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OBTAINING OF FUNCTIONAL SURFACE ACTIVE MONOMERS BASED ON ***TERT***-BUTYLPEROXY-6-HYDROXYHEXANOATE

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Abstract. The interaction of *e*-caprolactone with *tert*-butylhydroperoxide led to *tert*-butylperoxyhexanoate. Peroxymaleinate has been obtained by the reaction of *tert*-butylperoxyhexanoate with a maleic anhydride. Functional monomers have been synthesized by reactions of peroxymaleinate with propansultone and polyethylene glycol (PEG). The obtained compounds exhibit surface active properties, reducing a surface tension at the water-air interface.

Keywords: *e*-caprolactone, peroxides, surface active monomers, surface tension.

1. Introduction

Functional surface active monomers that have also been known as surfmers have shown the wide capability for creating reactive olygomers, polymeric particles with functionalized surface and drug delivery systems [1]. Within different types of surfmers special attention is paid to the ways of obtaining maleic surfmers. The singularity of such monomers is that they are almost incapable of homopolymerization and generally can form alternate copolymers [2]. Moreover, the insertion of substitutes of different nature and in a variety of combinations in their molecules allows regulating the colloid-chemical properties of such monomers within broad limits [3]. The use of surfmers during the emulsion and dispersion polymerization permits to control the size of latex particles and provides the fuctionalization of the surface of latex particles [4]. Also surfmers in such processes can perform the role of comonomers and at the same time act as a typical surfactant stabilizing the emulsion of the monomer. After the polymerization is completed polymers that contain the units of surfactants locate predominantly on the surface of polymeric particles. This provides the stability of colloidal systems and also allows inserting various functional groups on the surface of the polymeric particles with surfmers [5].

One knows an extensive range of maleic surfmers with hydrophilic polyethylene glycol, propanesulfone or triethylamine units and lipophilic alkyl [6], fluoroalkyl [7], olygomethylsiloxane [8] and saccharide blocks [9]. Surfmers which contain di-*tert*-peroxide groups in lipophilic block have also been described [10]. Primary alcohols with di-*tert*-peroxyfragment in *g*-position were used as initial compounds for obtaining peroxymaleinates [11]. The application of peroxide surfmers during the emulsion and dispersion polymerization permits inserting peroxide groups onto the surface of polymeric particles directly during the time of their formation. This allows performing various polymer-analog transformations on the surface of polymeric particles by free radical reactions involving peroxide groups on the surface.

However, such peroxides exhibit high thermal stability that constrains their application [12]. The applying of surfmers with peroxyester groups as comonomers for creating surface functionalized colloidal polymeric systems should also be attractive due to their lower thermal stability. The use of these compounds during the emulsion and dispersion polymerization can permit inserting peroxide groups on the surface of latex particles directly during the time of their formation, as well as allow performing various polymer-analog transformations on the surface of particles.

Also, various functional surface active monomers that have polimerizable group abstracted from the anchor functional group with the help of spacers that have different length and nature seem to be prospective compounds for obtaining colloidal systems with functionalized surface of interface [13]. Various bifunctional compounds can be used as spacers. However, it is known that the usage of typical bifunctional compounds (diols, dicarboxylic acids *etc*.) can lead to the

problems connected with a selective functional group transformation. Nevertheless, such problems can be omitted while using different heterocyclic reagents such as oxyranes, lactones, sultones. These mentioned compounds lead to monoaddition products during ring opening reactions. It is known that reactions with a ring opening of lactone lead to various functional derivatives of hydroxyacids [14]. The reaction of propiolactone with *tert*-butyl hydroperoxide is well studied and described [15]. However, the detailed information about the interaction of *e*- or *w*-lactones with hydroperoxides was not found. This reaction can also be a convenient method for obtaining various *w*-peroxide containing derivatives for creating peroxide monomers in which the peroxide group is distanced from a polimerizable C=C group.

So the aim of this work is to investigate the interaction of *e*- or *w*-lactones with *tert*-butyl hydroperoxide and to obtain surface active monomers with peroxyester groups.

2. Experimental

2.1. Initial Materials

Maleic anhydride (Merck) was additionally purified by distillation. Mp 325–325.6 K, bp 362 K/1.59 kPa. (Lit. mp 325.8 K, bp 475 K [16]).

Triethylamine (Merck) was additionally purified by distillation. Bp 361.8 K, d_4^{20} 0.7293, n_D^{20} 1.4007. (Lit. bp 362.7 K, d_4^{20} 0.7293, n_D^{20} 1.4009 [16]).

1,3-Propanesultone (Merck) was additionally purified by distillation under residual pressure. Bp 456 K/3 kPa, mp 304–305 K. (Lit. bp 453 K/3 kPa, mp 304–306 K [16]).

Polyethylene glycol monomethyl ether 550 (PEG MME 550) with average molecular weight 550 g/mol was commercially available from Aldrich.

tert-Butyl hydroperoxide (TBHP) was also additionally purified by distillation under residue pressure. Bp 308 K/2.6 kPa, d_4^{20} 0.8966, n_D^{20} 1.4010. (Lit. bp 406 K, d_4^{20} 0.8960, n_D^{20} 1.4006 [16]).

e-Caprolactone was synthesized by oxidation of cyclohexanone by peroxybenzoic acid [17]. The raw product was distillated under residue pressure. Bp 370.5 K/1.3 kPa, n_D^{20} 1.4629. (Lit. bp 369 K/1.3 kPa, n_D^{20} 1.4630 [16]).

Solvents *(dichloromethane, 2-propanol, hexane, ethyl acetate*) were used after additional purification [18].

2.2. Analysis

The individuality of the obtained compounds was confirmed by TLC method using Silica gel 60 F_{254} (Merck) sheets. The solvents hexane and ethyl acetate mixed in ratio 2:1, 1:1, 2:1 were used as the eluent and the length of the solvent front was 100 mm. Iodine vapors were used as a 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).

FT-IR spectroscopy was used to determine the products. Spectra were recorded in a thin film (for liquid compounds) and in a vaseline oil (for crystalline substances).

Organic peroxides were quantified by *iodometric titration (iodine value)* in the glacial acetic acid [19].

The acid value was determined by a potentiometric titration with 0.1 N solution of sodium hydroxide in the alcohol medium [20].

2.3. Differential Thermal Analysis

This analysis was performed by the method of complex thermal analysis using derivatograph Q-150 with Paulik-Paulik-Erdey system. Thermolysis was held in a dynamic regime with a heating rate of 2.5 K per minute. The weight of the sample was 50 mg. The sensitivity of differential thermal scale (DTA) was 100 mV, the sensitivity of thermogravimetric scale (TG) was 50 mg and the sensitivity of differential thermogravimetric scale (DTG) was 250 mV respectively. The aluminium oxide was used as the reference substance.

2.4. Surface Tension

The surface tension of water solutions of the obtained monomers was measured at 293 K by Du Noüy ring method [21]. The critical micelle concentration (CMC) of monomers was determined using surface tension isotherms of corresponding compounds.

2.5. Synthesis

tert-Buthylperoxy-6-hydroxyhexanoate (**2**). 1.12 g (0.0098 mol) of *e*-caprolactone and 8 g (0.082 mol) of TBHP were mixed and a droplet of $BF_3{\cdot}(C_2H_5O)_2$ was added. The mixture was stirred for 12 h at 323–328 K and filtered through a thin layer of aluminium oxide. The excess of TBHP was removed under reduced pressure. The crude product was chromatographed on silica gel eluting with the hexane-ethyl acetate gradient. The solvents were removed to give 1.4 g (70 %) of pure peroxide. n_D^{20} 1.4552, d^{20} 1.0182, M_R 53.6. Found, %: C 58.59; H 9.4. $C_{10}H_{20}O_4$. Calc., %: C 58.82; H 9.8. M_R 53.5. Found iodine value 7.4; calc. iodine value 7.8. IR, cm^{-1}: 1380, 1360, 1250, 1192 ($C(CH_3)_3$); 1776 (C=O); 1200 (C–O); 1000 (C–OO–C); 872 (O–O).

6-tert-Buthylperoxy-6-oxohexylmaleinate (**3**). To a solution of 1 g (0.01 mol) of maleic anhydride in 5 ml of dichloromethane 2 g (0.01 mol) of **2** and 0.1 ml (0.0007 mol) of triethylamine were added consequentially. The

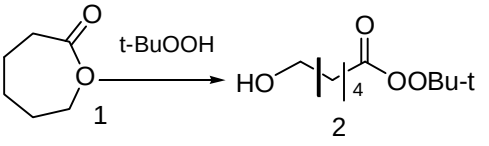
mixture was stirred for 24 h at 313 K. The solvent was removed to give 2.9 g (96 %) of **3**. Found acid value 182.23; calc. acid value 185.76. Found, %: C 55.45; H 6.98. $C_{14}H_{22}O_7$. Calc., %: C 55.63; H 7.28. IR, cm^{-1}: 3300-2500 (OH); 1640 (C=C); 1728 (C=O); 1240 (C–O); 1000 (C–OO–C); 872 (O–O).

Triethylamino 3-[(Z)-4-(6- tert-buthylperoxy-6-oxohexyloxy)-4-oxo-2-buthenoyloxy]-1-propansulphonate (**4**). To the solution of 2 g (0.0066 mol) of **3** in 6 ml of dichloromethane 0.8 g (0.0066 mol) of propanesultone and 0.7 g (0.0066 mol) of triethylamine were added consequentially. The reaction was stirred for 24 h at room temperature. After the evaporation of the solvent the resulting monomer was obtained with a quantitative yield as a yellow viscous liquid. Found, %: C 52.10; H 8.79; N 2.52; S 6.15. $C_{23}H_{46}O_{10}SN$. Calc., %: C 52.27; H 8.71; N 2.65; S 6.06. IR, cm^{-1} : 1240 i 1050 (SO_2), 1640 (C=C); 1728 (C=O); 1240 (C–O); 1000 (C–OO–C); 872 (O–O).

(6-tert-Buthylperoxy-6-oxohexyloxy)(methoxy polyethylene glycol-550)maleinate (**5**). To the 2 g (0.0066 mol) of **3** in 6 ml of dichloromethane 0.45 g (0.0033 mol) of phosphorus trichloride was added dropwise. The reaction was stirred for 5 h at 313 K. The resulting solution was decanted and was added dropwise at 283 K under stirring to the solution of 3.8 g (0.0066 mol) of PEG MME 550 and 0.7 g (0.0066 mol) of triethylamine in 10 ml of dichloromethane. The mixture was stirred for 30 h at 288 K and then filtered through a thin layer of aluminium oxide. The solvent was removed under reduced pressure and the yield of target was 85%. Found, %: C 55.87; H 8.92.$C_{39}H_{72}O_{19}$. Calc., %: C 55.45; H 8.53. IR, cm^{-1}: 1640 (C=C); 1728 (C=O); 1240 (C–O); 1000 (C–OO–C); 872 (O–O).

3. Results and Discussion

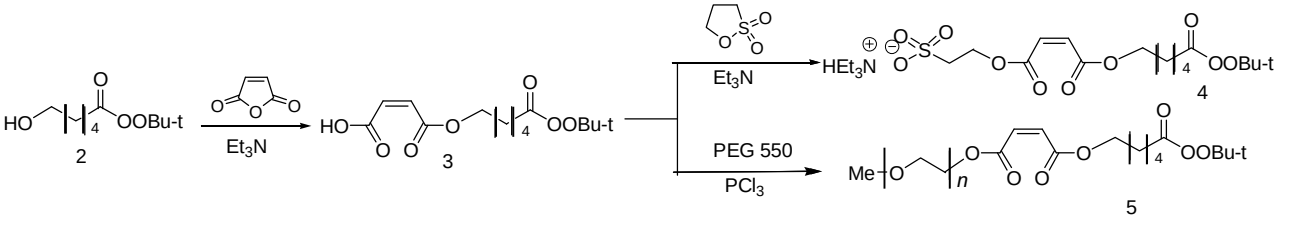
The interaction of *e*-caprolactone with *tert*-butyl hydroperoxide was studied. It was noticed that in the presence of boron trifluoride as a catalyst and at 323–328 K the reaction led to the aimed compound **2**:



The major side reaction under these conditions was the telomerization of the initial lactone. The increase of the molar ratio lactone: TBHP decreased the rate of telomerization. The use of the sevenfold molar excess of hydroperoxide minimized this reaction. It is notable that the employment of solvents such as 2-methyl-2-propanol did not influence the mentioned processes.

The presence of primary hydroxylic group distanced from the peroxyester fragment by the methylene chain made the compound **2** attractive as an intermediate product for creating novel surface active peroxide monomers.

The *e*-peroxyalkylmaleinate **3** was obtained by the reaction of **2** with the maleic anhydride. The interaction of propanesultone with **3** gave the anionic surface active monomer **4**. The reaction of **3** with polyethylene glycol monomethyl ether 550 led to the non-ionic surfmer **5**. The last interaction was carried out via the obtaining of the intermediate chloroanhydride of **3**.



Acylation of **2** by maleic anhydride was held under equimolar ratio of reagents in dichloromethane at 313 K. The trace amount of triethylamine was used as a catalyst. The complete conversion was achieved in 24 h under these conditions.

Sulphoalkylation of *e*-peroxyalkylmaleinate **3** by propanesultone was performed in dichloromethane at room temperature and in the presence of triethylamine (molar ratio of reagents was 1:1:1).

Chloroanhydride of **3** was obtained by the interaction of ε-peroxyalkylmaleinate with a phosphorus trichloride. The optimum temperature for this reaction was 313 K. This can be explained by the fact that under temperatures higher than 313 K the reduction of the peroxyester group can occur. Subsequent acylation of polyethylene glycol monomethyl ether (molecular weight 550 g/mol) by chloroanhydride of **3** at 283–288 K and in the presence of triethylamine as the acceptor of HCl led to the target monomer **5**. The reaction was performed in hexane and under equimolar ratio of reagents.

The results were confirmed by functional and elemental analyses and by IR spectroscopy.

Differential thermal analysis was performed for peroxide **2**. According to the results of this analysis the

intensive weight loss of the sample occurred under 373–448 K accompanied by the appearance of obvious exothermic effect on the DTA curve. The maximum of the exothermic effect was observed at 410 K. The maximum speed of the weight loss of the sample according to the DTG curve was observed at 411–413 K.

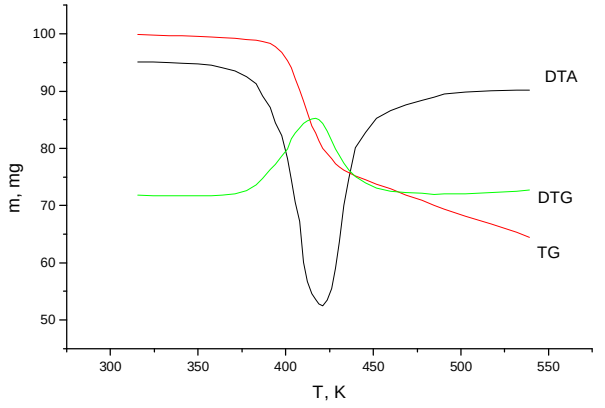


Fig. 1. Curves of the complex thermal analysis of peroxide **2**

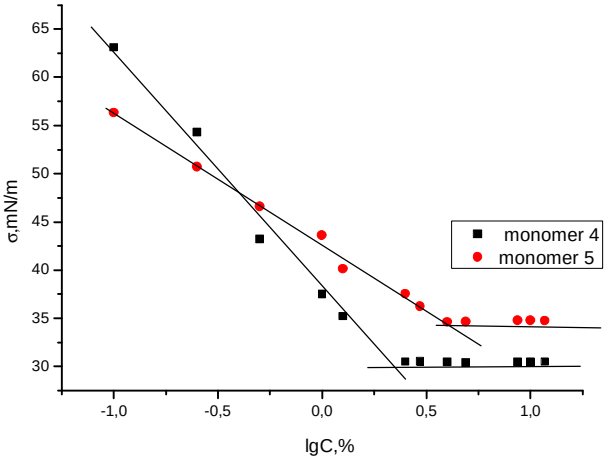


Fig. 2. The surface tension isotherms of monomers **4** and **5**

The surface tension of water solutions of the obtained surface active monomers was measured and their critical micelle concentrations and the surface tension above CMC were determined with the purpose of studying the colloidal properties of monomers **4** and **5**. The CMC for surfmer **4** was 2.5 % and the surface tension above CMC was 30.5 mN/m. The CMC for surfmer 5 was 3.7 % and the surface tension above CMC was 34.6 mN/m respectively.

4. Conclusions

It is established that the interaction of *e*-caprolactone with hydroperoxides led to the formation of peroxyester with the primary hydroxylic group. This compound is an attractive reagent for obtaining novel types of monomers with the peroxyester group. The resulting compounds with anionic and non-ionic hydrophilic blocks are typical surface active monomers that reduce surface tension at the water-air interface.

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СИНТЕЗ ФУНКЦІОНАЛЬНИХ ПОВЕРХНЕВО-АКТИВНИХ МОНОМЕРІВ НА ОСНОВІ *ТРЕТ*-БУТИЛПЕРОКСИ-6-ГІДРОКСИГЕКСАНОАТУ

Анотація. *При взаємодії e-капролактону з трет-бутилгідропероксидом одержано трет-бутилперокси-6-гідроксигексаноат, реакцією якого з малеїновим ангідридом синтезовано пероксидовмісний малеїнат. Взаємодією останнього з пропансультоном і поліетиленгліколем отримано функціональні мономери. Отримані речовини є типовими ПАР і знижують поверхневий натяг на межі вода-повітря.*

Ключові слова: *e-капролактон, пероксиди, поверхнево-активні мономери, поверхневий натяг.*