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Photopolymerization in Pluronic Lyotropic Liquid Crystals: Induced Mesophase Thermal Stability

Demetrius T. McCormick,[†] Kalena D. Stovall,[†] and C. Allan Guymon*[,‡]

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39401, and Department of Chemical and Biochemical Engineering, University of Iowa, Iowa City, Iowa 52242-1527

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ABSTRACT: Nanostructured polymers are of significant interest due to their potential use in applications ranging from ultrafiltration membranes to catalysis supports. To date, much research has focused on using small molecular weight surfactants that form lyotropic liquid crystals (LLCs) as polymerization templates or polymerizing reactive LLCs to form such nanostructure in polymers. LLC phases formed from small molecular weight surfactants, however, are in and of themselves neither thermally nor mechanically stable, often rendering it difficult to preserve the LLC structure throughout polymerization. A relatively new class of surfactant molecules, Pluronic block copolymers, may afford increased flexibility in nanostructure development when used as polymerization templates. This work has focused on the photopolymerization of water and oil-soluble monomers in Pluronic lyotropic liquid crystals. In particular, the effect that LLC order and monomer segregation behavior has on monomer polymerization rate has been examined. The order of the LLC mesophase has a significant impact on polymerization rate with faster polymerization occurring in the normal phases for the oil-soluble monomer hexanediol diacrylate (HDDA) and in the inverse phases for the water-soluble monomer poly(ethylene glycol) diacrylate (PEG-400-DA). In addition, the effect of monomer addition and polymerization on LLC order has been characterized, with retention of LLC order before and after photopolymerization. Mesophase thermal stability, or the persistence of an LC phase at elevated temperatures, has also been examined for the polymer/LLC hydrogels to determine how polymer nanostructure differences affect fundamental LLC properties. Interestingly, when PEG-400-DA is polymerized in the continuous domains of the hexagonal mesophase, the clearing point is increased more than 40 °C. However, when HDDA is polymerized in the discontinuous domains of hexagonal phase, the mesophase thermal stability increases only 25 °C. Conversely, when HDDA is polymerized in the continuous region of the inverse hexagonal phase, the clearing point increases more than 60 °C. The difference in polymer nanostructure that evolves during the polymerizations directly impacts the mesophase thermal stability. The LLC polymerization also affects the physical properties of polymer/Pluronic hydrogels with significant differences in compressive modulus observed based on the LLC phase in which the nanostructured polymer is generated.

Introduction

Nanostructured polymeric materials have the potential for use in a wide variety of applications ranging from catalysis and electrically conductive materials to ultrafiltration membranes and separations media.[1−6] A variety of approaches have been utilized to produce nanostructured polymers including self-assembled monolayers (SAMs),[7] Langmuir−Blodgett films,[8] lipid vesicle assemblies,[9] and macromolecular ordering induced by lyotropic liquid crystalline systems.[10−15] Lyotropic liquid crystals (LLC) can form a variety of supermolecular structures dependent on the nature of the surfactant used and the concentration of water present in the system. The specific geometry of each LLC mesophases has the potential to allow for a variety of different polymer architectures.[16−18] To utilize the geometries available in LLC systems, both the polymerization of reactive mesogens and the use of LLCs as polymerization templates have been examined to develop novel polymer nanostructures based on LLC morphology.

A large portion of the work related to the development of LLCs as polymerization templates has focused on small molecule surfactant/solvent systems.[19−25] Recently, a significant amount of work has examined the photopolymerization of reactive surfactant monomers and the polymerization of water- and oil-soluble monomers in nonreactive surfactant−water systems.[19−22] Through these investigations it has been demonstrated that the LLC morphology has a significant impact on the polymerization rate as well as the resultant physical properties of the polymers produced. When a reactive semifluorinated surfactant monomer was examined, for example, higher polymerization rates were observed when polymerization occurred in the more ordered LLC phases.[19] When polymerizations are conducted using nonmesogenic monomers in LLC solvents, the polymerization rate varied significantly with LLC order. The resulting physical properties changed significantly as well with a substantial difference in compressive modulus using different LLC phases for polymerization.[21]

While small molecule surfactants have been shown to be useful as polymerization templates, their LLC phases are not inherently mechanically stable.[26] The limited mechanical, and in some cases thermal, instability inherent in phases formed from small molecule surfactants severely limits the conditions under which polymeric materials can be generated and may prohibit certain applications if moderate shear rates or high temperatures are encountered. A relatively new surfactant system, Pluronic block copolymers, offers an

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[†] University of Southern Mississippi.
[‡] University of Iowa.
* To whom all correspondence should be addressed.

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attractive alternative. For potential use as polymerizations templates, these systems exhibit substantially greater mechanical stability that may enhance the ability to produce desired nanostructures.

Pluronics are ABA block copolymers of ethylene oxide and propylene oxide, consisting of two poly(ethylene oxide) (PEO) outer blocks and a center block of poly(propylene oxide) (PPO). Recently, a considerable amount of research effort has been devoted to understanding the organization of this interesting class of amphiphiles in aqueous solutions.[27−34] On the basis of these results, Pluronic block copolymers self-assemble in water to form a variety of LLC mesophases, thus opening a wide array of potential applications.[31−34] In addition to forming LLC structures in aqueous solutions, ternary systems of copolymer, water, and oil also can exhibit a significant array of polymorphism.[35] The variety of LLC phases that can be formed with Pluronics is typically greater than those formed from most small molecular weight surfactants. In addition, control over the PEO and PPO content and the molecular weight of the copolymer gives specific nanoscale control of the mesophase domain size and allows for the isolation of specific mesophases for a given surfactant system.[35] Such control of mesophase domain size gives Pluronic LLCs the potential for use in a number of applications ranging from catalysis to filtration membranes in which nanoscale control over pore diameters is crucial. The additional mechanical stability inherent in Pluronics can also potentially aid in mesophase retention during the polymerization process by inhibiting mesophase shifts. The greater thermal stability present in Pluronic systems could also allow for optimization of polymerization conditions that could lead to enhanced structure retention.

To take advantage of these properties, research has been performed in which Pluronics were investigated as polymerization templates for silica materials.[36−38] By using mixtures of block copolymers and small molecule surfactants to generate a hexagonal LLC mesophase, mesostructured silica monoliths can be developed with uniform pore sizes.[37] Other research has investigated using the block copolymer as the only structure directing amphiphile for the polymerization of sodium metasilicate. Using this approach, hexagonal and bicontinuous cubic mesophase order was retained in silica monoliths.[38]

While some research has investigated Pluronics as polymerization templates for inorganic polymers, little research has examined Pluronics as templates for organic polymers. Some research has been conducted investigating how Pluronic LLC order affects the photopolymerization kinetics of a methacrylate monomer.[39] Enhanced polymerization rates were observed when the monomer was polymerized in the ordered lamellar phase compared to the disordered isotropic phase. This polymerization rate enhancement is due to ordering of the monomer between the lamellar layers. These initial results suggest that the ordering of the Pluronic LLC has a significant impact on monomer polymerization, but scant evidence exists about the impact that the resulting polymer has on LLC order or if the LLC morphology is actually templated by the organic polymer. In addition, the impact of the resulting polymer nanostructure on overall LLC properties such as the isotropic clearing temperature, or mesophase thermal stability, has yet to be determined.

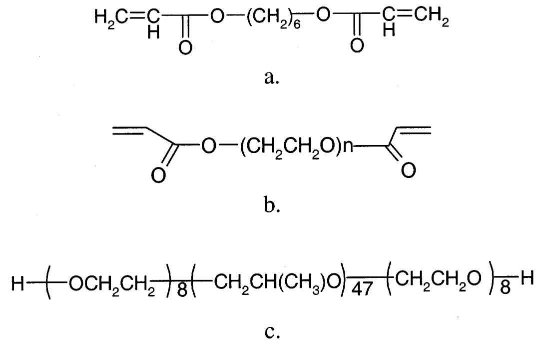


Figure 1. Monomer and LC structures of (a) hexanediol diacrylate (HDDA), (b) poly(ethylene glycol) diacrylate (PEG-400-DA), and (c) Pluronic L 92 (P92), which has a M_w of 3650 and 20% PEO content.

This research details the photopolymerization of water- and oil-soluble monomers in Pluronic/water surfactant systems. Polymerization kinetics were examined to determine the effect of LLC order on the polymerization rate. In addition, polarized light microscopy (PLM) was used to determine the effect of the polymerization process on LLC order. Polarized light microscopy was also utilized to investigate the mesophase thermal stability of the Pluronic and the resulting polymer/Pluronic hydrogels. Small-angle X-ray scattering was used to confirm the PLM results. Physical properties of the polymer hydrogels were also examined to study how differences in LLC order affect the macroscopic behavior of the resulting nanostructured materials. Through these studies, greater understanding has been gained regarding the use of Pluronics as polymerization templates for the generation of nanostructured polymeric materials.

Experimental Section

Materials. The water-soluble monomer used in this study was poly(ethylene glycol diacrylate) (PEG-400-DA: Polysciences, Warrington, PA), and the oil-soluble monomer used was hexanediol diacrylate (HDDA: Polysciences, Warrington, PA). The Pluronic block copolymer examined was L 92 (P92: BASF Corp., Mount Olive, NJ). Chemical structures of the monomers and liquid crystal are shown in Figure 1. Photopolymerizations were initiated using Irgacure 907 (Ciba Specialty Chemicals, Hawthorne, NY) for the lipophilic monomer and Irgacure 2959 for the hydrophilic monomer. All materials were used as received. The monomer/LC/water mixtures were prepared with initiator concentrations approximately 5 mol % of the total monomer double bond concentration. The 10% monomer concentrations denoted in the text represent the weight percent of monomer in the Pluronic/monomer/water mixtures. It is important to note that addition of monomer changes phase behavior slightly, but the overall clearing point remains virtually unchanged. The Pluronic/monomer samples were mixed thoroughly and centrifuged extensively to ensure homogeneity.

Characterization. Polymerization rate profiles were monitored using a differential scanning calorimeter (DSC 7; Perkin-Elmer) modified with a medium-pressure UV lamp. Polymerizations were initiated using 365 nm monochromatic light with an intensity of 1.5 mW cm^{-2} unless otherwise noted. The DSC sample cell was attached to a refrigerated circulating chiller to achieve isothermal conditions. For rate studies, the samples were heated above the isotropic transition temperature of the monomer/LC mixture and cooled to the appropriate polymerization temperature to ensure uniform thickness and sufficient thermal contact. The DSC sample cell was purged with nitrogen for 10 min prior to polymerization to mitigate oxygen inhibition. Polymerization rate was calculated as shown elsewhere.[19] The polymerization rate as shown has units of

1/s, giving a normalized rate that allows for facile comparison of systems with different monomer concentration and type.

Polarized light microscopy (Optiphot 2-pol; Nikon, Melville, NY) was used to determine the lyotropic liquid crystalline mesophases and the order of the mesophases after monomer addition and polymerization. For thermal stability studies, the samples were heated on a hot stage (INSTEC, Broomfield, CO), equipped with a temperature controller, to the desired temperature and held isothermally for several minutes before photographs were taken. Diffraction profiles of the Pluronic systems were measured using small-angle X-ray scattering (SAXS, Siemans XRD 700 WAXD/SAXS) with a Cu Kα line of 1.54 Å. Changes in SAXS behavior as a function of temperature were examined using a temperature-controlled SAXS cell.

Results and Discussion

Pluronic lyotropic liquid crystalline systems offer great potential as polymerization templates for the generation of nanostructured organic polymers. If nanostructured polymeric materials could be controllably developed, they could be used for a variety of applications ranging from separations media to nanocomposites.[2,3] Until recently, little research has been devoted to investigating polymerizations in lyotropic liquid crystalline systems, particularly in Pluronic block copolymer surfactant systems. Pluronic copolymer amphiphiles could be ideal for use as polymerization templates due to the variety of LLC mesophases that they can form as well as their inherent mechanical stability which can aid in structure retention and give additional polymer synthesis flexibility. In addition, significant nanoscale control of mesophase domain size is afforded through simple manipulation of block copolymer content, i.e., ratio of poly(ethylene oxide) and poly(propylene oxide) blocks, and copolymer molecular weight. Therefore, if nanostructure could be retained through polymerization, Pluronic LLCs, when used as polymerization templates, could yield novel and interesting nanostructured polymeric materials.

To fully understand the development of nanostructured polymeric materials in Pluronic LLCs, it is important to examine the polymerization behavior as LLC order is modulated to determine the effect that LC order has on the polymerization. The polymerization rate behavior may also give an indication of the segregation behavior of the monomer within the surfactant system which will ultimately determine the structure of a templated polymer. Figure 2 shows polymerization rate profiles of 10% PEG-400-DA in various LLC phases of P92. As the surfactant concentration increases, a substantial increase in the polymerization rate is observed when changing from the micellar phase to the hexagonal phase. An even faster polymerization rate is observed in the bicontinuous cubic phase, with a slight decrease in rate in the inverse micellar phase. It is interesting to note the differences in the polymerization behavior of the water-soluble monomer in the micellar and inverse micellar phases. The faster polymerization rate in the inverse micellar phase indicates that the monomer is segregated within the inverse micellar cores, which could lead to an increased monomer concentration and accelerated polymerization rate. When PEG-400-DA is polymerized in the micellar phase, the monomer is most likely dispersed in the continuous media, i.e., the aqueous solvent, and the reactive moieties would be less concentrated.

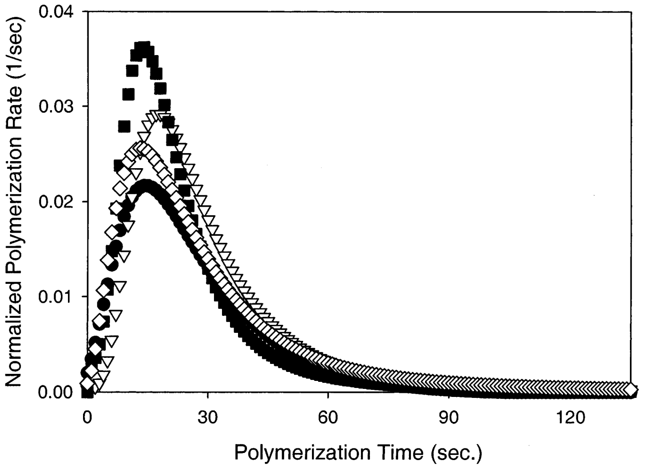


Figure 2. Polymerization rate profiles of 10% PEG-400-DA polymerized in various LLC phases of P92. Shown are the 20% P92-micellar phase (●), 44% P92-hexagonal phase (▽), 58% P92-bicontinuous cubic phase (■), and the 81% P92-inverse micellar phase (◇).

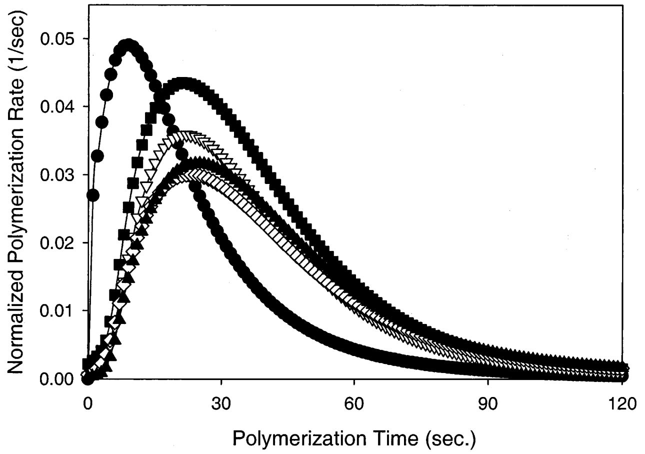


Figure 3. Polymerization rate profiles of 10% HDDA polymerized in the various LLC phases of P92. Shown are the 18% P92-micellar phase (●), 40% P92-hexagonal phase (▽), 58% P92-bicontinuous phase (■), 76% P92-inverse hexagonal phase (◇), and 82% P92-inverse micellar phase (▲).

The oil-soluble monomer, HDDA, exhibits slightly different polymerization behavior. Figure 3 shows the polymerization rate profiles of 10% HDDA in various P92 mesophases. In this case the fastest polymerization rate is observed in the micellar phase. The polymerization rate decreases significantly when the oil-soluble monomer is polymerized in the hexagonal phase, while the rate increases upon further surfactant addition to reach the bicontinuous cubic phase. When polymerizations are conducted in the inverse hexagonal and micellar phases, decreases in the polymerization rate are observed. The polymerization behavior of HDDA also gives indications regarding the segregation behavior of the monomer. The observation of a faster polymerization rate in the micellar phase compared to the inverse micellar phase indicates that the oil-soluble monomer is confined to the micellar cores. In addition, the observation of faster polymerization rates occurring in the hexagonal phase compared to the inverse hexagonal phase also indicates that the oil-soluble monomer is preferentially segregating in the hydrophobic PPO domains. Interestingly, the acceleration of the polymerization rate in the bicontinuous cubic phase for HDDA is similar to that observed for PEG-400-DA. This similarity is possibly due to similar segregation behavior of both monomers in the co-continuous surfactant/water domains of the bicontinuous cubic phase.

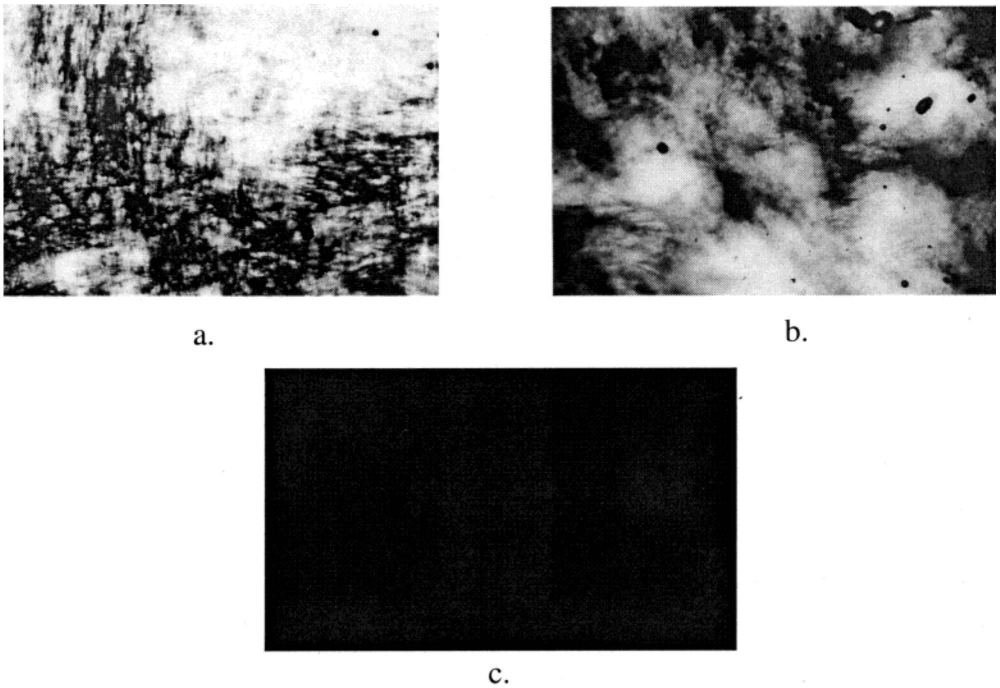

a. b. c.

Figure 4. Optical micrographs of 45% P92 in water at (a) 25 °C, (b) 40 °C, and (c) 75 °C.

While the polymerization behavior of the monomers helps to understand segregation behavior, it is still important to understand how the addition of monomer and subsequent polymerization affects the order of the LLC phase. To successfully generate templated nanostructured/polymer LLC materials, the original LLC phase of the monomer/surfactant gel must be retained throughout the course of the polymerization. Previous research using small molecule surfactants as polymerization templates has shown that the LLC phase can shift during the course of monomer polymerization;[24] however, recent research has shown retention of the parent LLC phase morphology by photopolymerizing monomers in surfactant systems.[19−22] Polarized light microscopy is a simple characterization technique that allows for the observation of the macroscopic LLC mesophase order in a monomer surfactant system before and after polymerization. Through observing the mesophase optical textures, the mesophases can be examined for homogeneity, phase retention after polymerization, and mesophase behavior at elevated temperatures. To characterize the effect of polymerizing PEG-400-DA and HDDA in Pluroinc surfactant systems, polarized light microscopy (PLM) was used to examine the optical textures of the neat Pluronic/water gels and the monomer/Pluronic/water gels both before and after polymerization. In addition, to compare the thermal stability of the polymer/Pluronic hydrogels to the neat Pluronic/water hydrogels, the samples were heated to various temperatures and the optical textures examined.

The addition of a polymer to a liquid crystal can potentially affect mesophase stability at elevated temperatures. Previous research has investigated the effect of polymerizing non-mesogenic monomers in thermotropic liquid crystals. Interestingly, a significant increase in mesophase thermal stability has been observed using appropriate monomers and polymerization conditions.[40−42] The mesophase was thermally stabilized through surface interactions between the polymer and the LC. In lyotropic liquid crystalline systems, examination of mesophase thermal stability could potentially provide evidence of successful templating of the parent LLC phase onto the organic polymer. When monomers are polymerized in the continuous region or the discontinuous region of an LLC mesophase, vastly different polymer nanostructures may evolve that could potentially lead to large differences in mesophase thermal behavior.

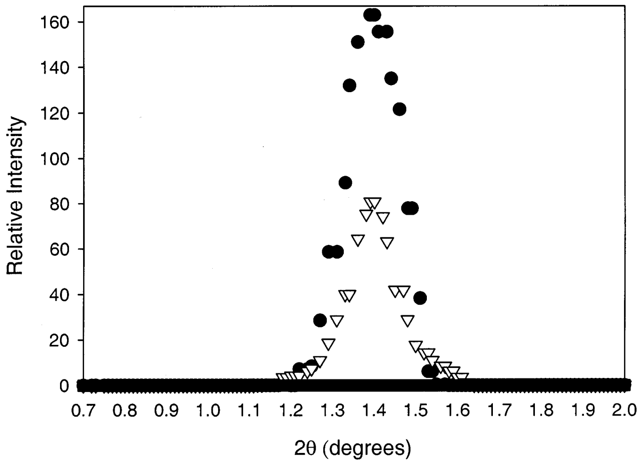


Figure 5. Small-angle X-ray diffraction profiles of 45% P92 in water at 25 °C (●), at 40 °C (▽), and at 75 °C (■).

Before examining the potential thermal benefits of a templated polymer, it is important to understand the phase behavior of P92 in water before addition of monomer and subsequent polymerization. Figure 4 shows polarized optical micrographs of 45% P92 in water at various temperatures. At ambient temperature, a classic hexagonal optical texture is observed. As the sample temperature is increased to 40 °C, a significant reduction in the birefringence of the hexagonal phase is observed, indicating a decrease in the order of the mesophase. In fact, 40 °C is very close to the clearing temperature of the hexagonal phase.[43] Further increases in sample temperature to 75 °C lead to a complete disruption of the hexagonal mesophase order, thus inducing a black picture under PLM.

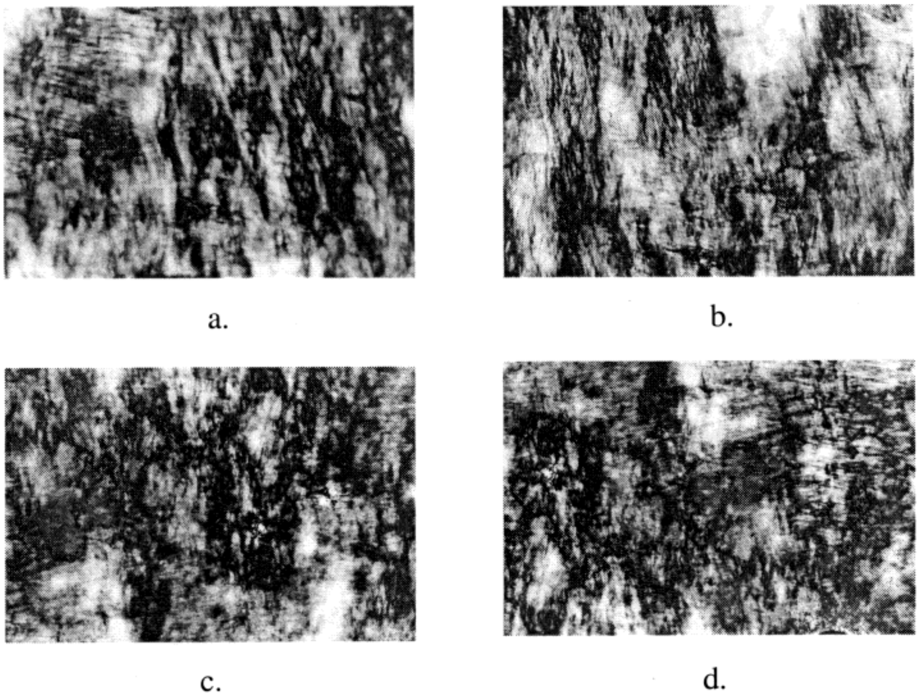

a. b. c. d.

Figure 6. Optical micrographs of 10% PEG-400-DA in 44% P92 in water (a) before polymerization at 25 °C and (b) after polymerization at 25 °C, (c) at 50 °C, and (d) at 75 °C.

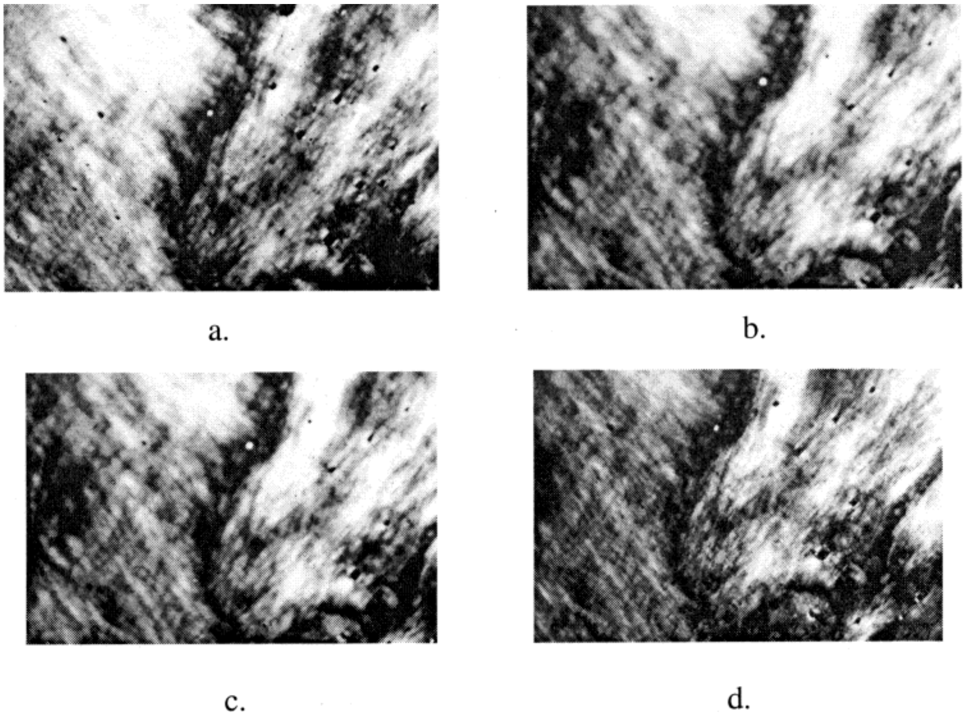

a. b. c. d.

Figure 7. Optical micrographs of 10% HDDA in 40% P92 in water (a) before polymerization at 25 °C and (b) after polymerization at 25 °C, (c) at 50 °C, and (d) at 65 °C. Note: the birefringence at 65 °C is transient and disappears after thermal equilibrium is reached.

As a complementary technique to PLM, small-angle X-ray scattering (SAXS), which measures the electron periodicity of a sample, was used to examine the diffraction profiles of the neat Pluronic/water sample at various temperatures. While polarized light microscopy gives microscopic evidence regarding the effect that monomer addition and subsequent polymerization has on LLC order, SAXS can be used to examine these samples on the nanoscale. The diffraction profiles of 45% P92 at various temperatures are shown in Figure 5. A sharp primary diffraction peak of 1.4° 2θ is observed at 25 °C. It is important to note that higher order diffraction peaks are typically observed for the hexagonal mesophase. Pluronics, however, form less discrete mesophases, so it is common to only observe the primary diffraction peak. As the temperature is increased to 40 °C, a sharp drop in the diffraction intensity is observed, indicating disruption of the hexagonal mesophase. When the sample temperature is increased further to 75 °C, no observable diffraction peak is evident due to the complete solvation of the surfactant. These results agree with previous characterization of this surfactant system.[43] If the incorporation of polymer increases the thermal stability of an LLC phase, changes in the optical textures and diffraction profiles should be observed with increase in temperature, similar to results seen in thermotropic LC systems. To determine whether such changes are observed, polarized microscopy and SAXS were utilized to examine the optical textures and diffraction profiles as a function of temperature for both HDDA and PEG-400-DA Pluronic systems.

Figure 6 shows polarized optical micrographs of 10% PEG-400-DA in 44% P92 before and after polymerization. After monomer addition the hexagonal phase is retained, indicating that the polar monomer does not significantly disrupt mesophase order. Interestingly, the clearing temperature also remains virtually unchanged. Upon polymerizing the monomer at ambient temperature in the hexagonal mesophase, the LLC order is preserved, indicating that the cross-linked polymer and the polymerization itself do not disrupt LC order. In fact, this optical texture is retained at 50 and 75 °C. The hexagonal optical texture is even observed at temperatures as high as 85 °C, although it is not nearly as intense as those seen at the other temperatures. The inclusion of the polymer within the hexagonal mesophase via photopolymerization has resulted in an approximately 45 °C increase in thermal stability of the LLC mesophase. The fact that the mesophase has been stabilized to such a significant degree points to the stabilization of the LLC morphology by the organic polymer. If the polymer were phase separated from the LC, such a striking degree of mesophase stabilization would not be expected.[40-42]

The nanostructured polymer resulting from the polymerization of PEG-400-DA encloses the hexagonal rods due to the segregation of the monomer in the continuous aqueous media. Further understanding of the templating effect of the LLC and the effect that the nanostructured polymer has on LLC properties can be gained through examining polymerizations for a monomer that partition in the discontinuous regions. The polymerization of HDDA in the hexagonal phase, for which the monomer segregates inside of the hexagonal rods, is a prime candidate to examine the impact of a discontinuous region polymerization. Optical micrographs of 10% HDDA in 40% P92 are shown in Figure 7. Before polymerization, the hexagonal mesophase is observed and is retained after polymerization at 25 °C, indicating that neither the monomer nor the polymer substantially affects the lyotropic liquid crystalline order. The hexagonal mesophase is observed at 50 °C, but the polymer/surfactant sample becomes isotropic at 65 °C. In this case, the increase in mesophase thermal stability is only 25 °C, whereas a 45 °C increase in mesophase thermal stability is observed for the PEG-400-DA sample in the same phase. The primary difference between the samples is that the PEG-400-DA polymer encloses the hexagonal rods and the HDDA polymer is primarily confined within the hexagonal rods. Through monomer selection, the mesophase thermal stability can be significantly altered in polymer/Pluronic systems. The observed differences in mesophase thermal stability provide evidence that the polymer nanostructure is templated by the LLC morphology.

SAXS was also used to examine the polymer/Pluronic hydrogels at various temperatures. The PEG-400-DA polymer hydrogel in 44% P92 exhibits a diffraction peak at 1.4° 2θ before polymerization, as shown in Figure 8a.

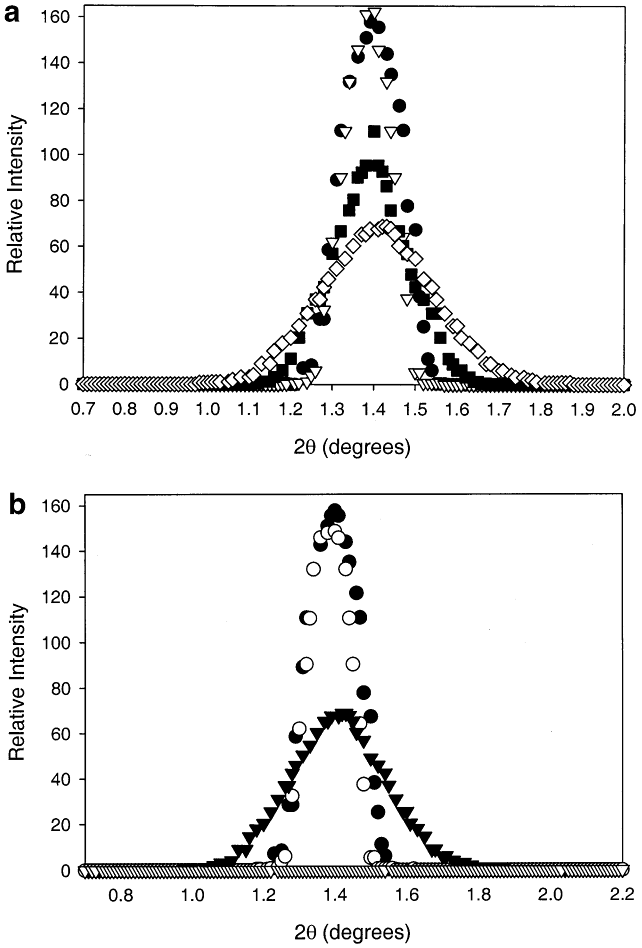


Figure 8. (a) Small-angle X-ray diffraction profiles of 10% PEG-400-DA in 44% P92 before polymerization (●) and after polymerization at 25 °C (▽), at 50 °C (■), and at 75 °C (◇). (b) Small-angle X-ray diffraction profiles of 10% HDDA in 40% P92 before polymerization (●) and after polymerization (▽) at 25 °C, at 50 °C (■), and at 75 °C (◇).

This peak and corresponding LLC order are retained after polymerization. As the sample temperature is increased to 50 and 75 °C, the diffraction peaks are retained though the intensity decreases. These results indicate that the LLC mesophase order in the polymer/Pluronic hydrogels is retained on the nanoscale, which does not occur in the neat Pluronic/water samples, especially at such elevated temperatures. When the HDDA polymer hydrogel samples are examined in Figure 8b, a sharp diffraction peak at 1.4° 2θ is again observed before polymerization with very little change in this peak observed after polymerization, indicating structure retention. Increasing the polymer hydrogel temperature to 50 °C causes a significant reduction in the diffraction intensity, signifying less order in the hexagonal mesophase. When the temperature is increased to 75 °C, no diffraction peak is observed, echoing the results observed with polarized light microscopy and SAXS of the nonstabilized Pluronic/water system. From the SAXS and PLM results, it is evident that the differences in polymer nanostructure have a profound impact on the thermal stability of the LLC mesophase. The observation of these thermal stability differences indicates that the morphology of the LLC mesophase is being templated onto the organic cross-linked polymers.

When PEG-400-DA is polymerized in the hexagonal phase, higher mesophase thermal stability is observed due to a stabilization of the LLC structure by the

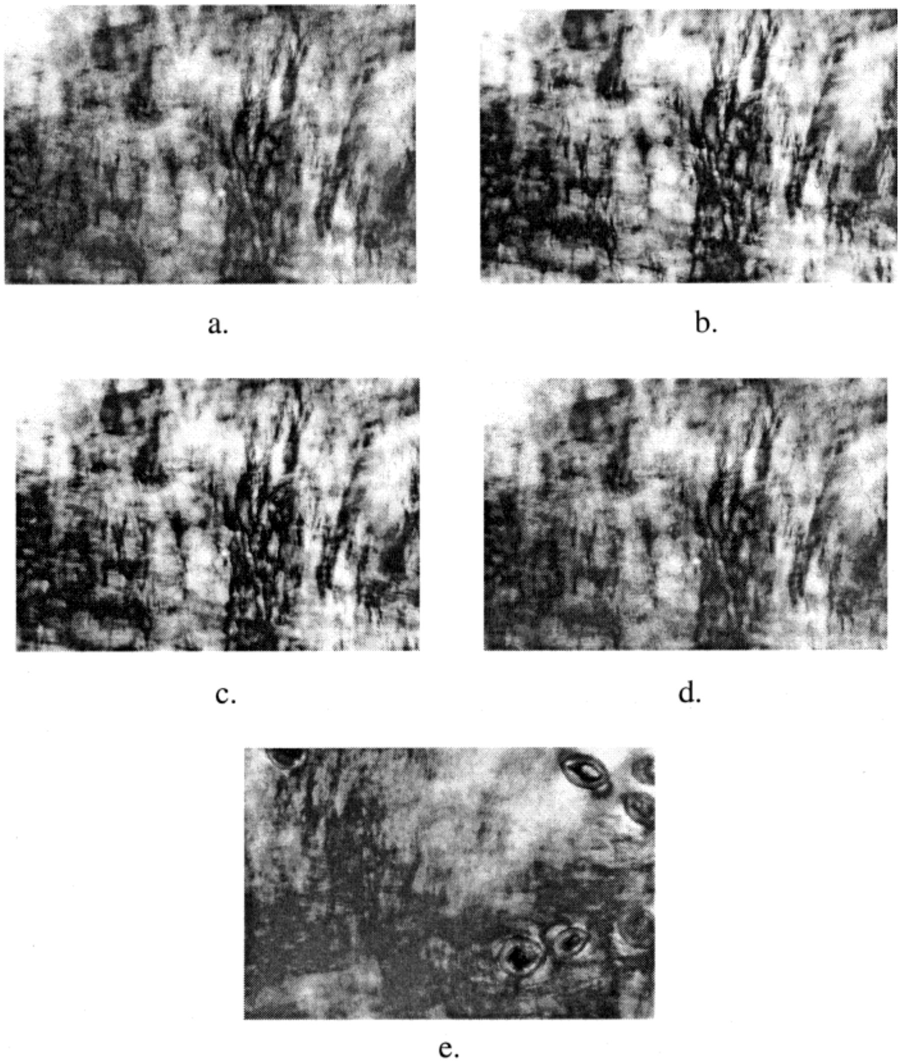
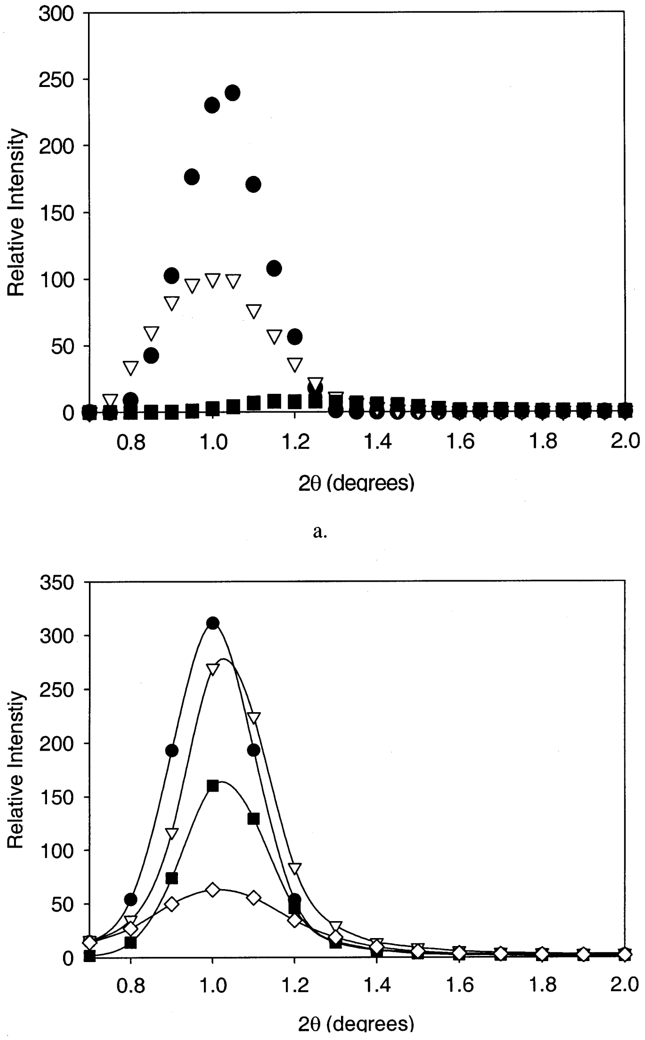


Figure 9. Optical micrographs of 10% HDDA in 76% P92 (a) before polymerization at 25 °C and (b) after polymerization shown at 25 °C, (c) at 50 °C, (d) at 85 °C, and (e) at 105 °C.

nanostructured polymer formed in the continuous phase. When the oil-soluble HDDA is polymerized in the inverse hexagonal phase, similar results may be observed as polymerization would occur in the continuous phase. Analogous to the hexagonal phase polymerization for PEG-400-DA, a continuous phase polymerization of HDDA may provide enhanced inverse hexagonal phase thermal stability. The optical textures of 10% HDDA in 76% P92 before and after polymerization are shown in Figure 9. Similar to the other monomer polymerizations in the Pluronic/surfactant systems, the inverse hexagonal mesophase texture is observed before and after polymerization. As sample temperature is increased to 50 and 85 °C, the inverse hexagonal mesophase persists. In fact, this mesophase optical texture is observed at temperatures as high as 115 °C. The clearing point of the inverse hexagonal phase is approximately 50 °C. The addition of polymer to the inverse hexagonal mesophase results in an over 60 °C increase in mesophase thermal stability. This result echoes those from the PEG-400-DA samples in the hexagonal phase and offers additional evidence that the polymer is templating the LLC morphology. For comparison, PEG-400-DA samples were examined at the same surfactant concentration to attempt polymerization in the inverse hexagonal phase. Unfortunately, the inverse hexagonal phase could not be isolated with these samples, so the discontinuous phase polymerization could not be conducted.

Small-angle X-ray scattering was also used to examine the thermal stability of a neat 85% P92/water sample (inverse hexagonal phase) and the HDDA/Pluronic system. Figure 10 shows the diffraction profiles of the inverse hexagonal phase of P92 in water as well as HDDA polymerized in the inverse hexagonal phase of P92. A sharp diffraction peak is observed for the neat P92/water sample at 25 °C at 1.1° 2θ. As the sample temperature is increased to 50 °C, a significant decrease in the diffraction peak intensity is observed due to disruption of the LLC order. At 75 °C, no observable diffraction peak exists due to the solvation of the block copolymer. The HDDA polymer exhibits the same diffraction peak at 1.1° 2θ both before and after polymerization. When the system is examined at 50 °C, the intensity of the diffraction peak is reduced, but the peak is still clear and distinct. At 85 °C, the diffraction peak broadens and is less intense but is still quite distinct, indicating that LLC order persists. This diffraction peak stays virtually the same at temperatures greater than 95 °C. The observation of the inverse hexagonal diffraction peak for the HDDA hydrogel at high temperatures again indicates that the polymer is acting to stabilize the mesophase at temperatures that far exceed those for stable phases of the parent LLC.



b.

Figure 10. Small-angle X-ray diffraction profiles of (a) 85% P92 in water at 25 °C (●), at 50 °C (▽), and at 75 °C (■). Also shown are diffraction profiles of (b) 10% HDDA in 76% P92 before polymerization (●) and after polymerization (▽) at 25 °C, at 50 °C (■), and at 75 °C (◇).

To further investigate mesophase thermal stability, 10% PEG-400-DA in 44% P92 was examined after the sample was heated to 50 °C before polymerization. Interestingly, as the sample temperature is increased for the PEG/Pluronic monomer sample, the mesophase shifts from a hexagonal phase at 25 °C to an optically isotropic phase (bicontinuous cubic) at 35 °C to a lamellar phase at 50 °C, as represented in Figure 11. The lamellar phase that results is not stable and disappears after holding the sample at 50 °C for a few minutes. This behavior is not observed for the neat 45% Pluronic sample, but the addition of ethylene oxide content from the monomer may lead to this interesting phase behavior in the monomer/Pluronic sample. To examine the templating effect of this LLC mesophase, PEG was photopolymerized at 50 °C, and the optical textures were examined after polymerization.

Figure 12 shows the optical textures of 10% PEG-400-DA in 44% P92 at 50 °C before and after polymerization. Before polymerization, the lamellar mesophase is apparent, and after 5 min of polymerization the mesophase structure has not changed substantially as indicated by PLM. Interestingly, after polymerization the mesophase is thermally stable at 50 °C indefinitely. Upon increase in sample temperature to 85 °C, the lamellar mesophase is still observed and is retained even when the temperature is lowered to 25 °C. The observation of the lamellar mesophase at 25 °C is significant. If the monomer/Pluronic sample is cooled slowly to 25 °C before polymerization, the hexagonal phase is re-formed, but after polymerization the lamellar phase is stable at room temperature. This observation truly underscores the fact that the LLC morphology is being templated in these systems, which consequently stabilizes the nanostructure of the LLC. If the polymer had phase-separated from the LC matrix or not adopted the nanostructure of the parent LLC morphology, such results should not be seen.

The generation of nanostructured polymer within an LLC mesophase can affect not only mesophase thermal stability but, depending on the type of polymer nanostructure that evolves, hydrogel physical properties as well.[21] Differences in physical properties such as compressive modulus can demonstrate the changes that are induced when lyotropic LCs are used as templates for nanostructured polymers. Figure 13 shows a plot of stress/strain profiles for 10% PEG-400-DA in 44% P92 polymerized at various temperatures. As mentioned previously, the modulation of temperature in this sample shifts the LLC mesophase from the hexagonal phase at room temperature, to a possible bicontinuous cubic phase at 35 °C, to a lamellar phase at 50 °C. The polymerization in the lamellar phase gives a stress/strain profile with a fairly small slope, indicating a low modulus nanostructured polymer hydrogel. When polymerization occurs in the bicontinuous cubic phase, the material initially has a slope, and therefore modulus, that is similar to the hydrogel generated in the lamella phase. The hydrogel, however, has a yield point at about 1.0×10^{-3} MPa. Polymerizing in the hexagonal phase yields a stronger polymer than is formed in the cubic or the lamellar phase, as indicated by the larger slope of the stress/strain profile. The difference in the stress/strain profiles and compressive modulus of these samples demonstrates the versatility afforded by using LLCs, specifically Pluronic block copolymers, as polymerization templates. Significant differences in polymer hydrogel physical properties are observed through simple manipulation of the LLC phase order. Interestingly, the amount of surfactant and polymer is constant in these systems, and the LLC mesophase is controlled simply by temperature. Therefore, it is possible to tailor the resulting polymer nanostructure and hydrogel physical properties in this system without changing surfactant concentration. These results indicate the great potential in using Pluronic LLCs as polymerization templates for the development of nanostructured polymeric materials.

Conclusions

Pluronic lyotropic liquid crystals offer a unique and versatile platform for the generation of novel polymeric nanostructured materials. Dependent on the polymeric architecture that evolves, polymers formed in Pluronic LLCs affect numerous mesophase properties. This work describes the photopolymerization behavior, nanostructure development, and mesophase thermal stability of water- and oil-soluble monomers in Pluronic LLC/water systems. When monomers of different chemical structure are photopolymerized in the various LLC phases of the Pluronic, different polymerization behavior is

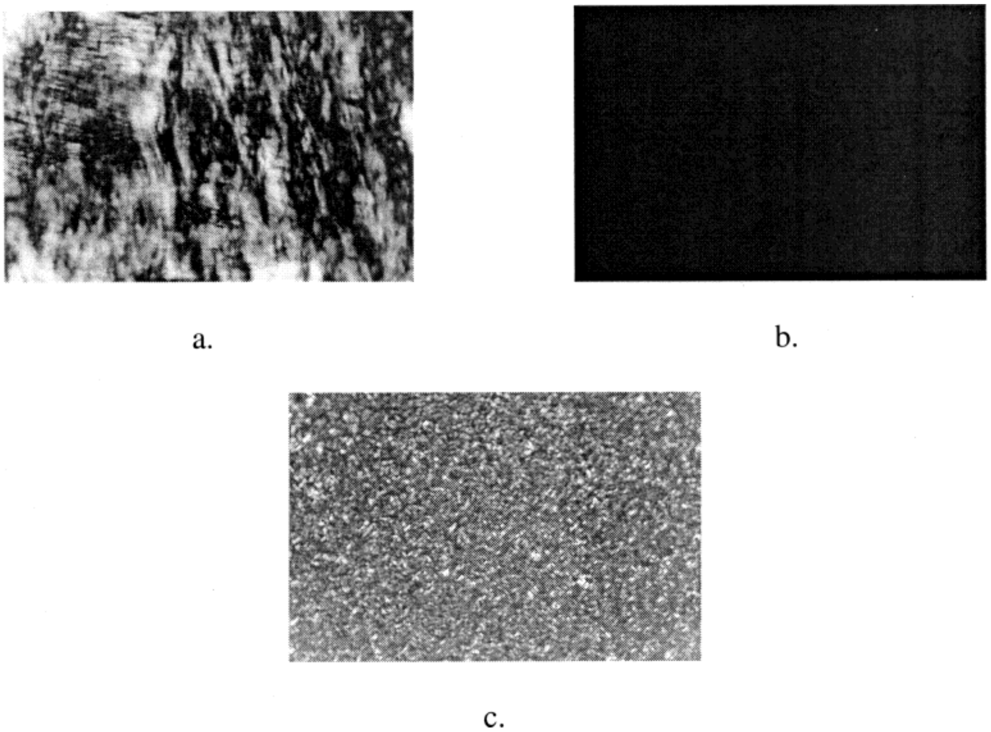


Figure 11. Optical micrographs of 10% PEG-400-DA in 44% P92 before polymerization at (a) 25 °C, (b) 35 °C, and (c) 50 °C.

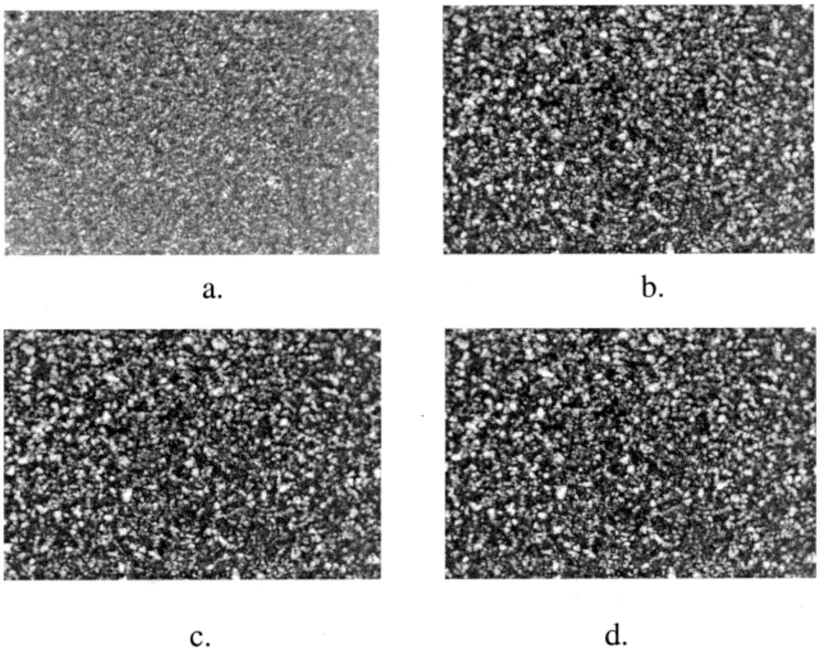


Figure 12. Optical micrographs of 10% PEG-400-DA in 44% P92 (a) before polymerization at 50 °C and (b) after polymerization at 50 °C, (c) at 85 °C, and (d) at 25 °C.

observed. Faster polymerization rates are observed in the normal phases for oil-soluble monomer systems, whereas accelerated polymerization rates are observed in inverse phases for water-soluble monomer systems. Interestingly, when polymerizations are conducting in the bicontinuous cubic phase, both types of monomer exhibit a relatively fast polymerization rate. These differences are directly related to the differences in segregation of the monomers in various LLC phases during photopolymerization. Additionally, the resulting nanostructured polymer has a significant effect on the thermal stability of the LLC mesophases. When PEG-400-DA is polymerized in the continuous region of the hexagonal mesophase, a 45 °C increase in hexagonal mesophase stability is observed. Polymerizations of HDDA in the hexagonal phase only result in a 25 °C increase in mesophase thermal stability. PEG-400-DA is polymerized in the continuous phase, around the hexagonal rods, whereas HDDA is polymerized in the discontinuous phase inside the hexagonal pores. On the other hand, when HDDA is polymerized in the inverse hexagonal phase, around the inverse hexagonal rods, a 60 °C increase in the inverse hexagonal mesophase thermal stability is observed. While increased thermal stability is observed for all polymer/LC systems, the results are especially striking when the polymer is

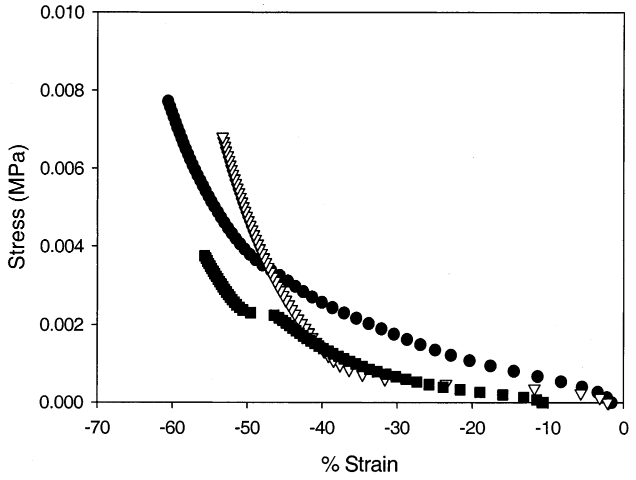


Figure 13. Stress/strain profiles of 10% PEG-400-DA in 44% P92 polymerized in the hexagonal phase (●), bicontinuous cubic phase (▽), and lamellar phase (■). The mesophases in this sample are modulated by temperature and not surfactant concentration.

formed in the continuous phase. Also, phases that are typically unstable or exist over a limited temperature range are also stabilized by polymerizing in the phase of interest as observed in the lamellar phase polymerization of PEG-400-DA. In addition, significant differences in the compressive modulus of polymer hydrogels of PEG-400-DA in P92 are observed with stronger materials being generated in the hexagonal phase compared to the bicontinuous cubic and lamellar phases.

References and Notes

(1) Reppy, M. A.; Gray, D. H.; Pindzola, B. A.; Smithers, J. L.; Gin, D. L. *J. Am. Chem. Soc.* **2001**, *123*, 363.
(2) Pindzola, B. A.; Hoag, B. P.; Gin, D. L. *J. Am. Chem. Soc.* **2001**, *123*, 4617.
(3) Hoag, B. P.; Gin, D. L. *Macromolecules* **2000**, *33*, 8549.
(4) Smith, R. C.; Fisher, W. M.; Gin, D. L. *J. Am. Chem. Soc.* **1997**, *119*, 4092.
(5) Miller, S. A.; Kim, E.; Gray, D. H.; Gin, D. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 3022.
(6) Armitage, B. A.; Bennett, D. E.; Lamparski, H. G.; O'Brien, D. F. *Adv. Polym. Sci.* **1996**, *126*, 53.
(7) Fendler, J. H. *Chem. Mater.* **1996**, *8*, 1616.
(8) Litvin, A. L.; Valiyaveettil, S.; Kaplan, D. L.; Mann, S. *Adv. Mater.* **1997**, *9*, 124.
(9) Archibald, D. D.; Mann, S. *Nature (London)* **1993**, *364*, 430.
(10) Gray, D. H.; Hu, S.; Juang, E.; Gin, D. L. *Adv. Mater.* **1997**, *9*, 731.
(11) Sellinger, A.; Weiss, P. M.; Nguyen, A.; Lu, Y.; Assink, R. A.; Gong, W.; Brinker, C. J. *Nature (London)* **1998**, *394*, 256.
(12) Werkman, P. J.; Wieringa, R. H.; Schouten, A. J. *Thin Solid Films* **1998**, *323*, 251.
(13) Srisiri, W.; Sisson, T. M.; O'Brien, D. F.; McGrath, K. M.; Han, Y.; Gruner, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 4866.
(14) Deng, H.; Gin, D. L.; Smith, R. C. *J. Am. Chem. Soc.* **1998**, *120*, 3522.
(15) Melosh, N. A.; Davidson, P.; Chmelka, B. F. *J. Am. Chem. Soc.* **2000**, *122*, 823.
(16) Tiddy, G. J. T. *Phys. Rep.* **1980**, *57*, 1.
(17) Miller, S. A.; Ding, J. H.; Gin, D. L. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 338.
(18) O'Brien, D. F.; Armitage, B.; Benedicto, A.; Bennett, D. E.; Lamparski, H. G.; Lee, Y.-S.; Srisiri, W.; Sisson, T. M. *Acc. Chem. Res.* **1998**, *31*, 861.
(19) Lester, C. L.; Guymon, C. A. *Macromolecules* **2000**, *33*, 5448.
(20) Lester, C. L.; Colson, C.; Guymon, C. A. *Macromolecules* **2001**, *34*, 4430.
(21) Lester, C. L.; Smith, S.; Guymon, C. A. *Chem. Mater.*, in press.
(22) Lester, C. L. Guymon, C. A. *Polymer* **2002**, *43*, 3707.
(23) Antonietti, M.; Hentze, H. P. *Colloid Polym. Sci.* **1996**, *274*, 696.
(24) Antonietti, M.; Caruso, R. A.; Göltner, C. G.; Weissenberger, M. C. *Macromolecules* **1999**, *32*, 1383.
(25) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 113.
(26) Gray, G. W.; Winsor, P. A. In *Liquid Crystals & Plastic Crystals*, 1st ed.; Gray, G. W., Winsor, P. A., Eds.; John Wiley & Sons: New York, 1974; Vol. 1, p 314.
(27) Ivanova, R.; Lindman, B.; Alexandridis, P. *Adv. Colloid Interface Sci.* **2001**, *89*−*90*, 351.
(28) Alexandridis, P.; Olsson, U.; Lindman, B. *Macromolecules* **1995**, *28*, 7700.
(29) Alexandridis, P.; Zhou, D.; Khan, A. *Langmiur* **1996**, *14*, 2442.
(30) Holmqvist, P.; Alexandridis, P.; Lindman, B. *Macromolecules* **1997**, *30*, 6788.
(31) Zhou, D.; Alexandridis, P.; Khan, A. *J. Colloid Interface Sci.* **1996**, *183*, 339.
(32) Alexandridis, P. *Macromolecules* **1998**, *31*, 6935.
(33) Holmqvist, P.; Alexandridis, P.; Lindman, B. *J. Phys. Chem. B* **1998**, *102*, 1149.
(34) Mortensen, K. *J. Phys.: Condens. Matter* **1996**, *8*, A103.
(35) Alexandridis, P.; Olsson, U.; Lindman, B. *Langmuir* **1998**, *14*, 2627.
(36) Attard, G. S.; Glyde, J. C.; Göltner, C. G. *Nature (London)* **1995**, *378*, 366.
(37) Kim, J. M.; Stucky, G. D. *Chem. Commun.* **2000**, 1159.
(38) Feng, P.; Bu, X.; Pine, D. J. *Langmuir* **2000**, *16*, 5304.
(39) Bowman, C. N.; Elliott, B. J. *ACS PMSE Proc.* **2000**, *82*, 344.
(40) Guymon, C. A.; Shao, R.; Holter, D.; Frey, H.; Clark, N.; Bowman, C. N. *Liq. Cryst.* **1998**, *24*, 263.
(41) McCormick, D. T.; Chavers, R.; Guymon, C. A. *Macromolecules* **2001**, *34*, 6929.
(42) McCormick, D. T.; Fordham, Z. W.; Guymon, C. A. *Liq. Cryst.* **2003**, *30*, 49.
(43) Svensson, M.; Alexandridis, P.; Linse, P. *Macromolecules* **1999**, *32*, 637.

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