.: 2: distances between scattering objects into organized solutions versus C16N32 concentration.

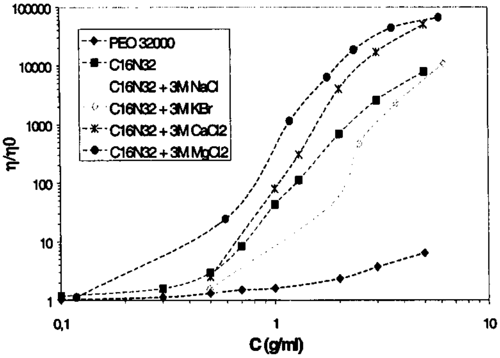

Fig.: 3:relative viscosity versus polymer concentration.

and in the presence of 3M KBr or $CaCl_2$. d sharply decreases at low concentration, then tends to stabilize. As one can note, $CaCl_2$ has no effect on d, KBr gives rise to a small increase of d.

Viscosity: The relative viscosity $\eta_r=\eta/\eta_0$ of PEO 32000 in pure water on the one hand and of C16N32 solutions in pure water and with 3M NaCl, KBr, $CaCl_2$ and $MgCl_2$ on the other hand is reported versus the concentration on figure 3. If at low concentration η_r of C16N32 does not differ from that of the equivalent unmodified PEO 32000, it is much higher for the associative polymer above a concentration of about 0.006 g/ml. With or without salt, the evolution of the relative viscosity with the concentration of the C16N32 solutions shows three different regimes. At low c, η_r is around 1 and does not increase a lot. Then a second regime takes place where η_r sharply increases with concentration but much more gently. Let us remind that for concentrations ranging between 0.1 g/ml and 2.2 g/ml with NaCl and between 0.5 g/ml and 1.25 g/ml with KBr, solutions of C16N32 have demixed. This explains the absence of experimental data in this range of c. If we exclude it, we can note that KBr and NaCl have no effect on η_r. At the contrary, in the presence of divalent cations, for a given concentration, η_r is much higher than in the presence of monovalent cations or with pure water.

Rheology: The curves of figure 4 show the evolution of the storage and loss modulii (G' and G") of C16N32 in pure water when the pulsation ω is increased. Despite the very low value of G' at low ω, G' and G"vary respectively as ω^2 and ω over a very large range of pulsation. This phenomenon is typical of that of a solution following a maxwellian behavior with one relaxation time ($\tau\approx10^{-2}$s). At $\omega\approx$ 0.05rad/s G' stops to decrease. Even if this plateau appears at very low value of G' (0.0007 Pa), it is reproducible and shows the existence of a second very slow relaxation mode.

$CaCl_2$ has major influence on the viscoelastic properties of the C16N32 solutions. The cross over is translated toward small frequencies (≈6rad/s (τ=0.16s) instead of more than 100 rad/s for the polymer in pure water). In the terminal zone, G' and G" follow power laws $G' \propto \omega^n$ and $G'' \propto \omega^p$ with n and p smaller than 2 and 1 respectively. Below 0.03rad/s one can observe a significant break of the slope for G' corresponding to a second relaxation time τ≈300s.

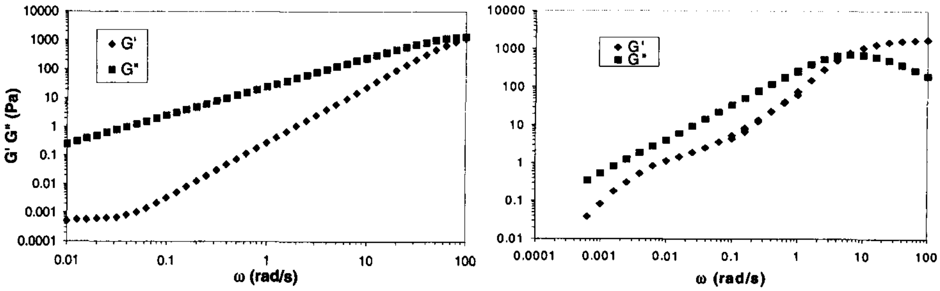

Fig. 4 : G' and G" versus w for C16N32 at 5% concentration and 5°C. (a) in pure water, (b) with 3M CaCl2.

Discussion and conclusion : From the knowledge about the influence of salts on the unmodified PEO solutions on the one hand, and about the associative properties of hydrophobically end-capped PEO in pure water, on the other hand, one could expect the following effects of salts on C16N32:

- decrease of solubility: the overlap of "flowers" should occur at higher concentration due to the collapse of corona, by analogy with what happens when PEO chain length decreases for a given hydrophobic tail (see Figure 5)
- increase of the aggregation number inducing an increase of the intermicellar distance
- slight decrease of viscosity related to the fact that intramolecular loops should be favored with respect to intermicellar bridges

Our experimental results seem to follow such predictions, in the case of monovalent cations, even if the viscosity depression is not significant. One can observe that organization of the micelles is not affected while corona repulsion was expected to be screened out by salts, even if the intermicellar distance is increased as expected.

At the contrary, the behavior observed with divalent cations is rather surprising. Indeed, instead to depress LCST of C16N32, $CaCL_2$ and $MgCl_2$ tend to improve its solubility. Moreover, these salts, which do not modify the structure of the solutions, strongly change their viscoelastic properties. It appears that the disengagement time of the aliphatic groups from the micelles characterized by the first relaxation time becomes much longer in the presence of Ca^{++} while viscosity increases. Besides, the elasticity is enhanced in the whole range of frequency and a second relaxation mode appears very clearly. Such a mode has already been observed in the case of PS-PMMA blends (8) and was attributed to a network type structure or to the alignment of the particles in the direction of the flow. Similarly, in our case, the second relaxation time may be correlated with the organized network deformation. Finally, the influence of salts on the associative properties of end-capped PEO depends on the nature of the cation. Such an observation may be explained by invoking specific interactions between PEO chains and divalent cations and localization of these cations at the next neighboring of the hydrophobic core.

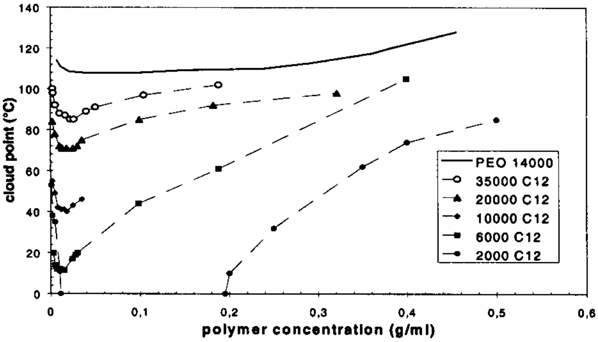

Fig. 5: cloud point temperatures versus concentration for PEO modified with C12 end groups.

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