Influence of Polymerization Conditions on Nanostructure and Properties of Polyacrylamide Hydrogels Templated from Lyotropic Liquid Crystals

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Lyotropic liquid crystals (LLCs) have recently been employed as polymerization templates to yield highly ordered nanostructured hydrogels, which have shown promise in biological separations and tissue engineering. To allow greater control of hydrogel structure using LLC templates, this study focuses on the influence of polymerization kinetics and temperature on ultimate polymer morphology and properties. A more in-depth understanding of these phenomena has been obtained through extensive examination of polymer structure with small-angle X-ray scattering (SAXS) and scanning electron microscopy (SEM). The impact of different polymerization rate and temperature regimes on polymer morphology was determined using isotropic, cubic, and hexagonal phases as polymerization templates. Polymer morphology varies dramatically depending on LLC phase template, while within a given phase changes in polymerization time scale and temperature greatly impact polymer structure. SAXS reveals a higher degree of retained liquid crystalline order using rapid polymerization at relatively low temperatures. SEM images demonstrate that rapid polymerization yields polymers with highly ordered network structures and nanoscale morphology. Less ordered, thermodynamically driven polymer features result from relatively slow polymerization. The degree of swelling in aqueous solution increases dramatically in ordered LLC phases relative to bulk polymerization, with lower swelling resulting from faster polymerization. Similarly, higher surface area results from polymerization in LLC media relative to isotropic systems, and surface area increases with increasing polymerization rate.

Introduction

Polyacrylamide hydrogels have received significant attention in recent years because of their broad application in drug delivery, biological membranes, and separations devices.[1−4] In conventional synthesis, which typically utilizes in situ thermal polymerization techniques, physical properties such as mechanical strength, pore size, and swelling are primarily regulated by adjusting the ratio of acrylamide and cross-linker. Although a wide range of pore sizes can be obtained through this method, material strength is often sacrificed to obtain large pores that are often necessary for efficient transport of large biomolecules.[1,2] Also, polymer surface area is quite low through bulk polymerization techniques, hindering applications in separations and tissue engineering. Several techniques to enhance polymer structure and facilitate more efficient separations have been proposed.[5−8]

One such approach, offering a number of advantages in the synthesis of polyacrylamide and other materials involves photopolymerization within lyotropic liquid crystalline media.[9−16] The periodic nanostructure inherent in lyotropic liquid crystals (LLCs) serves as a structure directing template, enabling synthesis of polymers with unique structure and physical properties. A variety of LLC structures, ranging from micelles that form at low concentrations of surfactant in polar solvent to hexagonal and lamellar phases at higher concentrations, may be used as the polymerization template. Several useful phases based on cubic lattice structures may also form at intermediate amphiphile concentrations.[17] As a result of the high degree of positional and orientational order, polymerization conducted within these anisotropic systems

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may produce polymers with geometries that cannot be achieved using traditional bulk or solution polymerization.[16,18] In contrast to conventional methods, synthesis using LLC templates can yield hydrogels that simultaneously exhibit significant swelling and remarkable mechanical strength, making them attractive candidates in membrane and tissue engineering applications.[9,11,13] The relative independence of pore size and cross-linker concentration indicates that the liquid crystalline structure plays a dominant role in polymer structure formation.[19] Careful selection of the LLC template phase may, therefore, allow significant control of polymer structure and properties through this method.

To better understand how liquid crystalline order influences the polymerization mechanism and structural development, several recent studies have investigated the polymerization kinetics of a number of monomers in LLC systems.[9−11,20−25] The polymerization rate of acrylamide in nonionic surfactant increases rapidly with increasing liquid crystalline order.[9,10] Studies with polar and nonpolar monomers, which exhibit significantly different polymerization behavior in LLC systems, indicate that monomer segregation and ordering may control the kinetics to a large degree.[22,23,25] Significant changes in the polymerization rate also result from variations in initiation efficiency in differently ordered LLC phases.[23,25] Such changes in photoinitiation have been correlated with substantial variation in polymer molecular weight in phases of different morphologies.[25] The dependence of polymer morphology on initiator and cross-linker concentrations in LLC systems indicates that the relative time scale of polymerization and demixing of polymer and surfactant may largely control polymer structure development.[12,13,26,27] While there is substantial evidence that the polymerization rate may largely influence the final polymer structure, the role of kinetics in LLC systems is not well-understood. A more in-depth study of the influence of kinetics in this promising method of synthesis could enable improvements in polymer structure and properties. Temperature may also play a unique role when using LLC systems as polymerization templates because the type and degree of LLC order varies with temperature. Understanding the effects of temperature on ultimate polymer structure could likewise lead to enhancement in the structure and properties of these hydrogels.

The goal of this study is to gain a more complete understanding of the role of polymerization kinetics and temperature in polymer structure and properties in LLC systems. The influence of liquid crystalline order on structural development will be studied using photo- and thermal initiation techniques. Photopolymerization exhibits a much more rapid rate than thermal polymerization and could yield substantially different polymer structure development. This study will allow a direct comparison of the role of kinetics while keeping composition and phase structure virtually constant. Because photoinitiation is relatively temperature independent, both photo- and thermal polymerizations can be conducted at the same temperature.[28] The degree of liquid crystalline order retained upon polymerization with each method will be examined using small-angle X-ray scattering (SAXS). Samples polymerized at different temperatures will be similarly studied. Polymer morphology will be directly studied using scanning electron microscopy (SEM). The relationship between polymer structure and physical properties, such as swelling in aqueous media and surface area, will be contrasted and compared for different polymerization rate and temperature regimes. As a result of this study further control in polymer structure will be possible through kinetic and thermal control of polymerization. By optimizing polymerization kinetics and temperature to yield the desired polymer structure and properties, improved materials for biological membranes and separation devices could be obtained.

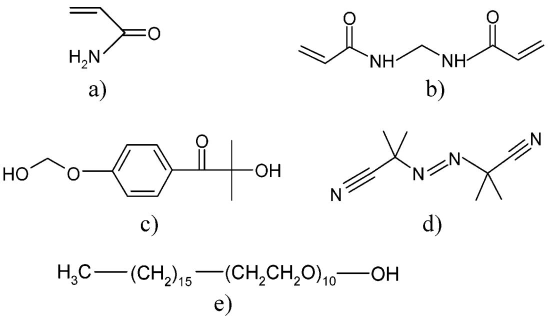

Figure 1. Chemical structures of the monomers, photoinitiators, and surfactant used in this study. Shown are (a) acrylamide (b) *N*,*N*-methylene bisacrylamide, (c) HEPK, (d) AIBN, and (e) polyoxyethylene (2) cetyl ether (Brij 56).

Materials and Methods

The monomers used in this study are acrylamide and *N*,*N*-methylene bisacrylamide (Acros). Polymerizations were initiated with the photoinitiator, 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (HEPK, Ciba Specialty Chemicals) and the thermal initiator 2,2′-azo-bis(isobutyronitrile) (AIBN, Aldrich). Liquid crystalline samples were synthesized using varying concentrations of the nonionic surfactant, polyoxyethylene (2) cetyl ether (Brij 56, Aldrich) and deionized water. The monomers, surfactants, and initiator were all used as received. Each sample contained 25 wt % of an acrylamide mixture (93 wt % acrylamide, 2.0 wt % *N*,*N*-bisacrylamide, and 5.0 wt % initiator) with appropriate amounts of deionized water and surfactant. Samples were mixed, centrifuged, and sonicated repeatedly until homogeneous gels were obtained. Figure 1 shows the chemical structures of the materials used in this study.

LLC morphology and phase boundaries were characterized with a polarized light microscope (Nikon, Eclipse E600W Pol) equipped with a hot stage (Instec, Boulder, CO) by examining the optical texture of each sample. For corroboration of microscopy data,

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phases were identified with SAXS by measuring ratios in *d*-spacing. These measurements were conducted utilizing a Nonius FR590 X-ray apparatus with a standard copper target Röntgen tube as the radiation source with a Cu Kα line of 1.54 Å, a collimation system of the Kratky type, and a PSD 50M position sensitive linear detector (Hecus M. Braun, Graz). By comparing SAXS profiles and poloarized light microscopy images from before and after polymerization, the degree of LLC structure retained upon polymerization was compared.

Morphology of the freeze-fractured polymer gels was examined using SEM (Hitachi S-4000). Prior to analysis, surfactant was removed by gradually exchanging water for ethanol. The ethanol was subsequently replaced by supercritical CO_2 using a BIO-RAD E3000 critical-point drying apparatus. The critical-point method employed has been shown to minimize collapse of the gel structure during drying.[29,30] The dried and freeze-fractured samples were sputter-coated using a Au/Pd target.

Polymerization rate data were acquired with a Perkin-Elmer differential scanning calorimeter. The emission spectrum from a medium-pressure UV arc lamp (Ace Glass) was used to initiate polymerizations. Light intensity was controlled with optical filters and by varying the distance of the sample from the lamp. Full spectrum, 60 mW/cm^2 light was used. Error caused by water evaporation was minimized by covering the approximately 5 mg samples with thin transparent films of FEP (Dupont fluorinated copolymer). Samples were purged with nitrogen for 6 min prior to polymerization to prevent oxygen inhibition. Isothermal reaction conditions were maintained during polymerization using a refrigerated circulating chiller. The polymerization rate, R_p, was determined as a function of time from the heat flow (Q) according to eq 1

$$R_p = \frac{Q[M_0]MW}{\Delta HM} \tag{1}$$

where $[M_0]$ is the initial monomer concentration, MW is the monomer molecular weight, ΔH is the enthalpy of polymerization of the monomer, and M is the sample mass.[31] Maximum rates were taken from the peak in the rate profiles obtained, and double bond conversion was calculated by integrating the heat flow profiles. For these studies the theoretical value of 18.5 kcal/mol was used as the heat evolved per reacted acrylamide double bond.[32] The relative standard error for these kinetic experiments was calculated by dividing the standard deviation of the maximum polymerization rate from five identical experiments by the average. The relative standard error for the vast majority of samples was less than 5%.

Polymer network swelling was determined gravimetrically after removal of the surfactant with ethanol and drying overnight under vacuum at 50 °C. Surface areas of the dried polymer samples were determined using the multipoint BET method with a Quantachrome NOVA 1200.

Results and Discussion

Polymerization within lyotropic liquid crystalline phases is a promising method of generating polymers with highly anisotropic morphologies and interesting physical properties. Through this method of polymerization final polymer morphology is determined to a large degree by the structure and order of the liquid crystalline phase. Great variety in polymer morphology may thus be obtained without changing the chemical makeup of the polymer but by simply varying the order of the reaction environment. In addition to the solvent order, several other factors play a role in polymer structure development in LLC systems, such as polymerization rate and temperature. Temperature has a compound role in LLC systems because LLC order as well as polymerization rate depend on temperature. Because liquid crystalline aggregates constantly undergo rapid structural transitions, the structure and properties of polymers synthesized in these ordered media may be highly dependent on the time scale of the polymerization. Several recent studies have shown complex polymerization kinetics in LLC systems that vary dramatically with LLC morphology.[9−11,20−22,24] Factors such as monomer segregation and initiation efficiency, which vary dramatically depending on LLC order, largely govern the kinetics.[23,25] Such changes in kinetics may largely affect how polymer structure develops in these systems. It has been suggested that the type of polymer structure formed in these systems depends on the relative rate of polymerization and demixing of polymer and surfactant.[8,12,13,26,27] Rapid polymerization would cause polymer networks to form at an earlier stage in the phase separation and may thus enable a higher degree of liquid crystalline order templated in the final polymer.

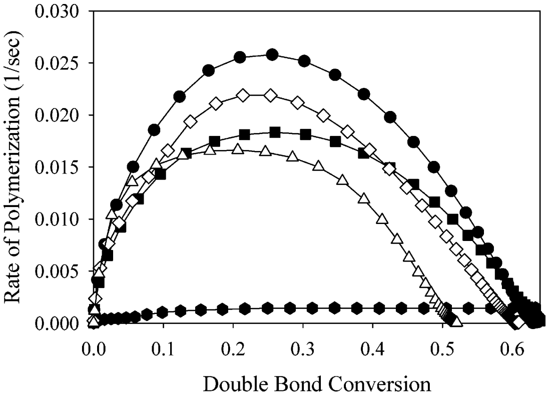

Figure 2. Polymerization rate vs conversion of 25% acrylamide initiated with 0.5 wt % HEPK. Shown are polymerizations in 0% (isotropic − ⬢), 40% (discontinuous cubic − ■), 50% (hexagonal − ●), 60% (hexagonal − ◇), and 70% (inverse micellar − △) Brij 56 in water.

To better understand polymer structure development in LLC systems, the influence of kinetics and temperature on polyacrylamide structure has been examined. Polymerization of acrylamide has been conducted in several liquid crystalline phases that form with varying concentration of the nonionic surfactant, Brij 56, in water. With a constant concentration of a 25 wt % mixture of acrylamide, cross-linker, and initiator, several well-defined and easily identified LLC phases form as the surfactant concentration is increased in water. To understand how the order of the liquid crystal influences the polymerization behavior, the polymerization rate was determined as a function of double bond conversion in the phases that form with varying concentration of Brij 56 in water. As shown in Figure 2, photopolymerization of acrylamide in an isotropic solution of water without added surfactant proceeds relatively slowly, requiring several hours to reach high conversion of double bonds. Polymerization

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in a cubic phase formed with 40 wt % Brij 56 results in dramatic rate acceleration, with double bond conversion exceeding 60% after 1 min. The rate of polymerization then increases another 50% in the hexagonal phase, in which the highest rate of polymerization occurs. A hexagonal phase persists at 60 wt % surfactant, although decreased birefringence and reduction in viscosity indicate a lower degree of order.[7,25] In this phase the polymerization rate is slightly less than that in the more defined hexagonal phase at 50 wt % surfactant but is still significantly higher than that in the other phases. Increasing the surfactant concentration to 70 wt %, to form an inverse micellar solution, results in a sharp decline in the polymerization rate. Interestingly, the inverse micellar phase, which forms at the highest surfactant concentration in this comparison, yields a similar polymerization rate to that in the cubic phase, which has the lowest concentration of surfactant. The polymerization kinetics are clearly not directly dependent on surfactant concentration but instead parallel the degree of orientational and positional order in the system.

A complex interaction of several variables accounts for the variation in polymerization rate in the different LLC phases. Previous studies indicate that close association of surfactant and monomer cause the monomer to adopt the order of the LLC phase.[9,10] The higher rates of polymerization in the more ordered phases in this system are consistent with increased monomer ordering. While changes in monomer order should expectedly exert significant influence over polymer structure, the change in the rate itself could additionally affect polymer formation. To decouple these effects and better understand the role of kinetics in the structural development, polymer structures resulting from the same LLC phase and different polymerization time scales should be compared. Using thermal and photoinitiators to initiate polymerization in the same phase could enable such a comparison. In this way the effect of kinetics can be examined over a wide range of rate regimes with minimal changes in sample composition. Photopolymerization of acrylamide in LLC systems occurs in less than 1 min when initiated with HEPK while a similar degree of monomer conversion requires approximately 4 h through thermal polymerization with AIBN. The initiator, which is used in low concentrations (0.5 wt %), is the only component that is varied.

To compare the structural influence of photo- and thermal polymerization, samples were examined with SAXS before and after polymerization. The triply periodic X-ray scattering profile of the unpolymerized sample with 40 wt % Brij 56 corresponds to a cubic phase as shown in Figure 3. Upon photopolymerization the primary and tertiary peaks occur at the same scattering angle as before polymerization although the secondary peak disappears completely. An additional peak appears after polymerization at 1.4° 2θ. This peak corresponds to the primary reflection of a sample consisting of monomer and surfactant in the same ratio with no added monomer, indicating that some of the surfactant behaves as if the polymer was completely purged from the system. The retention of the primary and tertiary peaks in the same scattering angle, on the other hand, provides evidence that complete phase separation of polymer and surfactant does not occur. Otherwise, the SAXS profile of the polymerized sample would exactly overlap that of the surfactant/water profile.[12] These results demonstrate that a relatively large degree of liquid crystalline order is retained upon photopolymerization. A sample with 40 wt % Brij 56 was thermally cured and similarly analyzed before and after polymerization. There is no perceptible change in liquid crystalline order before polymerization between samples with thermal and photoinitiators, likely because of the low initiator concentration used, and the otherwise identical composition. In agreement with the results from photopolymerization, a shoulder appears in the scattering profile of the thermally polymerized sample, indicating formation of a mixed phase. However, a larger decrease in scattering intensity occurs in the thermally polymerized samples, indicating a greater loss of liquid crystalline order. Because sample compositions and polymerization temperatures were nearly identical for both photo- and thermally polymerized samples, the differences in LLC order observed in the polymerized material from each method can be attributed to the different polymerization rates. Faster polymerization kinetics clearly enable the retention of higher degrees of liquid crystalline order.

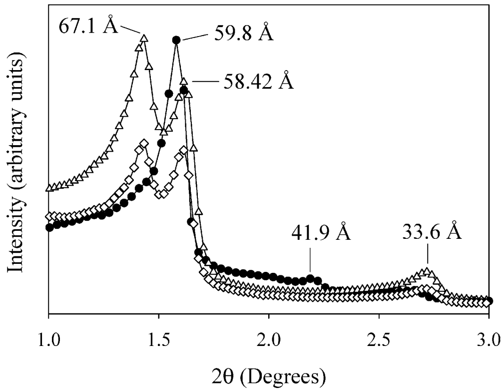

Figure 3. SAXS profiles of 25% acrylamide in 40% Brij 56 and water before polymerization (●), after photopolymerization (△), and after thermal polymerization (◇).

This type of SAXS analysis provides information about transitions in liquid crystalline order occurring during polymerization, which are related to the ensuing polymer structure development. However, SAXS alone does not provide direct information about polymer structure, especially when polymer coexists with a liquid crystalline phase.[7,8,16] Further morphological information of photo- and thermally polymerized samples was therefore obtained by extracting the surfactant and water at room temperature and viewing the freeze/fracture surface of the polymer with SEM. While the temperature of polymerization is different than the temperature at which the surfactant and water is removed, the network morphology should not be significantly changed with the slight change in temperature due to cross-linking and the high T_g of acrylamide polymers. The smooth, glassy morphology of polyacrylamide photocured in an isotropic phase of water without added surfactant is shown in Figure 4a. This sample from isotropic bulk polymerization provides a control to compare how polymer structure may vary when templated from ordered LLC phases. In contrast, a very well-defined sheet-like morphology, as shown in Figure 4b, results

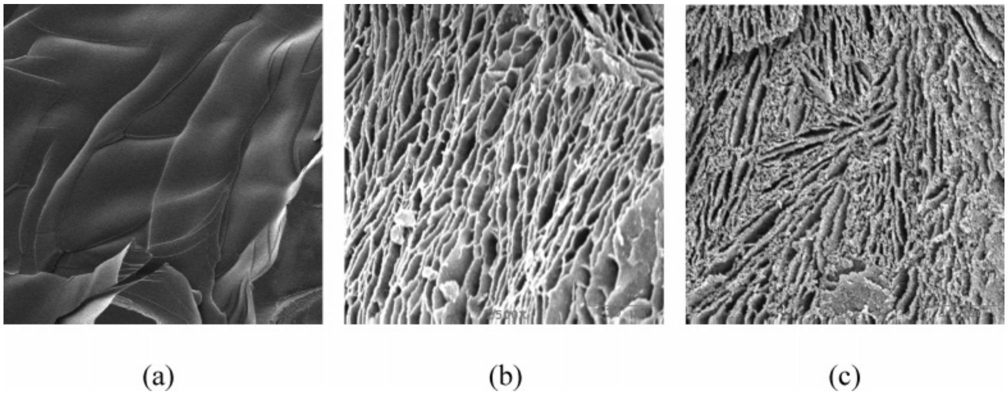

Figure 4. SEM images of polyacrylamide (a) photocured in the isotropic phase with 0 wt % Brij 56, (b) photocured in the cubic phase with 40 wt % Brij 56, and (c) thermally cured in the cubic phase of 40 wt % Brij 56. Surfactant and water were removed prior to imaging.

from photopolymerization of acrylamide in the cubic phase formed with 40 wt % Brij 56 in water. This image depicts a very porous polymer structure of similarly aligned channels, with width ranging from 500 nm to 1 μm and length from 2 to 10 μm, which are homogeneously distributed throughout the sample. Distinct grain boundaries visible in the polymer network indicate that monomer diffusion is directed by the LLC phase. This is consistent with the mechanism proposed by Antonietti et al. in which domain growth is regulated by the anisotropic transport properties of the liquid crystalline phase. The morphology of the thermally polymerized material shown in Figure 4c, while possessing a remnant of the lamellar structure of the photopolymerized material, exhibits a much different morphology. At low magnification a sheet-like morphology is visible along with a secondary structure filling the void space. Sheets are less defined and appear to splay out in a mushroom-like fashion from the surface, indicating phase separation of polymer and surfactant. These results could be, in part, due to differences in segregation within the LC as well. Previous studies[23,25] have shown that different photoinitiators can segregate in different regions of the LC. This behavior, in turn, can significantly change the polymerization rate. Even with this rate change, the polymer structure in using different photoinitiators is only slightly different, indicating that the large changes in structures observed here are a result of the significant difference in time scale of polymerization, not initiator segregation.

SEM images obtained with higher magnification provide further detail of the relationship between polymerization kinetics and final polymer structure. Under 13 000× magnification as shown in Figure 5a the photopolymerized sample reveals very little secondary structure. Clean void space with relatively smooth, approximately 500 nm to 1 μm thick channel walls are visible. The structure of the thermally polymerized sample as shown in Figure 5b is more heterogeneous, with the polymer that fills the void space within the channels exhibiting cauliflower-like morphology, such as might be expected from a thermodynamically controlled phase separation process. In corroboration with the SAXS data, these images reveal significant differences in polymer structures from photo- and thermal polymerization when conducted in a cubic LLC phase. The appearance of the spherical droplet structures in the thermally polymerized material shown in Figure 5b is indicative of thermodynamically controlled structural development, contrasting definitively with the more homogeneous, kinetically controlled polymer structure resulting from photopolymerization.

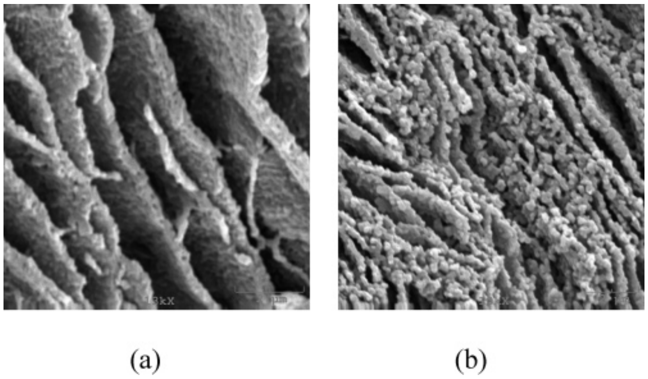

Figure 5. SEM images of 25% acrylamide (a) photo- and (b) thermally polymerized in the cubic phase of 40% Brij 56 and water. Shown are freeze-fractured samples after removal of surfactant and water.

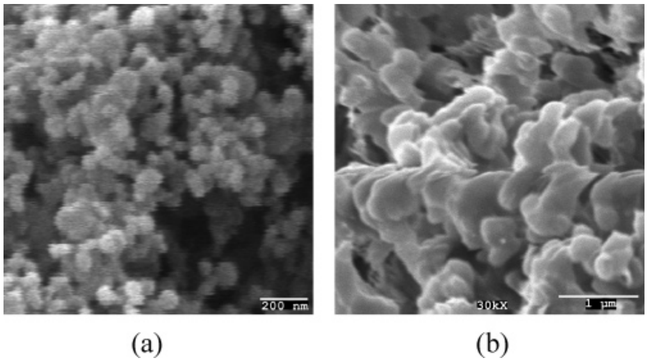

Figure 6. SEM image of polyacrylamide cured using (a) photo- and (b) thermal initiators in the hexagonal phase of 60 wt % Brij 56 in water. Images were taken after extraction of surfactant and water.

The structural development occurring in a hexagonal phase has similarly been examined to determine whether kinetics have similar influence in a different liquid crystalline phase. The SEM image of the polymer templated from a hexagonal liquid crystal is shown in Figure 6a. The morphology is typified by interconnected spherical globules with an average domain size of approximately 40 nm. Unlike polymers generated in the cubic phase, hexagonal samples lack a well-defined channel structure. The cauliflower-like appearance of this sample resembles the material filling the void space in the channels of the cubic samples polymerized through thermal polymerization. Slow polymerization kinetics were implicated in the formation of this type of structure in the cubic phase. In the hexagonal phase a similar structure results even with rapid photopolymerization kinetics. Although the surfactant concentration is higher in the hexagonal phase, the viscosity is much lower than that of the cubic phase.[8,17] The significantly lower viscosity is likely a driving force for the formation of such a structure. Diffusion of monomer and polymer is expectedly much faster and less positionally restricted. Even with rapid polymerization kinetics, a higher diffusion rate enables attainment of more energetically favorable spherical droplet morphology in this lightly cross-linked system. To determine further the influence of kinetics in polymer formation in a hexagonal phase, the thermally cured sample was similarly analyzed with SEM. Figure 6b depicts the morphology of thermally cured polyacrylamide in the 60 wt % Brij 56/water system. The structural units in this material have plate-like rather than spherical appearance and are significantly larger than those of the photopolymerized material. The larger size scale of the interconnected polymer structural units provides further evidence of a diffusion controlled process. The much slower rate of thermal polymerization allows more extensive demixing of polymer and surfactant. This is consistent with the relatively large decrease in liquid crystalline order that has been observed in the thermally polymerized material using SAXS. The smaller spherical globules of the photopolymerized sample signify more limited diffusion time before gelation impedes further transport. This structural comparison of the photo- and thermally polymerized samples, which are virtually identical, again demonstrates the significant role of polymerization kinetics in structure development.

Polymerization temperature is another factor with a significant role in polymer structure formation.[33] While temperature is obviously a critical consideration in all types of polymerization, the effect of temperature is compounded in LLC systems as liquid crystal phase behavior varies significantly with temperature. Even with constant surfactant concentration, changes in polymerization temperature alter the morphology of the liquid crystalline template thereby impacting ultimate polymer structure. To gain a clearer understanding of the role of polymerization temperature in structure development in LLC systems, samples polymerized at closely spaced temperature increments were examined with SAXS before and after polymerization. Figure 7 shows the SAXS profiles of polyacrylamide polymerized in a cubic phase at temperatures ranging from 25 to 80 °C. While the polymerization temperature is different for each sample, all SAXS measurements were taken at room temperature to allow direct comparison. Upon polymerization of the cubic sample, a peak appears at 1.4° 2θ, which corresponds to the position of the primary scattering peak of a sample with water and surfactant only in the same ratio. While this is indicative of phase separation, a relatively high degree of liquid crystalline order remains after the polymerizations conducted at lower temperatures. This is demonstrated by the retention of the peaks at 1.6° and 2.75° 2θ, which are in the same position as before polymerization. Each successive increase in temperature, however, yields an associated decrease in scattering intensity and correspondingly lower degrees of liquid crystalline order in the polymerized samples.

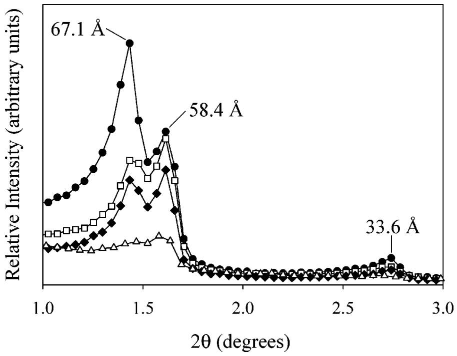

Figure 7. SAXS profiles of 25% polyacrylamide in the cubic phase of 40% Brij 56 and water after photopolymerization at 27 °C (●), 50 °C (□), 65 °C (◆), and 80 °C (△). While samples were cured at different temperatures, all SAXS measurements were taken after cooling the samples to 27 °C.

Polymerization at 80 °C completely disrupts the original liquid crystalline order of the cubic phase. Upon polymerization and cooling to room temperature, the sample exhibits weak scattering insufficient for phase identification, indicating relative disorder in the polymerized material. Because the phase becomes isotropic above 75 °C, polymerization conducted at 80 °C occurs in the randomly oriented solvent, and the polymerized sample may be expected to be isotropic. However, cooling the sample back to room temperature would allow reformation of an ordered liquid crystalline phase if surfactant and polymer were completely phase separated. The persistence of the relatively unordered phase after cooling the polymerized sample indicates that polymer and surfactant interact strongly before and during polymerization. Polymer structure in these systems appears to form through a template assisted mechanism rather than from complete phase separation.[24] These results provide additional evidence that the type and degree of order preserved during polymerization is not solely a function of surfactant concentration but is instead dependent on the orientation of the surfactant aggregates, which varies dramatically with temperature.

To determine how polymerization temperature affects the structure of the polymer itself, with the surfactant and water removed, polymers photocured at different temperatures were examined with SEM. Figure 8 shows the SEM images of polyacrylamide photocured at 27 °C, 50 °C, and 65 °C in the cubic phase formed with 40 wt % Brij 56 in water. Photopolymerization at 27 °C results in a sheet-like structure with interlayer spacing of ≈1 μm. The sheets are a well-defined, densely polymerized material, with relatively smooth surface and edges. The sample polymerized at 50 °C maintains similar interlayer spacing and approximately 1 μm × 5 μm channels. The surface and edges of the polymer sheet-like structure appear rougher and not as precisely defined as those of the sample cured at lower temperatures. Similarly, the sample polymerized at 65 °C appears even more rough and less defined, although the channel dimensions are not altered. The surface of this sample has a bubbly appearance. While the cubic phase is still intact at 65 °C, the phase becomes less stable as the surfactant aggregates

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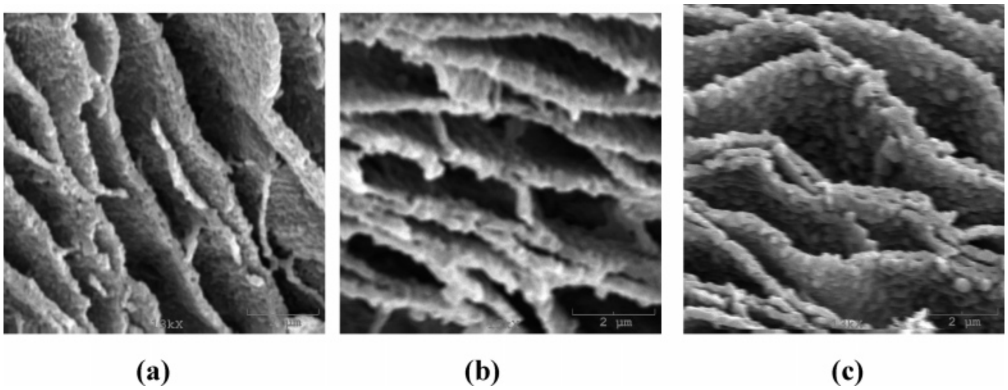

Figure 8. SEM images of polyacrylamide photocured in the cubic phase of 40 wt % Brij 56 and water at (a) 27 °C, (b) 40 °C, and (c) 65 °C. Surfactant and water were removed prior to imaging.

are more mobile at the higher temperature. The phase becomes less ordered at temperatures approaching the transition to an isotropic phase, which ultimately leads to a less defined polymer/surfactant interface. The higher degree of phase separation near the interface can explain the bubble-like texture of the polymer surface at this higher polymerization temperature. This interfacial blurring also results in increased polymer layer thickness.

The network structure of the polyacrylamide gels could influence a number of physical properties directly related to the potential performance of these materials in several applications. The dramatic variation in morphology resulting from polymerization in different phases and polymerization rates would, for example, expectedly influence the swelling behavior of these polymers. Swelling kinetics and maximal degree of swelling vary substantially with conventional hydrogels depending on cross-link density, and the swelling of polyacrylamide synthesized in a liquid crystal system may be affected similarly by the unique pore and channel structure. From the microscopy and SAXS results it is clear that polymerization kinetics and temperature play a very significant role in polymer network formation. To further correlate the polymerization kinetics with the structure and properties of these materials, the rates of swelling of photo- and thermally cured polyacrylamide hydrogels were compared. To eliminate the influence of temperature and simplify analysis, all polymerizations were conducted at 50 °C. Surfactant was removed, and the samples were dried before being placed in water. In Figure 9 the percent water uptake is plotted as a function of time for both photo- and thermally cured samples. The thermally cured samples exhibit the most rapid swelling kinetics, reaching equilibrium in 400 min. The photopolymerized samples, on the other hand, require 600 min to reach equilibrium. In addition, the thermally polymerized samples swell to a greater extent, taking up 750% of their original mass in water, whereas photopolyerized samples swell to equilibrium at 650% of their initial mass. The physical appearance of the swollen samples reveals important information about the network structure. The photopolymerized samples maintain their aspect ratio as they swell, indicating a uniform structure. In contrast, the thermally polymerized samples become warped as a result of a less homogeneous structure. This is consistent with the previously described SEM observations of these samples, in which a highly periodic network structure is observed only in the photopolymerized samples.

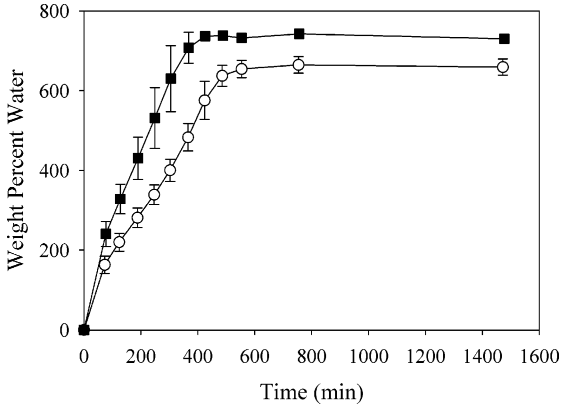

Figure 9. Swelling isotherms of 25% polyacrylamide photo- (○) and thermally (■) polymerized in the cubic phase of 40% Brij 56 and water. All samples were polymerized at 50 °C.

The higher degree of swelling in the thermally polymerized samples is interesting given their smaller apparent pore size. When compared to conventional cross-linked hydrogels, in which higher cross-link density leads to smaller pore size and a lower degree of swelling, it may be expected that the photopolymerized samples would exhibit the highest degree of swelling. However, the larger pores in this case do not result from a lower concentration of cross-linker but from rapid polymerization kinetics in a LLC mesophase. Swelling is affected by polymer/water interactions, diffusivity of water within the sample, which increases with porosity, and the elastic forces of the polymer, which counters the swelling.[34−36] The polymer filling the voids in the otherwise sheet-like structure of the thermally polymerized samples causes an apparent pore size smaller than the one that exists in the photopolymerized samples. However, it does not appear to reinforce the channels but instead decreases the elastic force by depleting polymer from the channels. The more defined network structure of the photopolymerized samples provides higher resistance to swelling despite the larger pores which would provide greater diffusivity to water. The combination

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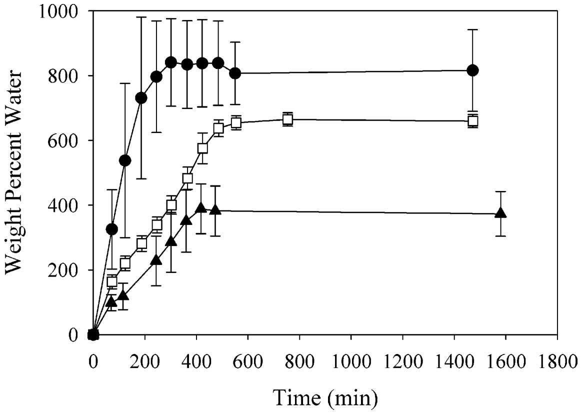

Figure 10. Swelling isotherms of 25% polyacrylamide in 40% Brij 56 and water for photopolymerization conducted at 27 °C (▲), 50 °C (□), and 70 °C (●).

of significant mechanical strength and large pores could be beneficial in tissue engineering applications.[1,2,5]

Similar comparison of the swelling was conducted with samples photopolymerized at different temperatures. As shown in Figure 10 the lowest degree of swelling occurs when photopolymerization is conducted at room temperature. The slope of the swelling isotherm is lowest for this sample, reaching equilibrium at four times its original mass. Faster swelling occurs in samples polymerized at 50 °C, with the mass of these samples increasing more than sixfold. The fastest swelling occurs for samples polymerized at 70 °C, the highest polymerization temperature in the study. This sample also swells to the highest degree, exhibiting an eightfold mass increase. The substantial increase in swelling may also be ascribed to the formation of a less defined network. While the sample polymerized at 25 °C is also highly porous, the network structure as depicted in Figure 8a is likely much more robust, yielding a lower degree of swelling. This is again evidenced by the physical appearance of the samples during swelling. The samples polymerized at lower temperatures maintain their aspect ratio during swelling while that of the sample polymerized at 70 °C changes substantially. Many of these samples start out as uniform polymer disks and become wedge shaped during swelling. The sample deformation as well as relatively high error in the swelling measurements is indicative of inconsistent structural formation at high polymerization temperatures.

To compare a wider range of sample compositions and the influence of LLC morphology on polymer structure development, the equilibrium swelling is plotted in Figure 11 with respect to surfactant concentration for photo- and thermally cured polyacrylamide. Samples polymerized in an isotropic solution of acrylamide and water are included in the study as a control to compare to those from ordered systems. The lowest degree of swelling is observed in the isotropic samples. With increasing surfactant concentration the swelling sharply increases, more than doubling in the micellar phase formed with 20 wt % surfactant. The highest degree of swelling occurs in the cubic phase with 40 wt % surfactant. Slight increases in surfactant concentration in the hexagonal phase minimally affect the swelling, but subsequent increases to 60 wt % surfactant leads to decreased network swelling. The decrease in swelling observed at 60 wt % surfactant indicates that swelling of these materials is not solely a function of surfactant content but that ordering of the surfactant aggregates also plays a critical role. As described previously, polymer structure varies significantly depending on the LLC phase. The decreased swelling in the hexagonal samples can be attributed to greater elastic forces in the polymer network. For each of the polymers synthesized in the ordered surfactant solutions, swelling occurs to the highest degree in the thermally polymerized samples. As mentioned previously, the rapid kinetics of photopolymerization yields a more robust network structure. The thermodynamically controlled structures from thermal polymerization, which possess remnants of a similar, although less robust channel structure, swell to a higher degree. Interestingly, the samples polymerized without surfactant exhibit the opposite trend, with the photopolymerized samples swelling to a higher degree. In these samples completely different dynamics, not dependent on polymer/liquid crystal phase separation, govern the structural development. Polymerization kinetics influence the structure in a much different way in these unordered systems.

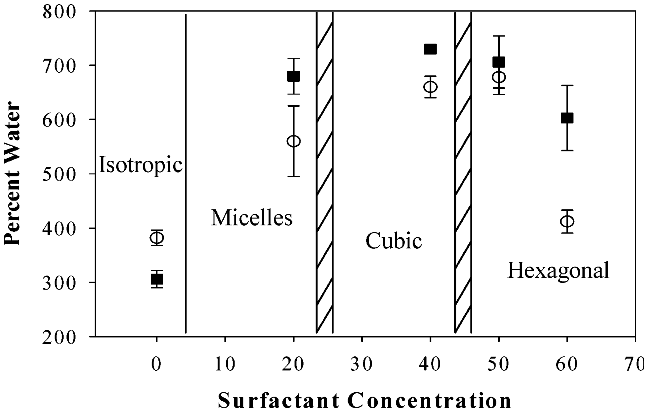

Figure 11. Equilibrium swelling of photo- (○) and thermally (■) cured polyacrylamide plotted as a function of Brij 56 concentration and the corresponding phase.

Table 1. Surface Area of Photo- and Thermally Cured Polyacrylamide Polymerized in Isotropic, Cubic, and Hexagonal Phases of Brij 56 in Water[a]

composition (LLC phase)	polymerization method	surface area (m^2/g)	standard deviation
0% Brij 56 (isotropic)	thermal	1.15	0.01
0% Brij 56 (isotropic)	photo	2.11	0.70
40% Brij 56 (cubic)	thermal	1.35	0.65
40% Brij 56 (cubic)	photo	5.49	1.63
60% Brij 56 (hexagonal)	thermal	3.20	0.38
60% Brij 56 (hexagonal)	photo	7.64	0.70

[a] Surfactant and water were removed prior to analysis.

Surface area is another physical property directly relevant to polymer performance in separations and biological applications. In addition to providing information about the performance potential of these materials, surface area measurements can provide further insight into the factors governing structural development in LLC systems. The surface area of polymers synthesized in the isotropic, cubic, and hexagonal phase is shown in Table 1. The influence of liquid crystalline order is evident from the rapid increase in surface area that occurs from isotropic samples polymerized without surfactant to the cubic and hexagonal phase. The surface area of the photopolymerized samples quadruples as LLC order increases, from 2 m^2/g in the isotropic phase to almost 8 m^2/g in the hexagonal phase. Upon examination of the SEM images of these materials the increase in surface area may be expected. The glassy morphology of the isotropic sample as shown in Figure 4a would expectedly yield low surface area while the spherical nanoscale domains of the hexagonal phase depicted in Figure 6a would obviously be much higher.

The surface area measurements also provide information about the influence of polymerization kinetics. Photopolymerized samples exhibit double the surface area of the thermally polymerized samples from each corresponding LLC phase. In the cubic phase the surface area is more than three times higher in the photocured samples. This may be explained by the higher degree of liquid crystalline order templated from the LLC during photopolymerization, as observed in the SAXS studies. From this study it is clear that a more uniform polymer structure with smaller domain size results through photopolymerization. The synthesis of more highly ordered polymers through rapid polymerization at low temperature along with the higher surface area obtained demonstrate that photopolymerization provides a more suitable method for polymerization in LLC media.

Conclusions

In this paper we present an extensive analysis of the influence of polymerization rate and temperature on polyacrylamide structure and property development in LLC systems. By comparing structures and properties resulting from photo- and thermal polymerization at the same temperature the influence of the polymerization time scale has been examined. Similar comparison of polyacrylamide photopolymerized at various temperatures has shown the unique influence of polymerization temperature in these highly ordered systems. Not only does polymer morphology vary from changes in the LLC template phase, but also the structure resulting for each phase is very dependent on the polymerization rate. Homogeneous polymer structures with well-defined features of relatively small size scale result from photopolymerization. The slower kinetics of thermal polymerization yield less ordered structures with larger feature size. Polymerization at room temperature enables retention of high degrees of liquid crystalline order, which becomes increasingly disrupted with higher polymerization temperature. The swelling of polyacrylamide in aqueous media is very dependent on the order of the LLC phase, and polymers templated from LLCs swell to a much higher degree than those from isotropic bulk polymerization. Within the ordered phases swelling is lower for the photopolymerized samples. The opposite is true with samples polymerized in isotropic media. Swelling increases dramatically with increasing polymerization temperature because of less robust channel structure. Surface area is likewise higher in LLC templated polymers but is much higher within each phase for photopolymerized samples because of higher degrees of liquid crystalline order templated through rapid kinetics. By regulating polymerization kinetics and temperature, significant control of polyacrylamide structure and properties has been demonstrated.

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