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ORIGINAL CONTRIBUTION

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A new approach towards redispersable polyelectrolyte–surfactant complex nanoparticles

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Abstract Redispersable and weakly cross-linked block copolymer particles with a core–shell structure were prepared by the use of a macroinitiator. Subsequent sulfonation of the polystyrene core and complex formation with a variety of cationic surfactants led to sterically stabilized, redispersable polyelectrolyte–surfactant complex particles with spherical shape and diameters of about 400 nm. Spontaneous microphase separation of the hydrophobic surfactant tails and the hydrophilic entities of the polyelectrolyte and the surfactant headgroups induces mesostructure formation within the particle cores. The characteristic lengths of the mesostructures formed depend mainly on the chain lengths of the surfactants and vary between 2 and 4 nm. For the first time, preformed nanoparticles were used as constrained nanogeometries for polyelectrolyte–surfactant complex formation.

Keywords Macroinitiator · Block copolymer · Polyelectrolyte–surfactant complex · Emulsion polymerization · Mesophase formation

Introduction

Polyelectrolyte–surfactant complexes form spontaneously when polyelectrolytes are mixed with surfactants of opposite charge [1, 2]. The formation of these complexes is driven by electrostatic interactions between the charged headgroups of the surfactants and the oppositely charged units of the polyelectrolyte, as well as by hydrophobic interactions between the alkyl chains. Also entropy contributes to the driving force of complex formation as a high number of counterions of the polyelectrolyte and the surfactant are released. Owing to phase separation of hydrophobic and hydrophilic entities long-range ordered mesostructured materials with a variety of morphologies are obtained. The charge density of the polyelectrolyte, its length and molecular architecture (e.g. linear, branched, grafted, block copolymers) have a strong impact on the morphologies formed, as well as the structure of the surfactants used for complexation. Depending on these factors, cubic, hexagonal and a variety of lamellar phases have been observed. Polyelectrolyte–surfactant complexes can be prepared simply by mixing surfactant and polyelectrolyte solutions. The complexes precipitate from solution at ratios close to an equimolar composition of charged polyelectrolyte groups and surfactant headgroups. In this way, mesostructured materials that are usually insoluble in common solvents and are nonredispersable are formed. For the study of gel-collapse processes bulk polyelectrolyte gels have also been used for the complex formation with surfactants [3].

For many potential applications (e.g. in drug delivery) and for the handling and processing of polyelectrolyte-surfactant complexes it can be advantageous to gain these materials as redispersable and well-defined particles [4]. One way to form redispersable particles of polyelectrolyte–surfactant complexes is to use double-hydrophilic block copolymers with at least one water-soluble, noncharged polymer block, for example, poly(ethylene oxide), and one polyelectrolyte block, for example, polymethacrylate anions, [5, 6, 7, 8]. By addition of oppositely charged surfactants (e.g. *N*-alkylpyridinium surfactants), particles are formed spontaneously that exhibit a mesostructured polyelectrolyte–surfactant complex core and a poly(ethylene oxide) shell, as first shown by Bronich et al. [5]. By this method, relatively monodisperse block ionomer complexes are obtained, which combine the properties of amphiphilic block copolymers and polyelectrolyte–surfactant complexes.

This report describes an alternative approach towards the synthesis of polyelectrolyte–surfactant complex particles. In contrast to all other approaches towards polyelectrolyte complexes so far, here the polymer matrix as a constrained nanogeometry for mesostructure formation by complexation is preformed. Therefore sterically stabilized latex particles with a poly(ethylene oxide) shell and a cross-linked polystyrene (PS) core were synthesized by free-radical emulsion polymerization of styrene and divinylbenzene. Poly(ethylene oxide) radicals were formed as the initiating species by redox reaction of the polymer with Ce^{4+} ions [9, 10]. After functionalization of the polymer particles by sulfonation and subsequent complexation with cationic surfactants, sterically stabilized polyelectrolyte–surfactant complex nanoparticles were formed. Characterization of the mesostructured and redispersable particles was performed by dynamic light scattering (DLS), transmission electron microscopy (TEM), elemental analysis, differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS).

Experimental

Synthesis of latex particles

Sterically stabilized PS nanoparticles were synthesized by means of emulsifier-free heterophase polymerization [9, 10]. In the first step, seed particles were synthesized. Subsequently, injection of styrene and 1,3-diisopropenylbenzene triggered the polymerization.

For the synthesis of the seed particles 8.4 g poly(ethylene glycol) (PEG, $M_n = 20{,}000$ gmol^{-1}, Fluka), 5 g HNO_3 (1 M, Aldrich), 0.63 g *N*-isopropylacrylamide (Acros, recrystallized before use) and 90 g deionized water were mixed in a glass reactor, equipped with a mechanical stirrer, a water-cooled condenser, a N_2 inlet and a heating jacket. The reaction mixture was heated to 60 °C and a continuous stream of N_2 was purged into the reaction mixture for 30 min to remove dissolved oxygen. Afterwards a solution 0.4 g $(NH_4)_2Ce(NO_3)_6$ (Aldrich) in 5 ml HNO_3 (1 M) was added. Styrene (12 g, Aldrich) and 1,3-diisopropenylbenzene (0.06 g, Aldrich) were continuously injected into the reaction mixture over a period of 40 min. Subsequently, the PS latex obtained was ultrafiltrated to remove inorganic salts and unreacted water-soluble polymers, ultracentrifuged and finally freeze-dried.

Functionalization of latex particles

A sulfonation reaction was used to functionalize the PS particles according to a standard procedure described in the literature [11]. In a typical reaction, 3 g dialyzed and freeze-dried polymer particles were redispersed in 60 ml dichloroethane (Aldrich). Concentrated sulfuric acid (4.4 g, Aldrich) and acetic acid anhydride (4.4 g, Aldrich) were dissolved in 30 ml dichloroethane and stirred for 5 min. This second solution was added dropwise to the stirred polymer particle dispersion at room temperature. Under reflux the reaction mixture was stirred and heated for 16 h at 50 °C. The yellowish precipitate formed was washed with 15 ml dichloroethane and dried at room temperature.

Preparation of polyelectrolyte–surfactant particles

Polyelectrolyte–surfactant particles were prepared by adding equimolar amounts of cationic surfactant to a dispersion of functionalized latex particles. For instance 0.175 g V140S was redispersed in 10 ml deionized water and mixed with a solution of 0.266 g dodecyltrimethylammonium bromide (DOTAB) in 10 ml deionized water. After stirring at room temperature for 3 h the mixture was dialyzed for 3 days to remove any residual surfactant. Subsequent freeze-drying of the purified solution resulted in white powders of polyelectrolyte–surfactant particles, which could be easily redispersed in deionized water. Other surfactants used for complex formation were tetradecyltrimethylammonium bromide (TTAB), cetyltrimethylammonium bromide (CTAB) and di(dodecydimethyl)ammonium bromide (DDAB), all supplied by Aldrich.

Analytical methods

Elemental analysis

The chemical composition of the complexes was determined by elemental analysis of CHNS using an Elementar Vario El apparatus.

Dynamic light scattering

Hydrodynamic particle diameters were determined by use of a NICOMP particle sizer (model 370, NICOMP particle sizing system, Santa Barbara, Calif., USA).

Polarized light microscopy

Optical textures of the complexes were studied with an Olympus BX50 optical microscope. The particles of the freeze-dried samples were placed between glass slides and observed at room temperature between crossed polarizers.

Transmission electron microscopy

Electron microscopy investigation was done with a Zeiss EM912 Omega transmission electron microscope, working with an acceleration of 120 kV. Dialyzed dispersions of the complexes were prepared by drying them on a carbon-coated copper grid without any further treatment. For ultramicrotomy freeze-dried samples were embedded in epoxy resin and microtomed using a Leica Ultracut UCT with a 45° diamond knife (Diatome). The thickness of the thin sections was about 50 nm. Owing to the sufficient contrast no staining techniques were applied.

Differential scanning calorimetry

The DSC measurements were performed with a Netzsch DSC200. The scanning rate was 10 Kmin^{-1} by applying two heating scans and one cooling scan in the temperature range 193–423 K.

Small-angle X-ray scattering

SAXS was performed using a vacuum Kratky camera (Anton Paar, model A-8054) equipped with image plates. Freeze-dried polymer samples were placed between polymer foils and measured under a vacuum. The scattering vector, s, is defined as $s=(2/\lambda)\sin(\theta/2)$, where θ is the scattering angle. The measurements were performed in an s range of $1\times10^{-2}\ \mathrm{nm}^{-1} < s < 9.0\times10^{-1}\ \mathrm{nm}^{-1}$.

Results and discussion

The use of water-soluble macroinitiators in aqueous emulsion polymerization is a convenient way to obtain redispersable polymer nanoparticles. From a morphological point of view, these particles are very similar to block copolymer micelles as they exhibit a core–shell structure. In particular, particles with a hydrophobic PS core and a hydrophilic poly(ethylene oxide) shell form when styrene is used as the monomer and poly(ethylene oxide) radicals as a macroinitiator. In this study, divinylbenzene was additionally used as a cross-linker and comonomer to induce morphological stability of the particles throughout the whole process of synthesis of sterically stabilized and redispersable, mesostructured nanoparticles. After emulsion polymerization, this process includes sulfonation of the PS core, redispersion of the cross-linked polyelectrolyte nanoparticles, and subsequently the complexation with cationic surfactants (Fig. 1). The amount of cross-linker was kept relatively low (0.5 wt% divinylbenzene with regard to styrene) to retain enough chain mobility within the polymer network for mesophase formation. The chain lengths of the alkyltrimethylammonium bromide surfactants used were C_{12} (DOTAB), C_{14} (TTAB) and C_{16} (CTAB). Additionally, DDAB was used as an example of complex formation by a double-tail surfactant.

Redispersable core–shell polymer nanoparticles are obtained by free-radical emulsion polymerization. The initiating species, a poly(ethylene oxide) radical, is formed by the reaction of Ce^{4+} with PEG with a molecular weight of 20,000 gmol^{-1}. The covalently bond poly(ethylene oxide) shell induces sterical stability of the polymer particles in dispersion. The hydrodynamic diameter of the freeze-dried and redispersed latex particles in water was determined as 386 nm by DLS. Subsequently, the PS core was sulfonated to obtain a polyelectrolyte network structure. The purified polyelectrolyte particles were redispersed in water. Excess cationic surfactant was added to the sulfonated particles to ensure saturation of the polyelectrolyte matrix by surfactant. In this way, the maximum uptake of surfactant as a function of the surfactant structure can be investigated. The chemical composition of the polyelectrolyte–surfactant complex particles obtained was determined by elemental analysis. The ratio of surfactant molecules to sulfonium groups was calculated directly from the molar ratio of nitrogen to sulfur, as all the surfactants used contain just one ammonium headgroup (Table 1).

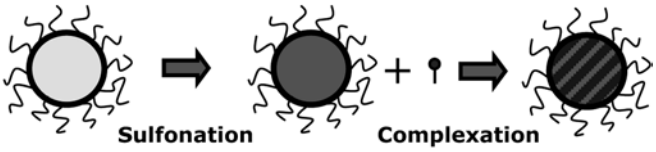

Fig. 1. Scheme of mesostructured nanoparticle synthesis

A stoichiometric complex of surfactant molecules and sulfonium groups is formed when DOTAB is used as the surfactant. The redispersed particles have an average hydrodynamic diameter of 648 nm. This increase in size compared to the nonmodified core–shell lattices (386 nm) is mainly due to the increase in mass by sulfonation and complexation. In the case of complex formation by surfactants with longer alkyl chains, the uptake of surfactant exceeds the stoichiometric ratio and increases up to 119% (V140S–CTAB). This effect can be explained by additional adsorption of the surfactant at the particle surface and the incorporation of excess surfactant within the mesostructure formed. This effect was also described earlier for block ionomer complexes [5]. The continuous increase in the stoichiometric ratio of surfactant cations and sulfonium groups with respect to the total number of carbon atoms of the surfactants alkyl chains is shown in Fig. 2.

By calorimetry (DSC), no phase transitions or hints of conformational changes were found within a temperature range of 193–423 K. This result is in contradiction to earlier investigations of bulk polyelectrolyte surfactant complexes of similar composition, where a transition towards a higher gauche content was detected

Table 1. Chemical composition, molar ratio, r, of surfactant to sulfonium groups and characteristic length, d, of the mesostructure formed (calculated from the first-order peak of small-angle X-ray scattering diffractograms)

Sample	wt% N	wt% C	wt% S	wt% H	r ($N_{\mathrm{cat}}/N_{\mathrm{an}}$)^{a}	d (nm)^{b}
V140S	0.055	36.49	13.45	11.86	–	–
V140S–DOTAB	2.880	65.51	6.582	11.72	1.001	2.95
V140S–TTAB	2.748	66.87	6.201	12.36	1.013	3.25
V140S–CTAB	2.638	67.74	5.805	12.74	1.039	3.70
V140S–DDAB	2.349	69.87	4.519	13.22	1.189	2.80; 3.10

[a] Degree of complexation calculated from $n(\mathrm{N})/n(\mathrm{S})$

[b] Calculated from small-angle X-ray scattering data

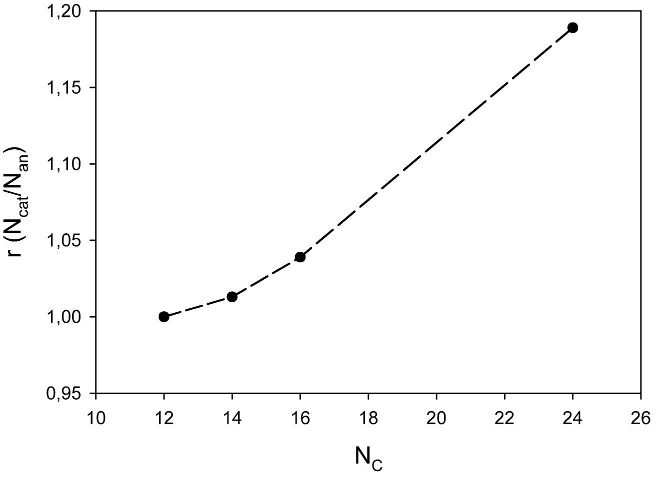

Fig. 2. Molar ratio of surfactant to sulfonium groups as a function of the total carbon numbers of the hydrophobic surfactant chains

owing to thermal expansion [12]. For the cross-linked polyelectrolyte–surfactant complex nanoparticles no significant transitions could be found. This effect is probably due to the limited chain mobility of the particle network structure rather than to the nanoparticle structure itself. Effects of the limited constraints (polymer particle size) could only be expected for particles smaller than the ones used for this study.

Transmission electron micrographs of the dried polyelectrolyte–surfactant complex latices show monodisperse, spherical particles with an average diameter of about 400 nm, as estimated from TEM of nonultramicrotomed samples. The morphology of the original particles was retained through the whole process of functionalization and complexation. The large difference in size compared to the hydrodynamic diameter of the redispersed particles (648 nm) can be explained by the deswelling of the hydrophilic moieties of the complex, as well as by the collapse of the poly(ethylene oxide) shell during drying. As a consequence of the latter effect, film formation takes place on the surfaces of the particles and this causes the impression of smeared contours (Fig. 3a). To investigate the inner structure of the particles, ultramicrotomed samples with an average thickness of 50 nm were investigated. Micrographs of an ultramicrotomed sample (sulfonated PS–TTAB) clearly show the core–shell morphology by the difference in contrast between the collapsed PEG shell and the polyelectrolyte–surfactant complex (Fig. 3b). The results from polarized light microscopy of the polyelectrolyte–surfactant particles give a first hint of the formation of mesostructured particles. The birefringence is relatively low compared to bulk polyelectrolyte complexes. This could be explained by the small domain sizes, which are limited by the constrained geometry of the parental latex particles (smaller than 300 nm).

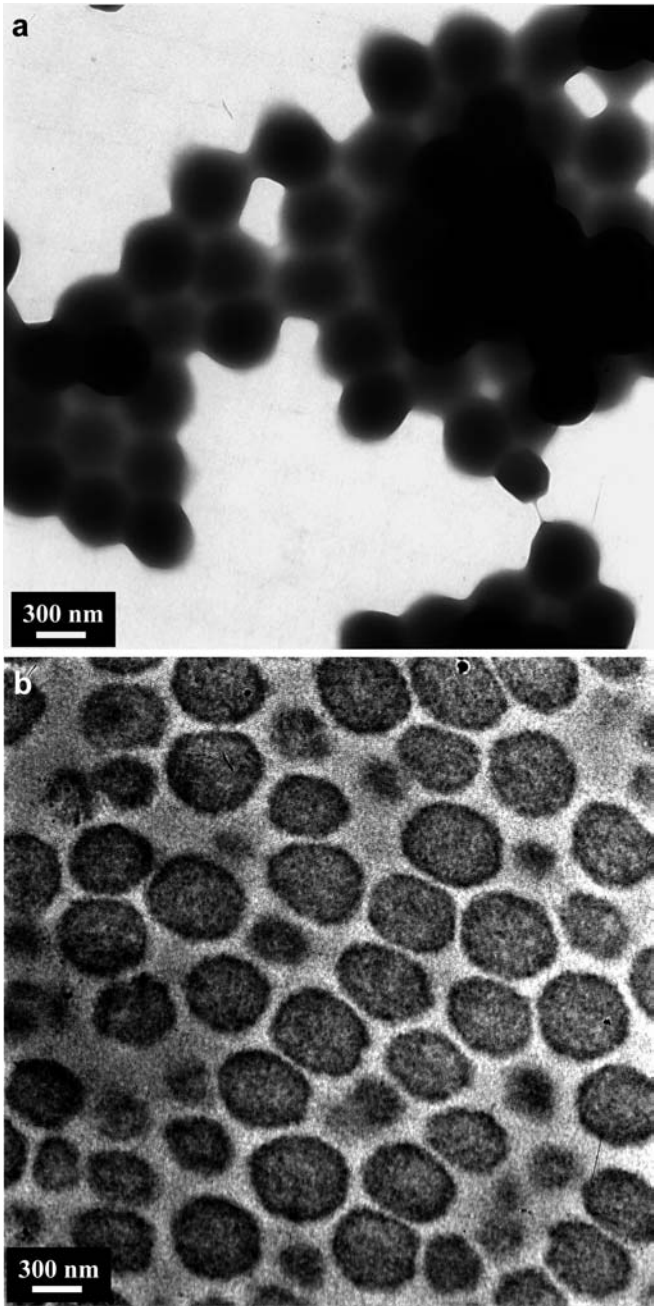

Fig. 3. Micrographs (transmission electron microscopy) of **a** dried and **b** ultramicrotomed samples of V140S–tetradecyltrimethylammonium bromide (*TTAB*)

SAXS was performed to determine the characteristic lengths of the mesostructures formed. The diffractograms of the sulfonated latex before complex formation and of the particles from complex formation with single-tail surfactants are shown in Fig. 4a. While the unmodified sulfonated PS particles show no order on the nanometer length scale, the surfactant-modified particles have long-range order with characteristic lengths of

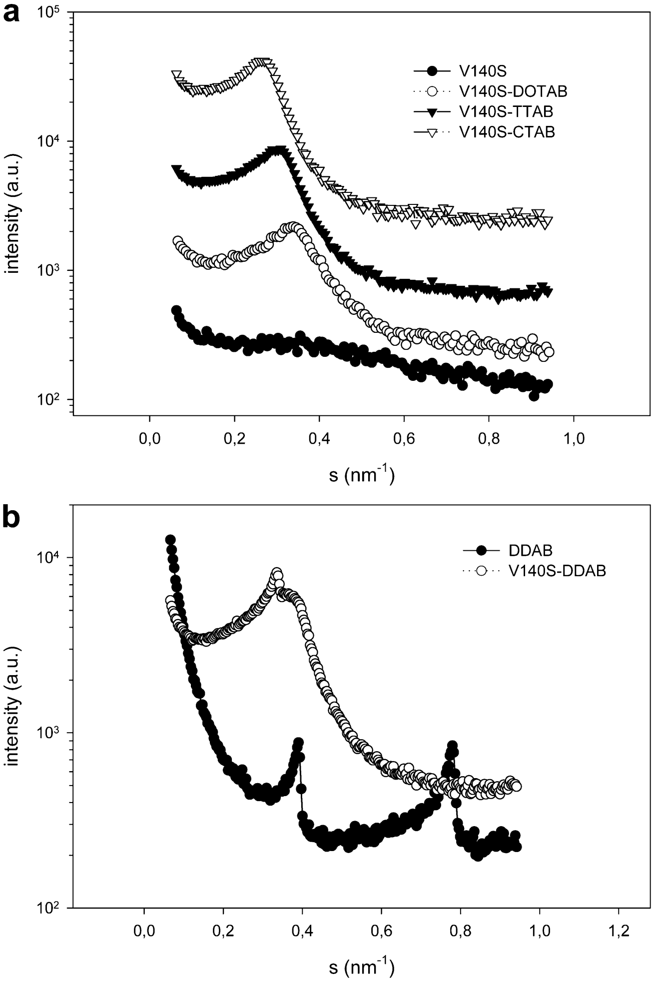

Fig. 4a, b. Diffractograms (small-angle X-ray scattering) of polymer particles: **a** Before complex formation (V140S) and after complex formation with the single-chain cationic surfactants DOTAB, TTAB and CTAB. **b** Diffractograms of bulk di(dodecydimethyl)ammonium bromide (*DDAB*) and of the complex V140S–DDAB

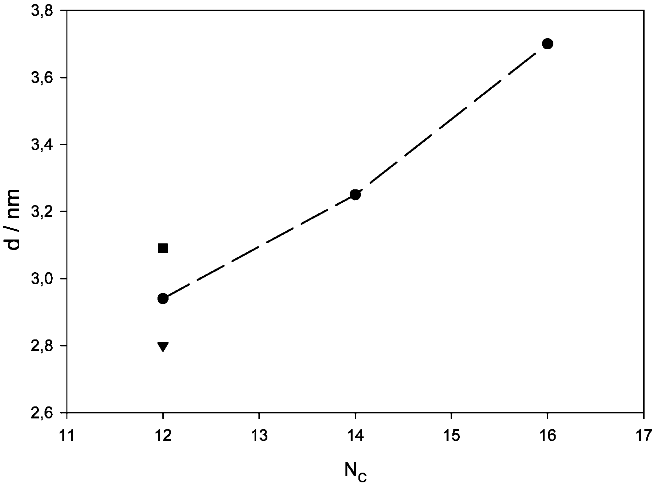

Fig. 5. Increase in characteristic lengths of the mesophases formed as a function of increasing surfactant chain lengths: complexes of single-chain surfactants (circles); two characteristic lengths of V140S–DDAB (*square* and *triangle*)

2.9–3.7 nm (Table 1). The characteristic lengths of the mesostructures formed increase with increasing chain length of the surfactant, as shown in Fig. 5. Higher-order reflexes are missing and the peaks are relatively broad, which hints at relatively low degrees of order. One reason for this effect might be the decrease in chain mobility due to cross-linking. On the other hand, the space-filling problem has also to be taken into account, as the constrained nanogeometry of the preformed polymer particles has to be considered as a limiting factor for long-range ordering. As similar bulk complexes described in the literature have a lamellar morphology [13], the observed structure might be best described as a disturbed lamellar phase.

The range of characteristic lengths of all the complexes is far too low to be explained by a typical bilayer structure of surfactant double layers separated from each other by ionic layers of polyelectrolyte. Rather more likely is the formation of an intercalated structure of two layers of surfactant chains [13].

The diffractogram of the complex nanoparticles formed with the double-tail surfactant DDAB is shown in Fig. 4b. In contrast to the single-chain surfactants, two reflexes close to each other are observed. They can be correlated with characteristic lengths of 2.8 nm for the very narrow first peak and 3.1 nm for the broader second peak, while the interlayer spacing of the lamellar surfactant bulk phase is 2.56. This clearly hints at the formation of a semicrystalline polyelectrolyte–surfactant phase, which was verified by DSC showing a melting peak at 40 °C.

Conclusions and outlook

A new approach towards polyelectrolyte–surfactant complex particles was described. Mesostructured polymer nanoparticles were formed by cross-linking emulsion polymerization, subsequent sulfonation and complexation with cationic surfactants. Owing to a covalently bonded poly(ethylene oxide) shell, the particles were redispersable even after complex formation. Morphological investigations revealed the core–shell structure of these particles, as well as mesostructure formation within the particle cores. The characteristic lengths of the mesostructures formed could be adjusted by the length of the alkyl chain of the surfactant between 2 and 4 nm. These relatively small values could be explained by an intercalated arrangement of surfactant chains. A semicrystalline morphology was obtained in case of complex formation with a double-chain surfactant. Future work will focus on a more detailed investigation of the morphologies formed, the swelling/deswelling behavior, as well as on the influence of constrained geometries on mesostructure formation.

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