

# Synthesis of Novel Oligo(primary-tertiary alkyl peroxides) via Oligocondensation Reactions under Phase Transfer Catalysis Conditions

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Received 19 November 2002; accepted 24 February 2003

**ABSTRACT:** Novel oligoperoxides, products of polycondensation of primary alkyl dibromide with tertiary dihydroperoxides, were obtained. The structure of the oligoperoxides was determined by gel permeation chromatography and nuclear magnetic resonance analyses. Their thermal properties were examined by differential scanning calorim-

etry, and a mechanism of the thermal decomposition was proposed basing on the gel chromatography–mass spectroscopy analysis of the degradation products. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 15–21, 2004

**Key words:** oligomers; initiators; polycondensation

## INTRODUCTION

Polymeric peroxides are the products of fine chemicals species. Several peroxy groups of different thermal stabilities incorporated in one polymer chain may be used as precursors in the free radical synthesis of block (graft) copolymers.<sup>1,2</sup> Our previous investigations showed, that oligo(tertiary-tertiary alkyl peroxides) may be obtained using di(tertiary hydroperoxides) and di(tertiary alcohols) with a moderate yield.<sup>3</sup> It is known, however, that simple peroxides can be obtained with good yields when phase transfer catalysis conditions are applied.<sup>4–6</sup> Novel bisperoxides were obtained<sup>7</sup> with good yields in reaction of sodium salts of cumene hydroperoxide or 2-(1-hydroperoxy-1-methylethyl)naphthalene with 1,4-dibromobutane or 1,10-dibromodecane as well as in reaction of the disodium salt of 1,4-bis(1-hydroperoxy-1-methylethyl)benzene with bromobutane or benzyl bromide using phase transfer catalysis (PTC) conditions similar to that described in the present work. The aim of the presented study is to check the possibility of the preparation of a novel kind of oligo(primary-tertiary alkyl peroxides) in the way of polycondensation under the PTC conditions.

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Contract grant sponsor: Polish State Committee for Scientific Research; contract grant number: 3 T09B 04618.

Contract grant sponsor: Rütgers Kureha Solvents GmbH Duisburg.

*Journal of Applied Polymer Science*, Vol. 91, 15–21 (2004)  
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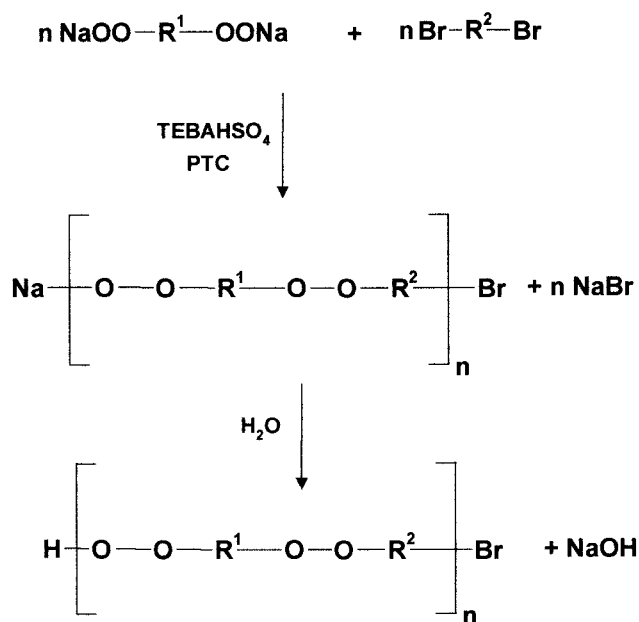
## EXPERIMENTAL

### Materials

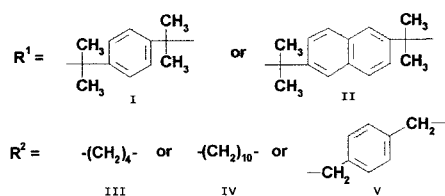
1,4-Dibromobutane 98% (Merck), tetra-*n*-butylammonium hydrogen sulfate 98% (Merck) and 1,4-bis(1-hydroxy-1-methylethyl)benzene 99% (Aldrich) were used without further purification. 1,4-Bis(1-hydroperoxy-1-methylethyl)benzene was prepared from 1,4-bis(1-hydroxy-1-methylethyl)benzene in the reaction with 63% H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> as a catalyst, mp 146.5–147.5°C (ref. 147–152°C).<sup>8</sup> Sodium salt of 1,4-bis(1-hydroperoxy-1-methylethyl)benzene was prepared in the reaction of 1,4-bis(1-hydroperoxy-1-methylethyl)benzene with methanol solution of NaOH as previously described.<sup>7</sup>

### General procedure for the preparation of oligo(primary-tertiary alkyl peroxides)

In a 100-mL thermostated glass reactor equipped with a stirrer, 10 mmol of sodium salt of dihydroperoxide and 50 mL of solvent (benzene or toluene) were placed. After 30 min, 10 mmol of dibromide were placed into reaction mixture. The mixture was reacted at 50°C for a given time. The progress of the reaction was monitored by iodometric analysis (concentration of peroxy- and hydroperoxy- groups).<sup>9</sup> Then the mixture was mixed with water. The organic layer was separated and washed with water. The organic layer was extracted with hexane, separated, dried over anhydrous MgSO<sub>4</sub>, and finally purified by column chromatography (silica gel, Merck, 70–230 mesh) using chloroform as eluent.



where:



Scheme 1

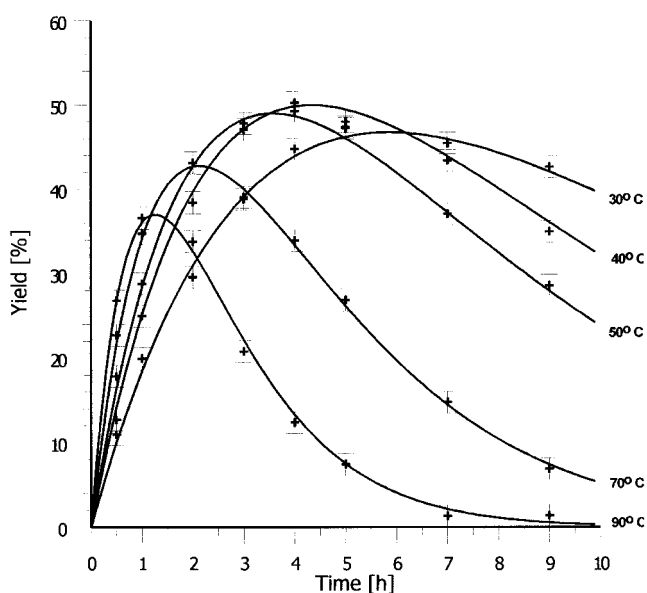


Figure 1 Temperature effect on the efficiency of the polycondensation of dihydroperoxide I (0.01 mol) with 1,4-dibromobutane III (0.01 mol).

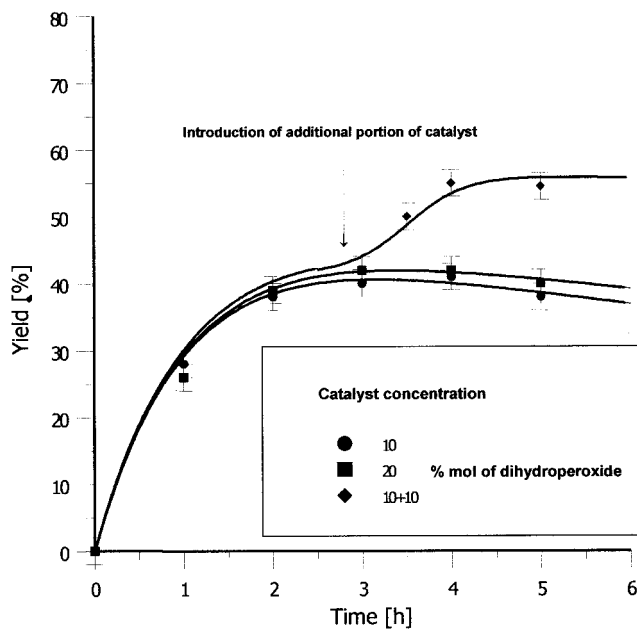
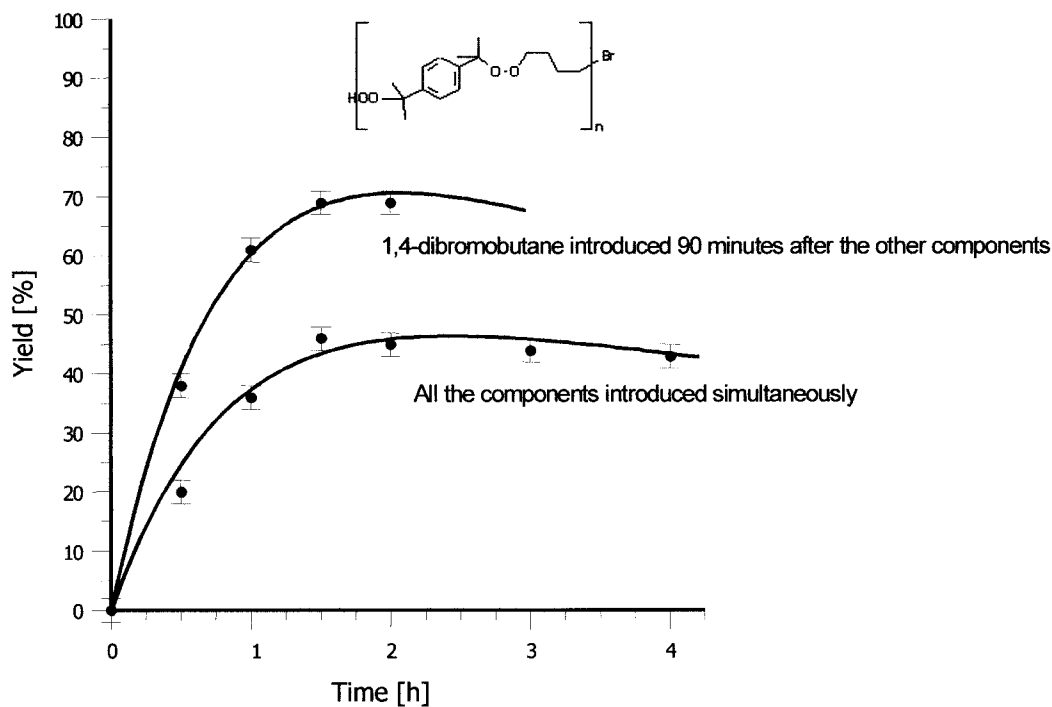


Figure 2 Additional portion of catalyst effect on the efficiency of the polycondensation of dihydroperoxide I (0.01 mol) with 1,4-dibromobutane III (0.01 mol) depending on the amount and way of applying the catalyst.



**Figure 3** The effect of introduction of the dibromo compound after the other components on the efficiency of the polycondensation of dihydroperoxide I (0.01 mmol) with 1,4-dibromobutane III (0.01 mol) depending on the way of applying 1,4-dibromobutane.

#### Instrumentation

$^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded in  $\text{CDCl}_3$  using a Varian Unity INOVA Plus 300 MHz multinuclear spectrometer; tetramethylsilane was used as an

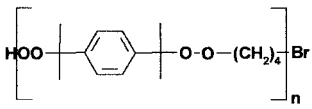
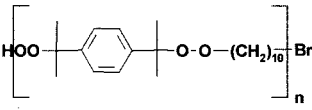
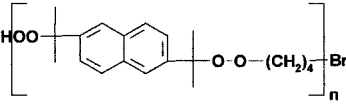
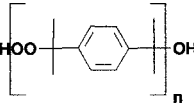
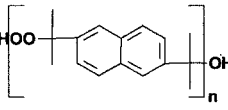
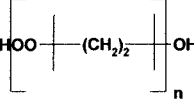
internal standard. Differential scanning calorimetry (DSC) analysis was performed at a heating rate of  $7.5^\circ\text{C}/\text{min}$  using a Polymer Laboratories STA 625 calorimeter. The molecular weights of oligoperoxides

**TABLE I**  
Oligo(primary-tertiary alkyl peroxides) Obtained in PTC Reactions<sup>a</sup>

Oligoperoxide	$n$	Yield (%)	$M_n$
 VI	1+4	48	378 734 1186
 VII	1+3	58	393 710 1117
 VIII	1+5	42	387 754 1179 1872

<sup>a</sup> Reaction conditions: temperature  $50^\circ\text{C}$ , catalyst  $\text{TEBAHSO}_4$  0,001 mol, dihydroperoxide 0,01 mol, dibromide 0,01 mol, benzene 50 mL, reaction time 4h.

TABLE II  
Decomposition Temperatures of Oligo(alkyl Peroxides)<sup>a</sup>

Oligo(alkyl peroxide)	$T_{\max}$
	149.8 171.2
	145.9 170.2
	151.0 175.0
	152.4 175.6
	154.8 176.7
	152.7 175.3

<sup>a</sup>Determined based on DSC analyses. Heating rate 7.5°/min.

were estimated by gel permeation chromatography (GPC) using polystyrene standards of low polydispersity. Gel chromatography-mass spectroscopy (GC-MS) analysis was performed using a Varian 3300 gas chromatograph equipped with a Finnigan MAT 800 AT ion trap detector. The temperature of the injection cell was 250°C; a capillary column of medium polarity (DB1701) was employed.  $T_{\max}$  was determined in open capillary tubes and the values were uncorrected.

## RESULTS AND DISCUSSION

### Synthesis of oligoperoxides

The polycondensation reaction was performed under solid-liquid phase transfer catalysis conditions. Tetraabutylammonium hydrogen sulfate was used as a phase transfer (PT) catalyst. The reaction of sodium salt of dihydroperoxide I (Scheme 1) with 1,4-dibromobutane III was selected as a model example of the performed investigations.

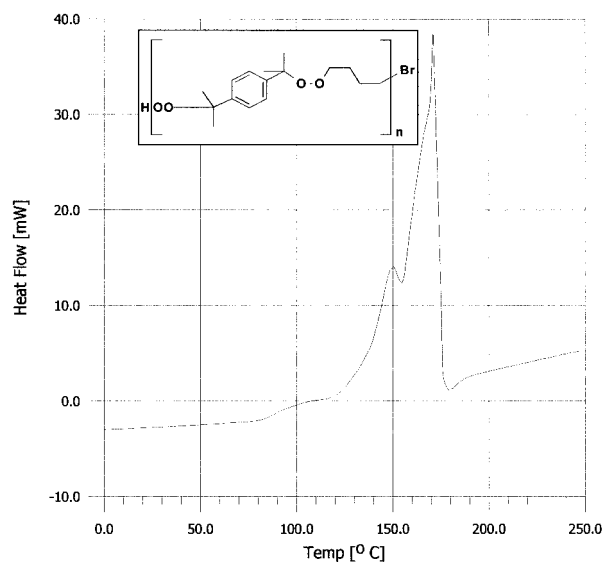
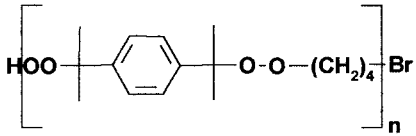
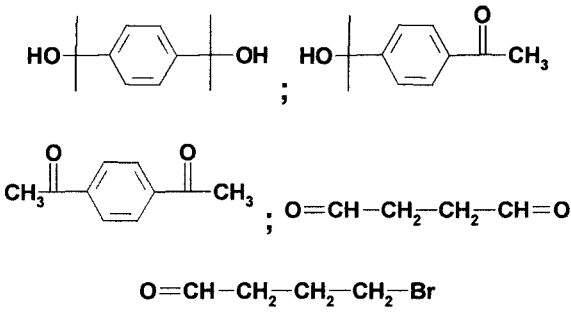
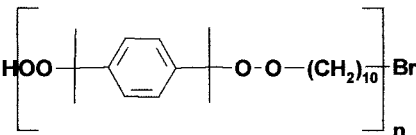
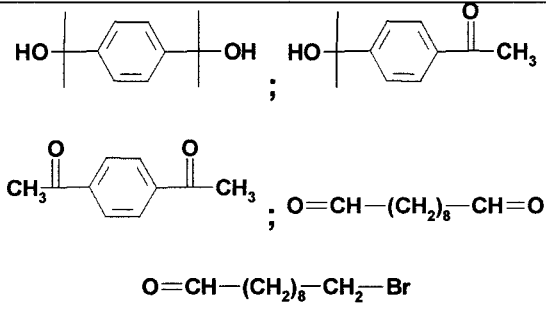
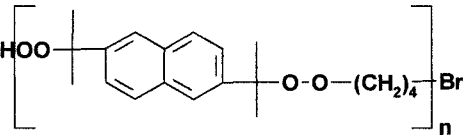
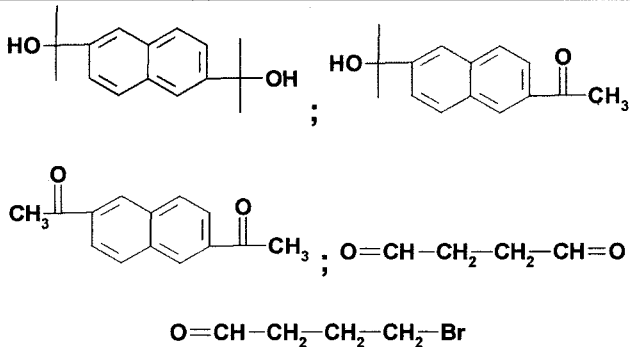


Figure 4 DSC thermogram of oligoperoxide VI.

TABLE III  
Products of the Thermal Decomposition of Alkyl Oligoperoxides Identified by GC-MS Analyses

Oligoperoxide	Products of thermal decomposition
 $\left[ \text{HOO} - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 - \text{O} - \text{O} - (\text{CH}_2)_4 - \text{Br} \right]_n$	 $\text{HO} - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{OH} ; \text{HO} - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{CH}_3$ $\text{CH}_3 - \text{C}(=\text{O}) - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{CH}_3 ; \text{O}=\text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}=\text{O}$ $\text{O}=\text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Br}$
 $\left[ \text{HOO} - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 - \text{O} - \text{O} - (\text{CH}_2)_{10} - \text{Br} \right]_n$	 $\text{HO} - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{OH} ; \text{HO} - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{CH}_3$ $\text{CH}_3 - \text{C}(=\text{O}) - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{CH}_3 ; \text{O}=\text{CH} - (\text{CH}_2)_8 - \text{CH}=\text{O}$ $\text{O}=\text{CH} - (\text{CH}_2)_8 - \text{CH}_2 - \text{Br}$
 $\left[ \text{HOO} - \text{C}(\text{CH}_3)_2 - \text{C}_{10}\text{H}_7 - \text{C}(\text{CH}_3)_2 - \text{O} - \text{O} - (\text{CH}_2)_4 - \text{Br} \right]_n$	 $\text{HO} - \text{C}(\text{CH}_3)_2 - \text{C}_{10}\text{H}_7 - \text{OH} ; \text{HO} - \text{C}(\text{CH}_3)_2 - \text{C}_{10}\text{H}_7 - \text{C}(=\text{O}) - \text{CH}_3$ $\text{CH}_3 - \text{C}(=\text{O}) - \text{C}_{10}\text{H}_7 - \text{C}(=\text{O}) - \text{CH}_3 ; \text{O}=\text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}=\text{O}$ $\text{O}=\text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Br}$

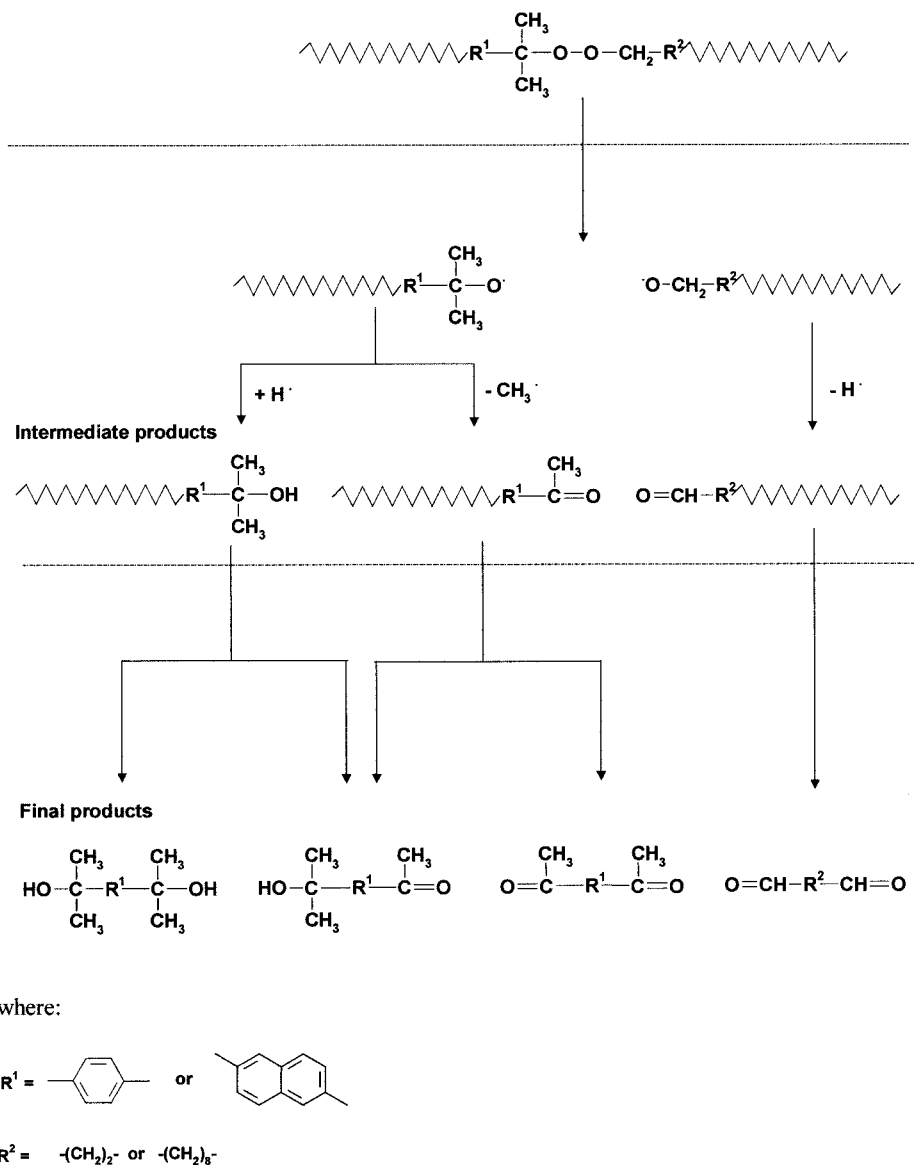
The temperature dependence of the studied process has been shown in Figure 1. At temperatures of 70 and 90°C the efficiency of the process reached its visible maximum, and then it dropped due to the sequence of the reactions of the product decomposition. Investigations carried out at lower temperatures indicated that in the region of 40–50°C the optimal yield of oligoperoxides (c.a. 50%) was achieved.

The influence of the amount of the catalyst and the way of its application into the reaction system on the process has been presented in Figure 2. A two fold increase of the amount of the catalyst introduced at the beginning of the reaction did not affect essentially any change in the yield of the oligoperoxides. The introduction of an additional portion of the catalyst after 2.5 h caused an increase of the yield to 58%. It might be the result of the partial deactivation of the catalyst during the reaction. It was also observed that

the yield of oligomeric peroxides depended on the way in which 1,4-dibromobutane was introduced (Figure 3). Contrary to the procedure when all the components were introduced simultaneously, a higher yield of 70% was achieved when 1,4-dibromobutane was introduced 90 min after the other components.

Some new oligomeric peroxides were obtained under conditions established for the reactions I and III. These are viscous oily substances, soluble in organic solvents, such as aromatic hydrocarbons, halogen hydrocarbons, acetone, methyl alcohol; and also in the vinyl monomers: methyl methacrylate and styrene.

The obtained products were composed of an oligomer mixture of various degrees of polycondensation and various chemical structures of the end groups. The molecular weight distribution and average molecular weights ( $M_N$ ) were determined. The



Scheme 2

oligoperoxides were characterized by GPC as well as  $^1\text{H-NMR}$  spectroscopy.

For all the studied oligoperoxides the polymodal distribution was indicated by GPC analysis conducted with the aid of high-resolution GPC columns (Table I). The  $^1\text{H-NMR}$  spectra of oligoperoxides exhibited resonance signals at ca 3.9 ppm, corresponding to methylene protons of the carbon atom next to the peroxy groups. There are also resonance signals at ca. 3.2 ppm, corresponding to methylene protons next to the bromine end groups. The  $^{13}\text{C-NMR}$  spectra of oligoperoxides exhibited resonance signals at 73 ppm corresponding to carbon (methylene) atoms connected with peroxy groups. The resonance signals at 82 ppm were from carbons (quaternary) that had been connected with peroxy groups.

### Thermal properties of the obtained oligoperoxides

The thermal properties of the investigated oligo(primary-tertiary alkyl peroxides) determined by means of DSC analysis have been presented in Table II and Figure 4. The prepared oligo(alkyl peroxides) possessed peroxy groups of different thermal stabilities. However, the values of their decomposition temperatures  $T_{\text{max}}$  were comparable in the case of all the obtained oligoperoxides. The investigated oligo(primary-tertiary alkyl peroxides) contained peroxide groups of different thermal stabilities, similar to as previously synthesized oligo(tertiary-tertiary alkyl peroxides).<sup>3</sup> The difference in their thermal stability was probably due the different location of the peroxy groups along the oligoperoxide chains. The results of the DSC analysis confirmed the presence of peroxy

groups of different thermal stabilities. It could be useful for the synthesis of block (graft) copolymers.

The composition of thermal degradation products of the oligo(alkyl peroxides) was evaluated by the GC-MS technique, as described previously.<sup>3</sup> For this purpose the oligomers were introduced into the GC injector chamber (the temperature of which was adjusted at 250°C) and the decomposition products formed after separation on the GC capillary column were analysed by quadrupole mass spectrometry.

Based on the MS spectra, the decomposition products were determined and listed in Table III. The thermal decomposition mechanism of the studied oligo(alkyl peroxides) was presented in Scheme 2. The homolytical scission of the oxygen–oxygen bonds was proposed as the first step of the oligo(alkyl peroxides) thermal decomposition process. The formed macroradicals were the subjects of further reactions with the formation of a hydroxyl group (hydrogen abstraction) or carbonyl group (due to the subtraction of methyl radical). The respective diketones, diols, and hydroxyketones were the final products of the decomposition process.

### CONCLUSIONS

The results of the presented works constitute an extension of our previous investigations on the relationship between the structure and properties of oligoper-

oxides. It has been revealed that oligo(primary-tertiary alkyl peroxides) contained peroxy groups of different thermal stabilities, similarly as previously synthesized oligo(tertiary-tertiary alkyl peroxides). The difference of their thermal stability was probably due to the different location of peroxy groups along the oligoperoxide chains. In the case of oligo(primary-tertiary alkyl peroxides) beside diketones, dialdehydes were detected as well as diols and hydroxyketones. Their formation could be due to the possible reaction of the alkoxy radical possessing two hydrogen atoms in  $\alpha$  position. The investigated oligo(primary-tertiary alkyl peroxides) could be obtained with yields of 42–70% under phase transfer catalysis conditions.

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