



Self-assembling of poly(ϵ -caprolactone)-*b*-poly(ethylene oxide) diblock copolymers in aqueous solution and at the silica–water interface

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Abstract

Small-angle neutron scattering is used to investigate the self-assembling behaviour of poly(ϵ -caprolactone)-*b*-poly(ethylene oxide) diblock copolymers with various block lengths (i) in aqueous solution, (ii) in aqueous solution with the addition of sodium dodecyl sulphate (SDS) and (iii) at the silica–water interface. Micelles are observed under our experimental conditions due to the very small critical micellar concentration of these copolymers (0.01 g/l). The poly(ϵ -caprolactone) core is surrounded by a poly(ethylene oxide) corona. The micellar form factors have been measured at low copolymer concentrations (0.2 wt%) under selected contrast matching conditions. The data have been fitted to various analytical models to extract the micellar core and corona sizes. SDS is shown to induce partial micelle disruption together with an increase of the poly(ethylene oxide) corona extension from 25% (without SDS) to 70% (with SDS) of a completely extended PEO₁₁₄ chain. Our data at the silica–water interface are compatible with the adsorption of micelles.

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1. Introduction

Uncharged water-soluble polymers are known to interact with ionic surfactants in aqueous solution and at interfaces [1,2]. Polymer-surfactant mixtures are widely used in many application fields, such as detergency, cosmetics, painting, etc. requiring surface conditioning. It is therefore

essential to characterize their properties and to be able to tune their behaviour both in aqueous solution and at the solid–liquid interface. The general purpose of our work is to analyse the behaviour of mixtures of two surfactants of different sizes, in water and at the silica–water interface: an amphiphilic water soluble diblock copolymer and an anionic classical surfactant, sodium dodecyl sulphate (SDS). The diblock copolymers investigated consist of a hydrophilic block of poly(ethylene oxide) (PEO) and a

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Table 1

Micellar structural parameters (core radius, R , and corona thickness, L) and adsorption results (adsorbed copolymer mass per silica surface unit, Γ) for the poly(ϵ -caprolactone)- b -poly(ethylene oxide) copolymers investigated

Copolymer	R (Å)	L (Å)	Γ (mg/m ²) (SANS data)	Γ (mg/m ²) (from adsorption isotherms)
PCL ₃ - b -PEO ₁₁₄	10 ± 1	92 ± 20		
PCL ₈ - b -PEO ₁₁₄	20 ± 5	86 ± 12	1.02	1.09
PMCL ₁₂ - b -PEO ₁₁₄	34 ± 3	76 ± 12	1.25	1.42
PCL ₁₆ - b -PEO ₁₁₄	37 ± 3	80 ± 16	1.31	1.63
PCL ₁₉ - b -PEO ₁₁₄	43 ± 3	70 ± 12	1.20	1.58

The adsorption data refer to copolymer concentrations corresponding to the adsorption plateau (saturation of the silica–water interface by the copolymer).

hydrophobic block of poly(ϵ -caprolactone) (PCL) or poly(γ -methyl- ϵ -caprolactone) (PMCL). The polymerization is well-controlled ensuring a low polydispersity. Five copolymers were selected for this study. They are listed in Table 1.

2. Experimental

Small-angle neutron scattering (SANS) experiments have been conducted at the Forschungszentrum Jülich (Germany) (FRJ-2 reactor, KWS-1 instrument) and at the Laboratoire Léon Brillouin (Saclay, France) (Orphée reactor, PACE instrument). Experiments have been performed in D₂O solutions and in the presence of deuterated SDS whose contrast was matched using a 92.5%/7.5% D₂O/H₂O mixture to observe only the copolymer micelles. Experiments at the silica/water interface used a 60%/40% D₂O/H₂O mixture to match the silica contrast. The silica particle sizes are in the 40–110 μm range. All measurements have been performed under neutral pH conditions and at room temperature.

3. Results

Due to the very low critical micellar concentration of the selected copolymers ($\text{cmc} \approx 0.01$ g/l) only micelles are observed by SANS in D₂O solutions. At low concentrations (0.2 wt%), the SANS signal reduces to the micellar form factor. The form factors have been analysed for the

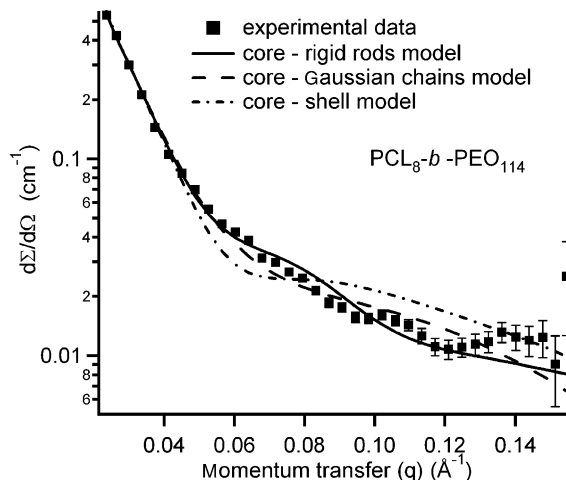


Fig. 1. Small-angle scattering cross-section for D₂O solution of poly(ϵ -caprolactone)₈- b -poly(ethylene oxide)₁₁₄ ($c = 0.2$ wt%). Full squares: experimental data (sample–detector distance = 8 m for the small q range and 2 m for the larger q range). Solid line: fit to the core-rigid rods model. Dashed line: fit to the core-Gaussian chains model. Dash-dotted line: fit to the core-shell model.

different copolymers using three different analytical models (core shell [3], core-Gaussian chains [4] and core-rigid rods [5]). All lead to compatible results but the best fits (Fig. 1) correspond to the core-rigid rods model, consisting in a dense hydrophobic core of radius R , surrounded by a corona of extended rods with an effective length L . The number of rods is equal to the aggregation number, N_{agg} . The micelle structural parameters resulting from this analysis are summarized in the second and third columns of Table 1. The corona

thickness lies in the 70–90 Å range: this corresponds to a moderate chain extension, equal to about 25% of a completely extended PEO₁₁₄ chain. Scaling relationships compatible with literature data [6,7] are found for the evolution of the core radius and the aggregation number as a function of the polymerization degree, N_b , of the hydrophobic block: $R \propto N_b^{0.80 \pm 0.06}$, $N_{agg} \propto N_b^{1.5 \pm 0.2}$. The global micellar size is nearly independent of the PCL block size: $(R+L) \propto N_b^{0.1 \pm 0.2}$.

The same methodology has been applied to obtain structural information on the micelles in the presence of an increasing concentration of deuterated SDS. Our results, summarized in Fig. 2, show that SDS induces a progressive disruption of the micelles leading to a release of free chains in the solution, whereas the corona of the remaining micelles reaches an extension of about 70% of a completely extended PEO₁₁₄ chain.

Scattering data have been obtained at saturation and half saturation of the silica–water interface by some of the copolymers listed in Table 1. The $q^2 I(q)$ data show a maximum at about 0.03 \AA^{-1} (Fig. 3), a situation which cannot be accounted for by a model involving the adsorption of free copolymer chains [8,9]. This suggests instead the adsorption of aggregates [10–12] separated by an average distance in the 100–200 Å range. A model has been developed involving the adsorption of core-rigid rods micelles with a hard

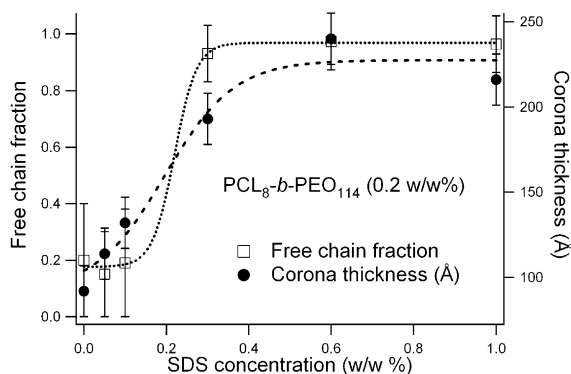


Fig. 2. Evolution of micellar disruption and corona extension for aqueous solutions of poly(ϵ -caprolactone)₈-*b*-poly(ethylene oxide)₁₁₄ in the presence of increasing amounts of SDS.

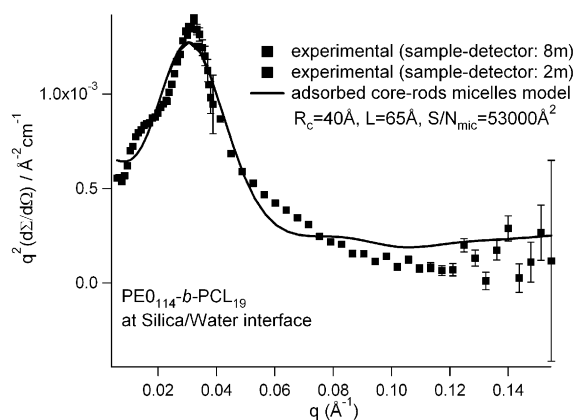


Fig. 3. Scattering data, in the $q^2 d\Sigma/d\Omega$ representation, for the PCL₁₉-*b*-PEO₁₁₄ copolymer adsorbed at the silica–water interface, under saturation conditions. Full squares: experimental data. Solid line: fit to the model for adsorbed core-rods micelles (see text).

sphere repulsive potential. Satisfactory fits of the model to the experimental data are obtained, as shown in Fig. 3. The adsorbed mass per unit surface which are deduced from this approach are given in Table 1 (4th column) and are in reasonable agreement with adsorption isotherm data (5th column). These isotherms have been determined by the total concentration depletion method using ¹H-NMR to measure the copolymer concentration remaining in the supernatant after separation of the silica particles by sedimentation. The micellar sizes are similar to those observed in solution.

4. Conclusions

Poly(ϵ -caprolactone)-*b*-poly(ethylene oxide) copolymers self-assemble into spherical micelles in aqueous solution. The SANS data are well accounted for by a model involving a dense core and moderately extended corona chains. Addition of SDS favours micellar disruption together with an increase of the corona thickness of the remaining micelles. Our data at the silica–water interface are compatible with the adsorption of micelles.

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