Polymerization in Surfactant Liquid Crystalline Phases

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We report the formation of cross-linked polysiloxane particles having rodlike and sheetlike morphologies by condensation of monomers in organized liquid crystalline mesophases of nonionic surfactants. The characteristic diffraction pattern obtained from the liquid crystalline surfactant assembly is preserved during polymer synthesis. The polymer colloids are rodlike when synthesized in a hexagonal mesophase and are sheetlike when synthesized in a lamellar mesophase. Interestingly, the size of the polymer particles is on the order of micrometers, viz. 3 orders of magnitude larger than the characteristic size of the surfactant mesophase. Thus, the polymers phase separate from the liquid crystalline phase during polymerization, and organize to resemble the mesophase geometry. The polymer particles are organized so as to minimize the elastic distortion of the surfactant mesophase after they phase separate. We speculate that the observed particle morphologies are formed due to the slow kinetics of polycondensation under our experimental conditions.

Introduction

Surfactants self-assemble into a variety of nanostructured "soft" organic phases[1] that can be exploited as structural motifs for spatial templating. Synthesis in the presence of surfactants can result in either a mesoporous material with a pore structure templated by the surfactant assembly, or in surfactant-directed formation of nanofibers or nanosheets. For example, the use of surfactants as structure-directing agents in the synthesis of zeolites has led to the development of inorganic matrixes with precisely engineered pore structures that are defined by the surfactant.[2] During the synthesis of these zeolites, silicate species condense around surfactant micelles and co-assemble to form surfactant−inorganic hybrids. Surfactant solutions have also been shown to direct the formation of silver[3] or gold[4,5] nanorods by reduction of their salt solutions. Recently, there have been reports of concentrated microemulsions,[6] or liquid crystalline gel phases of surfactants[7−11] or block copolymers[12,13] (high molecular weight analogues of surfactants) being replicated by dielec-

tric, metallic, or semiconducting solids. Since surfactants can assemble into hexagonal, lamellar, or spongelike liquid crystalline mesophases depending on the chosen molecule and the conditions of assembly, it is especially interesting to examine the possibility of using such mesophases as templates. Such template-directed synthesis might also be relevant for biomimetic schemes as phospholipid surfactant phases are commonly observed in nature and might be used for localization in biotransformations.[14]

Although replication of surfactant templates by metallic or inorganic solids has been demonstrated by several groups, replication by polymers remains challenging. The main difficulty during replication of the structure of surfactant assemblies is to preserve the organization of the surfactant molecules. The radius of gyration of polymers is comparable to the characteristic dimension of the surfactant mesophase, typically on the order of $1-10$ nm. Therefore, as monomer is converted to polymer, surfactant ordering is disrupted or the polymer separates from the surfactant mesophase to avoid the loss of conformational entropy from confinement[15] in the organized structure. This tendency to phase separate is often aggravated by the enthalpic penalty for the polymer to stay solvated in the surfactant. Therefore, when surfactant lyotropic phases were used as polymerization media to prepare gels,[16−22] the polymer phase separated during

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synthesis and these gels did not replicate the structure of the template. In some cases,[21,22] the gels comprised sheets formed from cross-linked polymer particles that were organized by the hexagonal surfactant mesophase. Several groups[23–26] have also attempted to polymerize monomers within bilayers of surfactant vesicles. Except in the case when equilibrium catanionic vesicles were used[26] as templates, this synthetic scheme leads to phase separation of the polymer as was reported in one detailed investigation.[27] Recently, Huang et al.[28] and Hulvat and Stupp[29] have reported electropolymerization of conductive monomers localized in surfactant hexagonal liquid crystalline phases to form polymeric nanowires. The nanowire diameter in these is around 100 nm[28] suggesting that the template is not directly replicated, but this aspect was not examined in detail. Moriguchi et al.[30] has reported the polymerization of a phenol−formaldehyde thermoset in the continuous phase of a surfactant hexagonal liquid crystalline phase, where the polymer precisely replicated the surfactant template. In another instance, Faul et al. have claimed some degree of success in replicating the template structure when polymerizing monomers in mechanically stable ordered phases formed by precipitation of polyelectrolyte−surfactant complexes.[31] These reports[30,31] are remarkable as the polymers form exact replicas of the templates and preserve the order in the liquid crystalline matrix phase.

Here, we report an unusual example of synthesis in surfactant liquid crystalline phases where the polymer particles are formed with the geometry of the mesophase but are micrometers in size (rather than nanometers, characteristic of the template). We chose nonionic C_nE_m surfactants for our templates—these are readily available and well characterized systems[1] that form hexagonal, lamellar, cubic, and the corresponding reverse phases in water, by appropriate choice of surfactant concentration and block lengths (n,m). Further, mixtures of C_nE_m surfactants give phase behavior that is characteristic of the molecular volume averaged "n" and "m";[32] thus, the desired phase can be obtained by suitable mixtures of available surfactants.

We have synthesized polysiloxanes by polycondensation of alkoxysilane monomers loaded into surfactant hexagonal or lamellar mesophases. While most researchers[16–26,31] have attempted free radical polymerizations in surfactant mesophases, the group of Schmidt[33–36] has reported the formation of monodisperse organosilicon nanoparticles or micronetworks of such nanoparticles using base-catalyzed polycondensation of alkoxysilane monomers in microemulsions of benzethonium chloride. Hydrolysis and condensation of alkoxy silanes to form polysiloxanes can be catalyzed by either acid or base[37–39] and the rate of condensation is strongly pH-dependent. Here, we examine the synthesis products obtained from *acid-catalyzed condensation* of dimethyldimethoxysilane, DMS (cross-linked by co-condensation with methyltrimethoxysilane, TMS) in hexagonal and lamellar phases of C_nE_m surfactants.

Experimental Section

Nonaethylene glycol monododecyl ether ($C_{12}E_9$) was obtained from Sigma. Polyoxyethylene(2) oleyl ether ($C_{18}E_2$) and polyoxyethylene(10) oleyl ether ($C_{18}E_{10}$) were obtained from Aldrich and mixed[32] in equal parts by weight to prepare $C_{18}E_6$. C_nE_m surfactants are prepared by ethoxylating fatty alcohols—HPLC (see Supporting Information) reveals that these materials comprise mixtures, viz. the "n" and "m" specified are averages. Dimethoxydimethylsilane (DMS, purity 99.5%) and methyltrimethoxysilane (TMS, purity 98%) were obtained from Aldrich. All chemicals were used without further purification. Distilled deionized water (resistivity = 18.2 MΩ-cm) from a Millipore Milli-Q system was used for all experiments.

We prepared the hexagonal phase by using a 50 wt % concentration of $C_{12}E_9$ in water, while the lamellar phase was prepared with 70 wt % of $C_{18}E_6$ in water. These liquid crystalline phases are gels that show a high viscosity and yield behavior.

Polymerization in the liquid crystalline gel phases was effected by adding the appropriate quantity of monomers to the surfactant in a clean glass vial, followed by addition of acidified water and vortexing for about a minute. In all our experiments, condensation was acid catalyzed using sulfuric acid (concentration from 0.01 to 0.5 M, having a pH of around 0.4 to 2). For example, polysiloxane rods were prepared in the hexagonal phase by adding 32 μL of DMS and 8 μL of TMS using a micropipet to 230 μL of $C_{12}E_9$ (total volume fraction of silane = 8%). This was vortexed for a minute after which 230 μL of acidified water (0.2 M sulfuric acid) was added to the mixture and vortexed until it was homogenized. The whole mass became transparent and highly viscous with few small bubbles in solution. This was then stored at room temperature.

The liquid crystalline gels were characterized using polarized optical microscope (Olympus-BX50) and small-angle X-ray scattering (Rigaku X-ray diffractometer, D-MAX-2500 using Ni-filtered

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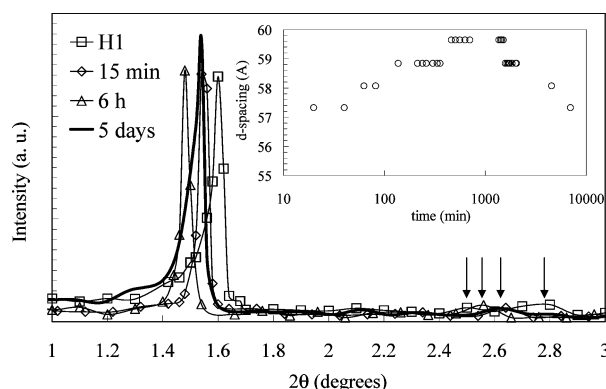(39) Deverux, F.; Boilot, J. P.; Chaput, F.; Lecomte, A. *Phys. Rev. A* **1990**, *41*, 6901.

Figure 1. Small-angle X-ray scattering from the hexagonal phase of $C_{12}E_9$ loaded with 4:1 DMS/TMS monomer as a function of time. The neat hexagonal phase is shown for reference (squares), and spectra are recorded 15 min (diamonds), 6 h (triangles), and 5 days (dark line) after monomer addition. All the scattering curves show a second-order peak at a *d* spacing that is $1/\sqrt{3}$ times the primary peak, characteristic of hexagonal ordering in the system. The small peak at $2\theta \approx 1.7°$ for the neat hexagonal phase might be attributed to the presence of a small fraction of impurities in the surfactant; we are unable to identify the origin of this peak unambiguously. The inset shows the variation with *d* spacing as a function of time on a linear-log scale.

Cu Kα radiation). Samples were prepared for SEM (Leica-S-440, accelerating voltage of 20 kV) by separating the polysiloxane particles from the surfactant gel by dispersing in ethanol. For TEM, the gel was dispersed in ethanol, and further cross-linking was terminated by addition of a large excess of trimethylmethoxy silane. This solution was used to spot the TEM grids. We used a JEOL1200-EX at an accelerating voltage of 80 kV.

FTIR measurements were made using a Perkin-Elmer 16-PC FT-IR. For the model experiments described in this paper, 1 mL of dodecane was mixed with 1 mL of acidified water (0.2 M sulfuric acid) in a vial and 150 μL of DMS was added to this. Samples (20 μL) of the top (dodecane) layer were withdrawn as a function of time for IR measurements made using standard KBr cells.

Results and Discussion

Addition of a mixture of DMS and TMS in a ratio of 4:1 by volume to the hexagonal phase of $C_{12}E_9$ leads to an increase in the *d* spacing in the X-ray diffraction pattern (Figure 1). Up to 8% (by volume) of the monomers can be added before the hexagonal phase becomes unstable and transforms into the oily micellar phase (see Supporting Information). As the aqueous phase in the surfactant mixture contains 0.2 M sulfuric acid, the monomers rapidly undergo acid-catalyzed hydrolysis. During hydrolysis, the surfactant-to-water ratio changes as water is "consumed" and methanol is formed. The swelling of the hexagonal mesophase observed by XRD is due to partitioning of the hydrolyzed monomers and methanol between the hydrophobic and hydrophilic regions of the assembly[40] and due to the change in surfactant/water ratio. With time, as the hydrolyzed

(40) The partitioning of methanol, DMS, and TMS between the hydrophobic core and the surrounding hydrophilic region of the surfactant assembly is one of the factors determining the *d* spacing. After hydrolysis, DMS and TMS partition differently. As the fraction of TMS to DMS in the added monomer is increased, the *d* spacing immediately after monomer addition is decreased. When only TMS is added, the *d* spacing decreases below that for the neat hexagonal phase. We will discuss this in detail in a subsequent publication; Wadekar, M.; Kumaraswamy, G.; et al. (in preparation).
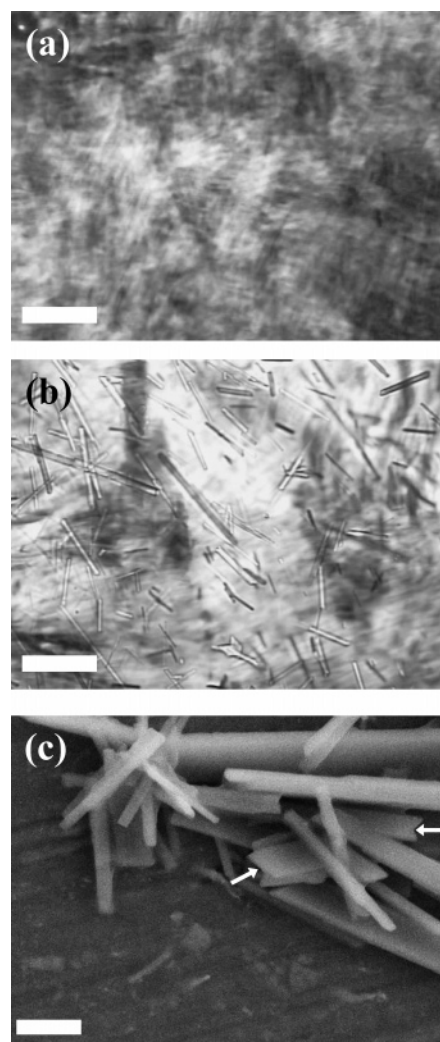

Figure 2. Polarized optical micrographs of (a) the neat hexagonal phase showing the characteristic liquid crystalline texture and (b) polysiloxane rods formed in the hexagonal phase. The liquid crystalline texture is apparent in the gel phase in the background in (b). The scale bars on the optical micrographs correspond to 50 μm. The last micrograph (c) shows an SEM image of polysiloxane rods synthesized in the hexagonal phase, formed after about 5 days from monomer addition. The scale bar corresponds to 6 μm. The white arrows indicate particles that are not rodlike.

monomers condense to form polysiloxanes, the *d* spacing first increases over a period of several hours, and then decreases over the next few days. The final *d* spacing is slightly higher than that immediately after monomer addition (Figure 1, inset). However, the XRD pattern always remains characteristic of a hexagonal phase and there is no significant decrease in the intensity of the scattering peak (Figure 1).

After 4−5 days, observation of the gel under an optical microscope reveals the presence of large rodlike polymer particles dispersed in the liquid crystalline surfactant phase (Figure 2b). The characteristic liquid crystalline texture[41] of the hexagonal phase is preserved and can be observed in the background, around the polymer particles (Figure 2a and b). On heating this sample above the clearing temperature

(41) The liquid crystalline mesophases formed in our experiments are high viscosity gels. Under the conditions of preparation, kinetic constraints prevent the formation of well-defined fan shaped textures characteristic of the hexagonal phase. However, the grainy textures observed in our micrographs compare well with literature reports—for example, Figure 2 in ref 22.
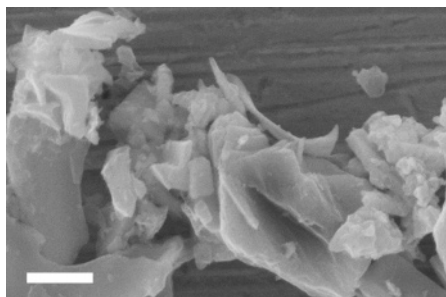
Figure 3. SEM of polysiloxane sheets synthesized in the lamellar phase of the $C_{18}E_6$ surfactant system. The scale bar corresponds to 5 μm.

of the hexagonal phase (around 40 °C), the liquid crystalline texture disappears and only the rodlike particles are visible under the microscope (see Supporting Information). We are unable to comment on the orientation of the rods in the gel as this might have been disturbed while transferring the sample from the vial to the microscope slide. The rodlike particles can be separated from the surfactant phase by repeated cycles of washing. FTIR of these particles confirm that they are composed of polysiloxane (see Supporting Information). The rods preserve their shape even after separation due to the cross-linking of the poly(dimethylsiloxane) by the TMS.

It is worth noting that rodlike particles are observed even when we condense neat DMS (with no TMS to cross-link) in the hexagonal phase (data not shown). Here too, the XRD *d* spacing shows the same behavior with time—first increasing when the monomer is added and then decreasing on condensation. However, addition of the cross-linker (TMS) is essential for the rods to retain their shape after separation from the gel. The rodlike particles formed by condensation of neat DMS collapse and lose their shape when they are transferred to a microscope slide after washing away the surfactant with methanol. Only when TMS is added do the particles retain their shape after the surfactant mesophase is washed away.

SEM shows that these rods are polydisperse with diameters up to 25 μm (the lowest diameter that we observed was 0.8 μm) and with lengths of up to 200 μm (Figure 2c). We also observe a few particles that are not rodlike (arrows in Figure 2c). The formation of irregularly shaped particles is a function of the ratio of DMS to TMS—with an increase in the fraction of TMS there is a higher incidence of irregular particles. At a DMS/TMS ratio of 100:1, the particles formed are almost exclusively rodlike, while for DMS/TMS ratios less than 1:4, we observe only irregular shapes in the optical micrographs rather than rods.

When we attempted synthesis of cross-linked polysiloxanes in a lamellar phase of $C_{18}E_6$, we observed behavior that is similar to that in the hexagonal phase: the lamellar phase is stable when swollen with up to 5% (by volume) of the 4:1 DMS/TMS monomer, and preserves the liquid crystalline phase while showing a decrease in the *d* spacing as condensation proceeds. SEM of the particles formed after 5 days shows polymeric sheets that are a few micrometers thick (Figure 3). Thus, the cross-linked polymer particles formed in both the hexagonal and lamellar matrixes have the same geometry as that of the parent mesophase.
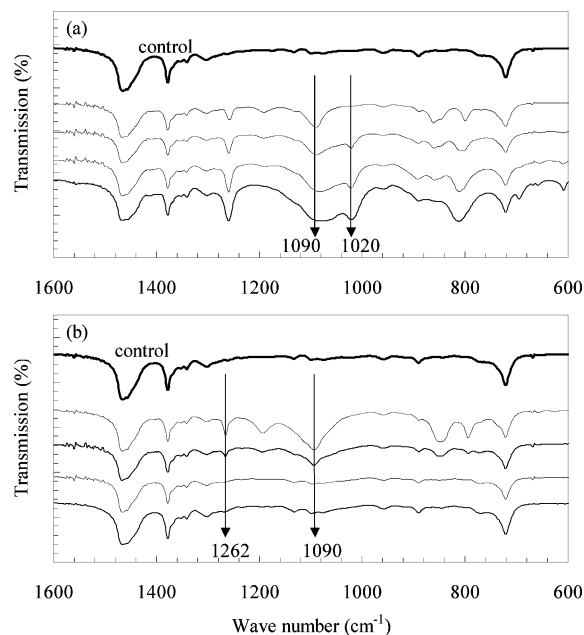

Figure 4. FTIR of the dodecane "oil" phase at various times after addition of (a) DMS and (b) TMS monomer. Spectra are shifted vertically for clarity and the dark control at the top is neat dodecane. Spectra from the top down are taken at intervals of 1 min, 30 min, 210 min, and 2 days in (a), and 1 min, 30 min, 120 min, and 2 days in (b).

The mechanism for the formation of the polymer particles is influenced by the localization of DMS and TMS in the liquid crystalline mesophase during hydrolysis and condensation. As this is difficult to investigate in the surfactant matrix, we used a model system and examined the hydrolysis and condensation of DMS (and of TMS in a separate experiment) in a dodecane/acidified water system, where the aqueous phase contains 0.2 M sulfuric acid. As the oil−water phases are immiscible, we sample the oil phase at regular intervals and use the FTIR signal from the asymmetric Si−O−Si bond stretch at a wavenumber of 1090 cm^{-1} to track the DMS or the TMS. Upon addition to the oil−water system, the DMS is initially confined to the oil phase (Figure 4a). As the DMS gets hydrolyzed and condensed, a broad doublet with peaks at 1090 and 1020 cm^{-1} grows. This corresponds to Si−O−Si stretching in molecules with more than 20 coupled siloxane units.[42] This suggests that the polymer formed by condensation remains in the oil phase (Figure 4a). TMS too is initially confined to the oil phase immediately after addition to the oil−water system (Figure 4b). However, in this case the peaks at 1090 cm^{-1} and at 1262 cm^{-1} (corresponding to the symmetrical methyl deformation) decrease in intensity with time. This indicates that as the TMS hydrolyzes and condenses to form a cross-linked polysiloxane, it moves out of the oil phase (Figure 4b). We can visually observe that the water phase becomes cloudy with time as the TMS hydrolyzes, moves into the water phase, and starts condensing (see Supporting Information). After several hours, the TMS cross-links to form a film that

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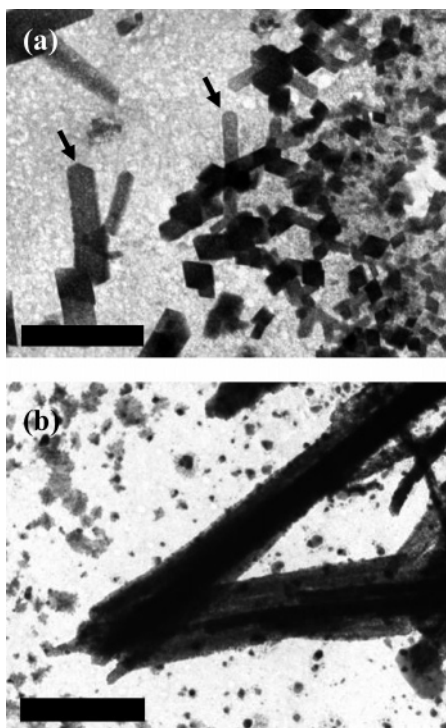
Figure 5. TEM of the polysiloxane particles extracted from the hexagonal gel phase 5 days after addition of 4:1 DMS/TMS monomer: (a) and (b) are images taken from different areas of the TEM grid and at different magnifications; the scale bars represent 500 nm in (a) and 1 μm in (b). We observe geometrically regular particles that are polydisperse in size in (a). The arrows indicate a few elongated objects. Two large elongated objects that appear to be formed by linking several elongated polysiloxane rods to form bundles are shown in (b).

Figure 6. Schematic of our proposed scheme for the formation of cross-linked polysiloxane particles that replicate the liquid crystalline gel templates. The filled circles represent DMS or hydrolyzed DMS, and the open triangles represent TMS or hydrolyzed TMS. The shaded area indicates the hydrophobic domains in the surfactant assembly that are separated by surfactants (not indicated) from the hydrophilic domains (in white). The arrows indicate progression with time. The spatial size of the cross-linked polysiloxane at the final stage extends beyond the figure to a size scale that is much larger than that of the surfactant mesophase.

is localized at the interface of water and dodecane. Although we cannot do FTIR in the aqueous phase, we can isolate the cross-linked TMS film and examine it. The film shows IR absorbances at 1035 cm^{-1} and 1118 cm^{-1} indicating the formation of an open chain siloxane network structure[42] (see Supporting Information). It is not possible to use FTIR to track DMS and TMS individually in similar experiments on monomer mixtures. For 4:1 DMS/TMS mixtures, FTIR of the oil phase shows a signature for polysiloxane (data not shown). However, in comparison to the experiment with neat DMS where only low molecular weight oligomeric products are formed, the polysiloxane formed with a mixture of DMS/TMS monomers is cross-linked and precipitates on addition of a small amount of nonsolvent acetone. This indicates that TMS is incorporated with DMS during condensation.

Further insight into the mechanism of formation of the polymer particles comes from TEM images of samples taken from the hexagonal gel 3 days after the addition of DMS/TMS monomer. While this sample already shows micrometer-sized rods in optical micrographs, TEM reveals the presence at the same time of particles that are tens of nanometers in size (Figure 5a). The particles observed in the TEM are geometrically regular and very polydisperse in size. We do not understand the reasons for this geometrical regularity. We also observe elongated structures (arrow in Figure 5a) and aggregates of these elongated structures (Figure 5b). It is possible (Figure 5b) that the elongated structures form by linking-up the smaller geometrically regular units. Electron diffraction from either the geometrically regular units or from
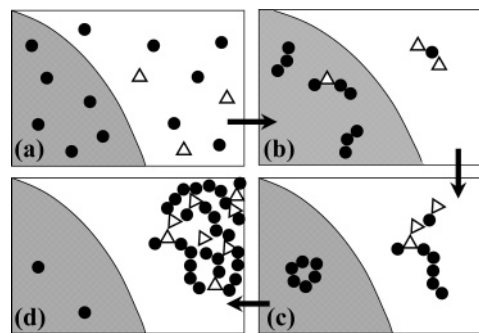
the elongated structures shows no crystalline ordering, as is expected. We are unable to probe low enough diffraction angles using this technique to determine whether the original ordering in the liquid crystalline surfactant template is preserved in these structures, but feel that this is unlikely.

The postulated mechanism for formation of the polysiloxane particles is summarized in Figure 6. The monomers are hydrolyzed as soon as they are added to the hexagonal/lamellar phase, and there is an increase in the d spacing of the surfactant assembly as it swells (Figure 6a). The monomers then condense over a period of several hours: during condensation, the DMS is cross-linked by the TMS and forms oligo- and polysiloxanes that are localized in the hydrophobic regions of the surfactant assembly (Figure 6b). Thus, the d spacing is further increased (Figure 6b). Gradually, as the molecular weight increases, the polymers phase separate from the surfactant mesophase (Figure 6c). As a function of time, the particles increase in size (and molecular weight) by cross-linking via the TMS units with other monomers and small particles ("accretion"). During condensation of the DMS/TMS mixtures, the polysiloxanes formed are not linear molecules, but might comprise cross-linked cyclics or other nonlinear architectures.[43] Eventually, the particles grow to a size that leads to significant elastic distortion of the liquid crystalline phase (Figure 6d). Further growth of the particles by accretion is directed by the liquid crystalline field and the particles grow anisotropically as suggested by the TEM images. In the case of the hexagonal phase they form rodlike objects, whereas in the case of the lamellar phase they form sheets.

(43) Condensation of neat DMS (with no added TMS) under the conditions adopted in our study does not lead to the formation of high molecular weight polymers, unlike the case reported by Schmidt et al.[33−36] In control experiments where we condensed the DMS in acidic aqueous solution, the oily product obtained comprised low molecular weight oligomers and did not show the presence of high molecular weight polymers in gel permeation chromatography. Further, extraction of the product from condensation of neat DMS in a hexagonal surfactant mesophase did not show the formation of high molecular weight polymers. This accords with the literature[37,47] on acid-catalyzsed condensation of alkoxysilane monomers and indicates that condensation of DMS leads to the formation of oligomeric or low molecular weight cyclic products. However, cross-linked products that readily precipitate in nonsolvent acetone are formed when a mixture of DMS and TMS are co-condensed.

When colloidal particles are dispersed in nematics, they are arranged so as to minimize the elastic penalty for distortion of the liquid crystalline phase. The elastic fields around the colloidal inclusions interact and align the particles into rows.[44,45] For free-radical polymerization in a hexagonal mesophase, these rows have been observed to cross-link to form sheetlike structures with a grainy, particulate texture.[22] In lamellar or smectic phases, theory predicts[44,46] that dispersed colloidal particles would gel into disordered networks, and this has been observed for the particles formed by free-radical polymerization in lamellar mesophases.[22] However, in our investigations, we observe that the particles are organized into geometries typical of the parent liquid crystalline phase.

What is the reason that the particles in our investigation organize into the same geometry as that of the surfactant mesophases while previous studies[16−22] using free radical polymerizations did not? We speculate that this might be due to the following reasons. First, we employ *polycondensation* to synthesize polymers in our experiments. In polycondensation, the molecular weight builds up slowly in the initial stages of the reaction, and high molecular weight species are formed only at high conversions. Further, in our experiments, the siloxane species condense at a pH that is near the isoelectric point of silica where the condensation kinetics of alkoxy silanes is slowest.[47] Therefore, the large polymer colloids observed in our experiments form by slow accretion of smaller particles over a period of days. Polymer particles obtained by condensation of monomers at significantly different pH, outside the range used here (more acidic, or basic, where condensation rates are rapid relative to near the isoelectric point) are irregular and do not replicate the geometry of either hexagonal or lamellar templates. Therefore, while polymer morphologies formed by free-radical polymerization accord with theories of particle organization in liquid crystalline phases, it is possible that the growth of polysiloxane particles in our experiments might necessitate a different explanation.

Conclusions

We have synthesized cross-linked polysiloxane particles by condensing dimethyldimethoxysilane and cross-linker trimethoxymethylsilane in lyotropic surfactant mesophases of nonionic C_nE_m surfactants. Under conditions that allow slow condensation of the polysiloxanes, the polymer particles formed have a geometry similar to that of the surfactant mesophase, viz. rodlike particles are formed in a hexagonal mesophase while sheetlike particles are formed in a lamellar phase. This has not been previously observed in investigations where free radical polymerization was used to prepare polymer colloids in surfactant mesophases. The polymer particles formed in our experiments are several micrometers in size, orders of magnitude larger than the characteristic repeat spacing in a surfactant mesophase. Rodlike or sheetlike morphologies are formed as the polymer particles phase separate from the mesophase, are organized by the liquid crystalline mesophase and cross-linked. We speculate that slow condensation and cross-linking kinetics, gradual build-up of molecular weight, and the nonlinear architecture of the polysiloxane molecules might allow the dynamic organization of the particles by the liquid crystalline mesophase, leading to the formation of the observed particle geometries.

Supporting Information Available: Experimental details, including characterization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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