Physical Properties of Hydrogels Synthesized from Lyotropic Liquid Crystalline Templates

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Recently, a considerable amount of research has centered on the synthesis of nanostructured hydrogels via the polymerization of monomers in lyotropic liquid crystal (LLC) phases. Because of the potential for controllable nanostructures, these materials have exhibited tremendous potential for a variety of applications. This work describes the impact of photopolymerization kinetics and polymer nanostructure on the physical properties of hydrogels synthesized from LLC templates. Both acrylamide and 2-hydroxyethyl methacrylate (HEMA) photopolymerize more rapidly in the highly ordered LLC phases, resulting in higher molecular weight polymers. The photopolymerization of these monomers in organized surfactant/water assemblies allow formation of highly ordered polymeric hydrogels. The ultimate physical properties appear to be a function of the different polymerization kinetics and polymer nanostructure. Nanostructured polyacrylamide hydrogels swell faster and to a greater extent than isotropic hydrogels. Compressive moduli are also higher for nanostructured polyacrylamide hydrogels when compared to isotropic analogues. The photopolymerization of HEMA results in nanostructured hydrogels, although some structural changes are evident. As a result of the different nanostructures, vastly different physical properties are observed. The isotropic polyHEMA hydrogels swell to a greater extent and considerably faster than any of the organized hydrogels. Additionally, the isotropic polyHEMA hydrogels exhibit higher compressive modulus than the hydrogels synthesized in the organized LLC phases. For both polyHEMA and polyacrylamide gels, different nanostructures produce different physical properties, implying that characteristics such as swelling and mechanical strength can be optimized simply by changing the parent LLC phase.

Introduction

Interest in the synthesis of novel hydrogels has recently been the focus of extensive research because of their promise and use in a variety of biomedical applications. Hydrogels consist of cross-linked hydrophilic polymers that are swollen but not solvated in water and have three-dimensional structures with ionic or covalent cross-links.[1] Additionally, other interactions such as hydrogen bonding and van der Waals forces can act as cross-links. Hydrogels have seen considerable application in separations of biomacromolecules, contact lens materials, drug delivery devices, and scaffolding for tissue engineering. Free-radical polymerization of acrylate and acrylamido monomers in isotropic solvents are often the means by which hydrogels are synthesized. These polymerizations yield gels with random morphologies and fairly wide pore size distributions. Therefore, the resulting polymers can exhibit relatively weak mechanical properties as well as a wide range of

swelling characteristics. The ability to controllably alter these characteristics in hydrogels is an important area of research. Considerable interest has been shown in the development of highly functional nanostructured gels to enhance and provide control over physical properties including swelling characteristics and modulus. Templating lyotropic liquid-crystal (LLC) phases onto these polymers has been proposed recently to control their nanostructure and thereby enhance material properties.[2-5]

LLCs are a class of liquid crystals that consist of two or more components, one being an amphiphilic molecule and the other being a solvent, which is usually aqueous. A variety of ordered structures exist when dispersing amphiphiles in water. At lower concentrations of amphiphile spherical micelles are formed that can be isotropically distributed in the aqueous phase or that

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can be packed into cubic lattices, forming an LLC phase. Other phases at higher concentrations of surfactant include the hexagonal, lamellar, and bicontinuous cubic morphologies.[6,7] All of the LLC phases formed typically have dimensions on the nanoscale that makes them promising for a variety of biomedical applications. However, LLC phases lack physical integrity as they exhibit the low viscosity typical of liquids, making them unsuitable for material applications. Therefore, templating these interesting geometries onto polymers would significantly aid in developing nanostructured hydrogels.

Templating the structure of LLC phases onto inorganic polymers has been examined extensively with ordered arrays formed from a variety of different surfactants and block copolymers.[8-10] Templating the LLC structure onto organic polymers has also been previously attempted. The polymerization of a variety of hydrophilic monomers in various LLC phases has been performed.[2,3,5,11,12] In these studies the resulting polymer morphologies are often a result of phase separation phenomenon and not a direct template of the parent LLC phase. In some cases, however, successful templating of LLC phases onto polymers has been reported. For example, the polymerization of acrylamide and other monomers in bicontinuous cubic LLC phases yields polymer networks with high degrees of order on the nanoscale, indicating that the original structure is retained.[4,13,14] These conflicting results imply that different polymerization conditions can determine whether LLC phases are true templates for the organic polymers or whether phase separation occurs. Additionally, the different types of polymer morphology obtained may impact the ultimate material properties. With a more complete understanding of the resulting polymer morphologies and the consequent impact on material properties, relationships between structure and physical properties may be attained, making it possible to tailor physical properties in polymeric hydrogels.

The polymerization kinetics of templated systems are significantly influenced by different LLC phases, which, in turn, can impact the molecular weight, cross-link density, and the ultimate physical properties. The impact of monomer organization on polymerization kinetics and the resulting polymer morphology has proven important in the polymerization of a variety of monomers in analogous thermotropic systems. The polymerization kinetics in thermotropic liquid crystals are heavily influenced by the phase structure in which they were polymerized. In turn, the kinetics also affect the final polymer architecture and properties.[15-17] The role of LLC morphology in the photopolymerization of monomeric amphiphiles has also been studied. Mesophases with higher degrees of order polymerize more readily and exhibit enhanced structure retention. The enhanced rates observed in the polymerization of monomeric amphiphiles in LLC phases are typically a result of depression in the termination rate due to diffusional limitations on the propagating polymers induced by the increased degree of LLC order.[18,19] Similarly, the templated photopolymerization kinetics of difunctional monomers exhibit a strong dependence on the LLC morphology. Monomers with different polarities segregate within different regions of the LLC phase and exhibit very different polymerization behavior. In these highly cross-linked systems the original nanostructures is retained to a large degree.[20,21]

The polymer morphology will depend strongly on the parent LLC phase in which the system is polymerized due to different reaction kinetics and thermodynamics. Correspondingly, the resulting polymer morphology may impact the physical properties of the hydrogel. The goal of this work is to elucidate how the physical properties of hydrogels prepared in LLC templates are affected by their ultimate polymer nanostructure. For this study, hydrophilic monomers will be polymerized in various LLC phases. The polymerization kinetics will be determined for the various LLC phases to understand how the ordered structures affect the polymerization itself. The LLC structure will be determined before and after polymerization to establish whether the polymer morphology is a template of the parent phase. Additionally, the physical properties including swelling behavior and compressive modulus of the hydrogels will be studied to determine the relationship between polymer morphology and material properties. This study will enhance the ability to control material properties in hydrogels through the concerted study of the polymerization, the resulting polymer morphology, and material properties. The ability to understand and control polymer nanostructure and material properties of hydrogels will be extremely useful in applications such as biological separations, materials for contact lenses, scaffolds for tissue engineering, and drug delivery devices.

Experimental Section

Materials. The monomers used in this study are acrylamide, *N,N*-methylene bisacrylamide, 2-hydroxyethyl methacrylate (HEMA, Acros), and poly(ethylene glycol)-400-dimethacrylate (PEG-400-DMA, Aldrich). The surfactants are the nonionic Brij 58 (Aldrich) and cationic dodecyltrimethylammonium bromide (DTAB, Aldrich). The chemical structure of the monomers and surfactants used are displayed in Figure 1. Irgacure 2959 (I-2959) photoinitiator was obtained from Ciba Specialty Chemicals Corporation (Tarrytown, NY). The monomers, surfactants, and initiator were all used as received.

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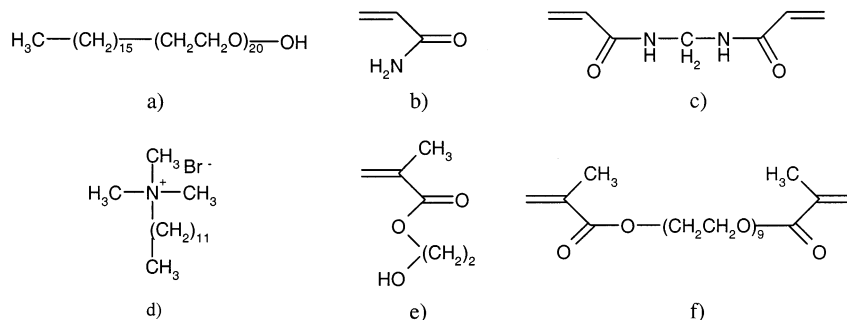(21) Lester, C. L.; Smith, S. M.; Guymon, C. A. *Macromolecules* **2001**, *34*, 8587.

Figure 1. Chemical structure of the monomers and surfactant used in this study. Shown are (a) Brij 58, (b) acrylamide, (c) *N,N*-methylene bisacrylamide, (d) dodecyltrimethylammonium bromide (DTAB), (e) 2-hydroxyethyl methacrylate (HEMA), and (f) poly(ethylene glycol)-400-dimethacrylate (PEG-400-DMA).
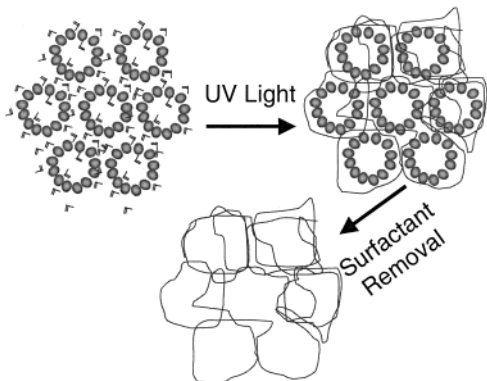

Figure 2. Diagram representing the successful templating of a hydrophilic monomer in an LLC phase. After photopolymerization, the surfactant is removed, leaving the nanostructured hydrogel.

The concentration of surfactant varied from 0 to 70 wt %. HEMA was added to the DTAB/water system at 20 wt %, whereas 25 wt % was utilized in the Brij 58/water system. Photoinitiator I-2959 was added at approximately 2%, and cross-linker was added at 1% of the monomer mass. Solutions were mixed thoroughly and centrifuged repeatedly to ensure homogeneity. The samples were flushed with nitrogen and refrigerated until use.

Hydrogels were synthesized by polymerizing 200 mg of sample in a flat-bottomed glass vial. The vials were fitted with septa, and the samples were placed through three freeze, thaw, and evacuation cycles to remove dissolved oxygen. The LLC samples were heated above their transition temperature so they could flow and form a film 1.0-mm thick. The vials were placed under a monochromatic (365 nm) UV light source for 30 min. Afterward, the films were removed and dialyzed extensively in deionized water to remove surfactant and other unpolymerized material. These films were then solvent-exchanged with acetone or ethanol and dried in a vacuum oven. A diagram outlining this process and the consequent LLC templating of the polymer is given in Figure 2.

Methods. Small-angle X-ray scattering (Siemens XPD 700P WAXD/SAXS with a Cu Kα line of 1.54 Å) was used to determine the phase behavior of the LLC mixtures and to determine the morphology of the polymeric gels. Bragg's law was used to determine the *d* spacing of the lyotropic mesophase and the resulting polymers. Characteristic textures of the various mesophases were examined by polarized light microscopy (Nikon Optiphot-2 pol) equipped with a hot stage (Instec, Boulder, CO) to corroborate data collected with SAXS. Polymerization exotherms were followed in real time with a modified Perkin-Elmer DSC-7. Polymerization rate was then calculated by a method described in detail elsewhere.[22] The heat of polymerization used for acrylamido and methacrylate monomers was 18.5 and 13.1 kcal/mol, respectively.[23]

To perform swelling studies, uniform disks 5.0 mm in diameter were cut from the dialyzed disks. These hydrogels of uniform dimensions were then dried and weighed. To determine the swelling kinetics, hydrogels were immersed in a bath of deionized water for a period of time. The hydrogel was removed periodically, patted dry, and weighed until no further uptake of water could be detected. The percent of water uptake *W* was determined with the equation shown below,

$$W = \frac{(W(t) - W_0)}{W_0} \times 100 \tag{1}$$

where $W(t)$ is the mass of the hydrogel at some point in time and W_0 is the mass of the dried gel.[24]

To obtain compressive stress/strain curves, uniform disks 5.0 mm in diameter were cut from completely hydrated, dialyzed disks. The samples were placed onto a compressive stress/strain clamp in a TA DMA 2980 Dynamic Mechanical Analyzer. The gels were then compressed at a rate of 0.0125 N/min up to 0.125 N. From the stress/strain profiles a compressive modulus was determined using a procedure described elsewhere.[25]

Results and Discussion

Nanostructured polymeric hydrogels offer considerable promise for many applications including enhanced separatory materials, and various biomedical materials. One route to nanostructured hydrogels is by polymerizing hydrophilic monomers in lyotropic liquid crystal (LLC) phase templates. The polymerization behavior of hydrophilic monomers is dramatically influenced by the organized LLC phases.[20,21] Conversely, the kinetics appear to play a role in the final nanostructure of the materials.[18,19] Even with this knowledge, little is known about such effects on the physical properties of these nanostructured polymers. Therefore, the goal of this work is to understand how the different LLC phases influence the polymerization itself and, conversely, how the polymerization influences the ultimate polymer morphology and the consequent physical properties. To accomplish these goals, the polymerization of two hydrophilic monomers, acrylamide and 2-hydroxyethyl methacrylate (HEMA), will be examined in the LLC phases of Brij 58/water and DTAB/water systems, respectively. These LLC systems have been selected as they display a wide range of stable LLC phases with

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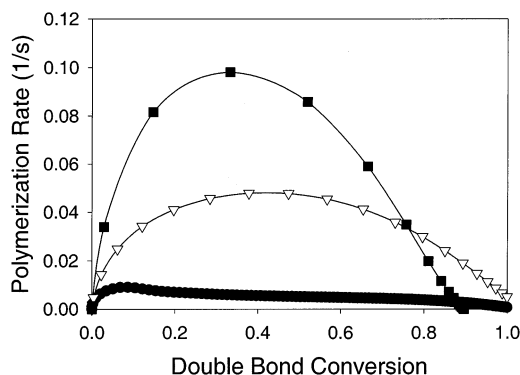
Figure 3. Polymerization rate profiles of 25 wt % acrylamide with increasing Brij 58 concentration in water as a function of double-bond conversion. Shown are 0%, isotropic (●), 20%, micellar (▽), and 40%, bicontinuous cubic (■) Brij 58.

Figure 4. SAXS profiles of 25% acrylamide in the micellar and bicontinuous cubic phases of Brij 58/water. Shown are a bicontinuous cubic system with 40% Brij 58, unpolymerized (●), and photopolymerized (▽), and a micellar solution with 20% Brij 58, micellar unpolymerized (■) and photopolymerized (◇).

changes in surfactant concentration. Additionally, for the Brij 58/water/acrylamide system the bicontinuous cubic liquid-crystalline phase is exhibited over a broad surfactant concentration.[12,21]

As described previously, the polymerization kinetics may be significantly influenced by LLC phase morphology.[21] To determine the impact in preparation of nanostructured hydrogels, the polymerization behavior of acrylamide was monitored in different LLC phases. In Figure 3 polymerization rate as a function of double-bond conversion is displayed for 25% acrylamide with increasing Brij 58 concentration. In the isotropic state the photopolymerization is extremely slow and takes nearly an hour to reach completion. When polymerized in micellar solutions at 20% Brij 58, the polymerization increases significantly. The fastest polymerization rate occurs when polymerizing in the highly ordered bicontinuous cubic LLC phase with 40% surfactant. In fact, the polymerization rate in the bicontinuous cubic LLC phase is fully 10 times that of the isotropic solution. These significant increases in polymerization rate result from various factors including diffusional limitations on the propagating polymers as well as segregation effects induced by the LLC phase.[21]

This reaction behavior may have significant implications in the development of the polymer molecular weight, nanostructure, and ultimate properties. Because of the depressed termination rate, it is reasonable to assume that polymers of higher molecular weight would be generated. To determine if such effects are present in the LLC/acrylamide system, viscosity average molecular weights were obtained for polyacrylamide synthesized without cross-linker in an isotropic solution containing no surfactant and for polyacrylamide formed in the faster polymerizing bicontinuous cubic LLC phase. The polyacrylamide synthesized in the isotropic solution has a viscosity average molecular weight of approximately 163000 g/mol. Interestingly, when the same bulk concentration of monomer is polymerized in the highly ordered bicontinuous cubic LLC phase, the viscosity average molecular weight increased to approximately 465000. This nearly 3-fold increase in molecular weight has significant implications for the resulting physical properties of the polymers. The increase in molecular weight is driven by a depression of the termination rate induced by diffusional limitations on the propagating polymer.[21]
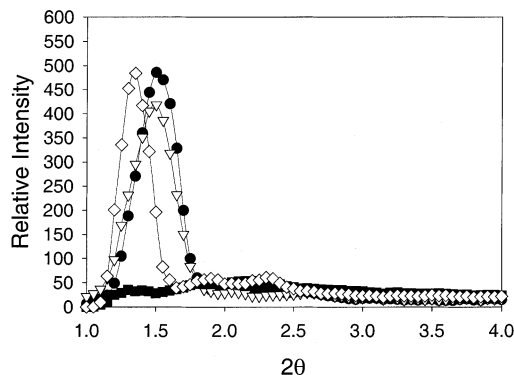
To understand how the reaction kinetics and LLC phase influence the developing nanostructure of the polyacrylamide gels, SAXS profiles were obtained before and after polymerization. In Figure 4 the SAXS profiles of the bicontinuous cubic phase formed by the 40% Brij 58 system with 25% acrylamide are displayed before and after polymerization. Also shown in Figure 4 is the SAXS profiles of the system with the same concentration of acrylamide polymerized in a micellar solution formed with 20% Brij 58. Before polymerization, the sample with 40% Brij 58 exhibits the triply periodic pattern, indicative of the bicontinuous cubic LLC phase. Upon polymerization the SAXS profile exhibits a similar triply periodic pattern with no difference in the peak positions. This pattern indicates that the polyacrylamide system appears to be retaining the order of the original LLC phase. The optical texture remains isotropic, providing further evidence for the successful templating of the bicontinuous cubic LLC phase onto the polyacrylamide gel. Similar results are observed at other compositions within the bicontinuous cubic LLC phase. On the other hand, no long-range order exists in the unpolymerized micellar solution with 20% Brij 58. Upon polymerization it is apparent, however, that the system becomes highly organized. The SAXS profile of the polymerized sample displays a triply periodic pattern, indicating that the developing polymer induces the formation of the bicontinuous cubic LLC phase.

Polymerization kinetics, molecular weight, and the final nanostructure of polyacrylamide are dramatically influenced by the LLC phase, which could also significantly alter the physical properties of the polymer formed. To study how polymerizing in LLC templates alters the physical properties of polyacrylamide, isothermal swelling studies were performed on dried and dialyzed gels that were synthesized in the various LLC phases. In Figure 5 the percentage of water uptake (W) is shown as a function of time for 25% polyacrylamide (with bisacrylamide as cross-linker) synthesized in Brij 58. Each swelling profile exhibits a relatively fast initial increase that slows after a few hours before approaching equilibrium. Significant differences are exhibited between the hydrogels with different morphologies. For example, the polyacrylamide hydrogel synthesized in the isotropic solution swells at a slower rate and ultimately swells to a lesser extent. The hydrogel
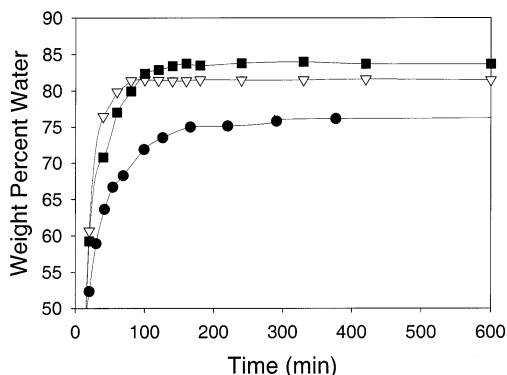
Figure 5. Water-swelling isotherms of polyacrylamide hydrogels formed from 25% acrylamide in the different phases of Brij 58/water. Shown are samples polymerized in 0%, isotropic (●), 10%, micellar (▽), and 40%, bicontinuous cubic (■) Brij 58.

polymerized from the micellar solution displays a significantly faster swelling rate and displays a higher percentage of water uptake. The nanostructured hydrogel polymerized in the bicontinuous cubic LLC phase swells more quickly than the isotropic hydrogel, but not as fast as the hydrogels synthesized in the micellar phase. Interestingly, the bicontinuous hydrogel swells to a greater degree than the hydrogels synthesized in the other phases.

To understand the swelling behavior further, the kinetics of water uptake can be analyzed by assuming second-order swelling kinetics. The swelling rate of hydrogels often obey second-order kinetics in which the swelling rate can be described by the following equation

$$\frac{\mathrm{d}W}{\mathrm{d}t} = k_\mathrm{w}(W_\infty - W_t)^2 \qquad (2)$$

where k_w is a kinetic rate constant for the swelling process, t is time, and W_∞ is the maximum percentage of water uptake. The integration and rearrangement of eq 2 results in the following equation

$$\frac{t}{W} = \frac{1}{k_\mathrm{w}} + \frac{1}{W_\infty}t \qquad (3)$$

where t/W can be plotted versus t to obtain k_w and W_∞ from the intercept and slope, respectively. When t/W is plotted as a function of time for the polyacrylamide hydrogels synthesized in the LLC phases of Brij 58/water, excellent linear fits were obtained, indicating that these materials obey second-order swelling kinetics.

In Table 1 k_w and W_∞ are displayed as a function of Brij 58 concentration and consequent LLC phase. As described previously, by changing surfactant concentration, different reaction kinetics, molecular weights, and nanostructures are observed. The minimum W_∞ is seen in the polyacrylamide hydrogel synthesized in the isotropic solution. With increases in surfactant concentration and corresponding changes in polymerization kinetics and nanostructure formation, W_∞ increases. Values of k_w in polyacrylamide hydrogels change even more dramatically when polymerized in the organized phases of Brij 58/water. The isotropic polyacrylamide gel exhibits the lowest k_w, implying that it exhibits the slowest swelling kinetics. The maximum k_w is observed in the polyacrylamide gel synthesized in the micellar
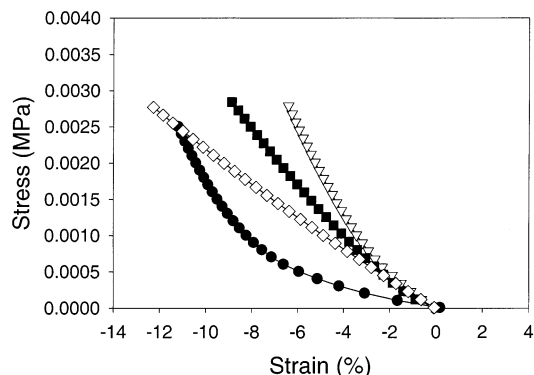

Figure 6. Compressive stress/strain profiles of polyacrylamide hydrogels formed from 25% acrylamide in the various phases of Brij 58/water. Shown are samples polymerized in 0%, isotropic (●), 10%, micellar (▽), 30%, micellar (■), and 40%, bicontinuous cubic (◇) Brij 58.

Table 1. Swelling Parameters of Polyacrylamide Hydrogels Synthesized in Various Phases of Brij 58 /Water

weight percent Brij 58	$k_\mathrm{w}{}^a$	$W_\infty{}^a$
0% (isotropic)	3.31	76.9
10% (micellar)	7.06	81.9
20% (micellar)	4.34	82.6
30% (micellar)	5.19	85.7
40% (bicontinuous cubic)	5.42	84.7
50% (bicontinuous cubic)	5.78	82.6

^{a} Relative standard error is <2%.

phase with 10% Brij 58. The faster swelling kinetics appear to be a result of the different polymer nanostructure formed when polymerizing from the micellar solutions. For polymers formed in the micellar solution at 20% Brij 58, k_w decreases but is still significantly higher than that of the isotropic gel. With further increases in surfactant concentration in the micellar region, and at higher concentrations to reach the bicontinuous cubic LLC phase, increases in k_w are observed. Interestingly, at 50% surfactant the k_w approaches that of the polyacrylamide gel polymerized in the micellar solution with 10% surfactant. The different swelling kinetics of polyacrylamide gels synthesized from 25% acrylamide in the different phases of the Brij 58 system indicate that nanostructure plays a large role in the permeation of water through these materials. Therefore, desired properties of polyacrylamide hydrogels could be tailored by polymerizing within different surfactant/water phases for various applications.

Different polymerization kinetics and polymer nanostructure could also possibly influence the mechanical properties of polyacrylamide hydrogels. To understand this influence, compressive stress/strain profiles were obtained of the various polyacrylamide hydrogels. In Figure 6 the stress/strain curves of dialyzed polyacrylamide hydrogels are displayed as a function of percentage of Brij 58 used in their synthesis. The isotropic polyacrylamide hydrogel displays a relatively small slope, indicative of a low-modulus material. Additionally, this particular hydrogel displays a yield point just below 7% strain. Interestingly, polyacrylamide hydrogels synthesized in surfactant/water phases display significantly different behavior. The nanostructured polyacrylamide gels from micellar solutions (10−30% Brij 58) and the polyacrylamide gel with the bicontinu-

Table 2. Compressive Modulus of Hydrated Polyacrylamide Hydrogels Synthesized in Various Phases of Brij 58/Water

weight percent Brij 58	$G (\times 10^{-3}$ MPa$)^a$
0% (isotropic)	2.10
10% (micellar)	5.91
20% (micellar)	6.72
30% (micellar)	6.06
40% (bicontinuous cubic)	6.09
50% (bicontinuous cubic)	4.32

^{a} Relative standard error is <4.0%.

ous cubic LLC phase morphology exhibit significantly higher slopes in the stress/strain profiles. The higher slope indicates that the nanostructured polyacrylamide gels are higher modulus materials. Additionally, the nanostructured hydrogels do not display a yield point over this range of applied stress in direct contrast to the isotropic gel.

To show this phenomenon more clearly, the compressive modulus (G) of the various polyacrylamide gels are displayed in Table 2 as a function of the concentration of Brij 58 utilized in their synthesis. At strains below 10%, the compressive modulus can be obtained from the slope of plots of τ versus $(\lambda - \lambda^{-2})$ as shown below

$$\tau = G(\lambda - \lambda^{-2}) \qquad (4)$$

where τ is the applied stress and λ is the ratio of deformed length over undeformed length of the hydrogel.[21] As would be expected from Figure 6, the lowest modulus material is that of the isotropic polyacrylamide hydrogel. On the other hand, nanostructured polyacrylamide gels synthesized from the organized phases of Brij 58 exhibit significantly higher compressive moduli. Polyacrylamide gels synthesized in the micellar and bicontinuous cubic phases display similar compressive strength until 50 wt % Brij 58 is reached, at which point a slight decrease is observed. The bicontinuous cubic polyacrylamide hydrogel synthesized in 50% Brij 58 still exhibits a significantly higher modulus than the isotropic hydrogel, however. It is important to note, however, that the same bulk concentration of monomer and cross-linker is utilized in synthesizing the hydrogels. The increase in effective cross-link density therefore implies that either the cross-linking efficiency is higher in the organized surfactant/water phases or that the ordered polymer morphology is increasing the mechanical integrity of the materials in some fashion. The polyacrylamide hydrogels that exhibit higher modulus also display higher degrees of swelling, which would typically indicate a lower degree of cross-linking. These results indicate that the polymer morphology itself drives the changes in properties and not simple differences in cross-link density.

To be able to synthesize nanostructured materials for a wide variety of applications and to determine if similar effects are also observed in other hydrogel-forming monomers, other monomer/LLC systems have been studied. The polymeric hydrogels from the water-soluble monomer 2-hydroxyethyl methacrylate (HEMA) have been used extensively in contact lens materials, devices for controlled release, and many other biomedical applications.[21] Interestingly, HEMA displays significantly different reaction behavior as well when photopolymerized in organized surfactant/water assemblies formed
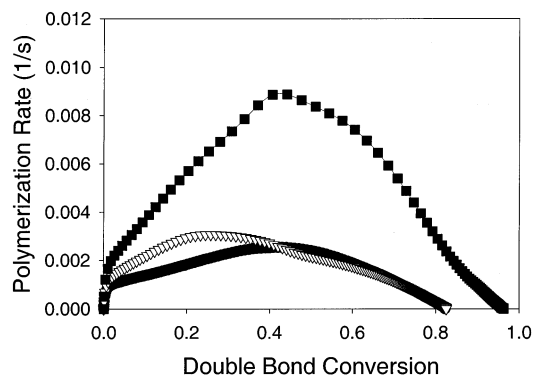

Figure 7. Polymerization rate profiles of 20 wt % HEMA with increasing DTAB concentration in water as a function of double bond conversion. Shown are 40%, discontinuous cubic (●), 50%, hexagonal (▽), and 60%, lamellar (■) DTAB.
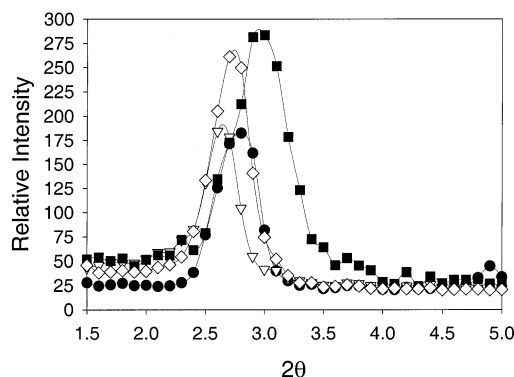

Figure 8. SAXS profiles of 20% HEMA in the hexagonal and lamellar phases of DTAB/water. Shown are a hexagonal system with 50% DTAB unpolymerized (●), and photopolymerized (▽), and a lamellar system with 60% DTAB unpolymerized (■) and photopolymerized (◇).

from LLC phases. In Figure 7 polymerization rate as a function of double bond conversion is shown for 20% HEMA in the various phases of DTAB/water. The photopolymerization of isotropic solutions of HEMA in water is so slow that it is exceedingly difficult to measure and obtain reproducible results with calorimetry, and therefore is not shown. As the surfactant concentration is increased to 40% DTAB (discontinuous cubic LLC phase), the polymerization rate is observable yet still relatively slow. Increasing the surfactant concentration further to 50% DTAB results in the formation of the hexagonal LLC phase, which yields a slightly faster polymerization rate. When polymerized in the lamellar LLC phase at 60% DTAB, a 5-fold increase in photopolymerization rate is observed from that observed in the discontinuous cubic LLC phase. This increase in photopolymerization rate has been shown in similar systems to be a result of depression of the termination rate brought about by diffusional limitations on the propagating polymers.[20] These results are similar to those observed in the Brij 58/water/ acrylamide system, indicating that LLC morphology drives the differences in the reaction kinetics.

To understand how the polymer morphology is influenced by the various LLC phases, small-angle X-ray scattering (SAXS) was used. In Figure 8 the SAXS profiles of unpolymerized and polymerized 20% HEMA in hexagonal (50% DTAB) and lamellar (60% DTAB) phases are shown. For the unpolymerized hexagonal
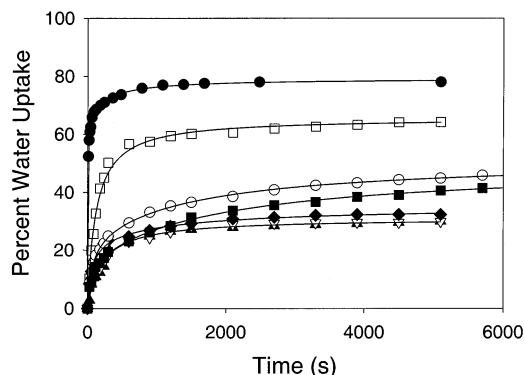
Figure 9. Water-swelling isotherms of polyHEMA hydrogels prepared with 20% HEMA in various phases of DTAB/water. Shown are samples polymerized in 0%, isotropic (●), 10%, micellar (□), 20%, micellar (▲), 30%, micellar (▽), 40%, discontinuous cubic (◆), 50%, hexagonal (○), and 60%, lamellar (■) DTAB.

Table 3. Swelling Parameters of PolyHEMA Hydrogels Synthesized in Various Phases of DTAB/Water

weight percent DTAB	$k_w{}^a$	$W_\infty{}^a$
0% (isotropic)	0.73	81.2
10% (micellar)	0.72	65.4
20% (micellar)	0.37	31.3
30% (micellar)	0.41	31.3
40% (discontinuous cubic)	0.47	33.2
50% (hexagonal)	0.40	47.4
60% (lamellar)	0.31	45.7

[a] Relative standard error is <2%.

sample a strong primary reflection is seen at approximately 2.8 2θ and a secondary reflection at approximately 4.8 2θ. The ratio of the d spacings is $1:3^{1/2}$, which is indicative of the hexagonal LLC phase.[6] Further confirmation of the phase was provided by the characteristic focal conic textures displayed by the 50% DTAB sample using polarized light microscopy. Upon photopolymerization the material still possesses long-range order but the primary peak position changes to slightly higher angles, indicating the development of slightly larger dimensions. The secondary peak also disappears entirely, indicating some structural changes of the parent LLC phase. For the unpolymerized lamellar sample, a single primary reflection at 3.1 2θ is observed. The lack of higher order peaks does not allow indexing of the phase type, but the optical textures of this sample clearly show the "oily streaks" and maltese crosses indicative of the lamellar LLC phase.[6] Upon polymerization the primary reflection has shifted to approximately 2.8 2θ, which corresponds to the formation of slightly larger dimensions as seen in the hexagonal LLC phase. The shift to larger dimensions could possibly be due to changes in the original LLC structure. These materials do remain birefringent when viewed through crossed polarizers, however, and no gross phase separation is observed. Therefore, even with some slight structural changes, it appears that unique nanostructured polymeric HEMA hydrogels are being synthesized.

With such drastic differences in the polymerization media, polymer nanostructure, and reaction kinetics of the HEMA/LLC system, it is reasonable to believe that the physical properties of these materials would also be heavily influenced. To study the influence of these features on the physical properties, water-swelling isotherms were obtained of polyHEMA films formed from 20% HEMA (with PEG400 DMA as cross-linker) in the various LLC phases of DTAB/water. Figure 9 displays the percentage of water uptake as a function of the DTAB concentration used to synthesize the various polyHEMA hydrogels. It is interesting to note that the swelling behavior exhibits almost the exact opposite behavior of the polyacrylamide hydrogels. For example, in comparison to hydrogels formed in LLC phases, the isotropic hydrogel swells very rapidly and to the greatest degree, whereas the isotropic polyacry-

lamide hydrogel swells much slower than the ordered systems and to a lesser extent. The polyHEMA hydrogel synthesized in the relatively dilute solution of isotropic micelles (10% DTAB) displayed slower swelling kinetics and swelled less. When polymerizing in more concentrated micellar solutions (20% and 30% DTAB) and in the discontinuous cubic LLC phase (40% DTAB), the swelling rate slows dramatically and the hydrogels swell only to about 30−40 wt %. Interestingly, when poly-HEMA is synthesized in the highly ordered hexagonal and lamellar LLC phases, the percentage of water uptake increases, though not to the degree of the isotropic hydrogels, and the kinetics are still much slower.

To understand these results in more detail, plots of t/W versus t were obtained. As with the polyacrylamide hydrogels, these plots were linear, indicating second-order swelling behavior. From the slopes and intercepts of the linear regression the parameters W_∞ and k_w were determined for polyHEMA hydrogels synthesized in the phases of DTAB/water. In Table 3 the rate parameter of swelling, k_w, and the equilibrium percentage of water uptake, W_∞, are displayed as a function of DTAB concentration and LLC phase used in the synthesis of the polyHEMA hydrogels. The highest rate parameter of swelling, k_w, is observed for the isotropic hydrogel. When polymerizing in the dilute isotropic micellar solution with 10% DTAB, k_w decreases to 0.72. k_w for the concentrated micellar solutions and the discontinuous cubic phase all decrease significantly with a local minimum observed for the hydrogel synthesized with 20% DTAB, which is approximately half the maximum observed for the isotropic system. Increasing surfactant concentration to 30% and 40% induces subsequent increases in k_w. These values, however, are still significantly lower than that observed for the isotropic hydrogel. PolyHEMA synthesized in the hexagonal LLC phase displays a slight decrease in the swelling rate from that of the discontinuous cubic LLC phase. Finally, the slowest swelling kinetics overall were observed in the polyHEMA hydrogel synthesized in the lamellar LLC phase, which exhibits a k_w value of 0.31.

The equilibrium percentage of water uptake also changes dramatically for hydrogels synthesized in the different phases of DTAB/water. The isotropic poly-HEMA hydrogel exhibits the maximum W_∞ value of 80%. W_∞ decreases slightly for the polyHEMA hydrogel synthesized in the dilute isotropic micellar solution. The equilibrium water uptake falls off dramatically for polyHEMA hydrogels generated from the more concentrated micellar solutions and the discontinuous cubic LLC phases. In fact, W_∞ for the micellar and discontinuous cubic LLC phase is 2.5 times less than the isotropic
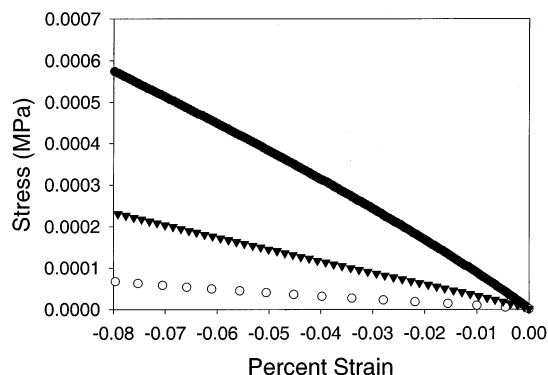
Figure 10. Compressive stress/strain profiles of polyHEMA hydrogels formed from 20% HEMA in various phases of DTAB/water. Shown are samples polymerized in 0%, isotropic (○), 40%, discontinuous cubic (▼), and 50%, hexagonal (■) DTAB.

Table 4. Compressive Modulus of Hydrated PolyHEMA Hydrogels Synthesized in Various Phases of DTAB/Water

weight percent DTAB	$G (\times 10^{-3}$ MPa)[a]
0% (isotropic)	2.20
10% (micellar)	2.41
20% (micellar)	1.11
30% (micellar)	0.52
40% (discontinuous cubic)	0.33
50% (hexagonal)	0.71
60% (lamellar)	0.96

[a] Relative standard error is <2%.

solution. Interestingly, when HEMA is photopolymerized in the lamellar and hexagonal LLC phases, W_∞ increases to approximately 45%, which is still considerably less than that of the isotropic hydrogel. The different swelling behavior of polyHEMA synthesized in the organized phases of DTAB/water implies that the polymers are cross-linked to different degrees and/or different polymer morphologies are influencing the physical properties.

Given the swelling results, it would be reasonable to assume that the physical strength of the hydrogels would be affected by the different polymer morphologies. To understand how polymer morphology influences physical properties, compressive stress/strain profiles of hydrated polyHEMA hydrogels were obtained. In Figure 10 the stress/strain profiles of samples formed with 20% HEMA are shown as a function of the LLC phase and DTAB concentration used to synthesize the hydrogels. In this case the highest slope magnitude is observed for the isotropic polyHEMA hydrogel, indicating a relatively high modulus. When polymerizing in the discontinuous cubic LLC phase, the slope of the stress/strain curve decreases to a minimum, and the modulus has decreased substantially. Intermediate values of the slope are observed for the polyHEMA hydrogel synthesized in the hexagonal LLC phase.

To illustrate this phenomenon more concisely, the compressive modulus (G) of polyHEMA hydrogels synthesized from 20% HEMA in various organized DTAB/water phases were determined as described previously. In Table 4 the compressive modulus of polyHEMA hydrogels is shown as a function of DTAB concentration used in their synthesis. As observed in the stress/strain plots, the isotropic hydrogel displays the highest modulus. The modulus increases slightly for the polyHEMA hydrogel synthesized in the dilute micellar solution with 10% DTAB. However, when increasing surfactant in the micellar solution, G decreases by a factor of 2. The polyHEMA hydrogel synthesized in the discontinuous cubic LLC phase (40% DTAB) yields the lowest modulus, fully 2.5 times less than the isotropic hydrogels. The polyHEMA hydrogels synthesized in the ordered hexagonal and lamellar LLC phases display an increase in G, though not to the level of the isotropic hydrogels. The decreases in compressive modulus indicate that these materials have a lower effective cross-link density than that of the polyHEMA hydrogels synthesized in the organized DTAB/water phases. It is important to note that the same bulk concentration of cross-linker and monomer was utilized in the synthesis of all the hydrogels. Interestingly, both swelling behavior and modulus of polyHEMA hydrogels are opposite to that observed in the polyacrylamide hydrogels. Some of these results could perhaps be explained by structural changes observed upon polymerization, but other possible factors could include the different LLC systems used, and inherent differences in the physical properties of the polymers themselves.

Conclusions

This work presents the influence of photopolymerization kinetics and polymer nanostructure on physical properties of hydrogels synthesized in lyotropic liquid crystal (LLC) phases. Acrylamide photopolymerizes more rapidly in the highly ordered LLC phases. The increase in polymerization rate for acrylamide monomers in ordered phases is induced by decreases in termination and increases in segregation. These kinetics changes also significantly increase the molecular weight. The original nanostrucuture appears to be retained when photopolymerizing acrylamide in the bicontinuous cubic LLC of Brij 58/water. Additionally, polyacrylamide hydrogels synthesized from micellar solutions exhibit long-range order after polymerization, indicating that LLC-type morphologies develop during polymerization. The physical properties of polyacrylamide hydrogels synthesized in the organized phases of Brij 58/water reflect the different polymerization behavior and resulting polymer morphologies. The nanostructured polyacrylamide hydrogels swell to greater degrees and at faster rates than the isotropic polyacrylamide gels. The compressive modulus of nanostructured polyacrylamide hydrogels is also higher than the isotropic hydrogels.

Similar and contrasting results are observed for polymerizations of HEMA in the LLC phases of DTAB/water. The fastest polymerization rate is observed in the highly ordered LLC phase. Upon photopolymerization some structural changes do occur. Specifically, the d spacing obtained from SAXS experiments increases slightly, and higher order reflections disappear. The LLC/polymer system still displays long-range order, however, and no gross phase separation is observed with polarized microscopy, indicating that nanostructured polyHEMA hydrogels are obtained. The different photopolymerization kinetics and polymer nanostructures give rise to extremely different physical properties. The isotropic polyHEMA hydrogels swell faster and to a much greater degree than any of the organized hydrogels. Additionally, the isotropic polyHEMA hydrogels exhibit higher compressive moduli when compared to

the hydrogels synthesized in the organized LLC phases. It is interesting to note that the physical properties of polyHEMA (swelling and modulus) are in direct contrast to those displayed by the polyacrylamide hydrogels. These differences may arise from the structural changes observed in the polyHEMA system and inherent differences in the physical properties of the two polymeric materials. This basic understanding of the impact of photopolymerization kinetics and polymer nanostructure on hydrogel properties will aid considerably in the development of a variety of applications that require controllable nanostructure and physical properties.

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