

Nanostructure Development of Polymers Templated from Lyotropic Liquid Crystals

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Introduction

Photopolymerization in lyotropic liquid crystalline media is a promising method for the synthesis of polymers with nanoscale architectural control. Through this method materials with monodisperse, nanometer sized pores can be obtained, with the specific pore size and other aspects of polymer structure adjustable through simple variations in the concentration and chemical structure of surfactant.¹ Recently polymers obtained through photopolymerization have been synthesized with indications of complete retention of the LLC mesophase structure in the polymerized material.²⁻¹⁰ However, the number of monomer/LLC systems that can be successfully templated and the applications currently benefiting from this technology are limited. Applications ranging from tissue scaffolds, size exclusion barriers, and catalytic supports could be greatly enhanced from the structural control afforded by this method if polymers with the desired chemistry could be templated.²⁻⁴ A greater understanding of the influence of monomer structure on mesophase retention and ultimate polymer nanostructure could not only help screen potential candidate monomers but also enable the application of LLC templating to a wider range of materials.

In this study the role of monomer chemical structure in ultimate polymer morphology has been examined. A series of analogous commonly used acrylate monomers with varying hydrophobic tail length have been polymerized in cubic, hexagonal, and lamellar phases. The influence of monomer hydrophobicity on LLC structure retention has been investigated. Polymerization reactions were monitored in real time to further probe how the local reaction environment varies with each monomer to provide insight into the development of polymer structure in these highly ordered solutions.

Experimental Section

Materials. The monomers used in this study were n-decyl acrylate (Polysciences), hexyl acrylate (Aldrich), and methyl acrylate (Aldrich). The surfactant chosen for this study was dodecyltrimethylammonium bromide (DTAB, Aldrich). Polymerizations were initiated with α,α -dimethoxy- α -phenylacetophenone (DMPA, Ciba Specialty Chemicals, Tarrytown, NY). The chemical structures of these materials are shown in figure 1.

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 of the various mesophases as well as phase transitions. Small angle X-ray scattering measurements were taken using a Nonius FR590 X-ray apparatus with a standard copper target Röntgen tube as the radiation source with a $\text{CuK}\alpha$ line of 1.54 Å, a camera, a collimation system of the Kratky type, and a PSD 50M position sensitive linear detector (Hecus M. Braun, Graz). LLC phase identities were confirmed by examining the ratio in d-spacing from X-ray scattering in corroboration with information from polarized light microscopy.

Polymerization rate profiles were monitored using a Perkin Elmer differential scanning calorimeter (DSC) modified with a medium pressure UV arc lamp. Polymerizations were initiated using full beam light with an intensity of 30 mW/cm². The DSC sample cell was attached to a refrigerated circulating chiller to achieve isothermal reaction conditions. Approximately 7 mg of monomer/LLC mixture was placed in an aluminum DSC pan. The DSC sample cell was purged with nitrogen for 6 min prior to polymerization to reduce oxygen inhibition. The polymerization rate was determined from the heat flow.¹¹

Results and Discussion

Polymerization rate, temperature, and LLC structure are critical parameters governing the structure of polymers synthesized utilizing lyotropic liquid crystalline templates.⁵⁻¹⁰ While all these factors are currently being investigated, this paper focuses on the role of monomer chemical structure and associated hydrophobicity as they are of primary consideration when screening materials for a specific application.

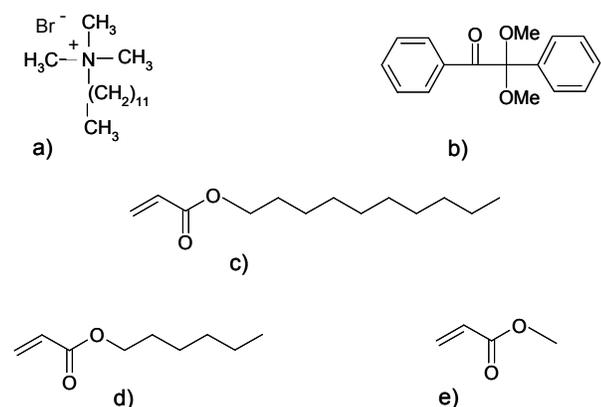


Figure 1. Chemical structures of monomers, surfactant, and photoinitiator used in this study. Shown are (a) dodecyltrimethylammonium bromide (DTAB) (b) α,α -dimethoxy- α -phenylacetophenone (DMPA), (c) n-decyl acrylate, (d) hexyl acrylate, and (e) methyl acrylate.

In contrast to the apparent preservation of the hexagonal phase observed with methyl acrylate, a significant disruption in LLC order occurs during polymerization of the hydrophobic n-decyl acrylate. Upon polymerization the d-spacing decreases substantially from 47.8 to 36.8 Å. The decrease in the scattering intensity is also much greater with n-decyl acrylate, dropping by more than half after polymerization. The polymerization of hexyl acrylate results in a shift of the primary scattering peak and decrease in intensity intermediate to that observed with methyl and n-decyl acrylate. These results show a clear trend of decreased retention of LLC morphology with increasing monomer aliphatic spacer length. Original LLC nanostructure is preserved most effectively with methyl acrylate and to a lesser degree with monomers of lower polarity, with substantial disruption in the phase structure apparent with n-decyl acrylate. Observation of the optical textures with polarized light microscopy before and after polymerization confirms this trend. With methyl acrylate the texture remains unchanged after

To study the effect of monomer hydrophobicity in the retention of LLC nanostructure, SAXS measurements were taken before and after polymerization using methyl, hexyl, and n-decyl acrylate. When 25 wt% of each monomer is used in samples with 50 wt% DTAB in water, a homogenous hexagonal phase forms. Before polymerization the SAXS profiles of these samples exhibit the characteristic 1:1/ $\sqrt{3}$ peak ratio of the hexagonal phase as shown in figure 2. To understand how polymerization affects the LLC structure of these samples, SAXS measurements were then taken after samples were polymerized. With methyl acrylate hexagonal phase structure appears to be preserved in the final polymer as the primary reflection remains in the same position and the d-spacing ratio of the scattering peaks is identical to that observed before polymerization. While the decrease in the intensity of the primary peak is indicative of less long range order, the overall sample morphology appears preserved to a large

polymerization while a slight dimming and some blurring of the texture occur with hexyl acrylate. With n-decyl acrylate the bright fan-like texture observed before polymerization largely disappears during polymerization and the image becomes quite obscured.

To gain insight into the polymerization behavior and better understand how monomer polarity may influence polymer nanostructure, the polymerization kinetics of these monomers were compared in various LLC phases that form as surfactant concentration is varied. Figure 3 shows the rate of

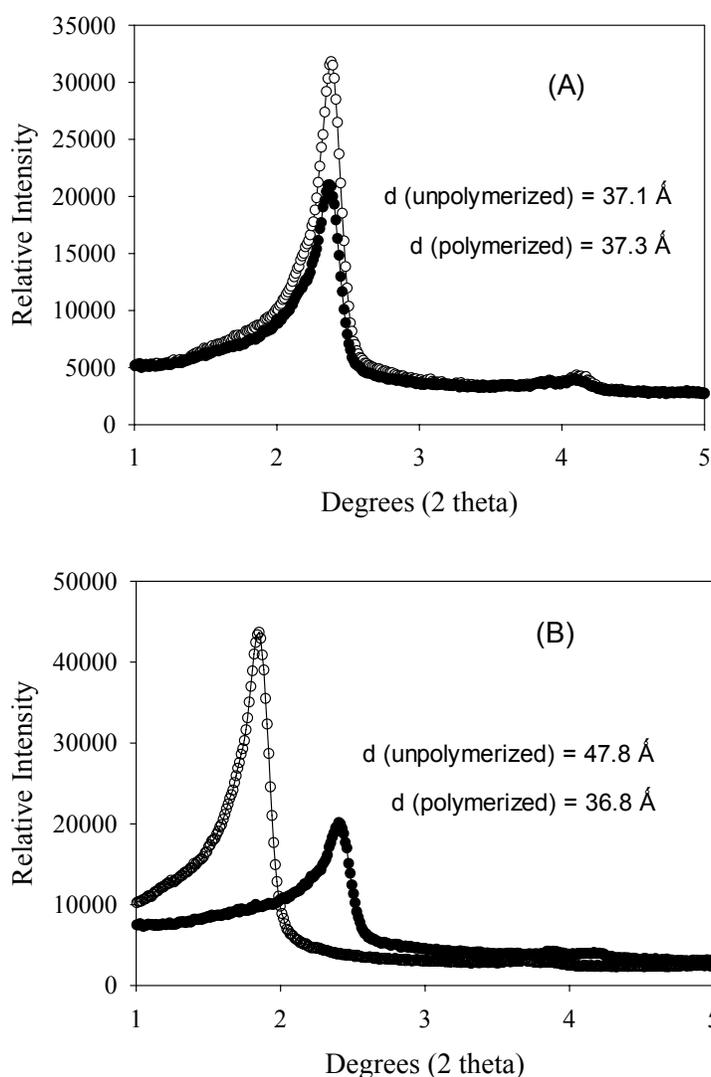


Figure 2. Small angle X-ray scattering profiles shown before (○) and after polymerization (●) for methyl acrylate (A) and n-decyl acrylate (B).

enhancement. 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.⁸⁻⁹ Previous studies have shown higher thermal stability and mechanical strength resulting from continuous phase polymerizations due to encapsulation of the surfactant aggregates by the

polymerization of 25 wt% methyl acrylate with respect to time in the cubic, hexagonal, and lamellar phases. The rate of polymerization of this monomer is highly dependent on the degree of order present in the system. In a relatively unordered micellar system formed at 30 wt% surfactant, polymerization occurs very slowly and does not reach high conversion even at long polymerization times. As the LLC order is increased to form the bicontinuous cubic phase, the rate of polymerization increases sharply. The rate further increases as the LLC transforms to a hexagonal 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.^{6,8-10} Similar experiments, which have been conducted with lower concentrations of monomer (15 wt%) also exhibit an increasing rate of polymerization in the more ordered system, but the increase is much less dramatic providing evidence that increases in localized double bond concentrations are the driving force for the rate

developing polymer.⁵ This may similarly explain why structure is retained to a significantly higher degree when polymerizing with the relatively water soluble methyl acrylate.

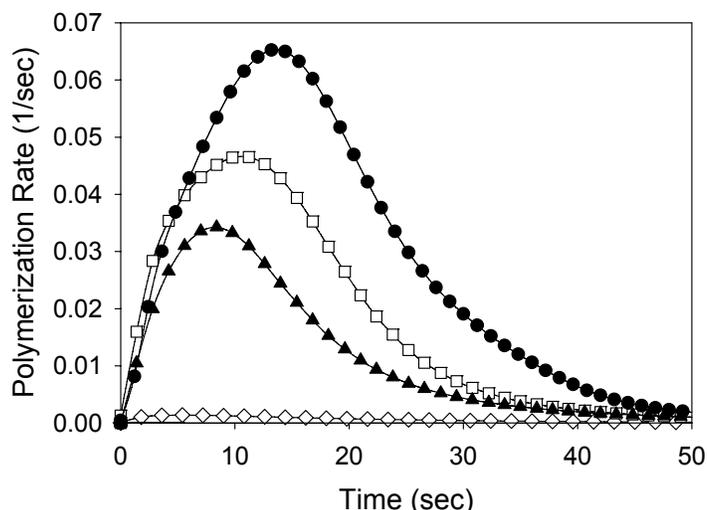


Figure 3. Rate of polymerization versus time of 25% methyl acrylate in the LLC phases of DTAB and water. Shown are 30% - micellar (\diamond), 40% - bicontinuous cubic (\blacktriangle), 45% - hexagonal (\square), 65% - lamellar (\bullet) DTAB.

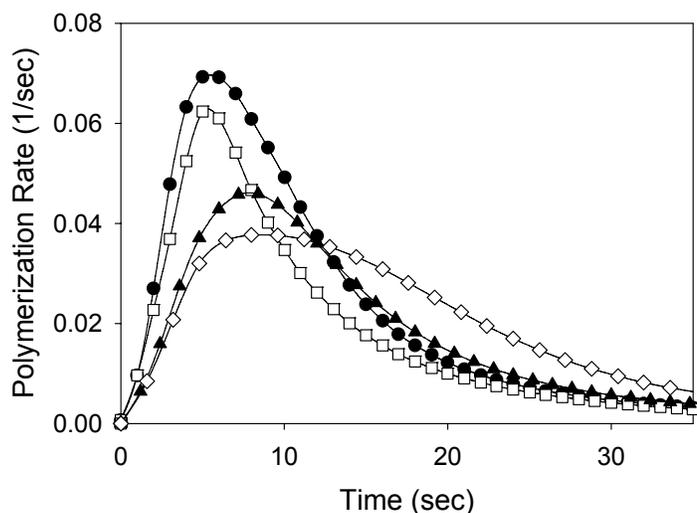


Figure 4. Polymerization rate with respect to time of 25% n-decyl acrylate in the LLC phases of DTAB and water. Shown are 40% - bicontinuous cubic (\bullet), 50% - hexagonal (\square), 55% - lamellar (\blacktriangle), and 60% - lamellar (\diamond) DTAB.

Polymerization of the oil soluble n-decyl acrylate in the same surfactant system yields contrasting kinetic behavior. The rate of polymerization with respect to time of this monomer is shown in figure 4 in several LLC phases that form as the concentration of DTAB is varied in water. The rate of polymerization is highest in the cubic phase, which forms at relatively low surfactant concentration and decreases rapidly with the transition to a hexagonal LLC morphology. The polymerization rate is lowest in the lamellar phase, about half that of the cubic phase. This trend, which is directly opposite to that observed with methyl acrylate, is consistent with polymerization of a monomer confined in nonpolar domains of the LLC.⁸⁻⁹ The localized double bond concentration in this region is highest in the cubic phase, in which the accessible nonpolar volume is low. The localized double bond concentration decreases in the hexagonal and lamellar phase due to higher surfactant concentration and larger nonpolar volume, leading to a decreasing rate of polymerization.

The contrasting degree of LLC phase retention of these acrylate monomers indicated by SAXS and PLM experiments likely results in large part to their segregation to separate regions of the LLC phase, which has been substantiated by the kinetic behavior of these monomers. The more robust framework of the polymer formed near and around the surfactant interface provides more stability to the LLC than that of polymer sequestered within the oil soluble cores of the hexagonal aggregates.⁵ When monomer locates within the nonpolar domains, the LLC phase appears to change significantly even before the polymerization. This is apparent from the relatively higher d-spacing observed with n-decyl acrylate before polymerization.

After polymerization the d-spacing decreases to a value similar to that observed with the more water soluble monomers. This interaction of n-decyl acrylate with the nonpolar region of the surfactant aggregates before polymerization appears to destabilize the hexagonal phase.

Conclusions

Monomer hydrophobicity largely determines the degree to which the LLC morphology is preserved upon polymerization. Acrylate monomers exhibit a clear trend of lower degrees of LLC nanostructure preservation with increasing nonpolar tail length. While the hexagonal phase is largely preserved upon polymerization with methyl acrylate, the same phase is largely disrupted by polymerization with n-decyl acrylate. Relatively water soluble monomers, which associate with the surfactant interface, enhance LLC phase stability by encapsulating the surfactant aggregates. Oil soluble monomers, which swell the micelles and cylinders of LLC aggregates, destabilize the LLC phase through nonpolar interactions and disrupt the original LLC structure during the polymerization.

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