Cross-Linking of Reactive Lyotropic Liquid Crystals for Nanostructure Retention

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In applications requiring nanoscale order, control over the structure formation is critical for appropriate function. Reactive surfactants forming reactive lyotropic liquid crystals (LLC) enable the formation of nanotructured polymers that exhibit enhanced physical properties when the original order is retained after polymerization. In this work, the use of a cross-linker to retain the LLC order for a monomethacrylate quaternary ammonium surfactant monomer in water during polymerization was explored. The cross-linker segregates to the polar regions of the surfactant assembly, likely near the quaternary ammonium group of the reactive surfactant. The use of a cross-linker enables the retention of the original LLC order after polymerization for hexagonal LLC phases that are not retained by other means. Increased polymerization rates are observed at low cross-linker concentrations. At higher cross-linker concentrations, the polymerization rates decrease because of a decrease in LLC order. More regular ordered morphologies are observed for systems that retain the hexagonal LLC order during polymerization. The resulting LLC order is also present after drying and swelling the polymer in water, therefore producing a polymer with robust LLC order. Enhancements in water uptake were also observed for polymers that retain the original order through cross-linking compared to systems that exhibit change in order. This behavior is directly related to the retention of the original LLC order.

Introduction

Generation of organic nanostructured materials has been of great interest recently because of great potential in applications such as separations, DNA delivery, tissue engineering, and catalysis.[1−4] Important in the ultimate properties of these materials is the rate of reaction and the conditions in which the reaction occurs. The reaction behavior is dependent on the order present in the system and the chemistry employed for synthesis.[5−8] Much of the work on producing organic nanostructured materials has focused on using polymeric templated systems.[9−12] The primary goals of templating polymer systems include control over polymer structure and reaction behavior in pursuit of functionally advanced materials that are not available through traditional bulk reactions.[9] Several systems have been explored for the creation of these materials such as catalytic polymerization, particles, and molecular imprinting.[13−16] Surfactant-based systems such as vesicles and lyotropic liquid crystals (LLCs) have also been widely studied.[17−19] The use of LLCs as templates has been examined because of the variety of potential structures that can be obtained.

Lyotropic liquid crystals (LLCs) exhibit periodic nanostructures that are dependent on concentration and temperature.[20] A variety of morphologies, ranging from micelles that form at low concentrations of surfactant in polar solvent to hexagonal and lamellar LLC phases at higher concentrations, can be formed. Other phases based on cubic lattice structures may also be observed at intermediate amphiphile concentrations.[21] Because of the high degree of positional and orientational order, polymerization conducted within

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these anisotropic systems may produce polymers with properties that cannot be achieved using the traditional bulk or solution polymerization. Recent work has shown that polymerization of poly(ethylene glycol) diacrylate (PEGDA) in lyotropic liquid crystals formed by a polyoxyethylene (10) cetyl ether (Brij 56) surfactant/water system creates a cross-linked polymer with controllable physical properties that exhibit a 3-fold increase in mechanical strength and diffusive transport compared to nontemplated systems.[22] Similar enhancement in swelling and permeability were obtained when templating a biodegradable monomer in LLC phases formed by using Brij 56.[23] Recent studies have also demonstrated that polymerization kinetics, the type of surfactant, and monomer segregation behavior have a significant role in the LLC templating process.[24−27] Although some of these studies demonstrate polymeric materials that resemble the original template, other studies show polymer morphologies that are much different from the original LLC. These differences arise as the interfacial energy of water and distribution effects induce phase separation of the growing polymer chain and surfactant.[28,29] Because the morphology of the organic polymer has a direct effect on the functionality of these materials, control of the polymer structure after polymerization has been a key objective of research in this area.

Nanostructured organic polymers have been created by the use of reactive thermotropic and lyotropic liquid crystals. For example, Broer and co-workers synthesized thermotropic liquid crystalline acrylate monomers where the order was preserved by in situ photopolymerization.[30,31]They demonstrated that the anisiotropic optical properties exhibited by the resulting liquid crystalline polymer can be varied through monomer structure design such as spacer length and substituents. Polymerization conditions also play a significant role.[31] The use of reactive surfactants that form reactive LLCs has been explored. Reactive LLCs have the advantage that the same surfactant forming the LLC structure is the monomer as well, therefore decreasing phase separation between the monomer and surfactant often observed in templated LLC systems. Several systems have shown retention of the original LLC order after polymerization. Gin and co-workers synthesized a series of sodium salts of styrene ether-modified fatty acids that form cross-linkable inverted hexagonal (H_{II}) phases in which the original order is preserved after polymerization.[32] They also synthesized triacrylate ionic surfactant monomers forming the H_{II} phase in which the dimensions can be varied just by changing the nature of the counterion.[33,34] Retention of the LLC order after polymerization was observed for the resulting cross-linked polymer. Columnar hexagonal phases of imidazolium and tris(alkoxy)phenyl moieties containing acrylate polymerizable groups have also been synthesized with retention of order after photopolymerization.[35] The resulting transparent polymer film exhibits anisotropic ion conductive properties that are dependent on the orientation of columns. These results suggest that the properties of these polymers are related to the nanostructure of the resultant polymer which is dependent on the surfactant monomer design and polymerization conditions.

As with templated LLC systems, the polymerization of reactive LLCs often results in organic nanostructures that are not thermodynamically stable which makes the structure difficult to retain and control during polymerization.[36] Previous research shows that the position of the polymerizable group, the aliphatic tail length, and temperature all have an effect in the structural evolution of reactive amphiphilic systems.[36−38] Recent studies in reactive LLCs formed by monomethacrylate quaternary ammonium surfactant monomers in water demonstrate that more ordered lamellar phases in which higher polymerization rates are exhibited are retained after polymerization, whereas the hexagonal phases are not retained.[36] The high speed of reaction associated with the lamellar phase seems to enable the “entrapment” of the LLC structure after polymerization, whereas the lower speed of reaction associated with the hexagonal phases enable the nanostructure to rearrange into a more stable structural conformation. Also, for polymerization in the hexagonal phases, increasing the nonpolar tail length of the reactive surfactant phase decreases the order of the system, forming a less-ordered polymer after polymerization. Although order seems to be an important factor in LLC structural development, most of the reactive systems that demonstrate structure retention are multifunctional surfactant monomers that create a cross-linked LLC polymer network. On this basis, it is reasonable to believe that introducing a cross-linking agent into the reactive LLC system would aid in the nanostructure retention. The goal of the present work is to systematically study the influence of cross-linking on the structure retention of monofunctional reactive LLCs. The hexagonal phases formed from these monofunctional quaternary ammonium surfactant monomers do not retain the original structure after polymerization.[36] For this study, a cross-linker will be added to the hexagonal LLC phase formed from photopolymerizable monofunctional

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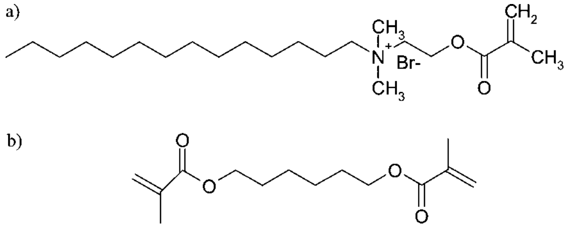

Figure 1. Chemical structures of the surfactant monomer (a) C14MA and cross-linker (b) HDDMA used in this study.

quaternary ammonium surfactant monomers in water in order to systematically study the effect of cross-linking on structure evolution. The degree of liquid crystalline order retained upon polymerization with increasing cross-linker concentration will be examined by using polarized microscopy (PLM) and small-angle X-ray scattering (SAXS). The photopolymerization kinetics will also be examined and related to the structure evolution. Polymer morphology will be directly studied using scanning electron microscopy (SEM). Material properties including swelling and robustness will be analyzed and related to the resulting polymer morphology.

Experimental Section

Materials. The cationic LLC monomer C14MA was prepared by reacting dimethylaminoethyl methacrylate (Aldrich) with tetradecylbromide (Aldrich) according to a method previously described.[40] In a typical synthesis, dimethylaminoethyl methacrylate is reacted with the tetradecylbromide in acetone at 41 °C for 4 days. After acetone evaporation, the product was precipitated in ethyl ether. White crystals were obtained after purification by recrystallization in ethyl acetate. The LLC systems presented in this research were prepared by mixing and centrifugating the reactive surfactant, cross-linker, water, and photoinitiator (Irgacure 2959 - Ciba) until a homogeneous mixture was obtained. Lauryl methacrylate (Aldrich), ethylene glycol diacetate (Aldrich), and 1,6-hexanediol dimethacrylate (HDDMA) (Aldrich) were used as received. The chemical structure of HDDMA and the surfactant monomer C14MA are shown in Figure 1.

Procedure. LLC phases for the different samples were characterized by small-angle X-ray scattering (SAXS) by measuring ratios in *d*-spacing calculated from the reflections in the corresponding sample profiles.[41] These measurements were conducted utilizing a Nonius FR590 X-ray apparatus with a standard copper target Röntgen tube as the radiation source with a Cu Kα line of 1.54 Å, a collimation system of the Kratky type, and a PSD 50 M position sensitive linear detector (Hecus M. Braun, Graz). LLC morphologies were also identified by examining the optical texture of the samples with a polarized light microscope (Nikon, Eclipse E600W Pol) equipped with a hot stage (Instec, Boulder, CO). By comparing SAXS profiles and polarized light microscopy images from before and after polymerization, a measure of LLC structure retention upon polymerization was determined.

Polymerization rate data were acquired with a Perkin-Elmer differential scanning calorimeter. The emission spectrum from a medium-pressure UV arc lamp (Ace Glass) was used to initiate polymerization. Light intensity was controlled with optical filters and by varying the distance of the sample from the lamp. A 365 nm wavelength filter with a light intensity of 1.5 mW/cm^2 was used unless otherwise mentioned. Error caused by water evaporation was minimized by covering the approximately 3.5 mg samples with thin transparent films of FEP (DuPont fluorinated copolymer). Samples were purged with nitrogen for 8 min prior to polymerization to prevent oxygen inhibition. The samples were also heated to 80 °C and cooled to 30 at 10 °C/min to ensure uniform thermal contact and thickness. Isothermal reaction conditions were maintained during polymerization using a refrigerated circulating chiller. The polymerization rate, R_p, was determined as a function of time from the heat flow (Q) according to eq 1

$$\frac{R_p}{[M]} = Q\left[\left(\frac{MW}{n\Delta H_p m}\right)_{\text{monomer1}} + \left(\frac{MW}{n\Delta H_p m}\right)_{\text{monomer2}}\right] \tag{1}$$

where MW is the monomer molecular weight, [M] is the concentration of reactive species, m is the mass of reactive species, n is the monomer functionality, and ΔH_p is the enthalpy of polymerization of the corresponding monomer.[42] For these studies, the theoretical value of 13.1 kcal/mol was used as the heat evolved per methacrylate double bond reacted.[43] Maximum rates were taken from the peak in the rate profiles obtained.

Polymer samples were made by pouring the previously mixed and centrifigated LLC monomer solutions into a nylon mold. The mold was placed into a nitrogen purged box for 10 min and then irradiated using a 365 nm UV light source (1.7 mW/cm^2) for 10 min. The resulting polymer sample was punched and then dried overnight in a vacuum oven before water uptake analysis. Morphology of the polymer was analyzed by using SEM (Hitachi S-4000). Samples were prepared by freeze-drying and freeze fracture techniques. Prior to analysis, the polymer was sputter-coated using a Au/Pd target.

Polymer swelling was determined gravimetrically by immersing dehydrated hydrogels into deionized water at room temperature. Swelling measurements were taken by removing the sample from the water, patting the surface dry, and then recording the mass of the hydrated polymer. Equilibrium water absorption was determined once the mass of a hydrated sample did not change significantly as a function of overall swell time. The water uptake (W) was determined by eq 2

$$W(\%) = \left(\frac{w_t - w_d}{w_d}\right)100 \tag{2}$$

where w_t is the equilibrium weight of the hydrated polymer sample and w_d is the weight of the dry polymer sample.

Results and Discussion

Polymers with nanostructures based on hexagonal LLC morphologies could be extremely beneficial for many applications such as separations and nanocomposite synthesis.[44−46] The use of reactive LLC monomers enables the creation of polymers that exhibit LLC morphologies by the formation of covalent bonds within the system. Typically, a polymer

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that exhibits different morphologies compared to the prepolymerized LLC is obtained because of phase separation during the polymer formation. Having control of the resulting polymer structure would enable the creation of materials that exhibit tunable morphology and consequent physical properties.

Recent work using monomethacrylate quaternary ammonium surfactant monomers with different nonpolar chain lengths shows that the hexagonal LLC phase is not retained during polymerization.[36] On the basis of such results, this work explores the use of cross-linking as a way to retain LLC phases. To accomplish this goal, the phase properties were studied before and after polymerization. The polymerization kinetics were also studied to elucidate the effect of the cross-linker on the LLC phase order and the effect of cross-linking on the polymerization rate and nanostructure evolution. From previous studies, it has been shown that C14MA surfactant monomer in water aggregates into micellar, hexagonal, and lamellar nanostructures.[36] In this study, the hexagonal structure is formed at a 7:3 C14MA:water ratio as determined by SAXS and PLM. By maintaining the ratio of C14MA and water constant, the segregation of the cross-linker in the hexagonal phase can be studied and its effect on the LLC phase quantified. At room temperature, the hexagonal phase is observed at up to 9.5% HDDMA, followed by a region where a mixture of hexagonal and cubic phases is observed. At concentrations above 12.3% HDDMA, an isotropic phase is observed as determined by PLM.

Previous research has used SAXS to understand the effect of the addition of a component on the lattice parameter of the LLC.[21,36,47] Pena dos Santos and co-workers showed by addition of oil and salt to the hexagonal phase formed from sodium dodecyl sulfate in water that the characteristic dimensions can be modulated therefore creating a stable nanoreactor for the creation of an inorganic material.[47] Lester and co-workers used the primary reflection of the SAXS profile to calculate the d_{100} spacings when adding different monomers to a dodecyltrimethylammonium bromide (DTAB) in water system.[21] More recently, the primary reflection of the SAXS profile has been used to understand the aggregation and quantify the characteristic dimension of monomethacrylate quaternary ammonium surfactant monomers with different nonpolar chain lengths in water.[36] Figure 2 shows the d_{100} spacing of the hexagonal phase as a function of the HDDMA added to the C14MA in water as calculated from the primary reflection of the SAXS profiles (see the Supporting Information). The incorporation of HDDMA within the hexagonal phase causes the d_{100} spacing calculated from the primary SAXS reflections to decrease. This behavior indicates a decrease in the characteristic size of the hexagonal arrangement. Adding approximately 8% HDDMA decreases the characteristic size by approximately 2 Å. The HDDMA segregates into the polar regions of the hexagonal phase because of polar interactions, more probably near the quaternary ammonium of the surfactant monomers, therefore compressing the structure. The addition of HDDMA also decreases the order of the LLC as reflected by a decrease in the clearing temperature and confirmed by less-defined textures, as determined by PLM.

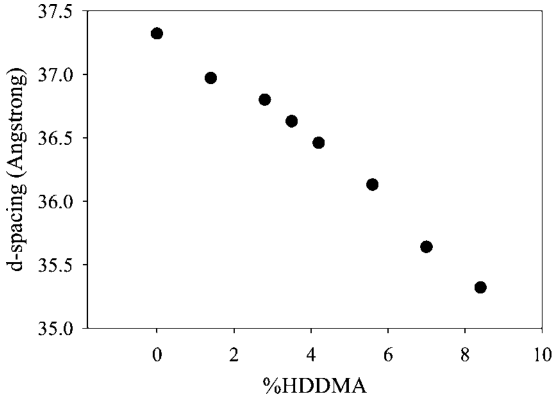

Figure 2. *d*-Spacing of the hexagonal phases formed at a 7:3 C14MA:water ratio at different HDDMA concentrations.

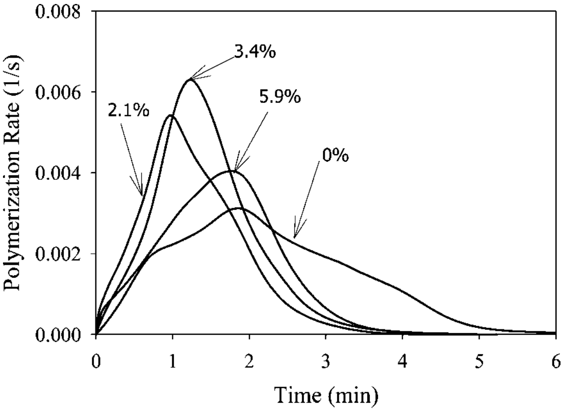

Figure 3. Polymerization rate versus time for the hexagonal phases formed using a 7:3 C14MA:water ratio at different HDDMA concentrations.

To be able to successfully generate polymeric materials with nanometer size morphologies, it is important not only to understand the structural evolution but also to develop an understanding of the polymerization behavior. Previous work has shown that the polymerization rate has a direct effect of the structure retention of templated and reactive LLC systems.[35,36] The polymerization kinetics were examined for the hexagonal phases over the whole range of cross-linker concentration. In Figure 3 the polymerization rate profiles in the hexagonal phase for different HDDMA concentrations are shown as a function of time. The polymerization rate behavior is greatly affected by the addition of the croslinker. When no cross-linker is present, two peaks in the polymerization rate profiles are observed. These peaks have been associated to changes in morphology during the polymerization process.[36] Adding 2.1% HDDMA not only increases the maximum polymerization rate by a factor of approximately two but also decreases the time it takes to reach the maximum polymerization rate by half. The increase in polymerization rate when adding a cross-linker has been associated in isotropic systems to an increase in the functionality of the system that causes higher cross-link density and decreases the mobility of propagating radicals thereby decreasing the termination rate.[47] The highest polymerization rate is observed for a concentration of approximately 3.4% HDDMA. Further increases in HDDMA

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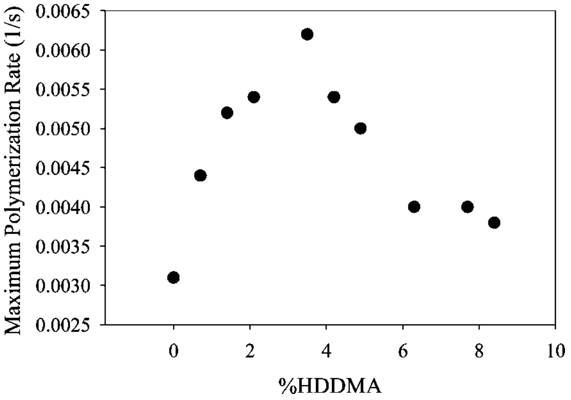

Figure 4. Maximum polymerization rate for a 7:3 C14MA:water ratio in water as a function of the amount of HDDMA added to the hexagonal phase.

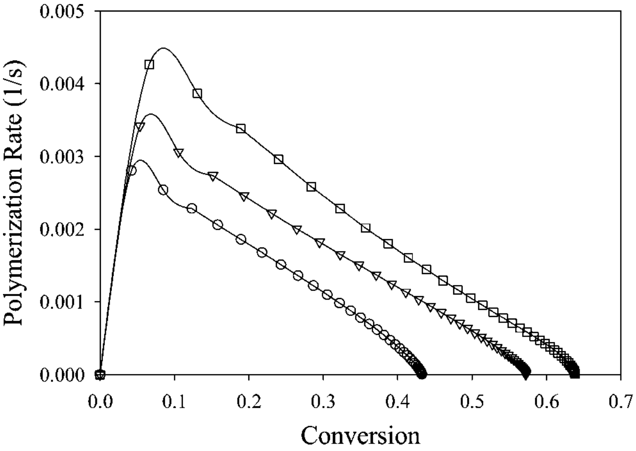

Figure 5. Polymerization rate versus conversion for a 9:1 lauryl methacrylate:ethylene glycol diacetate ratio at different HDDMA concentrations in water. Shown are 0% HDDMA (○), 9% HDDMA (∇), and 15% HDDMA (□).

concentration creates reactive hexagonal phases that exhibit lower polymerization rates. For example, increasing the concentration of HDDMA to 6% decreases the polymerization rate about 66% compared to the highest polymerization rate. This behavior could be due to a decrease in the order of the hexagonal LLC phases. Such a decrease is confirmed by less-defined textures and profiles using PLM and SAXS, respectively. It is important to mention that the second peak in the polymerization rate profiles disappears, suggesting that adding cross-linker changes the dynamics of the system and perhaps has an impact on the polymer evolution.

To illustrate this behavior in more detail, the maximum polymerization rates for a 7:3 C14MA:water ratio are plotted for various concentrations of HDDMA in Figure 4. Increasing the concentration of HDDMA increases the maximum polymerization rate until a concentration of approximately 3.4% HDDMA is reached. Further increase in cross-linker concentration decreases the maximum polymerization rate considerably. This behavior differs from the behavior observed for isotropic systems in which adding a multifunctional monomer to a monofunctional monomer system increases the polymerization rate due to a decrease in mobility of propagating radicals that induces a decrease in termination rates.[47] Because the LLC order decreases as the HDDMA is added, the subsequent decrease in polymerization rate could be induced by decreases in order with increasing HDDMA. Previous studies support this idea in that higher polymerization rates are observed in more ordered LLC phases.[21,35,36] At higher cross-linker concentrations, a slight disruption of the LLC structure results from the addition of cross-linker which, in turn, causes the polymerization rate to decrease.

To determine if the polymerization rate behavior is simply due to a decrease in order, the polymerization rate of a completely isotropic and disordered monomer was studied as a function of cross-linker added. Lauryl methacrylate (LaMA) was chosen as the monomer based on the structural resemblance with a similar aliphatic tail to the amphiphilic molecules under study. LaMA was dissolved in ethylene glycol diacetate (EGDAc) creating an isotropic system. The ratio of LaMA and EGDAc is kept constant for all the samples, whereas the amount of HDDMA is varied. Figure 5 shows the polymerization rate as a function of conversion for a ratio of LaMA to EGDAc of 9:1 with increasing amounts of HDDMA. Adding HDDMA at high concentrations increases the polymerization rate as expected. For example adding 15% HDDMA increases the polymerization rate about 66% compared to the system where no cross-linker is added. As explained before for isotropic systems, adding a multifunctional monomer to a monofunctional monomer system increases the polymerization rate because of a decrease in mobility of propagating radicals during the polymerization process that induces a decrease in termination rates. These results support the fact that a decrease in polymerization rate in the ordered C14MA/HDDMA system at high HDDMA concentrations is due to a decrease in the order of the hexagonal LLC phase.

From the polymerization kinetics, it is apparent that the polymerization behavior of reactive LLC systems is highly dependent on the order because the hexagonal phase is slightly disrupted at high cross-linker concentration and lower polymerization rates are seen. The decrease in order with more cross-linker may also have a significant impact in retention of phase morphology as well. To determine the impact of the cross-linker, SAXS was employed as the primary tool to characterize morphology changes of the LLC phases before and after polymerization. Figure 6a shows the SAXS profiles before and after polymerization for a 7:3 C14MA:water ratio adding 2.1% HDDMA. Before polymerization the SAXS profile exhibit a ratio between the primary and secondary reflections of $1:1/3^{1/2}$, indicating the presence of a hexagonal phase.[36] Upon polymerization a ratio of 1:2 between primary and secondary reflections is observed, which is indicative of a lamellar phase. Therefore, the hexagonal phase in the monomer state changes to the lamellar phase during polymerization. Similar results have been presented in previous work for hexagonal LLC phases formed using different nonpolar tail lengths of the reactive surfactant.[36] These results confirm that thermodynamics play an important role in the structure retention and evolution of reactive LLC systems. After polymerization, the molecules tend to form a structure that minimizes the interfacial curvature of the polymer in order to decrease the free energy

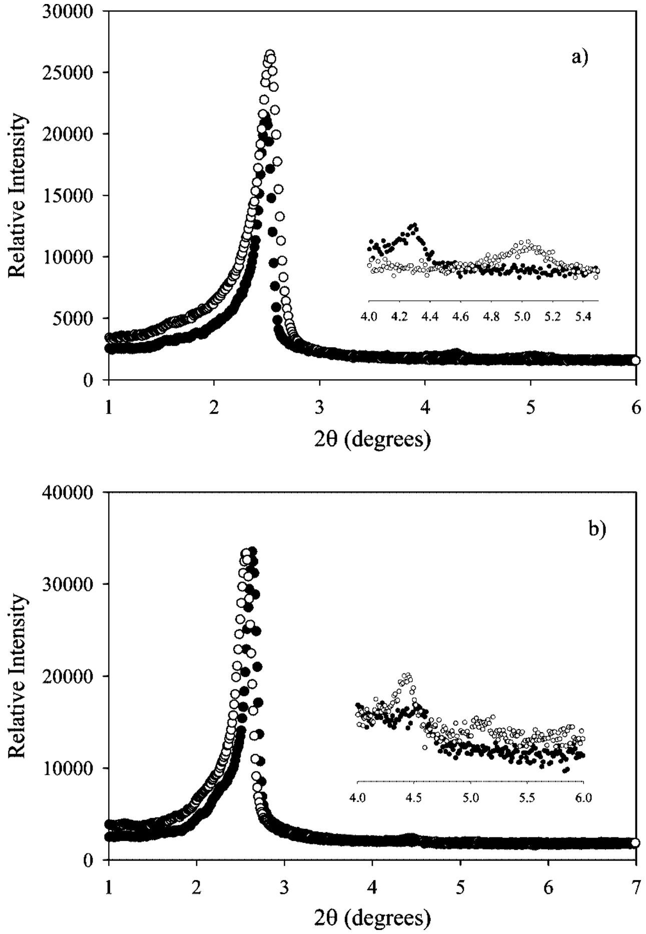

Figure 6. Small-angle X-ray scattering (SAXS) profiles for a 7:3 C14MA: water ratio with (a) 2.10% HDDMA and 8.34% HDDMA before (•) and after (○) polymerization.

of the system. Similar behavior is observed for the hexagonal phases formed adding up to 5.9% HDDMA. Interestingly, this behavior changes when using concentrations above 5.9% HDDMA, where the hexagonal LLC order is retained during polymerization as indicated by the SAXS profiles. This behavior is shown in Figure 6b for a ratio of C14MA to water of 7:3 with added 8.3% HDDMA. Before polymerization, the SAXS profile exhibits a ratio between the primary and secondary reflections of $1{:}1/3^{1/2}$, indicating the presence of a hexagonal phase. Upon polymerization, the sample still exhibits a ratio between primary and secondary reflections of $1{:}1/3^{1/2}$, indicating that the hexagonal phase is retained during polymerization. An increase in the ratio of peak height to width at half-width after polymerization of 20% is observed, as well as an increase in intensity of the secondary SAXS reflection, suggesting a possible increase in order. Also, the fact that a third reflection is SAXS profile is present after polymerization supports the fact that a more periodically ordered hexagonal LLC structure is being formed.

From the SAXS profiles, it is apparent that the original LLC phase is disrupted during polymerization for samples containing less than 5.9% HDDMA and retained for samples containing more than 5.9% HDDMA. To corroborate the basic structures resulting from the polymerization of these systems, PLM was employed. PLM provides a straightforward method of characterizing LLC phases based on the optical anisotropy present in these systems. Images a and b in Figure 7 show polarized light micrographs for a 7:3 C14MA:water ratio before and after polymerization, respectively. Before polymerization a focal conic texture is observed indicating the presence of a hexagonal mesophase. After polymerization, most of the hexagonal LLC order disappears producing spherulites distinctive of lamellar LLC phase. Images c and d in Figure 7 show polarized light micrographs for a 7:3 C14MA:water ratio with added 8.3% HDDMA before and after polymerization, respectively. Before polymerization, a focal conic texture is observed indicating the presence of a hexagonal mesophase. Interestingly, the phase texture does not change much after polymerization, indicating the hexagonal LLC phase is retained to some degree. Also, PLM shows that the hexagonal phase formed in the monomer state at a 7:3 C14MA:water ratio exhibits more defined textures compared to this system with added 8.3% HDDMA, confirming that adding a cross-linker decreases the hexagonal LLC order. The difference in LLC order before polymerization between samples that retain structure and samples that do not retain structure could indicate differences in the resulting polymer morphology and properties.[29]

SAXS analysis provides information about changes in liquid crystalline order occurring during polymerization, which are related to polymer structure development. To gain better insight of how retention of the hexagonal phase by the addition of cross-linking affects the resulting polymer morphology, we performed SEM studies. Figure 8a depicts the SEM image corresponding to a 7:3 C14MA:water ratio, which changes structures during polymerization from hexagonal to lamellar as determined by SAXS. Although it possesses some characteristics of the lamellar structure, it exhibits a much different morphology. At low magnification, a sheetlike morphology is visible along with polymer filling the void space that is more readily observed in the magnified image shown in Figure 8b. The polymer exhibits a porous surface of irregular aligned channels with width ranging from 500 nm to 2 μm. The irregularity and wide range of channel width could be due to the fact that a change in structure is occurring during polymerization therefore affecting the polymer formation by creating disorder. On the other hand, Figure 8c depicts a SEM image for a 7:3 C14MA:water ratio with 8.3% HDDMA, which retains the hexagonal structure during polymerization according to SAXS. The polymer exhibits a smooth surface with aligned channels that exhibit regular void spaces ranging from 50 to 500 nm. These ordered channels can be seen more clearly at higher magnifications, as shown in Figure 8d. The use of a cross-linker aids in structure preservation during polymerization therefore creating a polymer with ordered and more defined features. The presence of different morphologies observed could translate into differences in polymer physical properties and therefore in polymer functionality.

When exploring a material functionality, especially one with inherent nanostructure, the ability of the polymer to withstand changes in operating environment with minimal damage or alteration is very important.[48] SAXS analysis not

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(48) Schmidt, H. *Soft Mater.* **2006**, *4*, 143–164.

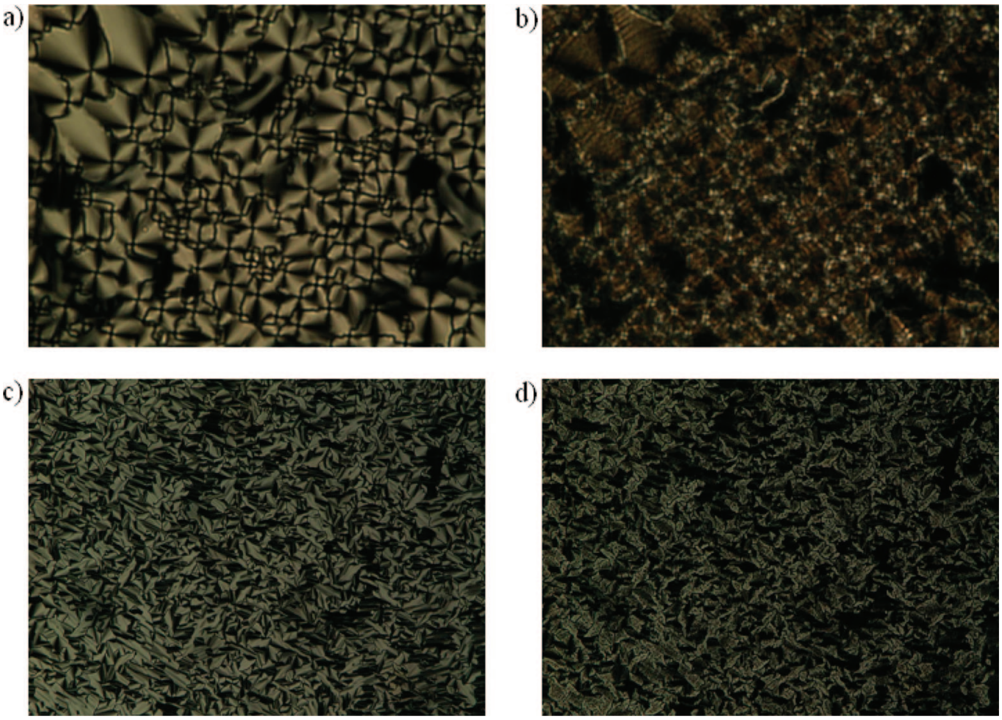

Figure 7. Polarized light microcroscopy pictures for the hexagonal phases. Shown are a 7:3 C14MA:water ratio (a) before and (b) after polymerization and a 7:3 C14MA:water ratio with 8.34% HDDMA (c) before and (d) after polymerization.

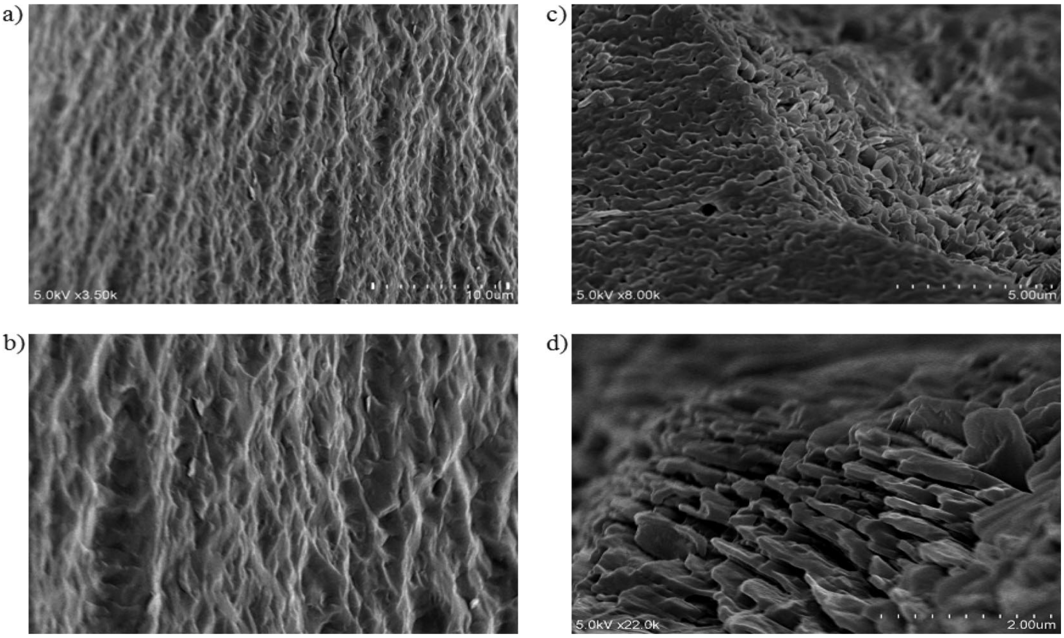

Figure 8. SEM images for the polymer formed at a 7:3 C14MA:water ratio with (a) 0% HDDMA, (b) 0% HDDMA at higher magnification, (c) 8.34% HDDMA, and (d) 8.34% HDDMA at higher magnification.

only provides information about changes in LLC order and structure preservation but also provides a way of understanding how the polymer behaves to those changes. For example, Figure 9 shows the SAXS profiles for the polymer formed using a 7:3 C14MA:water ratio with 8.3% HDDMA before and after polymerization and also after drying and swelling in water. It has been presented before that the ratio of primary and secondary reflections if the SAXS profiles before and after polymerization are the same ($1:1/3^{1/2}$) for this system, suggesting that the hexagonal phase is retained. Similar intensities for the samples before and after polymerization are observed suggesting similar order. After the sampes are dried in a vacuum oven overnight, the *d*-spacing from the primary reflection in the SAXS profile decreases because water is removed from the system. Even though a higher intensity is observed for the primary SAXS reflection, the ratio of peak height to width decreases, suggesting some order could be lost during the drying process. This is also supported by the disappearance of the second reflection in the SAXS profile. Interestingly, after swelling in water, the primary and secondary reflections in the SAXS profile are observed, again implying that hexagonal order is present.

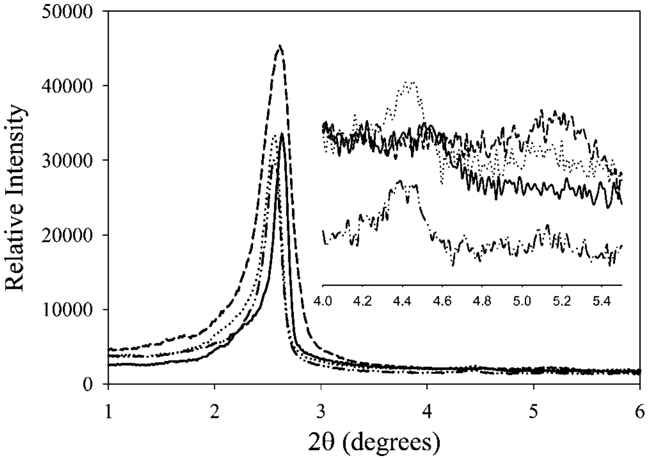

Figure 9. Small-angle X-ray scattering (SAXS) profiles for the hexagonal phase retained after polymerization using a 7:3 C14MA:water ratio with 8.34% HDDMA before polymerization (—), after polymerization (•••), after drying (---), and after swelling in water (-••-).

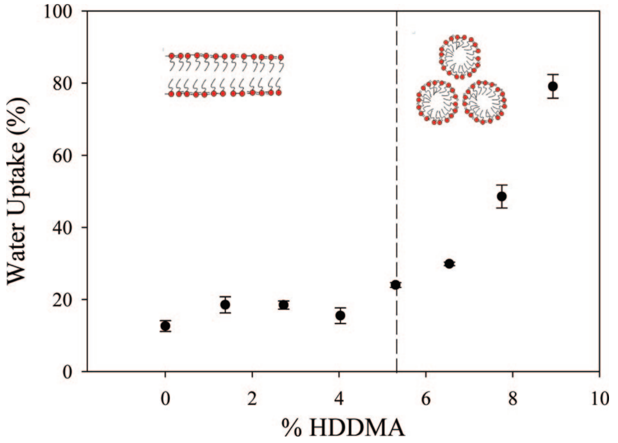

Figure 10. Water uptake for the system with a 7:3 C14MA:water ratio at different HDDMA concentrations. Polymers that retain the original hexagonal LLC phase exhibit higher water uptakes.

This behavior indicates that the resulting polymer exhibits a robust LLC structure that is retained through drying and reswelling.

To be able to better understanding the influence of LLC structure retention on the resulting polymer, the swelling in water was studied comparing systems with structure retention with systems that lose the original LLC order during polymerization. Figure 10 shows the polymer maximum water uptake as a function of the amount of HDDMA added to the hexagonal phase formed at a ratio of C14MA to water of 7:3. At low HDDMA concentrations, the maximum water uptake remains constant at about 20%. This behavior is observed for systems with up to 5.9% HDDMA, for which the hexagonal phase is not retained but changes to the lamellar phase during polymerization. By increasing the concentration above 5.9% HDDMA, when the original hexagonal structure is retained during polymerization, polymers are produced that exhibit a significant increase in water uptake. For example, the polymer formed by adding 8.9% HDDMA, which retains the hexagonal structure during polymerization, is able to uptake four times more water than the polymers formed with lower concentration of cross-linker that do not retain the original structure after polymerization. Interestingly, the water adsorption is significantly increased by adding a cross-linker. This behavior appears to be due to the retention of the structure after polymerization as indicated by SAXS and PLM. This behavior also differs from isotropic systems for which adding a cross-linker to a monofunctional monomer results in less water adsorption because of an increase in cross-link density and mechanical forces.[49] Also interesting is that polymerized HDDMA does not adsorb much water by itself since it forms a highly cross-linked and relatively nonpolar network. This behavior indicates that the resulting increase in water uptake is due to the retention of the hexagonal structure after polymerization and therefore the different morphologies obtained. The polymer formed without cross-linker, which exhibits a porous structure of irregular aligned channels with polymer filing the void spaces, exhibits a much lower water uptake compared to the polymer formed with 8.3% HDDMA, which exhibits a more ordered polymer structure with regular aligned channels. The higher water uptakes observed at high cross-linker concentration, where the hexagonal phase is retained during polymerization, can be attributed to the regularity of voids and homogeneity of the polymer that facilitates penetration of water into the polymer network. Preservation and disruption of the original LLC structure through polymerization induces significantly different polymer morphology and properties. As the water and unreacted monomer are removed after polymerization, regular and defined polymer channels are obtained. When the structure is not retained, the aggregation of molecules changes during polymerization because of phase separation. As the surfactant monomers reacts during phase separation, polymers with disordered features are produced after water removal.

Conclusions

In this study, the use of a cross-linker to retain the LLC order of a monomethacrylate quaternary ammonium surfactant monomer in water during polymerization is explored and the phase behavior studied. The cross-linker segregates to the polar regions of the LLC, more likely near the polar heads of the reactive surfactant, as observed by a decrease in *d*-spacing elucidated from the SAXS profiles. The hexagonal phase was observed to exist at concentrations up to 9.5% HDDMA followed by a transition region and isotropic phase at concentrations above 12.3% % HDDMA. The polymerization rate increases when adding HDDMA at low concentrations, while at concentrations above 3.4% HDDMA the rate decreases. The use of a HDDMA enables the retention of the original hexagonal LLC order after polymerization at concentration above 5.9% HDDMA as confirmed by using SAXS and PLM. The fact that a less defined hexagonal phase is observed by using PLM suggests that a decrease in LLC order drives the decrease in polymerization rates after the initial increase with small amounts of cross-linker. This behavior suggests that the polymerization kinetics are governed by competing effects between cross-linking and order. More regular and ordered morphologies are observed for polymers that retain the

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(49) Brazel, C. S.; Peppas, N. A. *Polymer* **1999**, *40*, 3383–3398.

hexagonal LLC order after polymerization as per SEM images. Also, the resulting polymer is stable after drying and swelling as observed by the retention of the polymer LLC order using SAXS. Polymer that retains the original LLC order exhibits increases in the water uptake by up to a factor of 4 compared with polymer with loss of original order when no HDDMA is added. This behavior is directly related to the retention of the original LLC order and the resulting regular and ordered polymer morphology.

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Supporting Information Available: Normalized SAXS profiles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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