Reactive Polymers on the Basis of Functional Peroxides

R. I. Fleychuk, A. M .Kohut, O. I. Hevus, S. Voronov*

Lviv Polytechnic National University, S.Bandera Str. 12, 79013 Lviv, Ukraine
E-mail: fleychuk@polynet.lviv.ua

Summary: The copolymerization constants of new monomer containing ditertiary peroxide groups with styrene have been determined. The peroxide monomers were prepared by the acylation of 3-(tert-butylperoxy)-3-methyl-1-butanol with methacryloyl chloride or maleic anhydride in the presence of tertiary amines. Peroxide containing copolymers were obtained by copolymerization of peroxyalkyl methacrylate and peroxyalkyl maleate with styrene.

Keywords: copolymerization; macroinitiators; monomers; peroxides; reactive polymers

Introduction

Peroxide copolymers are of the most efficient classes of the reactive modifiers for macro- and microsurfaces. Depending on peroxide group placement, these copolymers could be classified as those containing peroxide group: in the terminus of macrochain (telechelic); along the skeleton; and in the side substituents of polymer macrochain. These copolymers are obtained by the copolymerization of peroxide monomers (PM) with other ones (styrene, α-methylstyrene, vinyl acetate etc.),[1-4] by the reaction of dihydroperoxides with bifunctional compounds (chloroanhydrides of dicarboxylic acids, ditertiary diols, diisocyanates etc.)[5-7] or by the interaction of maleic anhydride copolymers with hydroxy peroxides.[8] Polymers having peroxide groups in side substituent of macrochain are of especial interest since they are able to initiate free radical processes, e.g. polymerization, grafting, structurizing etc. while retaining macrochain due to the homolysis of O-O bond under the influence of transition metals or heating. The peroxide derivatives of 2-methyl-5-hexen-3-yne-2-ol are the most studied monomers of this kind. Polyreactive plastics, rubbers, latexes, and peroxide surfactants were obtained on the basis of these monomers. However, the combination of the chemical-physical properties and the reactivity (solubility, activity in copolymerization reactions, temperature range of free radicals generation, and the activity of the radicals formed) limits partially the application of known PM sometimes.

The purpose of this work is a synthesis of reactive polymers on the basis of the new kind of peroxide monomers incorporating double carbon-carbon bond and peroxide group separated by alkyl spacer.

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Experimental

Materials

3-tert-Butylperoxy-3-methyl-1-butanol was synthesized according to the technique reported before.[9] Maleic anhydride from Aldrich was purified by vacuum distillation and kept under argon. Methacryloyl chloride from Fluka was used as supplied. Styrene from Aldrich was distilled under reduced pressure just before use. The initiator, 2,2'-azobis(isobutyronitrile), AIBN, from Merck was purified by recrystalization from anhydrous methanol for three times.

Analysis Methods

Individuality of the synthesized compounds was verified by thin layer chromatography with plates of Silica gel 60 F_{254} from Merck. The plates were developed in iodine vapour as well as by reflux with solutions of reagents forming coloured derivatives: N,N-dimethyl-1,4-phenylenediamine – with peroxide group, cerium ammonium nitrate – with hydroxyl one. IR spectra were recorded in thin film (for methacrylate **2**) or in tetrachloromethane solution (for maleate **3**) with a RS 1000 FT-IR spectrometer (UNICAM Analytische System GmbH). ^{1}H-NMR spectra were recorded using a Brucker 150 spectrometer at working frequency of 300 MHz, substance concentrations of 5...10%, internal standart – hexamethyldisiloxane. The average molecular weights of obtained copolymers were determined with a gel-permeation chromatograph "Waters" (200). The active oxygen content in the synthesized peroxide compounds and prepared polymers was determined by means of iodometry according to the known technique.[10] Functional groups in the synthesized substances were determined using the following techniques: carboxylic – potentiometric titration;[11] carbon-carbon double bonds – addition of $Hg(ClO_4)_2$ with following back titration by 0.01 N solution of thioglycolic acid.[12]

Synthesis of peroxide monomers

3-tert-Butylperoxy-3-methyl-1-butyl methacrylate **2** was obtained in petroleum-ether solution by the reaction of 4.4 g (0.025 mol) of hydroxy peroxide (**1**) with 2.6 g (0.025 mol) of methacryloyl chloride in the presence of 2.6 g (0.025 mol) of triethylamine at 0...5°C according to the technique described elsewhere.[9] 5.4 g amount of target methacrylate was obtained (yield 89%). IR spectrum, cm^{-1}: 830 (O-O), 955 (COOC), 1016...1110 and 1220 (C-O), 1210 (C-O), 1680 (C=C), 1722 (C=O). ^{1}H-NMR ($CDCl_3$), δ, ppm: 1.15 s (9H, t-Bu), 1.25

s (6H, $2CH_3$), 1.93 t (2H, CH_2), 1.94 s (3H, CH_3), 4.2 t (2H, OCH_2), 5.56 s and 6.07 s (2H, CH_2).

3-tert-Butylperoxy-3-methyl-1-butyl maleate **3** was obtained by the reaction of 17.62 g (0.10 mol) of 3-tert-butylperoxy-3-methyl-1-butanol and 9.8 g (0.10 mol) of maleic anhydride according to the technique reported before.[9] 23.8 g (yield 87%) amount of peroxyalkyl maleate was obtained. IR spectrum, cm^{-1}: 830 (O-O), 960 (COOC), 1210 (C-O), 1168 and 1280 (C-O), 1658 and 1640 (C=C), 1720 (C=O), 2500...3200 (HO). ^{1}H-NMR ($CDCl_3$), δ, ppm: 1.15 s (9H, t-Bu), 1.25 s (6H, $2CH_3$), 1.93 t (2H, CH_2), 4.21 t (2H, OCH_2), 6.42 and 6.47 (1H, CH), 6.36 d and 6.41 d (1H, CH), 10.34 s (1H, OH).

Copolymerisation procedure

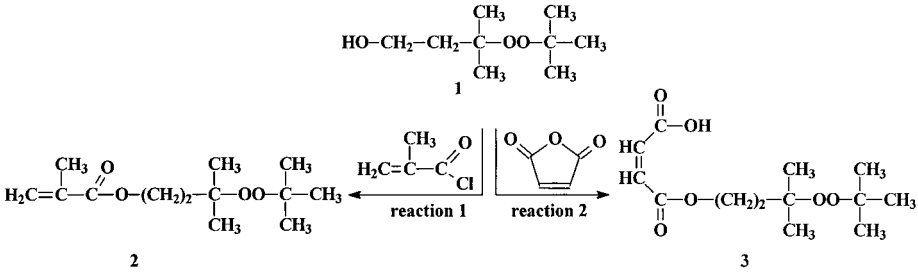
*Copolymerization of peroxyalkyl methacrylate **2** with styrene in solution.* The copolymerization was performed in ampoules under argon in which benzene, 3-tert-butyl-peroxy-3-methyl-1-butyl methacrylate, styrene, and 2,2'-azobis(isobutyronitrile) (2 wt % with respect to monomer mixture) were charged. The volume ratio of the solvent-monomer mixture was of 5 : 1, respectively. The ampoule contents were freezed, vacuumized and charged with argon for several times in turn. Ampoules were sealed after that and heated to 60°C for 2 h. The prepared polymers were isolated and purified by precipitation from benzene to methanol. Copolymer composition was determined from elemental analysis data and active oxygen content after drying in vacuum at room temperature up to constant weight.

*Copolymerization of peroxyalkyl maleate **3** with styrene in solution.* The copolymerization was performed in ampoules under argon, the volume ratio of the solvent-monomer mixture was of 5 : 1, respectively (solvent – benzene). 2,2'-Azobis(isobutyronitrile) was utilized as initiator (2 wt % with respect to monomer mixture). The ampoule contents were freezed, vacuumized and charged with argon for several times in turn. Ampoules were sealed after that and heated to 60°C for 2 h. The polymerization proceeded till monomer conversion of 13...18%. The prepared polymers were isolated and purified by precipitation from benzene to methanol. The polymers were dried in vacuum at room temperature up to constant weight and copolymer yields were calculated. Copolymer composition was determined from elemental analysis data, active oxygen content and acid number value.

Results and discussion

Obtaining of peroxide monomers

Peroxide monomer – methacrylic acid derivative – was synthesized by acylation of 3-tert-butylperoxy-3-methyl-1-butanol **1** with equimolar amount of methacryloyl chloride (Scheme 1, reaction 1). The reaction was carried out in organic solvent at 0...5°C in the presence of triethylamine as hydrogen chloride acceptor. The yield of 3-tert-butylperoxy-3-methyl-1-butyl methacrylate **2** was of 89%.



1 2 3

Scheme 1

It was failed to obtain peroxyalkyl methacrylate **2** by the esterification of 3-tert-butylperoxy-3-methyl-1-butanol with methacrylic acid in the presence of sulphuric acid as a catalyst or by interesterification of methyl methacrylate with hydroxy peroxide **1** at satisfactory yields due to the heterolysis of peroxide group catalyzed by mineral acids.

Hydroxy peroxide **1** and maleic anhydride were utilized as initial substances to prepare peroxide monomers – maleic acid derivatives. The interaction of equimolar amounts of 3-tert-butylperoxy-3-methyl-1-butanol and maleic anhydride was performed for 18 h at 30...40°C in the presence of catalytic amount of triethylamine (Scheme 1, reaction 2). The yield of 3-tert-butylperoxy-3-methyl-1-butyl maleate **3** was of 87%.

The structure of the synthesized substances has been confirmed by data of elemental and functional analyses, IR and NMR H^1 spectra. The characteristics of the obtained products are listed in Table 1.

Table 1. Characteristics of peroxide monomers – derivatives of methacrylic and maleic acids.

Product Number	Yield, %	d_4^{20}	n_D^{20}	MR_D Obtained/ Calculated	Obtained / Calculated, %		Formula	M Obtained/ Calculated
					C	H		
2	89	0.9388	1.4320	67.504/67.728	63.78/63.91	9.86/9.90	$C_{13}H_{24}O_4$	248/244.33
3[a)]	87	--	--	--	56.78/56.92	8.21/8.08	$C_{13}H_{22}O_6$	281/274.31

a) melting point 60.0...61.5°C.

The peroxide monomer **2** is a colourless oily liquid, and the monomer **3** is a crystalline substance. The peroxide monomers synthesized are safe for use and capable to be kept without the appreciable loss of active oxygen content for a long time. The monomer **3** has an essential advantage over the other kinds of known PM: it does not undergo self-initiated homopolymerization.

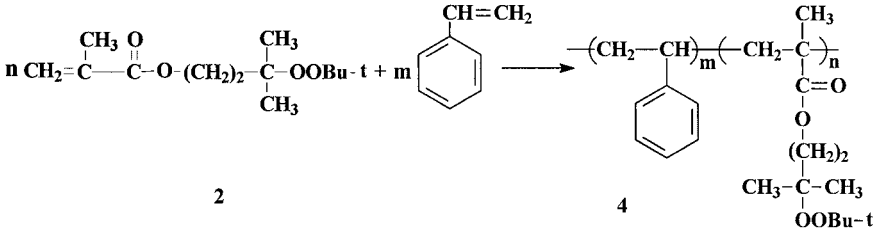
Obtaining of reactive copolymers

Copolymerisation of peroxyalkyl methacrylate with styrene

The copolymerization of synthesized peroxyalkyl methacrylate **2** with styrene in solution has been investigated in order to study its polymerizability (Scheme 2). The copolymerization was carried out for five monomer ratios (Table 2).

Unsaturated peroxide loss for side reactions is known to do not exceed 2...3% during copolymerization at 60-70°C.[13] It permits the utilization of known techniques for determination of copolymerization constants under these conditions.

The polymerization constants were calculated according to the Mayo-Lewis method using the composition equation in the integrated form:[14] $r_1 = 0.54$, $r_2 = 0.43$. Figure 2 represents the composition curve of the copolymer. One can see from Figure 2 that both copolymerization constants are less then 1 during copolymerization of peroxyalkyl methacrylate with styrene, i.e. every comonomer is added more readily to radical of another than to its own one. It is probably explained by the difference in polarities of double bonds of peroxyalkyl methacrylate and styrene. The product of r_1 and r_2 is of low value, that tesifies to the tendency of this system to form alternate copolymer.



Scheme 2

The polymers of linear structure are formed as a result of the performed copolymerization. The low value of average molecular weight of the prepared copolymers (about 12,500) testifies to this fact. Furthermore, 3-tert-butylperoxy-3-methylbutyl methacrylate undergoes mainly chain propagation reaction without peroxide group decomposition under

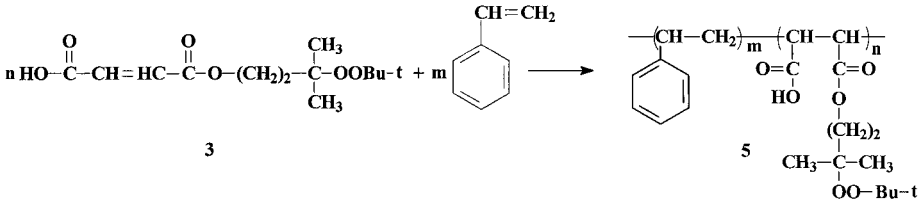
copolymerization proceeding conditions as it is indicated by active oxygen content of the final copolymers (see Table 2). The mentioned results coincide with data on copolymerization of other kind of ditertiary peroxide monomers reported in literature before.[15]

Table 2. Copolymerization of peroxyalkyl methacrylate (M_2) with styrene (M_1).

Monomer mixture composition, $[M_1] : [M_2]$	Elemental composition of copolymers, % w/w			Copolymer composition, $[m_1] : [m_2]$	Active oxygen content in copolymer, %	Average molecular weight of copolymer
	C	H	O			
0.7955 : 0.0483	79.23	8.72	11.97	0.7358 : 0.2642	2.99	11,200
0.6000 : 0.4000	74.53	9.09	16.37	0.5846 : 0.4154	4.09	12,100
0.3978 : 0.6022	71.25	9.33	19.39	0.4512 : 0.5488	4.84	12,600
0.1976 : 0.8024	68.13	9.57	22.27	0.2913 : 0.7087	5.56	13,100
0.0988 : 0.9012	66.27	9.72	24.00	0.1761 : 0.8239	5.99	13,200

Copolymerisation of peroxyalkyl maleate with styrene

The copolymerization of peroxyalkyl maleate **3** with styrene (Scheme 3) in solution was carried out for three monomer ratios (Table 3). Figure 3 represents the composition diagram of the copolymer.



Scheme 3

The copolymerization constants of peroxyalkyl maleate **3** with styrene calculated according to the method[14] were: $r_1 = 0.15$ (styrene), $r_2 = 0.04$ (peroxyalkyl maleate). One can see from the obtained copolymerization constants that the addition of the peroxide monomer **3** molecule to its own radical is hindered during the copolymerization with styrene because of steric factors. That is why, styrene mainly is added to the maleate radical as it is indicated by low copolymerization constant value ($r_1<1$). The average molecular weight of obtained copolymer **5** amounts to about 15,700.

Table 3. Copolymerization of peroxyalkyl maleate (M_2) with styrene (M_1).

Monomer mixture composition, $[M_1] : [M_2]$	Elemental composition of copolymers, % w/w			Copolymer composition, $[m_1] : [m_2]$	Active oxygen content in copolymer %	Acid number, mg KOH/g	Average molecular weight of copolymer
	C	H	O				
0.9046 : 0.0954	73.46	15.41	18.59	0.6988 : 0.3012	3.09	108.71	17,000
0.7562 : 0.2438	67.39	7.97	24.60	0.5260 : 0.4740	4.10	143.87	16,500
0.4829 : 0.5171	67.29	7.97	24.69	0.5227 : 0.4773	4.11	144.44	13,700

Peroxyalkyl maleate link content in the copolymers calculated from acid number value coincides with copolymer composition determined from active oxygen content. It points out the fact that copolymerization of peroxyalkyl maleate (**3**) with styrene undergoes without the appreciable decomposition of peroxide groups under process proceeding conditions. The composition of the synthesized copolymers calculated from functional analyses data corresponds to the composition determined from the results of elemental analyses. The formed copolymers are linear. The low value of average molecular weight and retaining peroxide groups under copolymerization proceeding conditions testify to such structure of the copolymers.

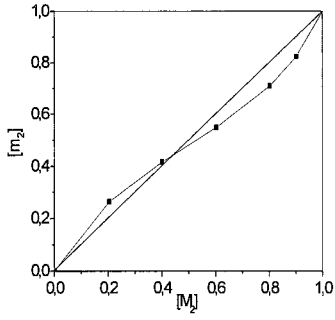


Fig. 1. The composition curve of the copolymer **4** of peroxyalkyl methacrylate (M_2) with styrene (M_1).

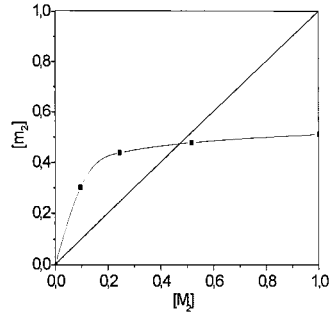


Fig. 2. The composition curve of the copolymer **5** of peroxyalkyl maleate (M_2) with styrene (M_1).

Conclusions

New peroxide monomers on the basis of unsaturated carboxylic acids have been synthesized by the interaction of hydroxy peroxide with derivatives of methacrylic and maleic acid. New reactive peroxide polymers with peroxide groups in side substituents of macrochain have been

prepared by the copolymerization of 3-tert-butylperoxy-3-methylbutyl methacrylate with styrene. The features of the radical copolymerization of peroxyalkyl maleate with styrene were studied and copolymerization constants were determined.

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