

Novel functional surface active monomers for synthesis of reactive surface active copolymers

Mykola Borzenkov, Orest Hevus

Department of Organic Chemistry, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandery street 12,
E-mail: nickborzenkov@gmail.com

Abstract – Novel surface active monomers based on derivatives of ω -hydroxy carboxylic acids have been synthesized. Synthesized monomers sufficiently reduce surface tension at the aqueous solution-air interface. The copolymerization of synthesized monomers with commercial monomers 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 obtained surface active copolymers can form the stable interpolyelectrolyte complexes with oppositely charged polymers.

Key words – synthesis, surface activity, surface active monomers, surface tension, surface active copolymers.

I. Introduction

The efficient way of creation of polymer colloids with 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. However, in contrast to traditional surfactants, surfmers due to presence of polymerizable units are incorporated into polymer backbone during the polymerization. Various surface active monomers that have polymerizable group and a functional group separated from each other via spacers of different length and nature are interesting prospects for developing of novel types of surface active copolymers. However, selective transformation of one of the two equally reactive functional groups is quite problematic. 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 functional surface active monomers for synthesis of reactive polymers utilizing lactones of 6-hydroxyhexanoic acid and 4-hydroxybutanoic acid as initial materials.

II. Experimental Part

Maleic anhydride, triethylamine, methacryloyl chloride, methacrylic acid, phosphoryl 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 commercially available from Sigma-Aldrich and were additionally purified by distillation. Poly(ethylene glycol) monomethyl ether 750 (PEG MME 750) with an average molecular weight 750 g/mol, poly(ethylene glycol) monomethyl ether 550 (PEG MME 550) with an average molecular weight 550 g/mol, and poly(ethylene glycol) 600 (PEG 600) with an average molecular weight 600 g/mol were commercially available from Sigma-Aldrich. *tert*-Butyl hydroperoxide was additionally purified by vacuum distillation. All solvents (hexane, ethyl acetate, dichloromethane, dioxane) were purchased from Merck and Sigma-Aldrich and purified according to known techniques prior to use.

IR spectra were recorded using Spectrod M80 spectrometer in a thin film (for liquid compounds) or in vaseline oil (for crystalline substances). $^1\text{H-NMR}$ spectra were recorded using a Bruker 150 spectrometer at a working frequency of 300MHz in DMSO- d_6 . Sample concentration was 5-10%, hexamethyldisiloxane was used as an internal standard. The purity of synthesized compounds was additionally confirmed by elemental analysis.

The characterization of surface activity of 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.

Copolymerization reactions were carried out in ethyl acetate as a solvent under argon atmosphere in soldered dilatometers with volume from 15 to 50 ml and with 0.05 ml as scaling factor. Azobisisobutyronitrile at concentration $5 \cdot 10^{-2}$ mol/L was used as initiator of polymerization. Obtained copolymers were isolated and purified by repeated precipitation. Emulsion polymerization was performed in thermostatic reactor equipped with stirrer and condenser under argon atmosphere.

III. Results

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 hydrophobic moiety were synthesized as follows. The derivatives of ω -hydroxy carboxylic acids and ω -bromo carboxylic acids obtained from corresponding lactones were used as initial compounds.

The reaction of lactones with unsaturated acids could be a promising method for the development of monomers having polymerizable fragment separated from the carboxylic group via polymethylene spacer of the defined length. Thus, the interaction of caprolactone with methacrylic acid was also studied. The resulted 6-methacryloyloxyhexanoic acid was used for synthesis of non-ionic surfmers containing poly(ethylene glycol) fragments and their phosphate derivatives.

The chemical structures of synthesized monomers are shown on Fig. 1:

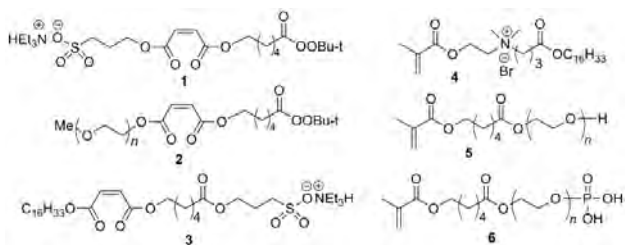


Fig. 1. Chemical structures of synthesized monomers

The synthesized monomers are typical surfactants, since they reduce the surface tension on aqueous solution – air interface. Therefore, the values of surface tension of aqueous solutions of the synthesized surface active monomers were measured and their critical micelle concentration and the surface tension above CMC were determined. The surface tension isotherms of synthesized surfmers are shown on Figures 2-4.

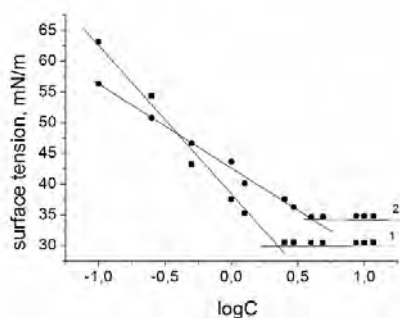


Fig. 2. Surface tension isotherms of monomers 1 and 2

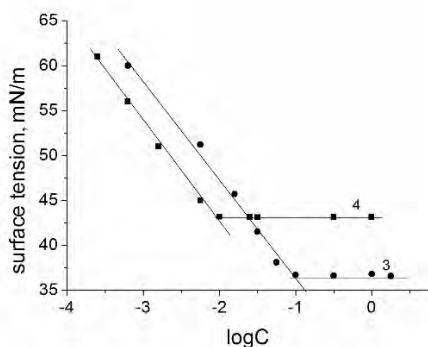


Fig. 3. Surface tension isotherms of monomers 3 and 4

Relatively high values of CMC for surfmers 1 and 2 could be explained by presence of relatively short hydrophobic tert-butylperoxyacyl fragment and strong hydro-

philic sulfonate group or long hydrophilic poly(ethylene glycol) chain. This promotes real solubility of monomers in water till higher concentrations, comparing to the other surfmers.

Lower values of CMC of surfmers 3 and 4 are caused by long cetyl chain which increases the hydrophobic character of the molecule and reduces solubility of monomer in water.

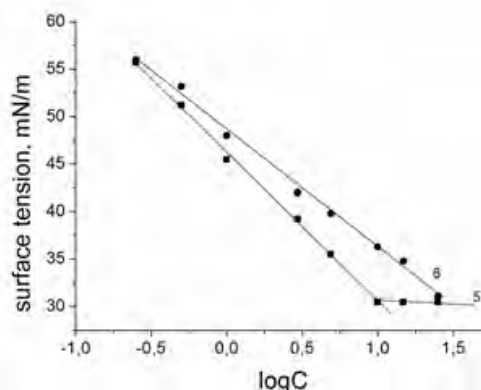


Fig. 4. Surface tension isotherms of monomers 5 and 6

The absence of inflection point on the surface tension isotherm of the monomer 6 could be explained by its strong hydrophilic character due to the presence of long poly(ethylene glycol) chain and the phosphate group.

The solution copolymerization of synthesized surfmers with peroxide containing monomer VEP and N-vinylpyrrolidone was carried out. The resulted copolymers are water soluble and reduce surface tension at aqueous solution-air interface.

The polymerization of styrene in the presence of peroxide containing non-ionic surfmer 2 was studied. During this process the peroxide containing surfmer acted as comonomer and as initiator at the same time.

Conclusion

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 in a wide range. The copolymerization of resulted surfmers with other monomers led to formation of surface active copolymers.