Photopolymerization in Polymer Templating[†]

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Primary objectives in templating of polymer systems include control over polymer structure and reaction behavior in pursuit of functionally advanced materials. Through such control, properties and features not accessible through traditional bulk polymerization are possible. In this review, recent developments in polymer templating are discussed that utilize benefits afforded through photopolymerization in the templating process. Photopolymerization not only is widely used and well-suited for templating applications but also is a highly effective tool with which to probe the kinetic behavior and structural evolution of templated polymers. Polymer templating encompasses a number of technologies and methods. Photopolymerization is prevalent in a number of these areas including linear chain templating or catalytic polymerization, organized particle templating, molecular imprinting, templating of assembled vesicles, and polymer templating in liquid crystals. In these systems the unique aspects of photopolymerization including fast reaction, spatial and temporal control, and temperature independence are often critical in obtaining desired reaction behavior and structure.

1. Introduction

Polymer templating has generated significant research interest over the last half-century as a means by which to control polymerization reactions and polymer structure. Numerous systems have been developed as templates that range from simple particles and linear polymer chains to complex nanostructured liquid crystalline aggregates.[1–4] The objectives of polymer templating have also expanded tremendously from early efforts to increase the molecular weight and microtacticity of linear polymers with templating additives, to selective membranes templated with functional porosity, and to recent endeavors in forming organic nanomaterials using the confined domains of self-assembling templates.[5–7] Such control is achieved using systems such as particle arrays, ions, linear polymer chains, vesicles, or liquid crystalline mesophases, to name a few.[8–13] Overall, monomer organization is one of the primary objectives in polymer templating, with the final goal of enhancing or altering the polymerization behavior, structure, or properties of the resulting polymer from what is typically attainable in bulk polymerizations. Photopolymerization, or polymerization initiated with light, has recently taken a prominent role in the development of systems with such unique characteristics.[7,14–16] Herein, a brief introduction of general polymer templating methods using alternative polymerization techniques is given. Further background regarding the unique aspects of photopolymerization is presented before highlighting the utility of photopolymerization in concert with polymer templating.

Many of the early forms of polymer templating used nature as an inspiration with the biosynthesis of proteins.[17,18] In fact, DNA transcription in which genetic information is templated from DNA to RNA is an important polymer templating process that is vital to life.[19] It is not coincidental that DNA transcription is similar to some synthetic polymer templating systems recently studied in which monomer closely associates and organizes along the backbone of a linear polymer chain acting as the template, analogous to the role of DNA.[1,20] This type of templating is often called catalytic polymerization because, upon initiation, enhanced polymerization rates compared to random bulk polymerizations are typically observed due to monomer preorganization.

Greater complexity over simple linear chain templates is realized in the form of dispersed particles that are organized within polymerizable media. The organization of the particles, typically through the application of an external force, allows a high degree of order and structure to be imparted on the prepolymer matrix that will then polymerize around the templating particles.[8,21] In another similar area of polymer templating, particles with distinct size, shape, or chemical functionality may be imprinted within a cross-linked organic matrix, creating site specific cavities within the templated polymer.[22–24] This specific niche of polymer templating has seen tremendous recent growth, generating molecular imprinted polymers (MIPs) that are highly selective to the particles and analogues of the particles with which they were templated. Consequently, while templating using dispersed particles is geared toward the fabrication of monodisperse membranes with specified pore size, molecular imprinting has been used more for the synthesis of membranes with specific binding selectivities for use in advanced separations applications.[8,25]

Because of recent interest in the synthesis of materials with submicron morphology, a great deal of polymer research and application has focused on the generation of materials using nanostructured self-organizing media as polymer templates. In fact, the use of self-assembling media as polymerization

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templates has recently been identified as one of the most promising approaches in the synthesis of organic nanomaterials.[7] To this end, the confined nanoscale domains of microemulsions and vesicles have each been explored extensively as templates for polymerization reactions.[13,26–30] Additionally, much current research and application in polymer templating focuses on the use of liquid crystals (LCs) to direct polymer structure. Liquid crystals are particularly well-suited for templating applications based on their ability to form different mesophases that possess highly ordered structural geometries ideal for directing polymerization reactions.[4,7] LCs used in polymer templating can typically be classified as either thermotropic liquid crystals (TLCs) or lyotropic liquid crystals (LLCs) in which the mesophase formation is determined primarily by temperature or concentration effects, respectively. The use of LC templates can be further divided into a number of specific areas including (1) polymer/LC composites in which the templated polymer is used to structurally reinforce the LC or induce unique electro-optic properties,[31–33] (2) polymerizable LC mesogens that self-assemble and then are covalently locked into place,[34–38] or (3) the use of a nonreactive LC system as a structure-directing agent for a separate polymerization reaction, after which the LC is typically removed from the organic network.[39–42]

As polymer templates grow in complexity, the preorganization of structure and subsequent polymerization in these systems result in a highly dynamic environment. For example, in LLC templating, a number of factors including thermodynamic interactions, solubility, reaction kinetics, functionality, and phase separation all directly contribute to the successful transfer of structure from the template to the growing polymer network.[43–46] Given the complexity of the LC systems before and during polymerization, it is not surprising that each templating method is associated with highly variable reports of templating success and failure. Some of most successful template replications were discovered in the early 1990s in the synthesis of mesoporous silicate materials in the presence of surfactant templating structures.[47,48] This initial work has developed into a rapidly expanding field resulting in numerous papers and achievements in generating uniform, tunable mesoporous silicate materials with nanometer pore dimensionality.[4,49–51] Similar interest and extensive research have also focused on the generation of organic nanostructured polymers templated from LLC assemblies. While some papers report the direct replication of template structure within the formed organic polymer, others state that phase separation of the polymer from the template is the primary mechanism directing the architecture of the growing network and prevents a direct transfer of structure from the template to the polymer matrix.[12,28,39–41,44,52] In fact, phase separation is one of the largest challenges in templating polymers within liquid crystal systems. Propagating polymer chains may directly influence the thermodynamic stability of the LLC/monomer formulations, resulting in phase separation and ultimately the destruction of the nanometer scale order of the LC system. In turn, much of the research in LLC polymer templating has focused on reducing phase separation through a greater understanding of the role of LLC stability, monomer chemistry, polymerization behavior, and environmental factors on the retention of template structure within the formed polymer network.[40,42,46,53]

In polymer templating, particular consideration must be given to the polymerization mechanism used in generating the templated polymer. Because the rate of polymerization, the growth mechanism, and the environmental requirements are often very different for each type, the choice of a particular initiation or polymerization strategy will often determine the degree of success in the templating process. Although a variety of polymerization mechanisms have been employed in previous templating studies including thermal, electrochemical, condensation, redox, etc.,[28,44,52–55] photopolymerization is particularly well-suited and is widely used in a number of templating applications. Photopolymerization, or more simply stated light-induced polymerization, has gained prominence in recent years for the pollution-free curing of polymer films as well as emerging applications in dental materials, electronic and optical materials, adhesives, conformal coatings, and high-resolution rapid prototyping of 3D objects.[14–16] These polymerizations can be conducted at a variety of temperatures as the initiation process is relatively independent of temperature. Additionally, great spatial and temporal control are inherent to these reactions based on the nature and flexibility that light provides in initiating the polymerization. These inherent advantages that have facilitated both significant industrial and academic interest in photopolymerization are interestingly often key factors between success and failure in templating applications. In addition, the highly controlled nature of photopolymerization allows this mechanism to be used as a tool to elucidate critical kinetic information about the polymerization.[56–58]

Early work by Ringsdorf and co-workers explored the use of photopolymerization to create membranes from polymerizable lipids which exhibit increased phase transition temperature.[59] Since then, the use of photopolymerization as a way to preserve structure and impart enhanced properties to the templated systems has increased substantially. The popularity of photopolymerization in templating applications stems from a number of key advantages that address main challenges in templating, including the natural phase separation that often occurs from the template as monomer is converted to polymer, the effects of nonuniform initiation leading to localized regions of polymer and monomer depletion, the limited stability of self-organized templates, and the rearrangement of the template upon polymerization.[52,60] As mentioned, inherent in photopolymerization is the ability to carry out the reaction independent of temperature.[61,62] This property is paramount in TLCs in which temperature directs the order of the templating system, making photopolymerization the only viable mechanism for TLC templating in different LC phases. The temperature control afforded by photopolymerization is also very beneficial in LLC templating, allowing the polymerization to be performed at the temperature at which the liquid crystal template is most stable.[46,63] In addition to temperature independence, the extremely rapid initiation rate compared to other modes of polymerization has made photopolymerization an attractive

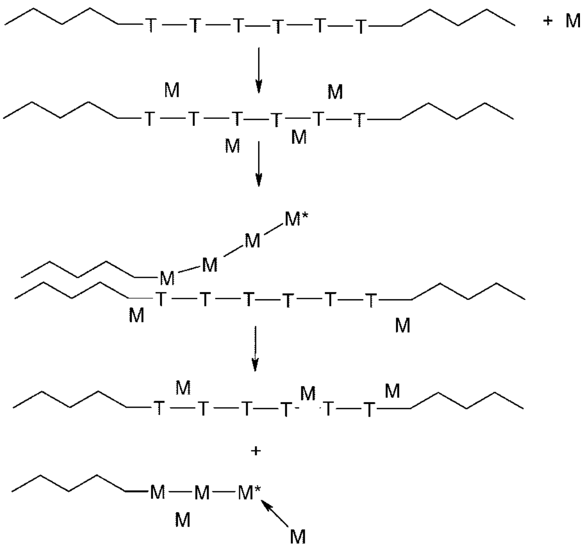

Figure 1. Linear chain template mechanism where −T−T−T− = template macromolecule, M = monomer molecule, and −M−M−M* = growing daughter chain radical. Adapted with permission from ref 68. Copyright 1990 Elsevier.

strategy in polymer templating.[14,15] Specifically, the rapid nature of photopolymerization may allow a polymer network to cross-link or lock in the structure of a template on a more rapid time scale than phase separation or reorganization of the template can occur, preventing significant phase separation or structure deformation in the templated polymer. Finally, initiation in photopolymerization is generally well controlled and uniform through the use of an appropriate light source, reducing the effects of a propagating polymerization front or undesired migration of monomer and nonuniform polymerization.[14,15,46,64]

While a number of successfully templated systems have been developed over the last few decades using a variety of reaction mechanisms, this review will focus on recent findings that directly use photopolymerization in polymer templating. In particular, five main templating areas will be covered herein including linear chain templating or catalytic polymerizations, organized particle templating, molecular imprinted polymers, templating of vesicles, and polymer templating in liquid crystals. The specific advantages of photopolymerization in producing unique templated materials will be highlighted along with discussion regarding the future role of photopolymerization in further advancements in the polymer templating field.

2. Templated or Catalytic Polymerizations

Early investigations into templated polymerizations focused on the use of macromolecule chains as templates for free radical polymerizations. Figure 1 diagrams the general scheme using linear polymer chains as templates for monomer organization and subsequent photopolymerization. The main premise behind this templating strategy is that monomer will closely associate with the linear polymer chains and a degree of organization will be imparted on the monomer prepolymerization. This ordering by the parent template chain serves to prolong macroradical life during polymerization and decreases the probability of chain termination.[1,56] Accordingly, most studies on this subject have primarily focused on the influence of the template on the polymerization kinetics of the propagating monomer as well as the structural effects of the template on polymer molecular weight and microtacticity of the growing daughter polymer.[5] Although templated polymerizations of this kind have been well studied in the past using a variety of polymerization mechanisms, recent work has employed photopolymerization, taking advantage of the benefits this initiation strategy has over other free radical polymerizations. For example, Matuszewska-Crwewik and co-workers recently published a series of articles in which templated photopolymerization of methacrylic acid was investigated.[56–58,65–67] In these studies, photopolymerization was used not only as the method to polymerize the templated polymer but also as a tool to understand the kinetic behavior of the templating system, elucidating such kinetic information as the propagation and termination rate constants of the reaction.

Generally in templated polymerizations, a higher photopolymerization rate is observed compared to nontemplated systems due to an increase in monomer organization and a considerable reduction of radical termination.[57] When the macroradicals are absorbed on the template, lower mobility and a lower tendency to recombine are expected compared to analogous reactions without a template. Interestingly, decreased mobility due to templating effects not only is associated with termination but also has been observed to direct a decrease in propagation rate constants due to steric effects, unfavorable spatial arrangements of reacting macroradicals, or disadvantageous positions of the fragments of the folded template macromolecules.[58] The interaction between monomer and templating polymer chains has also been postulated to play a critical role in whether templating effects such as enhanced kinetics or molecular weight growth are observed. It is not surprising that systems with a weak monomer−template interaction, such as the polymerization of methacrylic acid (MAA) using poly(ethylene glycol) (PEG) templating chains, exhibit no effect on the photopolymerization rate compared to nontemplated systems.[65] On the other hand, the photopolymerization of MAA using poly(vinylpyrrolidone) (PVP) displays definite templating effects such as monomer organization and a change in the kinetic rate constants of the polymerization due to the strong associative interactions between MAA and the PVP template.[66]

In addition to monomer−template associative interactions, studies have linked the photopolymerization kinetics of templated polymerizations to the molecular weight of the templating chains as well as to the ratio of template to monomer in these systems.[65,67] For example, increasing the molecular weight of PVP as a template for the photopolymerization of methyl methacrylate (MMA) was observed to increase both the conversion and polymerization rate of the daughter polymer. A similar relationship was found templating MMA with poly(vinyl acetate).[68] In addition to template molecular weight, these studies have demonstrated that increasing the ratio of polymer template to monomer directly increases photopolymerization rates by influencing both propagation and termination kinetic constants. One of the general themes in the studies described is that the relationships between the polymerization kinetics and the changes in the chemistry, molecular weight, or concentration of the templating chains are evidence that the daughter polymer is truly being templated by the macromolecule chains.

Further investigations into the mechanisms behind the observed kinetic increases in linear templated photopolymerizations have recently been conducted using a system of MAA templated with poly(*N*-acetyliminoethylene).[69] Interestingly, conversion profiles of the daughter polymer in this study can be divided into two stages. The reaction was followed by TEM to identify discrete steps of structural growth during the polymerization. First, early polymerization of MAA along the template backbone directs the association of the macromolecules into compact spherical particles that further aggregate into fibrils with a shape similar to a radial spherulite. This step is followed by the filling of the interfibrilar spaces in the aggregates to give compact spheres, allowing the formation of a three-dimensional network by association followed by precipitation. By comparing kinetic and microscopy data, it was concluded that the second growth rate of the bimodal conversion profile begins at the onset of the filling of the “spherulite-like” aggregates. These studies support the concept that both thermodynamic and kinetic factors are highly important in the structure formation of templated materials.

3. Particle Templating

Another form of polymer templating employs the use of particles dispersed with a degree of order within a polymerizable media. Recent studies have shown that the controllable alignment of templating particles, primarily accomplished using electric or magnetic fields, enables the formation of strings or column aggregates that can be used as structural templates for photopolymeric materials.[21] Park and coworkers studied how the aligned structure of silica−zirconia, glass, mica, and other particles is affected by the particle size, size distribution, shape, and concentration under an electric field.[21,70] Using SEM, it was found that the magnitude of the electric field and concentration of particles in a photopolymerizable urethane dimethacrylate play a key role in determining string length and agglomeration as well as both particle and aggregate structure alignment. Other factors such as particle shape and size distribution affect the aggregation rate and alignment of particles, allowing for optimization of the system and the formation of templating structures with narrower size distributions.[70]

One of the more significant factors in retaining order in the particle dispersed systems both before and during the early stages of photopolymerizations is the viscosity of the ordered solution. Typically, a high viscosity is desirable to slow particle motion and reduce sedimentation. One of the direct advantages of photopolymerization in these templating systems is that the temperature and thus the viscosity of the system can be specified and remain relatively constant until cross-linking of the polymer takes place. The increased heating necessary of thermal polymerizations would serve to decrease the viscosity of the medium and have detrimental effects on the order of the dispersed particles in the templated prepolymer formulation.[21] Additionally, the rapid initiation and kinetics associated with photopolymerization allow the medium to be quickly solidified around the dispersed particles, reducing the disruption that the phase change and migration may cause to the ordered particle arrays.

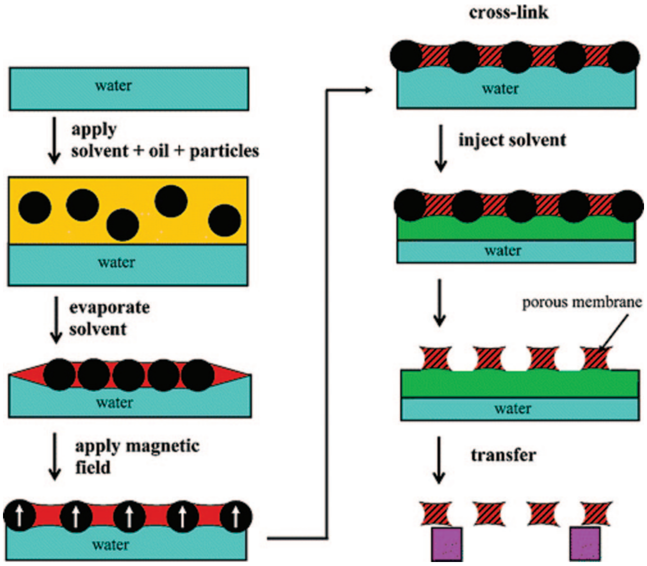

Figure 2. Scheme of the preparation of monodisperse nanoporous membranes using colloidal particles dispersed through the application of a magnetic field. Reprinted with permission from ref 8. Copyright 2005 American Chemical Society.

Ordered photopolymerizable particle systems have applications ranging from high strength polymer composites, and electrical conducting polymers, to monodisperse membranes.[8,21,70] In one particular study, thin membranes with uniform pore size were formed using a monolayer of colloidal particles dispersed through the application of a magnetic field. Figure 2 diagrams the scheme for the membrane preparation in this study. After photopolymerization and particle removal, organic membranes with monodisperse, controllable pores were formed. In further studies using repulsive particles as a template and specifying the particle diameter, researchers were able to tune the interparticle distances and pore sizes of these membranes.[8]

4. Molecular Imprinting

Molecularly imprinted polymers (MIPs), another form of templating in polymer systems, have garnered a great deal of interest over the past few decades due to their potential to form polymeric membranes or substrates that preferentially bind or retain certain species. Initial work by Wulff and coworkers introduced the idea of preparing synthetic polymers that are polymerized around template molecules that interact with the functional groups on the backbone of the polymer.[24,25,71] Removing the template leaves cavities within the cross-linked polymer matrix that are specific to the template molecule based on cavity size and stereochemical arrangement of functional groups within the cavity. Thus, the templated polymer will have a high binding affinity for the specific template molecule or analogue molecules similar to the mechanism an enzyme would use to bind certain

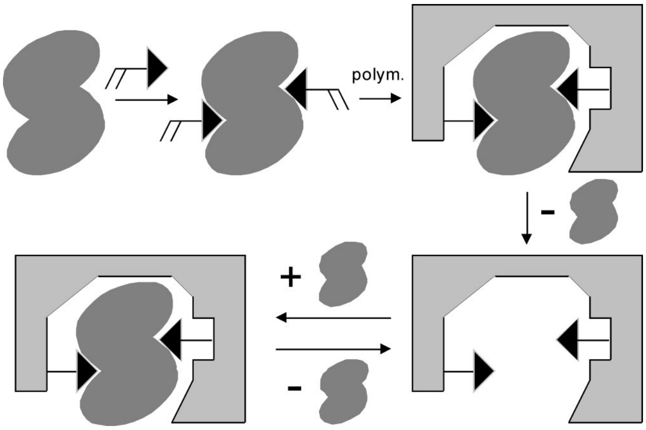

Figure 3. Outline of the mechanism for MIP binding site formation including, clockwise from upper left, complex formation between template and monomer, polymerization, removal of the templating particle from the cross-linked matrix, and selective rebinding of the template molecule or similar analogues. Reprinted with permission from ref 23. Copyright 2003 American Chemical Society.

molecules in a biological setting. Figure 3 diagrams the molecular imprinting strategy for creating selective sites in macroporous polymers.[72] A variety of inexpensive polymers may be imprinted with and tailored to a number of targeted compounds, making this strategy a rapid and simple route to generate polymers that combine the high selectivity of enzymes with the advantages of synthetic enzyme mimics.[25,72] Furthermore, polymeric materials that can be closely tailored to bind targeted compounds offer tremendous potential in separations as well as recognition elements for highly tailored immunoassays and chemical sensors.[73–75]

As with most templating methods, the polymerization mechanism plays an important role in the fabrication of MIP constructs. Photopolymerization is widely used in MIP synthesis and has been shown to play an integral role in the performance of MIPs due to the ability of the reaction to be carried out at room temperature.[74] Specifically, researchers have shown that the formation of a complex between the monomer and the template molecule, an integral step in setting up cavities with specific binding sites, is favored at lower temperatures.[75] It is thought that the increased temperatures required of thermal polymerization decrease the concentration of the monomer−template complexes and, in turn, decrease the number of specific binding sites in the cavity left by the template. In fact, in a direct comparison between thermal and photoinitiated polymerizations (at 60 and 5 °C, respectively) templating 9-ethyladenine as a targeted compound, the photoinitiated MIP at 5 °C was found to possess roughly 14 times the capacity for rebinding to 9-ethyladenine than the thermally formed construct.

Efforts to refine and improve the molecular imprinting process have primarily focused on the polymer scaffold and cavity left by the templating process. Early work by Wulff and others recognized that increased cross-linking in the polymer matrix, enhancing the robustness of the scaffold and cavity site, served to increase the specific recognition or selectivity of the matrix to the targeted molecule.[25] Systematic studies by Spivak and co-workers compared the effects of the cavity shape versus the functional group orientation within the cavity on the performance or selectivity of molecularly imprinted photopolymers.[76] Spivak found that the performance of MIPs with fewer template−functional monomer interactions was dominated by the shape selectivity of the cavity, while the particular orientation of the functional groups was the primary factor in MIPS with three or more template−functional group interactions. In general, the greatest selectivity was obtained with low template−functional group interactions, where the dominant mode of molecular recognition is through shape selectivity. In addition to selectivity, studies have focused on other aspects of MIP templating such as improving the overall reloading capacity of the templated matrix.[73,77,78] For example, Striegler and others were able to increase the reloading capacity of MIPs templated with particular oligosaccharides by introducing cross-linking agents with hydroxyl functional groups that favorably interact with the carbohydrate molecules.[77]

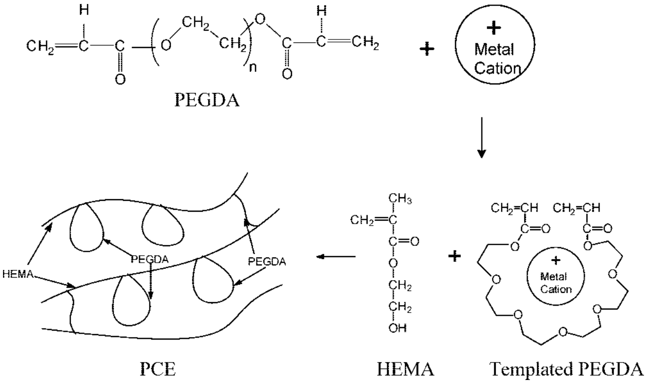

Figure 4. Synthesis scheme for the production of polymeric pseudocrown ethers using cationic metal particles. Reprinted with permission from ref 9. Copyright 1995 Taylor and Francis.

Similar to the use of functionalized particles in molecular imprinting, ionized particles have been used as templates in the creation of polymeric pseudocrown ethers in photopolymerizable systems.[9,79–83] These studies focus on the preparation of polymer-bound macrocyclic ligands in situ during a one-step polymerization based upon the tendency of oligomeric poly(ethylene glycol) diacrylate (PEGDA) monomers to naturally assume circular conformations. The presence of a templating cationic particle significantly decreases the mean end-to-end distance of the repeating units, bringing the unsaturated acrylate end groups closer to each other and further enhancing the formation of these cyclic molecules.[81] Figure 4 highlights the basic scheme for the production of pseudocrown ethers using PEGDA and hydroxyethyl methacrylate (HEMA) monomers.[9] Factors such as the solubility and the size of the cationic particles were found to affect the performance of this templating mechanism by directing the complexation between the monomer and the metal ion.[79–81] Furthermore, increasing the concentration and solubility of the templating ion increases the number of pseudocrown ethers formed.

In situ photopolymerization enables the creation of pseudocrown ethers at low cost and increased safety compared to traditional schemes in which a polymeric chain is functionalized with preexisting crown ethers.[83] Similar to other photopolymerizable systems, changes in the properties and structure of the pseudocrown ether polymers can be examined through the use of photopolymerization kinetic analysis. In one particular set of studies, the peak rate of reaction during autoacceleration was used as a measure of the mobility of the reacting species.[83] It was found that increasing the number of pseudocrown ethers decreases the cross-linking density of the system, therefore decreasing the autoacceleration that is typically observed in highly cross-linked systems. Exploring the practical applications of templated systems using pseudocrown ethers in a photopolymerizable matrix has focused on the creation of facilitated transport membranes.[82] As expected, these studies confirm that ion selectivity of the generated membranes are highly dependent on the type of metal cation used to create the pseudocrown ether in each system.

5. Vesicle Templating

Templating polymerizations in surfactant phases is a widely used pathway in the generation of synthetic materials exhibiting order on the nanometer size scale. Early efforts of polymerizing within surfactant generated templates focused on the polymerization of small oil-soluble monomers within vesicles. Vesicles, in general, have been investigated in great detail, leading to commercial application in the area of drug delivery due to their discrete geometry comprised of spherical stratums of lipid bilayers around a solvent entrapped core.[26,27] Polymerization within vesicles is primarily performed in an attempt to enhance the stability of liposomes by forming a covalently cross-linked polymer within the self-assembled bilayers of the vesicles.[84,85] Unilamellar vesicles that spontaneously form a single lipid bilayer sphere are particularly attractive templates for the synthesis of polymer nanoparticles or hollow nanocapsules as they are typically 50–100 nm in size, stable upon the inclusion of small hydrophobic monomers, and form a single-walled hollow sphere. Early work by Murtagh and Thomas explored this templating strategy using photoinitiation to polymerize styrene and divinylbenzene monomers within 40–100 nm vesicles, resulting in highly cross-linked polymer particles of similar dimensions.[45]

Photopolymerization has been explored to form stable vesicles for a number of years based upon significant advantages over other reaction mechanisms.[86] Foremost, the relative temperature independence allows the polymerization to be performed at the most stable temperature of the system, reducing morphological rearrangement of the vesicle structure.[84,87] Compared to thermal polymerization, the rapid initiation and polymerization rate inherent in photopolymerization may also allow the templated monomer to cross-link and stabilize within the vesicle bilayer on a more rapid time scale than phase separation of polymer from the template can occur, leading to a more direct replication of vesicle structure. Additionally, through the ability to shutter the light source and specify the intensity of the UV light, photopolymerization allows direct control over the degree of polymerization and rate of initiation in these systems.[88] This high degree of control over the reaction is particularly attractive in vesicle templating, as the polymerization can be tuned to the vesicle system and optimized in regards to template structure retention.

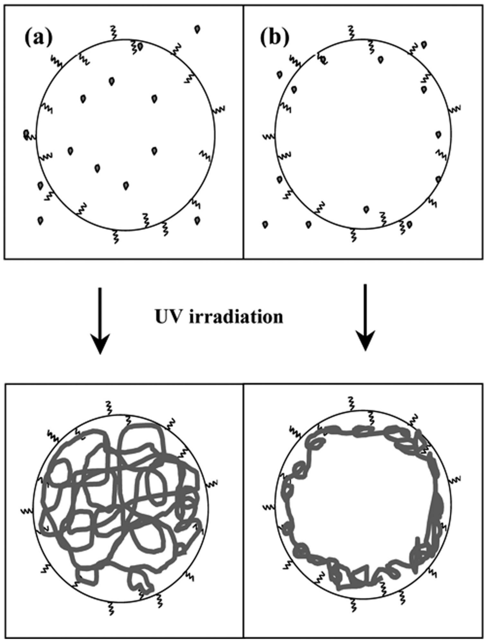

Figure 5. (a) Homogeneous distribution of photoinitiator in the vesicle leads to the formation of a polymer solid sphere. (b) Photoinitiator activated after immediate penetration through the liposomal membrane leads to the formation of a polymer hollow sphere. Reprinted with permission from ref 85. Copyright 2002 American Chemical Society.

A number of research groups have examined the use of vesicles as polymerization templates, investigating a variety of monomers, vesicle forming surfactants, and polymerization mechanisms.[11,26–28,88,89] In many reported cases, vesicle templating results in complete phase separation of the polymer from the vesicle bilayer, forming pure polymer beads attached to the larger vesicle structure.[60,89] However, many reports of vesicle templating using photopolymerization have demonstrated little to no disruption to the vesicle structure as well as enhanced properties and stability of the templated polymer system.[60,86,88,90] In one study, cross-linked copolymers of *N*-isopropylacrylamide (NIPAM) and tetraethylene glycol dimethacrylate (TEGDM) were photopolymerized within the inner monolayer of lipid vesicles. Becaused of the many advantages of photopolymerization described, the compolymerization of TEGDM and NIPAM resulted in minimal to no disruption of the vesicle, as postpolymerization TEM images confirmed the spherical shape and unilamellar bilayer structure of the template vesicle.[85]

In this particular study, anchoring specific monomers within the lipid bilayer of the templating vesicles also allowed the bilayer to serve as a permeation barrier for the photoinitiator, resulting in location-dependent photopolymerization near this membrane. Thus, the vesicles could be used to template both solid and hollow nanometer scale spheres depending on the location of the photoinitiator within each system. Figure 5 illustrates the schematic of how the temporal photoinitiator penetration through this membrane is thought to allow for the formation of photopolymerized hollow spheres using the vesicle template.[85] Finally, the stability of the polymer templated vesicles was significantly improved over pure EPC vesicles due to the presence of cross-linked polymer.

6. Liquid Crystal Templates

Liquid crystals (LCs) have been the focus of a great deal of recent research in polymer templating as their self-assembling geometries have shown promise as effective structure directing templates for polymerization reactions. Similar to polymerization in vesicles, the premise behind LC templating is to reinforce or replicate the structure of the LC-based template with a covalently linked polymer matrix. Extensive work in LC templating has been performed using both thermotropic LCs, in which the temperature of the system directs the order of the LC, or lyotropic liquid crystals, in which order is dictated by concentration effects. In both cases, photopolymerization is the polymerization mechanism of choice due to its many beneficial properties (temperature-independent reaction, rapid and controlled initiation) that are particularly well-suited for these templating applications.[14,15,61,62]

6.1. Thermotropic Liquid Crystal Templating. Thermotropic liquid crystals (TLCs) have primarily found use as polymer templates in polymer-stabilized liquid crystalline (PSLC) systems due to their unique anisotropy and order. PSLC systems are usually prepared by mixing a low-molar-mass liquid crystal and a photopolymerizable monomer into a uniform mixture. A particularly comprehensive review is available that covers the transfer of structure from the liquid crystal to the polymer network as well as the relationships between photopolymerization conditions and the resulting PSLC morphology.[91] Figure 6 depicts the formation of a PSLC system using photoreactive monomer.[91] The goal in polymeric/LC composites is to combine the advantages of the mechanical stability of polymers with the electro-optic properties of liquid crystals,[92] and thus a great deal of work has been devoted to the formation of ordered polymer networks from TLC templates. These studies generally conclude that TLC order, temperature, polymerization kinetics, solubility effects, and phase separation all play key roles in the resulting polymer network structure in PSLC systems.[91–95]

Adding to the complexity in TLC templated systems, many of the factors governing the templated network structure are not independent but rather closely interconnected, creating a dynamic system that ultimately directs the final polymer structure. For example, the order of the TLC system has proven to have a large influence over photopolymerization kinetics, increasing the polymerization rate when changing, for example, from an isotropic phase to an ordered smectic phase.[96,97] Monomer segregation and ordering in the liquid crystalline phases appear to be the primary factors responsible for the polymerization kinetic behavior observed in these systems. In PSLC systems, the liquid crystal not only acts as a structure-directing template but also allows the formed TLC composites to retain a degree of electro-optical functionality, an attribute that is often measured to gauge the performance of PSLC composites.[94,95]

Cholesteric liquid crystals (CLCs) have recently attracted considerable attention as templates for the creation of polymer-stabilized cholesteric liquid crystals (PSCLC) because of their potential applications in display technology, telecommunications, and fiber optics.[33,34,98–100] Figure 7 shows SEM pictures of PSCLC diffraction gratings in which the periodic structures are formed from polarized photopolymerization of a reactive monomer within the liquid

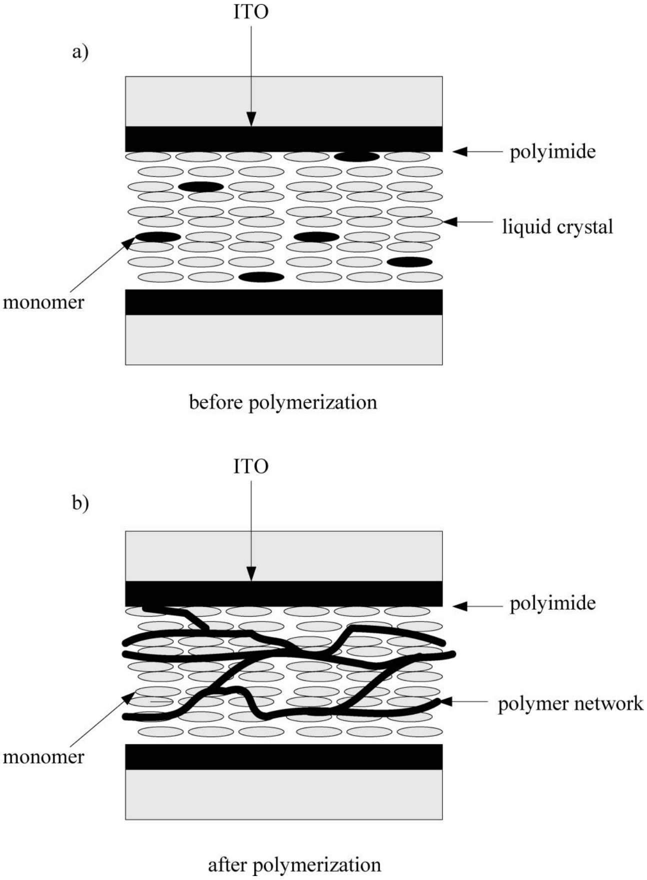

Figure 6. Schematic illustration of the fabrication of PSLCs. (a) Photoreactive monomers dissolved in a LC before polymerization. (b) Polymer network stabilizing the LC orientation after polymerization by UV irradiation. Adapted with permission from ref 91. Copyright 2000 Wiley-VCH Verlag GmbH & Co. KGaA.

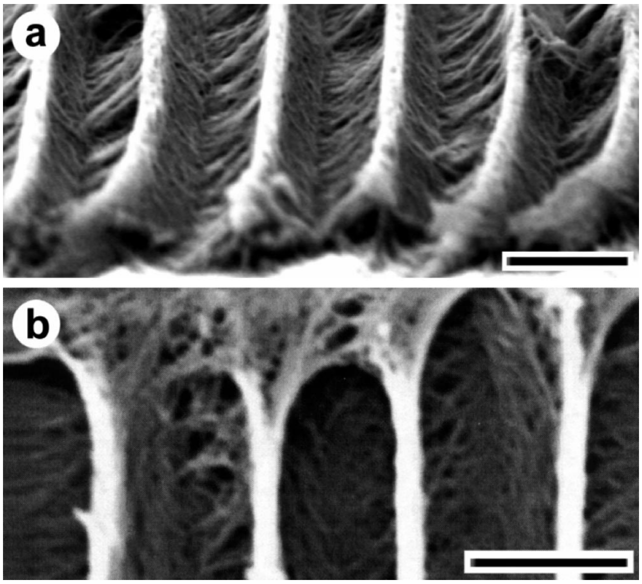

Figure 7. (a) SEM view of the RM257 polymer network profile between the substrates for PA-polarized UV cure. (b) Same as (a), except for PE-polarized cure. Reprinted with permission from ref 99. Copyright 2000 American Institute of Physics.

crystal director.[99] In recent studies, the growth mechanism in PSCLCs has been extensively investigated, leading to a proposed mechanism in which the cross-linking monomer reaches a critical molecular weight and then phase separates from the low-molar-mass LC template.[32,34] As part of the larger TLC family, the morphology of CLC templates and the resulting PSCLC composites are highly dependent on temperature, a factor that will influence solubility and phase separation during polymerization. In general, increasing the curing temperature results in PSCLC networks that are characterized by larger network mesh sizes.[93] Thus, the ability to control the temperature of the polymerization during PSCLC formation makes photopolymerization particularly attractive for these systems.

Similar to the thermodynamic behavior, the kinetic behavior of the PSCLC templated polymerization reactions will also influence phase separation in these systems and have a large influence over the morphology of the resulting materials.[32,95] For example, Dierking and co-workers found that by decreasing curing intensities and thereby reducing the rate of photopolymerization in a PSCLC system, polymer networks result with smaller average mesh sizes than if higher curing intensities are used. Because of the thermodynamic and kinetic influences on structure, it is not surprising that photopolymerization is predominantly used in the study and generation of PSCLCs in which the temperature and kinetics of the polymerization reaction may be closely controlled. In addition to temperature and kinetics, the molecular structure of the monomer and the interaction between the monomer and the LC component in the PSCLCs have all been shown to play an important role regarding the resulting polymer structure and electro-optic performance of these materials.[32,94,95]

Additional photopolymer LC template research has focused on the generation of polymer-stabilized ferroelectric liquid crystals (PSFLCs). Work in this area has primarily focused on the influence of adding a photopolymerizable monomer to the FLC on both the performance and electro-optic properties of the resulting polymer templated composites.[101] Similar to the LC templated polymerizations above, the photopolymerization rate was found to be higher in ordered FLC phases compared to isotropic phases.[102–104] Interestingly, decreasing the temperature of the system elicits increases in the polymerization rate, atypical behavior in most bulk polymerizations. Rather, the observed increase in polymerization rate was attributed to the increased order that is present in these systems at lower temperatures. In one particular study, monomers with different functionalities and structures were photopolymerized in both FLC and isotropic phases to determine the direct mechanism behind the anomalous rate behavior.[102] It was shown that increasing the order of the polymerization media, particularly at lower conversions, does not have an effect on the propagation rate constant, but rather decreases the termination constant considerably, driving the higher polymerization rates in the ordered FLC mesophases.

It was also demonstrated that monomer structure has an effect on the spatial organization of monomer−LC mixtures prior to polymerization and thus affects the polymerization kinetics.[96] For example, monomers with a structure similar to the FLC-directing mesogens tend to orient themselves with the LC molecules. On the other hand, nonmesogenic small molecules tend to segregate parallel to the layers in sheets as shown for a smectic phase. Furthermore, trends in electro-optic behavior have been found to be dependent on the type of polymer and polymerization conditions including the system temperature and the degree of cross-linking.[103,104] The electro-optic properties of PSFLC systems are influenced by the resulting morphology of these composites, suggesting that the optimization of these systems can be accomplished by using the appropriate monomer/FLC mixtures and polymerization conditions.[105]

Building on the kinetic studies of polymer/liquid crystal systems, much research has focused on understanding the polymer nanostructure evolution during the photopolymerization process. In these studies, varying the monomer used seems to have a large effect on not only the polymerization kinetics but also the resulting polymer/LC composite structure.[106] For example, fluorinated monomers exhibit enhanced polymerization rates compared to analogous aliphatic monomers even though each of these monomers segregate between the smectic LC layers before photopolymerization. Furthermore, it was observed that the network structures of cross-linking aliphatic and cross-linking fluorinated diacrylate monomers phase separate from the LC, whereas linear fluorinated polymers remain between the smectic layers and retain the prepolymerized order of the LC. It is hypothesized that the low surface energy of the linear fluorinated polymer decreases the driving force for phase separation from the liquid crystal template.[107] In a separate study, it was found that photopolymerizing *n*-decyl acrylate polymer within an isotropic LC phase results in low molecular weight chains compared to the generation of larger molecular weight chains using ordered nematic or smectic LC phase templates. By relating the low polymerization rates in the isotropic phases to the molecular weight and employing ^{1}H NMR, it was found that the decrease in molecular weight in the isotropic phase is mainly due to chain transfer effects.[108]

6.2. Lyotropic Liquid Crystalline Polymer Templating. In polymer templating within lyotropic liquid crystalline (LLC) media, the influence of the ordered media on polymerization kinetics and the subsequent relationship between kinetics and evolution of polymer structure have been central themes over the past few decades. Figure 8 depicts the general process of LLC templating using a nonreactive Brij 56 surfactant blended with a nonmesogenic photo-cross-linking monomer, poly(ethylene glycol) diacrylate (PEGDA).[109] Photopolymerization is widely used in LLC templating applications and thought to play a crucial role in the use of this media as a structural template. For example, the extremely rapid initiation rate inherent in photopolymerization has been suggested to enable better template structure retention by allowing the growing polymer to undergo significant cross-linking before phase separation can occur.[7,110,111] Furthermore, the ability to closely track the

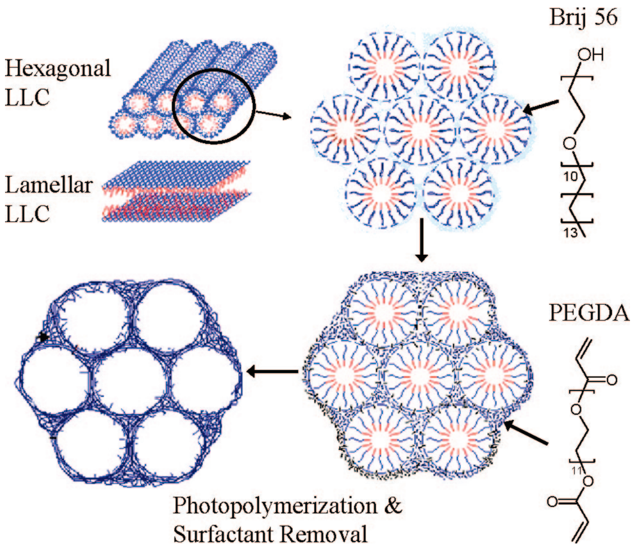

Figure 8. Representative LLC templating process, clockwise from upper left: hexagonal and lamellar LLC mesophase structures, 2D hexagonal LLC with Brij 56 surfactant chemical structure, 2D hexagonal LLC with dispersed PEGDA monomers, and photopolymerized PEGDA in continuous hexagonal arrangement with Brij 56 surfactant removed. Reprinted with permission from ref 109. Copyright 2007 American Chemical Society.

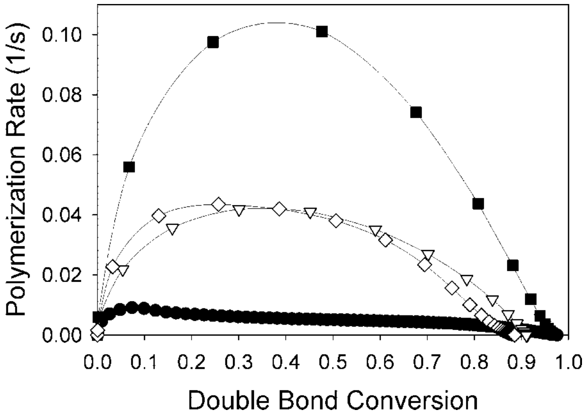

Figure 9. Polymerization rate of 25 wt % acrylamide at 25 °C with increasing Brij 58 concentration in water as a function of double-bond conversion. Shown are 0% isotropic (●), 20% micellar (▽), 40% bicontinuous cubic (■), and 70% inverse micellar (◇) Brij 58. Reprinted with permission from ref 42. Copyright 2003 American Chemical Society.

behavior and kinetics of the reaction allows photopolymerization to be used as a tool to probe the generation of structured networks within various LLC template morphologies.[108]

The influence of confined order on polymerization kinetics has been well documented in the past few decades, demonstrating significant deviations from traditional isotropic polymerizations.[114,115] In one particular study, the photopolymerization of acrylamide within a highly ordered bicontinuous cubic LLC template elicits a 10-fold increase in polymerization rate over isotropic solutions under the same conditions.[42] Figure 9 shows the significant increase in polymerization rate for the ordered polymerization of acrylamide templated within a bicontinuous LLC. Not coincidentally, independent reports have shown that photopolymerizations of acrylamide in bicontinuous cubic phases yield polymer gels that retain the original structure of the LLC, whereas polymerizations in other template geometries result in phase separation and a lesser degree of structure retention.[40]

The interesting effects of confined order on the polymerization kinetics of LLC templated systems has been further explored using a variety of different LLC mesophase geometries to template both polar and nonpolar monomers. In recent studies, it was found that nonpolar monomers segregate within the oil-soluble domains of LLC templates, exhibiting the highest polymerization rate in the micellar phase and lowest in the lamellar phase.[110] As the template transitions from micellar, to hexagonal, and finally to lamellar morphology, the size of the oil-soluble domains increases causing the localized double bond concentration within each domain to decrease, thus lowering the overall rate of polymerization. Further evidence supporting this theory is provided by photopolymerization of polar monomers within the hydrophilic domains of LLC mesophases in which the opposite trend is observed with polymerizations in the lamellar phase exhibiting the fastest rate.[110]

In addition to monomer partitioning, the segregation and mobility of polar and nonpolar photoinitiators of different size and chemistry have also been found to play an important role in directing the photopolymerization kinetics in LLC media. For example, a study using a bulky hydrophobic photoinitiator with nonpolar monomers observed the polymerization rate to increase with increased LLC template order, a trend that is opposite from that described previously regarding monomer partitioning.[112,113] The reverse trend is attributed to the increased initiator efficiency of the bulky photoinitiator in lamellar LLC morphologies that controls the polymerization kinetics in the system.

Based on these kinetic studies, an appreciation of the complexities inherent in photopolymerization within LLC ordered media is gained as both monomer and initiator chemistry, mobility, and location have all been found to play a significant role in determining the polymerization kinetics within the ordered templates. In the context of LLCs as templating agents for polymerizations, kinetic understanding is necessary as the relationship between LLC order and polymerization kinetics is hypothesized to be vital to the process of using these templates to generate a successful replication of structure within each particular polymer system.[40,110,111] Numerous reports have directly tied photopolymerization kinetics and structural development in LLC templated systems. For example, Lester and others found that the degree of structure retention of a cationic monomer mixed with its analogous LLC forming surfactant dodecyltrimethylammonium bromide (DTAB) was highly dependent on whether the template was of hexagonal, bicontinuous cubic, or lamellar geometry.[115] In this study, the fastest polymerization occurred in the lamellar LLC template which also showed the highest degree of structure retention. Although also showing evidence of parent template nanostructure, the slower polymerizing hexagonal and bicontinuous cubic templated networks exhibited slight changes from the original structure.

Additional studies investigating the relationship between kinetics and structural evolution in LLC templated polymers

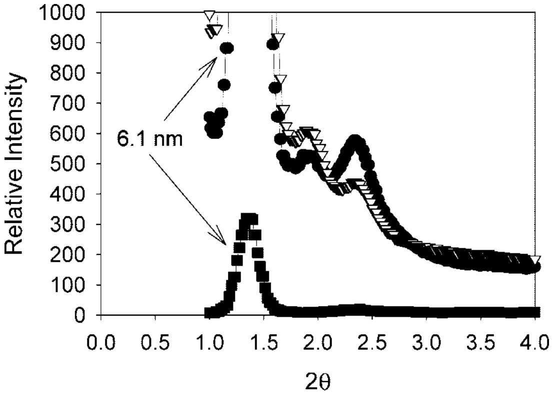

Figure 10. SAXS profiles at 25 °C of 25% acrylamide in the bicontinuous cubic phase of 40% Brij 58/water unpolymerized (●), photopolymerized at 25 °C (▽), and thermally polymerized at 60 °C (■). Reprinted with permission from ref 42. Copyright 2003 American Chemical Society.

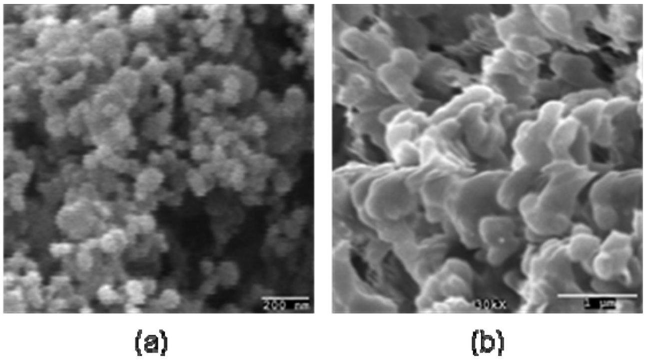

Figure 11. SEM image of polyacrylamide cured using (a) photoinitiators and (b) thermal initiators in the hexagonal phase of 60 wt % Brij 56 in water. Images were taken after extraction of surfactant and water. Reprinted with permission from ref 46. Copyright 2006 American Chemical Society.

have directly contrasted the rapid initiation of photopolymerization with slower thermally polymerized templated systems. One particular study examining the polymerization of acrylamide in various LLC mesophases observed considerable decreases in the small-angle X-ray scattering (SAXS) peak intensity profiles when the system was polymerized thermally as opposed to photochemically.[42] Figure 10 shows the SAXS profiles of bicontinuous LLC templated acrylamide polymerized using both photoinitiation and thermal initiation. In Figure 10, the significant reduction in scattering intensity as well as the loss of the secondary peaks in the thermally cured sample is reported to indicate a significant loss of template structure compared to the photopolymerized case.

In a similar study, also polymerizing acrylamide within the bicontinuous cubic LLC mesophase, SAXS and scanning electron microscopy (SEM) images indicate a greater loss of liquid crystalline order with the thermally polymerized samples.[46] Since both photoinitiated and thermal initiated polymerizations were performed at the same temperature in this study, the enhanced structure retention using photopolymerization was solely attributed to the enhanced kinetics of this type of reaction. Figure 11 shows SEM images of polyacrylamide polymerized within a hexagonal LLC using both thermal and photoinitiation methods. The enhanced resolution and definition of the structures in the photopolymerized LLC templated system are clearly observed in this figure as well as the much smaller feature size compared to the thermally polymerized system.

Additional results also explored the effect of increasing the temperature at which the photopolymerization took place from 25 to 80 °C (near the clearing temperature of the bicontinuous cubic LLC template).[46] Even though the cubic LLC phase was still intact at these high temperatures, the phase is less stable with more mobility in the ordered aggregates. Consequently, SAXS and SEM images of the templated acrylamide indicate a significant decrease in structure retention and a less defined polymer/surfactant interface when the photopolymerizations were carried out at temperatures approaching the transition to an isotropic phase. These studies directly illustrate the advantages of photopolymerization in LLC templating including rapid kinetics and the ability to polymerize at a temperature at which the template is most stable, resulting in nanostructured polymers that retain the original template order.

In addition to the kinetic/structural investigations during photopolymerization within LLC templates, much work has focused on inducing thermal or mechanical stability in LLC polymer composites postpolymerization as well.[116–120] In fact, the enhanced thermal or mechanical stability of these systems is often used as evidence of structure retention in polymer/LLC composites. Early studies regarding LLC mechanical reinforcement focused on unique liquid crystal forming cellulose derivatives in which anisotropy is induced by mechanical shearing, although the system inevitable returns to an isotropic state after a period of time.[116–120] Researchers found that by incorporating acrylic or methacrylic acid within these liquid crystal templates, the original birefringent pattern of the nanostructured template was not only retained upon photopolymerization, but the ordered polymer network served to disallow the relaxation of the liquid crystal back to an isotropic state. In addition to mechanical stability, many studies have demonstrated enhanced thermal stability of LLC systems using photopolymerized polymers to reinforce the orientation of the LLC assemblies. In a particular study incorporating both polar and nonpolar monomers into self-assembling Pluronic LLCs, McCormick and co-workers found that the parent template structure is not only retained postpolymerization, but the birefringent texture of the polymerized LLC composite is present at temperatures 30–60 °C above the natural clearing temperature of the prepolymerized systems.[63,108] Interestingly, the degree of structural reinforcement and enhanced thermal stability was found to be more dependent on whether the monomer was in the continuous phase of the LLC template as opposed to following the kinetic trends mentioned previously.

In applications that employ liquid crystals as polymerization templates, one of the key challenges is preserving the highly ordered structure of the parent template within the growing polymer network. The growing polymer chains in LLC templated systems will affect the thermodynamic stability of the lyotropic phase, often resulting in phase separation and the destruction of the nanometer scale order of the template.[41,49] Furthermore, confining the geometry of a cross-linked polymer network to the high degree of orientation of the LLC comes at a high entropic cost, usually decreasing the stability of the templating system.[44,52] However, studies using photopolymerization within LLC media provide optimism that, through a greater understanding of polymerization kinetics within LLC ordered phases, greater control over the structural evolution of the templated polymers may be realized. In addition, many of the cases mentioned in this review provide evidence that photopolymerization is advantageous over other mechanisms in reducing phase separation and retaining the LLC orientation in the generated polymer.

In an effort to restrict phase separation and its detrimental effects on templated structure, researchers have begun to explore polymer templating techniques using more mechanically stable forms of highly ordered LLC systems. For example, Co and others have recently shown that microemulsions of surfactant, oil, and sugar formulations can be readily processed into solid complex glasses with robust and controllable nanostructures.[119–121] By replacing the oil in these systems with an oily cross-linking monomer such as divinylbenzene (DVB), the glassy sugar formation can be used as a template to photopolymerize DVB into a polymer network with specific nanostructured architecture. As opposed to liquid crystalline templates, monomers in these studies are essentially polymerized within a solid crystalline nanostructured template that is able to withstand the phase separation forces that arise during polymerization.

Considerable work has focused on the self-assembling phase behavior of various sugars and surfactants suspended in oil.[121] Similar to aqueous LLC systems, mesophase and structure formation in these systems are largely dependent on surfactant type, concentration, system temperature, and sugar loadings. Though a variety of templating mesophases are possible, studies to date have primarily concentrated on bicontinuous sugar-based emulsions to structure growing polymers within a glassy template. Post polymerization, the sugar microemulsion template can be easily removed by dissolution in water. Interestingly, it was discovered that when a non-cross-linking and low glass transition temperature (T_g) monomer such as isobutylacrylate is used as the polymerizing constituent, the pores of the structured polymer collapse upon removal of the sugar template. However, the inclusion of a higher T_g, cross-linking polymer such as DVB results in polymerized networks that do retain nanostructured porosity after the template is removed.[119,120] Overall, these studies demonstrate that photopolymerization of DVB within a bicontinuous solid microemulsion is able to create organic polymeric membranes with nanometer scale pores by limiting phase separation during the templating process.

In yet another area of LLC templating, polymerizable surfactants can be assembled and photo-cross-linked into LLC geometries that have found use as templates for subsequent templated polymerizations. Studies in this area have primarily focused on the use of surfactants with vinyl functionality that readily assemble and can be photopolymerized into an inverse hexagonal (H_{II}) LLC phase with well-defined open pore structure.[35,36,122–125] Again, photopolymerization plays a key role in these systems, although in this case it facilitates the formation of the template itself rather than acting as the templating mechanism. The primary goal of this research is to employ the nanometer size domains of the organic host template to elicit property or catalytic enhancements on the polymerization that takes place within the ordered molecular arrays of the original LLC polymer. For example, as poly(phenylenevinylene) (PPV), a luminescent conjugated polymer, was templated within the porous channels of an inverse hexagonal polymerized LLC, an enhanced photoluminescence quantum yield with long-term stability was observed due to chain isolation and protection effects.[126] The improvement in photoluminescence behavior observed over traditional bulk polymerizations of PPV may direct these LLC templated nanocomposites toward a number of potential applications including light-emitting diodes.[36]

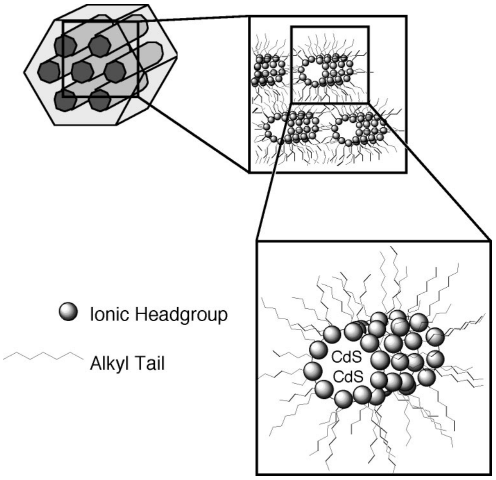

Figure 12. Templated formation of CdS particles within a polymerized liquid crystalline template. Reprinted with permission from ref 127. Copyright 1998 American Chemical Society.

Various reports have also explored the synthesis of inorganic species within the channels of a polymerized LLC template. In one such example, the confined nature and size constraints of the organic LLC photopolymerized template were found to directly influence the conversion and production of silica from the condensation of $Si(OEt)_4$.[127] In this study, only partial conversion was achieved after photoacid-catalyzed condensation compared to the full conversion typically obtained from nontemplated bulk systems. Similar template-mediated polymerization results were obtained for the production of CdS nanoparticles, behavior which was attributed to the expected diffusion limitations of additional monomer into the nanoscale pores of the H_{II} phase templating polymer. Figure 12 depicts the templated generation of CdS particles formed within the templated domains of an inverse hexagonal polymerized LLC formation.[127] These studies provide a basis for the synthesis of new inorganic and organic functionalized materials within the channels of LLC templates, highlighting the catalytic enhancements, reactant selectivity, and polymerization behavior within this unique environment.

In addition to generating controlled nanoscale porosity or sites for second-generation templated polymerizations, a primary goal of polymer templating using LLCs is to access control over the structure of a polymeric material on the nanoscale in an effort to enhance the properties of the polymer. It is expected that imposing a high degree of order on the nanometer size scale within a polymeric material will have direct implications on the overall physical properties of the polymer.[111,128] Furthermore, because of the significant changes observed in network structure by varying the particular LLC template, it is not surprising that researchers have observed very different polymer properties that are specific to the template that was used to structure each gel.[45,61,105,123] For example, one particular study found that templating a linear *n*-decyl acrylate within discontinuous cubic, hexagonal, and lamellar DTAB LLC mesophases results in specific changes in the molecular weight of the templated polyacrylate chains.[112] Thus, by dictating the template structure, a degree of control over the reaction, the resulting polymer molecular weight, and ultimately the physical properties of the templated polyacrylate is achieved.

Property control has also been explored with cross-linked hydrogels, templating polar monomers such as acrylamide, 2-hydroxyethyl methacrylate (HEMA), or poly(ethylene glycol) diacrylate (PEGDA) within the continuous domains of various LLC mesophases. Similar to the molecular weight study described, specific LLC mesophases elicit separate and significantly different properties compared to other template geometries or isotropic samples.[63,109,112,128] In one set of studies, a polyacrylamide gel templated with a bicontinuous cubic LLC structure was found to have a 10% increase in the maximum percentage of water uptake along with a 3-fold increase in compressive modulus over isotropic gels polymerized under the same conditions.[128] In this case and most LLC templating applications, the surfactant from the bicontinuous cubic template is removed, rendering the templated and isotropic gels chemically and compositionally equal prior to physical tests. Thus, the swelling and modulus differences between the two cases may be solely attributed to the templated architecture of the structured acrylamide gel. Furthermore, it is important to note that the simultaneous increase in both water uptake and the modulus of cross-linked acrylamide hydrogels in this study is atypical behavior in hydrogel engineering, demonstrating another unique result of nanostructured templating with LLCs. In fact, the modulus and water uptake in traditional isotropic hydrogels are often found to be interconnected, whereas increases in one property will directly compromise the other.[129,130]

Additional studies exploring the structure/property relationships of templated hydrogels have documented a 5−7-fold increase in surface area and a 4−5-fold increase in permeability as polyacrylamide and PEGDA hydrogels were photopolymerized within the highly ordered geometries of hexagonal, cubic, or lamellar structured LLCs.[46,110] These findings further demonstrate that the nanostructured aggregates of the liquid crystal, whether bicontinuous cubic, hexagonal, or lamellar in structure, dramatically increase the porosity of the resulting gel through polymerization within each template. In addition to the property enhancements observed with structured hydrogels, LLC templating also offers a degree of control over the properties of these materials. A recurring theme in the structure/property studies with templated hydrogels is that typically each templating geometry elicits a significantly different physical property.[46,63,109,128] Since the template can be closely controlled through surfactant concentration and reaction conditions, the physical properties of the gel can be modulated simply by specifying which LLC phase template to use. For example, Figure 13 demonstrates the relationship between LLC templated structure and the half-life release rate of a dye from PEGDA gels templated with various LLC mesophases.[109]

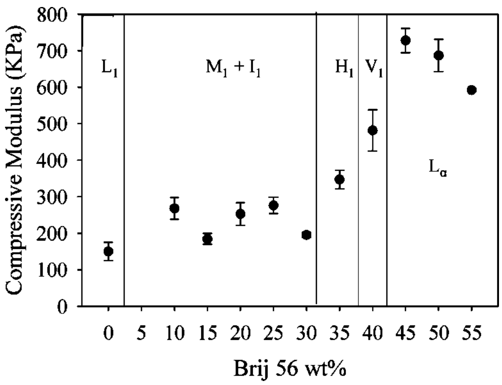

Figure 13. Release time required for Chicago Sky Blue dye from cross-linked 40 wt % PEGDA samples with increasing concentrations of Brij 56 surfactant to create specific polymer templated gels: L_1 = isotropic, M_1 = micellar solution, I_1 = micellar cubic phase, H_1 = hexagonal phase, V_1 = cubic phase, and L_α = lamellar. Surfactant is removed prior to release experiments. Reprinted with permission from ref 109. Copyright 2007 American Chemical Society.

Finally, the process of LLC templating biodegradable polymers has recently been explored.[131] In one study, the degradation time of a common biodegradable poly(lactic acid)−poly(ethylene glycol) (PEG−PLA) cross-linked hydrogel templated with a nanostructured lamellar LLC template was found to degrade in half the time required of the traditionally fabricated, isotropic biodegradable gel. The increased degradation rate over the isotropic gel was attributed to the increased swelling of the templated hydrogel, bringing in more water to cleave hydrolyzable PLA segments, as well as increased porosity due to templating effects, allowing degradation products to elute much faster from the templated hydrogel system. Again, since the templating surfactant is removed and both cases are polymerized under the same conditions, the biodegradation variance between the templated and isotropic hydrogels in this study was solely attributed to the altered network structure of the lamellar gel. Overall, the ability to closely control the properties of a hydrogel or polymer in general, such as porosity, swelling, modulus, and degradation, is one of the more promising aspects of LLC templating as this technique may be used to tailor and enhance the properties of a polymeric material without requiring the cost and resources of synthesizing new monomers.

7. Conclusions and Outlook

Polymer templating methods have evolved tremendously in recent years as researchers endeavor to gain structural control over polymerization reactions toward the generation of functionally advanced materials. This review covers some of the main strategies and recent developments in polymer templating while focusing on research that incorporates photopolymerization in the templating process. The templating strategies discussed include linear polymer chain templating, particle dispersion templating, molecular imprinted polymers, templating in vesicles, and templating within liquid crystal surfactant assemblies. Photopolymerization holds many advantages in polymer templating over other reaction mechanisms including temperature independence and rapid kinetics as well as a highly controlled polymerization in terms of rate, degree of polymerization, and spatial initiation. Additionally, photopolymerization not only is well-suited for and widely used to perform templating reactions but also can be effectively used as a tool to probe the kinetic behavior and structural evolution of the templated polymer structure. One of the general themes in polymer templating is that greater understanding and control over the polymerization reaction in terms of kinetics and polymer growth are critical toward the successful transfer of structure and organization from the template to the polymeric network. Numerous milestone achievements have been reported in templated photopolymers including enhancements in molecular weight and tacticity, generation of highly selective membranes, realization of highly specific induced network morphology, and the ability to direct and enhance the properties of templated polymeric materials.

Recently, polymerizations within highly organized mesoscale templates have been investigated as a potential processing method for nanostructured polymers with well-defined and controlled network architectures. This is an area with tremendous growth potential as templating is able to provide a simple and economic pathway toward the generation of nanostructured organic polymers with advanced properties. The combination of templating and photopolymerization is particularly well suited for growth in the biomedical arena[132] as nanostructured biomaterials may be able to address some of the highly complex biomaterial requirements that are constantly arising in tissue engineering and drug delivery applications. Already, ordered mesoporous materials generated using surfactant templates have been investigated to replace highly complex tissues such as bone and cartilage.[133] Similarly, polymer delivery vehicles templated using nanoscale self-assembled vesicles have demonstrated potential for advanced drug delivery applications.[26,27] In these endeavors, photopolymerization will continue to play a key role in the fabrication of nanobiomaterials through templating pathways.

The continued study of the kinetic and environmental influences on structural evolution in templating applications will lead to greater control over the templating process and result in polymeric materials with finely tuned architectures and properties. Photopolymerization will play a crucial role in this process, allowing enhanced control over the templated polymerization reaction as well as identifying the kinetic parameters and environmental conditions that lead to successful template structure transference. In turn, optimization of templating using photopolymerization will allow polymer templating to play a significant part in meeting the ever-growing demand for advanced functional materials that can be processed using simple and inexpensive methods.

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