Macromolecules

Volume 34, Number 25 December 4, 2001

Communications to the Editor

Acceleration of Polyacrylamide Photopolymerization Using Lyotropic Liquid Crystals

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Received July 23, 2001

Polyacrylamide has been used extensively in a variety of applications including electrophoretic media for the separation of biomolecules. Conventionally polymerized polyacrylamide gels have random morphologies with a wide distribution of pore sizes. This limits the size of biomolecules separated by electrophoresis as well as the overall resolution.[1] Additionally, these random morphologies result in a mechanically weak gel. To overcome these drawbacks of contemporary gels, recent work has proposed to control the polymer morphology by templating the unique nanostructure of lyotropic liquid crystals onto polymeric materials.[2−6]

Lyotropic liquid crystals (LLC) are ordered liquids that consist of an amphiphile and a solvent. LLC phases include hexagonal-packed rodlike micelles, bilayers, and discontinuous and bicontinuous cubic arrangements.[7] As LLCs possess nanoscale morphologies, they are ideal candidates for enhanced separations. Unfortunately, LLCs lack material robustness and are unsuitable for separatory applications. Therefore, templating these fascinating structures onto polymeric materials provides an attractive alternative for generating enhanced separation materials.

Previously, the templated polymerization of acrylamide, as well as other water-soluble monomers, has been performed in the LLC phases of a variety of ionic and nonionic surfactants. Often, the polymer morphologies obtained are a result of phase separation and not a direct template of the original LLC phase.[2,6,8] Other results have shown polymerizations of acrylamide in bicontinuous cubic phases yielding nanostructured polymer gels that retain the original structure of the LLC phase.[3] These contrasting results reveal the importance of understanding more about the polymerization itself. In fact, the polymerization kinetics have been implicated as a primary means by which the structure could be controlled. Despite their importance, very little information is available about the kinetics of polymer formation. It would therefore be of great value to develop an understanding of how the unique nanostructure of the LLC phases influences the polymerization mechanism and consequently controls the overall polymer morphology.

Such considerations have proven important in the polymerization of a variety of monomers in analogous thermotropic systems.[9−11] Additionally, LLC morphology in the polymerization of monomeric amphiphiles plays a predominant role. Mesophases with higher degrees of order polymerize more readily and exhibit enhanced structure retention.[12] The templated polymerization kinetics of difunctional monomers also exhibit a significant dependence on the LLC morphology.[13] The goal of this work is to understand the polymerization kinetics of acrylamide in the various mesophases of a nonionic surfactant/water LLC system in order to enhance the ability to controllably synthesize templated nanostructured gels. A systematic study of the polymerization of acrylamide in LLC phases will provide substantial insight into the role that organized media plays in the polymerization mechanism and will aid in optimizing conditions for the retention of the original lyotropic structure for a variety of applications.

To examine these aspects for an LLC phase templated acrylamide system, the nonionic surfactant Brij 58 was chosen (relevant chemical structures are shown in Figure 1). The phase behavior of the Brij 58/water/acrylamide system exhibits the bicontinuous cubic liquid crystalline phase over wide ranges of surfactant concentrations.[6] Specifically, with 25 wt % acrylamide and at concentrations of 40−60 wt % Brij 58 the bicontinuous cubic phase is observed using polarized light mi-

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10.1021/ma011314p CCC: $20.00
Published on Web 11/06/2001

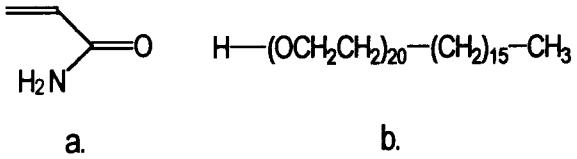


Figure 1. Chemical structures of (a) acrylamide and (b) Brij 58.

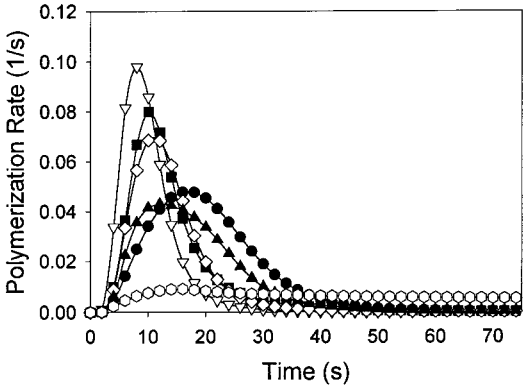


Figure 2. Polymerization rate vs time for 25 wt % acrylamide in the LLC phases of Brij 58/water with increasing Brij 58 concentration. Shown are 0 wt % isotropic (○), 30 wt % micellar (●), 40 wt % cubic (▽), 50 wt % cubic (■), 60 wt % cubic (◇), and 70 wt % inverse micellar (▼) Brij 58.

croscopy (PLM) and small-angle X-ray scattering (SAXS). Below 40% Brij 58 an isotropic micellar system is observed, whereas above 70% Brij 58 an inverse micellar phase is exhibited. In all cases Irgacure 2959 (2 wt % with respect to the monomer mass) was used as a photoinitiator, and photopolymerizations were performed using monochromatic UV light at 365 nm with an intensity of 4.0 mW/cm^2.

Other studies have shown that the LLC phase behavior in templated systems has a substantial effect on the polymerization kinetics.[13] To determine whether similar effects are observed in the templated acrylamide system, the polymerization was examined using photo-differential scanning calorimetry (DSC). All samples were covered with a UV transparent film (FEP Dupont) to prevent these samples from losing water in the DSC via evaporation. Rate profiles were obtained using photo-DSC as described elsewhere.[9] In Figure 2 the polymerization rate profiles are shown of samples with constant concentration (25 wt %) acrylamide and increasing weight percent Brij 58. The surfactant concentration range used allows study of polymerizations in the micellar, bicontinuous cubic, and inverse micellar geometries. Also included in Figure 2 is the rate profile of an isotropic solution with the same concentration of acrylamide in water but without surfactant. An extremely slow photopolymerization rate is observed for the isotropic solution. In fact, the isotropic solution polymerizes so slowly it is difficult to observe with calorimetry. When adding surfactant to reach a micellar system, a 5-fold increase in polymerization rate is observed. When the morphology of the ternary system is changed to a bicontinuous cubic liquid crystalline phase by increasing the Brij 58 to 40%, an extraordinary increase in the polymerization rate is observed. The peak polymerization rate in the bicontinuous cubic phase is over 10 times that of the isotropic solution and twice that of the micellar phase despite the fact that the same bulk concentration of acrylamide is utilized. Interestingly, the polymerization rate does not change

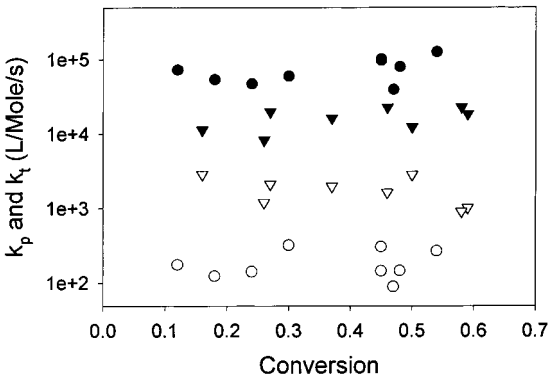


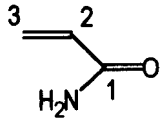
Figure 3. Termination (k_t) and propagation (k_p) rate parameters of 25% acrylamide in LLC phases of Brij 58/water, shown as a function of double-bond conversion. Given are k_t for 40% cubic (▼), k_t for 0% isotropic (●), k_p for 40% cubic (▽), and k_p for 0% isotropic (○) Brij 58.

to a great extent within the bicontinuous cubic phase. However, once the inverse micellar phase is reached, the polymerization rate is of similar magnitude to that of the normal micellar phase. That the inverse and normal micellar phases exhibit similar polymerization behavior further substantiates the importance of the LLC morphology on the polymerization kinetics.

To investigate what factors drive these striking differences in polymerization behavior, the apparent rate parameters of propagation (k_p) and termination (k_t) were determined by a method described in detail elsewhere.[9] In Figure 3 k_p and k_t for the isotropic solution and the bicontinuous cubic liquid crystalline sample consisting of 40% Brij 58, both with 25% acrylamide, are shown as a function of double-bond conversion. These samples correspond to the fastest and slowest polymerizing samples, respectively. Interestingly, the apparent rate parameter k_p is an order of magnitude higher for the faster polymerizing cubic sample as compared to the isotropic solution. This result is indicative of increased local concentration of the acrylamide monomer in the bicontinuous cubic phase.[9] If segregation were the only driving factor in increasing the polymerization rate, a similar increase in k_t should also be observed. However, the rate parameter k_t is significantly less for the bicontinuous cubic sample, indicating that not only are segregation phenomena occurring but ordering effects play a predominant role as well. In previous studies of thermotropic and lyotropic liquid crystalline systems, changes in polymerization rate in organized media have been shown to be due to one of the two phenomena described above,[9,10,12,13] but this system is unique in that both phenomena are observed. These insights on the role of ordered lyotropic structures on the photopolymerization behavior might have significant implications in polymer structure evolution in cross-linked systems as well as the molecular weight of linear polymers.

To determine how the LLC phases change the mobility of the acrylamide monomer and thus influence the polymerization behavior, ^{13}C T_1 spin−lattice relaxation times were determined for the carbonyl and both vinyl carbons of acrylamide in the isotropic and in the bicontinuous cubic LLC phase. As can be seen in Table 1, the isotropic solution exhibits relaxation times that are over 5 times longer than in the bicontinuous cubic phase. In the solution state longer T_1s are a result of a less hindered environment.[14] These results therefore indicate that the acrylamide monomers in the bicon-

Table 1. ^{13}C T_1 Spin−Lattice Relaxation Times for the Carbons of Acrylamide[a]



carbon	0% Brij 58 isotropic	40% Brij 58 cubic
1	49.6	10.1
2	5.04	1.08
3	2.50	0.55

[a] Relative standard error is less than 7%.

tinuous LLC phase are aggregating with the surfactant. Acrylamide monomers aggregated within the LLC phase would yield a higher local concentration of double bonds. With the polymerization occurring topologically along the interface, the propagating polymer chains would also be highly constrained and diffusion limited. Both of these observations are consistent with the observed polymerization kinetic results described earlier. It is also possible that lowered mobility of monomer species could result simply from concentration effects which also could decrease the termination rate. In this case, however, the concentration dependence of ^{13}C T_1 relaxation times is not as profound as what is observed in the differences between the isotropic state and the ordered phases.[15]

This work presents the photopolymerization kinetics of acrylamide monomers in the LLC phases of the Brij 58/water system. Acrylamide monomers polymerize slowly in isotropic water solutions. In micellar solutions of Brij58/water, however, at identical monomer concentrations, the polymerization rate is dramatically enhanced. When polymerized in the bicontinuous cubic phase, a 10-fold increase in polymerization rate is observed. These unprecedented differences in polymerization rate are a result of monomer segregation, which yields a higher local concentration and limits diffusion of the propagating polymer. ^{13}C T_1 relaxation times indicate that these kinetic results are driven by monomer aggregation with the surfactant in the LLC phase. The consideration of both these kinetic phenomena has tremendous implications on the developing polymer nanostructure, molecular weight, and material properties.

Acknowledgment. The authors acknowledge the Petroleum Research Fund and the National Science Foundation through a CAREER grant (CTS-0093911) for financial support.

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(15) ^{13}C T_1 spin−lattice relaxation times were obtained for isotropic solutions of increasing concentration of acrylamide. The relaxation times decreased with increasing acrylamide concentration, indicating that mobility was changing. However, the increases were less than 20%, indicating that the decrease in mobility observed in the bicontinuous cubic phase is predominantly a result of the LLC order.

MA011314P