

Chapter 2

Colloidal Properties of Surface Active Monomers

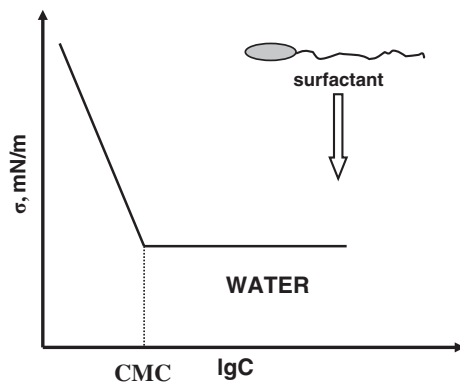
2.1 Colloidal Properties of Surfactants

A surfactants (“surface-active agents”) are defined as a materials that can greatly reduce the surface tension of water when used in appointed concentrations. This concentration is known as critical micelle concentration (CMC) determined as the concentration of surfactants above which micelles form and all additional surfactants added to the system go to micelles [1]. Surfactants are amphiphilic compounds containing both hydrophobic groups and hydrophilic groups [2]. Therefore, they contain oil-soluble and water-soluble components. The typical changing of values of surface tension of water when adding a surfactant is shown on Scheme 2.1.

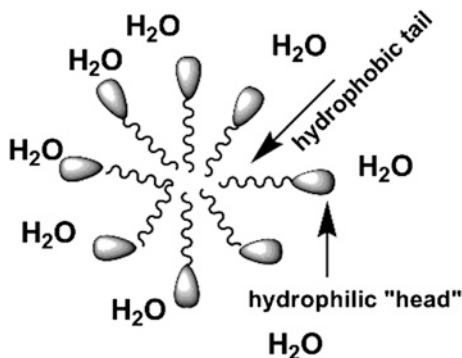
While reaching the CMC, the values of surface tension change strongly with the concentration of the surfactant [1]. After reaching the CMC, the surface tension is almost constant or changes with a lower slope. At the concentrations above CMC, the micelles, which are determined as an aggregate of surfactants, are formed [3]. From the bases of colloidal chemistry, it is known that the classical micelle in aqueous solutions consists of two main parts, namely the hydrophilic “head” regions in contact with solvent and hydrophilic tails in the micelle center [4]. The typical structure of micelle is shown on Scheme 2.2.

With the increase of micelle size, the micelle shape can change from spherical to rod-like or to dimensional disk-like aggregates. The self-assembly of surfactants depends on the length of alkyl chain, the nature of hydrophilic “head,” the salt concentration, pH, and temperature [5].

Specific amphiphilic molecules, such as lipids, are capable to form closed bilayer assemblies in aqueous solution known as vesicles [6]. Special attention is paid to these systems due to their ability to mimic biological cell membranes [7]. Vesicles are larger than micelles, which have a smaller surface curvature and higher degree of organization [6]. The simplest image of vesicle is displayed on Scheme 2.3.



Scheme 2.1.1 Typical surface tension isotherm showing the decrease of surface tension when surfactant is added. The inflection point corresponds to CMC

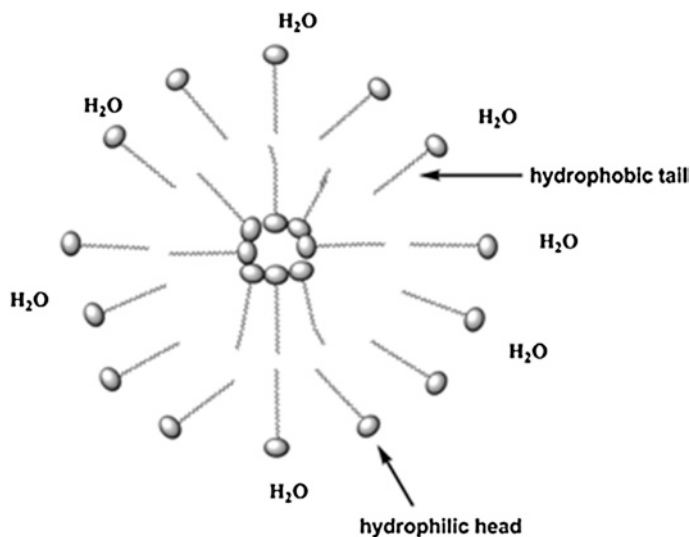


Scheme 2.1.2 The structure of typical micelle in aqueous solution

The above-described bases of surfactants colloidal properties are *background* of colloidal properties of surface-active monomers. Therefore, the next subchapter concentrates on colloidal behavior of surfmers.

2.2 Fundamentals of Colloidal Chemistry of Surface-Active Monomers

It was already told in introduction that surface-active monomers during the preparation of emulsion of monomers in water are located predominantly on the monomer droplet–water interface, thus acting as surfactants stabilizing the emulsion. Colloidal properties of surface-active monomers like in case of traditional surfactants depend on length and origin of lipophilic and hydrophilic fragments.



Scheme 2.3 The scheme of a vesicle formed in aqueous solution

Like typical surfactants, the surface-active monomers most commonly classified according to polar “head” group. A non-ionic surfmers have no charge groups in their “head.” If the charge on the “head” is negative, the surfmers are considered as anionic, and if the charge on the “head” is positive, the surfmers are called cationic. In case surfmer contains a “head” with two oppositely charged groups, it is called zwitterionic. This classification is displayed on the Scheme 2.4.

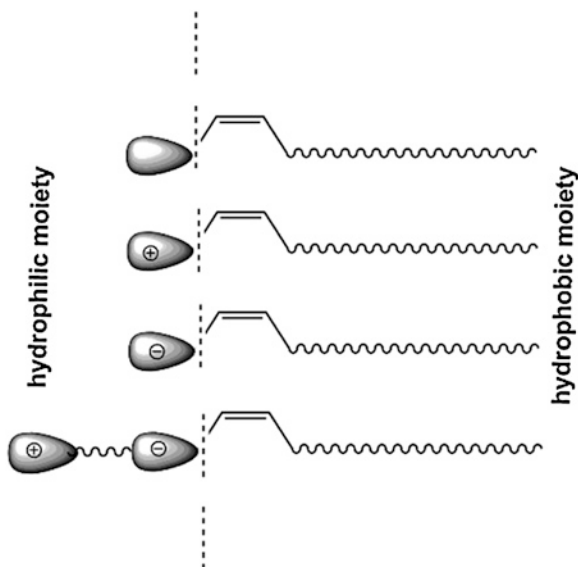
Some typical for surfmers ionic groups are shown on the Scheme 2.5.

The anionic hydrophilic group can influence on a range of parameters: the electrostatic stabilization, the sensitivity to pH, and electrolyte condition. Zwitterionic surfmers can be anionic and cationic or both depending on the structure and medium conditions.

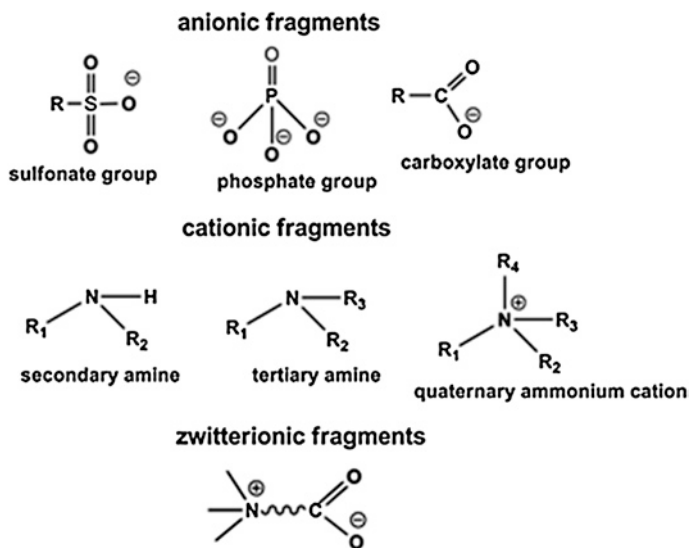
As it was told in introduction, polymerizable part in the molecule of surfmer could be located either in hydrophilic or hydrophobic part or between these two parts.

As opposite to typical monomers, surface-active monomers due to their surface-active properties are characterized by the micelle formation and the adsorption at interfaces [8]. Surfmers are capable to form both true and micellar solutions in water [9]. Also, the surface-active monomers which are structural analogous of phospholipids can form structures resembling biological membranes in solution (vesicles and liposomes) [10] and at the interface (monolayers and polylayers) [10]. Surface-active monomers provide an opportunity for developing hybrid nanosized reaction and templating media with constrained geometries [6].

CMC of surfmers is an essential characteristic and a key point for further application of these compounds. Actually, it is the concentration where the surfmer acts as micelle. Micellization is a strongly cooperative self-association process accruing at a narrow concentration of surfmer [11]. Surface tension measurements are



Scheme 2.4 Classification of surfmers according to polarity: non-ionic, cationic, anionic, and zwitterionic



Scheme 2.5 Some typical ionic groups incorporated in structure of surfmers

generally used for CMC determination. Nevertheless, there are other physical properties that can be used to monitor micelle formation and CMC determination. For example, the rate of increase in osmotic pressure falls into a plateau [11].

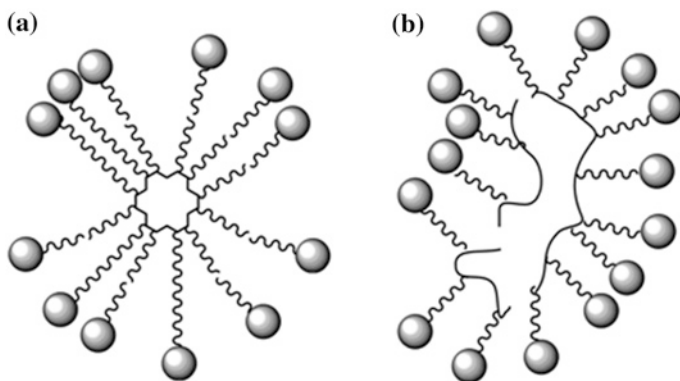
A sharp increase in turbidity is also observed by light-scattering techniques [11]. In conductance measurements, a marked decrease in the slope is observed after crossing CMC indicating that there are much less mobile charged units than expected from the individual surfactants molecules [11]. The so-called hydrophobic effect is considered as a main driving force in self-association that is an entropic driven process [3, 11]. The self-assembly of surfmers like in case of traditional surfactants depends on a range of factors such as length of hydrophobic tail, surfmer concentration, nature of hydrophilic moiety, pH, and temperature. The presence of long hydrophobic chain promotes the poor solubility of surface-active monomers. Therefore, the corresponding monomers form micelles under low concentrations. The introducing of hydrophilic groups of various nature and hydrophobic chains of different length gives an opportunity to vary the surface-active properties of synthesized surfmers in wide range. Since the first publications devoted to colloidal properties of surfmers were appeared, numerous of corresponding papers have been published. For the convenience, the following subchapters focus more on properties and polymerization of micelles, vesicles, mesophases or lyotropic liquid crystals, and microemulsions.

2.3 Properties and Polymerization of Micelles, Vesicles, Mesophases or Lyotropic Liquid Crystals, and Microemulsions

2.3.1 Micelles

One of the earliest publications devoted to micelle polymerization was made by Larrabee and Sprague [12]. The polymerization was only observed at concentration of surfmer above the CMC proving that micelle formation is essential condition of polymerization. This is a typical phenomenon observed with all surface-active monomers and is explained by “condensation effect of monomer” [13], which makes an accelerated propagation step [6]. Polymerization of surfmers in micelles and other self-assembled phases has been studied for at least 30 years. The polymerization process is strongly influenced by the structure and properties of the micelles. The term “polymerized micelle” was discussed in publications of Sherrington et al. [14–16]. He proposed that during the polymerization process, the formation of “polysoap,” an oligomeric species that exhibits micellar-like physical properties. The schematic representation of “polymerized micelle” and “polysoap” is shown on Scheme 2.6.

The monomer reactivity and location of polymerizable appreciably impact on the nature of polymerizable species [17]. During the last decade, it has observed a substantial advance in understanding both the structure and dynamics of polymerizable surfmer micelles. In the review published in 2012, the new insights yielded primarily by small-angle neutron scattering using high-flux sources were highlighted [18]. This technique provides further prospects for realizing and controlling topochemical polymerization in micellar systems.



Scheme 2.6 Schematic representation of “polymerized micelle” (a) and “polysoap” (b)

The physicochemical properties in aqueous solution of synthesized anionic gemini surfmer containing two anionic monomeric parts linked with an ethylene spacer and polymerizable methacryloxy groups covalently bound to the terminal of the hydrocarbon chains were studied [19]. In the region of low added electrolyte concentrations, the synthesized surfmer spontaneously formed spherical micelles in aqueous solution, which was confirmed with the Corrin-Harkins analysis (CMC vs. total counterion concentration) and cryogenic transmission electron microscopy. Al-Sabagh et al. [20] reported about the synthesis of novel surfmers with terminated terminal acrylate group on the hydrophilic moiety. In this work, the surface and thermodynamic parameters of the prepared surfmers were determined at 25 °C including surface tension and effectiveness maximum surface excess, and minimum surface area. Also, the standard free energy of micellization and adsorption were recorded. Micellization and surface-active properties of hydrocarbon and fluorocarbon surfmers were reported in a paper published in Langmuir [21]. The interaction between synthesized surfmers in aqueous micellar state and solubilization capacity was reported. The CMC, fractional charge per micelle, and standard free energy change of micellization were determined for polymerizable sodium itaconate monoesters in a paper published in 2013 [22]. The effect of hydrophobic chain length of synthesized surfmers on micellization parameters was reported. In another paper published in 2013 in Journal of Surfactants and Detergents, micellization and adsorption of new reactive surfmers based on modified nonyl phenol ethoxylates were described [23]. Bunio and Chlebicki [24] characterized sorbic acid amphiphilic polymerizable derivatives. Interfacial activity and micellar properties of synthesized compounds were investigated.

Suresh and Bartsch [25] performed the evaluation of a newly developed anionic surfmer, sulfonated 3-pentadecyl phenyl acrylate, in the emulsion polymerization of styrene and its effect on the polymer properties. The obtained results were compared with the commercially available non-reactive anionic surfactant sodium lauryl sulfate. The corresponding surfmer has a low critical micellar concentration value of 40.11 mg/L in comparison with 2,400 mg/L for sodium dodecyl sulfate.

Zaragoza-Contreros et al. [26] reported about anilinium dodecylsulfate surfmer prepared from aniline and sodium dodecylsulfate for synthesis of polystyrene/pol-aniline core-shell composites. The critical micellar concentration of the salt was determined using electrical conductimetry, which detected that the change of counter-cation, sodium by anilinium, reduced the CMC with respect to the conventional counterpart, sodium dodecylsulfate. In the paper published in 2012, mixed micelles composed of alcohol and hexadecyl trimethyl allylammonium chloride were constructed and their properties were studied [27]. An interesting result is reported in publication of Ohkubo et al. [28]. The authors synthesized and characterized the cationic gemini methacrylate surfmers. The equilibrium properties of surfmers in water were investigated by means of surface tension, and polymerization of resulted micelles was performed. The highly dispersed state of molecular assembly of gemini surfmer was considered as excellent property to prepare uniform polymer micelle without any flocculation of micelles. In the paper published in 2013 in *Journal of Dispersion Science and Technology*, the dynamics of surface activity and a range of parameters such as surface tension at the CMC, adsorption efficiency, and Gibbs free energy of the micellization were evaluated for novel cationic imidazolium surfmers [29]. The maximum surface excess concentration and minimum surface area/molecule at the air–water interface were also estimated. The micellar behaviors of surfmers of acrylamide type, sodium 2-acrylamido-tetradecane sulfonate and sodium 2-acrylamido-dodecane sulfonate, were studied [30]. It was found that the effects of the length of the hydrophobic hydrocarbon chain and the addition of electrolyte on the micellar behaviors for the anionic synthesized anionic surfmers of acrylamide type are similar to typical anionic surfactants. In the other paper, the micellization behavior of homopolymer of (2-acrylamido) ethyl tetradecyl dimethylammonium bromide was investigated [31]. In the paper published in 2012 in *Journal of Colloid and Interface Science*, an empirical model for the concentrations of monomeric and micellized surfactants as a consistent approach for the quantitative analysis of obtained data was presented [32]. The reported concentration model provided an objective definition of the CMC and yielded precise and well-defined values of physical parameters. Benbayer et al. [33] reported about characterization of novel hybrid hydrocarbon/fluorocarbon ammonium-type surfmers. The synthesized surfmers exhibited very low surface tension as well as low critical micellar concentrations. Obtained results indicated that the acrylic function has a pronounced effect on increasing the hydrophobic micelle character. In the paper published by Zhang et al. [34] in 2013, the comparison of properties were made for pressure adhesives generated via emulsion polymerization using both conventional and polymerizable surfactants.

The surface activity of reported maleic surfmers [35] with hydrophobic alkyl-, fluoroalkyl-, and oligomethylsiloxanic could be managed by the nature of hydrophobic blocks. It was found the surface activity decreased in the following range fluoroalkyl- > oligomethylsiloxanic > alkyl chain. The synthesized non-ionic and ionic monomers [36] based on derivatives of 4-hydroxybutyric acid and 6-hydroxyhexanoic acid exhibited significant surface activity, and introducing of hydrophilic groups of various nature and hydrophobic chains of different length

gives an opportunity to vary the surface-active properties of synthesized surfmers in wide range. Also, the synthesized recently saccharide containing monomers [37] are typical surfactants, since they reduce the surface tension on aqueous solution–air interface. As an example, the typical surface tension isotherms of some of above-mentioned surface are shown on Figs. 2.1, 2.2, and 2.3.

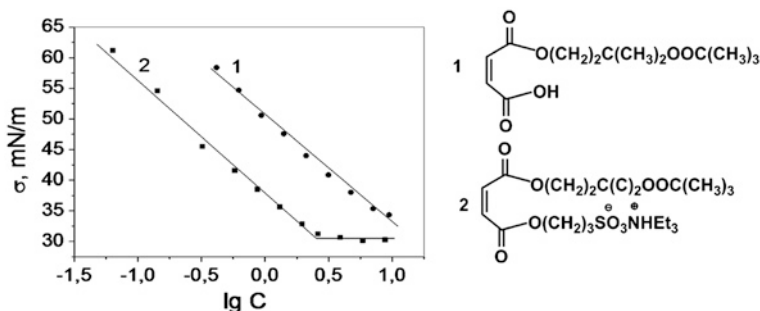


Fig. 2.1 Surface tension isotherms of synthesized maleate surfmers with containing di-tertperoxide group

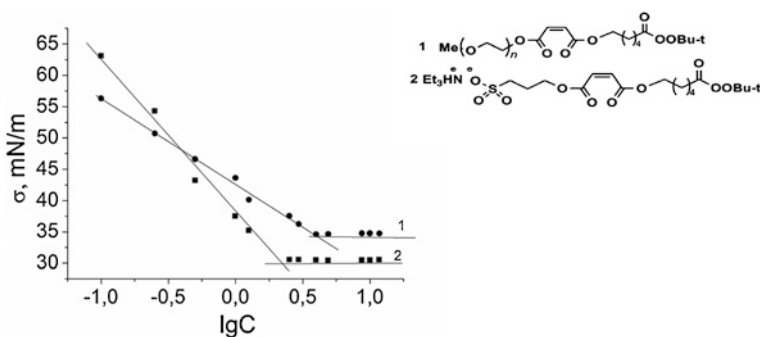


Fig. 2.2 Surface tension isotherms of surfmers containing peroxide groups synthesized from ε-caprolactone

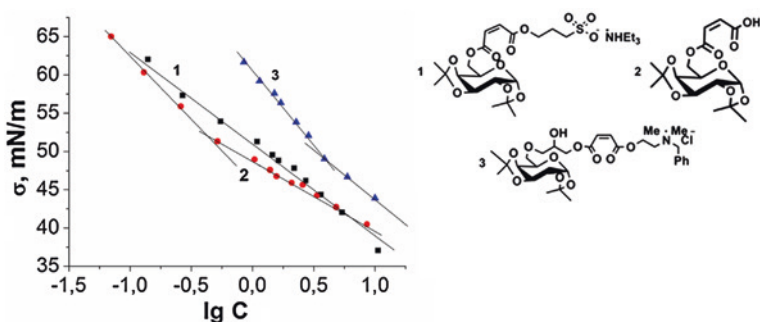


Fig. 2.3 Surface tension monomers of synthesized maleate saccharide containing monomers

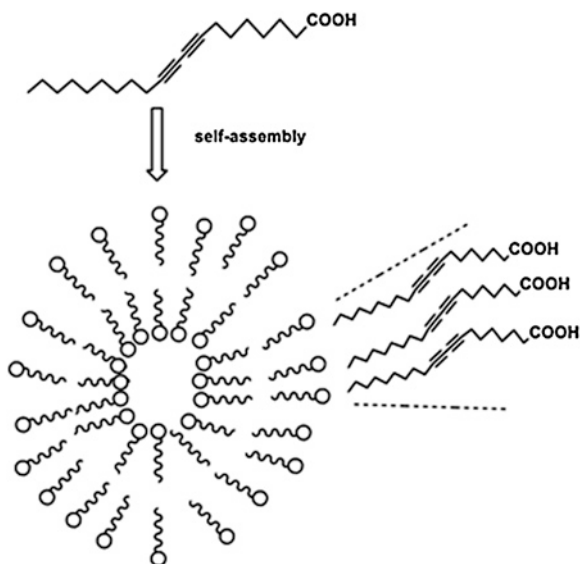
Unusual surface tension isotherms of saccharide containing surfmers could be explained by the capability of diisopropylidengalactoside fragment to form associates with water [38]. This changes the orientation of corresponding compounds at interface.

2.3.2 Vesicles and Bilayers

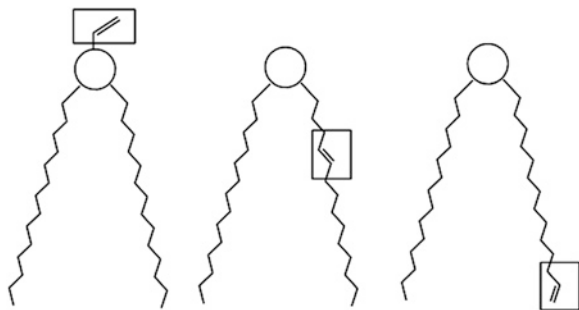
Synthetic vesicles unlike naturally occurring systems tend to revert back to the lamellar phase by vesicle fusion or they precipitate out from an aqueous dispersion [39]. One of the best strategies to overcome this problem is to lock in these structures by the employment of surfmers [40, 41]. Polymerizable vesicles are formed by the functionalization of vesicle-forming surfactant with polymerizable groups. The organization and aggregation of the monomers and their dynamics in the vesicular phase impact on polymerization process and the structure of resulted polymers. Vesicles and liposomes are able to solubilize hydrophobic substances in the interior of their surfactant bilayer. Using hydrophobic monomers, subsequent polymerization leads to the formation of polymer chains entrapped in the hydrophobic part of the membrane. The schematic structure of a vesicle formed by surfmer is shown on Scheme 2.7.

The description of polymerizable vesicles was firstly reported in a publication of Regen et al. [42]. The enhanced stability of resulted polymerized vesicles was additionally confirmed by the unchanged absorbance during the addition of ethanol. The unique character of the bilayer vesicles was used to synthesize novel polymer architectures not available by conventional methods [6]. This statement was confirmed by O'Brien et al. [43] while using novel two-tailed heterobifunctional

Scheme 2.7 Schematic structure of a vesicle formed by surfmer



Scheme 2.8 Locations of polymerizable groups in the structure of reactive lipids



lipid, containing a diene and a 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 simultaneous or selective polymerization, depending on the mode of initiation. The employing of 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 [6]. The schematic presentation of the different locations of polymerizable groups in the structure of reactive lipids is shown on Scheme 2.8.

Jung et al. [44] showed that styrene and divinyl benzene could be successfully copolymerized in a bilayer matrix composed of single- or double-chained quaternary ammonium surfmer bearing one or two terminal styrene groups. It was found that unilamellar vesicles were formed with monofunctional surfmer, while the bis-functional surfmer did not form vesicles itself, but could be incorporated into a matrix of monofunctional surfmer [6, 44]. The cross-linking activity of the bisfunctional surfmer enhanced the stability and produced rippled bilayer morphology [45].

Another interesting and prospective approach includes the utilization of vesicles with the polymerizable group as counterion. One unique feature of using a polymerizable counterion is the possibility of generating a coated vesicle or liposome in a net, in which the polymer network acts as a membrane that is not covalently linked but is electrostatically encasing the bilayers; the components of the lipid bilayer therefore retain their monomeric state [39]. Regen et al. [46] described surfmer with a potentially cross-linkable diallylammonium group as a counterion. One potential drawback with the Regen systems is that the diallylammonium counterions are known to undergo cyclopolymerization to produce linear rather than cross-linked systems and the extent of cross-linking in vesicles might have been limited. In the paper published in *Journal of Polymer Science* in 2004, counterion surfmers, dicetyldimethylammonium 4-vinyl benzoate, and dicetyldimethylammonium 3,5-divinyl benzoate were synthesized and, as expected, these surfmers formed both homo and mixed vesicles which were readily polymerized with a suitable radical photo-initiator [39].

To prepare vesicles with polymerizable bilayers lipids with polymerizable moieties usually needs to be synthesized, and this often involves multistep reactions. Therefore, Lee et al. [47] proposed an alternative, simpler approach based

on a commercially available, single-tailed surfactant, 10-undecenoic acid, a fatty acid with a terminal double-bond. It was shown that 10-undecenoic acid can also be induced to form vesicles by adjusting the pH: vesicles form at intermediate pH (6–8), whereas at higher pH, the vesicles are transformed into micelles. The presence of 10-undecenoic acid vesicles in the pH 6–8 range was confirmed using small-angle neutron scattering and cryotransmission electron microscopy. Subsequent thermal polymerization of 10-undecenoic acid bilayers was carried out using 2,2-dimethoxy-2-phenylacetophenone as initiator. Kaler et al. [48] synthesized cationic methacryloyloxyundecyl trimethylammonium bromide and anionic sodium 4-(ω -methacryloyloxyundecyl)oxy benzene sulfonate and showed that the microstructures formed by mixtures of these surfmers in aqueous solution include stable vesicles, the structure of which can be fixed by polymerization. Another interesting types of surfmers which are capable to form vesicles were introduced in a publication of Bordes et al. [49] published in *Langmuir* in 2007. In this work, a new family of polymerizable surfactants was synthesized starting from a 1:1 mixture of alkylcarboxylic acids (C_{10} – C_{16}) and norbornene methyleneamine. Light-scattering measurements and electron microscopy observations confirmed the spontaneous formation of stable vesicles ($90 \text{ nm} < d < 370 \text{ nm}$). Also, NMR experiments showed the enclosing of the norbornene part inside the vesicle membrane.

2.3.3 *Lyotropic Liquid Crystals*

Lyotropic Liquid Crystals (LLC) assemblies have garnered widespread attention in disparate areas of chemistry. Condensed high-curvature LLC or mesophases, with well-ordered periodic nanodomains offer great potential as templates for mesoporous inorganic materials, as media for biophysical studies of transmembrane proteins (“cubic lipidic phases”), and as therapeutic nucleic acid delivery vehicles [6]. LLCs form by the concentration-dependent supramolecular self-organization of amphiphilic molecules in water into soft materials having distinct hydrophilic and hydrophobic nanoscale domains with long-range periodic order. Moreover, the organized polar and non-polar domains in lyotropic liquid crystalline phases provide an excellent opportunity to produce polymers with geometries and functionalities which cannot be achieved through traditional bulk or solution polymerization. One of the ways that is used for generation of nanostructured material to LLC media is utilization of surfmers to form structured materials on a nanometer scale. The organization of surfmers in LLC phases can have a large influence on the polymerization behavior by changing the local concentration of reactive groups and restricting the diffusion of propagating monomers and polymers [50]. The hydrophilic and hydrophobic domains of LLC can allow confinement of reactants within well-defined dimensions. LLC monomer can assembled into lamellar, hexagonal, and cubic structures according to the molecular structure, type, and content of solvent and temperature. The importance of LLC order during polymerization of monomeric lipids is highlighted

in the publications of O’Brain et al. [43, 51] which demonstrate significant alteration of physical properties when lipids are polymerized in ordered LLC phases. The channel dimensions in the inverse hexagonal structure can be tailored by modifying the length of the hydrocarbon chain of surfmer [50]. Varying the position of the polymerizable group, the tail length, and the counterion of the head group, feature size may be tailored to allow tuning off the properties of resulted materials [50]. The development of functional materials with nanometer-scale architectures and the effect of these architectures on their chemical and physical properties are of great interest in materials design. The studies devoted to formation and polymerizations of LLC carried out in 1980th–1990th are well reported in works of O’Brien et al. [43], McGrath KM and Drummond [52], and McGrath [53]. The applications of polymerized LLC assemblies were discussed in a paper published in 2001 [54].

The biocontinuous cubic lyotropic liquid crystal networks formed by synthesized polymerizable gemini ammonium surfactants is reported in a paper published in 2010 [55]. Another types and application of novel gemini surfmers capable for forming the lyotropic liquid crystal networks is described in US patent published in 2013 [56]. The corresponding anionic surfmers containing at least seven carbon atoms may be used to prepare triply periodic multiply continuous lyotropic phase and polymers thereof that substantially retain triply periodic multiply continuous lyotropic phase structure. The application of ammonium-type gemini surfmers applied for the formation of LLC crystal network was also reported in another US patent published in 2012 [57]. In this patent, a new Q_I -phase gemini LLC monomer system has been developed. Homologs of this gemini ammonium-based monomer system exhibited Q_I phases that could be cross-linked with retention of the structure. The use of methacrylate surfmer, dodecyldimethylammonium ethyl methacrylate, for fabrication polymeric carbon nanotube–liquid crystal composites was reported by Kwon et al. [58]. The bare LC of corresponding surfmer and the dispersions showed columnar hexagonal phases. The nanotubes were well incorporated in the hexagonal LC phase where they induced a swelling of the structure. The advances in the design of polymerizable LLC assemblies are discussed in number of publications [59–62].

2.3.4 Microemulsions

Miniemulsions are a special class of emulsions that are stabilized against coalescence (by a surfactant) and Ostwald ripening (by an osmotic pressure agent) [63]. A major difference between emulsions and microemulsions comes from the amount of surfactant needed to stabilize the systems. 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 [6]. The basic feature of performing polymerization in microemulsion is that in these systems, nucleation can take place directly inside very small monomer droplets. The miniemulsions are produced by high-energy homogenization and usually yield stable and narrowly

distributed droplets with a size ranging from 50 to 500 nm. The first surveys in this field were carried out in the early 1980s by Stoffer and Thomas [64, 65]. In the pioneering studies, the utilization of non-polymerizable surfactants as stabilizers, such as sodium dodecyl sulfate, often led to phase separation. Later, it was found that incorporation of surfmers instead of traditional surfactant can solve the range of problems during miniemulsion polymerization [66]. The microemulsion polymerization in the presence of surfmers is discussed in the next chapter.

For conclusion, it should be said that surface-active properties of surfmers, namely the capability to form micelles and vesicles, and combination of the length of hydrophobic chain and a nature of hydrophilic part open a large opportunities for performing various polymerization techniques. The next chapter is devoted to polymerizable behavior of these compounds.

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