

Photopolymerization in Lyotropic Liquid Crystal Templates for Improved Polymer Properties

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Introduction

Materials containing organized structures on the micro- and nanometer size scale are generating significant research interest in applications ranging from biomaterials to microprocessors and optical sensors.¹ Of particular importance is the impact nanometer sized polymer structures have on ultimate material properties. Significant differences in polymer mechanical strength and transport may be observed between isotropic polymers and polymers containing ordered morphologies on the nanometer scale.² A developing method of generating nanostructure in organic polymers utilizes self-assembling lyotropic liquid crystals (LLCs) as structure directing photopolymerization templates. Photopolymerization in and of LLC templates has been used to generate polymers containing periodic nano-scale features with properties much different than isotropic counterparts with the same chemical composition.³ Although the impact of LLC order on polymer properties can be significant, it is often difficult to retain nanostructure throughout polymerization. Here, we describe methods of retaining the LLC order during polymerization through the use of reactive surfactants and step-growth polymerization mechanisms.

The self-organized geometries of LLC mesophases provide a useful method of generating nanostructure in organic polymers. LLCs are typically formed at higher concentrations of surfactant or amphiphilic molecules in a solvent such as water. The LLC geometries formed range from hexagonal packed cylinders to flat bilayer or sponge-like structures with the geometry of surfactant aggregation is dictated primarily by the concentration, polarity, and size of surfactant molecules. These self-assembled structures contain periodic water- and oil-soluble domains with nanometer size dimensions that are utilized as a template to segregate monomers into ordered geometries based on their polarity.⁴ For example, a hydrophilic monomer added to the LLC phase will preferentially segregate in the water soluble domains and adopt a geometry that directly resembles that of the LLC phase. The rapid initiation rates inherent in photopolymerization are then used to transfer the order of the template to the polymer. Unfortunately, thermodynamically driven phase separation events can generate a polymer with a structure that is much larger and more disordered than the original template. Phase separation is significant problem in LLC polymer templating because it precludes the control of useful polymer properties dependent on nanostructure.

Reaction conditions have a significant impact on the degree of LLC structure transferred to the polymer during polymerization. Factors including photoinitiator efficiency, solubility, and mobility as well as overall photopolymerization rate can greatly impact the final order of the polymer network. Additionally, the LLC monomer system should be sufficiently thermodynamically stable to allow photopolymerization to proceed at a rate faster than phase

separation processes in order to allow for successful retention of LLC structure during polymerization.⁵ Herein, we briefly describe methods of retaining the original LLC nanostructure in a templated polyacrylamide system by the addition of reactive surfactants to the liquid crystal phase. The attributes of thiol-ene photopolymerizations including fast kinetics and step-growth mechanism are also utilized to generate nanostructured thiol-ene polymers. The structure of these polymer systems that retain the LLC order have significantly different properties compared to traditional polymers with the same chemical composition.

Experimental

Materials

The reactive quaternary ammonium surfactant monomer C12A was prepared by reacting 2-(dimethylamino)ethyl acrylate (98%, Aldrich) with 1-bromododecane ($\geq 99.5\%$, Aldrich) according to previously described methods.⁶ Hydrogel forming monomers included acrylamide ($\geq 99\%$, Aldrich) and *N,N'*-methylenebisacrylamide (99%, Aldrich). The nonreactive quaternary ammonium surfactant cetyltrimethylammonium bromide (CTAB, $\geq 99\%$, Aldrich), release solute rhodamine B (dye content $\sim 95\%$, Aldrich), and photoinitiator 2,2-Dimethoxy-1,2-diphenylethan-1-one (Irgacure 651, Ciba Specialty Chemicals) were also used. Glacial acetic acid (Aldrich) was utilized as a solvent. Thiol-ene systems contained 1,3,5-Triallyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (TTT, Aldrich), pentaerythritol tetrakis(2-mercaptoacetate) (Aldrich), and Brij 52 surfactant (4T, Aldrich). Figure 1 shows the chemical structures of monomers and surfactants used. All chemicals were used as received.

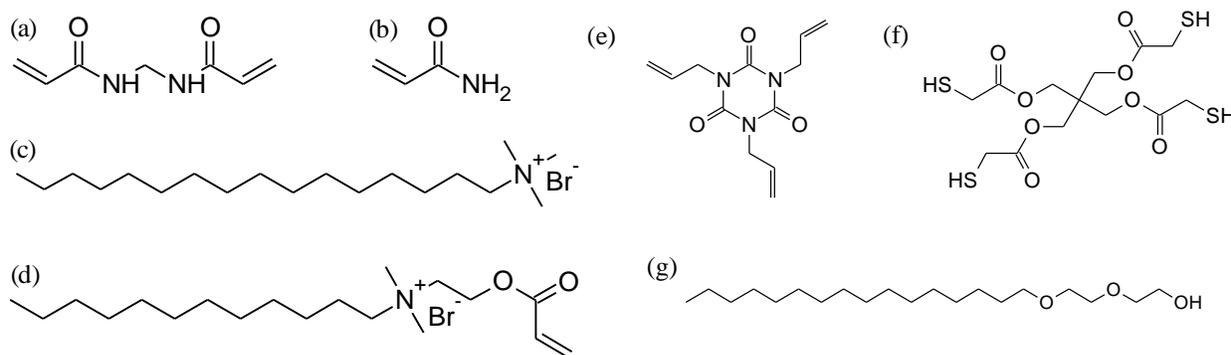


Figure 1. Chemical structures of monomers and surfactants used in this study. Shown are (a) *N,N'*-methylenebisacrylamide, (b) acrylamide, (c) cetyltrimethylammonium bromide (CTAB) surfactant, (d) acrylate functionalized quaternary ammonium surfactant, dodecyl-dimethyl-(2-prop-2-enoyloxyethyl)ammonium bromide, (C12A), (e) 1,3,5-Triallyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (TTT), (f) pentaerythritol tetrakis(2-mercaptoacetate) (4T), and (g) Brij 52 surfactant.

Methods

Lyotropic liquid crystalline templated samples were prepared by mixing particular concentrations of monomer, surfactant, deionized water, and photoinitiator. Isotropic samples were prepared by mixing specific concentrations of monomer and photoinitiator in deionized water. All samples contained 20 wt % acrylamide (95 wt % acrylamide and 5 wt % *N,N'*-methylenebisacrylamide mixture) and 1 wt % photoinitiator with respect to total monomer mass. Isotropic controls did not contain CTAB surfactant. All LLC templated formulations contained 50 wt % total surfactant which represents the total combined weight percent of CTAB and C12A surfactants. Sample homogeneity was achieved using centrifugation, mechanical agitation, heat sonication, and vortex mixing. Polymer disks were prepared by pipetting samples into borosilicate molds (15 mm diameter, 2 mm height), purging the samples with nitrogen for 8 minutes, and irradiating samples with a medium pressure UV arc lamp (Ace Glass) with an intensity of 1.5 mW/cm². All LLC templated thiol-ene system systems contain 85 wt % of an equimolar ratio of thiol and ene monomer based on functional groups and 15 wt % Brij 52 surfactant. Photopolymerization was initiated using Irgacure 651 at 1 wt % with respect to monomer mass. An aluminum salt based inhibitor (*N*-nitroso-*N*-phenylhydroxylamine Aluminum Salt) was used at a concentration of 0.05 wt % to increase the shelf-life of thiol-ene systems.

Characterization

The optical anisotropy of LLC samples was characterized before and after polymerization using a polarized light microscope (PLM, Nikon, Eclipse E600W Pol) equipped with a hot stage (Instec, Boulder, CO). PLM images were obtained by placing samples sandwiched between a glass microscope slide and coverslip on the microscope stage, heating, and allowing them to cool slowly at room temperature. Samples were photopolymerized with the UV light source described above. Optical textures were examined for birefringent patterns characteristic of ordered phases formed in the LLC samples. PLM images obtained before and after photopolymerization were compared to determine the extent of phase disruption that occurred as monomers polymerized into a cross-linked network. Polymer nanostructure was characterized with a Nonius FR590 small angle X-ray scattering (SAXS) apparatus using a standard copper target Röntgen tube with a Ni-filtered Cu K α line of 1.54 Å as the radiation source, a collimation system of the Kratky type, and a PSD 50M position sensitive linear detector (Hecus M. Braun, Graz). Phases were indexed by calculating the *d*-spacing ratios of scattering peaks. The scattering vector, *q*, was calculated from the angle of the scattered radiation and the X-ray wavelength. The compressive modulus of dehydrated polymer disks was calculated from the slope of stress-strain curves measured using dynamic mechanical analysis (TA instruments DMA Q800 series) equipped with a compressive clamp using previously established methods. Surfactant was removed via solvent exchange with acetic acid before mechanical testing.

Results and Discussion

To demonstrate how polymerizable surfactants may be utilized to retain nanostructure, reactive amphiphiles were added to a LLC monomer system found to phase separate from the parent template during photopolymerization and the structure was characterized before and after polymerization. An acrylamide system templated with the non-reactive quaternary ammonium

surfactant cetyltrimethylammonium bromide (CTAB) in water was selected as it was found form a well-ordered hexagonal LLC phase before polymerization and adopts a predominantly isotropic structure after polymerization. A polymerizable surfactant analogue of CTAB, C12A, that contains a reactive acrylate functional group attached to the ionic head group of the CTAB surfactant was chosen because it is known to retain LLC order well during polymerization in water. It is hypothesized that adding a reactive surfactant moiety that retains LLC structure will promote a greater degree of template order transferred to the polymer in a system that would otherwise phase separate.

Figure 2 shows the PLM images of acrylamide templated with different concentrations of C12A and CTAB before and after photopolymerization. The birefringence pattern and fan-like optical texture observed before polymerization in each of the LLC templated acrylamide samples is characteristic of the hexagonal LLC mesophase. After polymerization, acrylamide polymers templated with 50 wt % CTAB and water do not retain the optical texture characteristic of the hexagonal phase and have adopted an isotropic structure. (Figure 2b).^{3,3,7} Reactive C12A surfactant was added to the template while keeping total surfactant concentration constant to determine if small concentrations of reactive surfactant may be utilized to retain the hexagonal structure. Figure 2c and 2d shows PLM images for acrylamide templated with 45 wt % CTAB and 5 wt% C12A in water before and after polymerization. Although incorporating 5 wt % C12A into the template does not appreciably disrupt the hexagonal phase, it does not allow for retention of the structure after polymerization as indicated by the isotropic optical texture shown in Figure 2d. Reactive surfactant concentration was further increased to 10 and 15 wt % C12A to determine if higher concentrations of C12A are needed to retain the hexagonal LLC structure. Figure 2e and 2f shown the PLM images for acrylamide templated with 10 wt % C12A and 40 wt % CTAB in water before and after polymerization. Interestingly, incorporating 10 wt % C12A into the LLC template retains the original hexagonal structure after polymerization. The birefringent pattern observed after polymerization with 10 wt % C12A shown in Figure 2f is characteristic of the hexagonal LLC phase. Similar results are observed for the polymerization of acrylamide with 15 wt % C12A and 35 wt % CTAB as shown in Figure 2g and 2h, both of which display the birefringent patten of the hexagonal LLC phase.

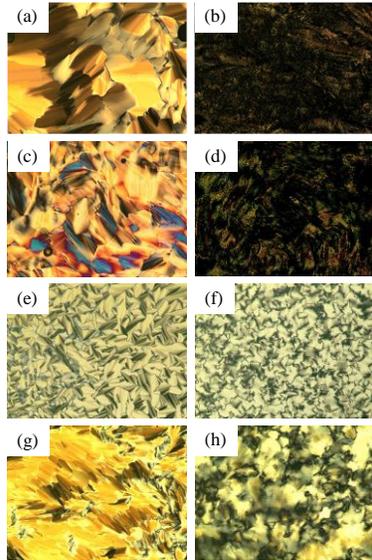


Figure 2. Polarized light micrographs of 20 wt % cross-linked acrylamide templated with different concentrations of CTAB and C12A surfactants (50 wt % total) in water before and after photopolymerization. Shown are 0 wt % C12A before (a) and after (b), 5 wt % C12A before (c) and after (d), 10 wt % C12A before (e) and after (f), and 15 wt % C12A before (g) and after (h) polymerization.

The strong birefringence intensity and well-defined optical texture observed after polymerization indicate that the parent template structure is preserved during the polymerization reaction when sufficient C12A is incorporated into the nonreactive CTAB template. To determine the impact of LLC order on mechanical properties, the compressive modulus of polymer samples was characterized using dynamic mechanical analysis. For comparison with LLC templated samples, isotropic controls containing the same chemical composition of LLC templated samples were prepared by replacing CTAB surfactant with water. The low concentration of C12A surfactant in isotropic samples is not sufficient to form LLC structures, yielding a polymer with an isotropic morphology and identical chemical composition to LLC templated samples. Isotropic controls represent the properties that are expected from a traditional or isotropic polymer that do not contain ordered morphologies.

Figure 3 shows the compressive stress-strain profiles for polymers templated with varying concentrations of C12A and their appropriate isotropic controls. It is apparent from Figure 3 that the slope of the stress-strain curves increases with increasing C12A concentrations for both LLC templated and isotropic polymers. However, the polymers that retain the original hexagonal LLC structure have a significantly larger modulus relative to their isotropic controls. In fact, the hexagonal LLC nanostructures of polyacrylamide samples templated with 10 or 15 wt % C12A display a compressive modulus about 50 and 60% greater than their isotropic counterparts of the same chemical composition, respectively. Because the hexagonal nanostructured polymers are compositionally identical to their isotropic controls that contain a random or disordered network structure, it is apparent that the directed hexagonal LLC structure is more resistant to deformation and generates an increase in mechanical strength.⁷

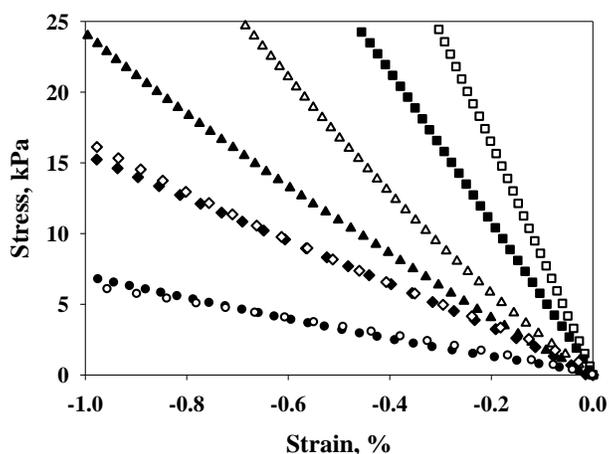


Figure 3. Stress-strain profiles of dehydrated polyacrylamide samples photopolymerized in the hexagonal LLC phase formed using varying concentrations of unreactive CTAB and polymerizable C12A surfactants. Also included are isotropic polyacrylamide controls with the same basic chemical composition of LLC templated counterparts. Shown are 0/50 wt % C12A/CTAB (\circ , phase separated), 0/0 wt % C12A/CTAB (\bullet , isotropic), 5/45 wt % C12A/CTAB (\diamond , phase separated), 5/0 wt % C12A/CTAB (\blacklozenge , isotropic), 10/40 wt % C12A/CTAB (Δ , hexagonal), 10/0 wt % C12A/CTAB (\blacktriangle , isotropic), 15/35 wt % C12A/CTAB (\square , hexagonal), and 15/0 wt % C12A/CTAB (\blacksquare , isotropic). CTAB surfactant was removed by solvent exchange prior to analysis.

Additional methods may be utilized to prevent phase separation events and better retain the original LLC order. In particular, reaction schemes that differ mechanistically in the buildup of polymer molecular weight may differ in the degree of template structure retained during polymerization. For example, chain polymerizations reach high molecular weight at low conversions as opposed to step-growth polymerization in which gelation and molecular weight buildup are observed at significantly higher conversions. Because solubility parameters, interaction parameters, and overall thermodynamic stability depend significantly on molecular weight it is expected that there may be a large difference in the degree of LLC template structure retained during polymerization. Thiol-ene systems are particularly interesting step-growth polymerizations with characteristics potentially useful in LLC systems including rapid polymerization rates and higher gelation points.⁸ LLC structure retention was examined in thiol-ene systems to provide useful comparison to chain polymerizations on the degree of LLC structure retained during polymerization.

The degree of structure retention for a step-growth polymerization was examined by photopolymerizing a thiol-ene monomer

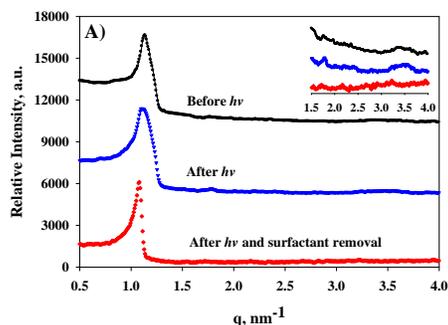


Figure 4. SAXS profiles for 85 wt % A) TTT:4T before and after photopolymerization and after Brij 52 surfactant removal by solvent exchange with ethyl acetate and drying.

mixture in a LLC phase and characterizing the structure before and after polymerization. Figure 4 shows the small angle X-ray scattering (SAXS) profile before polymerization, after polymerization, and after polymerization and surfactant removal for 85 wt % triallyl - triazine and tetra-functional thiol with 15 wt % Brij 52 surfactant. The ratios of *d*-spacing peaks in the SAXS profile before polymerization indicate the thiol and ene monomers are segregated into an ordered hexagonal LLC geometry before polymerization. After photopolymerization, the ratio of *d*-spacing and scattering intensity are retained, indicating that the polymer has adopted a hexagonal LLC structure. Also shown in Figure 4 is the SAXS profile obtained after photopolymerization and removal of Brij 52 surfactant from the polymer matrix by solvent exchange with ethyl acetate. Surfactant removal was greater than 95% as measured gravimetrically. Because the Brij 52 surfactant has been removed, the SAXS pattern represents the structure of the polymer and is not convoluted with diffraction from surfactant-polymer interactions. Interestingly, the SAXS pattern indicates a hexagonal LLC structure after photopolymerization and surfactant removal. The significant degree of template order retained in the thiol-ene system shown in Figure 4 suggests that polymerization systems that reach high molecular weight at the later stages of the reaction may aid in structure preservation.

Conclusions

Photopolymerization in self-assembling LLC phases is a promising method of generating nanostructure in organic polymers. The addition of a polymerizable surfactant to the parent template increase significantly the degree of LLC structure transferred to poly(acrylamide) during polymerization. Critical concentrations of polymerizable surfactant needed to retain the original hexagonal order which in turn generates a large increase in the compressive modulus compared to isotropic polymers with the same chemical composition but lacking periodic order. Finally, step-growth photopolymerization of thiol-enes in LLC templates appears to be another promising method of retaining the original LLC nanostructure during polymerization. These results may be utilized to retain the nanostructure in LLC templated systems and ultimately improve the properties of polymers for use in a growing number of advanced biological and industrial applications.

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