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Published on Web 02/25/2006

Solvent-Induced Morphological Transition in Core-Cross-Linked Block Copolymer Micelles

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Abstract: Microwave-assisted polymerization has been utilized to synthesize amphiphilic poly(2-ethyl-2-oxazoline-*block*-2-“soy alkyl”-2-oxazoline) diblock copolymers (PEtOx−PSoyOx). The amphiphilic block copolymers have been used to prepare aqueous spherical micelles consisting of a PEtOx corona and a PSoyOx core, which have been further cross-linked by UV irradiation. The morphology of these cross-linked micelles has been shown to reversibly change from spheres to short rods referred to as rice grains whenever the micelles were transferred from water into acetone, a nonselective solvent for the constituent blocks. This morphological transition has been attributed to the swelling of the slightly cross-linked PSoyOx core.

Introduction

When compared to low molar mass surfactants, block copolymer micelles are characterized by a much slower rate of intermicellar chain exchange that makes them interesting for a variety of applications.[1] The intermicellar exchange rate in block copolymer micelles has been studied by fluorescence techniques, for example, and has been shown to essentially depend on the nature of the constituent blocks (i.e., on the glass transition of the insoluble block, polarity, the overall chain length, and relative block lengths, as demonstrated by Creutz et al.[2]). On the other hand, a slow intermicellar chain exchange rate may be a problem during micelle preparation and may impede the formation of equilibrium micelles.[3] In this respect, “kinetically frozen micelles” are reported from amphiphilic block copolymers containing high T_g long hydrophobic blocks.[4] Whenever short amphiphilic block copolymers are considered, the intermicellar exchange rate increases and the resulting micelles become unstable. Moreover, even if the intermicellar exchange rate is slow, the majority of the self-assembled morphologies are likely to become unstable in a certain range of temperature, concentration, or pH.[5] As a consequence, the number of industrial applications developed thus far with these micellar systems is limited, essentially because of the lack of stability control. If applications are to be developed on the basis of such micellar structures, it is necessary to stabilize them to form objects with nanoscale dimensions. A way to circumvent these drawbacks consists of using short amphiphilic block copolymers ($M_n \approx 10\,000$ g mol^{-1}) containing low T_g cross-linkable insoluble blocks. In the first step, equilibrium micelles are obtained by dissolving these copolymers in a selective solvent for the coronal chains. Then the core-forming low T_g chains are cross-linked to lock the micellar structure. Such an approach has been previously used by several groups, as illustrated in ref 6. The cross-linking of the micellar core can be achieved by several methods, although radical UV-cross-linking seems to be one of the most promising routes since it does not require the diffusion of a cross-linker inside the core. In addition to radical cross-linking, methods of stabilization using other chemical reactions or noncovalent interactions such as H-bonding have been also considered, as recently reviewed by Lecommandoux and co-workers.[1]

Core-cross-linking by means of radical reactions requires that double bonds in block copolymers be exposed to UV−vis light,

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10.1021/ja057762k CCC: $33.50

generally in the presence of a radical initiator. Depending on the location of the cross-linking reaction in the aggregate, different situations can be distinguished. First, cross-linkable end groups can be attached to the block copolymers. This approach is illustrated by, for example, Maskos and co-workers, who synthesized α,*ω*-heterotelechelic amphiphilic poly(dimethylsiloxane)-*block*-poly(ethylene oxide) diblock copolymers.[7] After self-assembly of these copolymers into micelles, the methacrylic group carried by the PDMS block in the α-position was used to photo-cross-link the core of the micelles. More than one polymerizable group can participate in the stabilization whenever pendant double bonds are available on the core-forming blocks. Such an approach has been implemented by Liu and co-workers for block copolymer micelles containing UV-cross-linkable poly(2-cinnamoylethyl methacrylate) core-forming blocks.[8] Polybutadiene-based block copolymers are also good candidates for stabilization by UV-cross-linking. This has been demonstrated by, for example, Bates and co-workers for wormlike aqueous micelles prepared from poly(styrene)-*block*-poly(ethylene oxide) copolymers.[9] Another related strategy relies on stabilization in bulk prior to micellization. This approach indeed allows covalent capture of a particular morphology from the bulk state, as demonstrated by Stupp and co-workers, who synthesized triblock rod−coil oligomers that were found to self-assemble into mushroom-shaped nanostructures in the solid state.[10] The original bulk nanostructure was retained through cross-linking of the double bonds of the polybutadiene central block. A similar approach was used by Müller and co-workers to prepare the so-called “Janus” micelles from poly(styrene)-*block*-poly(butadiene)-*block*-poly(methyl methacrylate) triblock copolymers.[11]

In principle, any core-forming polymer blocks that contain aliphatic double bonds are prone to micelle stabilization by UV-cross-linking. Nevertheless, polymers based on unsaturated fatty acids have never been applied for this purpose to the best of our knowledge. In this article, we report on the microwave-assisted synthesis of poly(2-ethyl-2-oxazoline-*block*-2-“soy alkyl”-2-oxazoline) diblock copolymers (PEtOx−PSoyOx), on the formation of core-cross-linked aqueous spherical micelles from these copolymers, and on the sphere to short rod morphological transition observed whenever these micelles are transferred into a nonselective solvent for the constituent blocks. The SoyOx monomer is based on a sustainable resource, soybean fatty acids, and contains alkyl chains of variable length bearing on average 1.4 double bonds.[12] It is thus an ideal candidate for UV-cross-linking.

Experimental Section

Materials and Instrumentation. Dichloromethane (Biosolve Ltd.) was distilled over potassium before use. EtOx (Aldrich) was distilled over barium oxide and stored under argon. SoyOx (donated by Henkel) was purified over aluminum oxide with hexane as eluent. After drying over BaO, it was stored under argon. Methyl tosylate (Aldrich) was distilled and stored under argon. The polymerizations were carried out in an Emrys Liberator (Biotage, formerly Personal Chemistry) utilizing capped reaction vials. These vials were heated to 105 °C, allowed to cool to room temperature, and filled with argon prior to use. All microwave polymerizations were performed with temperature control (IR sensor). ^{1}H NMR spectra were recorded on a Varian Gemini 300 spectrometer. Chemical shifts are given in ppm relative to TMS. Gel permeation chromatography (GPC) was measured on a Shimadzu system with a SCL-10A system controller, an LC-10AD pump, a RID-6A refractive index detector, and a PLgel 5-μm mixed-D column with chloroform/triethylamine/2-propanol (94:4:2) as eluent, and the column oven was set to 50 °C (polystyrene calibration). Atomic force microscopy (AFM) measurements were obtained in the tapping mode with a Veeco Nanoscope IV Multimode microscope operated in air. Both height and phase images were recorded simultaneously. Etched Si tips with a resonance frequency of approximately 170 kHz and a spring constant of 15 Nm^{-1} were used, and the scan rate was in the range of 1 to 2 Hz. Transmission electron microscopy (TEM) was performed on a Leo 922 microscope, operating at 200 kV accelerating voltage in bright field mode. Dynamic light scattering (DLS) measurements were performed on a Malvern CGS-3 apparatus equipped with a He−Ne laser with a wavelength λ of 633 nm. The temperature was controlled at 25 °C. The method of the cumulants was generally used to analyze DLS results, while size distribution histograms were obtained by the CONTIN method. The polydispersity index (PDI) of the micelles was estimated from the $\Gamma_2/\ \Gamma_1^2$ ratio in which Γ_1 and Γ_2 represent the first and second cumulant, respectively.

Synthesis. A solution of 2-ethyl-2-oxazoline (0.68 g, 6.9 mmol) and methyl tosylate (16.1 mg; 0.086 mmol) in acetonitrile (1.0 g, 1.27 mL) was stirred for 13.33 min at 140 °C under microwave irradiation. The polymerization mixture was cooled to 38 °C, and the 2-“soy alkyl”-2-oxazoline (0.60 g, 2.0 mmol) was added under an inert argon atmosphere. Subsequently, the polymerization was continued for 3.33 min at 140 °C in the microwave synthesizer. The polymerization was quenched by the addition of water. The resulting polymer was analyzed after drying in a vacuum oven and used without further purification. ^{1}H NMR (CDCl$_3$): δ 7.71 (d, J = 8.1 Hz, 2H, CHCS tosylate), 7.16 (d, J = 8.1 Hz, 2H, CHCCH$_3$ tosylate), 5.45−5.20 (br, 26H, HC=CH), 3.6−3.3 (br, 172H, NCH_2CH_2N), 2.75 (br, 11H, HC=CH), 2.45−2.20 (br, 93H, C=OCH_2), 2.08−1.95 (br, 32H, CH_2), 1.65−1.50 (br, 18H, CH_2), 1.38−1.20 (br, 170H, CH_2), 1.20−1.03 (br, 112H, C$H_{3,\mathrm{EtOx}}$), 0.90−0.82 (br, 27H, C$H_{3,\mathrm{SoyOx}}$). Composition was calculated using the backbone and CH$_{3,\mathrm{SoyOx}}$ signals: PEtOx$_{68}$−PSoyOx$_{18}$. GPC: M_n = 9100 Da, PDI = 1.19.

Preparation of the Micelles. Micelles were prepared by dissolving the PEtOx$_{68}$−PSoyOx$_{18}$ copolymer in acetone at a concentration of 1 g/L. Water was added dropwise to trigger micellization. Acetone was then eliminated by dialysis (Spectra-Por membranes with a MW cutoff of 6000−8000 g/mol). The concentration of the micelles in water was set to 0.02 g/L after the dialysis process. UV-cross-linking was performed by exposing the micellar solution to UV light (dose of 20 J/cm^2) under stirring. For transferring the micelles from water to acetone or from acetone to water, two different procedures were used: dialysis against the appropriate solvent (i) or freeze-drying followed by redissolution of the obtained powder in the appropriate solvent under ultrasound (ii). It was found that clustering of micelles was minimized whenever procedure (ii) was applied.

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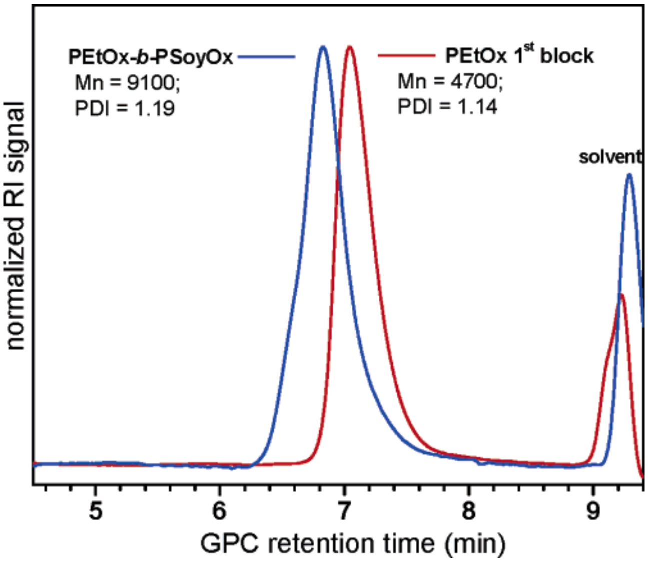

Figure 1. GPC traces for the $PEtOx_{68}$ first block and the final $PEtOx_{68}-PSoyOx_{18}$ block copolymer.

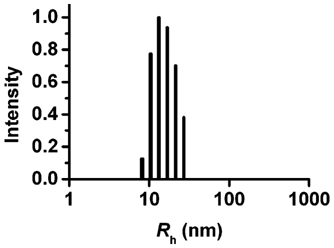

Figure 2. CONTIN size distribution histogram obtained before cross-linking for $PEtOx_{68}-PSoyOx_{18}$ micelles in water at a concentration of 0.02 g/L.

Scheme 1. Chemical Structure of the Investigated Poly(2-ethyl-2-oxazoline-*block*-2-“soy alkyl”-2-oxazoline) Copolymer

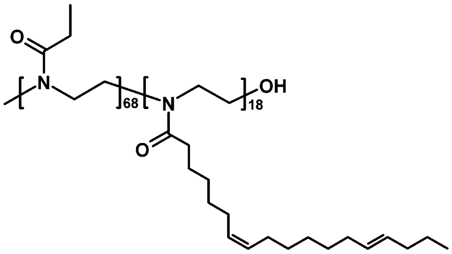

Table 1. Characteristic Features of the $PEtOx_{68}-PSoyOx_{18}$ Micelles as Measured by DLS and AFM

sample	*C* (g/l)	R_h (nm)[a]	PDI[b]	D_z (nm)[c]
a	0.02	13	0.057	5.2 ± 0.5
b	0.01	86	0.341	4.2 ± 0.8
c	0.003	102	0.158	12.1 ± 1.3
d	0.002	146	0.068	10.2 ± 0.8
e	0.001	118	0.289	12.4 ± 1.4

[a] R_h is the hydrodynamic radius of the micelles as measured by DLS. [b] PDI is the polydispersity index of the micelles as measured by DLS. [c] D_z is the diameter of the dried micelles in the *z*-direction (height) as measured by AFM.

Results and Discussion

Recently, the living cationic ring-opening polymerization of four differently substituted 2-oxazolines, namely 2-methyl-, 2-ethyl-, 2-nonyl-, and 2-phenyl-, was successfully performed in single-mode microwave reactors.[13,14] Due to the microwave irradiation, the polymerization was accelerated from several days to several minutes, which also allowed the easy preparation of block copolymer architectures via sequential copolymerization processes.[14] In this study, polymerizations were performed in CH_2Cl_2 at 140 °C under microwave irradiation. CH_2Cl_2 was used as solvent to ensure complete solubilization of the formed block copolymers. After polymerization of the first PEtOx block, the SoyOx monomer was added under argon followed by a second heating step to 140 °C. The resulting GPC traces clearly show that all polymer chains were chain-extended with SoyOx and that no “dead” PEtOx chains remained (Figure 1). In addition, ^1H NMR spectroscopy revealed that the double bonds of the SoyOx were unaffected by the cationic ring-opening polymerization. In the following, attention will be paid to the $PEtOx_{68}-PSoyOx_{18}$ sample, where the numbers in subscript represent the number-averaged degree of polymerization of the corresponding blocks. The polydispersity index of the investigated copolymer was 1.2, which is a reasonably low value. The chemical structure of this copolymer is depicted in Scheme 1.

Since it contains a major hydrophilic PEtOx block, the $PEtOx_{68}-PSoyOx_{18}$ sample is a good candidate for the formation of aqueous micelles. The bulk sample was, however, first dissolved in acetone at a concentration of 1 g/L, which is a good solvent for both blocks. DLS indeed confirmed that the copolymer chains were molecularly dissolved. Water was then added dropwise to trigger the micellization process. This procedure has the advantage to ensure an initial complete solubilization of the block copolymers as unimers and to erase any memory effect of the bulk structure.[3] Acetone was then gradually removed by dialysis against water. The micelles in pure water were characterized by DLS, AFM, and TEM. One single population of micelles with an average hydrodynamic radius of 13 nm was found by DLS (Figure 2 and Table 1). Spherical micelles were visualized by TEM and AFM for this sample (Table 1 and Figure 3). The $PSoyOx_{18}$ core-forming blocks were subsequently cross-linked by UV irradiation. The cross-linking step was performed under stirring, and the sample was exposed to different doses of UV light. An optimal dose of 20 J/cm^2 was found. Larger doses resulted in extensive intermicellar cross-linking as confirmed by the observation of a few larger objects in the AFM picture and by an important increase of the R_h in DLS. Some intermicellar cross-linking was observed even for the optimized UV dose of 20 J/cm^2, as indicated by the increase of the R_h from 13 to 86 nm (Table 1) and from the observation of a few clustered micelles in the corresponding TEM and AFM pictures. Lower UV doses resulted in inefficiently cross-linked micelles that could be redissolved as unimers in acetone. That intermicellar cross-linking is observed during UV irradiation strongly suggests that the initial uncross-linked micelles do experience chain exchange dynamics. As discussed in a recent article by Tenhu and co-workers, chain exchange between micelles could occur via two ways: insertion and expulsion of single chains and merging and splitting of micelles.[15] The observation of intermicellar cross-linking in the present study suggests that, at least, the

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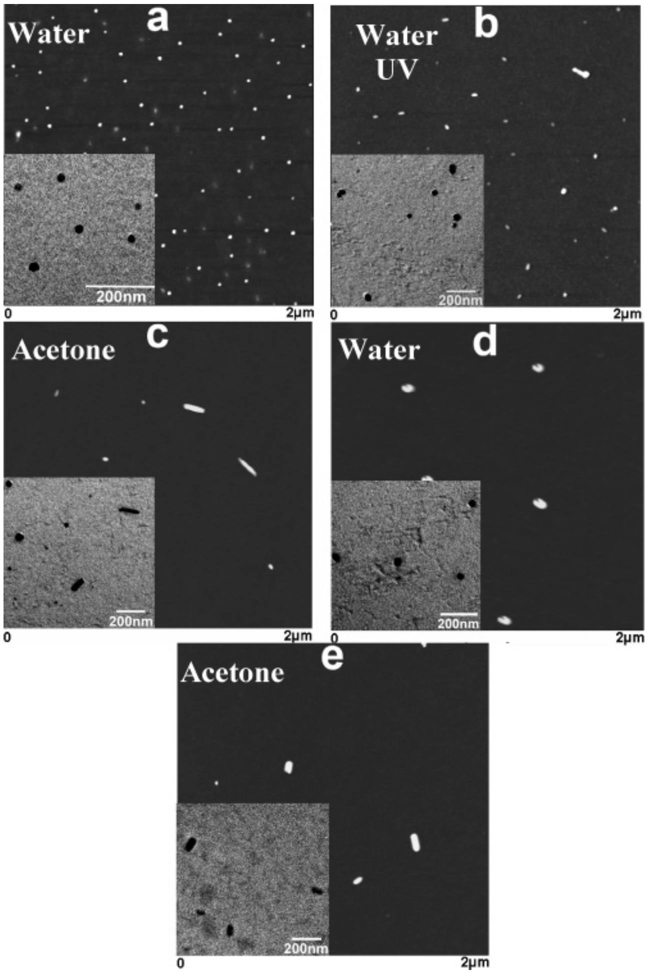
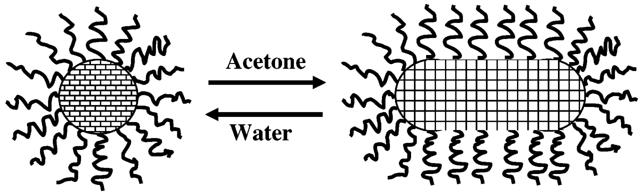


Figure 3. AFM (2 × 2 μm height contrast images) and TEM (inserted in the corresponding AFM pictures; the white scale bar represents 200 nm) images of $PEtOx_{68}-PSoyOx_{18}$ micelles initially prepared by addition of water to a solution of the unimers in acetone (a), solution a cross-linked in water (b), solution b freeze-dried and further dissolved in acetone (c), solution c dialyzed against water (d), and solution d freeze-dried and further dissolved in acetone (e).

Scheme 2. Representation of the Sphere to Rice Grain Morphological Transition



second mechanism is operative in our system. To validate the efficiency of the cross-linking process, the micelles (UV dose of 20 J/cm^2) were first freeze-dried and then redispersed in pure acetone. Micelles were now observed in acetone, confirming that the micellar structure initially formed in water was stabilized by the cross-linking process. Interestingly enough, TEM and AFM analysis of the cross-linked micelles in acetone revealed a different morphology. The micelles were no longer spherical but rather adopted a short rod shape, which has been referred to as rice grain morphology (Scheme 2). The formation of nonspherical micelles was also ascertained by DLS experiments in which the angular dependence of the apparent diffusion coefficient, D_{app}, was measured. The angle of measurement has been expressed as the square root of the scattering vector, q (Figure 4). In water, D_{app} is constant whatever the angle of observation, in agreement with a spherical morphology. In acetone, D_{app} increases with q^2, in agreement with the formation of nonspherical micelles with an elongated shape.[16] In some cases, more extended rodlike micelles were observed, but in any case, they were much shorter than the usually observed rodlike micelles.[17]

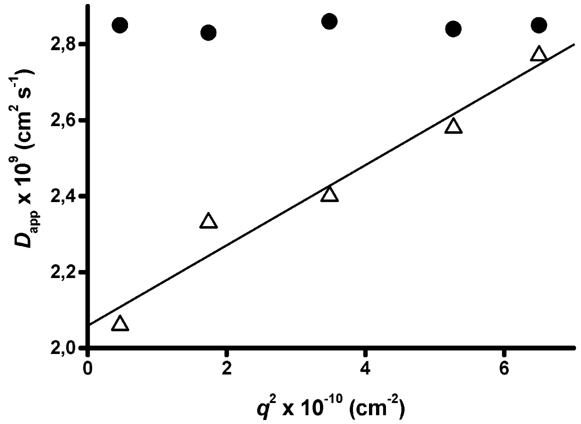


Figure 4. Angular dependence (q is the scattering vector) of the apparent diffusion coefficient, D_{app}, for the cross-linked spherical micelles of sample b in water (●) and of the rice grain micelles of sample c in acetone (△).

This morphological transition could be understood on the basis of the swelling of the $PSoyOx_{18}$ cross-linked core whenever the micelles are transferred into acetone. Indeed, swelling results in an increased volume for the cross-linked core. In case of a slightly cross-linked core, the $PSoyOx_{18}$ chains may experience sufficient mobility to trigger a morphological reorganization toward cylindrical micelles. It is indeed well-known that a spherical micellar morphology cannot accommodate indefinitely with a steadily increasing volume fraction of the core-forming chains for thermodynamic stability reasons.[4] At one critical point, the system should reorganize toward a cylindrical morphology to decrease its free energy. In the system under investigation (UV dose of 20 J/cm^2), we believe that the micellar core is cross-linked enough to keep the integrity of the micelles into acetone but still allows the core-forming chains to reorganize into a more stable cylindrical morphology. A careful examination of the TEM and AFM pictures revealed that some of the cross-linked micelles kept a spherical shape after their transfer into acetone. This is thought to result from a nonhomogeneous cross-linking among the initial micelles, which would then prevent the too-densely cross-linked micelles to reorganize into a rice grain morphology.

Because intermicellar chain exchange is prevented among cross-linked micelles, the morphological transformation would not lead to extended rods but would be rather limited to a single micelle or to the merging of a few micelles, as shown by the AFM and DLS results. The diameter of the $PSoyOx_{18}$ core for the rice grain micelles in acetone (10.2 nm as measured by

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AFM) is twice the diameter of the initial cross-linked spherical micelles in water, in agreement with swollen micelles.

Interestingly enough, the spheres to rice grains morphological transformation appears to be reversible. This has been ascertained by transferring the rice grain micelles from acetone to water by a dialysis process (Figure 3c). The micelles in water were then again observed as spherical objects (Figure 3d). DLS, however, indicates that most of these micelles aggregate into larger clusters. This could be accounted for by a lack of colloidal stability of the micelles in aqueous medium, which tend to aggregate. These clusters were observed in the corresponding AFM and TEM pictures (Figure 3d). In the last step, the latter micelles have been freeze-dried and redispersed in acetone. Rice grain micelles were again observed (Figure 3e). The size of the rice grain micelles (Figure 3e) is similar to the one previously observed (Figure 3c). This indicates that the formation of aggregates of micelles is not favored in acetone, in contrast to the situation observed in water. The micellar characteristic features, as measured by DLS (R_h) and AFM (D_z, diameter of the micelles measured in the z-direction), are systematically listed in Table 1 for all the investigated samples (i.e., from step a to step e). The lateral diameter D_{xy} as measured by AFM is believed to be affected by tip-convolution effects and certainly does not indicate the real size of the micelles in the dried state, which is why it has not been discussed in this article. The a to e sequence was repeated on another batch of $PEtOx_{68}$−$PSoyOx_{18}$ micelles, and essentially the same results were obtained. Finally, it should be noted that no sphere to rice grain morphological transition was observed for the highly cross-linked micelles (UV doses higher than 20 J/cm^2), although data analysis was difficult due to the presence of large supermicellar aggregates.

Conclusions

Microwave-assisted polymerization conditions were successfully used to synthesize PEtOx−PSoyOx amphiphilic block copolymers. Spherical aqueous micelles have been prepared from these copolymers whose cores have been slightly cross-linked by UV irradiation. These micelles have been transferred into a nonselective solvent, acetone, while keeping their integrity thanks to the cross-linking process. The core of the micelles in acetone is swollen, and a reversible morphological transition toward rice grain micelles is observed. As a further development, this micellar core swelling-induced morphological transition could be used to encapsulate and/or release molecules of interest. Other applications could also be envisaged in the field of self-assembled soft materials where our system could be used as a stimuli-sensitive templating medium or for the creation of smart surfaces.

Acknowledgment. H.H., A.M.J., and J.-F.G. thank the “Fondation Louvain” (mécénat Solvay) and the STIPOMAT ESF Program. R.H., M.A.M., and U.S.S. thank the Dutch Scientific Organization (NWO), the DPI, and the Fonds der Chemischen Industrie for financial support. Henkel is acknowledged for providing the SoyOx monomer.

JA057762K