

Effect of photoinitiator segregation on polymerization kinetics in lyotropic liquid crystals

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Abstract

Through photopolymerization lyotropic liquid crystalline (LLC) phases may be templated onto organic polymers to yield highly complex nanostructures. In order to understand the unique polymerization behavior controlling structural development in LLC media, the polymerization kinetics in these systems have been studied using several commercially available photoinitiators. Although monomer segregation and diffusional restrictions largely govern the kinetics in these systems, the initiation may also be influenced by changing LLC order and composition. Nonpolar monomers, which partition to the oil soluble domains of the LLC phase typically display the fastest rate of polymerization in micellar aggregates. The rate decreases in phases with larger nonpolar domains due to decreasing localized double bond concentration. Polar monomers exhibit the opposite behavior. However, the segregation of photoinitiator may contribute to significantly different trends in polymerization behavior. Relatively mobile initiators, displaying favorable interaction with water, yield a trend in polymerization that is governed primarily by monomer and diffusional effects. When bulkier, hydrophobic initiators are used, the polymerization appears much less dependent on these effects. Rather than the decreasing rate usually observed at higher surfactant concentrations, polymerization of oil soluble monomers with the less mobile initiators shows the opposite trend of increasing rate at higher surfactant concentration. This behavior likely results from increasing initiator efficiency of the bulky, hydrophobic initiator in the surfactant rich environment.

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1. Introduction

Various synthetic methods offering enhanced control of organic polymer nanostructure have been developed in recent years. The ability to control structural elements on increasingly smaller size scales could lead to considerable improvements in applications such as catalytic supports, separations media, drug delivery systems, and artificial implants [1,2]. Highly ordered structures with nanometer scale periodicity have been obtained through several template methods including molecular imprinting and colloidal crystal templating. Another interesting method involves templating the well-defined nanostructure of lyotropic liquid crystalline (LLC) phases onto organic

polymers utilizing photopolymerization [3]. The breadth of potential polymer geometries from the enormous variety of liquid crystalline structures makes this method promising for generating a wide range of complex polymer morphologies. Materials thus synthesized have the potential to improve the resolution of separation and microfiltration devices due to the monodispersity of pore size inherent in the nanostructure templated from the LLC phases, and show promise in regulated drug transport through tuning of pore size and porosity [1,4,5].

While a combination of several factors determines polymer structure, the size of pores and overall polymer geometry is dictated to a large degree by the morphology of the LLC template. Lyotropic liquid crystals are self-assembling structures consisting of a typically polar solvent and surfactant possessing low viscosities and the long range order of crystalline materials [3]. At appropriate concentrations of surfactant, several ordered structures with

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distinct and complex geometries may be observed such as spherical micelles, hexagonal arrangements of rod-like structures, and bilayer aggregates of the lamellar phase. Other phases, including bicontinuous cubic, discontinuous cubic, and the inverse of the above mentioned phases, can form at appropriate concentration and surfactant geometry.

While material applications of lyotropic liquid crystals are limited by their lack of mechanical strength and thermal stability, the ability to replicate the unique morphology of LLCs in more robust polymer resins and gels could facilitate production of novel nanostructured materials. Polymerization of amphiphilic monomers in various liquid crystalline phases, including hexagonal, inverse hexagonal, cubic, and lamellar has been performed recently with full retention of mesophase morphology in the polymerized material [6–9]. Successful templating of the LLC morphology from nonpolymerizable surfactant systems onto organic polymers has also been reported. The retention of various liquid crystalline phases has been accomplished through polymerization of acrylamide and several acrylate monomers using both nonionic and cationic surfactants [10,11].

The polymerization kinetics in ordered media are significantly different than in isotropic bulk polymerizations. The morphology of the liquid crystalline phase in thermotropic systems greatly influences the polymerization rate, which in some systems has caused the interesting trend of decreasing rate of polymerization at elevated temperatures [12,13]. Analogous studies of the polymerization kinetics of various monomers within lyotropic liquid crystalline media have elucidated the unique mechanism governing polymer structure development in these systems. As in thermotropic systems, the degree of lyotropic liquid crystalline order greatly influences polymerization kinetics. The kinetics in turn play a major role in polymer structure formation, with enhanced structure retention being correlated to faster rates of polymerization [9]. Monomer polarity determines their localization within the LLC and thus has a large effect on kinetics, ultimate polymer structure, and physical properties. The decreasing rate of polymerization of hydrophobic monomers as liquid crystal order increases results from increased diffusional limitations as well as lower local double bond concentration in the more ordered systems. The reverse trend of increasing rate with respect to LLC order occurs with polar monomers as their local concentration increases at higher surfactant concentrations [8].

Just as monomer hydrophobicity is a critical parameter governing polymerization kinetics and structure, the photoinitiator is another component of the system that may significantly influence kinetics and resulting polymer morphology. However, the effect of initiator chemical structure and solubility on polymerization behavior in liquid crystalline systems is not well understood. A few studies have focused on the role of photoinitiator hydrophobicity in emulsion polymerizations, which are analogous in many ways to LLC systems. Both the rate of polymerization and

conversion of styrene depend on initiator hydrophobicity when polymerization is conducted in miniemulsion [14,15]. Investigations of a surface active initiator designed for the microemulsion polymerization of styrene show the importance of initiator location within the system. The close association of surface active initiator with surfactant results in increased polymer molecular weight with anionic surfactants because radicals quickly recombine and fewer radicals enter the monomer droplets. With a cationic surfactant lower molecular weights and lower polydispersities were reported [16,17]. The localization of photoinitiator during microemulsion determines its photoinitiation efficiency to a large extent. When initiating radicals are primarily incorporated in monomer droplets, rapid termination from radical recombination has often been observed. Higher initiation efficiencies typically result when photoinitiator localizes within the dispersed medium [18–24]. Localization of photoinitiator may be even more critical in lyotropic liquid crystalline systems because of their higher surfactant concentrations and ordering.

To better understand the polymerization mechanism in lyotropic liquid crystalline media and consequently gain more control over polymer nanostructure formation, this study focuses on the role of photoinitiator in the polymerization kinetics in highly ordered surfactant solutions. Specific attention will be given to the relationship between initiator segregation and rate of polymerization as LLC order is modulated. Trends in polymerization rate with respect to degree of LLC order will be characterized and compared using several photoinitiators that exhibit different segregation behavior in the reaction medium due to differences in polarity and mobility. Photopolymerization kinetic data and initiator mobility information along with evidence of initiator localization will provide a greater understanding of the influence of photoinitiator on the polymerization behavior in these ordered LLC systems. This information could enable the selection of photoinitiator and the development of improved initiating molecules for optimum characteristics in a variety of polymer/LLC systems.

2. Experimental section

2.1. Materials

The monomers used in this study were hexanediol diacrylate (HDDA, Polysciences), poly(ethylene glycol)-400-dimethacrylate (PEGDMA, Polysciences), and acrylamide (Bio-Rad Laboratories). The two surfactants used were dodecyltrimethylammonium bromide (DTAB, Aldrich) and polyoxyethylene (10) cetyl ether (Brij 56, Aldrich). 2-Hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (HEPK, Irgacure 2959, Ciba Specialty Chemicals), 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone (DBMP, Irgacure 369, Ciba

Specialty Chemicals), α,α -dimethoxy- α -phenylacetophenone (DMPA, Irgacure 651, Ciba Specialty Chemicals), and the water soluble oligo (2-hydroxy-2 methyl-1-4(1-methylvinyl)phenyl propanone (HMMP, SarCure SR1131, Sartomer) were the photoinitiators that were compared. Chemical structures of these compounds are shown in Fig. 1. Lyotropic liquid crystalline phases were formed by mixing appropriate concentrations of surfactant, monomer, photoinitiator, and deionized water. Homogeneous liquid crystalline samples were obtained through repeated centrifugation and sonication.

2.2. Methods

Polymerization rates were monitored using a Perkin Elmer Diamond differential scanning calorimeter. The full emission spectrum from a medium pressure UV arc lamp was used to initiate polymerizations. Light intensity was controlled with neutral density filters and by adjusting the distance from the lamp to the sample. Approximately 5 mg of sample was placed in aluminum DSC pans and covered

with UV transparent thin films of FEP (Dupont fluorinated copolymer) to prevent evaporation of water. The DSC sample cell was purged with nitrogen for 6 min prior to polymerization to reduce oxygen inhibition. Samples were heated to 50 °C and then cooled to room temperature at 20 °C/min to ensure uniform sample thickness and good thermal contact. During polymerization isothermal reaction conditions were maintained using a refrigerated circulating chiller. The polymerization rate was determined from the heat flow, and maximum rates were taken from the peak of the rate profiles obtained [12]. The relative standard error for the kinetic experiments was calculated by dividing the standard deviation of the maximum polymerization rates from five identical experiments by the average. While significant differences in this error are observed from sample to sample, the relative standard error was less than 10% for the vast majority of systems.

A polarized light microscope (Nikon, Eclipse E600W Pol) equipped with a hot stage (Instec, Boulder, CO) was utilized for phase characterization by looking for characteristic textures of the various mesophases as well as phase

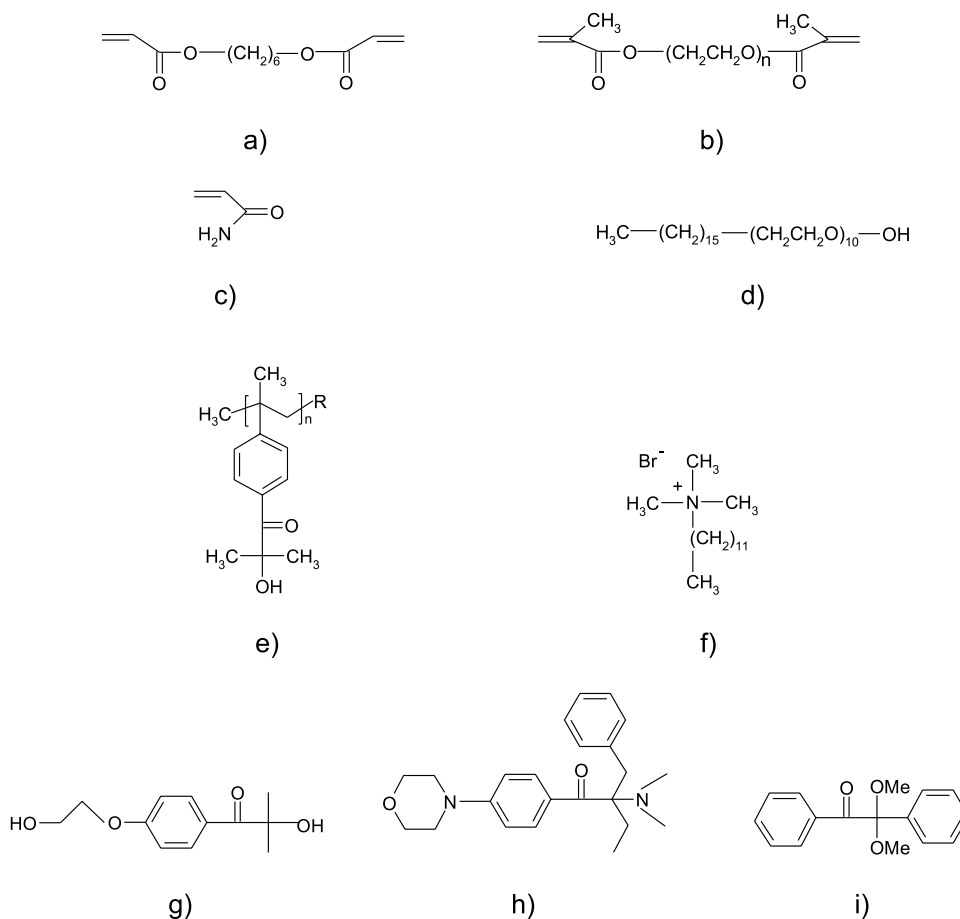


Fig. 1. Chemical structures of the monomers, surfactants, and photoinitiators used in this study. Shown are (a) hexanediol diacrylate (HDDA), (b) poly(ethylene glycol)-400-dimethacrylate (PEGDMA), (c) acrylamide, (d) polyoxyethylene (10) cetyl ether (Brij 56), (e) oligo (2-hydroxy-2 methyl-1-4(1-methylvinyl)phenyl propanone (HMMP), (f) dodecyltrimethylammonium bromide (DTAB), (g) 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (HEPK), (h) 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone (DBMP), and (i) α,α -dimethoxy- α -phenylacetophenone (DMPA).

transitions. Small angle X-ray scattering measurements were taken using a Nonius FR590 X-ray apparatus with a standard copper target Röntgen tube as the radiation source with a Cu K α line of 1.54 Å, a camera, a collimation system of the Kratky type, and a PSD 50M position sensitive linear detector (Hecus M. Braun, Graz). LLC phase identities were confirmed by examining the ratio in d-spacing from X-ray scattering in corroboration with information from polarized light microscopy.

Photoinitiator solubility in the liquid crystalline solutions was determined by preparing samples containing a range of photoinitiator concentration near the saturation point. The samples were lightly heated, centrifuged, and sonicated to dissolve the solid photoinitiator. Samples were kept at room temperature for 16 h and then examined for photoinitiator recrystallization. The photoinitiator concentration just below the saturation point was recorded. Concentration increments were spaced closely to minimize the relative error, which was generally less than 5% for all formulations.

NMR spectra were acquired using a Bruker Avance DRX-400 NMR spectrometer operating at a frequency of 100.6 MHz for ^{13}C . Inverse gated proton decoupled T_1 IR (T_1 inversion recovery) ^{13}C observe experiments were run with a 90° pulse corresponding to 9.45 μs . The number of scans varied from 624 for concentrated samples to 1400 for dilute samples. Between 7 and 10 T_1 time delay points were used to allow accurate determination of T_1 curves.

3. Results and discussion

Previous studies of the polymerization kinetics in liquid crystalline systems have characterized the effect of several factors such as mesophase structure, monomer ordering and polarity on the polymerization kinetics and the development of polymer nanostructure [8–11,25,26]. Significant rate enhancement has been observed in several systems when liquid crystalline order is increased. For example, the rate of acrylamide polymerization increases by a factor of ten when the liquid crystalline order is increased from the isotropic to the cubic phase and is also accompanied by significant increases in molecular weight [10,11]. Depending on monomer polarity, liquid crystalline order may affect the polymerization differently. The rate of polymerization of oil soluble monomers typically decreases with increasing surfactant concentration which induces higher LLC order. In contrast, the polymerization rate of water soluble monomers increases in more highly ordered mesophases. These opposite behaviors result primarily from monomer localization to distinct regions of the LLC. Nonpolar monomers segregate within the hydrophobic cores of micellar aggregates while polar monomers often associate with surfactant head groups in the continuous phase. Photoinitiators with different chemical structures may likewise interact differently within ordered media and become segregated to distinct regions of the LLC. The

polymerization kinetics may thus vary in different LLC phases not only from changes in local monomer concentration, but also from changes in initiator segregation. As polymerization kinetics have been directly implicated in polymer nanostructure development, segregation of photoinitiator could potentially impact the structure development and resulting properties of the polymers [9,27,28]. To understand the effect of initiator segregation on the polymerization mechanism, the photopolymerization kinetics using various monomers in liquid crystalline media have been examined with initiators of different chemical structure and hydrophobicity.

As the concentration of DTAB is increased in a system consisting of 10% HDDA and water, discontinuous cubic, hexagonal, and lamellar phases are observed at room temperature. The variety in LLC morphology allows examination of the effects of liquid crystalline order on the polymerization kinetics, and the use of different photoinitiators may elucidate how segregation of initiator affects polymerization behavior in these ordered systems. The initiators, HEPK and DBMP, were selected because they initiate by a similar α -cleavage mechanism yet exhibit distinct polarity and mobility. While HEPK is highly soluble in water, DBMP is hydrophobic and relatively bulky. To demonstrate the role of liquid crystalline order in the polymerization kinetics, Fig. 2 shows the polymerization profiles of 10% HDDA initiated with HEPK and DBMP in the cubic, hexagonal, and lamellar phases. The effect of liquid crystalline order on polymerization with both initiators is apparent from the significant rate changes that occur as LLC order is varied. Polymerization of 10% HDDA initiated with HEPK in the discontinuous cubic phase, which is observed at 40 wt% DTAB, yields the fastest polymerization for both initiators. As surfactant concentration increases for the HEPK system, inducing a change to the hexagonal phase, the rate of polymerization continually decreases. In the highly ordered lamellar phase that forms above 70 wt% DTAB the polymerization rate decreases to less than half the value in the cubic phase. The continuous decrease in polymerization rate of HDDA initiated with HEPK indicates the strong role of LLC order in controlling the polymerization behavior. Similar trends showing decreasing rate of polymerization with oil soluble monomers (HDDA and *n*-decyl acrylate) have been reported in the various phases of DTAB/water initiated with DMPA [8]. These studies show that apparent kinetic parameters of propagation and termination decrease in more ordered systems, indicating that decreasing local double bond concentration drives the decrease in rate observed in the more ordered liquid crystalline phases. The oil soluble HDDA, which segregates within the hydrophobic cores is most locally concentrated in the discontinuous cubic phase. The localized concentration of HDDA decreases significantly as the hydrophobic domains become larger in the hexagonal and lamellar system. Thus, the rate of polymerization of HDDA when initiated by HEPK

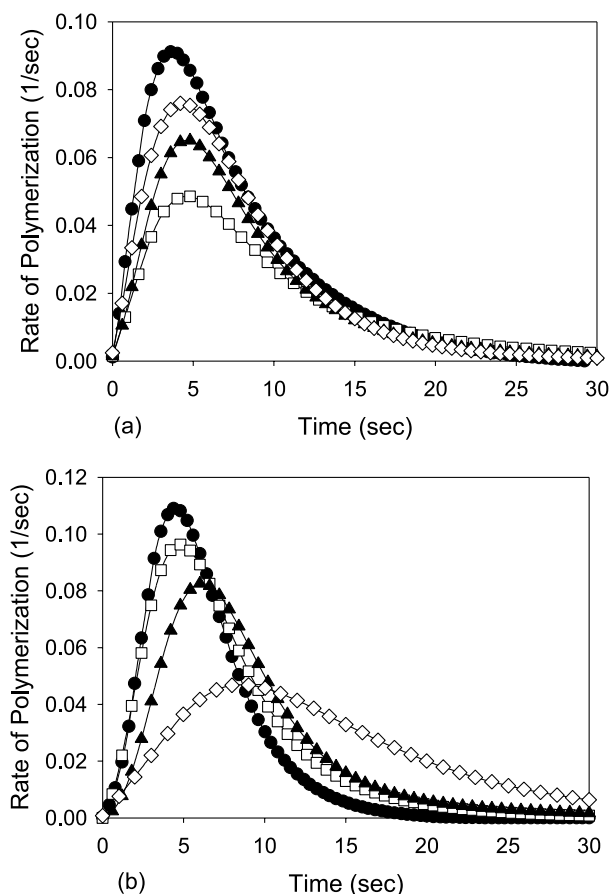


Fig. 2. Polymerization profiles of 10% HDDA initiated with (a) 1 wt% HEPK and (b) 1 wt% DBMP. Shown are polymerizations in 40%-discontinuous cubic (●), 50%-hexagonal (◇), 60%-hexagonal (▲), and 80%-lamellar (□) DTAB in water.

appears to be controlled primarily by monomer segregation within the ordered surfactant assemblies.

Striking differences in the polymerization behavior occur when DBMP initiates polymerization of HDDA within the same system. The rate of polymerization with this initiator is again highest in the discontinuous cubic phase formed at 40% DTAB. A dramatic decrease in rate is observed with the transition to a hexagonal phase formed at 50% surfactant concentration. In fact, the rate of polymerization is at a minimum in the hexagonal phase at this concentration of DTAB. The rate then increases at higher surfactant concentrations within the hexagonal phase and is further enhanced in the lamellar phase, in which the rate approaches that of the less ordered discontinuous cubic phase. This behavior is in direct contrast to the continual decrease in rate described previously with HEPK. The time required to reach the peak rate of polymerization also varies widely in the different liquid crystalline phases when initiating with DBMP. This is again in contrast to polymerization initiated with HEPK, in which the time to reach the peak rate of polymerization varies only slightly. With DBMP only 5 s are required to reach the peak polymerization rate in the cubic phase while nearly 10 s are required upon transition to

a hexagonal morphology. As surfactant concentration is further increased, the time to reach the peak rate of polymerization decreases with the accompanying increase in rate. In the lamellar phase the time at the maximum rate is once again 5 s, identical to that of the cubic phase. Differences in UV light absorbance and bond dissociation energy between the two initiators may account for differences in polymerization rate in the same LLC environment, but these factors do not explain the different trends in rate with respect to LLC order. While initiation with HEPK results in behavior consistent with monomer segregation phenomena, the increasing rate of polymerization observed with DBMP with increasing degrees of LLC order indicates that other factors control the rate with this initiator. Since the photoinitiator is the only component of the system that is different, the dissimilar trends in polymerization kinetics likely result from changes in photoinitiation [29].

In order to directly compare how LLC order influences polymerizations initiated with different initiators, Fig. 3 shows a comparison of relative maximum rates of polymerization of HDDA initiated with HEPK and DBMP in the various LLC phases. Relative maximum rates were calculated by dividing the maximum rate of polymerization in each phase by the maximum rate in the discontinuous cubic phase, in which the fastest polymerization occurs. By using relative maximum rates, the trends in polymerization kinetics can be compared closely even though the absolute rates in each trend may be significantly different due to distinctive UV absorption characteristics of the photoinitiators. The nearly linear decrease in the polymerization rate with HEPK as LLC order increases again indicates the strong role of monomer segregation in this system. On the other hand, the rate changes that occur with DBMP are inconsistent with monomer segregation. Although decreasing localized double bond concentration likely contributes to the large decrease in rate that occurs in progressing from

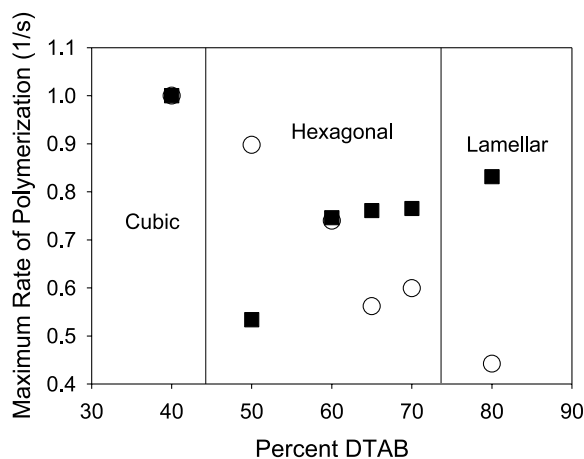


Fig. 3. Relative maximum rate of polymerization of 10% HDDA initiated with 1 wt% HEPK (○) and 1 wt% DBMP (■) in the LLC phases of DTAB/water with respect to DTAB concentration.

the cubic to the hexagonal phase, the magnitude of the rate decrease could be better explained by changes in initiator localization and mobility in the different LLC environment. The near doubling in rate that occurs as the surfactant is increased to yield the lamellar phase shows that changes in initiation are dramatic.

To determine whether similar effects are observed with these initiators for a water soluble monomer, PEGDMA was polymerized in the various phases of DTAB/water using HEPK and DBMP. To understand better how initiator segregation affects the polymerization behavior, HMMP, a water soluble emulsion based initiator was also used because of its likely partitioning within the continuous aqueous LLC domains. The relative maximum rate of polymerization of PEGDMA using these initiators in the various liquid crystalline phases of DTAB/water is shown in Fig. 4. A nearly identical trend of increasing rate with respect to LLC order is observed with HEPK and HMMP. With these initiators the rate is lowest in the cubic phase and increases by 50% in the hexagonal phase in direct contrast to the HDDA system for which the highest rate is observed in the cubic phase. With further increases in surfactant concentration that yield the lamellar phase, the polymerization rate is highest, approximately two times that of the cubic phase polymerization. Previous studies of the polymerization of water soluble monomers in this LLC system show that decreased termination drives the increase in rate exhibited with higher liquid crystal order. The constrained environment of the ordered system limits diffusion of the propagating polymer, which decreases the rate of termination and consequently leads to increased radical concentration and rate of polymerization in the more ordered systems. The decrease in termination rate indicates that PEGDMA is not freely solvated in the aqueous domains, but is instead closely associated with the polar headgroups of the surfactant/water interface. Other studies have shown similar aggregation of hydrophobically modi-

fied poly(ethylene glycol) with cationic surfactants [30]. Therefore, as the surfactant concentration increases, monomer becomes increasingly ordered along the LLC interface resulting in higher local double bond concentration, increased diffusional limitations on the growing polymer chain and consequently higher polymerization rates [8].

As mentioned previously for HDDA systems, liquid crystalline order influences the polymerization behavior in a significantly different manner depending on choice of photoinitiator. The maximum rate of polymerization of PEGDMA initiated with DBMP follows a distinctly different trend than that observed with the more water soluble photoinitiators, HEPK and HMMP. The polymerization rate decreases by 50% between the cubic and hexagonal phase in which a local minimum occurs. Subsequent increases in surfactant concentration result in rapidly increasing rates. Similarly, increased rate of polymerization is observed at higher surfactant concentration with HEPK and HMMP. However, the magnitude of rate increase is much greater for initiation with DBMP, in which a fourfold rate increase occurs between the hexagonal and lamellar phase. While monomer segregation and diffusional limitations with the water soluble PEGDMA should lead to increasing polymerization rates in progressing from the cubic to the lamellar systems regardless of initiator, the more rapid rate increase observed with the hydrophobic DBMP appears to result from an enhanced rate of initiation at higher concentrations of surfactant. As discussed previously, higher surfactant concentrations lead to increased rates in DTAB/HDDA systems when initiated with DBMP although monomer effects would typically induce the opposite trend, which is observed with the more water soluble and less bulky HEPK. It is logical to believe that enhanced rates of initiation, which may occur at higher surfactant concentrations, are likely responsible for the divergent trends in polymerization behavior that are observed with different photoinitiators.

A surprising result in these kinetic comparisons is the similarity of the polymerization kinetics between PEGDMA and HDDA when initiated by DBMP. In both cases the rate passes through a local minimum after a 50% reduction in rate from the cubic phase at 40% DTAB to the hexagonal phase at 50% DTAB. The rate then increases in the more ordered samples, albeit much faster in the polymerization of PEGDMA. While monomer segregation appears to be the primary driving force for polymerization behavior when initiated with HEPK, the polymerization trends with DBMP appear less dependent on monomer polarity. The similarity in the polymerization kinetics with two monomers of opposite polarity provides further evidence that photoinitiation of DBMP, which appears to be more rapid in more highly ordered surfactant solutions, is the dominant factor controlling the polymerization mechanism. The initiation behavior of DBMP appears to be highly dependent on LLC composition and order and may dictate the polymerization kinetics to a large degree.

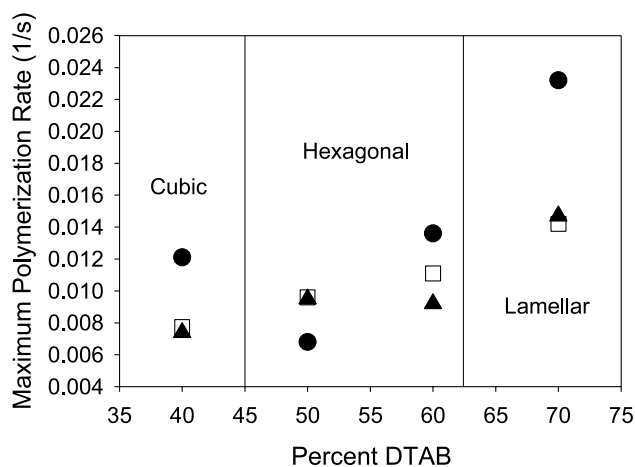


Fig. 4. Peak polymerization rate of 20% PEGDMA initiated with 1 wt% HEPK (□), HMMP (▲), and DBMP (●) in the LLC phases of DTAB/water as a function of DTAB concentration.

As seen from studies of microemulsions, which are analogous in many ways to LLC polymerizations, localization of photoinitiator to different regions within the system may have a large influence over the polymerization mechanism and ultimate polymer structure [17,18]. The polymerizations previously discussed were performed in LLC phases consisting of surfactant, water, and monomer. The solubility of photoinitiator in each component of these systems provides an indication of how initiator segregates within the system and may provide insight into the photoinitiation behavior. To determine whether differences in initiator segregation may cause the divergent kinetic behavior observed with different photoinitiators, the solubility of HEPK and DBMP was compared in the same LLC systems in which the polymerization kinetics were studied. The solubility of DBMP and HEPK is plotted with respect to DTAB concentration in Fig. 5 in systems of PEGDMA/DTAB/water, HDDA/DTAB/water, and also in DTAB/water alone. The initiator solubility may provide evidence regarding which component has the greatest impact on solubility and thereby extrapolate the segregation of each photoinitiator. From this study it is clear that the solubility

of both initiators increases dramatically with increasing surfactant concentration. A more than tenfold increase in the solubility of DBMP occurs as surfactant increases from 20 to 60 wt%. Although solubility increases very rapidly with DBMP, it remains lower than 1% for surfactant concentrations less than 45%. The solubility of HEPK also increases at higher surfactant concentration but the increase is less drastic, increasing by a factor of three between 20 and 60 wt% DTAB. Changing from the polar PEGDMA to nonpolar HDDA systems or even to neat DTAB/water has a much lower effect on the solubility of each initiator than simply increasing the surfactant. However, the small differences in solubility that are observed in each case are consistent with the hydrophobicity of these initiators. The solubility of DBMP, which is less than 0.05% soluble in water, is highest in HDDA/DTAB/water and is lowest in the PEGDMA/DTAB/water system. The minute difference in the solubility of DBMP in the DTAB/water system and the HDDA/DTAB/water system indicates that this initiator does not segregate preferentially within monomer rich domains. In fact, the rapid increase in solubility as surfactant increases indicates that DBMP likely resides primarily in the nonpolar tails of the surfactant.

HEPK similarly associates with surfactant as can be seen from the rapid increase in solubility at higher surfactant concentrations. However, this initiator interacts more favorably with water being 20 times more soluble in water than DBMP. This is also reflected by the higher solubility of this initiator in the DTAB/water system than the HDDA/DTAB/water or PEGDMA/DTAB/water systems. The neat DTAB/water solutions have higher water content than the LLC solutions containing monomer. While HEPK may preferentially reside in surfactant rich regions of the LLC, its favorable interaction with water shows that it may be relatively dispersed throughout the system, even in a system with relatively high water content and low surfactant concentration. Changes in surfactant concentration would therefore have less impact on initiator segregation and the photoinitiation mechanism than with DBMP.

The differences in photoinitiator segregation demonstrated by the solubility data provide understanding of the contrasting kinetics observed with the different initiators in LLC systems. When HEPK is used to initiate polymerization, the polymerization behavior is dominated by monomer segregation effects. This initiator is not only more water soluble but displays solubility approximately 10 times higher than that of DBMP for all of the compositions that were studied. It is therefore less likely to be segregated within the smaller hydrophobic domains of the LLC. On the other hand, the polymerization behavior observed with DBMP in the LLC systems appears dependent on a combination of initiator and monomer effects. Due to the high hydrophobicity and bulky chemical structure of DBMP, high localized concentrations of this initiator may occur in systems formed at low concentrations of surfactant. In this system DBMP may become sequestered in the

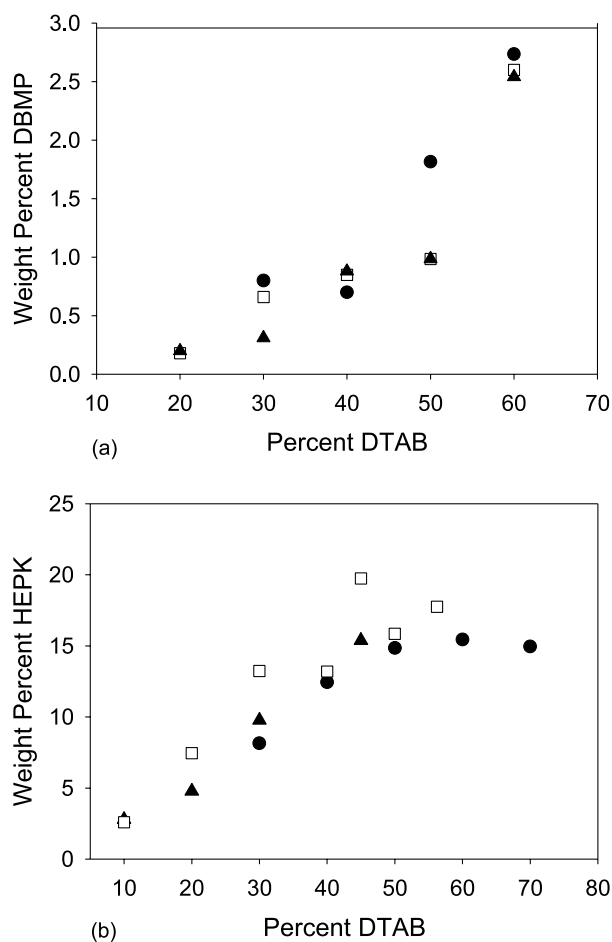


Fig. 5. Solubility of (a) DBMP and (b) HEPK in DTAB/water (□), PEGDMA/DTAB/water (▲), and HDDA/DTAB/water (●) as a function of DTAB concentration.

hydrophobic micellar cores, which at low surfactant concentration make up only a small portion of the system. The radicals formed upon exposure to UV light, being segregated within the small lyophobic domains, could readily recombine rather than escape to monomer rich locales to initiate polymerization [18]. With increasing surfactant concentration the initiator likely becomes more diffusely distributed in the system, decreasing the likelihood of recombination, enabling more radicals to initiate polymerization. Thus, the initiation efficiency of DBMP appears more dependent on LLC composition than that of more water soluble and less bulky initiators.

To understand further the role of photoinitiator segregation in LLC polymerizations, DBMP and HEPK were used to initiate polymerization of acrylamide in the LLC phases of Brij 56, a nonionic surfactant, and water. Polymerization in this system not only could help to verify the polymerization behavior observed in the DTAB/water system is not simply the result of interactions specific to a certain surfactant and initiator, but additionally allows the observation of the effect of initiator segregation when polymerization occurs in both continuous and discontinuous phases. With increasing surfactant concentration in a system of 25 wt% acrylamide and water, discontinuous cubic, hexagonal, and inverse micellar phases are observed. Fig. 6(a) shows the polymerization profiles of 25% acrylamide initiated with HEPK in the various mesophases of Brij 56 and water. Polymerization proceeds very slowly in the isotropic sample of acrylamide in water with double bond conversion remaining low even at extended polymerization times. The parallel between polymerization rate and LLC order is obvious from the sharp rate increase observed when polymerization occurs in the more ordered discontinuous cubic phase with 40% Brij 56 in water. As order increases to the hexagonal phase, the rate increases more than 30%. Variation of surfactant concentration within the hexagonal phase, in which the highest rates are observed, causes only slight changes in the polymerization rate, further demonstrating the role of liquid crystalline order in the polymerization behavior. Further increases in surfactant concentration induce transition to an inverse micellar phase, in which the rate of polymerization decreases to a value similar to that in the discontinuous cubic phase. This decrease in rate even with increasing surfactant concentration shows that polymerization behavior is governed primarily by LLC morphology and not surfactant concentration. Previous examination of this system shows that the rate of polymerization is governed by monomer ordering with higher localized double bond concentration and diffusional restrictions causing the elevated rate observed in the highly ordered hexagonal phase [10].

Contrasting results as shown in Fig. 6(b) are observed when DBMP is used to initiate polymerization of acrylamide in the same liquid crystalline phases. Monomer and surfactant concentration were identical to those used in the study performed with HEPK in order to isolate the effects of

photoinitiator on the polymerization behavior in LLC systems. It should be noted that changes in photoinitiator do not affect LLC phase behavior. As seen previously for initiation with HEPK, the lowest rate of polymerization is seen in the isotropic phase and rapidly increases in the discontinuous cubic phase of 40% Brij 56 and water. In contrast to initiation with HEPK, however, the transition to the hexagonal phase causes only a slight rate increase. Interestingly, the rate almost doubles as surfactant concentration is increased within the hexagonal phase. Another significant difference with DBMP is seen as surfactant concentration further increases causing the transition to the inverse micellar phase. The rate of polymerization in this phase is highest with the less soluble DBMP, almost double that of the discontinuous phase. With this initiator, the rate of polymerization is clearly not dictated solely by liquid crystalline order. Otherwise, the rate in the discontinuous cubic and inverse micellar phases should be similar as they are with HEPK, and the highest rate of polymerization would be seen in the highly ordered hexagonal phase. As with polymerization in the LLC phases of DTAB/water, polymerizations initiated with HEPK follow trends in rate that are predictable based on LLC order, whereas the rate of polymerization initiated with DBMP generally increases with increasing surfactant concentration.

Another factor that should be considered simultaneously with photoinitiator segregation is initiator mobility. In order to initiate polymerization photoinitiator must either be located in close proximity to monomer or be able to readily diffuse to monomer. In this regard initiator mobility could have a similar effect on polymerization behavior as initiator segregation. Just as viscosity widely varies in different LLC phases, photoinitiator mobility could also be dependent on LLC order. To determine whether photoinitiator mobility is influenced by changing lyotropic liquid crystalline phases, ^{13}C T_1 spin lattice relaxation times were measured in systems with varying concentrations of surfactant. The time constant, T_1 , is a function of the time required for relaxation of nuclear spin to an equilibrium state after application of an inversion pulse. In liquids high T_1 s typically correspond to higher degrees of atomic mobility [8,10]. To compare photoinitiator mobility within surfactant systems, Fig. 7 shows the relative T_1 spin lattice relaxation times of carbons from HEPK and DBMP as a function of DTAB concentration. T_1 values of the carbonyl (2) and aromatic (1) carbons, are compared because they are common structural elements of both initiators and are relatively close to the site of photolytic cleavage. All data points are normalized by values determined in acetone. With increasing surfactant concentration, the T_1 values of DBMP and HEPK carbons decrease indicating a less mobile environment for both photoinitiators. However, the mobility of the DBMP carbons appears to decrease much more rapidly than those of HEPK. The T_1 of the carbonyl carbons of DBMP decreases 98% from the isotropic solvent to the more ordered cubic phase, compared to a 90% decrease in T_1 for

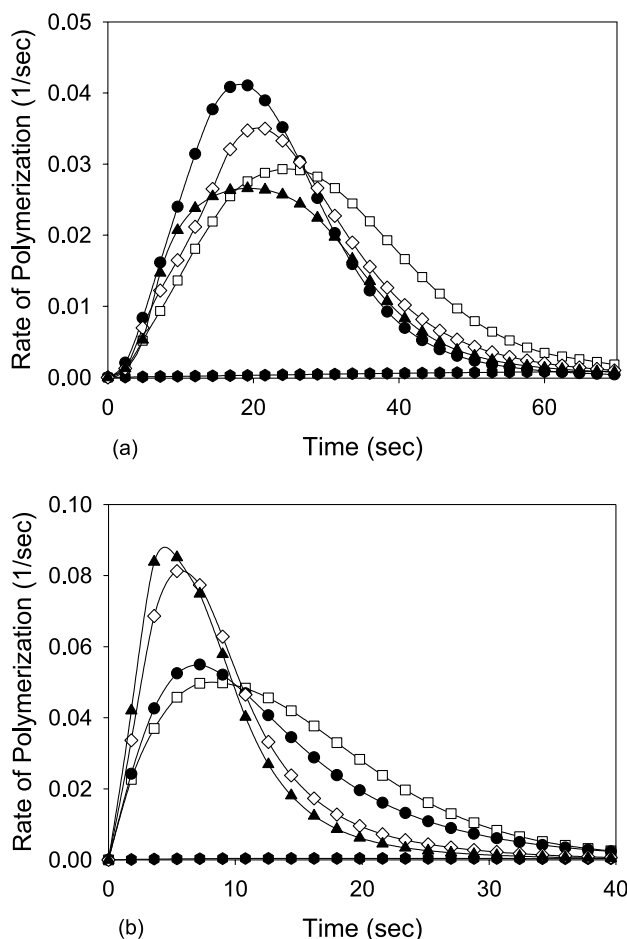


Fig. 6. Polymerization rate with respect to time of 25% acrylamide initiated with (a) 1 wt% HEPK and (b) 1 wt% DBMP. Shown are polymerizations in 0%-isotropic (●), 40%-discontinuous cubic (□), 50%-hexagonal (●), 60%-hexagonal (◇), and 70%-inverse micellar (▲) Brij 56 in water.

the carbonyl carbons of HEPK over the same composition range. The mobility of the aromatic carbons of DBMP similarly decreases more rapidly than those of HEPK. The

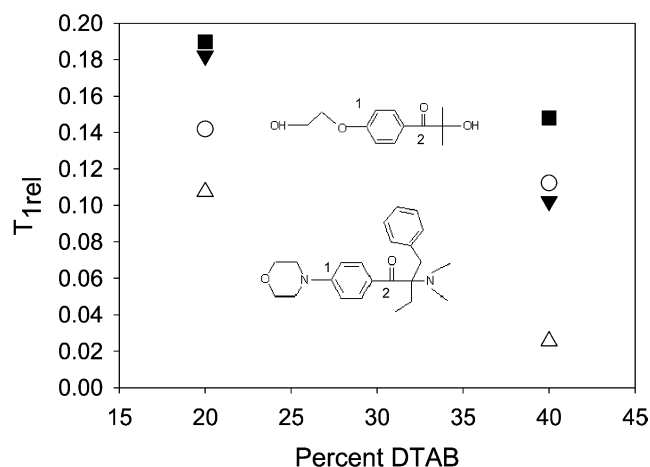


Fig. 7. Relative ^{13}C T_1 spin lattice relaxation times of the carbonyl-2 (Δ) and aromatic-1 (\circ) carbons of DBMP and carbonyl-2 (\blacktriangledown) and aromatic carbons-1 (\blacksquare) of HEPK as a function of DTAB concentration. All values are normalized by T_1 measurement in acetone.

decrease in mobility as surfactant concentration increases indicates that the initiators are not randomly solvated, but interact strongly with surfactant. The efficiency of hydrophobic initiators such as DBMP may therefore not only be affected by their segregation behavior but also by a decrease in the rate of diffusion to monomer in ordered LLC systems. As a result of the slower diffusion and isolation in surfactant rich domains, initiator fragments may be more likely to recombine than initiate polymerization. With the hydrophilic HEPK the decrease in rate of diffusion that occurs at higher surfactant concentrations should have less influence on the polymerization rate as this initiator is more diffusely located in the system, making recombination unlikely.

A better understanding of the effect of initiator mobility and segregation on the polymerization behavior in LLC phases can be obtained by comparing rates of polymerization in isotropic systems, where initiator mobility is relatively high, to that in more constrained reactive environments. Accordingly, the polymerization of neat HDDA was compared to the polymerization of 10% HDDA in the hexagonal phase synthesized using 50% DTAB in water. In order to gain understanding about the relative initiation efficiencies of DBMP and HEPK, each

initiator was used to polymerize neat HDDA as well as HDDA in the ordered system. The rate of polymerization of neat HDDA initiated with 0.03% DBMP was compared to that of 3% HEPK. The widely different absorption of UV light by these initiators necessitates the large difference in initiator concentration in order to obtain comparable rates of polymerization with each initiator. The polymerization rate of neat HDDA with both initiators is plotted as a function of time in Fig. 8(a). The rate is almost two times higher with DBMP in spite of its significantly lower concentration. This is a result of the disparate extinction coefficients of these initiators over the UV wavelengths used in the experiment.

When the same concentration of initiators as used above initiates polymerization of HDDA in the hexagonal mesophase of DTAB and water, the relative rate of polymerization with the two photoinitiators varies significantly from that of the neat polymerization. Fig. 8(b) shows the rate of polymerization of HDDA with these two initiators in the ordered surfactant system with respect to time. In the ordered system, the maximum rate of polymerization using HEPK is five times higher than the polymerization initiated with DBMP. If the efficiency of each initiator exhibits similar dependence on reaction conditions, then the ratio of polymerization rates using both initiators should also be similar in the neat HDDA and

the hexagonal phase polymerization. Instead it appears that the decreased rate of diffusion and the segregation of DBMP in the ordered system dramatically affect the polymerization rate causing the rate to decrease to less than 5% of that in the neat system. In contrast, the rate of polymerization initiated with HEPK in the ordered system is about 50% that in the neat system. These results are direct evidence of the higher sensitivity of the relatively bulky DBMP to the liquid crystalline environment. While the efficiency of both initiators may be different in the neat polymerization and the ordered system, the lower mobility and segregation phenomena occurring in the ordered LLC environment have the greatest influence on the efficiency of DBMP, which appears to decrease sharply in the LLC phases.

4. Conclusions

The polymerization kinetics in LLC media are highly dependent on the degree of orientational order within the reaction environment. While monomer segregation behavior and diffusional limitations significantly affect the rate of polymerization, segregation of photoinitiator is an additional factor influencing the polymerization kinetics in these systems. Differences in photoinitiator chemical structure and mobility cause initiators to partition in separate domains in the LLC and can result in significantly different polymerization behavior. When hydrophilic and more mobile initiators such as HEPK and HMMP are used the polymerization kinetics vary in the LLC phases in a manner consistent with monomer segregation, with increasing rates usually observed in mesophases that enhance local double bond concentration. With the relatively immobile, hydrophobic DBMP, a contrasting dependence on order occurs as a result of combined monomer and initiator effects. With this initiator the polymerization occurs more slowly at low surfactant concentrations as initiator radical recombination is more prevalent due to the cage effect in the small nonpolar domains. Rate enhancement occurs at higher surfactant concentrations as initiator becomes more diffusely dispersed in the system and the initiator radicals are more likely to initiate polymerization. These results imply that the rate of initiation with mobile, hydrophilic initiators varies little in LLC environments of different composition and morphology. On the other hand the rate of initiation with bulky, hydrophobic initiators appears highly dependent on LLC order and composition.

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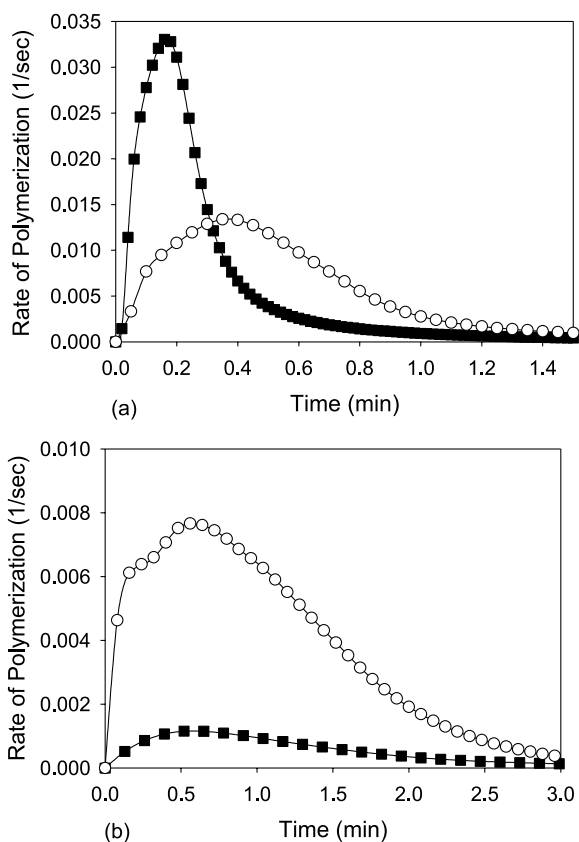


Fig. 8. Polymerization profiles of (a) neat HDDA and (b) 10% HDDA in the hexagonal mesophase with 50% DTAB/water initiated with 0.03 wt% DBMP (■) and 3 wt% HEPK (○) with 3.3 mW/cm² full beam light.

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