



Applications of polymerizable surfactants

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Abstract

Polymerizable surfactants ('surfmers') offer potential for developing hybrid nanometer-sized reaction and templating media. There has been a significant literature devoted to polymerization of, or in organized amphiphilic assemblies. This has led to the formation of a number of unique nano-materials including open-cell polymer networks, ultra-fine polymer latexes and inorganic/organic nano-composites, which exhibit novel properties, and would be unobtainable through conventional techniques. Amongst other parameters, surfmer composition and molecular structure play an extremely important role in the polymerization process, and essentially govern the final properties of the polymer. This review focuses on three main areas including the polymerization of micelles, vesicles, lyotropic liquid crystals or mesophases and microemulsions.

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1. Introduction

At the forefront of nanotechnology is the on-going quest to develop easily accessible reaction and templating media, which offer compositional and/or architectural control on a nanometer scale. Organized self-assembled surfactant phases have received a lot of attention as possible reaction and templating media; however, due to their dynamic nature, conventional surfactant structures are of limited use. Polymerizable surfactants ('surfmers'), on the other hand, offer potential for

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developing hybrid nanosized reaction and templating media with constrained geometries. In 1958, Freedman et al. [1] reported the first synthesis of vinyl monomers, which also functioned as emulsifying agents. Since this time, especially over the last 15 years or so, surfmers have received much attention. A wide variety of surfmers have been synthesized and studied by different groups worldwide [2–7]. A vast amount of literature exists in this field and there are a number of excellent reviews [8–12]. This review focuses on three main areas, including the polymerization of micelles, vesicles, lyotropic liquid crystals or mesophases and microemulsions.

2. Micelles

One of the earliest reports on micelle polymerization was by Larrabee and Sprague in 1979 [13], using γ -irradiation to polymerize aqueous micelles composed of sodium 10-undecenoate. Polymerization was confirmed by the disappearance of vinyl signals in the ^1H NMR spectrum. Furthermore, polymerization was only observed at concentrations above the c.m.c., demonstrating that micelle formation is a necessary condition for polymerization. This is a typical phenomenon observed with all surfmers, and is explained by a ‘condensation effect of monomer’ [8], which produces an accelerated propagation step. This would suggest polymerization is strongly influenced by the structure and properties of the parent micelles. Poly(sodium 10-undecenoate) was further characterized by Paleos et al. [14], who demonstrated, by electrical conductivity measurements, that the polymer exhibits a c.m.c. equal to zero. The phrase ‘polymerized micelle’; used by Paleos et al. to describe the polymer was later questioned by Sherrington et al. [15]. Sherrington has published a number of papers describing the synthesis and characterization of a wide scope of mono- and divalent quaternary ammonium cationic surfmers [16–19] and a series of alkyl pyridinium bromide maleate diester surfmers [20]. He proposed that the phrase, ‘polymeric micelle’, insinuates a topochemical polymerization, which involves the linking of monomers in such a manner that the final polymer geometry mirrors that of the original monomeric micelle, as shown in Fig. 1a. However, the fact that rapid monomer exchange between micelles is in the range 10^{-5} – 10^{-9} s [8], which on average is much smaller than the rate of chain propagation (10^{-2} – 10^{-6} s) [8], implies that monomer exchange occurs during the polymerization. This led Sherrington to believe a topochemical polymerization of a micelle is extremely unlikely. Instead he proposed that a more realistic representation was the formation of a ‘polysoap’, i.e. an oligomeric species that exhibits micellar-like physical properties (Fig. 1b).

The issue of stereoselectivity of the polymers formed from surfactant micelles is also an interesting subject. Previous reports demonstrate that both monomer reactivity and location of the polymerizable group have a profound effect on the nature of the polymerized species [21]. Dais et al. [21] have demonstrated how the position of a polymerizable methacrylate group in micelle-forming quaternary ammonium surfmers, and the corresponding polymers, causes pronounced differences in solubility, aggregation number, micellar size and molecular weight. Furthermore, ^{13}C NMR

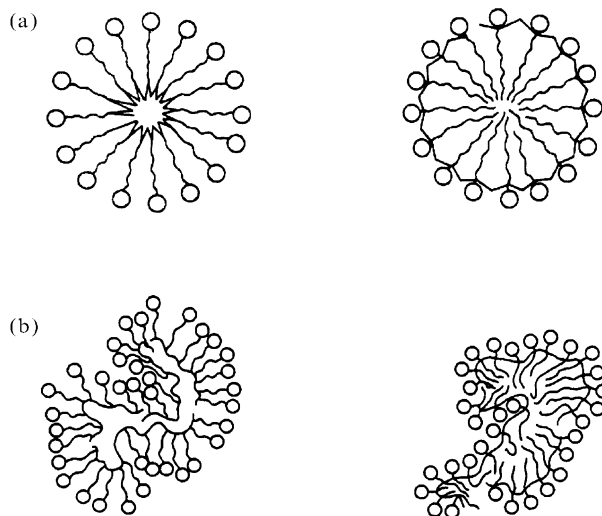


Fig. 1. Schematic representations of a 'polymerized micelle' (a) and a 'polysoap' (b) Reprinted with permission from reference [17]. © 1987 Elsevier.

spectroscopy was employed to elucidate the microstructure of the final polymers. They found that polymerization was essentially complete after just 5 min for the T-type surfmer (polymerizable moiety located in the hydrophilic head-group), whereas the H-type surfmer (polymerizable moiety located in the hydrophobic tail) took approximately 2 h [21]. This dramatic change was readily explained by a combination of the high concentration of methacrylate groups in the interior of the micelle for the T-type surfmer and the electrostatic repulsion between adjacent head-groups retarding the propagation rate for the H-type surfmer. The absence of any observed splitting patterns in the ^{13}C NMR spectrum in the latter case was indicative of a purely syndiotactic stereoregular polymer [21].

Polymerized micelles/polysoaps exhibit potential to function as catalysts, depending on the specifics of on micelle–substrate association, via electrostatic or hydrophobic interactions. The rapid dissociation equilibrium of conventional micelles is not favorable to association and, therefore, the catalytic process. The effect of micelle polymerization on the base-catalyzed hydrolysis of *p*-nitrophenyl hexanoate was studied by Roque et al. [22]. Various polymers and telomers were prepared from two monomeric methacrylic surfmers [22]. They found that polymerization led to a polymer capable of solubilizing hydrophobic solutes much more efficiently than their unpolymerized counterparts [23], and that they exhibited a higher catalytic activity, which increased with the degree of polymerization.

Fairly recently, Candau et al. [24–26] have developed multicomponent polymeric micelles (MCPMs) capable of specific solubilization of mutually incompatible hydrophobic compounds. These MCPMs formed well-segregated hydrophobic hydro- and fluorocarbon domains along a hydrophilic polyacrylamide backbone, as illus-

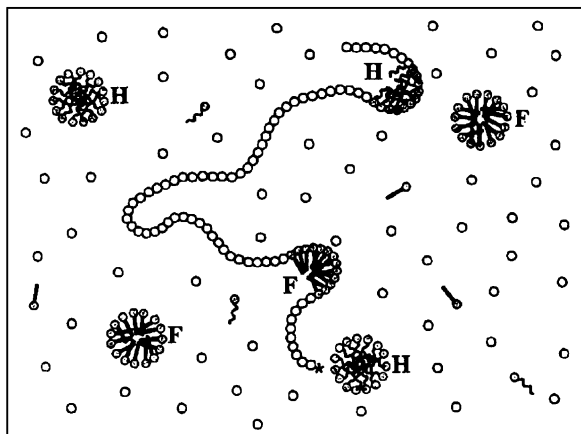


Fig. 2. Schematic representation of MCPMs proposed by Candau et al. Reprinted with permission from [26]. © 1999 American Chemical Society.

trated in Fig. 2. MCPMs were synthesized by an aqueous radical terpolymerization of a water-soluble monomer (acrylamide) with both hydrocarbon and fluorocarbon surfmers in the micellar state. Surface tension and conductivity measurements confirmed the demixing behavior of the two surfmers in the micellar state, and fluorescence experiments provided evidence of hydrophilic polymer chains composed of two different types of non-compatible hydrophobic microdomains.

In order to improve micelle polymerization and be able to effectively enhance templating of the parent micelles, an understanding of the kinetics and evolution of microstructure during reaction is essential. Recently published work by Kline [27,28] followed the evolution of microstructure, by small-angle neutron scattering (SANS) (Fig. 3), during the in situ free-radical polymerization of cetyltrimethylammonium 4-vinylbenzoate. The physical stability of the polymerized aggregates towards dilution and temperature change was also investigated. Kline [27,28] has shown that polymerization proceeded through a highly turbid phase, resulting in a stable, non-viscous solution where the cylindrical structure of the parent micelle is partially preserved. These polymerized aggregates were reported to be insensitive to temperature changes and dilution, whereas their parent rod-like structures rearrange to spherical micelles at elevated temperatures. The resulting polymerized cylinders are stable and redispersable, contrary to typical polymerized surfactants or 1:1 polymer-surfactant complexes.

This account by Kline clearly demonstrates, as suggested by Sherrington [15], that micelle polymerization does not represent a true templating (or topological) process, but is microstructure mediated in the sense that polymerization only occurs above the c.m.c., and the parent micellar structure does influence the final polymer morphology.

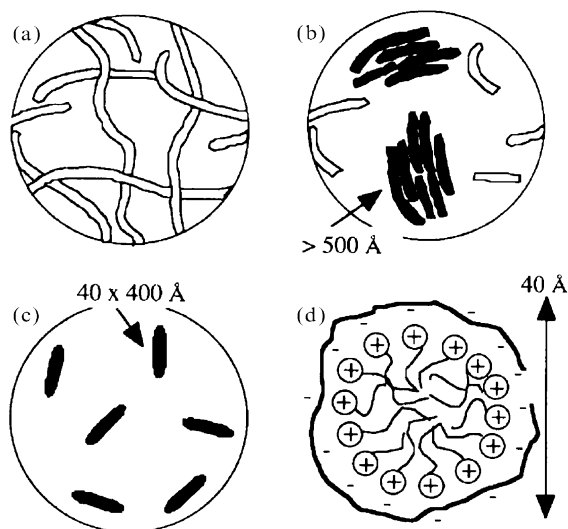


Fig. 3. Schematic representation of the evolution of microstructure of cetyltrimethylammonium 4-vinylbenzoate during polymerization. Reprinted with permission from reference [28]. © 1999 International Union of Crystallography.

3. Bilayers and vesicles

Specific amphiphilic molecules, such as lipids, are known to form closed bilayer assemblies, known as vesicles, in aqueous solution. Much attention has been devoted to these systems due to their ability to mimic biological cell membranes. Vesicles are larger than micelles, have a smaller surface curvature and a higher degree of organization. Lateral diffusion can occur within a layer, however, monomer exchange between vesicles is slow, and, therefore, these phases can be stabilized through polymerization without any dramatic change in morphology, or catastrophic phase separation.

The concept of polymerized vesicles was first introduced by Regen et al. [29] in 1980. Vesicles of cetyl(11-(methacryloyloxy)undecyl)dimethylammonium bromide were polymerized, yielding a clear stable solution. Polymerization was confirmed by ^1H NMR spectroscopy, and electron micrographs confirmed the presence of spherical vesicles. The enhanced stability of polymerized vesicles was demonstrated by the unchanged absorbance in the addition of ethanol. In contrast, non-polymerized vesicles showed a dramatic reduction in turbidity. Since these pioneering studies, there have been numerous reports on the synthesis and characterization of polymerized vesicles [30–33].

The unique character of bilayer vesicles has been used to synthesize novel polymer architectures not available by conventional methods. This was demonstrated by O'Brien et al. [34] using a novel two-tailed heterobifunctional lipid, 1-palmitoyl-2-(2, 4, 12, 14-tetraenehexadecanoyl)phosphatidylcholine, containing a diene and a

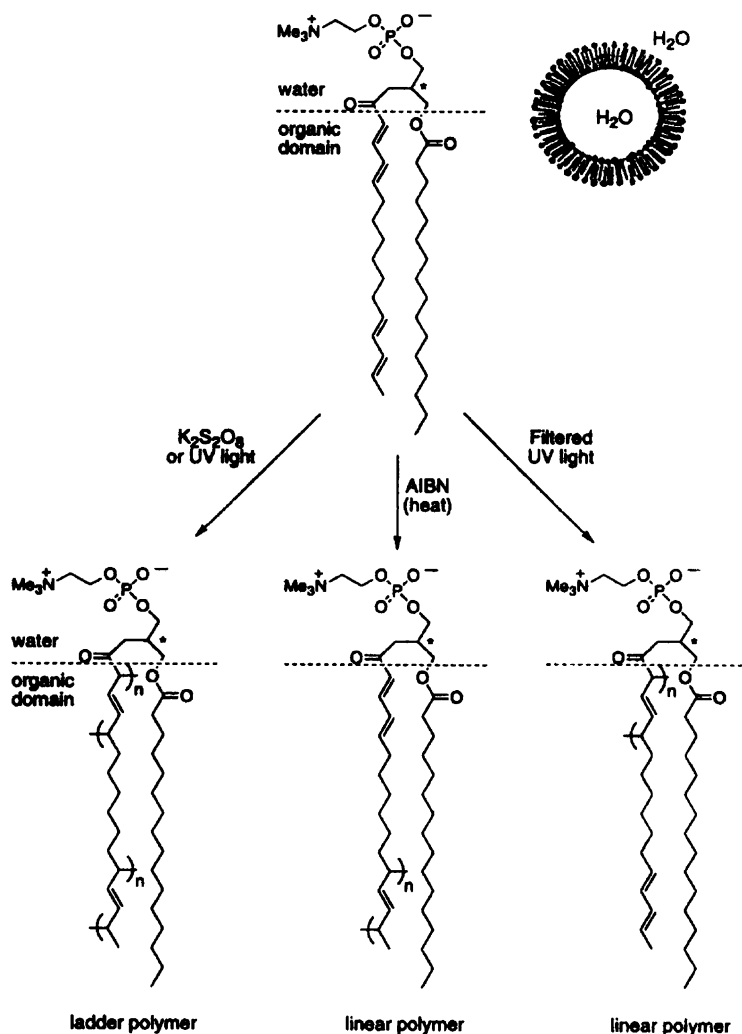


Fig. 4. Simultaneous and selective polymerization of 1-palmitoyl-2-(2, 4, 12, 14-tetraenehexadecanoyl)phosphatidylcholine. Reprinted with permission from reference [9]. © 1987 Elsevier.

dienoyl group in a single chain. The difference in polarity of the local environment of each reactive group within the vesicle made it possible to perform either a simultaneous, or selective polymerization, depending on the mode of initiation (Fig. 4). Polymerization of both groups proceeded through the 1,4-addition mechanism irrespective to the initiation chemistry [34]. The polymerized vesicles formed in each case were linearly-linked, as the addition of Triton X-100 disrupted their structures, and the dried polymers were soluble in organic solvents. Linear and cross-linked assemblies (Fig. 5), whether referring to monolayers, bilayers or non-

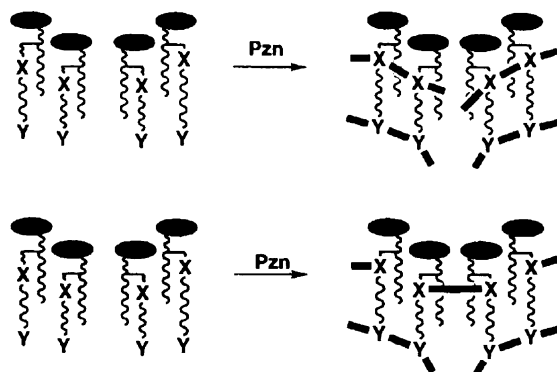


Fig. 5. Schematic representation of a ladder-like and cross-linked polymer. Reprinted with permission from reference [34]. © 1999 American Chemical Society.

lamellar phases, exhibit significant differences in physical properties such as permeability [35,36], chemical stability [37,38] and solubility [37,38]. The manner in which molecules link together in polymer chains largely depends on the number and location of reactive groups per monomer, as well as the mode of initiation. Bifunctional monomers containing polymerizable groups in both hydrocarbon chains typically afford cross-linked assemblies, yielding insoluble, intractable polymers [39]. Therefore, by employing mixtures of mono- and bis-substituted monomers allows the cross-link density of the poly(lipid) structure to be varied accordingly, and provides a convenient way of modifying the physical properties of the final polymer.

Jung et al. [40] proposed an alternative method in which bilayer vesicles can be used for preparing novel vesicle–polymer colloids. Initially, they investigated the effect of polymerizing styrene adsolubilized in a supported bilayer membrane composed of the non-polymerizable surfactant, dioctadecyldimethylammonium bromide. This attempt was unsuccessful as phase separation occurred irrespective of reaction conditions. However, Jung et al. [41,42] showed that styrene and divinylbenzene could be successfully copolymerized in a bilayer matrix composed of polymerizable surfactants, without any phase separation. Novel single- and double-chained quaternary ammonium surfactants were employed bearing one or two terminal styrene groups. A free-radical polymerization was carried out using the oil-soluble photoinitiator 2,2-dimethoxy-2-phenylacetophenone. They found that unilamellar vesicles were obtained with the monofunctional surfmer, whereas the bifunctional surfmer did not form vesicles itself, but could be incorporated into a matrix of the monofunctional surfmer. As demonstrated by O'Brien et al. [39] the cross-linking activity of the bifunctional surfmer enhanced stability, and produced a rippled bilayer morphology.

4. Lyotropic liquid crystals

Condensed high curvature lyotropic liquid crystals or mesophases, with well-ordered periodic nanodomains offer great potential as templates. Although conventional mesophases are more constrained than micellar and bilayer media, they are fluid, and their well-ordered structures can be easily disrupted by physical or chemical forces. One of the first reports on the polymerization of lyotropic liquid crystal phases was by Friberg et al. [43] in 1980. A free-radical polymerization was carried out on a hexagonal liquid crystal phase formed from sodium 10-undecenoate. IR spectroscopy showed the disappearance of the vinyl groups was consistent with essentially complete conversion and small-angle X-ray scattering and polarizing light microscopy monitored the structures. It was found that a structural change occurred during polymerization; the original hexagonal phase was converted to a lamellar phase with an amphiphilic layer thickness of 15.9 Å. This was linked to directional constraints of the end groups. In contrast to the polymerization of bilayers and vesicles, which has been well-established [30–33], the reaction of lyotropic liquid crystal phases, with retention of parent microstructure is rare. Most of the pioneering work carried out in the early 1980s centered upon the polymerization of lamellar phases [44,45].

The first successful representative example of polymerization of non-lamellar phases was carried out by O'Brien et al. [46]. A polymerizable mono-dienoyl-substituted phosphoethanolamine and bis-dienoyl-substituted phosphocholine were employed, containing an isomethyl branch at the chain terminus in order to adjust the lamellar-to-non-lamellar phase transition temperature to a convenient range for subsequent polymerization [47]. A 3:1 molar mixture was used, and at 60 °C an inverted hexagonal phase formed that was polymerized, to yield a hexagonal phase (stable over 20–60 °C). The same lipids at lower concentration were characterized by ³¹P NMR and transmission electron microscopy (TEM), and were consistent with a sample of isotropic symmetry as expected for a cubic phase. This sample was successfully polymerized, maintaining the initial structure.

McGrath [48–51] published a series of papers on the polymerization of mesophases. In the first of four parts, McGrath investigates the aqueous phase behavior, and effect of polymerization on two quaternary ammonium surfactants containing an allyl function in the head group; the single-chain allyldodecyldimethylammonium bromide and its double-chained counterpart allyldidodecylmethylammonium bromide. Using small-angle X-ray scattering (SAXS) and polarizing light microscopy (PLM) McGrath studied the effect of polymerization on a number of mesophases. In general, it was found that a maximum cross-linking of approximately 30% could be achieved with the single-chained surfmer, which agreed well with that found by Rodriguez et al. [52]. On the other hand, polymerization did not occur for the double-chained surfmer. Retention of the initial phase structure was evident, and McGrath assumed that the final structure was composed of a non-polymerized surfactant matrix interwoven with polymer chains. It was found that partial cross-linking of the mesophases enhanced their stability towards temperature changes. This low conversion was attributed to a reduced molecular mobility favoring

termination, as polymerization in dilute aqueous micelles was found to be essentially 100% [52]. McGrath conducted further investigations with ω -undecenyltrimethylammonium bromide; a surfmer containing a polymerizable allyl group at the chain terminus. It was found that mesophases formed by this surfmer could be polymerized to 40%, which was a slight improvement on its H-type analogue, but was still well below the 80% found for its non-aggregated form. The authors claimed that this was due to the aggregated liquid crystal domains acting as a cage, inhibiting polymerization. The increase in rigidity of the hydrocarbon chains led to a decrease in solubility at high surfactant concentrations, and reduced phase stability. However, the partially polymerized phase did exhibit an increased stability towards temperature changes. This led the group to investigate the effect of head-group type. Another T-type surfmer, sodium 10-undecenoate, was employed and, as before, only partial polymerization was achieved (approx. 30%), and where chains were in a fluid-like state (i.e. micellar and hexagonal phase) the original monomeric matrix was largely unchanged. In contrast, partial polymerization of the lamellar gel phase resulted in a phase transformation. To complete the study, McGrath investigated the effect of the polymerizable group. Dodecyldimethylammoniummethacrylate bromide, an H-type surfmer containing a large flexible hydrophilic moiety was investigated. In contrast, it was found that polymerization of both the non-aggregated and aggregated states went to near completion, producing a polymer that was insoluble in water. McGrath's investigations clearly demonstrate the influence surfmer architecture has on the polymerization process.

Further research by O'Brien et al. [53] led to the successful polymerization of an inverted hexagonal phase (H_2), formed by phosphoethanolamine; a di-functional phospholipid with a polymerizable dienoyl group in each chain. The dimensions of the H_2 unit cell were shown to be temperature-dependent prior to polymerization, and then fixed by polymerization at a desired temperature. Consequently, this permits the formation of encapsulated aqueous lipid nanotubes with 'tuneable' dimensions and the capability of acting as novel nanometer sized building blocks.

Significant advances in this area have been made by Gin et al. [54–57] who successfully polymerized an inverted hexagonal phase and synthesized a variety of novel materials inside the encapsulated aqueous nanochannels. In an initial effort a hexagonally ordered poly(*p*-phenylenevinylene) (PPV) nanocomposite was formed by mixing an aqueous solution of poly(*p*-xylylenedimethylsulfonium chloride), with monomer 1 (Fig. 6) and an organic solution of a radical photoinitiator (2-hydroxy-2-methylpropiophenone). The PPV precursor could be accommodated up to 20% by total weight and was assumed to reside in the cylindrical pores of the monomeric and polymeric surfactant templates, as it is a highly charged polyelectrolyte that is completely insoluble in non-polar media. The sample was photopolymerized with retention of microstructure, however, a slight volume contraction was observed. The nanocomposite could be fabricated into highly aligned free-standing thin films, or fibers depending on the method of preparation [54]. PPV entrapped in the aqueous nanochannels exhibited a significant increase in photoluminescence, which was attributed to separation and architectural control on the nanometer level.

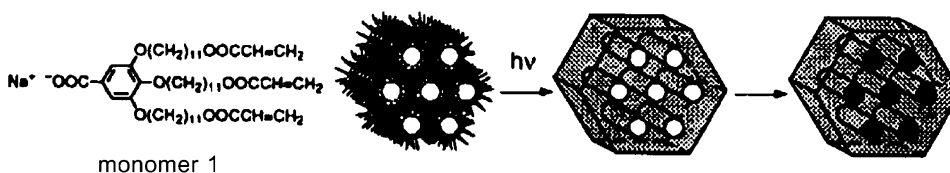


Fig. 6. Schematic representation of the formation of building blocks from the polymerization of the inverted hexagonal phase. Reprinted with permission from reference [54]. © 1999 American Chemical Society.

Having successfully demonstrated the novel templating effect of the inverted hexagonal liquid crystal phase, and the influence of size control on material properties, Gin et al. investigated the relationship between template geometry and surfmer architecture [55]. The effect of employing different metal cations, including transition-metals and lanthanide ions on the hexagonal assembly was investigated. Polymerization was monitored by the loss of acrylate bands (1637 and 810 cm^{-1}) using FT-IR spectroscopy. They found that samples containing metal ions of the same charge exhibited inverted hexagonal phases with very similar d_{100} spacings, regardless of metal ion size. Furthermore, samples containing trivalent lanthanide salts exhibited significantly smaller unit cell dimensions than their divalent transition-metal analogues. In addition, incorporation of these various counterions introduced new properties into the nanostructured polymer networks with the potential of performing chemistry.

In a recent publication, Gin et al. [57] proposed a new strategy for synthesizing catalytic Pd nanoparticles using a polymerized inverted hexagonal network formed by monomer 1. Initially, a Pd(II) salt of 1 was synthesized through an ion exchange with dichloro-(1, 5-cyclooctadiene)palladium(II) in acetonitrile. Although monomer 2 did form the desired inverted hexagonal network, attempts to cross-link the structure were unsuccessful, and resulted in a reduction of Pd(II) to Pd(0) causing disruption of the original microstructure. Instead, they found that carrying out an ion exchange on the cross-linked inverted hexagonal formed by monomer 1 led to a 95% exchange with retention of the parent microstructure. In order to create catalytically active Pd(0) particles in the matrix, the system was reduced with hydrogen gas, yielding a shiny black material. However, powder X-ray diffraction demonstrated that the order in the system disappeared on reduction. Roughly spherical particles with a diameter somewhat larger than the original nanochannels, 4–7 nm were observed through TEM, and a high catalytic activity was observed for hydrogenation and Heck coupling.

5. Microemulsions

Microemulsions exhibit unique microenvironments for performing chemistry and, therefore, there has been a lot of interest devoted to the use of these systems as host media for polymerization reactions. The majority of work in this area has

centered upon the polymerization, in, or of, one or other of the bulk phases to produce new polymeric materials. Stoffer and Bone [58,59] and Atik and Thomas [60,61] carried out pioneering research of polymerization in microemulsions in the early 1980s. Since this time there have been numerous attempts to prepare polymeric nanomaterials by polymerization of a suitable monomer (e.g. methyl methacrylate or styrene) in water-in-oil (w/o) [62,63] or oil-in-water (o/w) [64–69] microemulsions and bicontinuous (middle phase) [70–73] microemulsions. Polymeric materials were traditionally stabilized by non-polymerizable surfactants, such as sodium dodecyl sulfate (SDS) [58], and were usually found to be opaque and very often phase separated. Gan and Chew [74] discovered through incorporating polymerizable acrylic acid as a cosurfactant, stable transparent polymeric materials could be obtained at low water contents (<15 wt.% [74]). However, no well-defined microstructures were observed by scanning electron microscopy. They later found that by replacing SDS with a polymerizable surfactant, such as (11-acryloyloxy)undecyltrimethylammonium bromide, transparent nanoporous polymeric materials could be obtained [75–81]. Microporous polymeric composite electrolytes were obtained from microemulsion polymerization of 4-vinylbenzenesulfonic acid lithium salt, acrylonitrile and a polymerizable non-ionic surfactant, ω -methoxy poly(ethyleneoxy)_n undecyl- α -methacrylate. Polymerization proceeded very rapidly, forming a soft gel within 20 min. The polymerized microemulsion solids exhibited open-cell structures and a reduced specific conductivity compared to the parent, liquid microemulsion. Although, the extent of conductivity retention was shown to increase with water content of the precursor microemulsions. Furthermore, they demonstrated that water could be freely exchanged with organic solvents or electrolyte solutions in these microporous membranes. Such systems could find extensive use in electrochemical devices.

Microemulsion polymerization has also been used to synthesize highly functionalized nanoparticles. Larpent et al. [82] prepared styrene-in-water microemulsions using SDS and polymerizable cosurfactants, such as hydroxyalkyl acrylates or methacrylates. Polymerization went to completion and led to stable suspensions of well-defined highly functionalized nanoparticles in the 15–25 nm diameter range. This technique proved economically sound as a component of the surfactant system which is incorporated within the resulting polymer, and is a convenient way of controlling the level of surface functionality.

A similar method was employed by Tieke et al. [83], however, polymerizable surfactants were used instead of polymerizable cosurfactants. Styrene and 11-(acryloyloxy)undecyltrimethylammonium bromide formed transparent, o/w microemulsions without the addition of any cosurfactant. γ -irradiation-induced polymerization resulting in nanolatex particles, approximately 21 nm in diameter, composed of a copolymer with a mole ratio of styrene to surfmer of approximately 1.5:1. Excess surfactant self-polymerized, forming a homopolymer. The copolymerized surfactant formed a polar shell, which increased particle stability and allowed them to be easily redispersed in solution (Fig. 7a). They extended their study by investigating a H-type surfmer, (2-(methacryloyloxy)-ethyl)dodecyl dimethyl-

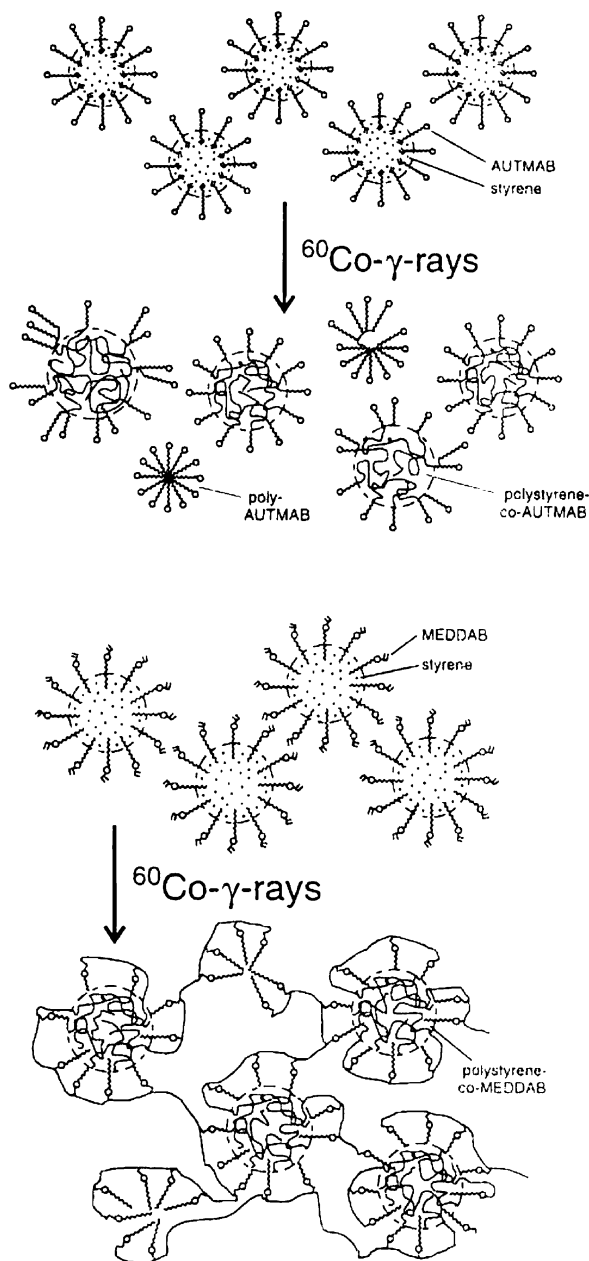


Fig. 7. Schematic representation of T/H-type surfmer copolymerized with styrene. Reprinted with permission from reference [84]. © 1999 American Chemical Society.

ammonium bromide [84]. Polymerization produced copolymers with a completely different morphology to that previously seen with the T-type surfmer. Highly organized, transparent nanogels with high water contents (Fig. 7b) and a large inner surface were formed, which could be used as potential drug delivery systems, chromatographic resins, or catalyst carriers. SANS experiments showed that the structure formed by the polymerized H-type surfmer closely resembled its monomeric analogue, whereas distinct changes were observed for the T-type surfmer. A relatively recent study by Tieke et al. [85] employed a combination of polymerizable and non-polymerizable surfactants. They found that by varying the composition of the amphiphilic interface larger single-phase microemulsion regions could be obtained, resulting in copolymers with a higher styrene content. This offers a versatile method for synthesizing amphiphilic copolymers of tailor-made composition, which cannot be prepared by any other polymerization technique.

Pileni et al. [86,87] proposed an alternative method for synthesizing nanoparticle latexes using surfmers, and showed for the first time that it is possible to obtain particles in the size range 2–5 nm. Reverse micelles in toluene were formed by didecyldimethylammonium methacrylate; a surfmer containing a polymerizable counterion. A UV-initiated free-radical polymerization was carried out, yielding stable latex particles similar in size to the original microemulsion droplets. Mackay and Pileni [87] extended this research by investigating the effect sodium methacrylate, added to the water cores of the reverse micelles had on the final polymer. They found sodium methacrylate in the aqueous cores caused an increase in the efficiency of cross-linking (50 to 83%), with a polydispersity index of 1.1. These particles also showed a tendency for film formation.

Mackay later produced inorganic–organic nanocomposites from a one-system reverse micellar synthesis [88]. CdS nanoparticles were prepared in reverse micelles, stabilized by Aerosol OT in a methyl methacrylate solvent. Polymerization produced opaque solids containing 20–80 nm aggregates of CdS nanoparticles. By employing a 1:1 weight ratio of methyl methacrylate and a polyethylene diacrylate, aggregation was eliminated but the solid remained opaque. However, replacing AOT with didecyldimethylammonium methacrylate led to the formation of a transparent solid matrix containing non-aggregated CdS nanoparticles.

On a similar theme, Hirai et al. [89] synthesized CdS and coprecipitated CdS–ZnS semiconductor nanoparticles in reverse micelles composed of cetyl-*p*-vinylbenzyltrimethylammonium chloride. Through an in situ free-radical polymerization using AIBN or visible light irradiation, these nanoparticles could be successfully incorporated into the polymerized matrix, whilst still maintaining their size and all important quantum size effects. As well as increasing stability, the polymerized PCV shell suppressed undesirable particle growth of the CdS. Although there was no direct linking between the CdS particles and the polymer matrix in both composites, PCV clearly acts as a rigid nanocapsule, capable of entrapping and immobilizing nanoparticles more effectively. However, this may limit the potential of the system to act as a photocatalyst. Furthermore, the PCV matrix was effective in stabilizing Au nanoparticles, as well as for CdS. Therefore, this technique does

not appear system specific, and might be employed as a general method for preparing and stabilizing inorganic nanoparticles.

6. Review conclusions

Since the pioneering surfmer synthesis, carried out by Freedman et al. [1], there has been a vast amount of literature published on the polymerization of, or in organized amphiphilic assemblies. This has led to the formation of a number of unique nanomaterials including open-cell polymer networks, ultrafine polymer latexes and inorganic/organic nanocomposites, which exhibit novel properties, and would be unobtainable through conventional techniques. Amongst other parameters, surfmer composition and molecular structure play an extremely important role in the polymerization process, and essentially govern the final properties of the polymer. For example, using analogous H- and T-type surfmers yields very different polymers with contrasting properties. Significant advances in this field over recent years reflect the high level of attention it has received, which will undoubtedly continue in the foreseeable future as the potential of nanotechnology projects to higher levels.

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