J Surfact Deterg
DOI 10.1007/s11743-014-1640-z

ORIGINAL ARTICLE

Synthesis and Properties of Novel Surface Active Monomers Based on Derivatives of 4-Hydroxybutyric Acid and 6-Hydroxyhexanoic Acid

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Received: 14 May 2013 / Accepted: 25 August 2014

Abstract Novel surface active maleate and methacrylate monomers based on derivatives of ω-hydroxy carboxylic acids have been synthesized. The monomers are comprised of hydrophobic alkyl chains and hydrophilic poly(ethylene glycol), quaternary ammonium, sulfonate and carboxylic fragments. Synthesized monomers sufficiently reduce surface tension at the aqueous solution-air interface. The copolymerization of synthesized monomers with 5-*tert*-butylperoxy-5-methyl-2-hexene-3-yne monomer and *N*-vinylpyrrolidone in solvent and emulsion copolymerization of synthesized peroxide containing surface active monomer with styrene have been carried out. The synthesized surface active monomers have been shown to be suitable emulsifiers for obtaining polystyrene colloid dispersions. It has been ascertained that the surface active copolymers obtained can form stable interpolyelectrolyte complexes with oppositely charged polymers.

Keywords Synthesis · Surface activity · Surface active monomers · Surface tension · Surface active copolymers

Abbreviations

IPEC	Interpolyelectrolyte complex
Surfmer	Surface active monomer
VEP	5-*tert*-Butylperoxy-5-methyl-2-hexene-3-yne

Introduction

The chemistry of polymeric and composite materials for biomedical applications has been intensively developed over the last decades [1–8]. Such materials possess special physical, mechanical and colloidal properties, essential for the creation of biocompatible implants [9–11], drug delivery systems [12–18], carriers of genetic materials [19–21] etc. In this sense, the properties of modern polymer materials with microheterogeneous morphology are determined not only by chemical structure of polymer but also by the nature of the interface and by processes occurring at interface [22]. The presence of various functional groups on the surface of polymeric particles facilitates performing varied reactions at the interface, namely forming implanted polymeric layers with desired properties [23], to immobilize various biomolecules [24], drugs [25], as well as luminescent, magnetic and other markers [26].

The efficient way of creation of polymer colloids with a functionalized interface consists of utilizing surface active monomers, also known as surfmers, during the polymerization of various monomers. 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 [27]. However, in contrast to traditional surfactants, surfmers due to presence of polymerizable units are incorporated into polymer backbone during the polymerization. The surfmer links due to their surface activity are located predominantly on the surface of polymeric particles [28] providing effective stabilization of the polymer colloid. Such polymer dispersion is considered cleaner, than that obtained with non polymerizable surfactants, which is important for biomedical applications.

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One of the first surveys on non-ionic polymerizable surfactants was published by the research group of Ottewill [29]. The authors synthesized polyethylene oxide containing macromonomer and used it for preparation of stable polystyrene latexes. In another paper, the synthesis and homopolymerization of polyethylene oxide containing macromonomers in water and toluene were reported [30].

Colloidal properties of surface active monomers as in the case of traditional surfactants depend on the length and origin of lipophilic and hydrophilic fragments. Variation of length and origin of lipophilic and hydrophilic fragments allows one to tailor the hydrophilic-lipophilic balance of the surfmer and its preferential location in the colloid system [31]. The nature of lipophilic fragment of the surfmer provides the affinity to different surfaces. Synthesized surface active monomers contain fragments of aliphatic alcohols or higher carboxylic acids as hydrophobic fragments and poly(ethylene glycol), carboxylate, sulfonate, phosphate and quaternary ammonium fragments as hydrophilic moieties.

The polymerization capability of such compounds, as in the case of typical monomers, is determined by the nature of the polymerizable fragment [32]. Variation of nature of polymerizable unit impacts on the polymerization capability of surfmers and on the microstructure of the copolymer backbone respectively. Nowadays, a wide range of maleate [33–37], (meth)acrylate [38–42] and styrene [43–46] surfmers have been synthesized.

Moreover, a number of papers [47–49] published in the 1990s were devoted to the behavior of macromonomers during copolymerization in the presence of surface active monomers. Thus, during the copolymerization of amphiphilic polyethylene oxide with styrene it was found that the polymerization rate significantly increases at concentrations of surface active monomer above the critical micelle concentration (CMC) [50]. Also the rate of copolymerization increases with increasing hydrophobicity of terminal aralkyl groups of the macromonomer due to formation of a micellar core. This type of copolymerization is known as micellar polymerization [51]. It was shown that during micellar copolymerization of macromonomers with styrene, hyperbranched polystyrene-grafted-polyethylene oxide capable of formation of monomolecular nanoparticles in aqueous solutions was obtained [50].

Additionally the surface active monomers contain various functional groups in their structure [52–54] providing the reactivity towards desired molecules or surfaces. Copolymerization of functional surfmers results in surface active copolymers which could be applied as efficient interface modifiers or carriers of biomolecules.

The surfmers containing a quaternary ammonium fragment or zwitterionic function are the promising reagents for creation of modifiers of negatively charged surfaces [55]. Moreover, cationic oligomers based on the above-mentioned surfmers perform efficient protein binding and can be used as carriers for nucleic acids, polypeptides, as well as some pharmaceutical substances [56]. For this purpose the synthesis of new cationic surfmers with quaternary ammonium fragment seems to be the prospective way for creation of polymers for efficient binding of negatively charged biomolecules. Surface active monomers with carboxylic groups are known to be prospective compounds for creation of anionic surface active copolymers applied for drug delivery as well as for binding of peptides and amino acids [57]. Incorporation in the surfmer structure of more hydrophilic anionic fragments such as a sulfonate group should improve the stability of complexes of copolymers containing links of the surfmer with positively charged centers of biomolecules.

Surface active copolymers with side peroxide links were applied as macroinitiators for the creation of block or branched carriers for drugs and nucleic acids during the last few years [58]. They are obtained by copolymerization of peroxide monomers, namely peroxide derivatives of vinylacetylenic alcohol, or peroxide-containing surfmers [59]. Utilization of peroxide-containing surfmers during emulsion or dispersion polymerization provides the location of peroxide groups onto the surface of polymeric particles directly during the polymerization process. Also this technique permits one to obtain surface active oligomers with a predictable structure containing peroxide groups as substitutes of the side chain [60, 61]. This allows one to perform various polymer-analogous transformations at the surface of polymeric particles by free radical reactions of peroxide groups.

However, the application of copolymer family containing di-*tert*-butyl peroxide for initiation of polymerization from the surface is limited due to high thermal stability of the peroxide group. The surfmers with peroxyester groups are more promising for creating surface functionalized polymeric colloids due to their lower thermal stability.

Various surface active monomers that have a polymerizable group and a functional group separated from each other by spacers of different lengths and nature are interesting prospects for developing novel types of surface active copolymers. Various fragments of bifunctional compounds (diols, dicarboxylic acids, diamines, etc.) that are used as spacers could be incorporated into the surfmer structure via successive interaction due to their functional groups. However, selective transformation of one of the two equally reactive functional groups is quite problematic. As a result, the final product contains impurities of bifunctional derivatives which is a serious issue in monomer synthesis.

Such problems can be avoided by using various heterocyclic reagents (oxiranes, lactones, sultones, etc.) since they are known to selectively form monosubstituted derivatives in ring opening reactions under mild conditions [62]. Lactones of corresponding carboxylic acids are particularly promising reagents for the incorporation of hydrophobic spacers. The utilization of lactones of different carboxylic acids and with various ring sizes allows varying hydrophilic-lipophilic balance and the position of polymerizable fragment relative to the other functional groups in molecule of surfmer.

In this study we report the synthesis of novel surface active monomers containing poly(ethylene glycol), carboxylic, sulfonate, quaternary ammonium hydrophilic fragments and *tert*-butylperoxy groups utilizing lactones of 6-hydroxyhexanoic acid and 4-hydroxybutanoic acid as initial materials.

Experimental

Initial Materials

Maleic anhydride, triethylamine, methacryloyl chloride were purchased from Merck and additionally purified by distillation. Phosphorus trichloride, 1,3-propane sultone, 1-hexadecanol were also purchased from Merck and used without further purification. ε-Caprolactone, γ-butyrolactone, *N*,*N*-dimethylaminoethanol, styrene, *N*-vinylpyrrolidone were obtained commercially from Sigma–Aldrich and were additionally purified by distillation. Poly(ethylene glycol) monomethyl ether 550 with average molecular weight of 550 g/mol was also commercially available from Sigma–Aldrich and used without additional purification. *tert*-Butyl hydroperoxide was additionally purified by vacuum distillation. VEP was synthesized from 2-methylhex-5-en-3-yn-2-ol and *tert*-butyl hydroperoxide according to a known technique [63] and purified by vacuum distillation. All solvents (hexane, dichloromethane, ethyl acetate, 2-butanone) were purchased form Sigma–Aldrich and purified according to known techniques [64] prior to use.

Synthesis of Intermediate Compounds

4-Bromobutyric acid was synthesized according to the technique described in [65]. The triethylammonium salt of 4-hydroxybutyric acid was obtained by interaction of γ-butyrolactone **1a** with triethylamine in aqueous solution. 1-Hexadecyl maleate was synthesized as it was reported in [66]. Chloroanhydride of 1-hexadecyl maleate **7** and chloroanhydride of 4-bromobutyric acid were synthesized via interaction of corresponding compounds with phosphorus trichloride according to the described method in [67]. 1-Hexadecyl-4-bromobutyrate **2** was synthesized by the reaction of chloroanhydride of 4-bromobutyric acid with 1-hexadecanol according to the described technique in [68].

*Synthesis of tert-Butylperoxy-6-hydroxyhexanoate **3***

First, 0.0098 mol (1.12 g) of ε-caprolactone **1b** and 0.068 mol (6.17 g) of *tert*-butyl hydroperoxide were mixed and a droplet of $BF_3 \cdot (C_2H_5O)_2$ was added. The mixture was stirred for 12 h at 50–55 °C and filtered through a thin layer of aluminium oxide. The excess *tert*-butyl hydroperoxide was removed under reduced pressure. The crude product was chromatographed on a silica gel column and eluted with a hexane–ethyl acetate gradient. The solvents were removed under reduced pressure to give 1.4 g (70 %) of pure peroxide **3**. d_4^{20} 1.0182; n_D^{20} 1.4552; M_R: 53.56; M_R (calculated): 53.55. Found, %: C 58.59; H 9.4. Calculated, %: C 58.82; H 9.8. ^{1}H NMR (DMSO-d_6), δ, ppm: 3.64 (t; $J = 6.46$ Hz; 2H); 2.32 (t; $J = 7.8$ Hz; 2H); 1.64 (m; $J = 7.61$ Hz; 4H); 1.4 (t; $J = 8.16$; 2H); 1.28 (s; 9H).

*Synthesis of 6-tert-Butylperoxy-6-oxohexylmaleinate **4***

To a solution of 0.01 mol (1 g) of maleic anhydride in 5 ml of dichloromethane 0.01 mol (2 g) of compound **3** and 0.0007 mol (0.1 ml) of triethylamine were added consequently. The mixture was stirred for 24 h at 40 °C. The compound **4** was further used for *in situ* synthesis of target surfmers and, therefore, was not identified.

*Synthesis of 4-(Hexadecyloxy)-N-(2-hydroxyethyl)-N,N-dimethyl-4-oxobutan-1-aminium bromide **10***

To a solution of 0.01 mol (1 g) of *N*,*N*-dimethylaminoethanol in 10 ml of 2-butanone 0.01 mol (3.76 g) of 1-hexadecyl-4-bromobutyrate, **2** was added and the mixture was heated for 15 h at 80 °C. The solvent was removed under reduced pressure to give the compound **10** with a quantitative yield (4.76 g). m.p. 50–53 °C; Found, %: C 60.15; H 10.57; Br 17.01; N 3.05. Calculated, %: C 60.00; H 10.42; Br 16.66; N 2.91.

The purity of the intermediate compounds was confirmed by thin layer chromatography and elemental analysis.

Synthesis of Surface Active Monomers

*Synthesis of Triethylammonium 3-[(Z)-4-(6-tert-butylperoxy-6-oxohexyloxy)-4-oxobut-2-enoyloxy]-1-propanesulfonate **5***

To a solution of 0.0066 mol (2 g) of compound **4** in 6 ml of dichloromethane, 0.0066 mol (0.8 g) of 1,3-propane sultone and 0.0066 mol (0.67 g) of triethylamine were added consequently. The reaction mixture was stirred for 24 h at ambient temperature. After the evaporation of the solvent, the monomer **5** was obtained with a quantitative yield (3.47 g) as slightly yellow viscous liquid. ^{1}H NMR(DMSO-d_6), δ, ppm: 9.47 (s; 1H); 6.33 (d; $J = 12.3$ Hz; 1H, = CH2); 6.22 (d; $J = 12.3$ Hz; 1H, = CH); 4.29 (t; $J = 6.38$ Hz; 2H); 4.16 (t; $J = 6.69$ Hz; 2H); 3.16 (q; $J = 6.69$ Hz; 6H); 2.73 (t; $J = 5.44$ Hz; 2H); 2.33 (m; $J = 7.12$ Hz; 2H); 2.16 (m; $J = 6.9$ Hz; 2H); 1.63 (m; $J = 7.72$ Hz; 2H); 1.33 (m; 11H); 1.28 (s; 9H) [69].

*Synthesis of (6-tert-Butylperoxy-6-oxohexyloxy)(methoxy polyethylene glycol-550)maleinate **6***

To a solution of 0.0066 mol (2 g) of compound **4** and 0.0066 mol (0.66 g) of triethylamine in 6 ml of dichloromethane, 0.0033 mol (0.45 g) of phosphorus trichloride was added dropwise. The reaction mixture was stirred for 6 h at 40 °C. The resulting solution was decanted and was added dropwise at 10 °C under stirring to a solution of 0.0066 mol (3.8 g) of polyethylene glycol monoethyl ester and 0.0066 mol (0.7 g) of triethylamine in 10 ml of hexane. The mixture was stirred for 20 h at 15 °C and then filtered through a thin layer of aluminium oxide. The solvent was removed under reduced pressure. The yield of monomer **6** was 85 % (4.6 g) ^{1}H NMR(DMSO-d_6), δ, ppm: 6.23 (d; 2H); 4.61 (t; 2H); 4.18 (t; 2H); 3.78 (t; 2H); 3.61 (m; 47H); 3.53 (t; 2H); 3.34 (s; 3H); 2.31 (t; 3H) CH2C(O)OO; 1.61 (m; 4H); 1.36 (t; 2H); 1.28 (s; 9H) [69].

*Synthesis of Triethylamino-3-[(Z)-4-hexadecyloxy-4-oxo-2-butenoyloxy-4-oxobutyloxanoate] **8***

To a solution of 0.01 mol (2 g) of triethylammonium salt of 4-hydroxybutyric acid and 0.01 mol (1 g) of triethylamine in 10 ml of dichloromethane, 0.01 mol (3.6 g) of chloroanhydride of 1-hexadecyl maleate in 10 ml of dichloromethane was added dropwise at 5–10 °C. The reaction mixture was stirred for 6 h at 10–15 °C. The precipitate of triethylammonium hydrochloride was filtered off and the solvent was removed to give 4.83 g (92 %) of compound **8**.

*Synthesis of Triethylamino-3-[(Z)-4-hexadecyloxy-4-oxo-2-butenoyloxy]-1-propanesulfonate **9***

This surface active monomer was synthesized with quantitative yield (2.84 g) from surfmer **8**. The technique was identical to the synthesis of surfmer **5**.

*Synthesis of N-(2-{[2Z]-3-carboxyprop-2enoyl]oxy}ethyl)-4-hexadecyloxy-N,N-dimethyl-4-oxobutan-1-aminium bromide **11***

To a solution of 0.0043 mol (0.42 g) of maleic anhydride in 5 ml of dichloromethane, a solution of 0.0043 mol (2 g) of compound **10** and 0.0007 mol (0.1 ml) of triethylamine in 5 ml of dichloromethane were added. The mixture was stirred at 40 °C for 24 h. The solvent was removed under reduced pressure to give 2.27 g (94 %) of monomer **11**.

*Synthesis of 4-(Hexadecyloxy)-N-(2-(methacryloyloxy)ethyl)-N,N-dimethyl-4-oxobutan-1-aminium bromide **12***

To a solution of 0.0043 mol (2 g) of compound **10** and 0.0043 mol (0.43 g) of triethylamine in 10 ml of dichloromethane, 0.0043 mol (0.44 g) of methacryloyl chloride solution in 5 ml of dichloromethane was added dropwise at 5–10 °C. The mixture was stirred for 6 h at 5–10 °C. The precipitate was filtered off and the solvent was removed under reduced pressure to give 2.3 g (90 %) of monomer **12**.

Polymerization Technique

Copolymerization reactions were carried out in ethyl acetate as a solvent under an argon atmosphere in soldered dilatometers with volumes from 15 to 50 ml and with 0.05 ml as the scaling factor. Concentration of monomers was varied in range from 1 to 4 mol/L. Azobisisobutyronitrile at concentration 5×10^{-2} mol/L was used as the initiator of polymerization. The copolymers obtained were isolated and purified by repeated precipitation by adding an excess of poor solvent (hexane) to a solution of copolymer in ethyl acetate. Isolated copolymers were dried under vacuum at ambient temperature to constant weight. Emulsion polymerization was performed in thermostatically controlled reactor equipped with a stirrer and condenser under an argon atmosphere. The conversion rate of monomers was determined by a gravimetric technique [70].

Analysis

The individuality of the obtained compounds was confirmed by thin layer chromatography using Silica gel 60 F_{254} (Merck) sheets. The solvents hexane and ethyl acetate mixed in ratios of 2:1, 1:1, 1:2 were used as eluent and the length of the solvent front was 100 mm. Iodine vapors were used as the general unspecific color reagent. Specific color reagents were used for discovering peroxide and carbonyl groups (*N,N*-dimethyl-1,4-phenylenediamine and 2,4-dinitrophenylhydrazine, respectively). IR spectra were recorded using a Spectrod M80 spectrometer in a thin film (for liquid compounds) or in Vaseline oil (for crystalline substances). ^{1}H-NMR spectra were recorded on a Bruker 150 spectrometer at a working frequency of 300 MHz in DMSO-d_6 (substance concentrations of 5–10 %, internal standard—hexamethyldisiloxane). The purity of synthesized compounds was additionally confirmed by elemental analysis.

Surface Tension

The characterization of the surface activity of the synthesized monomers and copolymers was characterized by surface tension measurements. These measurements were performed with a Du Noüy ring tensiometer at 20 °C. The CMC values of the monomers as well as surface tension above CMC were determined from the inflection points on the surface tension isotherms.

Interpolyelectrolyte Complexes (IEC) Formation

The formation of interpolyelectrolyte complexes was studied with conductometric titration. To the aqueous solution of ionic copolymer poly(vinyl acetate-*co*-maleic anhydride) with the number-average molecular weight 7,500 g/mol with hydrolyzed anhydride chains or poly(butyl acrylate-*co*-dimethylaminoethyl methacrylate) with the number-average molecular weight 12,000 g/mol the aqueous solution (1 % by weight) of synthesized copolymer containing units of the oppositely charged surfmer was added dropwise. Electrical conductivity was measured with a CON 2700 conductivity meter.

Particle Size Measurement

Particle size during IPEC formation and emulsion polymerization was determined using a light-scattering technique [71] in a plane-parallel cuvette in the wavelength range from 420 to 620 nm on a photocolorimeter LMF-72 M.

Results and Discussion

Synthesis of Surfmers

Novel anionic, cationic and non-ionic maleate or methacrylate surface active monomers containing fragments of *tert*-butylperoxy esters or higher alkyl esters of ω-hydroxy carboxylic acids as the hydrophobic moiety were synthesized as follows.

The derivatives of ω-hydroxy carboxylic acids and ω-bromo carboxylic acids obtained from corresponding lactones **1a,b** were used as initial compounds. The synthesis of corresponding derivatives of ω-hydroxy carboxylic acids is shown on Scheme 1:

Peroxyester of 6-hydroxy hexanoic acid **3** was synthesized by reaction of ε-caprolactone **1b** with sevenfold molar excess of *tert*-butyl hydroperoxide in the presence of boron trifluoride as a catalyst and at 50–55 °C.

Cetyl ester of 4-bromobutyric acid **2** was obtained in three stages. Firstly 4-bromobutyric acid was synthesized by interaction of γ-butyrolactone **1a** with hydrogen bromide in the presence of sulphuric acid. The reaction of resulted acid with phosphorus trichloride led to formation of chloroanhydride of 4-bromo butyric acid. The desired ester **2** with 90 % yield was obtained by interaction of the corresponding chloroanhydride with 1-hexadecanol. The reaction was carried out in dichloromethane at 10–15 °C and in the presence of triethylamine as the acceptor of hydrogen chloride.

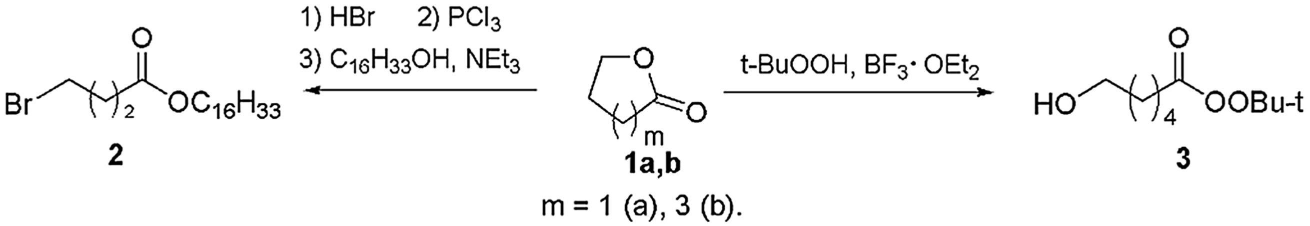
Peroxide containing maleate **4** was synthesized by acylation of peroxyester **3** with maleic anhydride. The acylation was performed at equimolar ratios of reagents in dichloromethane at 40 °C. A small amount of triethylamine was used as the catalyst. The synthesis of corresponding surfmers **5** and **6** is shown on Scheme 2:

The sulfonate surfmer **5** was synthesized by reaction of maleate **4** with 1,3-propane sultone. Sulfoalkylation was performed in dichloromethane at ambient temperature and in the presence of triethylamine (the molar ratio of the reagents was 1:1:1). Peroxide containing maleate **4** was also used for synthesis of non-ionic surfmer **6**. Thus, maleate **4** was converted to chloroanhydride by the interaction with phosphorus trichloride. Subsequent acylation of poly(ethylene glycol) monomethyl ether with corresponding chloroanhydride in the presence of triethylamine led to the formation of the target monomer **6**.

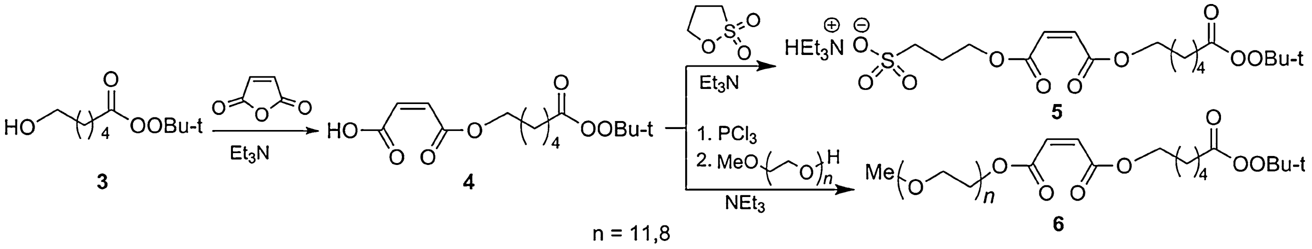
Synthesized surfmers **5** and **6** have relatively short hydrophobic fragments. Therefore, surfmers containing longer alkyl chains were obtained from 1-hexadecyl maleate and the cetyl ester of 4-bromobutyric acid **2**.

Thus, the carboxyl monomer **8** was synthesized by reaction of chloroanhydride **7** obtained from 1-hexadecyl maleate with a stoichiometric amount of triethylammonium salt of 4-hydroxybutyric acid in dichloromethane. Performing this reaction with 2 mol of triethylamine per 1 mol of chloroanhydride **7** the corresponding monomer was obtained in the form of the triethylammonium salt. The sulfonate surfmer **9** was synthesized via the reaction of an equimolar amount of monomer **8**, 1,3-propane sultone and triethylamine at ambient temperature after 24 h. The synthesis of surfmers **8** and **9** is shown on Scheme 3:

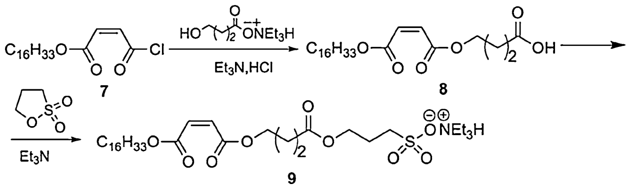
Methacrylate and maleate cationic surface active monomers **11** and **12** containing fragments of quaternized *N*,*N*-dimethylaminoethanol were synthesized according to Scheme 4:



Scheme 1 Synthesis of corresponding derivatives of ω-hydroxy carboxylic acids



Scheme 2 Synthesis of surfmers **5** and **6**



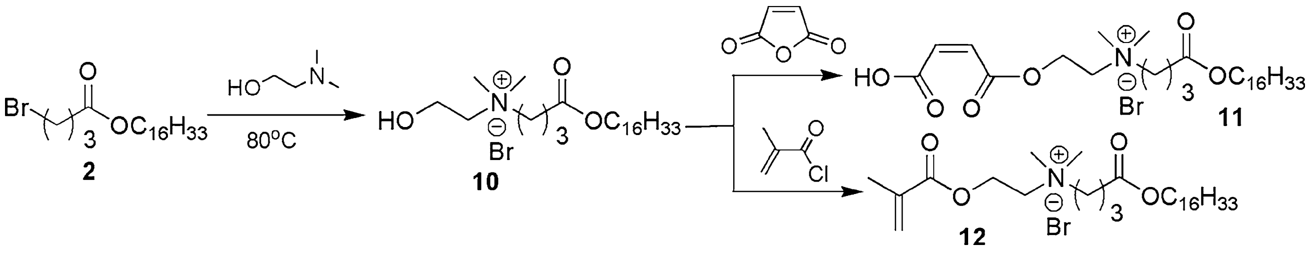
Scheme 3 Synthesis of surfmers **8** and **9**

For this purpose the quaternization of *N*,*N*-dimethylaminoethanol with hexadecyl 4-bromobutyrate was carried out. The reaction was performed during heating of equimolar amounts of ester **2** and *N*,*N*-dimethylaminoethanol in 2-butanone at 80 °C over 15 h. Acylation of the resulting compound **10** with maleic anhydride in dichloromethane at 40 °C in the presence of triethylamine led to the formation of maleate surfmer **11**. Surface active monomer **12** was synthesized by acylation of **10** with methacryloyl chloride. The reaction was performed at equimolar ratios of reagents in the presence of triethylamine and at 10–15 °C.

Characteristics of synthesized surface active monomers and their elemental composition are shown in Table 1.

The structure of monomers was also confirmed by IR and ^{1}H-NMR spectroscopy. Maleate fragments in the obtained maleate monomers are defined by absorbance bands at 1,090–1,240 cm^{-1} (υC–O), 1,635–1,640 cm^{-1} (υC = C), 1,728–1,740 cm^{-1} (υC = O). Absorbance bands at 1,035–1,220 cm^{-1} (υC–O), 1,640 cm^{-1} (υC = C), 1,724 cm^{-1} (υC = O) are assigned to methacrylate fragments in monomer **12**. In the ^{1}H-NMR spectrum of surfmer **12** two signals with chemical shifts of 5.55 ppm (s.,1H, CH_2=) and 6.09 ppm (s., 1H, CH_2=) correspond to protons of a methylene group. This can be explained by the *cis* or *trans* positions of the mentioned protons relative to the carbonyl group. The signal of methylene *cis*-proton is shifted downfield. The proton peak of the methacrylate methyl group is located at 1,95 ppm (s., 3H, CH_3–C=).

The presence of a *tert*-butylperoxy ester fragment in monomers **5** and **6** was confirmed by presence of absorbance bands at 1,250–1,192 cm^{-1} defining the vibrations of $C(CH_3)_3$ fragment and by the presence of a band with a maximum at 852 cm^{-1} (υO–O) [72]. In ^{1}H-NMR spectra of peroxide containing monomers **5** and **6**, the signal of *tert*-butyl fragment with chemical shift 1.28 ppm (s., 9H)



Scheme 4 Synthesis of surfmers **11** and **12**

Table 1 Characteristics of synthesized surfmers and their elemental composition

Surfmer	Yield (%)	m.p. (°C)	Elemental analysis (found/calculated) (%)				
			C	H	N	S	Br
5	Quantitative	1.4682[a]	52.47/52.37	8.36/8.49	2.66/2.69	6.08/6.03	
6	85	1.4410[a]	56.87/56.54	8.87/8.69			
8	92	34	67.75/67.60	9.71/9.86			
9	Quantitative	28–30	60.90/61.11	9.75/9.57	2.03/2.16	5.11/4.93	
11	94	45–48	58.37/58.13	8.75/8.99	2.10/2.42		13.51/13.84
12	90	34–36	61.65/61.42	9.49/9.69	2.37/2.56		14.27/14.62

m.p. melting point

[a] Refractive index

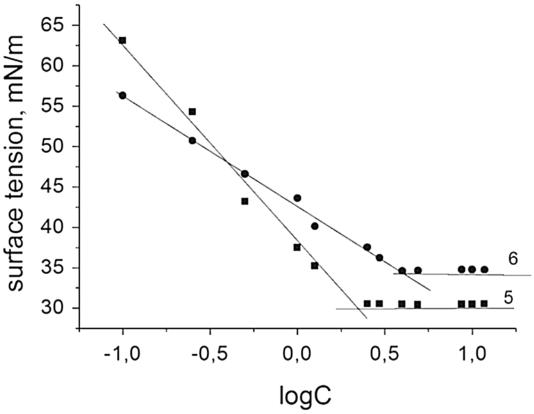


Fig. 1 The surface tension isotherms for the aqueous solution-air interface of surfmers **5** and **6**

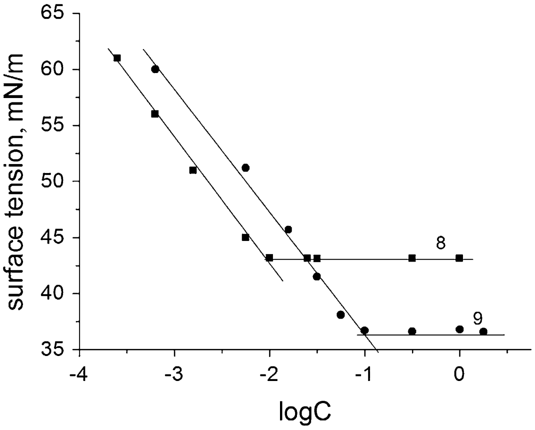


Fig. 2 The surface tension isotherms for the aqueous solution–air interface of surfmers **8** and **9**

was observed. Absorbance bands at 1,240–1,050 cm^{-1} corresponding to propylsulfonate fragment were observed in IR spectra of monomers **5** and **9**. In ^{1}H-NMR spectra of monomers **5** and **9** protons of propylsulfonate fragment are characterized by signals with the following chemical shifts—2.21 ppm (m., 2H), 2.94 ppm (t., 2H) and 4.33 ppm (t., 2H). The signal with chemical shift at 10.44 ppm corresponds to ammonium group (s., HN^{+}). Absorbance band at 1,104 cm^{-1} assigned to poly(ethylene glycol) fragment (υC–O) was observed in IR spectra of non-ionic monomer **6**.

Surface Activity of the Synthesized Monomers

The synthesized monomers are typical surfactants, since they reduce the surface tension at the aqueous solution–air interface. Therefore, the values of surface tension of aqueous solutions of the synthesized surface active monomers were measured and their CMC and the surface tensions above the CMC were determined. The surface tension isotherms of synthesized surfmers are shown on Figs. 1, 2 and 3. The CMC values and the values of surface tension above CMC are shown in Table 2.

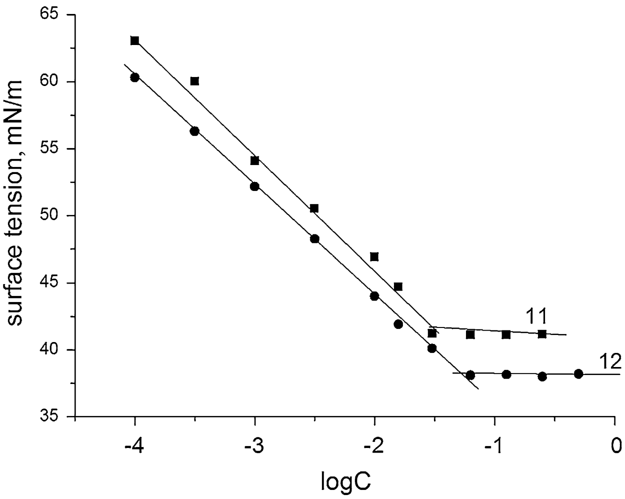


Fig. 3 The surface tension isotherms for the aqueous solution–air interface of surfmers **11** and **12**

Relatively high values of CMC for surfmers **5** and **6** could be explained by the presence of a relatively short hydrophobic *tert*-butylperoxyacyl fragment and a strong

Table 2 The value of CMC and surface tension above CMC of the synthesized surfmers

Surfmer	CMC (wt%)	Surface tension (mN/m)
5	2.5	31.2
6	3.7	34.6
8	0.01	43.17
9	0.1	36.7
11	0.03	41.2
12	0.06	38.1

hydrophilic sulfonate group or a long hydrophilic poly(ethylene glycol) chain. This promotes real solubility of monomers in water up to higher concentrations compared to the other surfmers.

Lower values of CMC of surfmers **8** and **9** are caused by a long cetyl chain which increases the hydrophobic character of the molecule and reduces the solubility of the monomer in water [73]. The higher value of the CMC of surfmer **9** is explained by the presence of a strong hydrophilic sulfonate group.

Monomers **11** and **12** contain hydrophilic quaternary ammonium fragments. The presence of a long hydrophobic chain promotes the poor solubility of the obtained cationic monomers. Therefore the corresponding monomers form micelles at low concentrations. The value of the CMC of surfmer **12** is slightly higher due to presence of carboxylic groups.

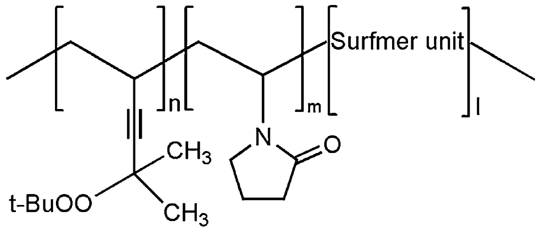
As it can be concluded, the introduction of hydrophilic groups of various natures and hydrophobic chains of different lengths gives an opportunity to vary the surface active properties of the synthesized surfmers over a wide range. It is worth mentioning that values of CMC reported in the literature for various types of surfmers vary over a wide range [27, 28, 33, 34, 40, 42]. Such values are significant for an insight into the interfacial behavior of amphiphiles according to previously published papers.

Synthesized anionic and cationic surfmers were utilized for obtaining surface active copolymers.

Copolymerization of Synthesized Surfmers with Vinyl Monomers

The solution copolymerization of synthesized surfmers with peroxide containing monomer VEP and *N*-vinylpyrrolidone was carried out. The general structure of the synthesized surface active copolymers is shown on Scheme 5:

The resulting copolymers are water soluble and reduce the surface tension at the aqueous solution–air interface. The surface tension isotherms of synthesized copolymers are shown on Fig. 4.



Scheme 5 General structure of synthesized surface active copolymers

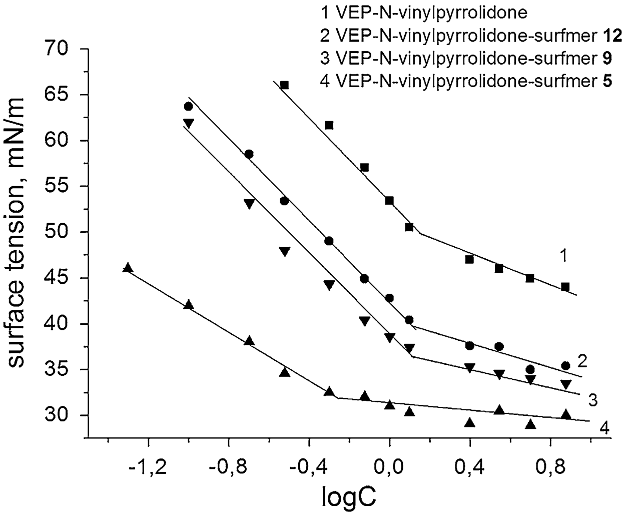


Fig. 4 The surface tension isotherms at the aqueous solution–air interface of synthesized copolymers

The incorporation of units of surface active monomers into the copolymer structure increases their surface activity in comparison to binary copolymer VEP–*N*-vinylpyrrolidone as can be seen in Fig. 4. The presence of inflexion points on the surface tension isotherms verifies the capability of the synthesized copolymers for association into supramolecular structures, similar to micelles of low molecular weight surfactants.

In contrast to low molecular surfactants, where micelle formation takes place as a phase transition at a certain discrete concentration, with the aggregation number approximately constant, the polymers are polydisperse with a varying number of functional groups per macromolecule. Therefore, the formation of micelles involves also the conformational changes and exchange of macromolecules between the solution and the micelles or interface, in order to reach packing with the minimum energy under given conditions. Though a fast decrease in surface tension below the CMC is explained by equilibrium adsorption at the water–air interface, similar to low molecular surfactants, a

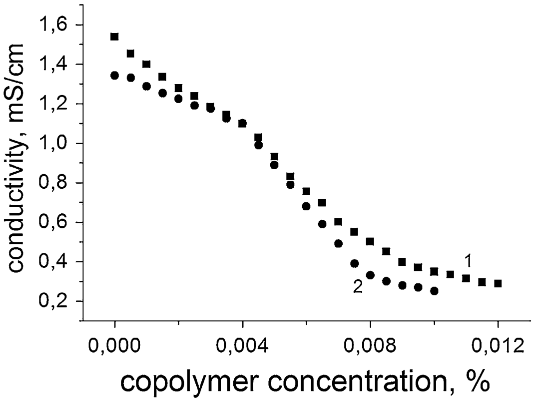


Fig. 5 The dependence of conductivity of ionic copolymer solution on the added amounts of 1 % solutions of oppositely charged copolymers. *Curve 1* corresponds to the solution of anionic copolymer poly(maleic anhydride-*co*-vinyl acetate) when adding the solution of VEP–*N*-vinylpyrrolidone—surfmer **12**. *Curve 2* corresponds to the solution of cationic copolymer poly(butyl acrylate-*co*-dimethylaminoethyl methacrylate) when adding the solution of VEP–*N*-vinylpyrrolidone—surfmer **9**

further decrease in the surface tension above the CMC is caused by further reorganization of the molecules.

Incorporation of units of ionic surfmers into the structure of VEP–*N*-vinylpyrrolidone macromolecules provides the polyelectrolyte properties, namely the capability to form IPEC with oppositely charged polymers.

Anionic copolymer poly(maleic anhydride-*co*-vinyl acetate) with hydrolyzed anhydride fragments and cationic copolymer poly(butyl acrylate-*co*-dimethylaminoethyl methacrylate) are used as models of anionic and cationic biopolymers [74]. Therefore, the study of IPEC formation between model copolymers and synthesized copolymers with surfmers fragments is an effective technique for the estimation of their ability to bind biopolymers, particularly nucleic acids.

During IPEC formation, the electrical conductivity of polyelectrolyte solution decreases due to the formation of insoluble pairs of oppositely charged ions attached to a polymer chain and therefore a decrease in the overall ion concentration.

The IPEC formation between anionic copolymer poly(maleic anhydride-*co*-vinyl acetate) with hydrolyzed anhydride fragments and synthesized cationic oligoelectrolyte VEP–*N*-vinylpyrrolidone—surfmer **12** as well as between cationic copolymer poly(butyl acrylate-*co*-dimethylaminoethyl methacrylate) (it is a cationic polymer in protic solvents, since ammonia groups act like Brønsted base, become protonated [75]) and synthesized anionic copolymer VEP–*N*-vinylpyrrolidone—surfmer **9** was studied with conductometric titration.

The dependence of conductivity of aqueous solutions of model copolymers on adding amounts of aqueous solutions of copolymers with surfmers units is shown on Fig. 5.

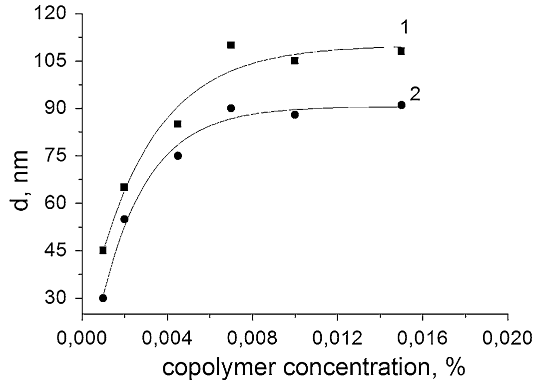


Fig. 6 The dependence of IPEC particles size on the added amount of 1 % aqueous solutions of oppositely charged copolymers. *Curve 1* corresponds to poly(maleic anhydride-*co*-vinyl acetate) with *N*-vinylpyrrolidone–VEP–surfmer **12**. *Curve 2* corresponds to poly(butyl acrylate-*co*-dimethylaminoethyl methacrylate) with *N*-vinylpyrrolidone–VEP–surfmer **9**

As can be seen from Fig. 5, the conductivity of the solution decreases during the interaction of oppositely charged oligoelectrolytes. The inflection was observed at equimolar ratio of copolymers.

Also, the size of colloid particles changes during addition of the oppositely charged copolymer as shown in Fig. 6.

The size of particles during the addition of oppositely charged copolymer increased at first. When a certain amount of oligoelectrolyte was added, the particle size remained practically unchanged.

The results obtained indicate the formation of stable IPEC during the interaction of the model and synthesized polyelectrolytes.

The formation of IPEC can be explained in nucleation and growth terms. On first addition of the countercharged electrolyte, the nucleation of IPEC takes place, but, since one of the polyelectrolytes is in excess, the IPEC are rich in this component, which still have vacant charged groups. Further addition of countercharged polymer leads to a saturation of IPEC and, a decrease in its charge to a value when nucleation of a new IPEC is favored. From this it can be concluded, that IPEC can be characterized with a certain finite aggregation number. The constant size above 0.040 % represents a certain steady state, when previously formed IPEC coexist with growing ones. Moreover, as it can seen from Fig. 5 the conductivity constantly decreases above 0.040. Only at around 0.01, does the conductivity reach a plateau, witnessing the termination of both nucleation and growth of IPEC. The fact, that the IPEC size does not increase dramatically after 0.01 % says, that already at 0.004, the size distribution is dominated with "passive" IPEC, having only a small, not detectable by light scattering, fraction of growing IPEC.

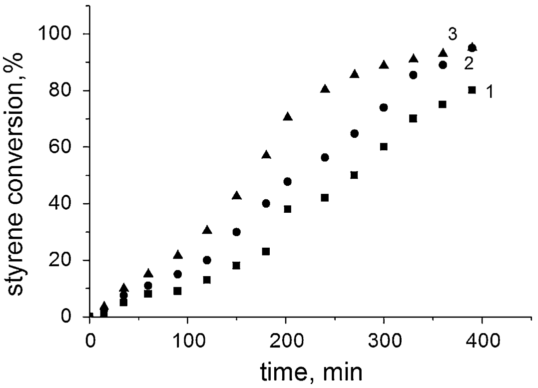


Fig. 7 The dependence of styrene conversion during self-initiated aqueous emulsion copolymerization of a mixture of styrene—surfmer 6 at 85 °C. The surfmer content in the monomer mixture was 10 (*curve 1*), 15 (*curve 2*) and 25 (*curve 3*) % (mol)

Emulsion Polymerization of Styrene in the Presence of Peroxide Containing Surfmer **6**

As mentioned in the introduction, emulsion copolymerization of functional surfmers with other monomers leads to the formation of polymer particles with functionalized surface. The emulsion copolymerization of styrene with various surface active monomers, conditions of process, characteristics of the resulting polymer particles are well elucidated in the literature. Hence, the polymerization of styrene in the presence of peroxide-containing non-ionic surfmer **6** was studied. The singularity of the process was that during the copolymerization, the peroxide-containing surfmer acted as a comonomer and as an initiator at the same time.

Therefore, the dissolution of surfmer **6** into styrene with subsequent dispersion of monomers in water allows us to obtain a stable monomer emulsion. The polymerization was carried out at 85 °C. The styrene conversion of 80–85 % was achieved in 6–7 h. The kinetic curves of styrene polymerization initiated with surfmer **6** are shown in Fig. 7.

It can be concluded from Fig. 7 that increasing the surfmer content leads to increasing of the polymerization rate content as it is known that increasing the emulsifier content leads to increases in the polymerization rate [76]. Stable dispersions of polymer particles with an average particle size of around 180 nm were formed during polymerization. The reported sizes of polystyrene particles resulted from emulsion polymerization vary in the range from 30 to 400 nm [31, 33, 61, 77, 78].

Conclusions

The synthesis strategy of novel ionic and non-ionic surface active monomers based on corresponding lactones of 4-hydroxybutyric acid and 6-hydroxyhexanoic acid was proposed and developed. The incorporation of various hydrophilic and hydrophobic groups tailors the surfactant properties of synthesized surfmers over a wide range. The copolymerization of the resulting surfmers with other monomers led to the formation of surface-active copolymers. Synthesized copolymers containing the units of ionic surfmers were shown to be capable of forming stable IPEC with oppositely charged copolymers. The synthesized peroxide-containing surfmer during emulsion polymerization acted as an effective surfactant initiator as well as the comonomer providing stable surfactant-free polymer dispersions.

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