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Ordering effects on the photopolymerization of a lyotropic liquid crystal

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Abstract

The synthesis of polymers bearing the highly ordered nanostructure of lyotropic liquid crystal (LLC) phases has recently been of great interest. This work describes the polymerization behavior and structural evolution of a cationic amphiphile in various LLC phases. The type and degree of LLC phases formed from this monomer depend strongly on the composition and temperature. By adding a nonpolymerizable surfactant a variety of LLC phases are formed including hexagonal, bicontinuous cubic, and lamellar morphologies while maintaining a constant monomer concentration. The highly ordered lamellar LLC phase exhibits the fastest polymerization rate with the slowest occurring in the hexagonal phase. The polymerization rates of the bicontinuous morphology were intermediate to the lamellar and hexagonal phases. The faster polymerization kinetics is due to diffusional limitations imposed on the propagating polymer by the highly ordered lamellar LLC phase. Also, the order of this LLC system has a strong dependence on temperature. At higher temperatures, the degree of LLC order and correspondingly the polymerization rate decrease. The original LLC phase morphology appears to be retained to the greatest extent in the faster polymerizing lamellar phase. The original nanostructure is also retained in the hexagonal and cubic LLC phases but with some slight changes in structure. This LLC structure is preserved at temperatures well exceeding the thermal phase transitions of the unpolymerized LLC samples. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Photopolymerization; Lyotropic liquid crystal; Polymer nanostructure

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1. Introduction

The generation of nanostructured materials has recently received much attention. Materials with morphologies on the nanometer size scale have shown promise in the synthesis of ultrafiltration membranes, drug delivery devices, and organic zeolites for catalysis [1,2]. Lyotropic liquid crystal (LLC) phases exhibit considerable promise for such applications as they possess a wide range of unique nanostructures. However, LLC phases lack stability and therefore are not useful as materials. For these reasons synthesizing polymers with the unique nanostructure of LLC phases has been of particular interest. One possible route to such materials is through the use of LLC forming molecules that can be polymerized.

LLCs are ordered liquids formed from an amphiphile and a typically aqueous solvent. When amphiphilic molecules are dispersed into water, a variety of ordered nanostructures or phases are formed. At low amphiphile concentrations spherical micelles are formed. These micelles can pack into discontinuous cubic arrays possessing long-range order. Rod-like micelles packed into hexagonal arrays and bilayer type aggregates are also possible forming the hexagonal and lamellar LLC phases, respectively. For some LLC systems, a bicontinuous cubic morphology exists at concentrations intermediate to that of the hexagonal and lamellar phases. Inverse phases can also form at extreme concentrations of amphiphile bearing the appropriate geometry and hydrophobic character [3]. Unfortunately, as mentioned earlier, LLCs lack mechanical stability and are unsuitable for material applications. Therefore, synthesizing polymers with these fascinating nanostructures is of great importance for potential applications in catalysis, separations, nanocomposite synthesis, and biomimetic materials.

Polymerizations of amphiphilic monomers in the micellar state has been studied extensively. Amphiphilic monomers containing anionic, cationic, zwitterionic, and nonionic polar head groups have been synthesized [4–9]. In general, monomers containing fairly reactive polymerizable groups such as acrylates, methacrylates, and acrylamides polymerize to high conversions; whereas, surfactants containing allylic groups form oligomers [10,11]. The mechanism of polymerization in the micellar state is influenced heavily by the order in the aggregates. For example, a cationic methacrylate surfactant polymerized faster and to a greater extent when dispersed in water above the critical micelle concentration as opposed to polymerizations performed in

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nonaggregating solvents [6]. Similarly, this phenomenon was reported for a nonionic polymerizable surfactant in which the monomer exhibited a dramatically faster polymerization rate in its micellar aggregates [8].

Some work has also been devoted to the polymerization of lyotropic assemblies of these surface-active monomers. Much of the research to date has examined the LLC systems prior to polymerization and after polymerization with primary focus on the retention of the original structure. The retention of lyotropic structure is problematic, and in many cases the morphology obtained upon polymerization is not the same as the original LLC structure. For example McGrath et al. [12–14] reported the polymerization of a series of polymerizable surfactants in their LLC phases. In the case of monomers containing allylic functionalities the original structure appeared to be retained upon polymerization. This retention was shown to be a result of the formation of oligomers and not high molecular weight polymers. Other studies determined the LC behavior of a quaternary ammonium methacrylate before polymerization. Polymers formed from this LLC surfactant in isotropic and micellar solutions were examined, but due to the sensitivity of the initiator, polymers formed in the LLC phases were not [15]. Some cases of retained LLC structure have been reported in the literature but with little detail about the mechanism of polymerization. For example, the normal hexagonal phase of a diene phosphonium amphiphile has recently been shown to retain its original structure upon polymerization [16]. LLC trifunctional acrylates and styrenic derivatives have been synthesized that adopt normal and inverse hexagonal phases. Upon polymerization the original structure is retained as a result of the high amount of cross-linking in the system [17–20]. Additionally, functional phospholipids have been synthesized and have been polymerized in their lyotropic mesophases. Retention of the original structures was reported in some cases depending on the type and placement of the polymerizable functionality, and the mode of polymerization [21–24]. Little information, however, is available regarding the role that these organized assemblies play in the kinetics of the polymerization and the structure of the developing polymer.

Therefore, not only do LLC monomers represent a great opportunity from a materials standpoint, but also they can yield insight into the impact of highly ordered arrays on the polymerization mechanism. Through studying the polymerization mechanism of LLC monomers, the ability to controllably generate nanostructured polymers may be attained. The polymerization kinetics in analogous thermotropic systems has proven to be important in the structural development of ordered polymers. For example, Hoyle et al. [25–27] have shown that the polymerization of thermotropic monomers is heavily dependent on the liquid crystalline morphology. Similar considerations have proven important in the polymerization of a variety of monomers in thermotropic liquid crystalline solvents [28–30]. Additionally, the templated polymerization kinetics of monomers solvated in nonpolymerizable LLC phases exhibit a strong dependence on the LLC morphology [31,32]. Polymerization kinetics appear to play a large role in structure retention of LLC systems. Recently, polymerization behavior and structure retention of a semi-fluorinated methacrylic acid derivative has been reported [33]. The polymerization rate of this semi-fluorinated LLC exhibits a tremendous dependence on the type and degree of order in the system. Rapid polymerization rates were observed in the lamellar mesophases that exhibit the highest degree of LLC order. With decreases in the degree of LLC order, the polymerization rate correspondingly decreased, reaching a minimum in the discontinuous cubic phase. Interestingly, the faster polymerizations yielded enhanced structure retention upon photopolymerization. Unfortunately, this system allowed the study of only two homogeneous LLC phases. In order to understand LLC polymerizations in a broader context, it would be beneficial to study a system that possesses a larger variety of mesophases.

The goal of this work is to understand the photopolymerization kinetics of a monomeric cationic surfactant in its various mesophases to enhance the ability to controllably synthesize nanostructured polymers based on lyotropic liquid crystalline assemblies. The systematic study of this monomeric LLC system will enhance the understanding of the impact of organized media on polymerization kinetics and conversely the role of polymerization kinetics on the ultimate structure. The LLC phase behavior will be determined for a cationic polymerizable amphiphile similar in structure to a nonpolymerizable analog that exhibits a wide variety of LLC phase morphologies. In order to understand the dependence of the type and degree of order in these systems, the photopolymerization kinetics of these organized assemblies will be monitored. The polymerization kinetics will be correlated to the LLC phase morphology. The LLC structure after polymerization will also be determined to further understand the role of polymerization kinetics in structure retention.

2. Experimental

2.1. Materials

The cationic LLC monomer was prepared by reacting dimethylaminoethyl methacrylate (Acros) with 1-dodecylbromide (Acros) according to a method described previously [6,15]. For simplicity the quaternized dimethylaminoethyl methacrylate has been designated C12MA in reference to its hydrophobic tail length. The analogous LLC forming surfactant dodecyltrimethylammonium bromide (DTAB) (Aldrich) was also used in this study as a nonpolymerizable mesogen. All LLC samples were formulated with deionized water or deuterated water (Aldrich). The chemical structure of these compounds is shown in Fig. 1. The photopolymerizations were initiated using Irgacure

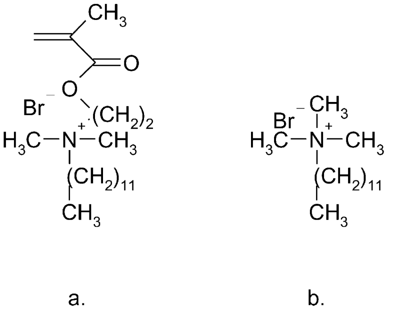

Fig. 1. Chemical structure of the monomer and surfactant used in this study. Shown are (a) quaternized dimethylaminoethylmethacrylate (C12MA), and (b) dodecyltrimethylammonium bromide (DTAB).

2959 (Ciba Specialty Chemicals, Tarrytown, New York). Approximately 1 wt% initiator with respect to the total monomer weight was incorporated into the LLC samples.

2.2. Procedure

Small angle X-ray scattering (SAXS) was used to characterize the phase behavior using a Siemens XPD 700P WAXD/SAXS with a Cu K_α line of 1.54 Å. Bragg's law was used to determine the *d*-spacing of the lyotropic mesophase both before and after polymerization. Confirmation of phase type was obtained through the characteristic ratios of the higher order peaks [3]. A polarized light microscope (Nikon, Optiphot-2 pol) equipped with a hot stage (Instec, Boulder, CO) was utilized to corroborate data collected with SAXS by looking for characteristic textures of the various mesophases as well as phase transitions. ^{14}N NMR was also used to determine the degree of order in the LLC systems. NMR spectra were acquired using a Bruker MSL-400 NMR spectrometer operating at a frequency of 28.9 MHz for ^{14}N. A standard 10 mm probe was used. Spectra were obtained using the DEPTH sequence to suppress ^{14}N background due to the probe [34]. The 90° pulse width was 22 μs, the probe dead time was 10 μs, and the acquisition time was 131 ms. The recycle delay was 600 ms, and no proton decoupling scheme was implemented. Spectra were typically acquired without spinning.

Reaction profiles were monitored in real time with a differential scanning calorimeter (Perkin–Elmer DSC-7) modified with a medium pressure UV arc lamp and quartz windows. Samples were covered with a thin film of FEP (DuPont fluorinated copolymer) to prevent evaporation of water. The DSC sample cell was also attached to a refrigerated circulating chiller (VWR Scientific Products—1150A) to maintain isothermal reaction conditions. The DSC cell was purged with nitrogen for 10 min prior to exposing the sample to the UV light source in order to prevent oxygen inhibition during polymerization. The samples were also heated to 80 °C and cooled to 30 °C at 10 °C/min to ensure uniform thickness and good thermal contact. The polymerizations were initiated with monochromatic 365 nm light at an intensity of 4.5 mW/cm^2.

The heat of polymerization was utilized to directly calculate the rate of polymerization. For this study the theoretical values of 13.1 kcal/mol was used as the heat evolved per methacrylate double bond reacted [35]. In order to determine individual rate parameters of termination and propagation, a series of after-effect experiments were performed. First, a lumped kinetic constant $k_p/k_t^{1/2}$ was measured as a function of time from the steady-state polymerization rate profile. By closing a light shutter between the UV light source and the sample at various times during the polymerization process, the initiation step is eliminated. The propagation and termination rate parameters can then be decoupled. This method of determining individual rate parameters is described in detail in Ref. [29].

3. Results and discussion

Nanostructured polymers could provide significant improvements for many applications such as catalytic media, nanocomposite synthesis, and biomimetic materials. Polymerization of LLC phase forming monomers may be an ideal way to synthesize such nanostructured materials. A variety of nanostructures is possible because of the different LLC phases. The dimensions of these different nanostructures can be tailored by the design of the polymerizable amphiphile and by changing the formulation of the desired LLC phase. Unfortunately, the polymerization of LLC monomers to form nanostructured polymers has proven difficult, yielding materials that are often not a function of the original LLC order. As stated previously, the goals of this work are to develop a better understanding of the photopolymerization kinetics of LLC monomers and to determine the impact that the LLC phase morphology and polymerization kinetics have on the resulting polymer. These research goals consequently require the selection of an LLC system that displays a variety of lyotropic morphologies. The quaternized dimethylaminoethyl methacrylate (C12MA) exhibits a wide variety of LLC phase behavior. In fact the C12MA/water system displays three distinct LLC morphologies as well as the isotropic micellar phase [15]. The critical micelle concentration of C12MA has been reported as 6.02×10^{-3} M [36]. The onset of LLC phase formation does not occur until a hexagonal LLC phase is observed after reaching approximately 60 wt% C12MA. Increasing the concentration further to approximately 80% C12MA induces a bicontinuous cubic phase. At concentrations above 90% a lamellar LLC phase is observed.

To obtain these different mesophases, the concentration of C12MA must be increased thereby increasing the concentration of double bonds. To be able to truly understand the impact that the LLC morphologies have on the polymerization kinetics, it is desirable that the double bond concentration be held constant. In order to modulate the phase behavior of this LLC system, small amounts of the analogous nonpolymerizable version of C12MA, i.e.

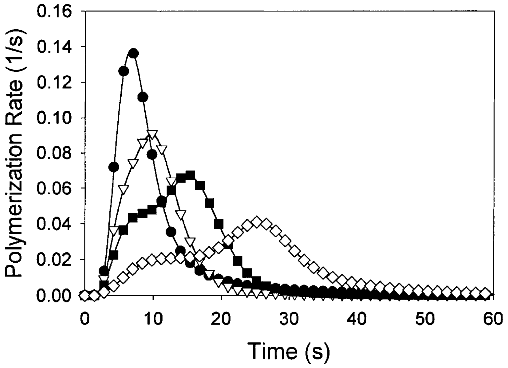

Fig. 2. Polymerization rate versus time for 75 wt% C12MA with increasing DTAB concentration in water. Shown are 0%: Hexagonal (◇), 5%: Cubic (■), 10%: Cubic/Lamellar (▽), and 15%: Lamellar (●) DTAB.

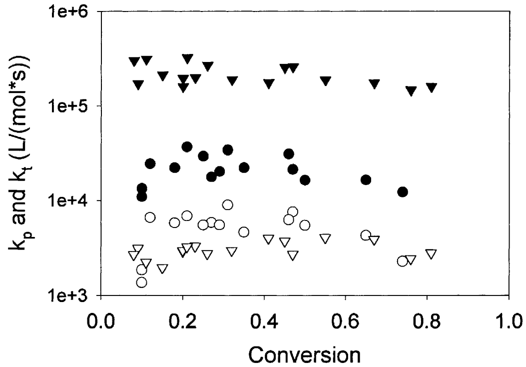

Fig. 3. Termination (k_t) and propagation (k_p) rate parameters of 75% C12MA in DTAB/water, shown as a function of double bond conversion. Given are k_t for 0%: Hexagonal (▼), k_t for 15%: Lamellar (●), k_p for 0%: Hexagonal (▽), and k_p for 15%: Lamellar (○) DTAB.

dodecyltrimethylammonium bromide (DTAB), were added to a constant concentration of C12MA. The addition of DTAB modulates the phase behavior almost identically to what would be observed with the binary C12MA/water system.

To determine if the different phases of the C12MA/DTAB affect the polymerization kinetics the polymerization rate profiles of 75 wt% C12MA with increasing DTAB concentration is shown in Fig. 2. Interestingly, the polymerization kinetics is dramatically influenced by the LLC morphology. In the hexagonal phase a relatively slow polymerization rate is observed. The rate profile of the hexagonal phase also exhibits some irregularities with significant rate acceleration at later stages of the reaction, which may indicate structural rearrangements and/or phase separation upon polymerization [25]. When 5 wt% DTAB is added, the bicontinuous cubic phase is formed, and the rate is significantly enhanced while the time to reach the maximum rate shifts to much earlier times. Further addition of surfactant changes the LLC phase to a binary mixture of the lamellar and cubic phases. This mixed phase exhibits a faster polymerization rate than either the homogeneous cubic or hexagonal mesophases. The fastest polymerization rate is observed in the lamellar mesophase. In fact, the lamellar morphology peak polymerization rate is five times that of the hexagonal LLC phase even though both systems have the same concentration of methacrylate groups. Interestingly, the double peak and late rate acceleration observed in the hexagonal phases becomes less prevalent as the surfactant concentration increases, and has completely disappeared for the fastest polymerizing lamellar system.

As the concentration of double bonds is held constant, the polymerization rate enhancements could be a result of one or two factors. One reason for significantly different polymerization rates in different phases could be the existence of different solution dynamics of the polymerizing system. It is possible that diffusional limitations are imposed on the propagating polymer very early in the polymerization in the more highly ordered LLC phases. Another factor that could heavily influence the polymerization rate is the interfacial curvature of the aggregates. The hexagonal LLC phase exhibits the highest degree of interfacial curvature with successive decreases of curvature into the bicontinuous cubic and lamellar LLC phases. Therefore, with lower interfacial curvature the polymerizable double bonds would be more closely aligned, causing a dramatic change in the polymerization behavior. Individual factors governing the polymerization kinetics including the termination and propagation rate parameters can provide information as to which process dictates the changes in polymerization kinetics.

To understand the mechanisms that drive the changes in polymerization kinetics of the various LLC phases of the C12MA/DTAB/H_2O system, after effect experiments were performed. Fig. 3 shows the individual apparent rate parameters of propagation and termination for the lamellar and hexagonal phases of this LLC system. As described previously the lamellar phase exhibits the fastest polymerization rate while the hexagonal is the slowest. Interestingly, the termination rate parameter for the lamellar phase is an order of magnitude lower than that of the hexagonal phase, which will yield more propagating radicals and consequently a higher overall rate. This behavior has also been observed in other polymerizable amphiphile systems with the polymerizable group located near the polar headgroup [33]. Other work has shown depressed termination rates for analogous thermotropic systems as a result of diffusional limitations on the growing polymer chain which consequently impedes termination [29]. For this LLC system the apparent rate parameter of propagation is also slightly higher in the faster polymerizing lamellar LLC phase. An increase in the propagation rate is indicative of a local increase in the concentration of double bonds [27]. The combined effects of diffusional limitations on the propagating polymer in addition to the segregation of the polymerizable group are the driving forces for the five-fold increase in polymerization rate.

The polymerization kinetics of this system appear to be heavily dependent on the LLC phase morphology. Another

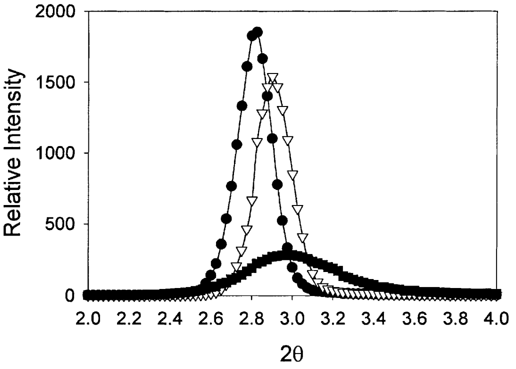

Fig. 4. SAXS profiles of 75% C12MA in water (hexagonal phase) with increasing temperature. Shown are profiles at 25 °C (●), 40 °C (▽), and 55 °C (■).

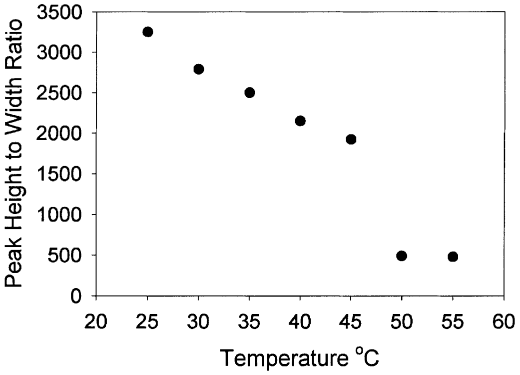

Fig. 5. SAXS peak height to width at half-height ratio of 75% C12MA in water with increasing temperature.

factor that changes the dynamics and morphology of the LLC system, and perhaps the polymerization behavior as well, is temperature. The C12MA/DTAB/water system exhibits significant phase changes with temperature. For example, the hexagonal LLC phase formed by 75% C12MA in water exhibits a transition temperature at approximately 45–50 °C as determined by polarized light microscopy, SAXS, and ^{14}N NMR. At temperatures below the transition temperature even within the hexagonal phase the degree of LLC order changes with increasing temperature. In Fig. 4 the SAXS profiles of the 75% C12MA system which exhibits the hexagonal phase are shown with increasing temperature. At 25 °C a well-defined sharp peak exists as a result of the high degree of order in the hexagonal phase. After increasing the temperature to 40 °C, the peak is still present but the relative intensity of this peak has dropped and shifted to slightly higher scattering angles. This change indicates that the overall order of the phase is decreasing and slight structural changes are occurring as well. After reaching 55 °C the sharp reflection resulting from the hexagonal phase has drastically changed to a very short, broad peak. This behavior is a result of the phase changing from the highly ordered hexagonal LLC phase to an isotropic micellar system with faster dynamics and lower order.

To show this decrease in LLC order more clearly, the peak height to width at half-height ratio of the primary reflection in the SAXS profiles were calculated and plotted as a function of temperature in Fig. 5. This ratio has proven to be a reliable measure of the degree of order in an LLC system and has shown direct correlation to polymerization kinetics of LLC systems [33]. The highest ratio is observed at 25 °C because of the high degree of LLC order. With subsequent increases in temperature the peak height to width ratio decreases in a linear fashion indicating a decrease in the LLC order. Above 45 °C the peak height to width ratio drops precipitously as would be expected at temperatures above the phase transition.

Another useful technique that provides direct information about the order in appropriate LLC systems is ^{14}N NMR. Naturally abundant ^{14}N is a quadrupolar nuclei that exhibits a quadrupolar splitting pattern in the NMR signal when placed in an anisotropic environment such as an LLC phase. The magnitude of this splitting pattern is indicative of the degree of orientational order in the LLC system. In Fig. 6 the ^{14}N NMR spectra of 75% C12MA is shown at temperatures of 30, 40, and 50 °C. Both 25 and 40 °C spectra are in the hexagonal phase, whereas the spectra obtained at 50 °C shows the behavior of the isotropic micellar phase. At 30 °C the hexagonal LLC phase exhibits a sharp splitting pattern resulting from the anisotropy of the system. With increases in temperature, the magnitude of the splitting decreases as the hexagonal phase loses some of its positional and orientational order. Additionally, at 40 °C an isotropic line appears indicating that the hexagonal phase coexists with an isotropic phase. At 50 °C the spectra resolves into an isotropic singlet as a result of the complete loss of the LLC order.

This splitting pattern can be used as a direct measure of the degree of order in an LLC system. In Fig. 7 the magnitude of the quadrupole splitting (Hz) of ^{14}N nuclei of the quaternary nitrogen in C12MA is shown for the hexagonal phase at 75% C12MA in water as a function of temperature. At 25 °C the magnitude of splitting is at a maximum. When increasing the temperature to 35 °C, the order of the

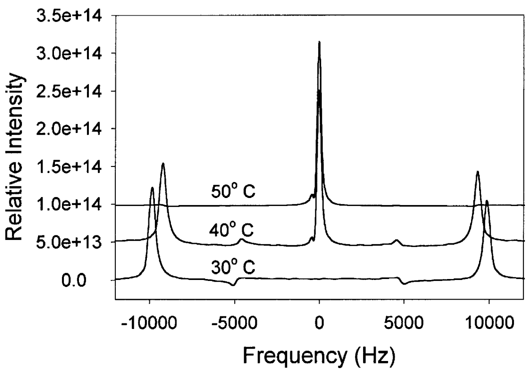

Fig. 6. ^{14}N NMR spectra of the quaternary nitrogen in the hexagonal LLC phase with 75% C12MA in water as a function of increasing temperature.

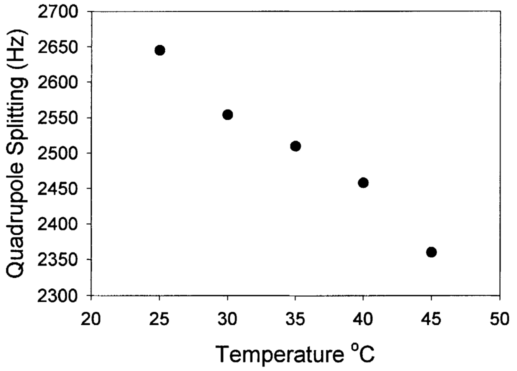

Fig. 7. Quadrupolar splitting from ^{14}N NMR spectra of the quaternary nitrogen of 75% C12MA in water with increasing temperature.

hexagonal phase and consequently, the quadrupole splitting decrease. Subsequent increases up to 45 °C yield similar decreases in the quadrupolar splitting indicating a continuous decrease in LLC order as a function of temperature. The ^{14}N spectra at temperatures exceeding 45 °C exhibit a single peak, indicating that the transition from the ordered hexagonal phase to an isotropic phase has occurred. These results mirror almost exactly those obtained from SAXS. With increased temperature, the order decreases almost linearly with temperature until the phase transition is reached.

Clearly, with increases in polymerization temperature the dynamics and ultimate degree of order in the LLC system change dramatically which may in turn influence the polymerization behavior. To determine the effect of temperature on polymerization behavior, the polymerization rate profiles of 75% C12MA samples are shown in Fig. 8 as a function of temperature. The magnitude of the peak polymerization rate in this case is virtually unaffected by the changes in degree of LLC order, unlike the kinetic results shown previously in which the magnitude of the peak polymerization rate changes tremendously with changes in LLC morphology. The time to reach the peak polymerization rate, on the other hand, is significantly different for the various polymerization temperatures. For example, the polymerization at 25 °C, which demonstrates the highest degree of LLC order, reaches its peak polymerization rate rapidly. When increasing the temperature to 35 °C and correspondingly decreasing the degree of LLC order, the polymerization rate profile shifts to higher times and takes almost twice as long to achieve the peak rate. The maximum polymerization rate is reached at even longer times at 45 °C, which corresponds to a hexagonal LLC phase exhibiting the lowest degree of order.

To be able to display all of the temperatures studied, the time to peak polymerization rate is plotted as a function of temperature in Fig. 9. The fastest polymerization occurs at the lowest temperature, which corresponds to the sample with the highest degree of LLC order. Increasing the temperature and thereby decreasing the LLC order of the system yields successively longer polymerization times. The time to peak rate has an almost linear response to the decrease in LLC order with increasing temperature up to the phase transition of 45 °C. Upon reaching the isotropic phase at 50 °C, the time to peak rate is at a maximum of approximately 30 s, which is well over twice that observed in the polymerization of the hexagonal phase at 25 °C. These changes in this case are very striking in that the polymerization rate decreases even with increased temperatures. Interestingly, the rate behavior appears to be directly dependent on the degree of order. The order, as observed with ^{14}NMR and SAXS, decrease in a linear fashion with increasing temperature. The time to maximum polymerization rate also changes linearly with increasing temperature, underscoring the direct dependence of the polymerization on the LLC order.

From these results, it is clear that the type and degree of LLC order significantly influence the polymerization kinetics. However, it is also of great importance to understand how the polymer structure develops upon photopolymerization and how the polymerization kinetics may influence this structure. The role of photopolymerization and its impact on structure retention is critical as well. To determine if the original LLC phase structure is being retained in these systems, polarized light microscopy was performed before and after polymerization. A polarized micrograph of unpolymerized 75% C12MA in water is shown in Fig. 10(a). This micrograph exhibits classic

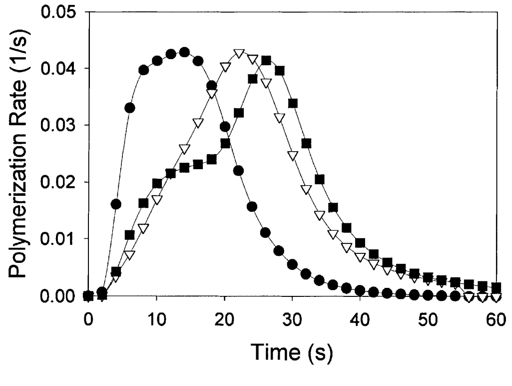

Fig. 8. Polymerization rate versus time for 75 wt% C12MA with increasing temperature. Shown are 25 °C (●), 35 °C (▽), and 45 °C (■).

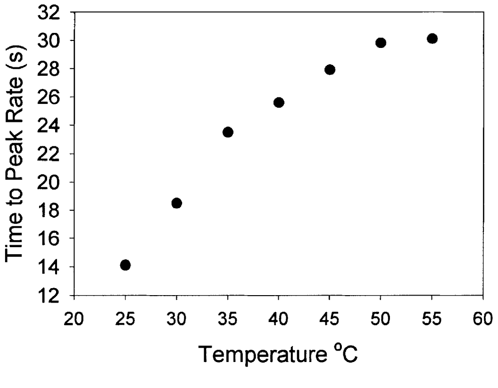

Fig. 9. Time to maximum polymerization rate for 75% C12MA in water (hexagonal) at different temperatures.

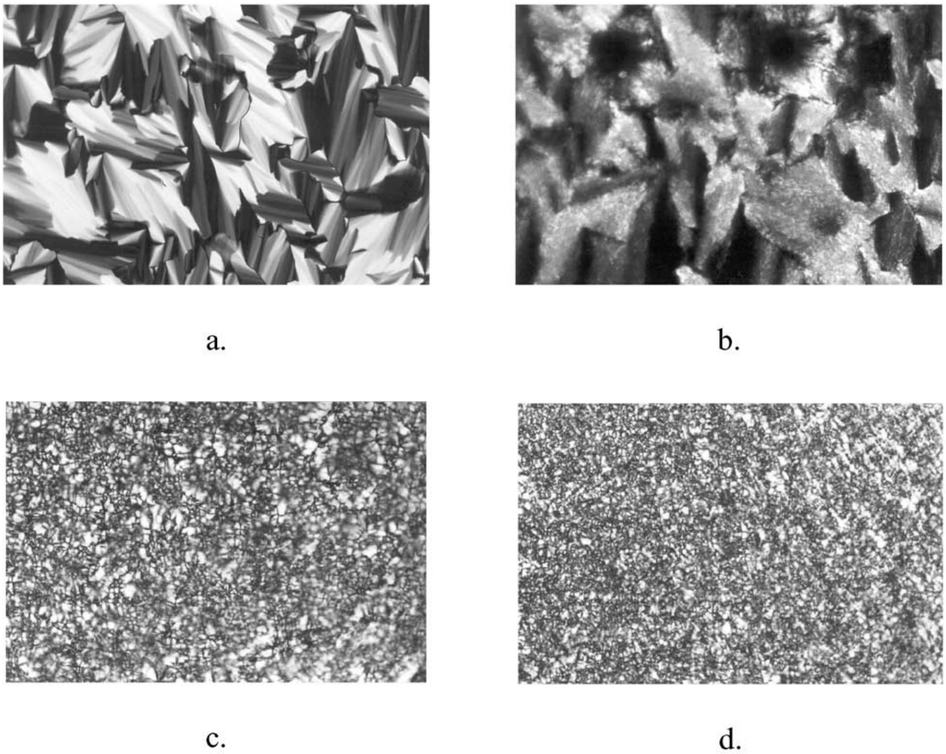

Fig. 10. Polarized light micrographs of 75% C12MA in water with 0% (hexagonal) and 15% (Lamellar) DTAB. Shown are (a) unpolymerized hexagonal, (b) polymerized hexagonal, (c) unpolymerized lamellar, and (d) polymerized lamellar LLC phases.

fan-like focal conic textures which are indicative of the hexagonal LLC phase. Upon polymerization (Fig. 10(b)) the sample remains birefringent, indicating that the polymerized sample possesses anisotropy. However, the texture does appear slightly different after polymerization. The fan-like structures coarsen somewhat indicating that the structure is experiencing a subtle change in structure upon polymerization. In Fig. 10(c) the polarized micrograph of 75% C12MA with 15% DTAB in water exhibits a mottled texture with evident maltese cross structures. This texture is well documented to be indicative of the lamellar phase. After photopolymerization the sample not only remains birefringent, but also the texture is virtually identical to that of the unpolymerized sample. This behavior implies that the LLC structure is retained. This enhanced structure retention may, in fact, be due to the faster polymerization kinetics of the lamellar sample. Additionally, the incorporation of the nonpolymerizable DTAB may stabilize the polymerizing LLC.

It does appear that the hexagonal phase may undergo some structural changes during polymerization. To determine the extent of change, the 75% C12MA system was further characterized with SAXS to determine if the degree of order changes upon polymerization. In Fig. 11 SAXS profiles of 75% C12MA in water are shown both in the monomeric and polymeric state. The unpolymerized profile displays a primary reflection at a scattering angle of 2.72° that correspond to a *d*-spacing of 32.1 Å. A secondary peak also exists at 4.71° that corresponds to 18.8 Å. The ratio of these peak positions and their *d*-spacings are $1:1/3^{1/2}$ indicative of a hexagonal LLC phase. After photopolymerization both primary and secondary peaks shift to slightly lower scattering angles but the ratio of the peak positions remain constant showing that the polymerized sample retains the original hexagonal structure. The slight increase in dimensions could account for the subtle differences in the polarized micrograph in Fig. 10(b).

An overall goal of this research is to synthesize robust materials utilizing photopolymerization to form LLC phase structures. The original LLC phase appears to be retained, but the question remains whether this order persists at

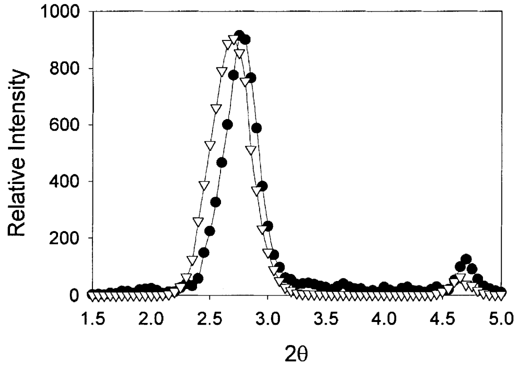

Fig. 11. SAXS profiles of 75% C12MA in water at 25 °C, shown are unpolymerized (●), and polymerized (▽).

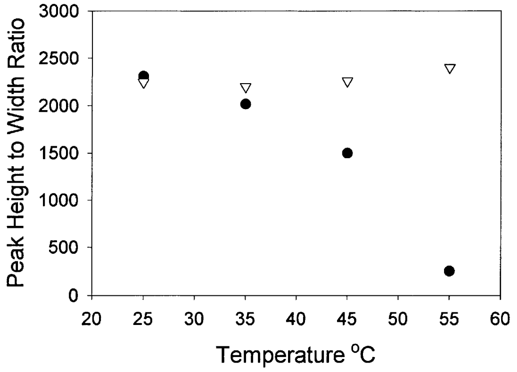

Fig. 12. SAXS peak height to width at half height ratios with increasing temperature of 75% C12MA in water unpolymerized (●), and polymerized (▽).

elevated temperatures. To answer this question, the peak height to width at half-height ratios from SAXS profiles of cured and uncured 75% C12MA in the hexagonal phase are depicted as a function of temperature in Fig. 12. The uncured LLC phase exhibits a very high ratio resulting from a very sharp peak in the SAXS regime at room temperature. When the temperature is increased to 35 °C, the hexagonal LLC phase is still present but the peak height to width at half-height ratio decreases somewhat. At 45 °C this measure of the degree of order decreases by more than 30% as the phase transition is approached. At temperatures above the phase transition, a very low peak height to width at half-height ratio is observed due to the lack of LLC structure. Interestingly, the cured sample exhibits a very similar ratio to the unpolymerized sample at 25 °C. Increasing the temperature to 40 °C causes no decrease in the degree of order of the polymerized sample. At temperatures exceeding the phase transition the original LLC order is still retained. Not only is the original degree of order retained in the polymerized system at temperatures exceeding the phase transition, but also perhaps a slight increase in the degree of order may be induced. This behavior suggests that the thermal treatment may allow the polymerized sample to organize to an even greater degree.

As the bicontinuous cubic phase exhibits no birefringence, small-angle X-ray scattering experiments were performed on unpolymerized and polymerized samples to determine if the structure is retained in this phase as well. In Fig. 13 the SAXS profiles of 75% C12MA with 5% DTAB are shown with increasing temperature. The SAXS patterns observed at 25 °C exhibit a strong primary reflection at approximately 3.0° that corresponds to 30.3 Å. Additionally, a peak is observed at a higher scattering angle corresponding to 24.8 Å. The ratio of these two *d*-spacings correspond to the ratio $2^{1/2}$:$3^{1/2}$ indicative of a bicontinuous cubic phase [3]. After heating the sample to 85 °C the SAXS profile changes to a single extremely broad peak that has shifted to higher scattering angles and correspondingly lower *d*-spacings. The broadened peak at 85 °C is due to the change in phase from the highly ordered bicontinuous cubic LLC phase to that of an isotropic micellar phase of surfactant and water. After polymerization at room temperature, the sample is still highly ordered as evidenced by the sharp reflections in the SAXS profiles. For this polymerized sample the primary reflection is observed to shift to lower scattering angles at 25 °C. Specifically, the *d*-spacing of the primary reflection has increased to 33.0 Å for a total change of 3.0 Å from the unpolymerized LLC phase. The secondary peak shifts to lower scattering angles as well. In fact, the secondary peak shifts to the same extent as the primary peak indicating that the bicontinuous cubic structure is retained. When the polymerized sample is heated above the unpolymerized sample phase transition to 85 °C, the sharp reflections (both primary and secondary) remain virtually unchanged. It is important to note for the phases in which retention is observed that photopolymerization is used. These structures are in direct contrast to those observed when the polymer is formed via other mechanisms. The photopolymerization not only provides rapid polymerization to trap the structure, but also allows polymerization at more thermodynamically favorable temperatures. The retention of LLC order above the phase transition gives strong evidence that the goal of generating robust materials with LLC nanostructures has been achieved.

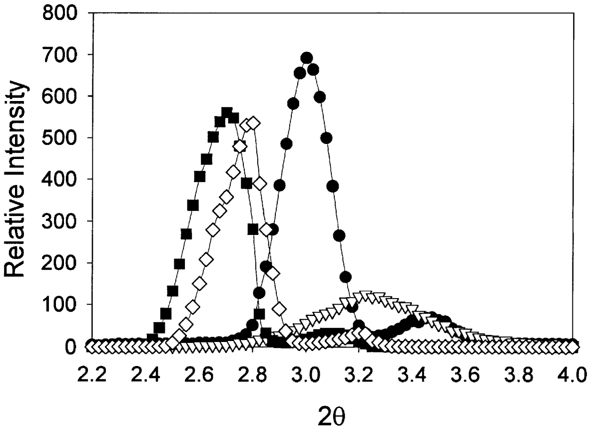

Fig. 13. SAXS profiles of 75% C12MA with 5% DTAB in water with increasing temperature. Shown are profiles of the system unpolymerized at 25 °C (●), and at 85 °C (▽), polymerized at 25 °C (■), and at 85 °C (◇).

4. Conclusions

The polymerization kinetics of the quaternary ammonium surfactant C12MA in water depend dramatically on the LLC morphology. The C12MA monomer exhibits a variety of LLC phases including hexagonal, cubic, and lamellar that can be modulated by adjusting the DTAB concentration, while keeping the double bond concentration constant. Interestingly, the fastest polymerization rates are observed in the highly ordered lamellar LLC phase with the slowest seen in the hexagonal LLC phase. The bicontinuous cubic LLC phase exhibits rates intermediate to the hexagonal and lamellar LLC phases. These differences in polymerization kinetics are predominantly due to diffusional limitations on the propagating chains. Additionally, order of the C12MA LLC system exhibits a significant dependence on temperature. At lower temperatures, higher degrees of order are observed with SAXS and quadrupolar NMR. With subsequent increases in temperature, the degree of order in the hexagonal LLC phase decreases until the transition to an isotropic phase is reached. The time to achieve peak polymerization rate is directly dependent on the observed degree of order in the system. At lower temperatures with higher degrees of LLC order, the time to reach the maximum polymerization rate is considerably less than the time to reach this maximum rate with lower degrees of LLC order at higher temperatures. The use of photopolymerization also allows LLC structure retention in all of the studied phases. The original LLC phase structure appears to be retained to the greatest extent in the faster polymerizing lamellar phase. The original nanostructure is also retained in the hexagonal and cubic LLC phases, though with some slight changes in structure. In fact, the original LLC structure is preserved at temperatures well exceeding the phase transitions of the unpolymerized LLC samples. In summary, the photopolymerization of the LLC phase forming monomer C12MA exhibits drastically different polymerization kinetics as the type and degree of LLC morphologies change. The retention of the original LLC nanostructure is also retained upon photopolymerization yielding considerable opportunity for applications requiring controlled nanostrucutures.

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