365d Investigation of Factors Influencing Phase Retention in Lyotropic Liquid Crystal Template Polymerization

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Photopolymerization in lyotropic liquid crystalline (LLC) media has recently been utilized to generate nanostructured polymers with the potential to enhance applications ranging from size selective barriers, drug delivery devices, to catalytic supports. By this method of polymer synthesis, nanometer scale architecture can potentially be regulated through careful selection of the liquid crystalline template. A number of variables including polymerization rate, monomer structure, and phase type influence the degree to which these ordered structures may be retained in more robust polymeric materials. The polymerization kinetics could play a particularly important role in the structure and properties of these polymers as the ability to template LLC nanostructure may depend on the relative time scale of polymerization and phase separation.

To understand further the role of polymerization kinetics in the ultimate structure and properties of templated polymers, the structure/property relationship of photo and thermally polymerized hydrogels has been compared. From small angle X-ray scattering and polarized light microscopy observations, original LLC order appears more directly preserved through photopolymerization, presumably because of the relatively rapid polymerization rate. The higher incorporation of LLC morphology in photopolymerized samples may be implicated in their significantly different physical properties. Photopolymerized polyacrylamide hydrogels exhibit surface areas more than three times that of thermally polymerized samples of similar chemical composition. The greater incorporation of LLC nanostructure allowed through photopolymerization also influences the swelling properties of these polymers. Photopolymerized hydrogels swell to a lower degree than thermally polymerized samples, likely resulting from relatively smaller pores, with dimensions more closely aligned with the original LLC template.

The degree to which LLC order may be preserved upon polymerization also appears dependent on monomer polarity. The role of monomer polarity in LLC structure retention was examined using a series of analogous single acrylate monomers possessing varying hydrocarbon tail length. Sample structures were analyzed before and after polymerization with small angle X-ray scattering and polarized light microscopy. The photopolymerization kinetics of the monomer/LLC samples were monitored with photo-differential scanning calorimetry to understand the local reaction environment influencing polymer structure development. Original structure of a hexagonal phase appears directly preserved with relatively polar acrylates, possessing short hydrocarbon tails, while it is increasingly disrupted by the polymerization of less polar monomers. Enhanced phase stability with more polar monomers likely results from their localization to the hydrophilic continuous phase near the surfactant interface. Less polar monomers tend to interact with and swell the hydrophobic domains of LLCs, inducing changes in phase behavior even before polymerization and significant disruption of liquid crystalline order during polymerization.