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Micellar structure of amphiphilic poly(2-oxazoline) diblock copolymers

C. M. Papadakis,^{a*} R. Ivanova,^a K. Lüdtkke,^b K. Mortensen,^c P. K. Pranzas^d and R. Jordan^{b,e}^aPhysikdepartment E13, Technische Universität München, James-Frank-Str. 1, 85747 Garching, Germany,^bLehrstuhl für Makromolekulare Stoffe, Department Chemie, Technische Universität München, Lichtenbergstr. 4,85747 Garching, Germany, ^cDanish Polymer Centre, Risø National Laboratory, 4000 Roskilde, Denmark,^dInstitut für Werkstofforschung, GKSS-Forschungszentrum Geesthacht, 21502 Geesthacht, Germany, and^ePolymer Research Institute, Polytechnic University, Six Metrotech Center, Brooklyn, NY 11201, USA.

Correspondence e-mail: christine.papadakis@ph.tum.de

Amphiphilic diblock copolymers from poly(2-oxazoline)s in aqueous solution can form micelles. By means of small-angle neutron scattering, we have found that poly[(*n*-nonyl-2-oxazoline)-*b*-(methyl-2-oxazoline)] [P[(NOx)-*b*-(MOx)]] diblock copolymers in aqueous solution form micelles of core-shell type. We have determined the core radius and the shell thickness of the micelles. Comparing the values obtained to the stretched lengths of the blocks leads to the conclusion that the P(NOx) core blocks are stretched, whereas the P(MOx) shell blocks are coiled.

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1. Introduction

Amphiphilic block copolymers in aqueous solution display a rich phase behavior. They are known to form micelles and micellar gels of different kinds (*e.g.* Price, 1982; Riess *et al.*, 1985; Piirma, 1992; Tuzar & Kratochvil, 1993; Webber *et al.*, 1996; Hamley, 1998; Alexandridis & Lindman, 2000). Poly(2-oxazoline) diblock copolymers constitute a versatile system to systematically study the aggregation behavior, because their architecture is readily varied, and homopolymers, diblock copolymers and triblocks from two or three chemically different monomers, for instance, can be synthesized (Komenda, 2000; Komenda & Jordan, 2003; Lüdtkke, 2005). The degree of hydrophilicity is controlled by the nature of the side group: A methyl group results in a hydrophilic monomer, whereas a 2-*n*-nonyl group leads to a hydrophobic monomer (Litt *et al.*, 1969). Furthermore, functionalization such as fluorescence-labeling is possible, and, in this way, tracer polymers which are identical to the non-labeled polymers are available (Bonné *et al.*, 2004). This enabled us to study the micelle formation of two poly[(*n*-nonyl-2-oxazoline)-*b*-(methyl-2-oxazoline)], P[(NOx)-*b*-(MOx)], diblock copolymers in aqueous solution using fluorescence correlation spectroscopy (FCS) (Bonné *et al.*, 2004). The critical micelle concentration (CMC) could be detected at very low polymer concentrations ($\sim 10^{-5}$ M).

We report here on a small-angle neutron scattering (SANS) study of the inner structure of the micelles formed by P[(NOx)-*b*-(MOx)]. The polymers were dissolved in mixtures of D₂O/H₂O chosen so that they match the scattering length density of either block. The concentration was chosen far above the CMC, *i.e.* unimers (single dissolved polymers) are present only in negligible amounts. We find that the micelles are of core-shell type and that the core blocks are stretched, presumably because of the comb-like structure.

2. Experimental

We have studied a P[(NOx)₁₀-*b*-(MOx)₃₂] diblock copolymer, where the subscripts denote the average degree of polymerization of the two

blocks. The synthesis has been previously described (Lüdtkke, 2005; Bonné *et al.*, 2004). The polymer was dissolved at a concentration of 10 wt% (21×10^{-3} M) in D₂O/H₂O. The mixing ratio was chosen in such a way that either the P(NOx) core or the P(MOx) shell were contrast-matched (see Table 1). For this purpose, the scattering length densities of P(NOx) and P(MOx) were calculated on the basis of mass densities calculated using the group contributions for the amorphous polymers (van Krevelen, 1990): 0.93 g cm⁻³ for P(NOx) and 1.06 g cm⁻³ for P(MOx). The solutions were annealed at 333 K for 12 h.

SANS experiments were carried out at SANS II at Paul-Scherrer-Institut, Switzerland. The intensities were brought to an absolute scale and corrected for the background scattering by subtracting a constant. The resulting intensity profiles were analyzed using the Generalized Inverse Fourier Transform (GIFT) module of the PCG software (Glatter, 1977, 1980; Bergman *et al.*, 2000). From the pair distance distribution function, $p(r)$, the core radius and the shell thickness were determined. The interaction between the micelles was modeled with the Percus–Yevick approximation (Brunner–Popela & Glatter, 1997), and the hard-sphere radius, R_{HS} , was found.

3. Results and discussion

In previous tracer experiments with FCS, we have determined the hydrodynamic radii of the unimers and micelles as well as the critical micelle concentrations of two similar P[(NOx)-*b*-(MOx)] diblock

Table 1
Solutions studied using SANS and results.

Block matched	D ₂ O/H ₂ O volume ratio	Core radius (Å)	Shell thickness (Å)	Hard-sphere radius (Å)
P(MOx)	23/77	26 (2)	–	81 (11)
P(NOx)	11/89	–	39 (3)	89 (6)

copolymers (Bonné *et al.*, 2004, 2007). Diblock copolymers which were fluorescence-labeled at the end of the P(NOx) or the P(MOx) block with tetramethyl rhodamine isothiocyanate (TRITC), but which were otherwise chemically identical, served as tracers. The fluorescence-labeled unimers were found to have hydrodynamic radii of 14 (4) Å [P[(MOx)₄₀-b-(NOx)₇]-TRITC] and 13 (2) Å [P[(NOx)₁₀-b-(MOx)₃₂]-TRITC], respectively. The micellar hydrodynamic radii amount to 130 (20) Å for P[(MOx)₄₀-b-(NOx)₇] and 113 (9) Å for P[(NOx)₁₀-b-(MOx)₃₂], and the CMCs to $7.4 (16) \times 10^{-6} M$ and $22 (7) \times 10^{-6} M$, respectively.

In order to determine the inner micellar structure, to relate the sizes found to the block lengths and thus to deduce the chain conformation, we have performed SANS measurements on solutions of a similar polymer, P[(NOx)₁₀-b-(MOx)₃₂] in D₂O/H₂O mixtures. The polymer concentration was chosen far above the CMC. Most of the polymers are thus present as micelles, and the fraction of unimers is negligible. The azimuthally averaged and scattering curves are shown in Figs. 1(a) and 1(c). The pair distance distribution functions (Figs. 1b and 1d) are in good agreement with spherical core-shell micelles with P(NOx) forming the core and P(MOx) the shell. The resulting fitting parameters are given in Table 1. Both D₂O/H₂O ratios lead consistently to a hard-sphere radius of 80–90 Å.

The determined micellar dimensions (core radius + shell thickness) amount to $26 + 39 = 65$ Å. This value is smaller than the hydrodynamic radii of the micelles determined by FCS, which is reasonable, because the hydrodynamic radius includes both the micelle and the water shell attached to it. Comparing the core radius of 26 Å to the dimension of the P(NOx) block gives information about the chain conformation: The stretched length of the P(NOx) block is 37 Å as estimated from the monomer length of 3.7 Å (Bonné, 2006). We conclude that the P(NOx) block is stretched from the surface of the core to the center, which is probably caused by the *n*-nonyl side groups.

The shell thickness of 39 Å is smaller than the stretched length of the P(MOx) block (111 Å). The P(MOx) block is thus coiled which is consistent with the much shorter side groups than in P(NOx).

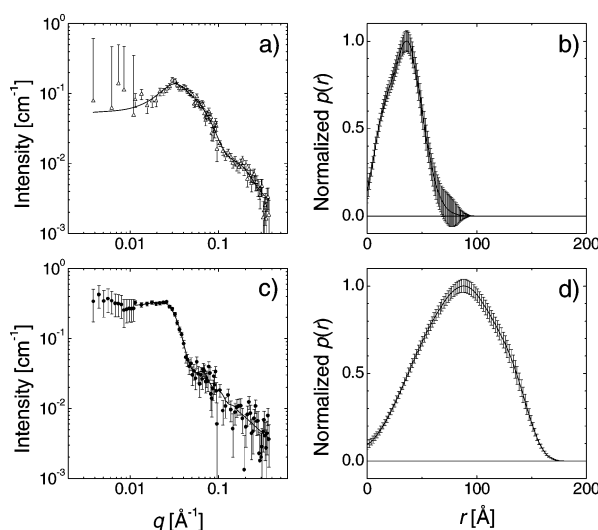


Figure 1

SANS intensity profiles, where $q = 4\pi \sin(\theta/2)/\lambda$ is the scattering vector, θ the scattering angle and λ the wavelength (left), and corresponding pair distance distribution functions, where r is the real space distance (right), from solutions of P[(NOx)₁₀-b-(MOx)₃₂] in D₂O/H₂O. (a), (b) P(MOx) block matched, (c), (d) P(NOx) block matched. The D₂O/H₂O ratios used are given in Table 1. The lines in (a) and (c) are fits determined with GIFT.

4. Conclusions

We conclude that P[(NOx)₁₀-b-(MOx)₃₂] diblock copolymers form spherical core-shell micelles. The core block is stretched, whereas the corona block is coiled. It is not straightforward to apply statistical models relating the core radius and the shell thickness to the number of segments in each block because the degrees of polymerization of the two blocks are very low and because each monomer is an amphiphile. Such polymers have been shown to assume conformations very different from the random coil (Vasilevskaya *et al.*, 2006). Moreover, the *n*-nonyl side groups lead to a comb-like conformation which is different from the usual random coil.

The poly(2-oxazoline) system allows studies of the effect of architecture on the micellar size, shape and structure, and we have studied P[(MOx)-b-(NOx)-b-(MOx)] triblock copolymers and P[(MOx)-*r*-(NOx)] random copolymers as well (Bonné *et al.*, 2007). Furthermore, poly(2-oxazoline)s containing fluorinated side groups are attractive candidates for the formation of multicompartment micelles (Komenda *et al.*, 2006; Ivanova *et al.*, 2007).

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