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Organisation and shape of micellar solutions of block copolymers

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Abstract

Diblock copolymers of polymethacrylic acid sodium salt, forming the hair, and styrene derivatives have been studied in aqueous solutions by SANS and by SAXS. The influence of both the chemical nature and the length of the hydrophobic block on the size and shape of micelles have been investigated. The micellar core size is in agreement with the theoretical evaluation for copolymers with a short hydrophobic sequence. In contrast, in case of larger hydrophobic blocks, the measured size is incompatible with a star-like model. Various hypotheses are presented for the latter.

Keywords*:* Micelles; Polymers; Small-angle neutron scattering; Surfactants

1. Introduction

Micelles of diblock copolymers in a solvent selected for one of the species have received considerable interest [1-4]. In contrast to inverse micelles that have been extensively studied by SAXS [5], few results have been published on the SANS analysis of ionic polymeric micelles. The purpose of this paper is to analyse the size, shape and spatial order of micelles as a function of the nature and length of the components. A series of SANS and SAXS experiments have been carried out on poly(styrene-b-methac-rylic acid Na salts) and poly(*tert*-butylstyrene-b-methacrylic acid Na salts) at various concentrations ranging from 1% to 10% and in different H_2O/D_2O mixtures. In order to selectively analyse the components of the micelle, perdeuterated polystyrene has been used. The relative composition of the diblock copolymers has also been varied.

2. Results

Below a concentration (in g/100 ml) of about 5% to 10% (depending on the micellar composition), homogeneous solutions are obtained in contrast to the 10% concentration, which gives rise most often to gels. SANS experiments have been performed at the LLB (Saclay) on the small angle diffractometer PACE. The spectra are recorded at different sample-to-detector distances: the ***q*** range extends from 0.004 to 0.2 Å^{-1}.
In Fig. 1, the SANS scattered intensity *I(q)* versus *q* is shown for a given micellar composition as a function of the concentration c (c = 0.01, 0.03, 0.05, 0.07 and 0.1) at two different sample-to-detector distances. The intensity ***I(q)*** is the product of the form factor ***P(q)*** and the interference function ***S(q)*** which modulates the spectrum below 0.05 Å^{-1}. After subtraction of these oscillations, it is shown that the shape of the micelles is independent of the concentration (the curves are parallel).

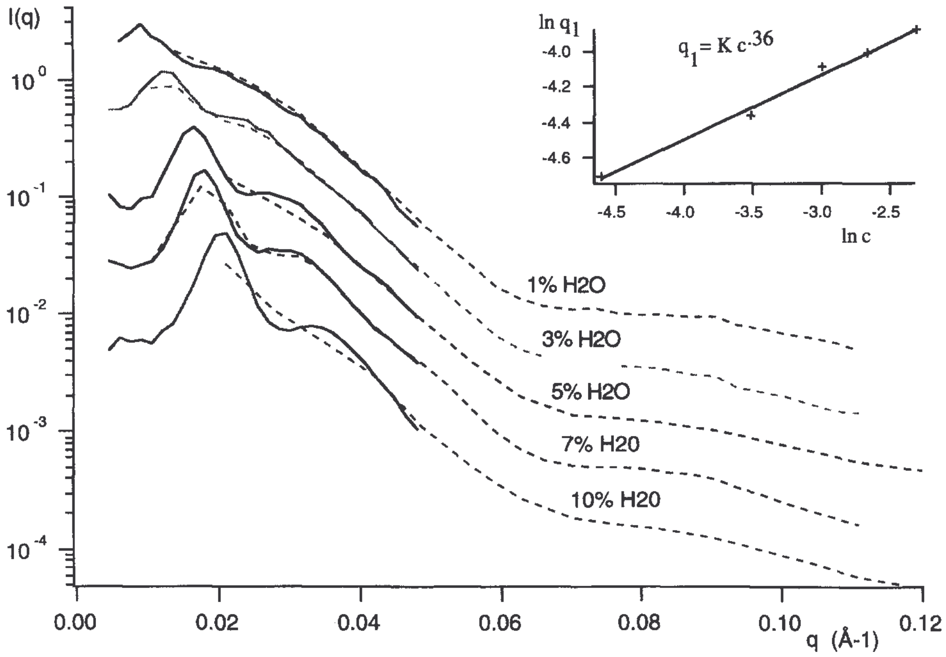

Fig. 1. The total diffracted intensity I(q) at different concentrations (in g/100ml) of $PS_d(22)$-b-MANa(23). The numbers between brackets give the number of monomers in the block copolymer. The polystyrene is perdeuterated. The measurements have been made at λ = 6 Å and at two different distances (full line: d = 4.65 m, dotted line: d = 1 m). In the inset, the position of the first maxima of I(q) is plotted as a function of the concentration.

Roughly, the SANS experiments are largely sensitive to the (deuterated) core, whereas the SAXS experiments are sensitive to the hair. The combination of both techniques gives in Table 1 the gyration radii of different compositions of PS_d-PMANa copolymers. The dimensionless product of the gyration radius R_g by the first minimum of *P(q)*, q_{min}, is $R_g q_{min} = 3.48$ for a (monodisperse) sphere. In our systems, we found larger values that indicate either a dispersion of the size or an ellipticity of the micelle (or both). We observe that the short symmetric copolymers (Table 1) have radii substantially larger than the length of the stretched insoluble block (which is roughly equal to the number of monomers times 2.5 Å. Calculations for the volume of the core of the micelles based on the intermicellar average distance obtained by the interference function *S(q)* (see below) accurately confirms the value of the core radius. In addition, determination of the hydrodynamic length by lightscattering gives the total length of the micelle in agreement with scattering data.

Table 1: Radii obtained by combining SANS and SAXS

Composition	R_{core} (Å)	$q_{min}R_g$	$R_{external}$
$PS_d(23)$-b-PMANa(25)	72	4.5	145
$PS_d(23)$-b-PMANa(70)	60	4.6	190
PtBS(19)-b-PMANa(76)	50	4.4	200
PtBS(23)-b-PMANa(30)	77	5.0	210

In contrast to the case of the short symmetric block copolymers, the asymmetric copolymers in which the hair is larger than the core, are simpler to characterise. They fit well with an elliptic shape and the core size corresponds to a stretched insoluble part. Coming back to the case of the symmetric (giant) micelles, the experimental data cannot be explained by a micelle with a dense spherical or elliptical core made of an insoluble part and a hair swollen by the solvent. The hypotheses of a vesicle structure has to be considered and it is compatible with recent data from electron microscopy.

The spatial order between micelles gives rise to the interference function *S(q)* which gives pair correlation functions *g(r)* by a Fourier transformation. This function *S(q)* is extracted by dividing the total diffracted intensity *I(q)* by a Guinier law $P(q) = P(0)\exp(-q^2 R_g^2/3)$ in the small *q* range. The resulting oscillating function $S(q) = I(q)/P(q)$ has successive maxima q_t such that $q_2/q_1 = 1.8$, is a characteristic value of normal liquids. An analysis of the first minimum as a function of the concentration gives a simple power law: $q_1 = Kc^{0.36}$ This expresses that the interatomic distance is proportional to c^{-036}, and close to c^{-033}, which is the signature of a repulsive interaction between micelles. However, in some cases, e.g. (PtBS(19)-b-PMANa(76)), we observed an original structure factor appearing with a splitting of the peaks into narrower peaks which is the signature of an incipient crystallisation.

Acknowledgements

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