Polymer 49 (2008) 2260–2267

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Aliphatic chain length effects on photopolymerization kinetics and structural evolution of polymerizable lyotropic liquid crystals

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ARTICLE INFO

Article history:
Received 22 December 2007
Received in revised form 12 February 2008
Accepted 16 February 2008
Available online 5 March 2008

Keywords:
Lyotropic liquid crystals
Photopolymerization
Surfmer

ABSTRACT

Polymerizable lyotropic liquid crystals (LLCs) have the potential advantage of producing materials with anisotropic morphologies and nanometer size dimensions with potential in applications, such as drug delivery, catalysis, and tissue engineering. With the goal of more clearly understanding the factors involved in LLC phase retention after polymerization, this work describes the effect of aliphatic tail length in the amphiphilic molecule on order, polymerization kinetics, and structural evolution of reactive LLC systems. The polymerization kinetics are influenced by the LLC phase morphology with increases in the polymerization rate as the LLC phase increases in order. Enhanced polymerization rates are a result of an apparent increase in the termination and propagation rate parameters, induced by a local increase in monomer concentration due to segregation effects in the LLC phases. Polymerization in hexagonal phases formed from reactive amphiphiles with longer aliphatic tails exhibit lower polymerization rates when compared to systems with shorter aliphatic tails, suggesting that the order of the hexagonal phase decreases as the aliphatic tail increases. Two peaks are observed in the polymerization rate profiles when polymerizing in the hexagonal and cubic phases, with the second peak becoming more pronounced as the aliphatic tail length increases and the order of the LLC phase decreases. This effect appears to be due to changes in morphology during the polymerization process as the hexagonal phase morphology changes significantly during the polymer formation. Different behavior is observed for polymerizations in the lamellar phase for which the LLC phase is retained after polymerization.

1. Introduction

Recently, significant efforts have been devoted to create materials with controllable nanometer scale dimensions because of the impressive properties that are accessible [1–3]. The increased ratio of surface area to volume present in many nanoscale materials opens new possibilities for unique applications in surface-based science, such as drug delivery, catalysis, and tissue engineering [4–6]. Several materials have been created that exhibit nanometer size scale dimensions and also exhibit enhanced physical properties, such as inorganic zeolites and block copolymers [7,8]. Other nanostructured materials have been created using templates with nanometer size dimensions [9]. One such template, lyotropic liquid crystals (LLCs), has shown promise in enabling formation of organic crosslinked nanostructured polymers [10–12].

Lyotropic liquid crystals (LLCs) are amphiphilic molecules that arrange in the presence of water into highly ordered systems with periodicity on the nanometer size range. The type of assembly that forms is dependent on concentration, temperature, and packing preference of the molecule [13]. Spherical micelles form at low amounts of surfactant in water at the critical micelle concentration. With higher concentration the order of the system may also increase with hexagonal arrangements of cylindrical micelles. The layered structure of the lamellar phase, with much less curvature, may result at even higher surfactant concentrations. Other phases, including bicontinuous cubic, discontinuous cubic, and the inverse of the above-mentioned phases, may form at appropriate concentration and surfactant geometry. LLC mesophase formation is dependent on a number of factors that dictate the way these amphiphilic molecules aggregate. These factors include volume of the organic portion, area of the amphiphilic head group, and average critical length to the expected curvature as described by the critical packing parameter [14,15]. Curvature in LLC phases allows minimization of the bending energy [16]. Packing also dictates the overall order of a system, which is a critical factor in producing nanostructured materials. A limitation with the use of ordered LLC phases in nanostructured applications is that they have properties of fluids, and therefore the ordered structures can be easily disrupted by chemical or physical changes. For this reason synthesizing polymer with the unique nanostructured order of LLCs phases has been of great interest.

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doi:10.1016/j.polymer.2008.02.047

Polymers that display nanostructured LLC properties exhibit properties that are highly influenced by the original degree of order of the system. Mechanical strength, permeability, and network swelling have been shown to be dependent on the LLC phase in which the polymerization occurs [17]. The dependence that the pre-polymerized LLC order of templated system has on reactivity and kinetics has also been study extensively by different researchers. For example, the polymerization kinetics are dependent on the LLC phase in which the polymerization is initiated and on the polarity and segregation of the reactive monomers [18]. Other studies have shown that different combinations of monomers and LLC phases result in polymer morphologies that are not truly templated from the original LLC since the interfacial energy of water and distribution effects induce phase separation of the growing polymer chain and surfactant [19]. Other work has studied the effects in the type of polymerization and temperature in similar systems [20]. Less ordered polymers are formed and lower degrees of liquid crystalline order are retained when using thermal polymerization compared to fast reacting photopolymerization. Recent results have also shown that LLCs can be used to produce mesophase segregated composites from incompatible monomers systems [21].

Special attention has been given recently to polymers that have LLC structures and that can be used for new applications requiring a high degree of mechanical stability and nanoscopic order [22,23]. Polymerizable LLC systems may enable creation of nanostructured materials by preserving the original structure using covalent bonds. Unfortunately, the polymerization often results in organic nanostructures that are not thermodynamically stable and, in most cases, presents difficulties in retaining and controlling the structure during and after the polymerization. Several investigators have studied other factors that affect the structure evolution in polymerizable surfactant systems, such as lipids, microemulsions, and glucose based surfactants [24–26]. From these experiments it was found that the position of the polymerizable group, aliphatic tail length, temperature, and kinetics influence the structural evolution of reactive amphiphilic systems. A number of studies have indicated that polymerization kinetics can provide a direct relation to the original order in polymerizable LLCs [18,27]. For example, polymerization kinetics of an amphiphilic cationic reactive molecule in its various mesophases have been correlated to the LLC phase morphology in order to provide a better understanding on the impact of polymerization kinetics on the ultimate polymer structure [27]. Interestingly, polymerization kinetics are dramatically influenced by LLC morphology and temperature. Increasing the temperature and thereby decreasing the LLC order of the system induced successively longer polymerization times. LLC order appears to be retained upon polymerization as confirmed by the use of polarized light microscopy. Similar results have been observed for a copolymerization process of a quaternary ammonium surfactant monomer and styrene by using γ-irradiation [28]. The reactivity is higher in the ordered lamellar phase in comparison to less ordered phases. This behavior is due to the higher mobility of the styrene molecules in the layered structure of the lamellar phase in comparison to the cylindrical micelles in the hexagonal phase. After polymerization, the hexagonal phase is more stable but the order is slightly reduced. The cubic phase was also stabilized. Therefore, for this system the resulting copolymer is very stable regardless of the LLC mesophases.

As outlined, the polymerization process of LLC monomers is often quite difficult and may present difficulties in retaining and controlling the structure. Therefore, before polymeric LLCs' materials with controlled structure can be developed, the variables that affect their order before, during, and after polymerization need to be understood. Some variables including pre-polymerization order, crosslinking, and type of monomer have shown significant impact on structure retention of polymerizable LLC systems. This research details the photopolymerization of a series of LLC forming reactive surfactants in water in order to elucidate order effects due to changes in LLC phase. Polymerization rates were correlated with aliphatic tail length for different reactive surfactants forming different LLC phases enabling detailed order characterization. Samples before and after polymerizations were characterized enabling to determine the effect of order and non-polar tail length on the polymer structural evolution. Polarized light microscopy (PLM) was used to determine the effect of the polymerization process on LLC order. In addition, small-angle X-ray scattering (SAXS) was used to confirm the PLM results. SAXS was also used to better understand the effect of the pre-polymerization order on the resulting polymer order.

2. Experimental

2.1. Materials

The cationic LLC monomers C12MA, C14MA, and C16MA were prepared by reacting dimethylaminoethyl methacrylate (Aldrich) with dodecylbromide (Aldrich), tetradecylbromide (Aldrich), and hexadecylbromide (Aldrich), respectively, according to a method previously described [29]. In a typical synthesis dimethylaminoethyl methacrylate is reacted with the corresponding alkyl bromide 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 chemical structure of the LLC monomers is shown in Fig. 1. The LLC systems presented in this research consist of the reactive surfactant, water, and photoinitiator (Irgacure 2959 – Ciba). Lauryl methacrylate (Aldrich) and ethylene glycol diacetate (Aldrich) were used as received.

2.2. Procedure

LLC morphology for the different samples was characterized 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). Phases were also identified with small-angle X-ray scattering (SAXS) by measuring ratios in *d*-spacing calculated from the reflections in the corresponding sample profiles [30]. 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). By comparing SAXS profiles and polarized light microscopy images from before and after polymerizations, the degree of LLC structure retained upon polymerization was determined.

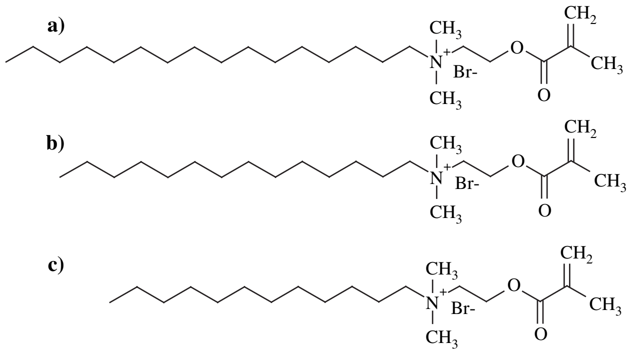

Fig. 1. Chemical structures for the polymerizable amphiphilic molecules used in this study. Shown are (a) C16MA, (b) C14MA, and (c) C12MA.

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 °C 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 as explained in previous publications [31]. Maximum rates were taken from the peak in the rate profiles obtained, and double bond conversion was calculated by integrating the heat flow profiles. For these studies the theoretical value of 13.1 kcal/mol was used as the heat evolved per methacrylate double bond reacted [32].

Apparent rate parameters for k_t and k_p were measured through a series of after-effect experiments. The steady-state polymerization rate was utilized to determine the lumped kinetic constant, $k_p/k_t^{1/2}$ as a function of time by using Eq. (1):

$$\frac{-\mathrm{d}[M]}{\mathrm{d}t} = \frac{k_p}{k_t^{1/2}}[M][\phi(I_{ABS})]^{1/2} = \frac{k_p}{k_t^{1/2}}[M]R_i^{1/2} \qquad (1)$$

where ϕ is the quantum yield of initiating radical formation, $[M]$ is the monomer concentration, R_i is the rate of initiation, and I_{ABS} is the intensity of light absorbed. By closing the light shutter between the UV light source and the sample at various time intervals during the polymerization, the initiation step was eliminated and the exotherm decay was analyzed by Eq. (2) to give k_p/k_t from the slope of a plot of reciprocal exotherm rate versus time:

$$\frac{1}{R_p} - \frac{1}{R_{po}} = \frac{2k_t t}{k_p[M]} \qquad (2)$$

where R_p is the polymerization rate at time t, R_{po} is the initial rate of polymerization, and $[M]$ is the monomer concentration at time t. The propagation and termination rate parameters can then be decoupled. The methodology of determining individual rate constants is also described in detail elsewhere [33].

3. Results and discussion

Polymerization of amphiphilic molecules functionalized with polymerizable moieties represents a promising route to produce nanostructured materials that exhibit enhanced material properties. The properties of the resulting polymer are often dependent not only on the LLC phase in which the polymerization is initiated but also on the polymerization kinetics. The goal of this work is to understand the effects induced by aliphatic tail length of the amphiphilic molecule on order, polymerization kinetics, and structure evolution of reactive LLC systems. This goal requires the selection of polymerizable amphiphilic molecules that exhibit a variety of LLC phases. Quaternary ammonium surfactant molecules like dodecyltrimethylammonium bromide (DTAB) display different LLC phases including hexagonal, bicontinuous cubic, and lamellar phases. The amphiphilic molecules used in this study are analogous to DTAB and contain a methacrylate group that can be reacted to form covalent bonds during polymerization.

Different non-polar tail lengths for the polymerizable LLCs were used in this study as shown in Fig. 1. For example, C12MA in water displays a wide range of LLC phases including the discontinuous cubic, hexagonal, bicontinuous cubic, and lamellar phases [34]. Similar phase behavior is observed for C14MA. The lamellar phase is not observed for C16MA under the concentration range explored. LLC phases exhibit characteristic dimensions that can be tailored by the size of the surfactant molecule and concentration. As can be seen in Fig. 2, the d_{100}-spacings for the unpolymerized samples calculated from the primary reflections in the SAXS profiles decrease as the concentration of the surfactant increases and the LLC phase changes from the hexagonal to the bicontinuous cubic phase for all aliphatic chain lengths. This contraction in *d*-spacings is due to the close packing of the amphiphilic molecules as more molecules and less water is present in the system. As the concentration of surfactant increases, the change in hydrophilic interactions between the surfactant head groups and hydrophobic interactions at the hydrocarbon–water interface induces the surfactant molecules to associate in a different way in order to minimize the entropy of the system [14]. As the aliphatic tail length of the reactive surfactant molecule increases the *d*-spacing also increases at the same concentration. This result is reasonable given that at the same LLC phase and concentration, a larger size repeating structure is expected as the length of the aliphatic chain of the surfactant molecule is increased.

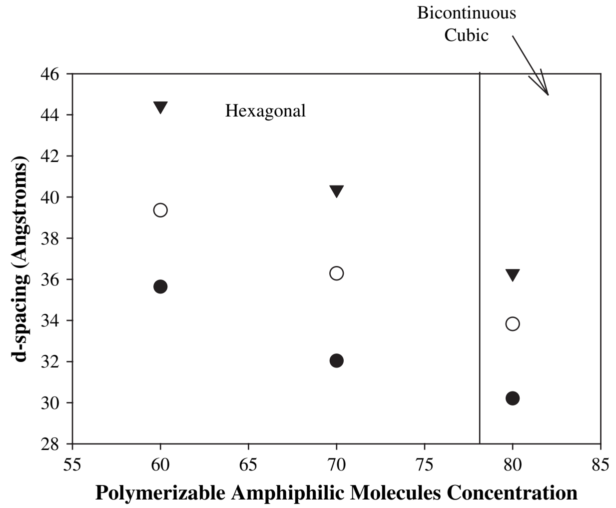

Fig. 2. *d*-Spacing of various polymerizable amphiphilic molecules in water at various concentrations as determined by the primary reflection of the SAXS profiles: shown are C12MA (●), C14MA (○), and C16MA (▼) in water.

In order to understand the influence of the order of the reactive LLC system on the polymerization rate, the polymerization behavior in different phases was studied. For these systems the reactive surfactant concentration was increased from 40% to 90% as this concentration range exhibits the discontinuous cubic, hexagonal, bicontinuous cubic and lamellar phases. Interestingly, the polymerization kinetics of reactive surfactants with different aliphatic chain lengths exhibit different polymerization behaviors. Fig. 3a–c shows that polymerization rate as a function of time for C12MA, C14MA, and C16MA in water, respectively. The main difference between these reactive surfactant molecules is the non-polar tail length ranging from 12 carbons for C12MA to 16 carbons for C16MA. The polymerization rate behavior is significantly different as phase behavior changes with increasing concentration of reactive surfactant monomer. The reaction rate increases as the LLC phase is changed from the optically isotropic discontinuous cubic phase, to hexagonal, and then to lamellar. In Fig. 3a it can be seen that for C12MA the maximum polymerization rate is similar for the discontinuous cubic and mixture of discontinuous cubic and hexagonal phases formed at 50% and 60% C12MA, respectively. Increasing the concentration to 75% C12MA forms the hexagonal phase which exhibits

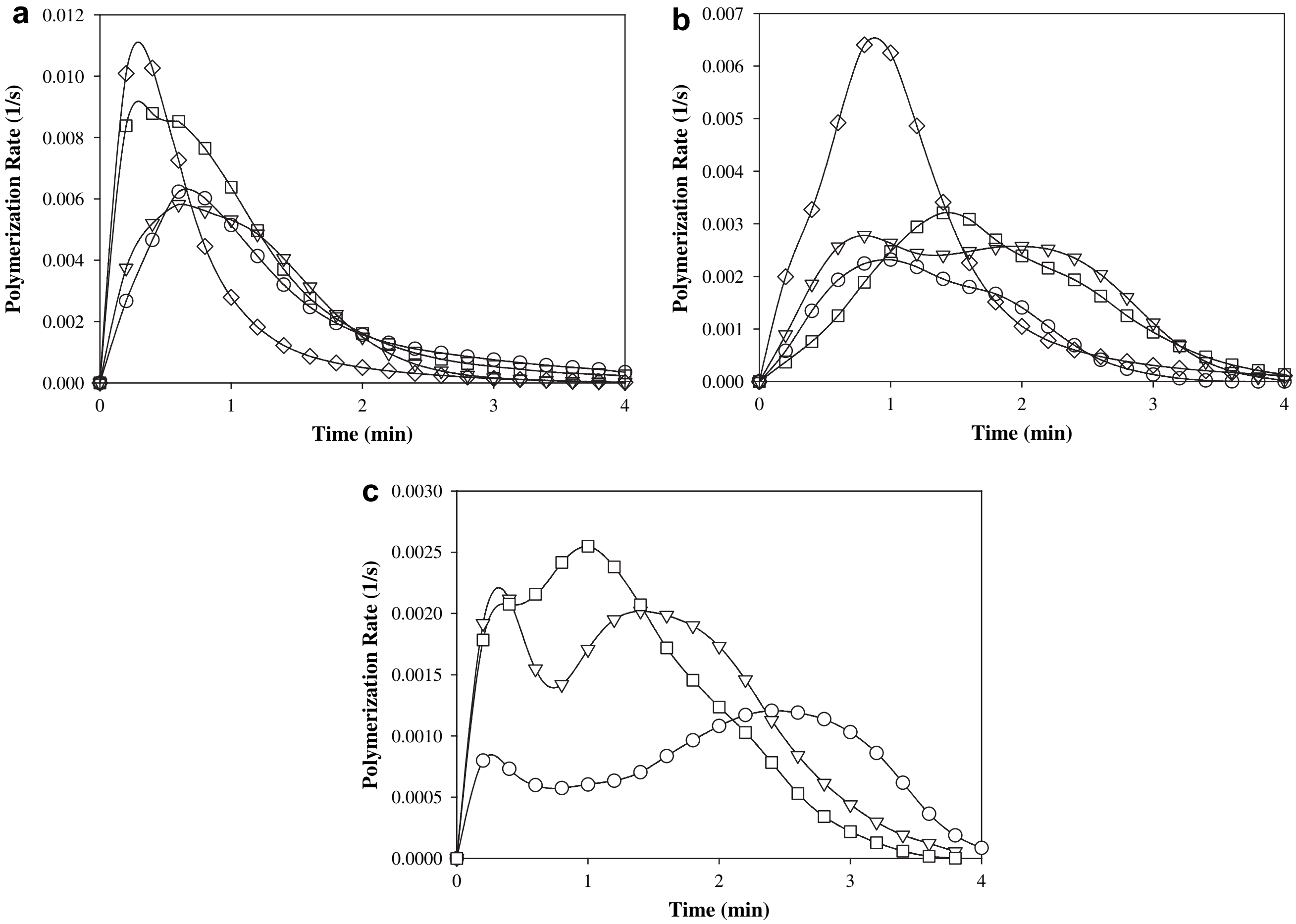

Fig. 3. Polymerization rate as a function of time for C12MA, C14MA, and C16MA in water. Shown are (a) 50% C12MA – cubic (○), 60% C12MA – cubic/hexagonal (▽), 75% C12MA – hexagonal (□), 90% C12MA – lamellar (◇) in water; (b) 50% C14MA – cubic (○), 55% C14MA – cubic/hexagonal (▽), 65% C14MA – hexagonal (□), 90% C14MA – lamellar (◇) in water; and (c) 40% C16MA – cubic (○), 50% C16MA – cubic/hexagonal (▽), 65% C16MA – hexagonal in water (□).

higher polymerization rate. The fastest polymerization rate occurs at 90% C12MA corresponding to a lamellar phase morphology. The maximum polymerization rate in the lamellar phase is observed to be almost twice that in the discontinuous cubic phase for C12MA.

Similar behavior is observed for C14MA as shown in Fig. 3b. The polymerization rate increases slightly between the cubic and the transition between the discontinuous cubic and hexagonal phases formed at 50% and 55% C14MA, respectively. Increasing the concentration to 65% C14MA forms the hexagonal phase which exhibits an increase in polymerization rate about 1.5 times that observed in the cubic phase. Further increase in concentration forms the lamellar phase with a maximum polymerization rate more than three times that of the discontinuous cubic phase. For C16MA the lamellar phase is not observed but the polymerization rate in the hexagonal phase is approximately double that of the discontinuous cubic phase as shown in Fig. 3c. It is important to note that two peaks are observed in the polymerization rate versus time curves for the hexagonal and cubic phases. This behavior may be attributed to autoacceleration effects associated to an increase in viscosity during the polymerization process or also changes in phase morphology [35].

To explain the increase in the polymerization rates when increasing the LLC order, after-effect experiments were performed to determine apparent rate parameters of propagation, k_p, and termination, k_t. In this experiment apparent k_p and k_t values were calculated from the steady-state polymerization rate and dark reaction exotherm decay assuming an initiation efficiency of 0.6 in both the hexagonal and lamellar phases. Fig. 4 depicts the apparent propagation and termination rate constants for the rapid polymerization in the lamellar phase and the slower polymerization in the hexagonal phase using the C14MA-water system. This system

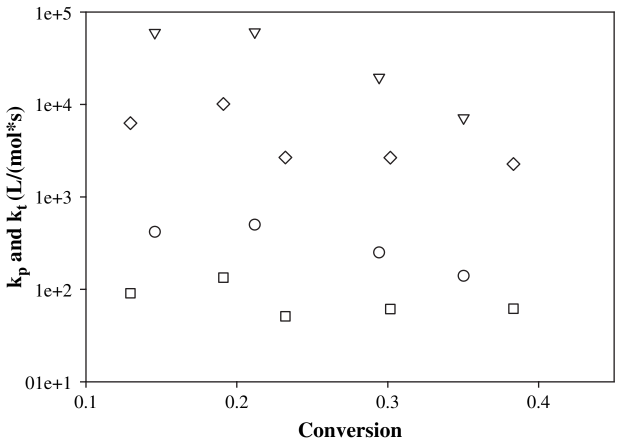

Fig. 4. Termination (k_t) and propagation (k_p) rate parameters of C14MA in water as a function of double bond conversion at 30 °C. Shown are k_p for 80% C14MA – lamellar (○), k_p for 65% C14MA – hexagonal (□), k_t for 80% C14MA – lamellar (▽), and k_t for 65% C14MA – hexagonal (◇).

was chosen because of the large increase of the polymerization rate between lamellar and other phases. Over a range of conversions polymerization in the lamellar phase exhibits a k_p an order of magnitude higher than the polymerization in the hexagonal phase which could explain the increase in reaction rate. However, a similar increase is also observed for the k_t values in the lamellar phase, which indicates faster termination rates which should reduce the overall rate. Since the polymerization rate based on a steady-state radical assumption is dependent on $k_p/k_t^{1/2}$, a similar increase of both k_p and k_t will produce an overall increase in the polymerization rate. The increase in the magnitude of the kinetics constants at different conversions suggests an increase in local monomer concentration due to segregation effects in the LLC phases as presented by Lester and coworkers [27]. This behavior is possible since a higher localized concentration of double bonds is present in the lamellar phase compared to the hexagonal phase due to the packing shape or molecular conformation of the surfactant molecules. With lower interfacial curvature the polymerizable double bonds would be more closely aligned in the lamellar phase, causing a dramatic change in the polymerization dynamics. The methacrylate groups will be much closer to each other especially when compared to the curved surface of the hexagonal phase.

In order to determine if this behavior is simply due to increased concentration or if order enhances the polymerization rate, a completely isotropic and disordered system composed of lauryl methacrylate in ethylene glycol diacetate (EGDAc) was employed as a control. Lauryl methacrylate (LaMA) was chosen as the monomer because of the structural resemblance with a similar aliphatic tail to the amphiphilic molecules under study. Fig. 5 shows the polymerization rate as a function of time for LaMA in EGDAc at different concentrations. Similar to the amphiphilic systems under study the normalized polymerization rate increases as the lauryl methacrylate concentration is increased. The maximum polymerization rate almost doubles when polymerizing at a concentration of 95% LaMA compared to 50% LaMA. Similarly, the maximum polymerization rate for the reactive LLC systems under study approximately doubles for a similar range of concentrations. Even though a higher light intensity was employed in the LaMA system as compared to the LLC systems, the polymerization rate is much slower. Complete polymerization occurs in approximately 20 min compared to approximately 5 min for the reactive LLC monomer systems. These results confirm that the enhancements in polymerization rates observed in the ordered LLC system are due to the combined effects of diffusional limitations on the propagating polymer in addition to the segregation of the polymerizable groups [36].

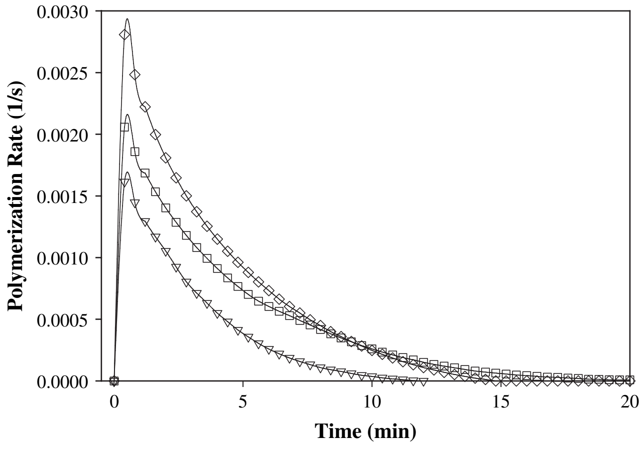

Fig. 5. Polymerization rate as a function of time for lauryl methacrylate (LaMA) in ethylene glycol diacetate (EGDAc). Shown are 50% LaMA (▽), 65% LaMA (□), and 95% LaMA (◇) in EGDAc.

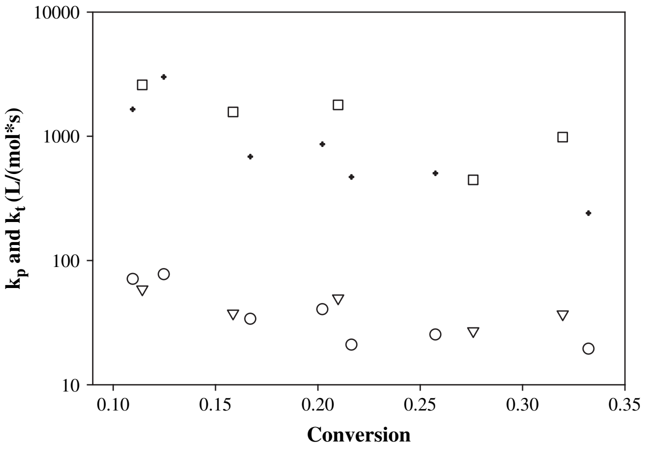

Fig. 6. Termination (k_t) and propagation (k_p) rate parameters of lauryl methacrylate in ethylene glycol diacetate (EGDAc) as a function of double bond conversion at 30 °C. Shown are k_p for 95% lauryl methacrylate (▽), k_p for 50% lauryl methacrylate (○), k_t for 95% lauryl methacrylate (●), and k_t for 50% lauryl methacrylate (□) in EGDAc.

Another important observation is that the shape of the polymerization rate versus time curves for LaMA does not indicate the two peaks observed in the reactive LLC systems. This result, and the fact that all the lamellar phases formed retained the original LLC order after polymerization, supports the idea that the shape of the polymerization rate curve observed for some reactive LLC systems could be due to the presence of the ordered nanostructures and may be due to changes in morphology during the polymerization process.

To further understand the polymerization rates result with increases in concentration for the completely isotropic and disordered system composed of LaMA in EGDAc, after-effect experiments were performed. Fig. 6 depicts the apparent propagation and termination rate constants, designated k_p and k_t, for 50% and 95% LaMA. Over a range of conversions both systems exhibit approximately the same k_p values. However, a slight decrease in k_t values is observed for the sample containing 95% LaMA compared to the sample containing 50% LaMA indicating a decrease in the termination rate. This classical behavior for polymerizable systems is due to the fact that as the propagating radicals becomes larger and the viscosity of the system increases, it is more difficult for the propagating radicals to terminate [37]. The presence of highly ordered morphologies in LLCs changes the polymerization dynamics to be dependent on diffusional limitations due to the organization and segregation of double bonds compared to diffusional limitations due to viscosity changes during the polymerization process for disordered isotropic systems. Therefore, different kinetics are observed between LLC systems that possess anisotropic order compared to completely disordered systems.

As mentioned before the primary goal of this work is to understand the effect that the aliphatic tail length of the amphiphilic molecule has on order, the polymerization kinetics, and structure evolution of reactive LLC systems. In order to accomplish this goal the hexagonal phases formed at 75% C12MA, 65% C14MA, and 65% C16MA in water were studied before and after polymerizations. To characterize the hexagonal phases formed using different aliphatic tail lengths, SAXS was employed. Fig. 7 shows the SAXS profiles for the hexagonal phases formed with 75% C12MA, 65% C14MA, and 65% C16MA in water while the *d*-spacings for each reflection are shown in Table 1. All samples exhibit a ratio between the primary and secondary reflections of $1:1/3^{1/2}$ before polymerization, which is indicative of a hexagonal phase. Upon polymerization all the samples exhibit a ratio between primary and secondary reflections of 1:2, which is indicative of a lamellar phase. Therefore, for all the hexagonal phases formed with LLC of different non-polar

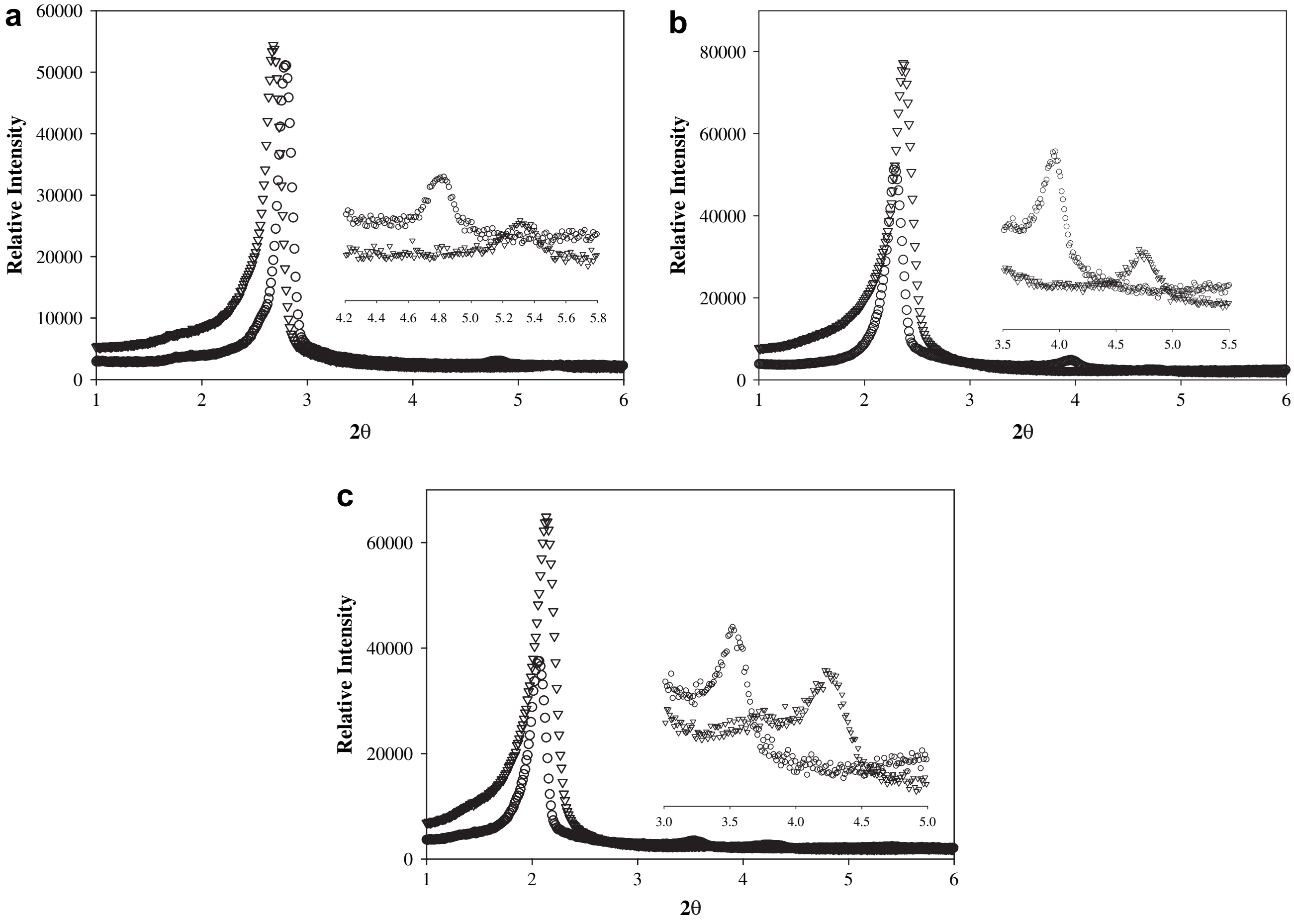

Fig. 7. SAXS profiles for the hexagonal phases formed at (a) 75% C12MA, (b) 65% C14MA, and (c) 65% C16MA in water before (○) and after (▽) polymerizations.

Table 1
SAXS reflections for hexagonal LLC phases

	75% C12MA		65% C14MA		65% C16MA	
	Primary reflection [Å]	Secondary reflection [Å]	Primary reflection [Å]	Secondary reflection [Å]	Primary reflection [Å]	Secondary reflection [Å]
Before polymerization	30.75	17.73	37.45	21.58	41.47	23.76
After polymerization	32.02	16.02	36.22	18.02	40.18	20.07

tail lengths the structure changes to the lamellar phase. These results confirm that thermodynamics have 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 of the system.

From the SAXS profiles it can be appreciated that the original LLC phase is disrupted during polymerization. In order to corroborate these results, PLM was employed. PLM provides a straightforward method of characterizing LLC phases based on the anisotropy present in these systems. Polarized light micrographs before and after polymerizations for the different hexagonal phases are shown in Fig. 8. For the 75% C12MA sample the polarized micrographs exhibit defined conical textures prior to polymerization that are indicative of an ordered hexagonal phase. After polymerization the sample remains birefringent, but the conical textures are significantly disrupted indicating a loss of order. Increasing the aliphatic tail and forming the hexagonal phase at 65% C14MA decreases the order as indicated by less defined conical textures. Further increase in the aliphatic tail with the hexagonal structure at 65% C16MA decreases the order to a greater extent. This result is in accordance with previous research indicating that increasing the aliphatic tail length increases the disorder at the end of the aliphatic tail due to hydrophobic interactions which may cause disruption of the liquid crystal [25]. Increasing the aliphatic tail also affects the packing parameter which dictates the shape and structure tendency of formation in surfactant systems [14]. This result is also supported by a significant decrease in the ratio of the SAXS primary reflection peak height to width ratio as shown in Fig. 9a. This ratio has been used in previous research as a way to compare order in LLC systems [37]. The peak height to width ratio for the hexagonal phase formed at 75% C12MA is almost twice that of the hexagonal phase formed at 65% C14MA. The hexagonal phase formed at 65% C16MA exhibits a height to width ratio that is slightly lower than that of the hexagonal phase formed at 65% C14MA. After polymerization the samples become opaque with this effect being more pronounced as the aliphatic tail length increases. The observation of an opaque sample indicates that some of the anisotropic character is being lost and changes in morphology are occurring as the polymer phase separates during the polymerization process. Increasing the aliphatic

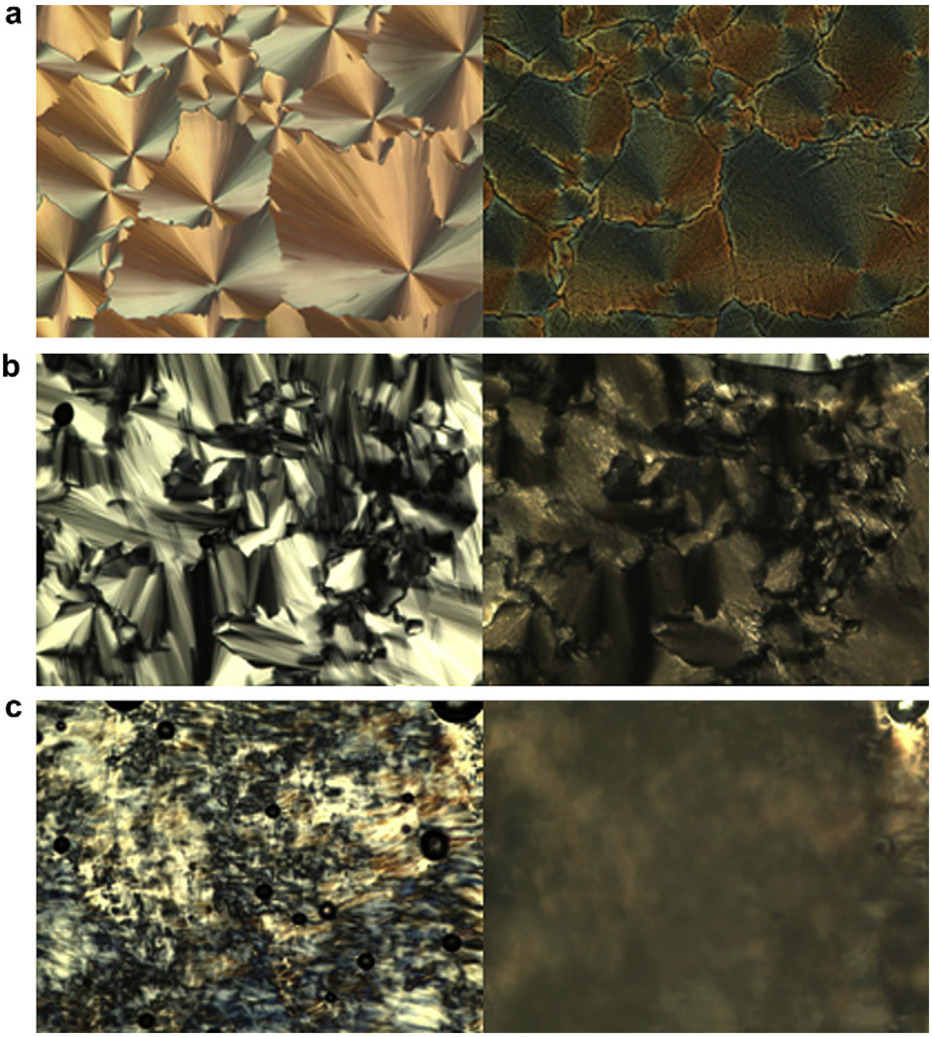

Fig. 8. Polarized light micrographs for the hexagonal phase formed at (a) 75% C12MA, (b) 65% C14MA, and (c) 65% C16MA in water. Unpolymerized and polymerized samples are on the right and left, respectively.

chain of the reactive surfactants decreases the order of the LLC phases formed and therefore increases the tendency of these LLC systems to change conformation during polymerization.

The SAXS and PLM results in conjunction with the polymerization kinetics presented enable us to characterize the LLC phases before and after polymerizations and further understand the structural evolution mechanism in polymerizable LLC systems. The pre-polymerization LLC order is dependent on the aliphatic tail length and is strictly related to the polymerization behavior. The maximum polymerization rate decreases for the hexagonal phase as the aliphatic tail length increases, suggesting that less order is present. As the aliphatic tail length increases from C12MA to C16MA, forming less ordered hexagonal phases, the two peaks observed in the polymerization rate profiles become more pronounced suggesting that the polymerization rate behavior could be due to the formation of the lamellar structure due to phase separation during the polymerization process as presented by the PLM and SAXS results. These results suggest the possibility of using the polymerization kinetics as a way to describe the polymer evolution during the reactive LLC polymerization process.

The order of the LLC phase before polymerization may also play a role in the order of the resulting polymer structure. In order to understand the effect of LLC phase stability on the resulting polymer order, the intensity change in the SAXS primary reflection before and after polymerizations is presented in Fig. 9b for the different hexagonal phases formed at 75% C12MA, 65% C14MA, and 65% C16MA. As the stability of the hexagonal structure decreases, the intensity of the primary SAXS reflection after polymerization decreases significantly. This result suggests that the LLC phase is more resistant to change when it is more ordered before polymerization. We can presume that a more ordered lamellar structure is being formed from the less ordered hexagonal structure because of the easier disruption of the phase during polymerization. Similar results have been obtained for reactive thermotropic liquid crystals in which the order changes from an isotropic phase to a more ordered smectic phase after polymerization [38].

From these results we can observe that LLC monomers apparently reorganize during polymerization from the hexagonal to the lamellar phase. As the photopolymerization starts by the exposure of the photoinitiator with UV light some molecules react that are in the same micellar rod and between rods in the hexagonal structure. As the polymerization proceeds the hexagonal phase becomes unstable and the molecules start rearranging in search of a thermodynamically stable conformation which leads to a partially reacted lamellar phase. The secondary peak observed in the polymerization rate curve is associated to the reorganized and partially reacted lamellar phase since a higher polymerization rate is observed for this highly ordered phase. This behavior has also been seen in previous results for reactive thermotropic liquid crystals in which the

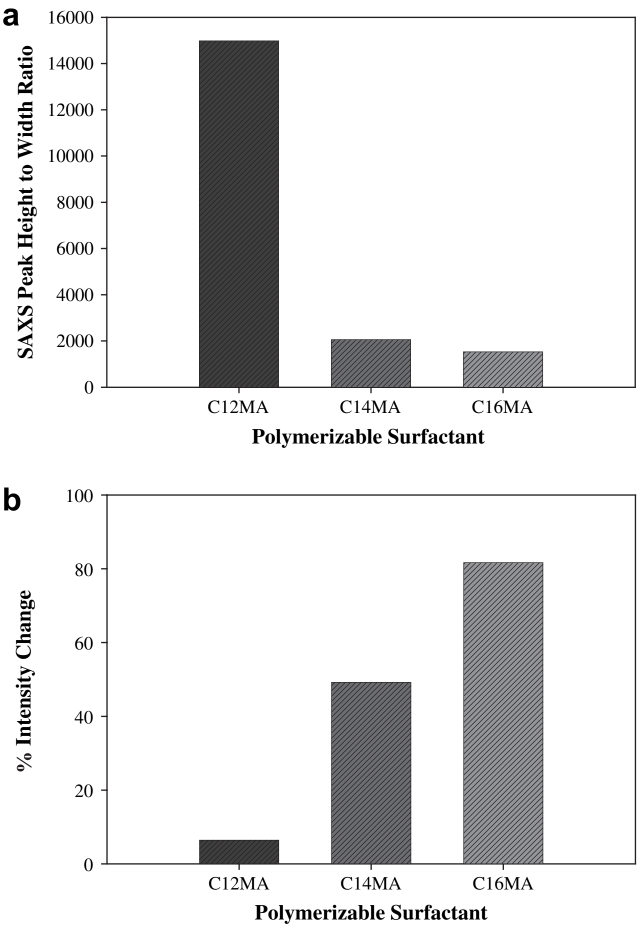

Fig. 9. (a) Ratios of peak height to width at half-height for the hexagonal phases formed at 75% C12MA, 65% C14MA, and 65% C16MA in water and (b) SAXS primary peak intensity change when polymerizing the hexagonal structure formed at 75% C12MA, 65% C14MA, and 65% C16MA in water.

presence of two peaks in the polymerization rate profiles was related to a change from an isotropic to a birefringement medium [39].

4. Conclusions

In this work the effect of the aliphatic tail length in a polymerizable amphiphilic molecule on order, polymerization kinetics, and structure evolution of reactive LLC systems is detailed. The polymerization kinetics are influenced by the initial LLC phase morphology with increases in the polymerization rate as the LLC phase order increases. This behavior is a result of an apparent increase in the rate of propagation and termination rates induced by higher local concentrations of reactive molecules in the more concentrated and ordered lamellar phase compared to other phases with lower concentration and order of reactive molecules. Less ordered hexagonal phases are formed by increasing the non-polar tail length of the amphiphilic molecule. During polymerization the original hexagonal LLC structure changes to a lamellar morphology. This change is reflected by two peaks in the polymerization rate profiles for the hexagonal and some cubic phases where a secondary peak, which indicates an increase in polymerization rate, corresponds to the formation of a lamellar structure. On the other hand, when systems exhibit a lamellar LLC morphology, the phase structure is retained through polymerization suggesting that more ordered LLC phases are more resistant to changes when polymerized.

Acknowledgements

The authors thank NSF for financial support of this project through PECASE CBET0328231 and CBET0626395 grants and the U.S. Department of Education for a GAANN fellowship.

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