Novel Surface-Active Succinate Monomers and Initiators for Obtaining Reactive Polymers

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Summary: Novel surface-active monomers and initiators were synthesized by successive treatment of cumylsuccinic anhydride with 3-*tert*-butylperoxy-3-methyl-1-butanol or poly(propylene glycol) acrylate and 1,3-propane sultone with triethylamine. The surface tension isotherms on the air-water solution interface were obtained. The critical micelle concentrations (cmc) as well as the surface tension at the cmc were determined for these substances. The complex thermal analysis of the obtained inisurf was carried out and the possible mechanism of decomposition of its peroxide group was proposed. The synthesized compounds were shown to be suitable reactive surfactants for obtaining styrene latexes.

Keywords: colloids; cumylsuccinic anhydride; initiators; monomers; surfactants

Introduction

Utilization of surfactants with reactive functional groups, particularly monomers (surfmers) and initiators (inisurfs), provides new possibilities for construction of grafted polymer nanolayers on the surfaces of diverse origin, creation of polymers with complex architecture, ''core-shell'' particles and other composites as well as stabilization of polymer colloid systems.[1–3] A lot of papers is devoted to utilization of such compounds in the processes of dispersion[4] and emulsion[5,6] polymerization. Unlike common surfactants, they are capable of grafting to the surface by means of covalent bonds.[7–9] Thus, they become unable to desorb, and therefore their efficiency as stabilizers and compatibilizers is greatly increased.

At present, succinate surfactants are widely used in the industry for stabilizing polymer suspensions and emulsions. On the other hand, surface-active compounds containing aromatic (benzene, naphthalene) fragments are known to possess several useful properties for obtaining styrene colloid systems, stabilizing mineral pigment dispersions (titanium (IV) oxide, zinc oxide), etc. Since colloids on the basis of styrene type monomers (styrene, α-methylstyrene, divinylbenzene, etc.) are commonly used in the industry of high-molecular compounds, the synthesis of functional succinate surfactants containing aromatic fragments is necessary for obtaining effective stabilizers of such systems.

The present work is devoted to the synthesis of novel surface-active monomers and initiators on the basis of cumylsuccinic anhydride (CSA), suitable for obtaining reactive polymers.

Experimental Part

Materials

Maleic anhydride and cumene form Fluka were purified by vacuum distillation before utilization. N,N-Dimethylformamide (DMF) from Aldrich was purified according to known technique.[10] Triethylamine from Aldrich was distilled at atmospheric pressure. 1,3-Propane sultone and poly(propylene glycol) acrylate (average molecular weight M_n ca. 475) from Aldrich were used

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without purification. Surface tension measurements were carried out in distilled water.

3-*tert*-Butylperoxy-3-methyl-1-butanol was synthesized according to the technique.[11]

Analytical Methods

The course of the reactions was controlled by means of gas-liquid chromatography by estimation of the reagent consumption with a "Selmihrom-1" chromatograph (Ukraine) (Teflon column length – 1 m, diameter – 3 mm, carrier – "Columpack T" with 2% w/w of "Carbowax 40M"). The furnace temperature was programmed from 50 to 200 °C (heating rate – 15 °C/min, detector – katharometer, detector current 180 mA). IR spectra were recorded in thin films (for liquids) as well as in tetrachloromethane solution or Vaseline (for crystalline materials) with a "Specord M80" spectrophotometer. ^{1}H-NMR spectra were recorded using a Brucker 150 spectrometer at a working frequency of 300 MHz in DMSO-d$_6$ (substance concentrations of 5…10%, internal standard – hexamethyldisiloxane). The surface active characterization of synthesized surfactants was carried out by means of surface tension measurements. These measurements were performed with a du Noüy ring tensiometer at 20 °C. Complex thermal analysis was carried out using the "Derivatograph Q-1500D", Paulik-Paulik-Erdey system (MOM, Hungary). The experiments were conducted in dynamic mode in oxygen atmosphere with a heating rate of 1.25 K/min (sample weight – 200 mg, sensitivities: TG scale – 200 mg, DTG scale – 500 μV, DTA scale – 100 μV). The samples were heated to 250 °C (Standard – aluminium oxide). The styrene conversion during emulsion polymerization in the presence of the surfmer (**3.2**) was estimated by means of solid residue content determination.

Synthesis of Reactive Surfactants

Cumylsuccinic anhydride (**1**). To a solution of 13.0 g (0.13 mol) of maleic anhydride in 98.0 g (0.820 mol) of cumene under argon atmosphere at 85 °C, 0.17 g (0.0007 mol) of benzoyl peroxide was added with intensive stirring. The mixture was kept at 85 °C for 6 hours under argon, then unreacted cumene and maleic anhydride were removed by vacuum distillation. The residue was dissolved in 30 ml of anhydrous benzene, the appeared crystals were filtered off. Then, 20 ml of anhydrous hexane was added to the filtrate and the solution was decanted from brownish oligomeric adducts. The procedure was repeated 3 times (60 ml of hexane total). The solvents were removed by distillation and the obtained residue was kept in vacuum for 3 hours to give 24.6 g of yellowish crystals (yield 85%). Found, %: C 71.31; H 6.62. $C_{13}H_{14}O_3$. Calcd, %: C 71.54; H 6.47. IR spectrum, cm^{-1}: 704, 768 and 3086 (C_{ar}–H), 1220 (C–O), 1376 and 1392 ($C(CH_3)_2$), 1448, 1496 and 1600 (C_{ar}–C_{ar}), 1792 and 1860 (C=O). ^{1}H NMR (DMSO-d$_6$), δ, ppm: 1.41 s (3H, $C\underline{H}_3$); 1.47 s (3H, $C\underline{H}_3$); 2.60 m, 2.90 m (2H, $C\underline{H}_2$); 3.66 m (1H, $C\underline{H}$); 7.34 m (5H, $C_6\underline{H}_5$).

Monosuccinates (**2.1**) *and* (**2.2**) were obtained as follows: To a solution of 2.18 g of cumylsuccinic anhydride (**1**) in 6 ml of anhydrous DMF, 0.01 mol of a hydroxy containing compound (3-*tert*-butylperoxy-3-methyl-1-butanol or poly(propylene glycol) acrylate) and 0.20 g (0.002 mol) of triethylamine were successively added with stirring. The obtained mixture was kept with stirring at 40 °C for 12 hours, then the solvent was removed by vacuum distillation. The Monosuccinates were formed in quantitative yield.

For peroxide containing succinate (**2.1**): Found, %: C 58.08; H 8.59. $C_{22}H_{34}O_6$. Calcd, %: C 57.89; H 8.67. ^{1}H NMR spectrum, δ, ppm: 1,10 s (6H, $C(C\underline{H}_3)_2OO$); 1,12 s (9H, $C(C\underline{H}_3)_3$); 1,32 m (6H, $PhC(C\underline{H}_3)_2$); 1,70 m (2H, $CHC\underline{H}_2$); 1,83 m (1H, $C\underline{H}CH_2$); 2,51 t (2H, $C\underline{H}_2C(CH_3)_2$); 4,01 t (2H, $C(O)OC\underline{H}_2$); 7,33 m (5H, $C_6\underline{H}_5$); 10,34 s (1H, OH).

The Succinate monomer (**2.2**) was used for obtaining monomer (**3.2**) in situ and, therefore, was not identified.

The typical procedure for obtaining *compounds* (**3.1**) *and* (**3.2**) is as follows: To a solution of 0.01 mol of monoester (**2.1**) or (**2.2**) in 6 ml of DMF, 1.22 g (0.01 mol) of 1,3-propane sultone and 1.01 g (0.01 mol) of triethylamine were added. The mixture was kept with stirring at 40 °C for 6 hours, then, the excess of triethylamine as well as the solvent were removed by vacuum distillation. The desired products were obtained in quantitative yield.

For inisurf (**3.1**): Found, %: C 58.08; H 8.59. $C_{31}H_{55}NO_9S$. Calcd, %: C 58.28; H 8.53. IR spectrum, cm^{-1}: 704, 776 and 3080 (C_{ar}–H), 880 (O–O), 930 (C(O)OC), 1040 and 1164 (SO_2), 1200 (peroxide C–O), 1230 (C–O of ester), 1360 and 1392 ($C(CH_3)_2$ and $C(CH_3)_3$), 1472 (C_{ar}–C_{ar}), 1728 (C=O), 2500 and 2683 (NH^+). ^{1}H-NMR (DMSO-d_6), δ, ppm: 1.10 s (6H, $C(C\underline{H}_3)_2OO$); 1.11 s (9H, $C(C\underline{H}_3)_3$); 1.19 t (9H, $^+NH(CH_2C\underline{H}_3)_3$); 1.32 m (6H, $PhC(C\underline{H}_3)_2$); 1.84 m (2H, $CHC\underline{H}_2$); 1.97 m (1H, $C\underline{H}$); 2.44 t (2H, $C\underline{H}_2C(CH_3)_2$); 2.50 m (2H, $CH_2C\underline{H}_2CH_2$); 3.09 q (6H, $^+NH(C\underline{H}_2CH_3)_3$); 3.40 t (2H, $C\underline{H}_2SO_3^-$); 3.98 t (2H, $C(O)OC\underline{H}_2CH_2CH_2$); 4.02 t (2H, $C(O)OC\underline{H}_2CH_2C(CH_3)_2$); 7.31 m (5H, $C_6\underline{H}_5$); 9.11 s (1H, $^+N\underline{H}$).

For surfmer (**3.2**): Found, %: C 59.25; H 8.74. $C_{45,84}H_{80,69}NO_{14,95}S$. Calcd, %: C 60.06; H 8.81. IR spectrum, cm^{-1}: 704, 770 and 3080 (C_{ar}–H), 930 (C(O)OC), 1032, 1150 and 1180 (SO_2), 1240 (C–O), 1360 and 1376 ($C(CH_3)_2$), 1452 (C_{ar}–C_{ar}), 1632 (C=C), 1732 (C=O), 2512 and 2696 (NH^+), 3030 (CH_2=).

Results and Discussion

Novel surface-active initiators and monomers were obtained by a two-step synthesis on the basis of cumylsuccinic anhydride (CSA) according to Scheme 1.

Cumylsuccinic anhydride, the starting material, can be synthesized on the basis of commercially available cumene and maleic anhydride (MA). The method of synthesis of anhydrides of such type is described in the literature.[12] The interaction between alkylarenes and MA was carried out in the presence of di-*tert*-butyl peroxide (DTBP) at 150 °C and at a molar ratio arylalkane: MA: DTBP as 10…15: 1: 0,007. The maximum yield of aralkylsuccinic anhydrides increased from primary to tertiary arylalkanes. In the case of *p*-cymene it was 76%, and for *p*-ethylisopropylbenzene it was 87%. The MA conversion was 85% and 88% respectively. The addition products were isolated, however, as the corresponding dicarboxylic acids, not as anhydrides.

Therefore, the novel technique of cumene addition to MA was developed. According to this technique the reaction was carried out in the presence of benzoyl peroxide (BP) initiator at 80–120 °C and the molar ratio cumene: MA: BP as 7…10: 1: 0.007.

The yield of anhydride (**1**) was established to increase with the temperature increase. Oligomeric adducts of anhydride (**1**) and other MA molecules were formed as by-products. Their yield decreased with a decrease of the reaction time as well as with an increase of the cumene excess. This tendency is observed for all the reactions of this type involving alkylaromatic hydrocarbons.

During the interaction of CSA with functional alcohols bearing a peroxide group (3-*tert*-butylperoxy-3-methyl-1-butanol) or a double bond (polypropylene glycol acrylate) in the presence of triethylamine catalyst in DMF solution at 20–40 °C, the peroxide containing succinate (**2.1**) and the succinate monomer (**2.2**) were obtained respectively. These surface-active products can be isolated as individual substances or used for synthesis of final reactive surfactants in situ. Treatment of these half-esters with equimolar quantities of 1,3-propane sultone and triethylamine resulted in the formation of the inisurf (**3.1**) and the surfmer (**3.2**) respectively in nearly quantitative yields.

The structure of the synthesized compounds was confirmed by elemental analysis data as well as IR and ^{1}H-NMR spectroscopy.

The surfactant properties of the obtained compounds were studied. The surface tension isotherms of their water solutions are shown in Figure 1.

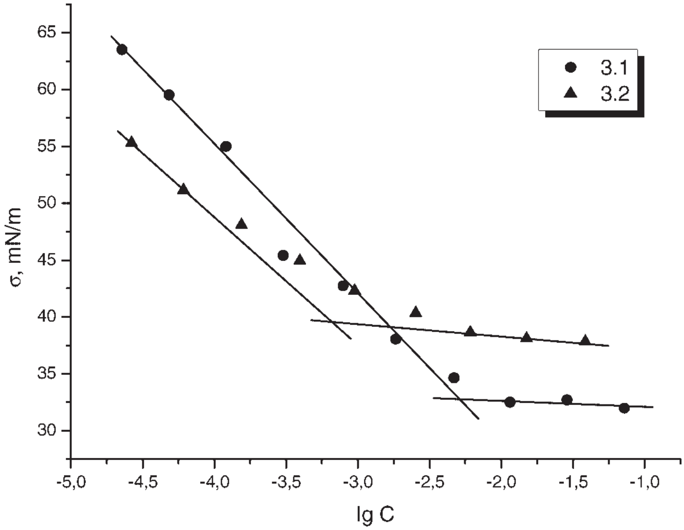


Figure 1.
Surface tension isotherms on the air-water solution interface of surfactants (**3.1**) and (**3.2**).

The synthesized surfmer and inisurf are obviously surface active compounds since the water surface tension is reduced when these substances are added. Both compounds are colloid surfactants. Their surface tension decreases almost linearly with increasing concentration and becomes constant above the concentration that corresponds to their critical micelle concentration (cmc). The cmc values of the investigated compounds as well as the surface tensions at the cmc were determined from the inflection points on the surface tension isotherms. The results are listed in Table 1.

A complex thermal analysis of synthesized inisurf (**3.1**) was carried out in order to study the thermal stability of its peroxide group. Thermogravimetric curves of the samples under investigation are given in Figure 2.

Table 1.
Critical micelle concentration (cmc) and the surface tension at the cmc of the synthesized compounds.

Compound	cmc		σ_{cmc}
	% w/w	mol/l	mN/m
3.1	0.316	0.0051	32.8
3.2	0.061	$6.6 \cdot 10^{-4}$	39.2

The thermolysis of the sample was accompanied by the appearance of an exothermic effect on the DTA curve in the temperature range of 133–198 °C with a maximum at 171 °C. A weight loss of approximately 22% was observed on the TG curve in this temperature range. A subsequent weight loss connected with further destruction of the substance was observed on the TG curve with the increase of temperature.

On the basis of this tendency the following mechanism of the thermal decomposition of the inisurf (**3.1**) was proposed (Scheme 2).

The validity of the shown mechanism was confirmed by the analysis of the volatile decomposition products by means of gas-liquid chromatography. Thus, according to the chromatographic data, the acetone content in the gaseous mixture was almost 2 times higher than the content of *tert*-butyl alcohol.

On the basis of the thermogravimetric curves, the kinetic parameters of the decomposition process of the peroxide group of

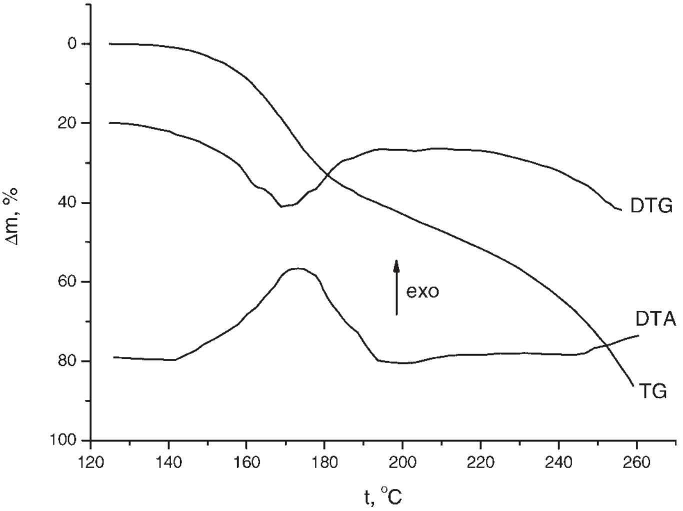


Figure 2.
Thermogravimetric curves of decomposition of peroxide containing succinate (**3.1**).

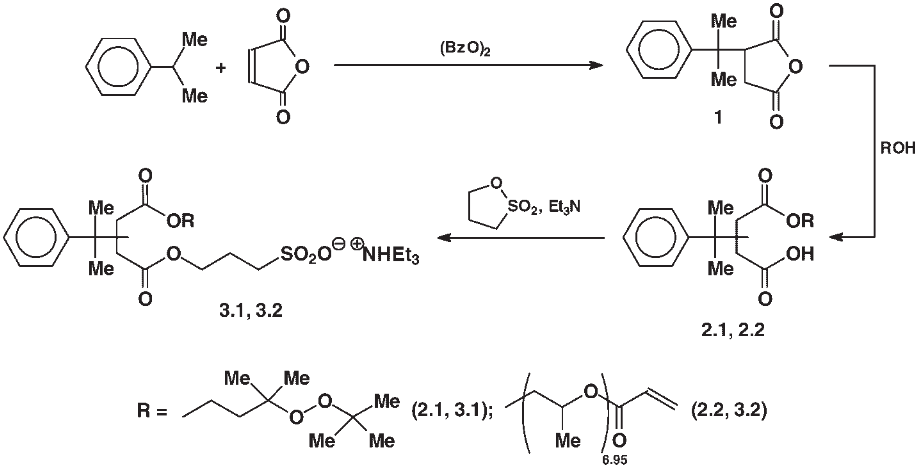
the inisurf (**3.1**) were determined according to Lipskis' differential method.[13,14] The calculation was carried out on the basis of a modified kinetic equation together with the least-squares method:

$$\frac{dW}{W_k dt} = \ln\frac{Z}{q} - \frac{E}{RT} + n\ln\left(1 - \frac{W}{W_k}\right),$$

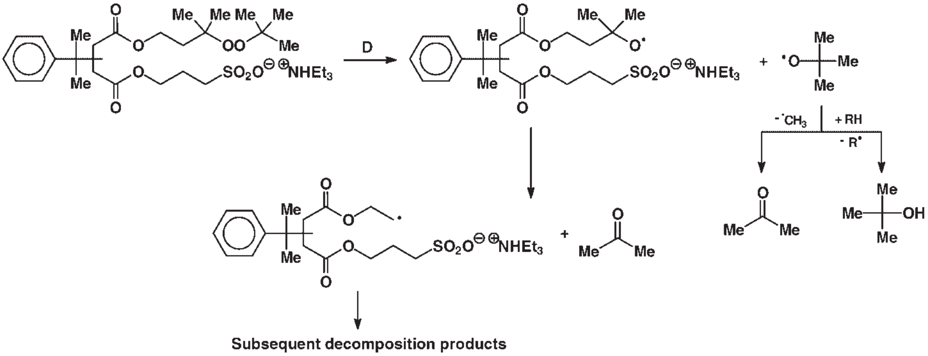
with: W –weight loss of sample at temperature T (determined on the TG curve), mg; W_k –total weight loss of sample on the certain stage, mg; T – temperature, K; E – sample activation energy, kJ/mol; n – reaction order; Z – pre-exponential factor; q – sample heating rate, K/sec.

The activation energy of decomposition, the pre-exponential factor, and the reaction order are calculated to be $E = 150{,}3$ kJ/mol, $Z = 8{,}26 \cdot 10^{16}$, and $n = 1{,}67$. Such values are typical for induced decomposition.

The synthesized reactive surfactants were shown to be good emulsifiers for



Scheme 1.
Synthesis of novel reactive succinate surfactants.



Scheme 2.
Possible decomposition mechanism of peroxide containing succinate (**3.1**).

obtaining styrene colloids. Thus, introduction of the surfmer (**3.2**) into styrene with subsequent dispersing of the monomer in water (weight ratio surfmer: styrene: water as 1…5: 100: 1000) allows to obtain stable monomer emulsions, which do not separate for a long time. The Initiation of polymerization by ammonium persulfate at 70 °C resulted in formation of stable polystyrene latexes. The polymerization rate was established to increase with increasing surfmer concentration in the reaction mixture. Depending on the quantity of surfmer involved, a monomer conversion of 80–90% was achieved in 2.5–8.5 hours.

Conclusions

On the basis of available raw materials, novel acrylate surfmers and peroxide inisurfs derivatives of cumylsuccinic acid were synthesized. The obtained compounds were shown to possess surface activity, since they reduce the surface tension at the air – water solution interface. The synthesized peroxide was demonstrated to generate free radicals during thermal decomposition. The synthesized compounds were shown to be suitable emulsifiers for obtaining styrene colloid systems.

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