

# Effect of Photoinitiator Solubility on Polymerization in Lyotropic Liquid Crystalline Media

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## Introduction

Nanostructured polymers have recently received considerable attention because of their potential to advance many diverse applications. Significant research has focused on synthesizing these polymers using lyotropic liquid crystalline (LLC) templates. The goal of this method is to produce polymeric gels with structures templated from the original surfactant system.<sup>1</sup> Extensive synthesis of inorganic polymers has relied on this method. Recently liquid crystalline nanostructure has also been templated onto organic polymers with full retention of structure.<sup>2-7</sup> The structures formed through this method of synthesis are highly dependent on polymerization kinetics. Significant understanding of the unique polymerization mechanism in LLC material has resulted from monitoring the polymerization kinetics of many monomer/LLC systems. These studies have revealed the roles of the monomer and liquid crystal components in the structure development of the resulting polymers.<sup>4,5</sup> Monomers of different polarity display significantly different polymerization kinetics and also result in drastically different polymer structures due to their segregation in different domains within the liquid crystalline system.

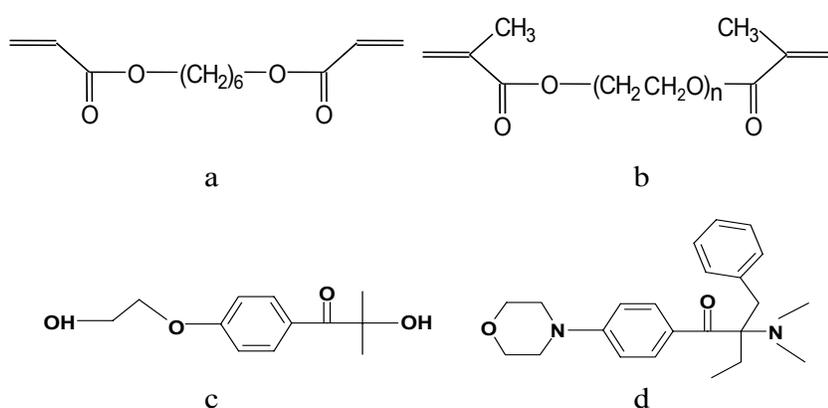
The photoinitiator is another component of the system that greatly affects the polymerization kinetics and structure formation. In microemulsions the initiation efficiency is highly dependent on initiator solubility.<sup>9</sup> However, the effect of initiator chemical structure and solubility on polymerization behavior in liquid crystalline systems is not understood. In this study the effect of initiator solubility and structure on polymerization kinetics in liquid crystalline media has been investigated. Several photoinitiators were used to initiate polymerization in solutions of varying LLC order. The trends in polymerization rate with respect to LLC order from these initiators were characterized and compared.

## Experimental Section

**Materials.** The monomers used in this study were hexanediol diacrylate (HDDA, Polysciences) and poly(ethylene glycol)-400 dimethacrylate (PEGDMA, Polysciences). The LLC system consisted of dodecyltrimethylammonium bromide (DTAB, Aldrich) and deionized water. Irgacure 2959, an  $\alpha$ -hydroxyketone and Irgacure 369, an  $\alpha$ -amino-ketone (Ciba Specialty Chemicals, Tarrytown, NY) were used to initiate the photopolymerizations. The chemical structures of these materials are shown in figure 1.

**Procedure.** 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 and phase transitions of the various mesophases.

The polymerization rates were monitored using a Perkin Elmer differential scanning calorimeter. Polymerizations were initiated using the full emission spectrum from a medium pressure UV arc lamp. Light intensity was controlled with neutral density filters and by adjusting the height of the lamp. Samples of approximately 5 mg were placed in aluminum DSC pans and covered with UV transparent thin films of FEP (Dupont fluorinated copolymer) to prevent



**Figure 1.** Chemical structures of monomers and photoinitiators used in this study. Shown are (a) hexanediol diacrylate, (b) poly(ethylene glycol)-400 dimethacrylate, (c) Irgacure 2959, and (d) Irgacure 369.

determined from the heat flow as shown elsewhere.<sup>9</sup> Maximum rates were taken from the peak of the rate profiles obtained.

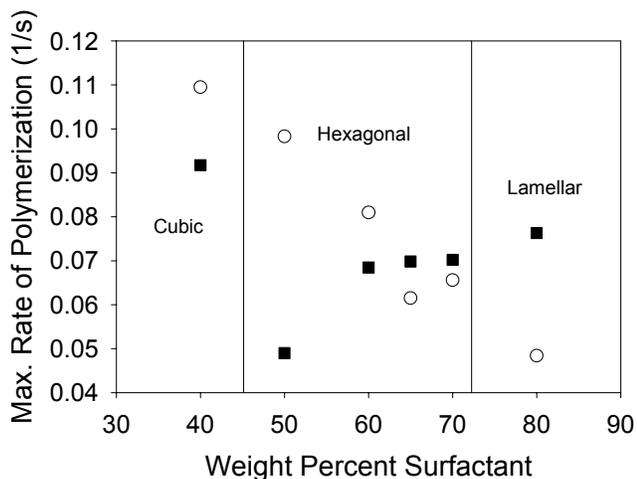
Photoinitiator solubility in the liquid crystalline solutions was determined by preparing samples containing a range of photoinitiator concentration near the saturation point. The samples were lightly heated, centrifuged, and sonicated to dissolve the solid photoinitiator. Samples were kept at room temperature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

## Results and Discussion

Polymerizations in liquid crystalline media exhibit interesting kinetics not seen in bulk polymerizations. Fundamental information about the structure development and interesting polymerization mechanism in liquid crystalline systems have resulted from previous investigations detailing the effect of LLC order on the rate of polymerization.<sup>3</sup> Many factors that typically influence the rate such as monomer and initiator concentration remain critical in LLC systems while additional factors such as the degree of order in the system also play an important role. The same interactions responsible for the self assembly of liquid crystalline order tend to segregate monomers and other components to specific domains depending on their solubility within the system. The segregation and diffusional restrictions in these ordered reaction environments have been characterized by studying the trends in rate of polymerization of polar and nonpolar monomers with different degrees of LLC order. Significant differences in polymerization kinetics were observed depending on monomer polarity and segregation characteristics.<sup>4</sup>

Recently the dependence of polymerization behavior on photoinitiator solubility has also been investigated in LLC media. Significant differences in polymerization behavior are observed when using different photoinitiators for the polymerization of HDDA and PEGDMA in the various LLC phases of DTAB and water. A comparison of the maximum rates of polymerization of HDDA initiated with Irgacure 2959 and Irgacure 369 is plotted with respect to surfactant concentration in figure 2. When Irgacure 2959 is used to initiate photopolymerization of HDDA in the cubic, hexagonal, and lamellar LLC phases, the rate of polymerization is highest in the least

evaporation of water. The DSC sample cell was purged with nitrogen for 6 min prior to polymerization to reduce oxygen inhibition. The samples were heated to 50° C and then cooled to room temperature at 20° C/minute to ensure uniform sample thickness and improve thermal homogeneity. During polymerization isothermal reaction conditions were maintained using a refrigerated circulating chiller. The polymerization rate was



**Figure 2.** Peak polymerization rates of 10% HDDA in the LLC phases of DTAB/water as a function of DTAB concentration. Polymerizations were initiated at 30°C using Irgacure 2959 (○) and Irgacure 369 (■).

behavior is in contrast to initiation with Irgacure 2959 in which the rate is lowest in the lamellar phase and less than half the rate in the cubic phase.

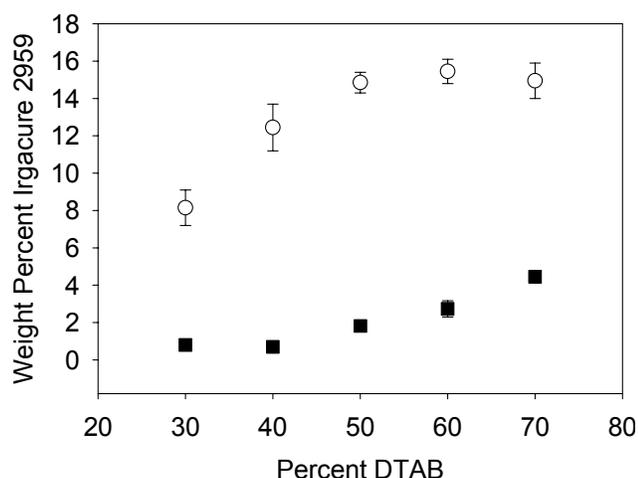
Although differences in UV light absorbance and initiator efficiency cause expectedly different rates for different photoinitiators, these contrasting trends in polymerization rate with increasing degree of LLC order indicate that other factors are altering the polymerization mechanism. Photopolymerization of HDDA initiated with several other initiators that have been studied follow similar trends of decreasing rate of polymerization with increasing LLC order. Other oil soluble monomers such as n-decyl acrylate show similar polymerization behavior with these same initiators as LLC order is increased.<sup>4</sup> The trend in polymerization rate in these systems suggests that monomer segregation is largely controlling the rate. Of the LLC phases studied, oil soluble monomers have the highest local concentration in the cubic phase where they are sequestered within the small micellar aggregates. Hydrophobic monomers thus show the highest rate of polymerization in this phase. The more ordered geometry of the hexagonal and lamellar phases results in lower localized monomer concentrations and the rate therefore decreases in these phases. In contrast, when Irgacure 369 is used to initiate polymerization of HDDA, the initial decrease in rate between the cubic and hexagonal phase is followed by a steadily increasing rate of polymerization as surfactant concentration is increased in the hexagonal and lamellar phases. This polymerization behavior is inconsistent with what would be predicted based on monomer segregation alone. The rate of polymerizations initiated with Irgacure 369 must therefore be controlled by other factors in addition to monomer segregation. Since the photoinitiator was the only system component that was varied, the dissimilar trends in polymerization kinetics likely result from differences in the photoinitiation step of the polymerization mechanism.<sup>10</sup>

Just as monomer solubility and segregation account for large differences in the polymerization behavior of oil and water soluble monomers in surfactant solutions, differences in photoinitiator solubility and segregation are the likely cause of the different rate trends seen in these polymerizations. To understand the effects of photoinitiator solubility on the polymerization kinetics, the solubility of Irgacure 2959 and Irgacure 369 was determined in gels containing 10

ordered cubic phase and lowest in the highly ordered lamellar phase. A similar trend was reported in the literature for HDDA and other oil soluble monomers in the various phases of DTAB/water initiated with Irgacure 651.<sup>4</sup> However, a different trend is observed when Irgacure 369 is used to initiate polymerization of HDDA. With Irgacure 369, the rate of polymerization decreases by almost half when the concentration of surfactant is increased to induce a change from the cubic to the hexagonal phase. The lowest rate occurs in the hexagonal phase at 50% DTAB concentration. The rate of polymerization then continues to increase with increasing surfactant concentration, and the rate of the lamellar phase polymerization is only slightly less than the rate of the cubic phase polymerization. This

wt% HDDA and varying concentrations of DTAB and water. The solubility of each initiator was determined over a wide range of surfactant concentrations to understand whether changes in solubility were linked to the changes in polymerization kinetics that occur over the same composition range. As shown in figure 3 the solubility of Irgacure 2959 is more than 8 ten times greater than that of Irgacure 369 for DTAB concentrations ranging from 0 to 50 wt%. As surfactant concentration increases the solubility of both photoinitiators increases sharply. However, the solubility of Irgacure 369 increases more quickly than Irgacure 2959 and is only 4 times less than that of Irgacure 2959 at 80% DTAB. These differences in solubility parallel the differences in kinetics seen with these two initiators.

Initiators with solubilities above a certain threshold value appear to follow decreasing rates of polymerization with increasing degrees of LLC order. This trend was observed with Irgacure 2959 and Irgacure 651, which have similar solubility in the various mesophases of DTAB/water.

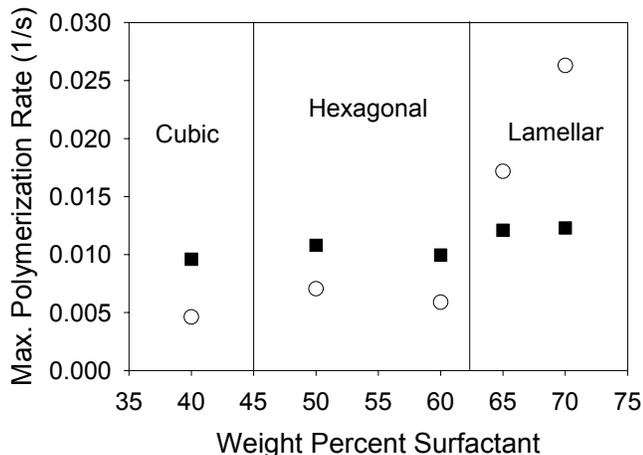


**Figure 3.** Solubility of Irgacure 2959 (○) and Irgacure 369 (■) with respect to DTAB concentration.

Sarcure SR 1131, an emulsion based initiator with significantly higher solubility than any of the other initiators that were studied also showed the same decreasing trend in rate with respect to LLC order. For all of these initiators the rate appears dependent primarily on segregation of monomer. Conversely, the rate of polymerization initiated with Irgacure 369 follows a trend that is controlled by limitations in photoinitiator efficiency. Due to the very low degree of solubility of Irgacure 369 and its association with surfactant, initiating radicals quickly recombine by the cage effect and thus slow the initiation process and result in lower rates of polymerization. The increasing rate of polymerization initiated with Irgacure 369 at higher surfactant concentrations results from

improved initiator solubility as well as more favorable LLC geometry. The enhanced solubility at higher surfactant concentration allows higher rates of initiation and polymerization as initiating radicals are less likely to terminate by primary recombination.

To determine the effects of initiator solubility on the polymerization of a water soluble monomer, PEGDMA was also polymerized in the various phases of DTAB/water using Irgacure 2959 and Irgacure 369 to initiate polymerization. Figure 3 shows the maximum rate of polymerization of PEGDMA in the LLC phases of DTAB and water. The polymerization rate increases with increasing DTAB concentration for both photoinitiators. However, the degree of increase is not the same for each initiator. When Irgacure 369 is used, the rate increases by a factor of 5 between the hexagonal and lamellar phases. With Irgacure 2959 the rate increases less than 20% between these same phases. The increase in rate seen with both photoinitiators through the progression from cubic to the lamellar phase occurs due to higher segregation of the water soluble PEGDMA in the more ordered LLC phases. Water soluble monomers such as PEGDMA which dissolve in the continuous aqueous phase surround the micelles in the cubic phase in which polymerization occurs relatively slowly. Local monomer concentration increases in the hexagonal phase and higher rates of polymerization result. Local ordering peaks in the lamellar phase where the highest rates of polymerization occur. While both initiators produce



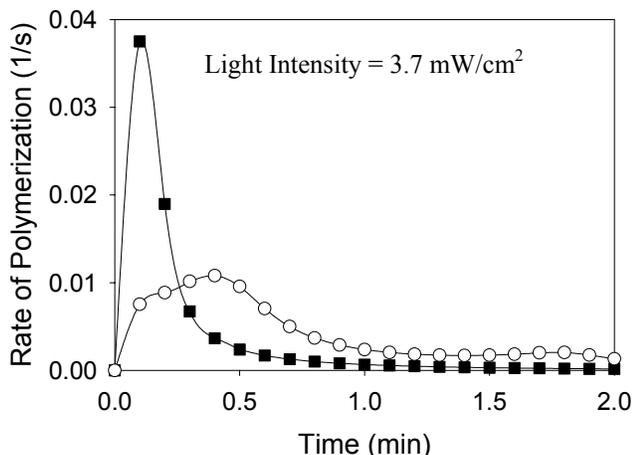
**Figure 3.** Peak polymerization rates of 20% PEGDMA initiated at 30°C with Irgacure 2959 (■) and Irgacure 369 (○) in the LLC phases of DTAB/water as a function of DTAB concentration.

Irgacure 369 is thus due to increasing monomer segregation combined with improved initiation efficiency in the more highly ordered LLC phases.

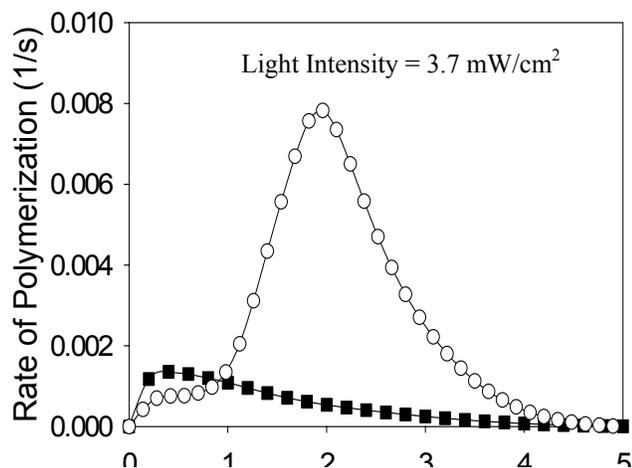
The rate of polymerization initiated with Irgacure 2959 increases from the cubic to the lamellar mesophase primarily because of monomer segregation effects. Changes in initiator efficiency are less significant when initiating with Irgacure 2959 than with Irgacure 369. Since Irgacure 2959 has relatively high solubility in the PEGDMA/DTAB/water system even at low concentrations of surfactant, primary radical termination is less prevalent and increases in surfactant concentration do not greatly enhance photoinitiation efficiency. Consequently the increase in the rate of polymerization with increasing LLC order is less dramatic when Irgacure 2959 is used to initiate polymerization of PEGDMA.

A better understanding of the effect of reaction conditions on the mechanism can be gained by comparing rates of polymerization of a particular monomer/initiator combination in different reactive environments. Accordingly, the polymerization of neat HDDA was compared to the polymerization of 10 wt% HDDA in the hexagonal phase synthesized using 50 wt% DTAB in water. In order to measure the relative initiation efficiencies of Irgacure 369 and Irgacure 2959, 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 wt% Irgacure 369 was compared to that of 1 wt% Irgacure 2959. The widely different absorption of UV light by these initiators necessitated the large difference in initiator concentration in order to compare rates of polymerization with each initiator. The polymerization rate of neat HDDA with both initiators is plotted as a function of time in figure 4. The rate is almost 4 times higher with Irgacure 369 in spite of its significantly lower concentration. This result alone provides little insight into the relative efficiency of photoinitiation and is caused by the disparate extinction coefficients of these initiators over the UV wavelengths used in the experiment. However, a comparison of the relative rates with each initiator in the neat HDDA to those from the liquid crystalline polymerization can provide the relative initiation efficiency of each initiator under the respective polymerization conditions.

similar trends in polymerization rate with respect to LLC order, differences in photoinitiator solubility likely cause the different magnitudes of change in the polymerization rate that is observed with the two initiators. When initiating polymerization with the less soluble initiator, Irgacure 369, the rate increases rapidly due to improved solubility at higher surfactant concentrations. As the initiator becomes more soluble in the medium, it becomes less locally concentrated and termination by recombination is less frequent. More radicals initiate polymerization due to the improved initiation efficiency and the rate of polymerization increases with increased liquid crystalline order. The rapidly changing rate of polymerization that occurs when initiating with



**Figure 4.** Polymerization profiles of neat HDDA initiated with 0.03 wt% Irgacure 369 (■) and 1 wt% Irgacure 2959 (○).



**Figure 5.** Rate of polymerization versus time of 10% HDDA in hexagonal mesophase of 50% DTAB in water. 0.03 wt% Irgacure 369 (■) and 1 wt% Irgacure 2959 (○) were used to initiate polymerization.

When the same concentration of both initiators was used to initiate polymerization of HDDA in the hexagonal mesophase of DTAB and water, the relative rates of polymerization with the two photoinitiators varied significantly from that of the neat polymerization. Figure 5 shows the rate of polymerization of HDDA with these two initiators in the ordered surfactant system with respect to time. The maximum rate of polymerization in the LLC environment using Irgacure 2959 was 5 times higher than the polymerization initiated with Irgacure 369. If the efficiency of each initiator showed a similar dependence on reaction conditions then the ratios of polymerization rates using both initiators would be similar in the neat HDDA and in the hexagonal phase polymerization. Instead, the rate of polymerization of HDDA initiated with Irgacure 369 decreases much more quickly than with Irgacure 2959 from the neat polymerization to the polymerization in the DTAB/water solvent. Using Irgacure 369 the rate decreases 95% while it decreases by only 33% with Irgacure 2959. These results are direct evidence of the relatively higher sensitivity of Irgacure 369 to the liquid crystalline environment. While the efficiency of both initiators is less in the ordered system than in the neat monomer, the efficiency of Irgacure 369 is significantly less than that of Irgacure 2959 in the LLC solution. The low solubility of this hydrophobic initiator causes it to be highly segregated in discrete domains in the LLC phases of the HDDA/DTAB/water system. The resulting high local initiator concentration has a

negative effect on initiator efficiency as radicals rapidly terminate by recombination.<sup>8,10-12</sup>

## Conclusions

Photoinitiator solubility influences the efficiency of the initiator and therefore plays a large role in the polymerization kinetics within LLC media. The trends in rate of polymerization with increasing degree of LLC order vary significantly depending on the solubility and efficiency of the photoinitiator. Initiation efficiency in the LLC environment is relatively high with Irgacure 2959 and changes little through the different phases. Consequently, the trend in polymerization rate with respect to LLC order depends primarily on localized monomer concentration.<sup>4</sup> When the less soluble Irgacure 369 initiates polymerization, the monomer ordering effects of the LLC also influence the rate of polymerization, but changes in initiator efficiency are more extreme and thus have a larger role in governing the polymerization kinetics. Future work will continue

investigating the dependence of initiator efficiency on LLC order as well as its relationship to final polymer structure.

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