Photopolymerization of functionalized lyotropic liquid crystalline systems

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Introduction

Nanostructured polymers have recently received considerable attention because of their potential applications in a wide range of applications. Significant research effort has focused on synthesizing these polymers using lyotropic liquid crystalline (LLC) not only as templates but by using reactive surfactants that form reactive LLC systems in which the original LLC order can be preserved after polymerization by the formation of covalent bonds. 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.[1] The dependence that the pre-polymerized LLC order of the templated system has on reactivity and kinetics has also been study extensively by different researchers. From these studies it was shown that the structures formed are highly dependent on polymerization kinetics. Significant understanding of the unique polymerization mechanism in LLC material has resulted from monitoring the polymerization kinetics of many LLC systems. Understanding the polymerization kinetics is a valuable tool that helps in the understanding of polymer formation and nanostructure development and therefore more research in needed in the area.

Several investigators have studied the factors that affect the structure evolution in polymerizable surfactant systems such as lipids, microemulsions, and glucose based surfactants.[2-4] From these experiments it was found that the position of the polymerizable group, temperature, and the aliphatic tail length influence the structural evolution of reactive amphiphilic systems. It is not surprising that the polymerization kinetics play an important role in better understanding these systems. A number of studies have indicated that polymerization kinetics can provide a direct relation to the original order in polymerizable LLCs.[5,6] In this study the effects that the non-polar tail length and location of the reactive group of the surfactant molecule and crosslinking have on the polymerization kinetics are presented. The trends in polymerization rate with respect to these variables are characterized and compared.

Experimental Section

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.[7] In a typical synthesis dimethylaminoethyl methacrylate is reacted with the corresponding alkyl bromide in acetone at 41°C for four 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 figure 1. The LLC systems presented in this research consist of the reactive surfactant, water, and photoinitiator (Irgacure 2959 - Ciba).

Procedure. A polarized light microscope (Nikon, Eclipse E600W Pol) equipped with a hot stage (Instec, Boulder, CO) was utilized for phase characterization by looking for characteristic textures and phase transitions of the various mesophases. Polymerized and unpolymerized samples were also characterized by small-angle X-ray scattering (SAXS). Bragg's law was used to determine d-spacing of the LLC system. 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 50M position sensitive linear detector (Hecus M. Braun, Graz).

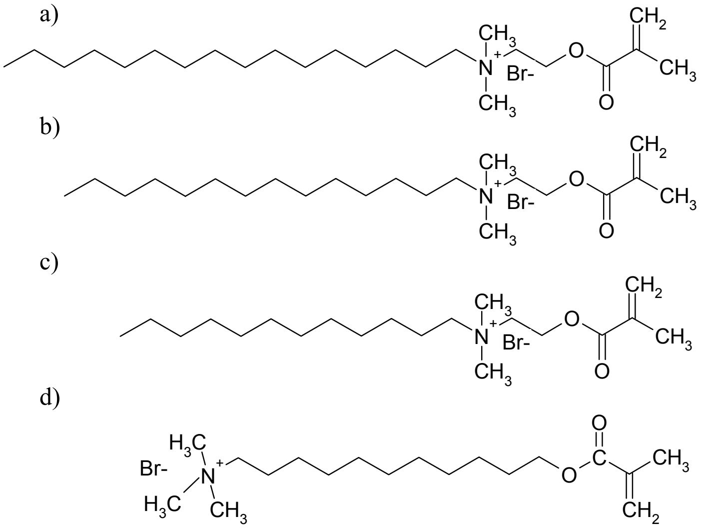

Figure 1. Chemical structures for the polymerizable amphiphilic molecules used in this study. Shown are a)C16MA. b)C14MA. c)C12MA. and d)PM1.

The polymerization rates were monitored using a Perkin Elmer differential scanning calorimeter. Polymerizations were initiated using the full emission spectrum from a medium pressure UV arc lamp. Samples of approximately 5 mg were placed in aluminum DSC pans and covered with UV transparent thin films of FEP (Dupont fluorinated copolymer) to prevent evaporation of water. The DSC sample cell was purged with nitrogen for 7 min prior to polymerization to reduce oxygen inhibition. The samples were heated to 80° C and then cooled to room temperature at 20° C/minute to ensure uniform sample thickness and improve thermal homogeneity. During polymerization isothermal reaction conditions were maintained using a refrigerated circulating chiller. The polymerization rate was determined from the heat flow as shown elsewhere.[8] Maximum rates were taken from the peak of the rate profiles obtained.

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. Many factors that typically influence the rate such as monomer design and temperature remain critical in LLC systems while additional factors such as the degree of order in the system also play an important role. The same interactions responsible for the self assembly of liquid crystalline order tend to segregate monomers and other components to specific domains depending on their solubility within the system. Addition of other molecules to the system, such as co-surfactants or crosslinkers, could also affect the dynamics of the system and thereby affect the polymerization behavior.

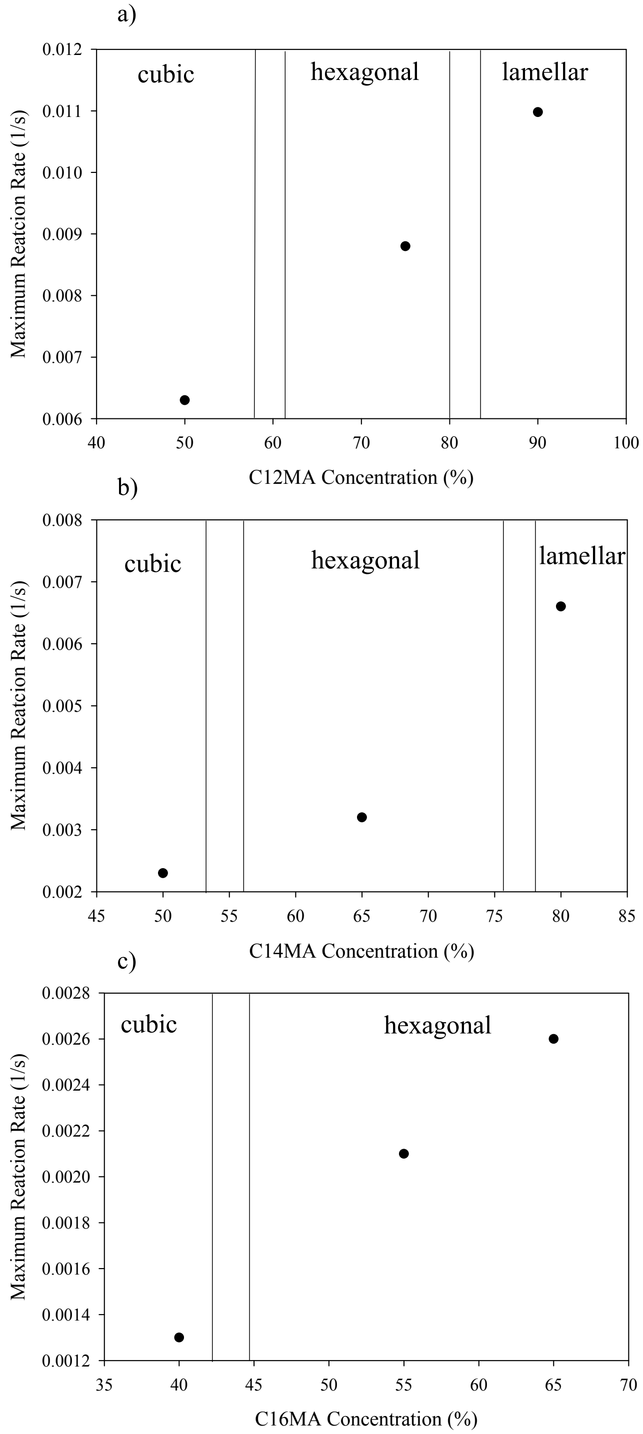

Figure 2. Maxiumum polymerization rates as a function of time for increasing concentrations of C12MA (a), C14MA (b), and C16MA (c) in water.

Non-Polar Tail Length: Different non-polar tail lengths for the polymerizable LLCs were used in this study as shown in figure 1. In order to understand the influence of the order of the reactive LLC system on the polymerizarion 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 cubic, hexagonal, and lamellar phases.[9] Interestingly, the polymerization kinetics of reactive surfactants with different aliphatic chain length exhibit different polymerization behavior. Figures 2-a, 2-b, and 2-c show the maximum 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 twelve carbons for C12MA to sixteen 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 increased in order from the optically isotropic cubic phase, to hexagonal, and then to lamellar. In figure 2a it can be seen that for C12MA the maximum polymerization rate increases from the cubic formed at 50%C12MA to the hexagonal LLC phase formed at 75%C12MA. 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 cubic phase for C12MA.

Similar behavior is observed for C14MA as shown in figure 2b. 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 cubic phase. For C16MA the lamellar phase is not observed but the polymerization rate in the hexagonal phase is approximately double that of the cubic phase as shown in figure 2c. 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 autoaceleration effects associated to an increase in viscosity during the polymerization process or also changes in phase morphology.[10]

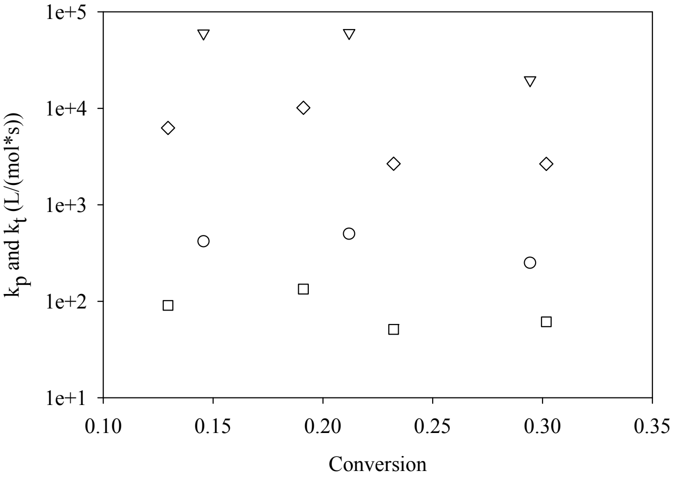

Figure 3. Termination (k_t) and propagation (k_p) rate parameters of C14MA in water as a function of double bond conversion at 30°C. Shown are k_p for 80% C14MA-lamellar (○), k_p for 65% C14MA-hexagonal (□), k_t for 80% C14MA-lamellar (∇), and k_t for 65% C14MA-hexagonal (◊).

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. Figure 3 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 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 that is 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.[6] 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. Interestingly, as the non-polar tail increases the reaction rate is lowered for the same LLC phase, suggesting that less ordered LLC phases are formed. This behavior could have an effect on the resulting polymer structure as it has been shown that the order has an impact on the polymer development in LLCs.

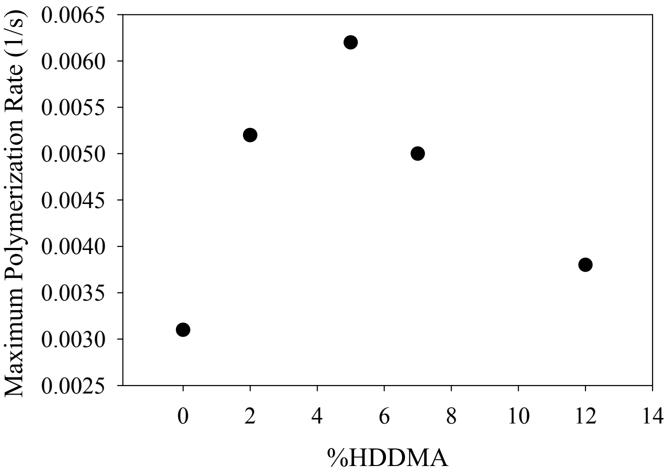

Figure 4. Polymerization rate as a function of time for 70%C14MA (hexagonal phase) in water at different temperatures. Shown are polymerizations at 30°C cubic (–), 50°C cubic-hexagonal (····), and 70°C hexagonal (**---**).

Crosslinking: Crosslinking the LLC structure has shown to promise as a way to retain the original structure after polymerization overcoming thermodynamic limitations associated with phase separation.[11] By using SAXS the type of phase can be characterized. For a system composed of C14MA, water, and HDDMA the hexagonal structure is observed up to 15% HDDMA with respect to surfactant monomer concentration at room temperature. The d-spacing, calculated from the primary peak, decreases as the HDDMA is added, indicating that the unpolymerized structure is being compressed. This suggests that the HDDMA molecules are segregating in the polar region, most likely near the polar heads. Crosslinking at 2mW/cm^2 enables retention of the hexagonal structure from 9%HDDMA to 15%w/w HDDMA. After polymerization both the primary and secondary peaks shift to slightly lower scattering angle but the ratio of the peak position remains constant showing that the polymerized sample retains the original hexagonal phase. Also, based on the intensity of the secondary peaks it can be said that the hexagonal phase is more ordered in the polymer with 12% to 13%HDDMA.

To better understand how the cross-linker influence the kinetics in this highly ordered system the polymerization rate was examined. For the hexagonal phase formed at 70%C14MA and adding different amounts of HDDMA the polymerization rate and the maximum polymerization rate increase as the HDDMA is added at low concentrations (up to 3%HDDMA) as shown in figure 4. This behavior is observed when adding a cross-linker to a completely disordered system. At high concentrations the rate of change of the polymerization rate and the maximum polymerization rate decrease. At these concentrations the hexagonal phase begins to be disrupted by the addition of HDDMA. This behavior indicates that there are two competing effects affecting the polymerization kinetics. At low HDDMA concentrations, where the conditions for phase formation don't change significantly, the cross-linker effect becomes more important. This behavior differs at high concentration where the hexagonal structure is disrupted by the addition of HDDMA into the polar regions of the LLC. The crosslinking effect on structure retention at high HDDMA concentrations becomes more important and pronounced than the LLC order therefore decreasing the polymerization rate.

Location of reactive group: The polymerization kinetic of different monomer segregated and templated in LLC phases have been studied before. Polar monomers have different polymerization behavior than non-polar monomers. These monomers segregate into different regions of the LLC. This work shows that variations in polymerization kinetics are expected with different LLC morphologies during photopolymerization of organic monomers of different nature. This behavior could have an impact in the resulting polymer morphology and final structure retention. Similarly, the location of the reactive group in the surfactant molecule for reactive LLC systems could have an effect on the polymerization kinetics due to the segregation of reactive groups in polar and non- polar regions of the LLC. To gain insight into the polymerization behavior and better understand how the location of the reactive group may influence the polymerization kinetics of these systems, the polymerization rate of surfactant molecules with different designs were compared in various LLC phases. DTAB was chosen as non-polimerizable surfactant in order to modulate the phase curvature of the system while maintaining a constant amount of double bonds. Figure 3a shows the rate of polymerization of 50%C12MA at different DTAB concentrations in water. C12MA has the reactive group near the polar head therefore the double bonds should be segregated into the polar regions of the LLC. As the LLC order is increased to form the hexagonal phase, the rate of polymerization increases sharply. The rate is maintained as the LLC transforms to a bicontinuous cubic phase, and the highest rate of polymerization occurs in the highly ordered lamellar phase. This interesting increase in rate observed with increasing surfactant concentration in more ordered liquid crystalline reaction environments is similar to that observed in previous studies of water soluble monomers, in which the rate enhancements were attributed to a combination of higher monomer ordering and increased localized double bond concentration.[12-14] This kinetic data demonstrates that polymerization occurs primarily in the continuous phase where an increase in localized concentration would be expected at higher surfactant concentration.

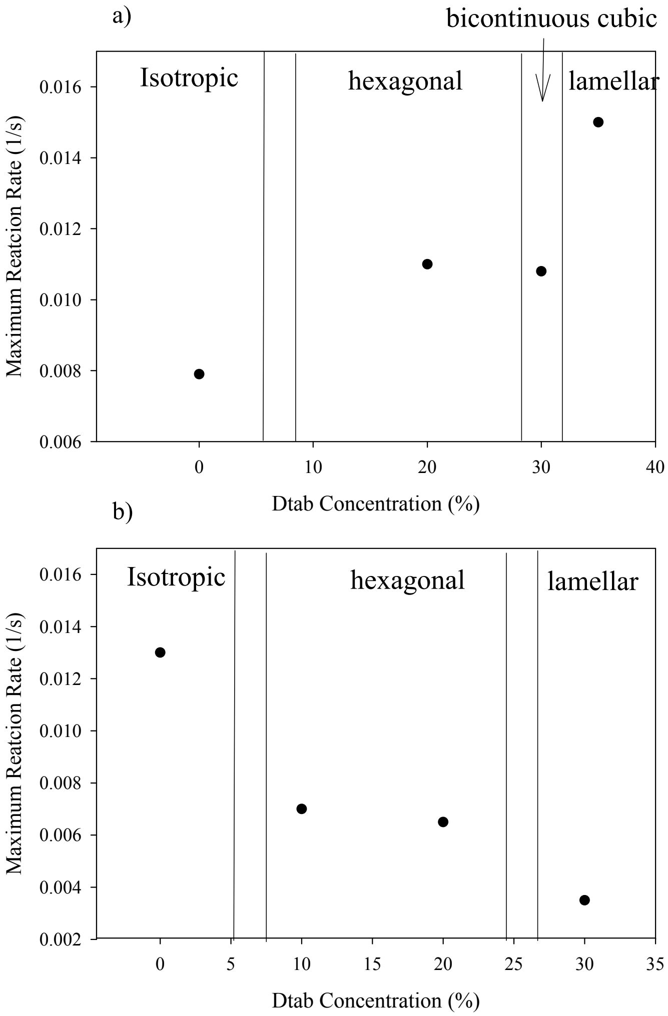

Figure 5 Maxiumum polymerization rates as a function of time for a)C12MA-DTAB and b)PM1-Dtab in water.

Polymerization of PM1, who has the reactive group in the non-polar tail in the same non-reactive surfactant system yields contrasting kinetic behavior. The rate of polymerization with respect to time of this monomer is shown in figure 5b in several LLC phases that form as the concentration of DTAB is varied in water. The rate of polymerization is highest in the isotropic phase, which forms when no surfactant is present and decreases rapidly with the transition to a hexagonal LLC morphology. The polymerization rate is lowest in the lamellar phase, about four times that of the isotropic phase. This trend, which is directly opposite to that observed with C12MA, is consistent with polymerization of a monomer confined in non-polar domains of the LLC.[6,13] The localized double bond concentration in this region is highest in the isotropic phase, in which the accessible non-polar volume is low. The localized double bond concentration decreases in the hexagonal and lamellar phase due to higher surfactant concentration and larger non-polar volume, leading to a decreasing rate of polymerization. The fact that different kinetics are observed when using different reactive surfactant systems could lead the creation of material that exhibit different properties as seen before for templated systems.[15]

Conclusions

Here we present the effect of several variables on the photopolymerization kinetics in reactive LLC systems. For the system composed of a quaternary ammonium methacrylated surfactant, where the reactive group in near the polar head, and water, the more ordered lamellar exhibit higher polymerization rates. The non-polar chain length seems to affect the polymerization kinetics by affecting the order of the system. The polymerization kinetics was studied when adding a crosslinker for LLC structure retention. At low crosslinker concentration the polymerization rate increases while at high concentrations the reaction rate decreases due to the hexagonal phase disruption. Still, the hexagonal phase is retained at high crosslinker concentrations. The polymerization of surfactant monomers with different position of the reactive group shows different kinetics. Surfactants with the reactive group near the polar head exhibit increases in polymerization rates when the order increases while surfactants with the reactive group in the non-polar tail exhibit decreases in polymerization rates. This behavior is due to segregation effects within the LLC phase. The differences in polymerization kinetics could impact the resulting polymer structure as different polymerization dynamics are observed

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