

SHORT
COMMUNICATIONS

Synthesis of Peroxide Monomers Based on Unsaturated Carboxylic Acids

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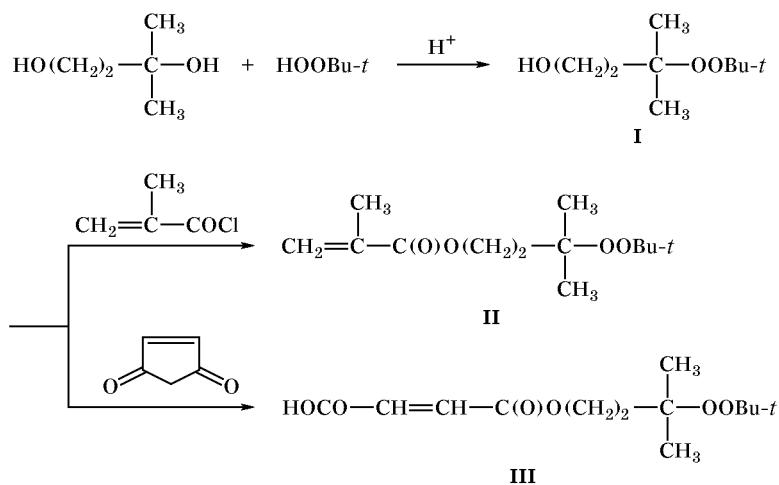
Peroxide monomers, i.e., compounds whose molecules contain double carbon–carbon bonds and peroxy groups, are used in the preparation of copolymers having peroxy groups as substituents in the macrochain. Such copolymers are efficient modifiers and activators of polymeric surfaces [1]. Among peroxy monomers in which the peroxy group is linked to two tertiary carbon atoms, only derivatives of isopropenylbenzene [2] and 2-methyl-3-hexen-5-yn-2-ol [3] are known.

The goal of the present work was to synthesize new peroxy monomers derived from methacrylic or maleic acid and 3-*tert*-butyldioxy-3-methyl-1-butanol. Initial hydroperoxide **I** was prepared by alkylation of *tert*-butyl hydroperoxide with 3-methyl-1,3-butanediol in the presence of sulfuric acid. Monomers **II** and **III** were obtained by acylation of compound **I** with an equimolar amount of methacryloyl chloride or maleic anhydride, respectively (Scheme 1). The products are stable to shock and friction, and they can be

stored for a long time without loss of active oxygen. Copolymerization of **II** and **III** with other monomers, such as styrene, α -methylstyrene, etc., gives rise to peroxy-containing copolymers.

3-*tert*-Butyldioxy-3-methyl-1-butanol (I). To a mixture of 39.7 g (0.38 mol) of 3-methyl-1,3-butanediol and 35.7 g (0.38 mol) of *tert*-butyl hydroperoxide we added dropwise with stirring at 35–40°C 57.2 g (0.38 mol) of 65% sulfuric acid. The mixture was stirred for 2 h at that temperature, diluted with an equal volume of water, neutralized with MgO, and extracted with hexane. The organic layer was separated and dried over MgSO₄, the solvent was distilled off, and the residue was distilled under reduced pressure. Yield 57.1 g (85%), bp 64°C (1.3 kPa), $d_4^{20} = 0.9216$, $n_D^{20} = 1.4266$, $MR_D = 49.05$ (calcd. 49.38). IR spectrum, ν , cm⁻¹: 960 (COOC), 820 (O–O), 1200 (C–O), 1020 (C–OH), 3368 (OH). ¹H NMR spectrum, δ , ppm: 1.15 s (9H, *t*-Bu), 3.77 t (2H, OCH₂), 1.83 t (2H, CH₂), 1.25 s (6H, 2CH₃),

Scheme 1.



2.25 s (1H, OH). Found, %: C 61.57; H 11.59. *M* 170 (by cryoscopy in benzene). $C_9H_{20}O_3$. Calculated, %: C 61.33; H 11.44. *M* 176.25.

(3-*tert*-Butyldioxy-3-methylbutyl) methacrylate (II). To a mixture of 4.4 g (0.025 mol) of hydroxy peroxide **I**, 2.6 g (0.025 mol) of triethylamine, and 15 ml of hexane we added dropwise at 5–10°C 2.6 g (0.025 mol) of methacryloyl chloride, and the mixture was stirred for 2.5 h. The precipitate was filtered off and was purified by chromatography on aluminum oxide of activity grade II using hexane as eluent. Yield 5.4 g (89%), $d_4^{20} = 0.9600$, $n_D^{20} = 1.4400$, $MR_D = 67.50$ (calcd. 67.72). IR spectrum, ν , cm^{-1} : 955 (COOC), 830 (O–O), 1210 (C–O). 1H NMR spectrum, δ , ppm: 1.15 s (9H, *t*-Bu), 1.25 s (6H, 2CH₃), 1.93 t (2H, CH₂), 1.94 (3H, CH₃), 4.2 t (2H, OCH₂), 5.56 s (1H, CH₂), 6.07 (1H, CH₂). Found, %: C 63.62; H 9.92. $C_{13}H_{24}O_4$. *M* 248 (by cryoscopy in benzene). Calculated, %: C 63.91; H 9.90. *M* 244.32.

(3-*tert*-Butyldioxy-3-methylbutyl) hydrogen maleate (III). A mixture of 17.6 g (0.1 mol) of peroxide **I** and 9.8 g (0.1 mol) of maleic anhydride was kept for 18 h at 35–40°C. It was then diluted with 35 ml of hexane and cooled to 15°C, and the

precipitate was filtered off. Yield 23.8 g (87%), mp 60–61.5°C. IR spectrum, ν , cm^{-1} : 960 (COOC), 830 (O–O), 1210 (C–O). 1H NMR spectrum, δ , ppm: 1.15 s (9H, *t*-Bu), 1.25 s (6H, 2CH₃), 1.93 t (2H, CH₂), 4.21 (2H, OCH₂), 6.36 d and 6.41 d (1H, CH), 6.42 and 6.47 (1H, CH), 10.34 s (1H, OH). Found, %: C 56.78; H 8.21. $C_{13}H_{22}O_4O$. *M* 281 (by cryoscopy in benzene). Calculated, %: C 56.92; H 8.08. *M* 274.31.

The IR spectra were recorded on a Specord 80M spectrophotometer from samples prepared as thin films (compounds **I** and **II**) or dispersed in mineral oil (**III**). The 1H NMR spectra were measured on a Bruker 150 instrument (300 MHz) from 5–10% solutions in chloroform-*d* using hexamethyldisiloxane as internal reference.

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