Effects of Temperature on Neutron Scattering from Aqueous Solutions of Hydrophobically Modified Poly(ethylene oxide)

Emmanuel Beaudoin[1], *Oleg Borisov*[1], *Alain Lapp*[2], *Jeanne François*[1*]

[1] Laboratoire de Physico-chimie des Polymères, UMR 5067 UPPA/CNRS, Hélioparc, 2 Avenue du Président Angot, 64053 Pau, France
[2] Laboratoire Léon Brilloin, CEA Saclay, 91191 Gif-sur-Yvette, France

Summary: The effect of temperature on the structure of aqueous dispersions of hydrophobically end-capped poly(ethylene oxide) (PEOM) was investigated by small angle neutron scattering (SANS). Polymers with hydrogenated or deuterated n-octadecyl end-groups were studied in heavy water or in a mixture heavy water / water, respectively. In the latter case the PEO chains were selectively matched. In all the cases, the scattering curves were characterised by a main peak which revealed organisation of polymers into micelles consisting of hydrophobic cores surrounded by repulsive PEO coronae. Measurements were performed in the semi-dilute regime where micelles coronae overlap. At constant polymer concentration, an increase in temperature leads to decreasing solvent strength of water for the PEO chains and decreasing repulsion between the PEO coronae. As a result, the intensity of the peak in a mixture of water /heavy water *decreases* with temperature On the contrary, in heavy water, the peak of the scattered intensity increases with *increasing* temperature. This scattering behaviour is interpreted on the basis of a scaling theory of the semi-dilute solutions of star-like polymer micelles .

Keywords: associating polymers, poly(ethylene oxide), micelles, neutron scattering

Introduction

Hydrophilic poly(ethylene oxide), PEO, chains with aliphatic end-groups, (α,ω-modified PEO or PEOM), self-assemble in aqueous dispersions to form "flowers" like micelles[1-6] (Figure 1). The aliphatic end groups associate in water to make dense cores, while the PEO chains remain embedded in the aqueous environment and constitute swollen micellar coronae. The PEO-based amphiphilic copolymers are particularly interesting because solubility of PEO in water can be easily tuned by varying temperature or salinity[7]. Micellization occurs above a well defined critical concentration, CAC, which is generally measured by fluorescence or light scattering[2,4-6]. Another concentrational threshold, C*, corresponds to

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the overlap of micelles_and to an abrupt jump in viscosity associated to the formation of the inter-micellar bridges. Above C*, SANS curves are characterised by a main peak which indicates repulsion between PEO coronae [1-3]. As has been demonstrated in ref. 8, such behaviour is very similar to that of star like polymers and can be modellized on the basis of the scaling theories of the semi-dilute solutions of star like polymers. [9-11]

The aim of the present paper is to study the effect of temperature, i.e., that of the solvent strength on the static structure of the semi-dilute solution of flower-like micelles, as it is manifested in the SANS behaviour. We demonstrate that selective matching of the PEO coronae enables to separate the contributions related to inter- and intra-micellar correlations.

As a result, we obtain quite unusual scattering patterns as a function of temperature. The evolution of the scattering curves is interpreted and quantitatively modelled on the basis of scaling theory for the structure of semi-dilute solutions of star-like polymer micelles.

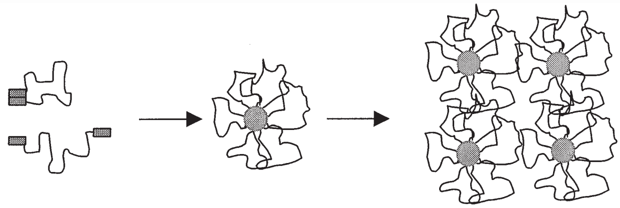

Figure 1 Schematic representation of association of PEOM

Theory

Structure of the micellar solution.

We assume that all end-functionalized PEO chains are associated into micelles, i.e. we neglect the contribution of dissociated chains which is negligible at concentrations above the CAC. Each micelle comprises N_{ag} di-functionalized chains. The core of the micelle is formed by $2N_{ag}$ aliphatic chains and has the shape of a sphere of radius $R_{C.}$ The volume fraction of alphatic chains in the core is close to unity due to their hydrophobicity. As long as the radius of the core, R_C , is negligible in comparison to that of the corona, R, the micelle can be assimilated to a star-like polymer [9,10] with $2N_{ag}$ branches. In dilute solution, the PEO corona can be presented as an array of concentric shell of close-packed blobs. The blob size, $\xi(r)$, increases with the distance r from the centre of the micelles as $\xi(r) \cong r\, N_{ag}^{-1/2}$. The polymer concentration in the corona decreases with r as $C(r) \sim r^{(1-3\nu)/\nu}$, where ν is the Flory exponent (ν=3/5 under good solvent conditions). The steric repulsions in the corona and the extension of the coronal chains decrease with decreasing solvent strength (that is, with increasing temperature in case of PEO) as R~ $(\Theta - T)^{1/5}$, where $\Theta \approx 373$ K is the LCST for the infinitely long PEO chains.

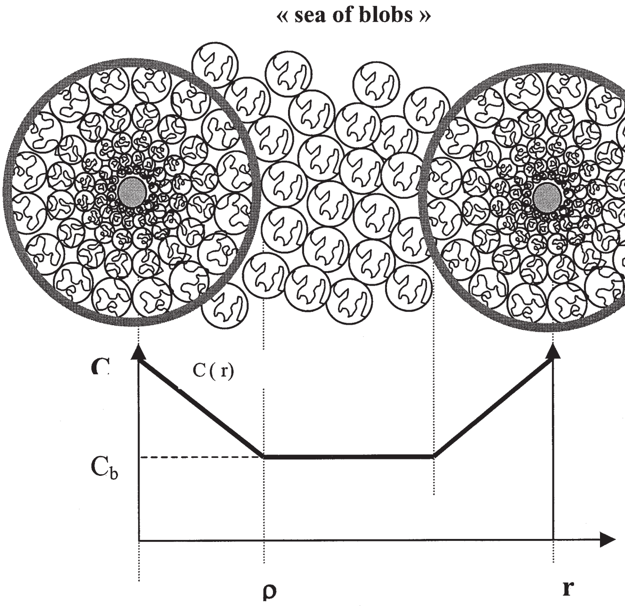

Figure 2 Blob picture of semi-dilute solutions of star like micelles

The semi-dilute solution of the star-like micelles is schematised in Figure 2 where the overlapped regions of the coronae constitute semi-dilute polymer solution which can be viewed as the "sea of blobs" of constant size ξ. An unperturbed structure of the corona equivalent to that in the dilute regime is preserved within the radius $\rho \le R$.. The monomer concentration profile is also schematically presented in Figure 2. The concentration inside the "sea of blobs" is uniform and we denote it as C_b. The concentration in the unperturbed internal regions of the micellar coronae decreases as a function of the distance *r* from the centre of the micelles reaching the value of C_b at the edge of the unperturbed part, i.e., at $r=\rho$. The radius ρ of the unperturbed internal region of the coronae depends on the overlap degree of the micelles, i.e., on C/C* and can be found from the condition $C(\rho)=C_b$, that leads to

$$\frac{1}{3\nu} r_c^{\frac{1-3\nu}{\nu}} \left[1 - \frac{3\nu - 1}{3\nu} r_c^{\frac{1}{\nu}} \right]^{-1} = \frac{C}{C^*} \qquad (1)$$

where r_c is the ratio between $\rho(C)$ and the radius of the micelle in the dilute regime, R, i.e., $r_c = \rho(C)/R$. As follows from eq 1, $r_c=1$ (i.e. $\rho = R$) at $C = C^*$. The overlap concentration $C^* \sim R^{-3}$ and, therefore, increases with an increase in temperature as $C^* \sim (\Theta - T)^{-3/5}$. Hence, at fixed concentration of the solution, the ratio $r_c = \rho(C)/R$ increases with increasing temperature.

We remark, that the aggregation number, N_{ag} , in general case also depends on temperature and concentration, as it is determined by the balance of repulsive steric interaction in the micellar corona and excess free energy of the core interface. As has been predicted theoretically[11] and proved experimentally[8], the concentrational dependence of N_{ag} becomes important at $C \gg C^*$. Our experimental results (see below) indicate, that in the range of temperatures studied in present work, the temperature dependence of N_{ag} is negligibly weak .

Scattering from semi-dilute micellar solution

a) PEO chains are matched

In case when PEO chains are matched the contribution to the scattered intensity is that of the micelle cores only. The scattering intensity can be presented as

$$\Delta I_c(q) = \frac{\Delta b_1^2}{N_A} C N_{ag} \frac{M_a^2}{M_w} P_c(q).S(q) \qquad (2)$$

where $P_c(q) = [\frac{3}{(qR_c)^3}(\sin qR_c - qR_c \cos qR_c)]^2$ is the formfactor of the unifom spherical core and S(q) is the structure factor which accounts for the repulsive interaction between the micellar coronae (C is the concentration of polymer (g/cm^3), M_w is the weight average molecular weight (g/mol) , $N_A = 6.022.10^{23}$ mol^{-1} is the Avogadro number, Δb_l and M_a are the contrast length and the molecular weight of the aliphatic chains, respectively). As long as the temperature dependences of N_{ag} and Δb_l are negligible, the variation of temperature affects only S(q) via temperature dependent monomer-monomer and corona repulsions.

b) PEO chains are not matched

In this case the scattering intensity from semi-dilute solution can be decomposed into two contributions [12,13]:

$$\Delta I(q) = \Delta I_s(q) + \Delta I_b(q). \qquad (3)$$

The first one, ΔI_s, describes scattering due to correlated fluctuations in the positions of unperturbed internal regions of micelles; while the contribution ΔI_b, is due to local fluctuations in the concentration of monomers both in the "sea of blobs" and inside unperturbed internal regions of the micellar coronae.

$$\Delta I_s(q) = \frac{\Delta b_2^2}{N_A} N_{ag} \overline{M_w C} \left[\frac{3v-1}{v} \left(\frac{\rho}{r} \right)^{1/v} \right]^2 P(q)\, S(q) \qquad (4)$$

(where Δb_2 is the contrast length of PEO) and the structure factor S(q) depends on the effective interaction potential between the depleted micelles.

For the calculation of the form factor P(q) of the overlapped micelles we have to take into account that 1) the central-symmetrical monomer density profile C(r) extends up to $\rho(C)$ and 2) the background concentration C_b has to be subtracted from C(r), that corresponds to the effective reduction of the contrast for depleted micelles embedded in the semi-dilute polymer solution (the "see of blobs") of concentration C_b. As a result, one gets:

$$P(q) = \left[\frac{4\pi \int_0^{\rho(c)} \frac{\sin(qr)}{qr} (C(r) - C_b) r^2 dr}{4\pi \int_0^{\rho(c)} (C(r) - C_b) r^2 dr} \right]^2 \qquad (5)$$

Using a simple relation between the polymer density *C(r)* inside unperturbed region of the micellar corona and the density C_b in the sea of blobs :

$$\frac{C(r)}{C_b} = \left(\frac{r}{\rho} \right)^{\frac{1-3v}{v}} \qquad (6)$$

we obtain:

$$P(q) = \left[\frac{\int_0^{\rho(c)} \frac{\sin(qr)}{qr} \left(\left(\frac{r}{\rho} \right)^{\frac{1-3v}{v}} - 1 \right) r^2 dr}{\int_0^{\rho(c)} \left(\left(\frac{r}{\rho} \right)^{\frac{1-3v}{v}} - 1 \right) r^2 dr} \right]^2 \qquad (7)$$

By setting the lower integration limit in eqs 5 and 7 equal to zero, we neglect a difference between the power-low decay and constant concentration of aliphatic chains within a small region $r<R_c$, and slightly underestimate scattering from the cores, which is anyhow negligible under non-matching conditions.

The contribution $\Delta I_b(q)$ to the scattered intensity is expressed similarly to the case of a semi-dilute polymer solution as a function of the average concentration of monomers per unit volume $\overline{C}$.

$$\Delta I_b(q) = K_I \overline{C}^2 (\Delta b_2)^2 \frac{\xi^3}{1+q^2\xi^2} \qquad (8)$$

where K_I is a numerical prefactor and ξ is the (average) correlation length which depends on $\overline{C}$. By the approximation leading to eq 8 we effectively smear out locally higher monomer concentration (and, as a result, locally smaller correlation length) in the internal unperturbed regions of micelles. We expect, that due to the power-law monomer density profiles inside unperturbed regions of micelles, this approximation affects only the numerical pre-factor in the expression for ΔI_b. Moreover, at sufficiently high concentration the contribution of the unperturbed internal regions of micelles to the overall solution concentration and to $\Delta I_b(q)$ becomes negligible and $\overline{C}$ approaches C_b .

Experimental

Materials

The preparation of the samples has been already described. Two samples were used in this study: 35000C18 and 35000CD18, (molecular weight 35000 $g.mol^{-1}$ and polydispersity index 1.02), end capped by two aliphatic chains of 18 carbons respectively hydrogenated or deuterated.

Small angle neutron scattering (SANS)

SANS experiments were performed on PAXY spectrometer at Léon Brillouin Laboratory (LLB, Paxi instrument, CEA, Saclay, France) and at Laue Langevin Institut (Ill Grenoble, D22 intrument). Scattering ranges covered were $0.003 < q(Å^{-1}) < 0.22$ and $0.018 < q(Å^{-1}) < 0.15$, respectively. The temperature was varied between 5 °C and 70 °C.

Samples 35000C18 and 35000CD18 were studied in heavy water (major contribution to scattering from PEO chains, 10 and 35 $g.ml^{-1}$) and. in a mixture water /heavy water (82.4/17.6 % v/v) (PEO matched, 35 $g.ml^{-1}$), in a temperature range from 5 to 72°C. As has been discussed elsewhere, the variation of the length scattering density of PEO with temperature can be neglected.

Results and discussion

Figure 3 allows the comparison of the evolution of scattering curves for the same polymer (D35CD18 at 0.35 g.ml^{-1}, that is larger than C*) in the mixture water / heavy water (a) and in heavy water (b). Figure 3a shows that with increasing temperature, the magnitude of the scattering peak which results from correlations in the positions of the micellar cores (which are the only ones visible under matching conditions) progressively decreases. Moreover the second peak which is well pronounced at 25 °C appears only as a shoulder at 53 °C and 72 °C. This reflects, as expected, weakening of repulsions between micelles coronae upon decreasing solvent strength. However, in heavy water (not matching conditions for PEO, Figure 3b), we observe the opposite trend in the evolution of the scattering curves: the peak is absent at 25°C but progressive appears and increases in magnitude with increasing temperature.

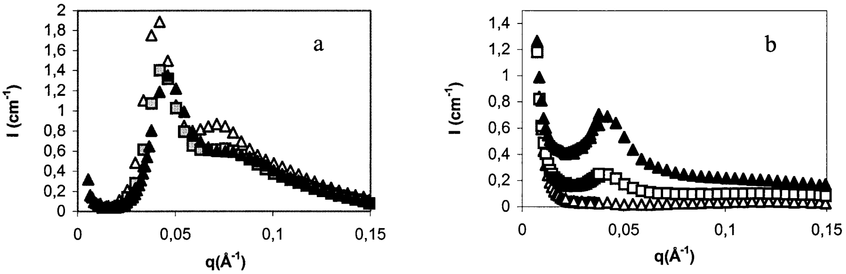

Figure 3 Evolution of the scattering curves with temperature a) matched PEO b) unmatched PEO (△=25°C ; □= 53°C: ▲= 72°C)

Figure 4 represents the evolution of the scattering curves as a function of concentration at constant temperature. The position of the peak is shifted towards high q values that refects decrease of the average distance between micelles. The magnitude of the peak I_{max} does not vary monotonically: it passes through a maximum at approximately C* and then decreases with concentration in the range of semi-dilute solutions, as illustrated in figure 5 where I_{max} is plotted as a function of polymer concentration for different temperatures ; As expected, C* at which I_{max} passes through a maximum, increases with increasing temperature.

The observed scattering behaviour can be qualitatively understood from theoretical arguments presented above. Indeed, the scattering intensity described by eqs 3,4,7,8 reveals interesting features as a function of concentration and temperature (solvent strength). Repulsive interaction between crowded micellar coronae manifests itself in a maximum in S(q): the position of the maximum is inversely proportional to the average distance between the centres of micelles, while the magnitude of the maximum depends on the strength of the inter-micelle repulsion. Therefore, ΔI_s (q), is peaked.

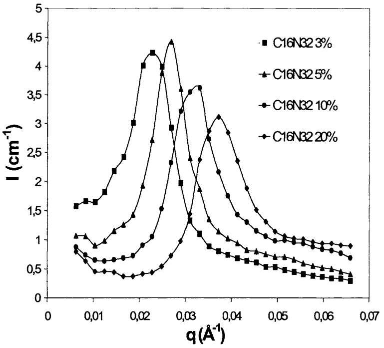

Figure 4 Scattering curves of 35000C18 at various concentrations (T=25°C)

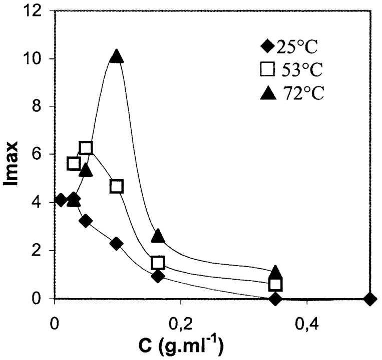

Figure 5 Magnitude of the scattering peak versus concentration at various temperature

On the contrary, ΔI_b (q), is a monotonically decreasing function of q.

With increasing concentration of the solution in the range of C>C*, the fraction of the volume filled by the uniform "sea of blobs", as well as the background concentration C_b, increase. On the contrary, the size of unperturbed internal regions and excess polymer concentration in these regions, C(r) – C_b, decrease. As a result, relative contribution of ΔI_s (q) to the overall scattering intensity decreases and the scattered intensity is dominated by the second term, which describes scattering due to local monomer density fluctuation, just as in conventional semi-dilute solution and does not exhibit any peak. Therefore the peak in ΔI (q) progressive disappears with increasing polymer concentration.

The effect of temperature on the scattering patterns appears to be even more peculiar. An increase in temperature at constant concentration C > C* of the solution leads to an increase in C* and to a decrease of the ratio C/C*., i.e., is equivalent to the shift of the solution conditions towards C*. Therefore, the relative contribution of the uniform "sea of blobs", ΔI_b (q), to the overall scattering intensity *decreases* and the maximum in ΔI (q), which is weak or absent at sufficiently high polymer concentration and low temperature, becomes more pronounced at higher temperature. This re-appearance of the maximum should not, however, be confused with enhancing repulsion between micelles (which normally leads to growth of the peak in S(q)). On the contrary, an increase in temperature (decreasing solvent strength) should lead to weakening of repulsive interactions between overlapped micellar coronae and to decrease in the maximum in S(q). This behaviour of S(q) manifests itself in the scattering experiments under the conditions of matching of the PEO coronal chains, when the temperature dependence of $\Delta I(q)$ is only due to that of S(q), see eq 2.

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