555c Photoinitiation and Monomer Ordering Phenomena in Polymerizations Conducted in Lyotropic Liquid Crystalline Phases

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Through photopolymerization lyotropic liquid crystalline (LLC) phases may be templated onto organic polymers to yield highly ordered nanostructures with potential applications in ultrafiltration, catalysis, and various biological applications. In order to understand the unique polymerization behavior which ultimately determines polymer morphology in these highly ordered systems, the polymerization kinetics of several monomers have recently been examined using a number of commercially available á-cleavage photoinitiators. The rate of polymerization in these systems exhibits an interesting dependence on LLC order. While association of polar monomers with the continuous phase leads to increasing polymerization rate in more ordered LLC phases, nonpolar monomers exhibit the opposite trend due to segregation in the discontinuous region of the phases studied.

To understand the underlying factors controlling the kinetics in these ordered systems, rate constants of termination and propagation (kt and kp) were determined using differential scanning calorimetry (DSC). The decreasing rate in more ordered LLC phases observed with nonpolar monomers likely results from a localized decrease in the double bond concentration in phases with higher surfactant concentration, evidenced by a decrease in kt and kp in more highly ordered phases. The increasing rate of polymerization observed with polar monomers and increasing LLC order may result from decreased diffusional restrictions on the propagating polymer in the more ordered environment, which is indicated by a decrease in kt.

Although monomer segregation and diffusional limitations largely govern the kinetics in these systems, initiation efficiency may also vary with changing LLC order and could likewise influence the polymerization kinetics. Polymerization conducted with relatively mobile initiators, displaying favorable interactions with water, yields a trend in polymerization that is consistent with the above mentioned kinetics, which are governed primarily by monomer segregation and ordering. However, bulkier, more hydrophobic initiators exhibit polymerization behavior much less dependent on these effects. Rather than the decreasing rate typically observed at higher surfactant concentrations, polymerization of oil soluble monomers with relatively bulky, hydrophobic initiators exhibits the opposite trend of increasing rate at higher surfactant concentration. To understand whether changes in initiation efficiency may cause this distinct behavior, DSC experiments were conducted using a free radical inhibitor to determine the relative initiation efficiency of several inititiators in different LLC phases. These studies indicate that the initiation efficiency with relatively bulky, hydrophobic initiators increases substantially in more ordered systems while the efficiency of smaller, less hydrophobic initiators, which are less hindered by LLC topology, is relatively independent of LLC order. By incorporating relative efficiency information in the analysis of propagation and termination rate parameters, the individual contributions of monomer segregation and photoinitiation behavior to the polymerization kinetics have been differentiated, and a more complete model of the polymerization behavior in LLC media has been developed.