

Polymerization of and within self-organized media

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Abstract

Self-organized surfactant solutions, such as microemulsions, vesicular solutions or dispersions, or lyotropic mesophases can serve as templates for the structure directed synthesis of organic polymers. Recent developments of templating within these equilibrium nanostructured fluids are reviewed. Depending on the template structure and the reaction conditions, the outcomes may be polyampholytes, amphiphiles, nanoparticles, hollow spheres, or mesoporous polymers. For each structure and morphology, the final product materials reflect a delicate balance between phase behavior and the reaction and mass transfer parameters that set structure. Experimental and theoretical aspects of reaction kinetics and thermodynamics such as monomer partitioning, swelling behavior and polymerization-induced phase separation are discussed.

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1. Introduction

The synthesis of materials with submicron morphologies is of increasing interest, and a goal of modern materials science is to control structure and the chemical and physical properties of supramolecular materials on a nanoscopic scale. The use of self-organized surfactant solutions as reaction templates or media is one of the most promising approaches towards the synthesis of functional inorganic and organic nanomaterials, such as nanoparticles, hollow spheres, membranes or mesoporous bulk materials [1,2[•],3–5^{••},6].

The general idea behind these templating approaches is to turn the fragile structure of a dynamic, self-organized molecular assembly into a mechanically and chemically stable supramolecular material. In the case of so-called direct templating the morphology of the polymeric product resembles the structure of the template. When polymerizable surfactants are used this process is called ‘synergistic’ and the material obtained is the cured template. On the other hand, a ‘transcriptive’ synthesis results in a product that is a copy of the

template structure, as results for example when monomer polymerizes around the self-assembled template. In some cases even when the template structure is not retained during polymerization the self-organized reaction medium can still direct polymer growth. In this way new and typically hierarchically morphologies are formed, and these are interesting subjects for the study of dissipative structure formation in self-organized media. Such cases of indirect templating are called ‘reconstructive’ synthesis [7^{••}].

The main developments of polymerization within self-organized media are summarized in a number of valuable review articles [1,2[•],3–5^{••},6]. This article will focus only on recent trends and achievements in templating within microemulsions, vesicles and lyotropic mesophases. The templating of organic polymers within other self-organized media, such as thermotropic liquid crystals [8], block-copolymer bulk phases [9], colloidal crystals [10], or polyelectrolyte–surfactant complexes [11], will not be considered in detail here.

2. Microemulsion polymerization

Microemulsions are thermodynamically stable mixtures of water, oil and surfactant that exhibit either a discrete microdroplet or a bicontinuous sponge-like structure. Most usually direct (o/w) or inverse (w/o)

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microemulsions are used for the synthesis of ultrasmall polymer particles. These nanoparticles are typically characterized by diameters between 5 and 100 nm, a narrow size distribution, and a small number of polymer chains per particle [12^{••}]. Like in other heterophase polymerization techniques, the presence of the continuous domain (water or oil) allows control of the polymerization temperature and the final product is a high molecular weight polymer dispersion with low viscosity. Because microemulsions are thermodynamically stable, unlike macro- or miniemulsions, the initial state of a microemulsion before polymerization depends only on composition and temperature (at constant pressure), and this allows intrinsic control and reproducibility of the product properties. Mechanistic studies show that in microemulsion polymerization usually only a very small fraction ($\sim 1/1000$) of the micelles are initiated and grow into polymer particles [13]. The main functions of the surfactant are isolation of monomer in confined nanodroplets, stabilization of the growing polymer particles, and limitation of polymer growth by creating a dynamic boundary the monomers must cross. The resulting polymer beads are typically much larger than the original microemulsion droplets. Therefore, microemulsion polymerization is a reconstructive template synthesis [5^{••}].

There has recently been considerable effort devoted to mechanistic and kinetic investigations of microemulsion polymerization from both experimental and theoretical points of view. Compared to other self-organized media, such as bicontinuous microemulsions or lyotropic mesophases, the discrete structure of direct and inverse microemulsions simplifies study of the details of monomer/polymer/surfactant interactions and can help isolate the importance of nucleation and monomer transport processes. These investigations provide a better general understanding of complex polymerization mechanisms in self-organized media and enable the prediction of reaction kinetics and molecular weight and particle size distributions [14].

In contrast to macroemulsion polymerization, the reaction kinetics of microemulsion polymerization is characterized by only two polymerization rate intervals; the interval of constant rate characteristic of emulsion polymerization is missing (Fig. 1) [15]. Particles are generated continuously during the reaction by both homogeneous and micellar nucleation mechanisms. As the solubility of the monomer in the continuous domain increases, homogeneous nucleation becomes more important [16]. For microemulsion formulations containing short-chain alcohols as cosurfactants (which can be avoided by proper study of phase behavior) the chain length of the cosurfactant strongly affects the polymerization kinetics, apparently because of changes of the polarity of the continuous domain and variation of monomer partitioning [17].

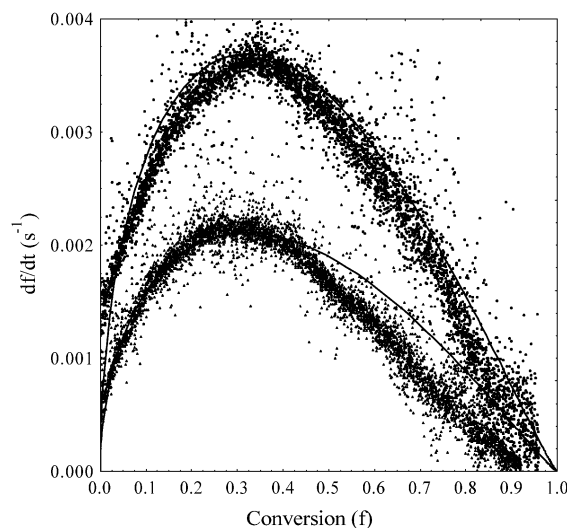


Fig. 1. Experimental and model rate vs. conversion profiles for the polymerization of hexylmethacrylate in a microemulsion stabilized by the surfactant DTAB (Reproduced from [19]). The two curves are for initiator concentrations of 0.045 (top) and 0.015 (bottom) wt.% relative to the amount of monomer in the microemulsion. The solid lines are predictions of the Morgan model [14].

In polymerization of a direct microemulsion, monomer partitioning between polymer particles and uninitiated micelles via diffusion through the aqueous phase determines the concentration of monomer at the polymerization loci. This partitioning plays an important role in determining polymer particle formation and growth [13,14,18]. Small-angle neutron scattering (SANS) measurements of monomer partitioning between polymer particles and monomer-swollen micelles show that the monomer concentration profile in the polymer particles over the course of polymerization depends strongly on the properties of the starting microemulsion. In some cases nonlinear monomer partitioning, non-negligible bimolecular termination and diffusion limitations to propagation have to be taken into account to achieve a proper description of the process [19]. Especially for initial microemulsion compositions close to a phase boundary, monomer partitioning can be significantly nonlinear [20]. Theoretical models that account for these factors can predict the observed molecular weight and particle size distributions [12^{••}].

Other mechanistic studies showed that the type of emulsion employed (macro or micro) can strongly effect termination reactions and, consequently, polymer properties [21]. For example, in microemulsion polymerization of vinyl acetate (VA) chain transfer to monomer, not to polymer, is the main termination mechanism. Thus, the polymer has a lower degree of branching than does polyvinyl acetate produced by emulsion polymerization, which terminates predominately by chain transfer to polymer.

The kinetics of polymerizations in inverse systems have also been studied [22–24]. Owing to the interplay between transport phenomena, polymerization, and initiation and nucleation rates, a complex evolution of the overall polymerization rate was observed for the inverse microemulsion polymerization of 2-methacryloyl oxyethyl trimethyl ammonium chloride (MADQUAT) [24]. When initiation by UV light in presence of azo-bis (isobutyronitrile) was used instead of metabisulfate initiation, the more regular polymerization kinetics were observed and described by a mathematical model [23].

A major drawback of conventional microemulsion polymerization is the high surfactant to monomer ratio usually needed to form the initial microemulsion. One strategy to overcome this problem is to develop more efficient surfactant systems, such as by varying counterion, the use of amphiphilic block copolymers as cosurfactants, or the synthesis of new surfactants that form microemulsions with improved solubilization properties. Gemini surfactants are an example of the latter approach [25]. Semi-empirical correlations such as cohesive energy ratio and hydrophile–lipophile balance concepts, can be used to optimize emulsion and microemulsion formulations. But even for these optimized formulations the amount of surfactants and monomer used in the initial formulation are comparable [26•].

Surfactant can be used more efficiently in semi-continuous or fed polymerization processes. Because the polymerization rates and conversions for microemulsion polymerizations are high compared to those of other techniques (e.g. solution polymerization), several polymerization cycles can be run in a short period of time by stepwise addition of new monomer. After each cycle most of the surfactant is available to form a microemulsion again. One example is the semi-continuous microemulsion polymerization of VA, where latices with high polymer content (~ 30 wt.%) were obtained at relatively low surfactant concentrations (~ 1 wt.%). Particle sizes and molecular weights were much smaller than those obtained by macroemulsion polymerization [27].

A mixture of surfactant and polymerizable surfactant has been used for a fed microemulsion polymerization of styrene. After nucleation within the initial microemulsion, additional monomer and polymerizable surfactant is added by a continuous feed. This approach produced latices with a particle diameter of approximately 50–80 nm, a solids content up 17 wt.%, and a polymer/surfactant ratio of up to 15 [28]. Hollow-fiber feeding was used to polymerize not only styrene, but also methyl methacrylate (MMA) and butyl (methacrylate), with comparable efficiencies [29•]. In this case sodium dodecylsulfate and 1-pentanol were used as stabilizers and a redox initiator system was employed.

Inverse microemulsion polymerization is an attractive approach to the synthesis of high-molecular-weight

water soluble polymers that can, for instance, be used as flocculants. Recently, the semi-continuous polymerization of inverse microemulsions was also reported. In this way polyampholyte latices based on N-isopropylacrylamide have been synthesized with low particle sizes (~ 70 nm) and high polymer contents (~ 20 wt.%) [30]. Continuous inverse microemulsion polymerization could be an attractive technique for large scale synthesis, as demonstrated by the polymerization of MADQUAT in a continuous stirred tank reactor [31].

Another major trend in microemulsion polymerization is the fabrication of functionalized nanoparticles with certain physical, chemical or biological properties. Viable approaches towards microlatex functionalization are copolymerization, variation of polymerization techniques, polymer-analogue reactions, or surface modification by adsorption.

As microemulsions enable the mixing of hydrophobic and hydrophilic compounds in confined nanogeometries, they can be used for the copolymerization of hydrophobic and hydrophilic monomers. This approach is an interesting way to form polyampholytes [32] or amphiphilic polymers. Amphiphilic copolymers of styrene and a polymerizable surfactant were obtained by γ -ray initiated direct microemulsion polymerization [33]. The copolymer composition was adjusted by partial substitution of the reactive surfactant with a non-reactive surfactant. Cross-linking of this type of latex might be an interesting way to synthesize amphiphilic particles. Inverse microemulsions can also be used for copolymerization of hydrophilic monomers and reactive surfactants [34], as well as for the synthesis of multiblock ionomers by polymerization of ionic and hydrophobic monomers [35]. The lengths of the ionic blocks and the glass temperature of the polymer can be tuned by variation of the monomer ratio.

In addition to free-radical polymerization, which is still the most established microemulsion polymerization technique, oxidative, electrochemical, living or interfacial polymerizations can be carried out. Electrically conducting polyaniline nanoparticles were synthesized by oxidative polymerization within inverse microemulsions [36,37], as well as within direct anionic and nonionic micelles [38]. Electrically conducting polythiophene was obtained from electrochemical polymerization of 3,4-ethylenedioxythiophene within direct microemulsions [39]. In these cases the main function of the microemulsion is to increase the solubility of the monomer in the aqueous reaction medium. Controlled free-radical polymerization has been used for the synthesis of fluorinated copolymers [40]. Due to the large polymerization rate within the microemulsion, the living process required only very small amounts of initiator. A complex kinetic model for this polymerization was developed and validated.

Functionalization by copolymerization was also used for the synthesis of metal-complexing nanoparticles [41•]. A metal binding cyclam-monomer was co-polymerized within an aqueous microemulsion of styrene (St) and divinylbenzene (DVB). The particles obtained showed high metal-binding selectivity and affinities, and were soluble in aqueous and organic media. An example of biological functionalization of microlatices is the immobilization of protease enzymes in a two-step procedure [42].

Particle morphologies more sophisticated than the typical ‘solid and dense’ polymerization product can also be fabricated using microemulsions. Core-shell nanoparticles have been obtained by a two-stage microemulsion polymerization beginning with a polystyrene seed [43]. Addition of butyl acrylate in a second step yielded a core-shell poly(styrene)/poly(butyl acrylate) morphology. The small particle size of the microemulsion latex led to improved mechanical properties compared to similar products produced by emulsion polymerization. Superparamagnetic nanoparticles with a magnetite core and a poly(methacrylic acid)-co-poly(hydroxyethyl methacrylate) shell were synthesized in a single inverse microemulsion [44]. The nanoparticles were formed in a two-stage process and recovered by magnetic separation. Insulin nanocapsules for drug delivery purposes were obtained by interfacial polymerization of ethyl 2-cyanoacrylate within a biodegradable microemulsion [45]. The resulting particles had a diameter of approximately 150 nm and exhibited a central cavity surrounded by a single polymer wall.

Hollow polymer particles can be made by etching away the core of a core-shell particle. For example, after the synthesis of core-shell particles with a cross-linked polystyrene shell, the poly(methyl methacrylate) core was dissolved with methylene chloride [46••]. The diameter of the resulting hollow capsules could be adjusted between 15 and 30 nm by variation of the surfactant to monomer ratio. The shell thickness was approximately 2–5 nm (Fig. 2). A more direct approach towards hollow nanocapsules is the cross-linking polymerization of styrene at the interface of isooctane microdroplets [47].

Applications of the different kinds of polymer nanoparticles synthesized in microemulsions range from photographic processes to pharmaceuticals [48].

Mesoporous polymeric materials can be obtained by polymerization within the sponge-like bicontinuous microemulsions. In a few cases, e.g. when a macromonomer is used as a polymerizable surfactant, the original template structure is retained and nanoporous polymer networks are obtained. The compatibility of the polymer network with the microemulsion phase seems to be enhanced by the amphiphilic character and the slow dynamics of a reactive surfactant [49]. In many other cases the polymer morphologies obtained are structured

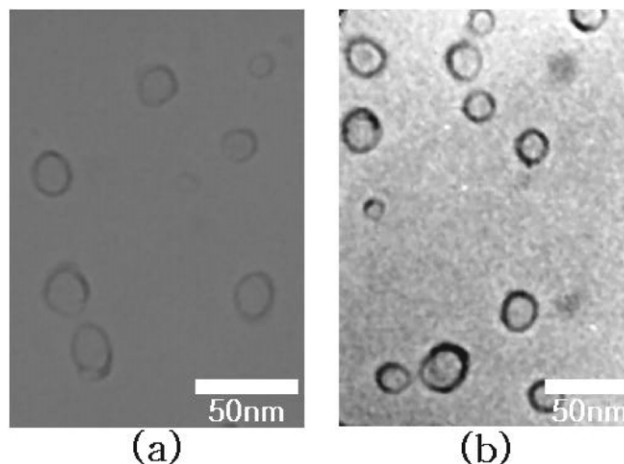


Fig. 2. Hollow polystyrene particles obtained from microemulsion polymerization of core-shell particles and subsequent core etching. (Reproduced with permission from [46••].)

on a length scale much larger than the parental sponge phase, and are the result of separation of the polymer matrix from the microemulsion phase [50,51]. Nonetheless, because of their high porosity and the continuous pore structure these gels have interesting properties. For this reason most recent publications about bicontinuous microemulsion polymerization deal with applications of these porous bulk polymers as, for example, nanofiltration membranes [52].

Functionalization of bicontinuous polymer gels was realized by incorporation of electrolyte solutions [53], metal-ions [54] or ruthenium(II) complexes [55], resulting in conducting composite electrolytes that could become the basis for devices such as chemical sensors. Superparamagnetic bicontinuous composites were obtained from biomimetic mineralization of magnetite within a bicontinuous polystyrene-co-poly(acrylic acid) gel [56]. Optically transparent PbS-polymer nanocomposites synthesized within a bicontinuous microemulsion showed large optical nonlinearity that was attributed to a surface-induced separation of delocalized charges and localized holes [57]. Potential applications for materials with enhanced optical properties are optical computing or real-time holography.

Interestingly, polymer nanoparticle dispersions with a very narrow particle size distribution can be obtained from polymerization in (and phase separation from) bicontinuous phases [26•]. This process might be an interesting alternative to the unstable and turbid inverse latices prepared by classical inverse emulsion polymerization, as the microlatices produced by microemulsion polymerization are remarkably stable. Compared to the result of polymerization in microemulsions with a discrete microdroplet structure, the non-cross-linked polymers obtained by polymerization within the bicontinuous phase are characterized by a slightly lower molecular

weight [58]. Also, the final conversions for the copolymerization of VA and 2-ethylhexyl acrylate were found to depend strongly on the initial structure of the microemulsion [59].

3. Polymerization of vesicles

Vesicles are discrete spherical assemblies formed by lipids, surfactants, polymers or proteins. They consist of closed bilayer shells with an entrapped solvent core. Potential applications include drug-delivery systems, biosensors, and encapsulation [60,61••].

Generally two broad classes of vesicles can be distinguished, either uni- or multilamellar vesicles that form after shearing and that are stable only kinetically, and equilibrium vesicles that form spontaneously and are stable with time. Most vesicular systems show a multilamellar, onion-like morphology with each vesicle being formed by a number of bilayers. These so-called liposomes have typically diameters ranging from hundreds of nanometers up to several microns. By applying high shear such as by sonication or extrusion, multilamellar vesicles can often be transferred into kinetically stabilized unilamellar vesicles. In contrast, unilamellar equilibrium vesicles form spontaneously in some mixtures of anionic and cationic surfactants without any additional energy input. Their equilibrium size is typically in the range of 50–100 nm and does not change with time after equilibration. Both kinds of vesicles can be used as templates for the synthesis of polymer nanoparticles or hollow nanocapsules.

Three different approaches towards the templating of vesicles are described in literature. One is the polymerization of standard monomers, i.e. styrene (St) or MMA, within the vesicle bilayers. More common is the use of vesicle-forming polymerizable surfactants, such as lipids or unsaturated amphiphilic block copolymers. In the third case these two approaches are combined and monomers and polymerizable surfactants are copolymerized.

The polymerization of hydrophobic standard monomers within the bilayers of kinetically stabilized vesicles of the surfactant dioctadecyldimethylammonium bromide (DODAB) was described in a series of papers. Because of phase separation of the polymer matrix from the bilayers the polymer did not resemble the vesicle structure, and instead more complex vesicle-polymer hybrid morphologies were obtained (Fig. 3) [62]. The non-cross-linking polymerization of styrene produced the so-called parachute architecture, which is characterized by a single polystyrene bead that is attached to a pure surfactant vesicle bilayer. Addition of cross-linker or copolymerization of styrene and butyl methacrylate could not prevent phase separation, but resulted instead in the formation of multiple beads. In this case several polymer beads were attached to one vesicle bilayer to

give a ‘necklace’ morphology. The copolymerization of styrene with a small amount of polymerizable surfactant gave a ‘wrapped parachute’ or ‘matrioshka’ structure, wherein each parachute vesicle-polymer hybrid is encapsulated in a unilamellar vesicle. Retention of the vesicle structure was only achieved by the copolymerization of styrene with a vesicle-forming polymerizable surfactant, or by polymerization of cross-linker within prepolymerized vesicles of the same surfactant [63•].

The mechanism of the parachute morphology formation was investigated by pulsed-laser polymerization experiments that provided simultaneously kinetic data and thermodynamic information on the locus of polymerization [64•]. This study indicated that polymerization occurs in small polymer nuclei that separate from the bilayer, and this morphology was confirmed by a detailed SANS study [65]. Characterization by micro-DSC, fluorescence studies, surfactant lysis and atomic force microscopy revealed that the parachute morphology consists of a pure surfactant bilayer and an attached and completely phase-separated polymer latex bead [66]. The presence of the polymer bead inside the vesicle bilayer strongly affects the dynamics and the electro-optic behavior of the vesicles [67].

Direct templating without morphological changes and by use of common monomers, such as styrene and DVB, was realized by the use of equilibrium vesicles [68••]. The catanionic templates formed by standard surfactants are characterized by spontaneous assembly into unilamellar vesicles. These vesicles can swell with monomer (DVB or DVB/styrene mixtures), and subsequent thermally initiated free-radical polymerization resulted in hollow polymer spheres with diameters approximately 60 nm and shell thicknesses lower than 10 nm (Fig. 3) [69]. The nanoparticles are stable enough to withstand dialysis, vacuum drying and resuspension aided by adsorption of nonionic surfactant. Redispersible polyelectrolyte nanocapsules were obtained by sulfonation of the polymer. The stability of these polymerizable vesicles results from the high cross-link density of poly-DVB, the compatibility of the aromatic surfactants and polymer, and perhaps from the ability of the bilayer to rearrange to accommodate the growing polymer. An alternative route to synthesis of polyelectrolyte hollow spheres is cross-linking UV-polymerization of acrylic acid esters within the bilayers of dioctadecyldimethylammonium chloride followed by saponification [70]. The particles obtained change size reversibly with changes in salt concentration or pH.

The monomer isodecyl acrylate reacts differently when polymerized within bilayers of fluorinated or hydrocarbon lipid [71••]. Polymerization in bilayers of the non-fluorinated lipid resulted in phase separation and the formation of a parachute-like morphology. However, polymerization within the fluorinated lipid bilayers yielded a homogeneous distribution of the polymer and

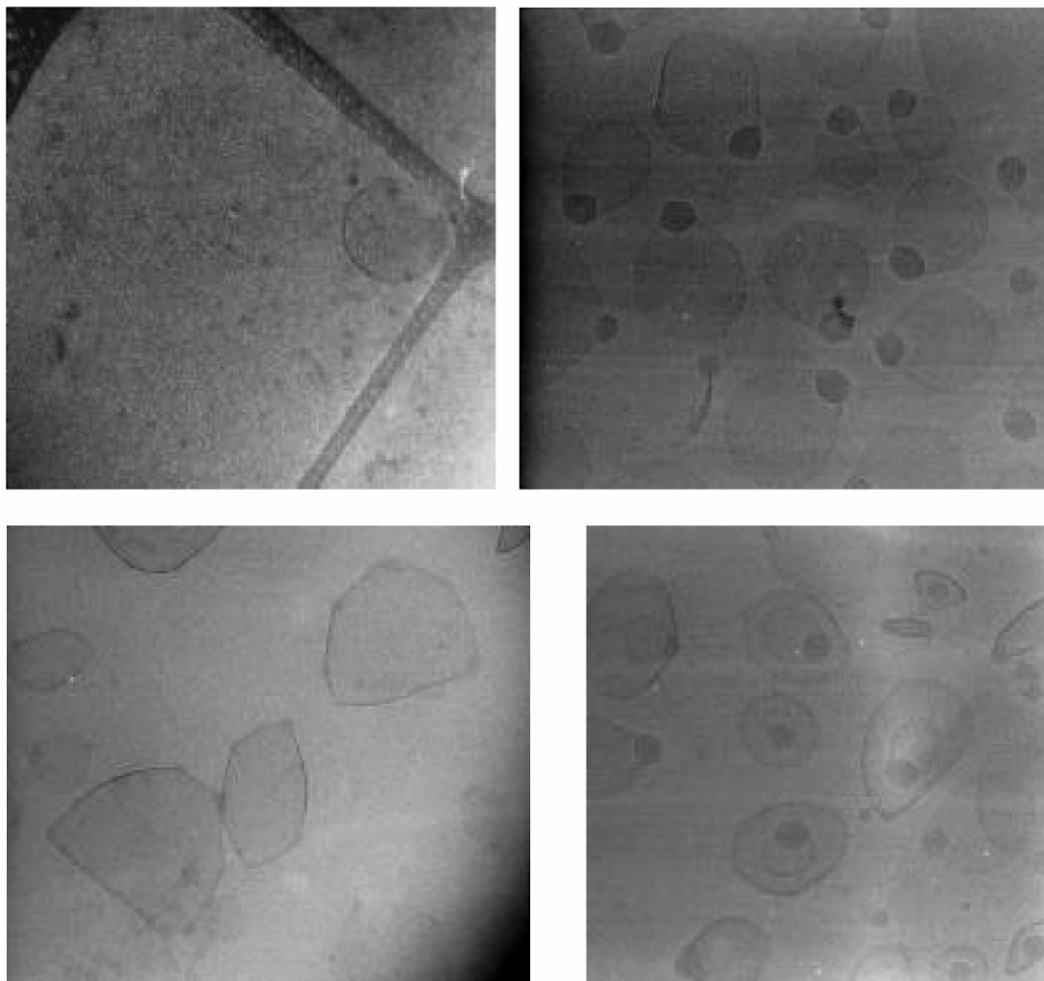


Fig. 3. Different polymer morphologies from vesicle templating: Hollow polymer spheres (top left) [68^{••}], parachutes (top right) [67], necklaces (bottom left) [62], and matrioshka structures (bottom right) [17]. (Adapted with permission from [62,67,68^{••}].)

retention of the vesicle structure. The lower molecular weight and the higher polymerization rates observed for the reaction in the fluorinated bilayers suggested that the more confined and non-expandable character of the fluorinated bilayers plays a role in the synthesis.

Biological functionalization of liposomes stabilized by polymerization of hydrophobic methacrylate monomer was achieved by encapsulation of enzymes and incorporation of natural channel proteins into the bilayer [72[•]]. Lipid vesicles can also serve as templates for sequence-selective polycondensation of dipeptides [73].

For most synergistic templating approaches polymerizable lipids are employed. One factor determining the success of this approach is the final cross-linking density, which depends on the ratio of mono- to bifunctional lipids in the bilayer and on the site of the reactive group [74]. Not surprisingly, when the reactive site is close to the glycerol backbone the polymerization is substantially more efficient than when the group is in the ω -position on the hydrophobic chains. The type of initiation also

plays an important role in determining the final product. Photopolymerization of heterobifunctional lipids yielded only oligomers, while cross-linked vesicles were obtained by redox initiation of the same system [75]. Redox initiated polymerization of liposomes prepared from heterobifunctional lipids resulted in polymeric ‘nanoballoons’ that were stable against freeze-drying and rehydration [76^{••}].

An acetylenic phosphocholine derivative was used for γ -ray polymerization of vesicles prepared by extrusion [77]. The resulting hollow particles remained structurally intact upon freeze-drying and subsequent redispersion in water. γ -ray polymerization was also used to cross-link vesicles formed by a variety of dienoyl-functionalized phosphocholines [78], and the resulting polymeric vesicles resisted freeze-thaw damage.

Ring-opening polymerization of lipids carrying dithiolane rings was performed for the encapsulation of proteins [79] and fluorescence markers [80]. The polymerized vesicles were resistant to surfactant disruption

and thermal perturbation. Owing to the mild polymerization conditions the activities of the encapsulated enzymes were not affected, and antibody formation was two times more efficient than that for the non-polymerized drug delivery liposomes.

Curvature modulation by addition of suitable cosurfactants, e.g. polyhydroxylated telomers, was explored for the polymerization of hydrocarbon glycolipid surfactants [81]. In this way disorganization of the bilayer and precipitation were suppressed during polymerization. Polymerization of fluorocarbon derivatives of the same glycolipids also led to successful synergistic templating, even without use of a cosurfactant.

Another approach to synergistic template synthesis is by the cross-linking of vesicle-forming amphiphilic block copolymers. UV-polymerization of methacrylate endgroup-functionalized block copolymers yielded polymer nanocapsules [82]. However, their stability was not high enough to withstand drying and redispersion without disruption, a condition probably reflecting a low degree of cross-linking with regard to monomer repeating units. These vesicles were suitable for biological activation by encapsulation of enzymes and incorporation of channel proteins into the bilayer [83]. Free-radical cross-linking of giant-vesicle forming poly(ethylene oxide)-*b*-polybutadiene block copolymers resulted in hollow capsules that were stable against drying, redispersion and lysis by addition of solvents [84[•]]. Rupture tensions and other physical properties were measured as a function of the cross-linking degree using micropipet aspiration methods.

4. Polymerization within lyotropic mesophases

As is the case for other liquid crystals, lyotropic mesophases combine both the flow properties of liquids and the long-range order of crystals. As they are thermodynamically stable they form spontaneously, as do microemulsions or equilibrium vesicles. They show long-range order in one (lamellar phases), two (hexagonal phases), or three (cubic phases) dimensions. Their phase behavior at constant pressure depends not only on temperature, as it is the case for thermotropic liquid crystals, but also critically on solvent type and concentration. Their morphological complexity enables their potential use for templated synthesis not only of nanoparticles, but also of bulk materials with isotropic or anisotropic morphologies.

As is the case for polymerization within vesicle bilayers, most studies deal with the synergistic templating of lyotropic mesophases by polymerization of surfactants [85]. However, polymerization of monomers in a surfactant template has considerable advantages over polymerization of amphiphilic monomers. Firstly, because the phase behavior of common surfactants is known or relatively easily measured, it is easy to modify

known mixtures to produce the desired template. Secondly, the effect of added monomers often can be predicted and if necessary compensated for changing phase behavior parameters such as temperature. Finally, the cost of specially synthesized surfactants is such that large scale applications will be dramatically restricted. For these reasons there are also numerous examples of polymerization of standard monomers within lyotropic mesophases with the aim of transcriptive synthesis for the fabrication of a one-to-one copy of the template. Again, only in relatively few studies have a combination of both polymerizable surfactant and monomer been explored.

Phase separation is the common outcome when standard monomers are employed for polymerization within lyotropic mesophases [86]. Nonetheless, the resulting solids typically have high porosities and surface areas and so still show very interesting properties. For example, hydrogels made this way respond quickly to changes in pH or ionic strength because of rapid ion transport within the porous polymer [87[•]].

As described above for the polymerization of styrene within the bilayers of DODAB vesicles, the polymerization of styrene within a bicontinuous cubic phase of the same surfactant also produced macroscopic phase separation [88^{••}]. Similar diffraction patterns before and after polymerization were found by small-angle X-ray scattering, and the viscous nature of the cubic phase first suppressed the expulsion of the polymer. However, cooling and storage of the samples eventually caused macroscopic phase separation into a polymer-rich and a surfactant-rich phase. The morphology of the polymer was not investigated.

Earlier studies showed that a liquid-crystalline reaction medium can still direct polymer growth during polymerization-induced phase separation and will yield hierarchical morphologies (Fig. 4a) [89]. A recent investigation gave more insight into the mechanism of dissipative structure formation within self-organized media [90^{••}]. The cross-linking polymerization of styrene within inverse hexagonal sodium bis (2-ethylhexyl) sulfosuccinate (AOT) phases resulted in phase-separated, but nanostructured polymer gels (Fig. 4b). Polymer nanoparticles with a diameter of approximately 100 nm formed, phase separated at an early stage of polymerization, and then fused into polymer strands that made up extended polymer sheets. The extension and definition of these polymer layers depended strongly on the cross-linking degree and polymerization kinetics. A suggested mechanism for the dissipative structure formation is based on the role of anisotropic viscosities and transport properties within the single domains of the hexagonal template. Analogous morphologies were found for colloidal ordering by thermally-induced phase separation of silicon oils within nematic liquid crystals [91^{••}], and for the sol-gel synthesis of silica within

inverse hexagonal AOT mesophases [92]. Modeling of these highly non-equilibrium dynamic processes offers better understanding of dissipative structure formation of polymers within self-organized media [93,94].

The surface topology of lyotropically templated polyacrylamide hydrogels was studied by AFM [95]. Surface areas increased systematically with increasing surfactant concentration. Another interesting effect of a confined lyotropic reaction media is its influence on polymerization kinetics [96]. For the photopolymerization of acrylamide within a nonionic cubic mesophase a tenfold increase in polymerization rate was observed compared to solution polymerization at identical monomer concentrations.

Significant differences were found for the polymerization of monomers with different polarities within lyotropic phases of the non-reactive surfactant dodecyltrimethylammonium bromide (DTAB) [97]. Nonpolar monomers partitioned to the oil-soluble domains while polar monomers segregated at the water/surfactant interface. Owing to the higher local concentration, polymerization rates of nonpolar monomers were higher in the micellar phase than in hexagonal or lamellar phases. For polar monomers the opposite behavior was observed, with the fastest polymerization occurring in the lamellar phase.

The most common approach for synergistic templating within lyotropic mesophases involves the use of polymerizable surfactants. Although the final materials often show no significant porosity after purification and drying, in many cases the internal interfaces become accessible by swelling with polar or non-polar solvents. Even in cases where the polymerization is not complete there is often an increase in the stability of the phase to temperature change or solvent addition.

The synergistic synthesis of nanostructured cubic polymer gels was realized by copolymerization of dienylyl



Fig. 5. Transmission electron micrograph of a polymerized dienylyl substituted lipid, cross-linked in a cubic mesophase; scale bar = 100 nm. (Adapted with permission from [98].)

substituted lipids [98]. No phase transitions or changes in dimensions were observed with temperature changes for the polymerized sample. Furthermore, the polydomain square lattice of the purified gel matrix could be visualized by TEM (Fig. 5). In contrast, copolymerization of monoacylglycerol and 1,2-diacylglycerol in a cubic lyotropic state did not result in a continuous gel structure [99]. Linear polymer chains were obtained instead, and the cubic morphology was destroyed by addition of organic solvent. Similar polymerizations in the inverted hexagonal phase yield an increased stability of the lyotropic phase against temperature changes [100].

For the polymerization of amphiphilic phosphonium dienes, 3,4,5-tris (ω -acryloxyalkoxy)benzoate salts or styrene ether-modified fatty acid, high conversions of up to 90% were observed [101–104]. Homopolymerization and copolymerization of the lyotropic phases with the cross-linker DVB resulted in freestanding, mechanically stable films. X-ray diffraction and polarized light microscopy showed the hexagonal order before and after

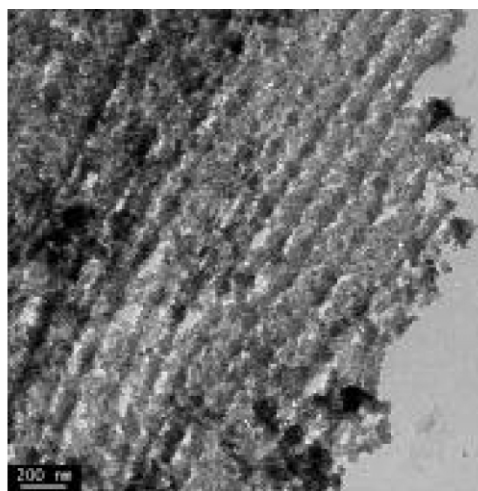
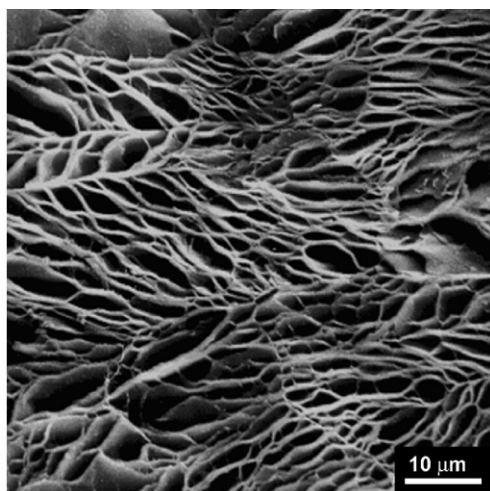


Fig. 4. Polymer gels with hierarchical structures formed by polymerization-induced phase separation within lyotropic mesophases [89,90••].

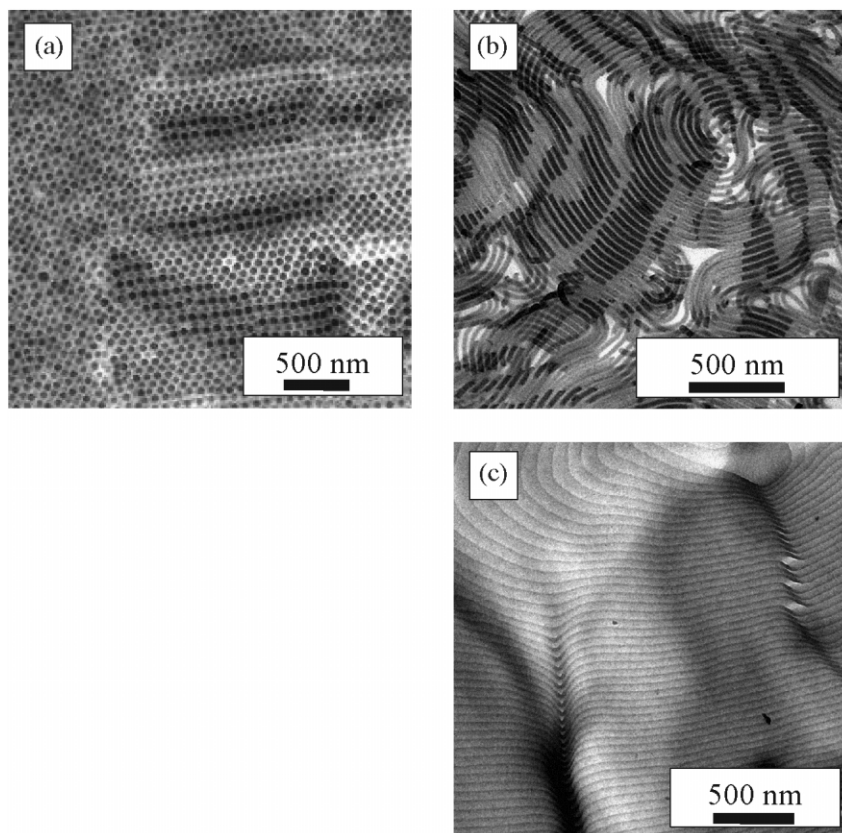


Fig. 6. Micrographs of cross-linked poly(butadiene)-*b*-poly(ethylene oxide) gels, templated in cubic (a), hexagonal (b), and lamellar (c) phases. (Reproduced with permission from [114].)

polymerization. The cross-linked polymer gels can be employed for templated nanocomposite formation or as heterogeneous catalysis [105].

Copolymers with amphiphilic properties were synthesized within lyotropic phases of oleic acid [106–108]. The polymeric surfactants obtained by copolymerization of amphiphilic monomers within lamellar phases showed improved surface activity and formed uni-molecular micelles through coiling of the hydrophobic chains [108].

Poly(oxyethylenes) with polymerizable, hydrophobic endgroups were cross-linked within oriented lamellar phases of the ternary system $C_{12}E_5$ /decane/water [109]. Cross-linked and oriented polymer gels were obtained that retained their lamellar morphology after extraction of the template, and which showed one-dimensional swelling by water.

Complete or partial ‘locking in’ of the initial lyotropic structure was realized by balancing mixing polymerizable surfactants so that they retain the same preferred curvature before and after cross-linking [110,111].

γ -ray polymerization is an efficient strategy for the reaction of the polymerizable cationic low molecular weight surfactants (2-methacryloyl)ethyl)dodecyltrimethylammonium bromide and (11-methacryloylunde-

cyl)trimethylammonium bromide in cubic and hexagonal binary phases [112]. The nanostructured gel products retained their morphology during drying and reswelling with hydrophilic or hydrophobic solvents. Cholesteric morphologies of higher molecular weight cellulose derivatives in water were also successfully cross-linked by γ -ray polymerization [113]. γ -irradiation has been employed for the synergistic templating of lyotropic mesophases formed by poly(ethylene oxide)-*b*-polybutadiene block copolymers [114]. Cross-linking within lamellar, hexagonal and cubic mesophases resulted in mechanically and chemically stable, transparent polymer gels (Fig. 6). The retention of order was proved by small-angle X-ray scattering, SANS and electron microscopy. No significant porosity could be determined by BET because of the highly compact character of the dried polymer gels. The gel morphology was stable against temperature changes, extraction, drying and reswelling with polar or nonpolar solvents. Electron microscopy of ultramicrotomed samples provided detailed views of lyotropic morphologies, defect structures, morphologies of transition states, and the topological effects of concentration, block length ratio and molecular weight of the block copolymer template [115].

Kinetic studies were also performed for the synergistic templating of lyotropic mesophases [116]. Due to the diffusional limitations of the propagating chains, the polymerization kinetics depended strongly on the liquid crystalline morphology. For the polymerization of a quarternized dimethylaminoethyl methacrylate within lyotropic phases formed by mixtures with DTAB, the polymerization rate decreased as the phase morphology changed from lamellar to bicontinuous cubic to hexagonal. Morphological studies of the polymer products after purification were not performed.

For the polymerization of a semifluorinated alkyl methacrylic acid an increase of the polymerization rate with the degree of order of the lyotropic mesophase was reported [117]. The maximum conversion for the γ -ray polymerization of allyldimethyldodecylammonium bromide within lamellar phases was restricted to 35% within hexagonal and cubic mesophases, while it was 100% in micelles [118]. The difference was explained by differences in molecular mobility favoring termination reactions.

5. Templating within self-organized media—some general considerations

Templating within organized solutions is a much more complex process than suggested by the simple picture of ‘casting’ a surfactant assembly. A polymerization reaction within a highly dynamic self-organized medium progresses in a continuously changing physico-chemical environment. As the monomer phase is substituted by a polymer phase, changes of the polarity of the dispersion medium and the partitioning of each compound occur. Many monomers show some degree of surface activity and consequently segregate at the assembly’s interface. Therefore, polymerization can cause phase transitions by driving changes in the interface curvature. More severe effects arise due to the loss of entropy or chemical incompatibility of the polymer with the surfactant, and this commonly drives phase separation and concomitant disruption of the initial structure. In these cases the surfactant phase still coexists with the demixed polymer phase, so there are usually no significant changes of optical textures or diffractograms recorded before and after polymerization. For this reason the existence of a liquid crystalline or microemulsion phase after polymerization, as verified for example by small-angle scattering, cannot be the lone determinant of whether or not direct templating occurred. Only characterization of the purified polymer matrix can provide evidence about the actual polymer morphologies formed. Of course, the process of extraction of the template may itself cause morphological changes, but a viable templating reaction should produce materials capable of withstanding such environmental changes.

Given the dilemma that phase separation induced by polymerization is always the enemy of direct synergistic or transcriptive templating using a complex fluid, two strategies can be developed for the synthesis of ordered supramolecular materials. One is to suppress phase separation by adjusting thermodynamic and kinetic parameters, either in the original formulation or, perhaps, by changing conditions as the reaction proceeds. To do this, and to realize true one-to-one templating, several approaches are described above. They are: (i) kinetic stabilization by the use of surfactants with slower exchange dynamics (e.g. amphiphilic block copolymers), (ii) polymerization within templates with long rearrangement times (e.g. hexagonal and cubic phases), (iii) thermodynamic adjustment of the surfactant/monomer/polymer mixture (e.g. by matching the molecular structure to induce some attractive interaction and by this compatibility, as was done for DVB polymerization in equilibrium vesicles), (iv) cross-linking of the polymer matrix to ‘compensate’ for the entropy loss caused by producing the polymer matrix in a confined nano-geometry (e.g. monomers with a high number of reactive entities per molecule can be fully cross-linked at low conversions, or small multifunctional monomers such as DVB that intrinsically form cross-linked networks).

Another strategy for the synthesis of ordered materials, not yet fully developed, is to make use of the high sensitivity of the interaction between polymer gel chemistry and surfactant mesophase chemistry. When aiming at the reconstructive templating of polymers with even more complex morphologies, this sensitivity can be used as a powerful tool for the synthesis of new hierarchical polymer structures. One example is the colloidal ordering of polymer gels by polymerization-induced phase separation within inverse hexagonal phases [90]. Modern theory will provide new insights and a better understanding of dissipative structure formation within these highly dynamic, non-equilibrium processes.

6. Conclusions

Thermodynamically stable self-organized media, such as microemulsions, vesicles and lyotropic mesophases display highly ordered structures on a nanometer scale. Because of their lack of mechanical stability and their sensitivity to environmental changes they are unsuitable for material applications. Templated synthesis of polymers within these phases is therefore employed to obtain ordered, nanostructured materials for potential applications including separations, catalysis, drug delivery, nanocomposite synthesis and as biomimetic materials.

Polymerization of organic monomers within surfactant solutions provides materials that usually cannot be obtained by conventional bulk or solution polymerization. Most strategies of polymer templating aim at the fabrication of one-to-one copies of the surfactant assem-

blies. In this way sometimes nanoparticles, hollow capsules, or mesoporous bulk polymers can be obtained. The success of true one-to-one templating depends strongly on balancing thermodynamic and kinetic parameters, e.g. monomer partitioning and diffusion, exchange dynamics and template rigidity, the use of cross-linkers and the compatibility of surfactant, monomer and polymer. By adjusting these parameters, separation into polymer-rich and surfactant-rich phases can be suppressed and the initial template structure preserved. A better understanding of the interplay of these parameters will allow and improve systematic approaches towards the design of nanostructured polymers.

In other approaches, polymerization-induced phase separation within self-organized media is employed for the colloidal ordering of hierarchically structured polymers. The supramolecular morphologies obtained by reconstructive templating usually show order on length scales from nano- to micrometer. In future this exciting field of research, where modern theory and polymer gel chemistry meet, will gain more attention and provide deeper insight into dissipative structure formation within non-equilibrium systems.

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