

Templating hydrogels

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Abstract Templating processes for creating polymerized hydrogels are reviewed. The use of contact photonic crystals and of non-contact colloidal crystalline arrays as templates are described and applications to chemical sensing and device fabrication are illustrated. Emulsion templating is illustrated in the formation of microporous membranes, and templating on reverse emulsions and double emulsions is described. Templating in solutions of macromolecules and micelles is discussed and then various applications of hydrogel templating on surfactant liquid crystalline mesophases are illustrated, including a nanoscale analogue of colloidal crystalline array templating, except that the bead array in this case is a cubic array of nonionic micelles. The use of particles as templates in making core-shell and hollow microgel beads is described, as is the use of membrane pores as another illustration of confinement templating.

Keywords Hydrogel · Templating · Photonic crystal · Emulsion templating · Double templating

Introduction

The syntheses of novel zeolites and nanoporous materials by templating on surfactant mesophases has been well established and very extensively reviewed [1–4]. The dynamic range in pore size is controlled by the length scale of the surfactants used in the templating, and typically are limited to lengths less than 100 nm and more usually to less than 30 nm.

Advances in pore size control were obtained when it was found that photonic crystals derived from bead arrays [5] and random bead arrangements [6] could be used to template diverse nanoporous, mesoporous, and microporous materials. Here the bead diameter controls the length scale of the final pores obtained.

In both of these approaches, the underlying templates provide a negative image of the final pore structure and the interstices constitute the volumes that are filled with a new phase during the initial stages of the templating chemistry. Almost any conceivable phase may be inserted in mesoporous to microporous bead assemblies [7, 8]. Once the interstices are filled with a new phase, the templating phase, surfactant mesophase, or bead assembly, are removed by dissolution or by pyrolysis. If the templating phase is a metal oxide, it is usually dissolved by aqueous HCl or other acid (aqueous HF in the cases of silica and titania); if the templating phase is a polymer that dissolves (such as polystyrene (PS) in toluene) the composite is subjected to dissolution by being placed in a solvent bath. If the templated phase is inorganic and thermally robust, a polymeric templating phase is removed by pyrolysis. The filling of mesophase interstices by organic polymerization has recently been reviewed [9–10].

In this review we focus upon templating involving polymeric organic hydrogels. Hydrogels are important

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classes of composite materials for many reasons. Foremost among these is the utility hydrogel coatings provide in facilitating interfacing synthetic materials with biological tissues [11]. No less importantly is the role hydrogels play in drug delivery systems, particularly in retarding the adsorption of proteins onto injected and implanted surfaces. Hydrogels also offer diverse applications in device fabrication and in chemical and physical testing.

Templating on photonic crystals

We consider two general types of photonic crystals fabricated by bead assemblies. The first is the type wherein the beads are in physical contact with their nearest neighbors (12 nearest neighbors in the fcc or in the hcc structures). This type of structure offers the greatest number of degrees of freedom in producing new materials. We denote such systems as “contact” photonic crystals, since nearest neighbors are in physical contact with each other. The second type of photonic material we examine is derived from crystalline arrays of charged beads, where nearest neighbors do not physically contact one another. These materials are known as colloidal crystalline arrays, CCA. In this type of material the beads also adopt an fcc or bcc lattice structure. Such arrays of charged beads form under stringent conditions of low ionic strength in aqueous suspension or in other solvents. Charge repulsion between such beads induces crystallization.

One of the chief limiting factors in utilizing photonic crystals of the first type is the tremendous activation present in their crystallization or 3D assembly. Debord and Lyon [12] used the thermal responsiveness of hydrogel particles in an attempt to circumvent some of this activation. Centrifugation was used to physically concentrate the particles, and then this concentrate was subject to a number of heating and cooling cycles. The PNIPAM poly (*N*-isopropyl acrylamide) hydrogel is known to condense or compress upon heating and it expands upon cooling. These cycles provided thermally induced mechanical annealing and greatly increased the crystallinity of the concentrated assembly.

3D contact photonic crystal templating Takeoka and Watanabe [13] used silica (contact) photonic crystals to template crosslinked hydrogels. *N*-isopropylacrylamide (NIPAM) and methylene bisacrylamide (MBA) were dissolved in 1,4-dioxane and perfused through air-dried silica photonic crystals and then polymerized using benzoyl peroxide as thermal initiator. After polymerization was completed, these silica-hydrogel composites were soaked in 5% aqueous HF to dissolve the templating silica. The resulting hydrogel with periodic structure (a reverse opal

structure of voids left by the silica) exhibited structural colors resulting from Bragg reflections in the visible. Due to the changes in refraction index at hydrogel/void boundaries, these gels mostly were opaque to transmitted light, but iridescent to reflected light because of this periodic (photonic crystal) structure. This iridescence is illustrated in Fig. 1. Silica particles of 0.5, 4, 6, and 10 μm diameter were used in preparing templating photonic crystals and subsequently templated hydrogels. Optical micrographs proved the periodic structures of the final hydrogels [13]. The porous structure greatly facilitated volume equilibration of these templated gels, in comparison to bulk gel samples, when subjected to changes in temperature. The authors observed facilitated equilibration to the volume changes occurring at a rate 1,000-fold faster for the templated gels. The periodic porous structure was retained on thermal cycling through the volume phase transition domain.

Contact photonic crystals built from 450-nm diameter polystyrene beads were grown in a flow cell [14]. The resulting crystals were used to template polyacrylamide by infusing aqueous 47.9% acrylamide, 3.8% methylene bisacrylamide, and 0.4% diethoxyacetophenone (photo-initiator) solution into the interstices. UV irradiation was used to drive polymerization. The templating beads were removed by soaking in toluene. The resulting inverse opal hydrogel is soft but has a sufficiently strong modulus that it can be handled. Its reflectance spectrum in the visible shifts with humidity, as the hydrogel equilibrates at different water uptakes and swelling states as humidity varies. This photonic material can thus be used as a relative humidity

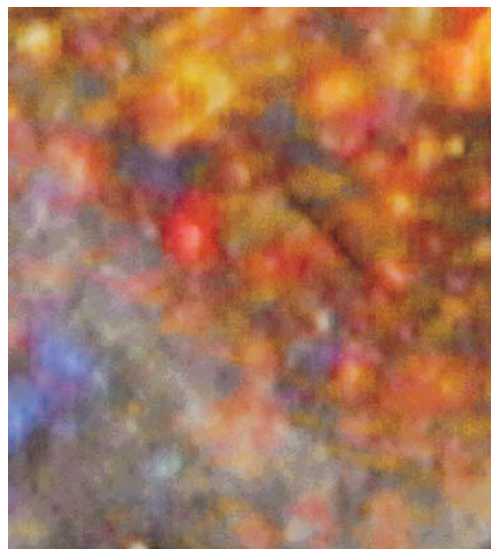


Fig. 1 Iridescent color resulting from the diffraction and scattering of visible light by the periodic structure of the PNIPAM/bisacrylamide crosslinked gel. Reproduced by permission from [14]; copyright 2002 by the American Chemical Society

sensor. Similar hydrogel sensors templated on contact photonic crystals were used by Braun and coworkers to fabricate colorimetric pH [15] and glucose [16] sensors. Recently Matsubara et al. fabricated temperature sensitive hydrogels using similar inverse opal templating methods for crosslinked PNIPAM hydrogels that also incorporated monomers bearing azobenzene groups, making the hydrogels photoresponsive [17].

2D contact photonic crystal templating A very interesting double templating method for preparing 2D arrays of microgel beads was demonstrated by Sakai et al. [18]. A hexagonally close-packed array of silica beads (the first template) was produced by simple drying of an aqueous suspension of monodisperse silica beads. After drying, this monolayer was infused with styrene so that the styrene film just covered the bead monolayer. This styrene was then polymerized using thermal initiation over 30 h at 40 °C. This silica-polystyrene film was then soaked in 5% aqueous HF to dissolve the silica, and to produce the second template, the polystyrene encased negative image of the silica bead hexagonal array. A glass slide is then activated by coating with a silane-propylmethacrylate layer. The air-dried polystyrene template is then filled with NIPAM and MBA in ethanol, containing a photoinitiator (2,2-dimethoxy-1,2-diphenylethan-1-one; Irgacure 651), sandwiched to the activated glass slide, and polymerized under a UV lamp. The polystyrene template was then removed by dissolving it in toluene and the crosslinked hydrogel was soaked in water. Because of the glass slide activation, the monolayer of hexagonally arranged microgel beads is chemically attached to the slide. When the beads are subjected to temperature cycling they swell to very tightly pack at, for example, 20 °C, and shrink to separated beads at high temperature (40 °C) (Fig. 2).

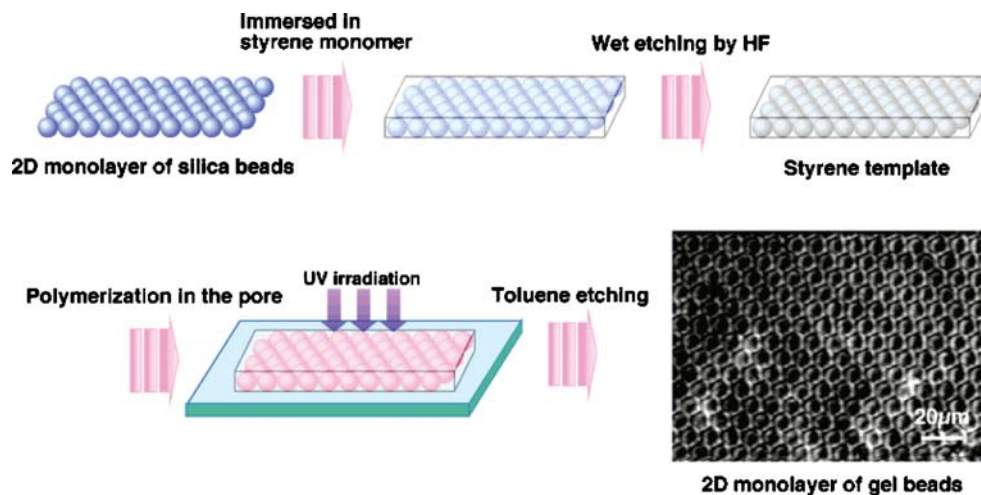
It is noteworthy that Tsuji and Kawaguchi [19] developed an alternative method to produce monolayers of

microgel bead arrays. In their work the separation distance between beads was controlled by the length/thickness of a surface layer of hairy polymer.

3D templating on colloidal crystalline arrays Asher and coworkers in an extensive body of work have shown that fcc colloidal crystalline arrays of submicron to multimicron diameter beads may be imparted a solid modulus by polymerizing hydrogels in the aqueous spaces between the beads [20]. While such CCA have been known for some time [21, 22], it was the templating of hydrogels provided by Asher and coworkers that have made such CCA much more useful, since they now can be handled as soft solid materials.

Because of the suspension and fluidic nature of CCA, thermally initiated polymerization of hydrogels in the aqueous fluid phase generally is too disruptive to the crystalline array and leads to unsatisfactory degradation of crystalline order among the beads. For this reason UV irradiation has usually been used to effect hydrogel polymerization. This need has been partially overcome by using PS particles that contain superparamagnetic iron oxide nanoparticles and a locally applied magnetic field gradient [23]. The charged PS/iron oxide composite particles self assemble into CCA in deionized water, but the packing is significantly affected by proximal magnetic field gradients. A locally applied uniform magnetic field was found to induce interparticle magnetic moments that produced a repulsive force in the plane perpendicular to the magnetic field and an attractive force in the direction parallel to the field [24]. This innovative use of applied fields makes it possible to obtain CCA self-assembly under high ionic strength conditions, when crystallization would otherwise not be obtained due to insufficient repulsion between beads. Foulger and coworkers introduced the use of PEG-based hydrogel monomers as alternatives to acrylamide-based hydrogels in such CCA-based templating

Fig. 2 Fabrication process of a 2D monolayer of gel beads by the double-template polymerization method. The optical micrograph illustrates the product gel beads. Reproduced by permission from [19]; copyright 2007 by the American Chemical Society



[25]. Such a PEG-monomer-templated hydrogel was used to demonstrate mechanochromic responses of the PCCA (polymerized CCA) [26]. Foulger and coworkers also have recently reported general schemes for using Click-Chemistry to functionalize bead particles in PCCA post-hydrogel templating to incorporate large numbers of dyes per bead [27].

The use of thermoreversible hydrogels with such CCA can produce a variety of devices. Thermoreversible-based CCA in a bcc structure composed of 100 nm particles [28] of poly(*N*-isopropylacrylamide), PNIPAM, provide a very temperature sensitive probe, where the narrow bandwidth extinction at about 530 nm increases five-fold in magnitude over the 24 to 35 °C interval. Here the index of refraction changes dramatically as the diffuse hydrogel condenses on itself as the temperature is raised. In an alternative approach to realizing a photonic thermometer [29], PS beads of 99 nm diameter were used to form a CCA in a bcc lattice and a thermally reversible hydrogel, PNIPAM, was polymerized in the continuous phase to lock-in the structure. In this material the overall lattice constant changes with temperature and the peak extinction wavelength shifts from 700 nm to 450 nm as temperature shifts from 10 to 35 °C. Bead-encapsulated Oil Blue N has been used to make such bead arrays very sensitive to heating effects and the resulting index of refraction changes have been demonstrated to produce fast optical switching [28, 30]. Nanosecond optical switching has also been demonstrated [31].

Such hydrogel-templated PCCA have also been suitably modified to provide chemical sensors. Doping the hydrogel monomers with ligand-monomers suitable for binding some chemical anlyate generally will lead to a lattice expansion or contraction upon binding, leading to a colorimetric Bragg diffraction shift in the PCCA [24, 32–34].

An interesting double templating CCA approach has been reported by Foulger and coworkers [35]. Instead of aqueous polyacrylamide, an aqueous PEGylated methacrylate ($M_n=360$) is used as the monomer and a PEGylated dimethacrylate ($M_n=550$) is used as crosslinker in preparing photopolymerized PCCA of PS beads (109 nm diameter). The resulting PCCA was air dried and then vacuum dried and then soaked in 2-methoxyethyl acrylate (MOEA) for 2 days. The swollen sample was then infused with some EGDMA and photoinitiator and photopolymerized to produce the resulting PCCA composite photonic band gap material. This material proved useful as a novel compressive stress sensor.

Similarly, templated hydrogel composites have been used to fabricate hybrid piezoelectric actuators for rejection wavelength tuning [36, 37] and for mechanochromic tuning of photoluminescent dyes [38]. PCCA comprising electroactively coated silica particles were used for electroactively tuning the stop band properties of PCCA [39]. A strain

sensor based on such arrays by pressure tuning [40] was also demonstrated.

Hydrogels on emulsion templates

The importance of emulsions with aqueous gel phases has been recently reviewed [41]; a major application area is in food grade emulsions and aqueous proteins are prime candidates for formulating the continuous phase hydrogels.

Emulsion templating Kim and coworkers demonstrated a supercritical CO₂ (scCO₂) in water emulsion templating method to prepare microporous hydrogels [42]. A fluoro-nated surfactant and polyvinyl alcohol (PVA) were used as dispersing agents and a mixture of acrylamide and methylene bisacrylamide (as crosslinking agent) were introduced into the aqueous solution, along with calcium derived by dissolving CaO and potassium persulfate as initiator. Supercritical CO₂ was introduced and emulsified and then the emulsion was heated to 60 °C and 280 bar while the aqueous phase underwent chain radical polymerization. The calcium ions formed particles of calcium carbonate that further stabilized the aqueous/scCO₂ interfaces, aiding the surfactant and PVA cosurfactant stabilization. After depressurization the CO₂ escapes the matrix and leaves an open cell structure, such as that illustrated in Fig. 3. The interfacial calcium carbonate can be removed by washing the matrix with aqueous acid.

Reverse emulsion templating The recent surge in developing Pickering emulsions where nanoparticles of various

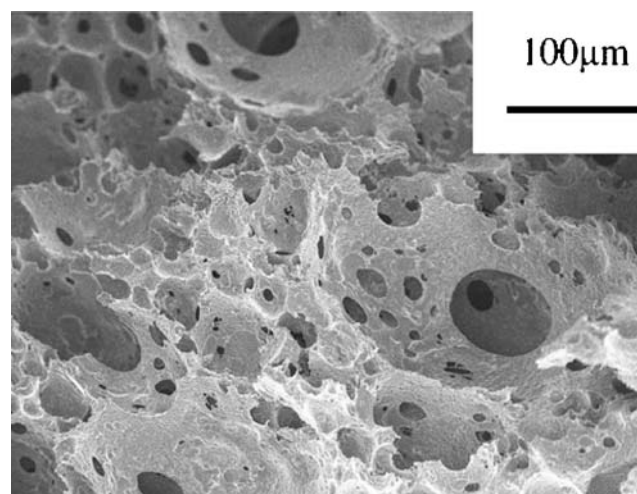


Fig. 3 SEM image of fracture surface of the CO₂ templated porous CaCO₃/PAM composites produced from CO₂ in water emulsion with the loading of Ca(OH)₂ was 3% (w/v to water) and the content of surfactant FC4430 was 12% (w/v to water). Reproduced by permission from [43]; copyright 2007 by Elsevier

types are used to stabilize emulsion droplets instead of surfactants or polymeric dispersing aids has also been applied to formulating and stabilizing reverse emulsions (water in oil emulsions). Recently, hydrogel beads have been produced with shells of partially fused colloid particles, and such beads have been called colloidosomes. Applications have included aqueous agarose stabilized in shells of epoxy resin microrods [43] and agarose stabilized by polystyrene latex-based shells [44]. Further applications have included the formulation of magnetic colloidosomes using shells stabilized with nanoparticles or Fe_3O_4 [45]. It is anticipated that such colloidosomes have high potential for controlled release and drug delivery applications in addition to food and cosmetic applications [46].

Water in oil emulsion templating of hydrogel core shell beads [47] was demonstrated using alginate as the hydrogel core material and porous calcium carbonate as the shell material. Sunflower oil was used as the continuous oil phase. The colloidosome-templating process is illustrated in Fig. 4. Calcium carbonate is particularly useful as a sacrificial stabilizer, because it can easily be removed [47] by dissolution after gently suspending the crosslinked hydrogel core shell particles in a mild HCl solution.

Double emulsion templating Zhang and coworkers [48] demonstrated a double emulsification method to produce

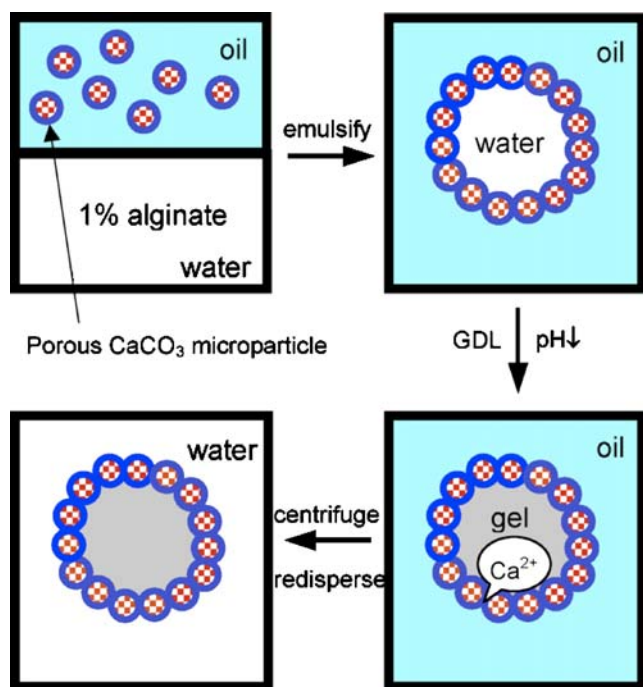


Fig. 4 Schematic illustration of the process for preparing colloidosomes based on stabilization of Pickering types of CaCO_3 microparticles at the interfaces of the aqueous hydrogel droplets. Reproduced by permission from [48]; copyright 2008 by Elsevier

crosslinked hydrogel porous particles. The hydrogel phase comprised sodium alginate and a small amount of hexylethylcellulose. These polymers produced an interpenetrating network that resulted in greater mechanical stability of the resulting hydrogel microparticles. An oil in water emulsion was then prepared with liquid paraffin, with oil droplets approximately $2\ \mu\text{m}$ in diameter being obtained. These paraffin droplets templated the ultimate pores obtained. This oil in water emulsion was then emulsified in chloroform, for example, obtaining double emulsion droplets about $100\ \mu\text{m}$ in diameter. This double emulsion was also mixed with aqueous calcium ion and glutaraldehyde to provide crosslinking and then the highly volatile phase was removed by drying and the paraffin was extracted with aqueous ethanol.

Macromolecule and micellar templating

Various templating methods have been demonstrated to create pores in hydrogel matrices [49–51]. Macromolecules and micelles of various sizes are included in the hydrogel monomer solution to be polymerized and then the subsequent removal of these steric blocking objects after polymerization leaves pore size distributions mirroring the dimensions of these nanotemplates. Templating gels with up to 20% sodium dodecyl sulfate (SDS) affected electrophoretic separations of SDS–protein complexes [49]. A bicontinuous phase of didodecyldimethylammonium bromide was used to template a poly(methyl methacrylate) gel [50]. More recently porous hydrogels have been studied using theoretical and simulation methods in evaluating micellar pore size effects on hydrogel creation and separation performance in GPC applications to separating globular proteins [51].

Templating on LC mesophases

Various hydrogels have been templated on liquid crystalline mesophases of surfactants where the templates are very similar to those used in preparing inorganic zeolites as discussed in the Introduction to this review. Infusion of hydrogel into the liquid crystalline interstices is done similarly as metal alkoxides in the zeolite syntheses, but the hydrogel polymerization is then done via UV irradiation or by thermal initiation, rather than by solvothermal conversion. Most of this work has been pursued by Guyman and various collaborators using templates based on the nonionic surfactant Brij 56. The phase diagram of this surfactant in water is illustrated in Fig. 5 [52], where the various LC (liquid crystalline) phases are indicated. Brij 56 is a trademark for $\text{C}_{15}\text{E}_{10}$.

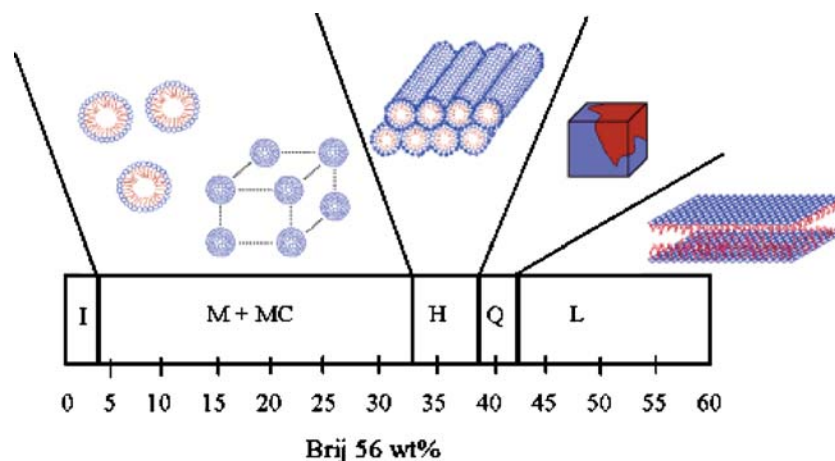


Fig. 5 Aqueous phase diagram of Brij 56 at 27 °C in 40% PEGDA. *I* represents an isotropic solution phase of monomeric surfactant and micelles, *M+MC* represents a coexistence domain of micelles and cubic micellar liquid crystals, *H* is a hexagonal phase of cylindrical

micelles, *Q* is a bicontinuous cubic phase where surfactant bilayers separate two separate continuous domains, *L* is a lamellar phase. Reproduced by permission from [53]; copyright 2007 by the American Chemical Society

The photopolymerization of acrylamide and of hydroxyethyl methacrylate (HEMA) in various of these LC mesophases was studied in detail [53]. Both acrylamide and HEMA were found to photopolymerize more rapidly in the more highly ordered (increasing amount of Brij 56; see Fig. 5) LC mesophases. For the resulting polyacrylamide systems, the more highly ordered mesophases swelled faster and further, and they also exhibited larger mechanical storage moduli. For the polyHEMA systems, the opposite trends in swelling and mechanical moduli were observed. The porous structure obtained from the cubic phase of Brij 56 at 40% *w/w* surfactant is illustrated in Fig. 6 where the smooth structure obtained in solution without any added surfactant is compared with the porous structure obtained before and after surfactant removal [54]. These studies also found that faster polymerization rates resulted in retention of smaller length scales, a trend often reported in similar studies of microemulsion polymerization.

Effects of Brij 56 LC mesophase structure on templated hydrogels derived from polyethyleneglycol diacrylate (PEGDA; $M_n=575$; ~11 oxyethylene groups between acrylates) were examined [52] using photopolymerization. Similarly to acrylamide, increases in swell rate, degree of swelling, mechanical modulus, and diffusion rates were all observed to increase with increasing surfactant and increasing mesophase order.

Templating on cubic micellar gels The thermoreversible gel nature of aqueous Pluronic-type triblock copolymer systems has been very well documented since the work of Malmsten and Lindman [55]. The micelles that form self-assemble into cubic gel phases when increasing temperature induces partial dehydration of the PEO corona segments. Such segments on nearest neighbors provide interactions that produce cubic arrangements of the constituent micelles. Such thermoreversible gels were examined as possible

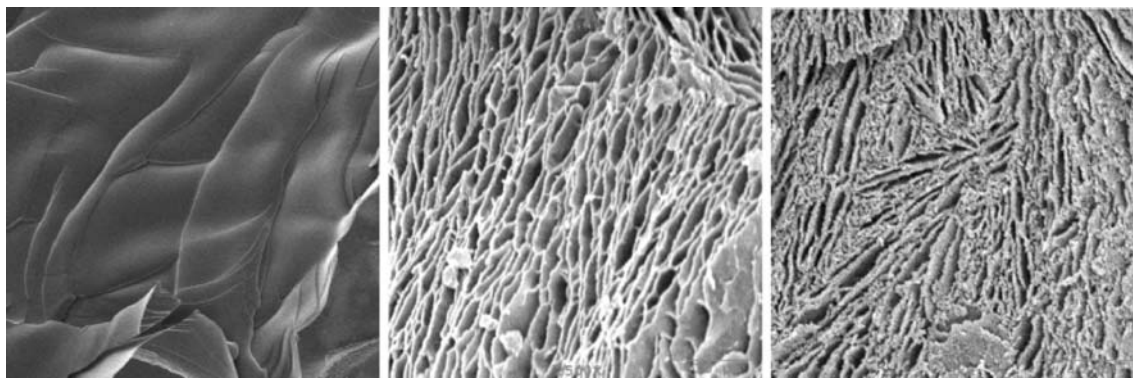


Fig. 6 SEM of photopolymerized polyacrylamide in (*left*) isotropic state without any Brij 56; (*middle*) cubic phase of Brij 56 at 40% *w/w*; (*right*) cubic phase of Brij 56 at 40% *w/w* after removal of the

surfactant. Reproduced by permission from [55]; copyright 2006 by the American Chemical Society

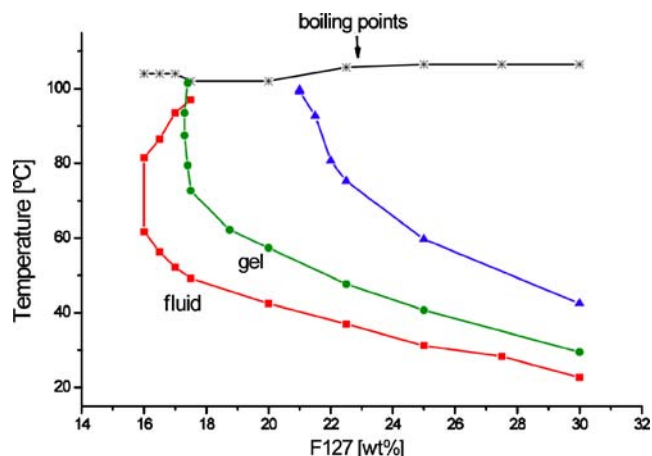


Fig. 7 Phase diagrams for F127 in 20 (filled square), 30 (filled circle), and 40% (filled triangle) (w/w) aqueous acrylamide at up to 30% (w/w) F127 (Texter et al. (2006) unpublished)

fouling release coatings for marine applications, since it is known that PEO greatly retards protein adsorption, a step believed to be the beginning of biofilm formation in fouling [56]. Since such gels are thermoreversible and would quickly dissolve at lower temperatures, it was decided to see if the cubic micellar gel phase could be used to template a crosslinked hydrogel phase to better encapsulate the micelles and to thereby provide an erodible fouling release coating. Motivation for such an approach is provided by the extensive innovation of Asher et al. described above in producing practical colloidal crystalline array materials for sensors, filters, and optical switches.

Illustrated in Fig. 7 are phase diagrams for F127 in 20, 30, and 40% (w/w) acrylamide. To the left of each of these liquid–gel boundaries is a liquid phase, with gel to the right. At 20% acrylamide, one can also pass from gel to liquid prior to boiling by increasing the temperature. At all of the concentrations where gelation occurs, it occurs thermoreversibly on increasing temperature. Basically similar phase diagrams were obtained for other hydrogel monomers, such as pentaethoxymethacrylate and hexylethoxyacrylate. In thin coatings UV polymerization was found useful. Ther-

mally initiated polymerization at 90 °C was also investigated. In Fig. 8 the thermally initiated polymerization of three different compositions are illustrated. The composition in Fig. 8 (left) is almost transparent, exhibiting a bluish Tyndall effect where there has been some small amount of ripening. The composition in Fig. 8 (right) is opaque and white, and indicates the onset of microphase separation. The essential retention of transparency in the one case illustrated means that the hydrogel templating was achieved without significant disruption of its underlying cubic phase structure.

Templating on particles

Gold nanoparticles were used by Singh and Lyon [57] as templates for producing hollow PNIPAM beads. Citrate stabilized gold nanoparticles are first coated with amine-terminated oligomers of *N*-isopropylacrylamide at room temperature where the oligomers are in an expanded random coil state. The temperature is then raised to 70 °C so that the adsorbed oligomers condense upon the surface to form a layer upon which to nucleate further PNIPAM condensation. NIPAM monomer and optional comonomers (acrylic acid, 4-acryloyl-*N*-ethylmaleimide) and methylene bisacrylamide as crosslinker with ammonium persulfate as initiator are added and a shell of crosslinked PNIPAM is condensed around the surface modified gold nanoparticles. After separating the shelled nanoparticles by centrifugation, the Au cores are dissolved with aqueous KCN.

Liposomes have been used to template alginate microgel beads [58]. Liposomes are first prepared in a solution of sodium alginate. The liposomes are then isolated, washed, and suspended in a calcium solution, where the calcium ions diffuse into the liposomes and physically crosslink the alginate when the liposomes are subjected to heating and cooling cycles that cross the T_m of the bilayer membrane. Studies using different liposomes sizes shows that one to one copies of the liposome cores were made by the alginate microgels.



Fig. 8 Polymerization with thermal initiation at 90 °C of (left) 25% F127, 20% PEG5MA, 5% PEG400DA; (middle) 20% F127, 20% PEG5MA, 5% PEG400DA; (right) 20% F127, 40% PEG5MA, 5% PEG400DA (Texter et al. (2006) unpublished)

Confinement templating in pores

Using membrane pores to template by confinement has been very successfully applied to making metallic nanorods of various compositions and to making conducting polymer rods. Yan and coworkers have shown [59] that membrane pores can also template PNIPAM microgels. Polycarbonate membranes 10- μm thick and having 0.8- μm diameter pores were used as templates. Membranes were first soaked in dilute aqueous H_2O_2 solutions of NIPAM and crosslinker (methylene bisacrylamide) to fill the pores, superficially dried, irradiated with UV, and then soaked in water to remove unreacted monomer and non-crosslinked oligomers. The cylindrical microgels were then released by dissolving the polycarbonate membranes in methylene chloride and the microgel particles were concentrated by filtration and then washed in a series of solvents, after which the microcylinders were stored in water under refrigeration. Optical microscopy confirmed the dimensions of the product microcylinders approximately matched those of the templating pores.

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