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Reactive surfactants – chemistry and applications
Part I. Polymerizable surfactants

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Abstract: Reactive surfactants, due to their versatility, are being rapidly developed and they are finding more and more applications. The aim of this paper is to present recent advances in the chemistry and technology of functional surfactants: surfmers (polymerizable surfactants), inisurfs (surface-active initiators), and transurfs (surface-active transfer agents). Reactive surfactants, beside other advantages, are also environmentally friendly and their use can reduce costs of chemical processes.

In this part of a brief review, basic information about reactive surfactants is presented and surfmers are described and discussed. Surfmers combine properties of surfactants (surface activity) and monomers (ability to polymerize). They are widely used for emulsion polymerization, but their other, more sophisticated applications include miniemulsion stabilization, nanomaterials synthesis, drug-delivery systems, and hydrogels.

Keywords: polymerizable surfactant, surfmer, surface-active monomer, polymerizable emulsifier, emulsion polymerization, nanomaterial, drug-delivery system, hydrogel.

Surfaktanty reaktywne – chemia i zastosowania
Część I. Surfaktanty zdolne do polimeryzacji

Streszczenie: Ze względu na wszechstronność zastosowań reaktywnych surfaktantów następuje szybki rozwój metod syntezy tej grupy związków. W artykule zaprezentowano najnowsze osiągnięcia chemii i technologii reaktywnych surfaktantów: surfmerów (surfaktantów zdolnych do polimeryzacji), inisurfów (powierzchniowo czynnych inicjatorów) oraz transurfów (powierzchniowo czynnych środków przeniesienia łańcucha). Zastosowanie reaktywnych surfaktantów może uczynić proces chemiczny bardziej przyjaznym środowisku i obniżyć koszty jego prowadzenia.

W tej części artykułu przedstawiono najważniejsze informacje dotyczące reaktywnych surfaktantów oraz opisano szerzej surfmery, które łączą w sobie właściwości charakterystyczne dla surfaktantów (aktywność powierzchniowa) oraz monomerów (zdolność do polimeryzacji). Surfmery są szeroko stosowane w polimeryzacji emulsyjnej, ale mają również inne, bardziej wyrafinowane zastosowania, takie jak: stabilizacja miniemulsji, synteza nanomateriałów, systemy dostarczania leków i hydrożele.

Słowa kluczowe: surfaktant zdolny do polimeryzacji, surfmer, monomer powierzchniowo czynny, emulgator zdolny do polimeryzacji, polimeryzacja emulsyjna, nanomateriał, system dostarczania leków, hydrożel.

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Due to many regulations concerning environment protection and safety of chemical processes, solvent-based systems are being substituted with aqueous systems. This tendency is also present in polymers production and results in growing importance of emulsion polymerization. Moreover, in many fields new forms of delivery are required, *e.g.*, micro- and nanoemulsions, concentrated emulsions, or suspoemulsions. It results in the need to develop new surfactant systems [1]. The synthesis of a surfmer by Freedman *et al*. in 1958 [2] is considered to be the first step in development of a new class of compounds – reactive surfactants.

Reactive surfactants have the ability to covalently bind to the dispersed phase. As a result they cannot be displaced from the interface as easily as traditional surfactants, which are only physically bonded. Permanent attachment to the dispersed phase have also environmental and economic advantages. It results in lower use of surfactants and smaller contamination of sewage. Reactive surfactants can be used to obtain redispersable lattices [3], latexes with functionalized surface [4], or dispersions with increased stability [5]. It is worth mentioning that they are widely applied in industrial processes to obtain inkjet inks [6–9], water-thinnable alkyd resins for coating purposes [10–11], and other coating compositions [12]. Reactive surfactants can be also used for many advanced applications, *e.g.*, nanoparticles stabilization, drug-delivery systems, hydrogels, and many others.

There are three basic groups of reactive surfactants: surfmers – polymerizable surfactants, inisurfs – surface-active initiators, transurfs – surface-active transfer agents. All this three groups of reactive surfactants form micelles in aqueous solutions above the critical micelle concentration (*cmc*). It is worth mentioning, that reactive surfactants can be either relatively small molecules, or macromolecules.

The most popular among reactive surfactants are surfmers, which are commercially available and used in large scale chemical processes. The use of inisurfs and transurfs is more problematic. In addition to dispersion stability, the concentration of inisurf affects polymerization rate and the concentration of transurf affects molar mass distribution [13]. Furthermore, the cage effect makes the efficiency factor of inisurfs very low [14, 15]. For these reasons, it is harder to optimize the polymerization process while using inisurfs or transurfs.

SURFMERS

Surfmers, also known as polymerizable surfactants, surface-active monomers, polymerizable emulsifiers, monomeric surfactants, or monomeric emulsifiers, are the largest group of reactive surfactants. Polymerizable surfactants act in emulsion polymerization both as a surfactant and as a co-monomer. Usually, emulsion stabilization is their main objective, and the ability of copolymerization is an extra advantage, which can eliminate purification step after polymerization, which is necessary when using traditional surfactants. Polymerizable surfactant simply builds into polymer structure and does not remain in reaction mixture. It also prevents migration of a surfmer to the interface (polymer/air and polymer/substrate) in films formed of the lattice. It results in better properties of the coating and reduces water sensitivity, adhesion, or gloss [16–18].

Aside from emulsion polymerization, surfmers can be used for more sophisticated purposes, *e.g.*, for drug-delivery systems, hydrogels, nanomaterials, and encapsulation.

Structure

Surfmer consists of three parts:

– a hydrophobic moiety;
– a hydrophilic moiety;
– a polymerizable moiety – usually with a double bond.

Surfmers can be anionic, cationic, or non-ionic.

Polymerizable surfactants can have various polymerizable moieties. Most popular moieties are:

– acrylic/methacrylic [19–21];
– vinylbenzyl [22–25];
– maleic [26–28].

A great advantage of maleic-based surfmers is the fact, that they do not enter homopolymerization, but copolymerize with most vinyl monomers [29].

The polymerizable moiety can be localized either at the hydrophobic part of the surfmer, or at the hydrophilic part.

Properties

Surfmer reactivity is very important aspect. It needs to be well balanced. If the surfmer is too reactive in a polymerization process, it will quickly build into growing polymer chain and get buried inside lattice particle, which may cause problems with emulsion stability. On the other hand, to low reactivity results in very low incorporation of surfmer into lattice. There is of course no ideal surfmer, but some balance needs to be found to get a stable polymerization process and good surfmer incorporation [30]. Optimal surfmer behavior is to maintain low surfmer conversion at the beginning of the process and reach high conversion at the end of the polymerization [31]. When it comes to *cmc*, its value should be low. In that case, aqueous phase polymerization of the polymerizable surfactant is limited and the risk of forming polysoaps, which can cause bridging coagulation of lattice particle, is minimized [4, 32]. Requirements for the optimal performance of surfmer during emulsion polymerization have been excellent described by Asua and Schoonbrood [13].

Surfmers can be divided into three groups, which differ in the type of the hydrophilic moiety. The hydrophobic moiety is in most cases a hydrocarbon chain, but polysiloxane [33], polycaprolactone [34], or poly(propylene oxide) [24, 35–37] chain can also be used.

The hydrophilic moieties in anionic surfmers are:
- phosphates [24, 37];
- sulphates [38, 39];
- carboxylates [40–43].

There is a large number of commercially available anionic surfmers. They are produced by Sigma-Aldrich (483729, 454974), Clariant (Emulsogen APS 100, APS 104, APS 100 S, APG 2019), Croda (Maxemul 6106 and 6112), Ethox (E-Sperse RS-1596, RS-1618, RS-1684, RX-202), Evonik (Visiomer MPEG 750 MA W).

Cationic surfmers in most cases are quaternary ammonium salts. An important group of cationic surfmers are gemini surfmers.

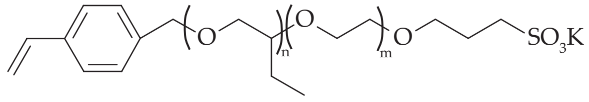
In case of non-ionic surfmers, the hydrophilic moiety is usually a poly(ethylene oxide) chain [22, 34, 44]. Hydrophilic moiety can be also based on, *e.g.*, polyglycidol [45] or glucose [46]. The hydrophobic moiety is usually a long hydrocarbon or poly(propylene oxide) chain.

Commercially available non-ionic surfactants are produced by Clariant (Emulsogen RAL 100, RAL 109, RAL 208, RAL 307, R 100, R 109, R 208, R 307), Croda (Maxemul 5010, 5011), GEO SC (Bisomer EP100DMA, EP150DMA, PEM63P HD) and Ethox (E-Sperse RS-1616, RS-1617, RX-201).

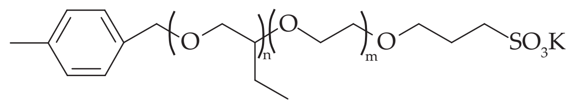
Applications

Emulsion polymerization of acrylate monomers, gemini surfmers, styrene and styrene copolymers, and other monomers

Guyot's group investigated the use of styrene containing block-copolymers as polymerizable surfactants in emulsion polymerization of core-shell acrylic latexes [47]. The authors have found that copolymers containing a large amount of the monomer units are formed. The uncopolymerized surfmer [Formula (I)] can be desorbed from the particles, but it was incomparably more strongly adsorbed than the nonreactive surfactant [Formula (II)].



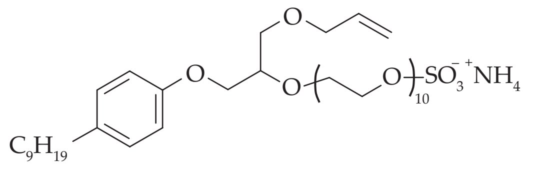
(I)



(II)

The latex prepared with a surfmer can be washed without aggregation, whereas a latex prepared with an analogue nonreactive surfactant was rapidly flocculated. From the nuclear magnetic resonance spectroscopy (NMR) data the authors estimated that about 5 % of the surfmer units remained in the serum, most probably as copolymers, while only a part of the hydrophilic poly(ethylene oxide) sequence was mobile enough to participate to the steric and electrosteric stabilization of the particles. A nonreactive surfactant (II) is more distributed in the water phase than an analogue surfmer.

The effects of the type and amount of the surfactant, allyloxy nonylphenol propyl polyoxyethylene ether sulfate [Formula (III)], and reactive cosurfactant stearyl methacrylate [Formula (IV)] on the miniemulsion polymerization of acrylate monomers were studied by Li *et al.* [48]. The results obtained by them showed that the resultant polyacrylate miniemulsion had a high monomer conversion rate and a low coagulum fraction, which were affected little by the surfactant and cosurfactant type.



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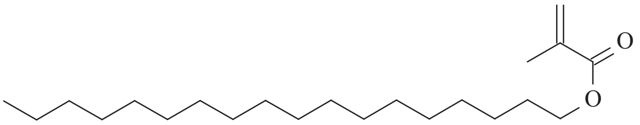
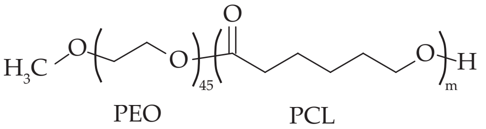


(IV)

Tan *et al.* [34] reported synthesis of similar amphiphilic diblock [Formulas (V), (VI)] and triblock copolymers [Formulas (VII), (VIII)] consisting of central poly(ethylene oxide) (PEO) as a hydrophilic segment and poly(3-caprolactone) (PCL) as hydrophobic segments. These block copolymers were end-functionalized by esterification with linoleic acid (LA), which contains reactive allylic double bonds.

Diblock copolymers:



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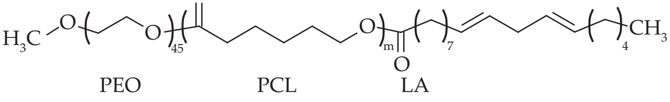
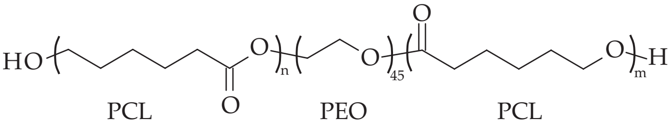


(VI)

Triblock copolymers



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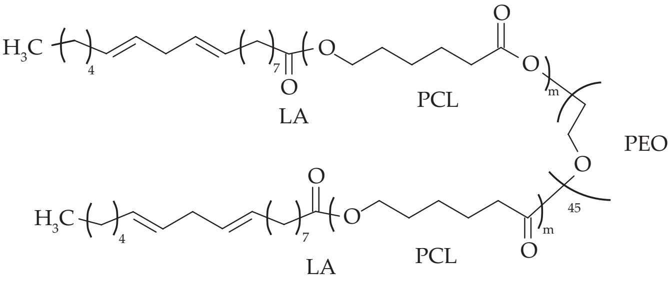
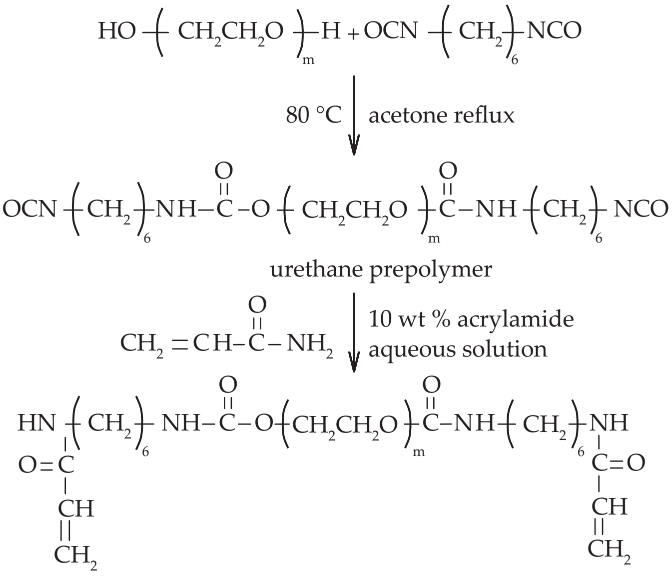


(VIII)

The latices of PMMA prepared with LA-functionalized diblock and triblock copolymers yielded narrow particle size distributions and particle sizes of 180 and 370 nm, respectively, whereas latices prepared with typical surfactant – sodium dodecyl sulfate (SDS) had a particle size of 90 nm. After extraction of the latex particles with methanol, the amounts of the unextractable (either buried or copolymerized) LA-functionalized diblock and triblock copolymers were 10 and 24 % of the initial amount of surfactant added, respectively. Control experiments with a stearic acid containing diblock copolymer showed that the amount of buried surfactant in PMMA latices was *ca*. 6.5 %.

Jung *et al.* [49] presented other acrylic group-terminated polyurethane macromonomer surfmer obtained from urethane prepolymer and acrylamide (Scheme A), which was applied for as a reactive stabilizer in the dispersion polymerization of methyl methacrylate in methanol.

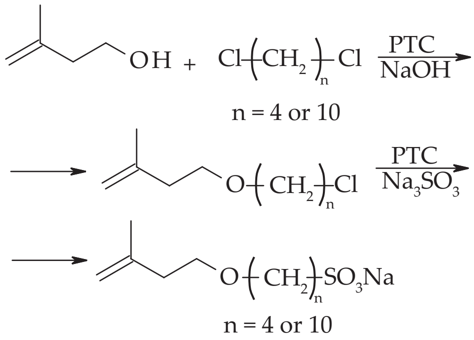


Scheme A

The authors obtained monodisperse PMMA microspheres that had good uniformity with 20 wt % macromonomer content. The macromonomer acted as an effective stabilizer, and therefore the monodisperse stable and cross-linked PMMA microspheres could be prepared.

Schoonbrood and Asua [31] have defined the optimum conditions of use of polymerizable surfactants, namely anionic maleic surfmers in various emulsion copolymerization systems including styrene, acrylates, and vinyl acetate. They have found that the reactivity ratios were the most important variable controlling the incorporation of the surfmer into the polymer chains. The surfmer conversion also depended on the particle size: the larger the particle size, the lower the surfmer conversion. They have found that when the surfmer copolymerized well with the monomers attaining high conversions from the beginning of the process onward, a significant part of the surfmer was buried in the particle interior, leading to unstable latexes.

Recently, Roy, Favresse, and Laschewsky [50] presented a new type of sulfonated anionic surfmer terminated with an isobutenyl reactive group (Scheme B), and its alternating copolymerization with fumarates and maleimides.

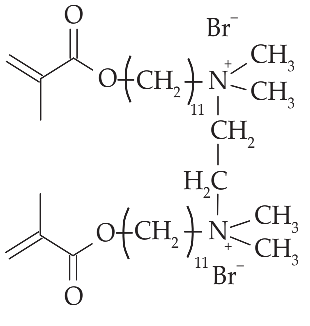


Scheme B

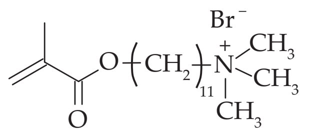
The authors claim, similarly to Schoonbrood and coworkers [51], that the "ideal" surfmer should have a polymerizable group of rather lower reactivity in comparison to polymerized monomers. Otherwise, the surfmers are mostly fixed to the latex particles at the beginning of the emulsion polymerization, and will be buried in the course of the process leading to poor stability of the latexes. Thus, the relatively low reactivity of the novel surfactant monomer towards acrylics and vinyl monomers should be particularly advantageous for stabilizing growing latex particles.

Recently, polymerizable gemini surfactants have attracted increasing attention for their novel physicochemical properties. Gemini surfactants contain two monomeric surfactants linked with a spacer. In comparison to typical monomeric surfactants they present lower critical micelle concentration (*cmc*), a lower surface tension measured at the *cmc*, spontaneous formation of vesicles and worm-like micelles even at relatively low concentrations, and a lower Krafft temperature and good water solubility in the case of ionic gemini surfactants. When gemini surfactants are used the total consumption of chemicals in industrial products is reduced and therefore they can be recognized as environmentally friendly materials [52]. Due to their excellent adsorption and micellization capability at low concentration they exhibit remarkable physico-chemical properties attractive for materials for many applications.

Usually, gemini surfmers contain polymerizable groups, such as acrylate one, and two ammonium groups, *e.g.*, *N*,*N*,*N'*,*N'*-tetramethyl-*N*,*N'*-bis(11-methacryloyloxyundecyl)ethylene diammonium dibromide [53].



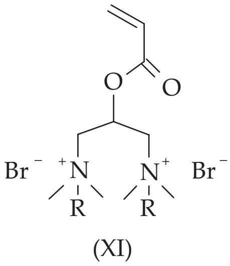
(IX)



(X)

Abe and coworkers [53] showed that the polymerizable cationic gemini surfactant [Formula (IX)] containing methacryloxy groups at the terminal of each hydrophobic chains have no contact with the air/water interface in the monolayer, whereas for the corresponding monomeric surfactant [Formula (X)], the methacryloxy group contacts at the interface forming a looped configuration like a bolaamphiphile. Polymerized micelles of the gemini surfactant are fairly small monodisperse and spherical particles with a mean diameter of 3 nm. The aggregation properties of such gemini surfactant in the condition of added electrolytes have been investigated by the same group [54].

Li *et al*. [55] showed that the polymers built of polymeric gemini surfactant with acrylic group in the spacer exhibited novel selfassociation behavior and were expected to be good functional materials. Very recently, the same group compared obtained results with the use of gemini surfmer to those of single-chain surfmer [56]. They reported that the gemini surfmers [Formulas (XI), (XII)] possess low critical micellar concentration (*cmc*) value and the surface tension value at *cmc* (γ_{cmc}). The introduction of the acryloxyl group into surfactant resulted in a higher degree of ionization and micropolarity of aggregate. These results the authors attributed to the existence of intramolecular dipolar interaction between the carbonyl of acryloxyl group and the cationic nitrogen atom. This increases the hydrophobicity and the regularity of the molecule, which induces the formation of tighter and larger size aggregate in comparison with reference gemini surfactant [Formula (XIII)] without the acryloxyl group.



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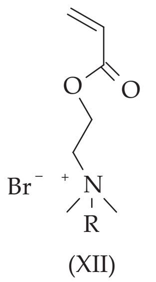

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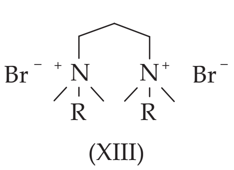
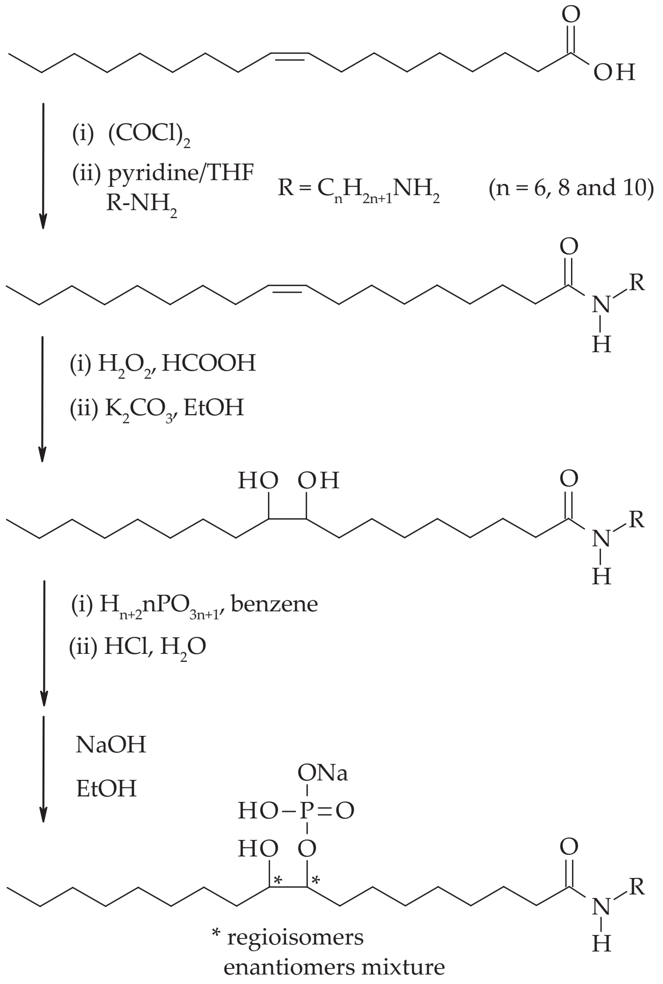


(XIII)

R = dodecyl, tetradecyl, hexadecyl

Semi-fluorinated gemini surfactants containing acrylic group located in the linkage between the two hydrophilic heads were synthesized to evaluate their surface active properties alongside with their antibacterial and antifungal properties [57]. Moreover, Caillier and coworkers showed that the introduction of a polymeric moiety into the spacer lead to advanced functional materials.

Abe's group developed three types of oleic-based gemini surfactants: anionic phosphate- (Scheme C) [38], sulfonic- [58], carboxylic-, and non-ionic sugar-type surfactants [52].



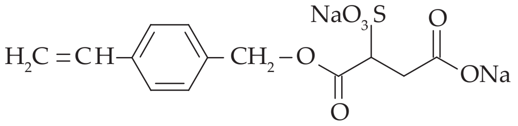
Scheme C

New sorbic acid amphiphilic derivatives with quaternary ammonium groups as gemini polymerizable surfactants were proposed by Bunio and Chlebicki [59].

Arz [60] claimed that the combination of anionic surfactants with non-ionic polymerizable ones lead to stable dispersions, which can be used as a binder for lacquers and paints.

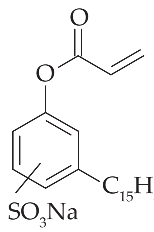
He and Zhang [61] revealed that acrylic pressure-sensitive adhesives obtained with the use of polymerizable surfactant showed adhesion properties and water resistance better than those of conventional ones. These differences the authors attributed to the different migration abilities of the surfactants. Similar results were obtained by Severtson's group [62]. As emulsifiers the authors used ammonium salts of sulfonated nonylphenol ethoxylates. The polymerizable surfactant contained a reactive double bond at its phenyl ring allowing for participation in free-radical polymerization.

Guyot's group [25, 63] investigated preparation of miniemulsions of styrene or methyl methacrylate in the presence of a styrenic polymerizable surfactant – vinylbenzylsulfosuccinic acid sodium salt [Formula (XIV)].

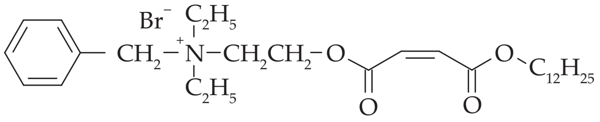

(XIV)

Anionic surfmer, containing less reactive allyl terminal group, namely sodium undec-10-enoate ($CH_2{=}CH(CH_2)_8COO^-Na^+$), was proposed and used for styrene emulsion polymerization initiated by ^{60}Co γ-rays by Wang and Huang [64]. The authors claimed that resultant latex particles had good monodispersity. The colloidal stability of the latex prepared with that surfmer was better than that prepared with a conventional surfactant. The obtained latexes with droplet diameters in the range 100–250 nm indicated excellent stability when potassium persulfate was used as an initiator. The authors revealed that the size of the particles was further increased by using these latexes as a seed polymerization of the monomer in the presence of another polymerizable non-ionic surfactant. Guyot and Goux [65] presented dodecyl monoester of maleic acid as a cheap and efficient anionic stabilizer for the emulsion polymerization of styrene. The authors claim that such simple reactive surfactant can be applied in rubber industry where polymer products are recovered upon flocculation.

Suresh and Bartsch [40] applied anionic polymerizable surfactant – sulfonated 3-pentadecyl phenyl acrylate [Formula (XV)], in emulsion polymerization of styrene. They have found that behavior of surfmer containing polymers resembles that of plasticized ionomers.

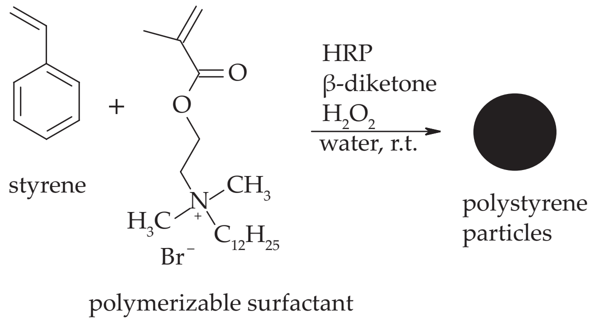

(XV)

A polymerizable cationic dialkyl maleic emulsifier with hydrophobic chain ($R = C_{12}H_{25}$) [Formula (XVI)] was investigated in batch emulsion copolymerization of styrene and butyl acrylate [66]. Guan group revealed that such maleic emulsifier has lower *cmc* and surface tension compared with cationic cetyltrimethyl ammonium bromide emulsifier.


(XVI)

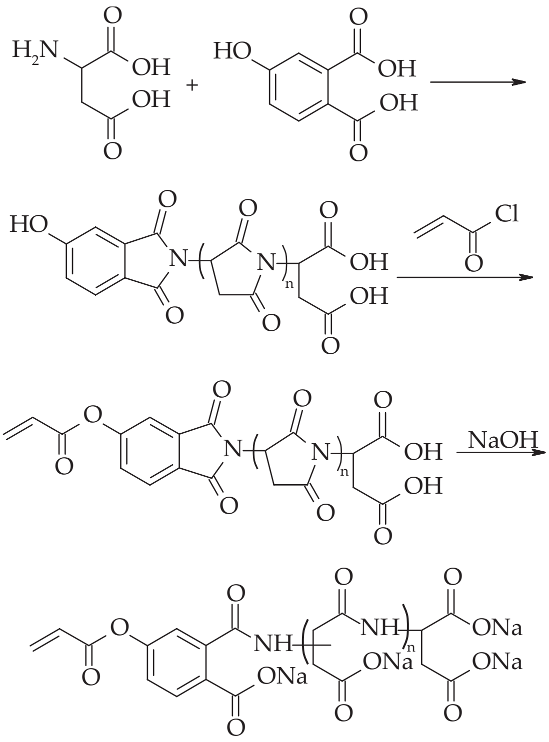
Zhang, Kang, and Luo [67] have revealed emulsion copolymerization of styrene-butyl acrylate-acrylic acid which was carried out using single or combined polymerizable emulsifiers, such as hydroxypropyl methacrylate sodium sulfate, sodium vinyl sulfate, and vinyl alkylphenol polyether sulfates. The copolymerization was proceeded in the presence of colloidal nano-SiO_2 dispersion and obtained films exhibited high hardness and water-resistance.

Kohri *et al.* [68] applied polymerizable surfactant such as *N*,*N*-dimethyl-*N*-*n*-dodecyl-*N*-2-methacryloyloxyethyl ammonium bromide (Scheme D) for enzymatic miniemulsion polymerization of styrene using a horseradish peroxidase (HRP) as an enzyme and in the presence of H_2O_2/β-diketone as initiating system.



Scheme D

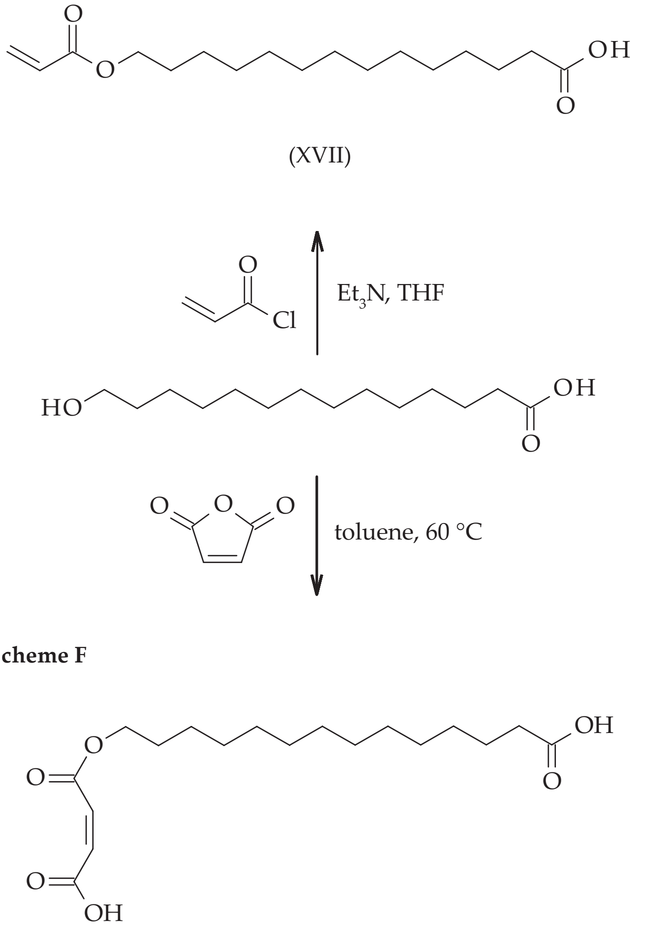
Interesting biodegradable and polymerizable surfactant – sodium polyaspartate with an acryloyloxy end group (Scheme E) was synthesized by Tomita and Ono [69].



Scheme E

The authors used this polymerizable stabilizer in dispersion copolymerization of styrene in a mixture of ethanol and water. The polyaspartate macromonomer acted as an effective stabilizer and yielded submicron-sized polymeric particles in dispersion polymerization carried out in polar medium. The particles were smaller than those prepared when polyaspartate surfmer without acrylic group was used as a dispersion stabilizer.

Recently, Hu *et al.* [43] presented anionic polymerizable surfactants obtained from biobased ω-hydroxy fatty acids. Synthesis of ω-acryltetradecanoic acid [Formula (XVII)] and ω-maleate tetradecanoic acid [Formula (XVIII)] are shown in Scheme F.



(XVII)

Scheme F

(XVIII)

It was found that both surfmers were effective surfactants in the emulsion polymerization of styrene, yielding stable latexes, small particle sizes, and reasonably fast polymerization rates. The particle sizes ranged from 52 to 155 nm, when applied at loadings from 10 to 1 wt % of surfactant to styrene.

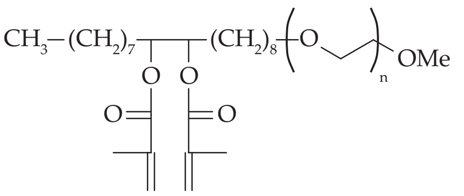
Reactive surfactants were also used for polymerization and copolymerization of other monomers. Kitzmiller *et al.* [70] used an allylsulfosuccinate as surfmer in miniemulsion copolymerization of vinylacetate and vinylethylhexanoate. Authors demonstrated vinylethylhexanoate in miniemulsion, and also the gain in nucleation efficiency obtained by the addition of surfmer to the formulation.

Nanostructured droplets and capsules

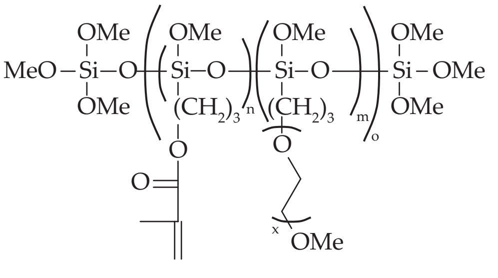
Very recently, Taden and coworkers [71] proposed stabilization of reactive emulsions *via* cross-linkable surfactants. Emulsion droplets were stabilized by an interfacial reaction between the active material and the reactive surfactant. Polyaddition-type reaction between an amine and a reactive cross-linkable surfactant ("cross-surf") containing epoxy groups was used as a model system. High sheer force miniemulsification was utilized to obtain small, narrowly distributed nanodroplets. Miniemulsion droplets were not densely covered with surfactant molecules and often referred to as "critically stabilized" [72]. The proposed cross-surfs are able to stabilize reactive compounds without the need of dense encapsulation. Reactive epoxide surfactants were utilized for interfacial polyaddition with amine nanodroplets and followed by isothermal titration calorimetry experiments that clearly indicate an interface deactivation with an ultrathin stabilization layer formed.

Crespy *et al.* [24] described synthesis of polymer particles and nanocapsules stabilized with PEO/PPO containing polymerizable surfactants in miniemulsion.

Different types of cross-linkable surfactants are currently being developed by authors of this review. First of the cross-surfs was fatty acid-based non-ionic surfactant containing two methacrylic groups [Formula (XIX)]. Second type is a group of graft copolymers with polysiloxane as the main chain and poly(ethylene glycol) and methacrylic side chains [Formula (XX)]. Both of this cross-surfs are to be applied as shell-forming agents for encapsulation of hydrophilic liquids [*e.g.*, low molar mass poly(ethylene oxide)] in emulsion polymerization. They are supposed to form a durable shell due to their cross-linking ability.



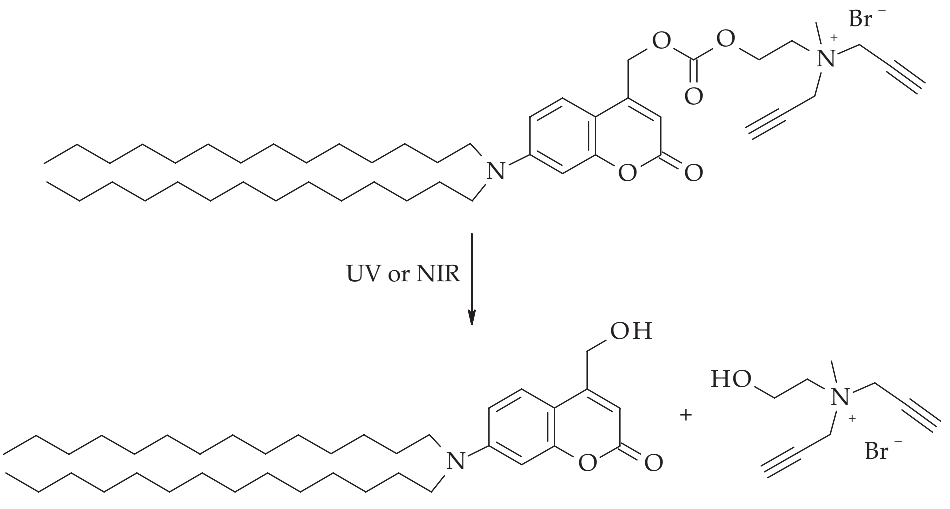
(XIX)



(XX)

Drug-delivery systems

Very recently, Dong and coworkers [73] revealed the use of an amphiphile that contains a coumarin unit and alkynyl groups, as a two-photon-cleavable segment and polymerizable groups for stable drug-delivery systems. The reactive surfactant was obtained from a coumarin derivative as the two-photon-cleavable unit with hydrophobic chains of tetradecyl groups and hydrophilic ammonium group. The coumarin unit was alkylated with *n*-tetradecyl bromide and then coupled with dipropargyl aminoalcohol. The latter one was finally converted into ammonium moiety in the reaction with bromoethane.



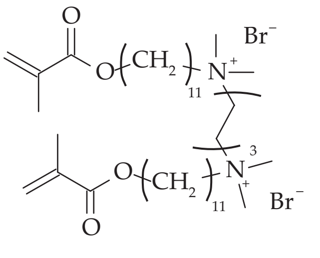
Scheme G

Such amphiphile formed a vesicle-type assembly, which can be stabilized by *in situ* "click" polymerization. Hydrophobic guests can be encapsulated within the vesicle membrane and can be released from the vesicle by UV or near-IR (NIR) irradiation, through splitting up the amphiphilic structure of the product (Scheme G).

Biodegradable gemini surfactants with gemini quaternary ammonium groups containing biodegradable amide and ester groups also were investigated by Pisárčik and coworkers [74]. Therapeutic effect of the so-called "soft" drugs is based on the presence of easily decomposable chemical groups in the drug molecule. In the process of biodegradable drug or disinfectant design it is important to select the "proper" decomposable chemical group with respect to the corresponding molecule conformation in the bulk and at the phase interface to allow easy interaction of the decomposable group with the respective decomposing agent (usually enzyme). The authors have found that the surfactant molecules containing an ester group occupy smaller area at the air/water interface than those with an amide group, mainly due to the higher conformational flexibility of ester groups.

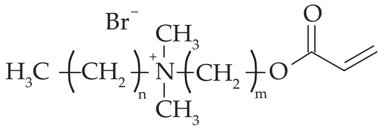
Abe's group [75] reported potential application of the gemini surfmers in stimulus-responsive material and nano-structural template. Organic capsules have been fabricated using the polymerizable gemini surfactant, namely1,2-bis[dimethyl(11-methacryloyloxy)undecylammonio]hexane dibromide [Formula (XXI)] as a single wall component.

The apparent hydrodynamic diameter of the capsule was reversibly changed in response to a change in ionic strength: *e.g.*, the increase in electrolyte concentration results in deswelling of the capsules, presumably due to the decreased electrostatic repulsion between quaternary ammonium groups within the polymerized film. Such a swelling/deswelling nature enables the control of the capture and release capabilities of glucose into/from the capsule core.

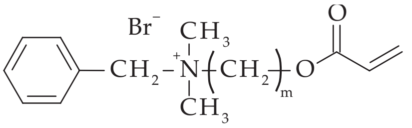


(XXI)

Guittard's group [76] synthesized polymerizable surfactants with quaternary ammonium groups [Formulas (XXII), (XXIII)] and used them as antibacterial and antifungal materials.



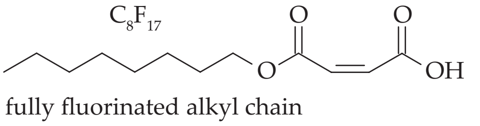
(XXII)



(XXIII)

They have found that increasing length of the spacer between the acrylic part and the ammonium group had a favorable effect on the minimal inhibitory concentration and minimal lethal concentration results. The introduction of perfluorinated chains in the molecular structure of quaternary ammonium gemini surfactants have led to antimicrobial agents [77, 78]. They exhibited peculiar bacteriostatic properties as compared to commercial available references and to a hydrocarbon analogue.

Similar fluorinated surfmer was used for miniemulsion polymerization of styrene and *n*-butyl methacrylate [79]. Mono-fluoroalkyl maleate [Formula (XXIV)] acted as a surfmer providing efficient stability to obtained dispersion and functionalization of particle surface with fluoro-groups.



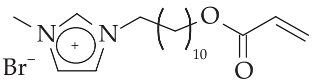
(XXIV)

Hydrogels

In recent years, the preparation and study of intelligent hydrogels have attracted much of scientific interest. Intelligent hydrogels exhibit reversible phase transitions in response to external stimuli such as temperature, pH, light, kind of solvent, and ionic strength, indicated by changes of volume or transparency [80, 81].

Friedrich and coworkers [82] presented photoreactive and thermoresponsive *N*-isopropylacrylamide (NIPAM) – surfmer copolymer hydrogels containing 4,4′-di(6-sulfato-hexyloxy)azobenzene (DSHA) dianions. The functional hydrogels are obtained in a two steps. First, a micellar aqueous solution of [11-(acryloyloxy)undecyl]trimethylammonium bromide (AUTMAB) and NIPAM was exposed to ^{60}Co-γ irradiation, and a thermoresponsive copolymer gel was obtained. Second, DSHA is included by shrinking the gel at 50 °C and subsequent reswelling in an aqueous solution of DSHA disodium salt at 20 °C.

England, Yan, and Texter applied a polymerizable ionic liquid surfactant, namely 1-(11-acryloyloxyundecyl)-3-methylimidiazolium bromide (ILBr) [Formula (XXV)], for copolymerization with methyl methacrylate (MMA) in aqueous microemulsions at 30 wt % ILBr [83].



(XXV)

Homopolymers and copolymers of ILBr and MMA were prepared by thermally initiated microemulsion polymerization at various compositions in bicontinuous and reverse microemulsion subdomains. The reaction products varied from being gel-like to solid. The authors obtained regular cylindrical pores in interpenetrating ILBr-*co*-MMA and PMMA networks by anion exchange in the absence of templates.

CONCLUSION

Reactive surfactants are a rapidly developing group of chemical compounds. They can be divided into three main groups: surfmers, inisurfs, and transurfs. Surfmers are commercially available and widely used for emulsion polymerization, but have also more advanced applications, *e.g.*, drug-delivery systems, encapsulation, hydrogels, or nanoemulsions stabilization. Their unique combination of surface activity and ability to copolymerize not only guarantees enhanced properties of the resulting lattice, but can also reduce cost and environmental footprint of the process by elimination of the purification step.

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