SYNTHESIS OF PEROXY OLIGOMERS USING 1,2-EPOXY-3-TERT-BUTYL PEROXYPROPANE

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Abstract. The possibility of peroxy oligomer synthesis has been studied by three methods: telomerization of diepoxy derivatives of ethylene glycol or Bisphenol A using 1,2-epoxy-3-tert-butyl peroxypropane as telogen, modification of phenol-formaldehyde resins by 1,2-epoxy-3-tert-butyl peroxypropane and polycondensation of phenol containing –O–O– bonds with formaldehyde. The peroxy oligomers obtaining conditions have been established and 7 new oligomers with peroxy groups have been synthesized. The structures of synthesized oligomers have been verified by chemical and spectral methods.

Key words: polycondensation, telomerization, modification, peroxide, oligomer, resin.

1. Introduction

The compounds containing labile –O–O– bonds in their structure are the sources of free radicals. That is why they are used as the initiators for polymerization reactions of unsaturated compounds, as well as curing and vulcanizing agents of polymeric systems [1, 2]. Peroxy groups presented in the oligomer and polymer molecules are used at the same time as initiating (so called crosslinking or curing) and modifying agents of polymeric systems [3-8]. It is caused by the decomposition of –O–O– bonds in the oligomer or polymer molecule results in the formation of oligomeric or polymeric radicals, correspondingly. Above-mentioned radicals initiate the linear or three-dimensional polymerization affecting in such a way the properties of formed polymer.

Previously the possibility of oligomeric peroxides obtained by the interaction between epoxy resins and hydroperoxides of aliphatic and aromatic types has been shown [3-6]. Non-organic bases [3], Lewis acids [6] and ammonium quaternary salts [4] may be the catalysts for the reactions of such type. Synthesized peroxides with labile –O–O– bonds may be used as crosslinking agents of polymeric systems [5, 9].

This work deals with the possibility of the peroxy oligomers synthesis using 1,2-epoxy-3-tert-butyl peroxypropane (EP) by the following formula:

$$\text{CH}—\text{CHCH}_2\text{OOC(CH}_3\text{)}_3 \text{O}$$

The EP molecule contains two reactive groups in its structure: –O–O– bond and epoxy group. The peroxy group can be decomposed at 373 K and higher temperatures with the formation of free radicals [6]. The epoxy group can react with the compounds containing mobile hydrogen atom [10]. Using EP as a reagent at the temperatures below 373 K, when –O–O– bond is not decomposed, we can obtain compounds with peroxy groups.

The synthesis of peroxy oligomers in the presence of EP has been carried out by the following reactions:

– telomerization between the diepoxy derivatives of glycols or diatomic phenols and glycols or phenols using EP as a telogen;
– modification of the existing phenol-formaldehyde resins by EP;
– polycondensation between the formaldehyde and peroxy monomer synthesized from the phenol and EP.

2. Experimental

2.1. Starting Reagents and their Purification

EP used in this work was synthesized by the following reaction:
EP synthesis was carried out in a three-necked reactor equipped with a mechanical stirrer, thermostat and funnel at 313–318 K during 3 h. Some excess of the tert-butyl hydroperoxide (1.1 mol per 1 mol of epichlorohydrin) and equimolar amount of potassium hydroxide were used for the reaction. After the synthesis the organic layer was separated from the aqueous one and dried by the waterless NaSO₄. Then it was rectified at 314 K and residual pressure of 1–2 gPa. EP had following characteristics: the refractive index \( n_D^{20} = 1.4180 \), the epoxy number (e.n.) 29.4% (theoretical e.n. 29.45%), active oxygen content [O\text{act}] \( 10.8 \% \) (theoretical [O\text{act}] \( 10.96 \% \)).

The peroxy derivative of Bisphenol A (DP) was synthesized by the following reaction:

\[
\text{CH}_2\text{CHCH}_2\text{OOC(CH}_3\text{)}_3 + \text{KOH} \rightarrow \text{CH}_2\text{CHCH}_2\text{OOC(CH}_3\text{)}_3
\]

One mole of Bisphenol A and 1500 ml of dry diethyl ester were loaded in a three-necked reactor equipped with a mechanical stirrer, thermometer and reflux condenser with the tube filled with a chlorinated calcium. Etherate of boron trifluoride (4 g) and of EP (2.5 mol) were added. The reacting mass was sustained at 303 K during 2.0–2.5 h, then neutralized by the alkali-aqueous solution. The volatile products were distilled and the residue was vacuumed within the temperature range of 323–328 K and pressure 1–2 gPa. The yield of obtained DP was 76 %. Its molecular mass \( M_n \) was 400 (the theoretical value 374); the active oxygen content was 4.20 % (the theoretical \( [O\text{act}] \) 4.28 %).

**Bisphenol A** was purified by toluene recrystallization. Its melting point \( mp \) 429 K (value reported in literature equals to 429–430 K) [11].

**Epichlorohydrin, ethylene glycol** was purified by distillation under vacuum. The main fraction was dried by the sodium sulfate and rectified repeatedly. Physicochemical constants were in agreement with those reported in literature.

Diglycidyl ether of ethylene glycol (DGEEG) was obtained via the procedure described in [10]. It had following characteristics: the boiling point was 401 K under 13.3 gPa, \( n_D^{20} = 1.4439 \), e.n. was 49.40 %. Product characteristics were the same as those reported in literature [10].

**Phenol formaldehyde resin (PhFR)** was obtained by condensation of 1 mol of phenol with 0.8 mol of formaldehyde (40%-aqueous solution) at 353–363 K during 2 h in the presence of alkali. The molecular mass \( M_n \) 340.

**Dimethylvinylthynyl-p-oxyphenylmethane-formaldehyde resin (DMEPMFR)** was obtained in an analogous way as PhFR using dimethylvinyl-p-oxyphenylmethane instead of phenol. \( M_n \) 380.

**Phenol, KOH, NaOH, potassium and sodium isopropylates, solvents and etherate of boron trifluoride** are produced by the Aldrich firm.

### 2.2. Analytical Methods

The number-average molecular masses \( M_n \) of the synthesized compounds and oligomers were determined by cryometry using benzene or dioxane as the solvent. The active oxygen content \( [O\text{act}] \) for the compounds or oligomers was determined by iodometry. The epoxy number (e.n.) was determined using back titration of
hydrochloric acid acetone solution by 0.1 N alkali solution. Methylol groups (–CH₂OH groups) and free formaldehyde were determined via the procedure described in [13].

2.3. Spectral Methods

Infrared spectra (IR) were obtained using a dispersive Perkin-Elmer apparatus with the relevant absorption range in 4000–400 cm⁻¹ region.

Proton magnetic resonance (¹H-NMR) spectra were recorded by the BS-487c spectrometer of Tesla, Brno, Czech Republic, at the frequency ν = 80 MHz in carbon tetrachloride. Hexamethyldisiloxane was used as an internal standard. The chemical displacements of group signals were determined by evaluating positions of symmetry centers of these signals.

2.4. Experimental Procedure

2.4.1. Determination of synthesis conditions for peroxy oligomers via telomerization

The synthesis of peroxy oligomers by telomerization was carried out in a three-necked reactor equipped with a mechanical stirrer, thermometer and funnel. Bisphenol A was dissolved in the isopropyl alcohol. 50%-Aqueous solution of potassium or sodium hydroxide was added to the mixture at 313–333 K. Using potassium or sodium isopropylate as a catalyst, 50%-aqueous solution in the isopropyl alcohol should be prepared. DGEEG and EP were added and the mixture was sustained during 1–7 h. The reacting mass was cooled to the room temperature, dissolved in benzene and neutralized by 30%-aqueous solution of acetic acid. The organic layer was washed by water and volatile products were distilled at 323–328 K and residual pressure 1–3 gPa. Synthesized oligomers were analyzed to determine the content of peroxy ([O]ᵦₒ) and epoxy (e.n.) groups. The molecular mass and functionality on the basis of end –O–O– bonds were determined.

The functionality (f) of synthesized oligomers was calculated by the formula:

\[ f = \frac{M}{M_{eq}} \]

where \( M_{eq} = \frac{M_p}{C_p} \) 100; \( M \) and \( M_p \) are the molecular masses of peroxy oligomer and peroxy group, correspondingly; \( C_p \) is the concentration (mass %) of the peroxy group in oligomer.

2.4.2. Determination of synthesis conditions for peroxy oligomers via modification of phenol-formaldehyde resins

PhFRs were modified by EP in a three-necked reactor equipped with a mechanical stirrer with a valve, thermometer and funnel. 40%-aqueous solution of potassium hydroxide was added to the resin dissolved in tert.-butyl alcohol. Using etherate of boron trifluoride as a catalyst, waterless benzene was the reaction medium. Then EP dissolved in tert.-butyl alcohol or waterless benzene was added dropwise to the mixture during 30 minutes. The reaction mass was sustained at 313–323 K during 2.0–3.5 h, cooled to a room temperature and neutralized by 5%-aqueous solution of acetic acid. Toluene was added and the mixture was transferred to the separation funnel. The organic layer was separated, washed by water and vacuumed at 313 K till the mass became constant. The active oxygen content was determined for synthesized products.

DMEPMFR modification by EP was studied in a same way, only the temperature and reaction time were different. The temperature was 288–328 K and duration 1.0–3.5 h.

2.4.3. Determination of synthesis conditions for peroxy oligomers via polycondensation

The polycondensation of DP with formaldehyde was studied in a reactor equipped with a mechanical stirrer, thermometer and reflux cooler. Synthesized oligomer was purified by thrice-repeated reprecipitation with water out of acetone.

3. Results and Discussion

3.1. Obtaining of Peroxy Oligomers via Telomerization

The synthesis of peroxy oligomers via telomerization using EP as a telogen may be described by the following equation:

\[
\begin{align*}
\text{CH}_2\text{CH} & \text{R CHCH}_2 + 2 \text{HO R' OH} + 2 \text{CH}_2\text{CHCH}_2\text{OOC(CH}_3)_3 \rightarrow \\
& (\text{CH}_3)_3\text{COOCH}_2\text{CHCH}_2\text{O R' OH CH}_2\text{CHCH}_2\text{OOC(CH}_3)_3 \quad n \text{OH OH OH}
\end{align*}
\]

where \( R = \text{--CH}_2\text{OCH}_2\text{CH}_2\text{O--} \) or \( \text{--CH}_2\text{OC}_6\text{H}_4\text{C(CH}_3)_2\text{H}_4\text{OCH}_2-- \); \( R' = \text{--C}_6\text{H}_4\text{C(CH}_3)_2\text{C}_6\text{H}_4-- \) or \( \text{--CH}_2\text{CH}_2-- \); \( n = 0–3 \)
In order to determine the optimal conditions for the peroxy oligomer synthesis the effect of the ratio between starting compounds, catalyst nature and reaction temperature on the characteristic of obtained compounds was examined.

The experiment procedure is given in Subsection 2.4.1. The process was studied using the reaction between Bisphenol A, DGEEG and EP as an example, within the temperature range of 313–333 K. The Bisphenol A : DGEEG : EP ratio was 2 : 1 : (1.5–4.0). Sodium and potassium hydroxides, as well as isopropylates of the mentioned alkali metals were used as catalysts by the amount of 14–56 % depending on the EP content. The obtained results are represented in Figs. 1 and 2 and Tables 1 and 2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst amount, depending on EP content, mol %</th>
<th>$[O]_{\text{act}}$, %</th>
<th>e.n., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH</td>
<td>14</td>
<td>0.85</td>
<td>5.0</td>
</tr>
<tr>
<td>KOH</td>
<td>28</td>
<td>1.00</td>
<td>1.8</td>
</tr>
<tr>
<td>KOH</td>
<td>42</td>
<td>1.05</td>
<td>–</td>
</tr>
<tr>
<td>KOH</td>
<td>56</td>
<td>1.00</td>
<td>–</td>
</tr>
<tr>
<td>NaOH</td>
<td>28</td>
<td>0.80</td>
<td>5.5</td>
</tr>
<tr>
<td>Potassium isopropylate</td>
<td>28</td>
<td>0.95</td>
<td>1.9</td>
</tr>
<tr>
<td>Sodium isopropylate</td>
<td>28</td>
<td>0.77</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Note: The reaction temperature is 313 K, reaction time is 4 h and Bisphenol A:DGEEG:EP ratio is 2:1:2.5 mol

Accumulation of peroxy groups (see Fig. 2) passes maximum at 323 K. If we compare the obtained results with those presented in Table 2, we can see that the increase of reaction duration increases the total content of peroxy groups in oligomers, that is verified by the increase of peroxy oligomer functionality (see Table 2).

<table>
<thead>
<tr>
<th>Reaction time, h</th>
<th>Molecular mass, $M_n$</th>
<th>$[O]_{\text{act}}$, %</th>
<th>Functionality, f</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>380</td>
<td>0.81</td>
<td>0.19</td>
</tr>
<tr>
<td>2</td>
<td>490</td>
<td>1.05</td>
<td>0.32</td>
</tr>
<tr>
<td>3</td>
<td>550</td>
<td>1.25</td>
<td>0.43</td>
</tr>
<tr>
<td>4</td>
<td>640</td>
<td>1.25</td>
<td>0.50</td>
</tr>
<tr>
<td>5</td>
<td>800</td>
<td>1.10</td>
<td>0.55</td>
</tr>
<tr>
<td>6</td>
<td>940</td>
<td>1.03</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Note: The reaction temperature is 233 K, Bisphenol A : DGEEG : EP ratio is 2:1:2.5 mol

We have established the following optimal conditions for the synthesis of peroxy oligomers by telomerization using EP as the telogen: process temperature
Synthesis of Peroxy Oligomers Using 1,2-Epoxy-3-Tert-Butyl Peroxypropane

is 323 K, duration is 5 h, Bisphenol A:DGEEG:EP ratio is 2:1:2.5 moles. The amount of potassium hydroxide is 28 mol % depending on EP amount.

Results obtained in such a way were used for the synthesis of PO-I peroxy oligomer (see Subsection 3.4.1). PO-II oligomer was synthesized in the same way using DGEBP, Bisphenol A and EP and PO-III oligomer – using DGEEG, EG and EP. The characteristics of PO-I, PO-II and PO-III oligomers are presented in Table 5.

PO-I, PO-II and PO-III oligomers are stable, soluble in the acetone, benzene, chloroform and other organic solvents, viscous and light-yellow compounds. The structures of synthesized oligomers are confirmed by IR- and PMR-spectroscopy. Absorption bands at 910 cm\(^{-1}\) are absent in the IR-spectra of these oligomers. This fact indicates the absence of epoxy groups in the compounds, that is adjusted with the results represented in Table 5. Data of PMR-spectroscopy also indicate the absence of epoxy groups. Protons signals in the area of 2.3–3.1 ppm were not found in the PMR-spectra of synthesized oligomers. At the same time there are weak absorption bands at 870–860 cm\(^{-1}\) in the IR-spectra, typical for the stretching vibrations of –O–O– bonds, there is also the doublet of gem-dimethyl vibrations at 1380 and 1360 cm\(^{-1}\) relating to the (CH\(_3\))\(_3\)C-group and indicating the presence of peroxy groups in the oligomer molecules.

The presence of –O–O– bonds in the compounds is also verified by PMR-spectroscopy. Protons signals of (CH\(_3\))\(_3\)C-group introduced into oligomer molecule by the telogen (EP) were detected in the area of 1.16–1.20 ppm. The presence of hydroxy groups formed by the opening of epoxy ring in the DGEEG or DGEBP and EP molecules was confirmed by the IR- and PMR-spectroscopy. The wide absorption band at 3400–3350 cm\(^{-1}\) was detected in the IR-spectra and protons signals at 4.88–5.55 ppm – in PMR-spectra, which are able to shift towards upper field at the heating to 313 K. The presence of etheric bonds is confirmed by the protons signals in the area of 3.52–3.88 ppm and absorption band in the IR-spectra at 1100 cm\(^{-1}\). The presence of Bisphenol A molecule in the peroxy oligomer is confirmed by the protons signals at 1.51 ppm corresponding to the CH\(_3\)–C–CH\(_3\) groups.

3.2. Obtaining of Peroxy Oligomers via Modification of Phenol-Formaldehyde Resins by EP

Molecules of PhFR and DMEPMFR contain reactive phenol group able to react with an epoxy group of EP in the presence of the catalyst [10].

The synthesis of peroxy oligomers based on mentioned resins and EP is carried out by following reaction:

\[
\begin{align*}
\text{OH} & \quad \text{CH}_2\bigg[\text{OH} & \quad \text{CH}_2\bigg] & \quad \text{OH} + \text{CH}_2\text{CHCH}_2\text{OOC(CH}_3\text{)}_3 \\
\text{C(CH}_3\text{)}_3 & \quad \text{O} & \quad \text{O} & \quad \text{O} \\
\text{CH}_2 & \quad \text{CH} & \quad \text{CH}_2 & \quad \text{OH} \\
\text{CH(OH)} & \quad \text{CH}_2 & \quad \text{OH} & \quad \text{OH} \\
\text{C(CH}_3\text{)}_3 & \quad \text{O} & \quad \text{O} & \quad \text{O} \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{OH} & \quad \text{OH} \\
\text{O} & \quad \text{O} & \quad \text{O}
\end{align*}
\]

here \( R = \text{H} \) or \(-\text{C(CH}_3\text{)}_2\text{Ca"C—CH}=\text{CH}_2\)
The potassium hydroxide and etherate of boron trifluoride were used as the catalysts. The experimental procedure is described in Subsection 2.4.2.

The results of the investigations concerning the effect of EP amount and reaction time on the active oxygen content in the presence of alkali are represented in Table 3.

**Table 3**

The dependence of active oxygen content \([\text{O}_{\text{act}}]\) in the oligomer on the reaction time and amount of EP and catalyst

<table>
<thead>
<tr>
<th>Content (in moles) per one phenol group</th>
<th>Time, h</th>
<th>([\text{O}_{\text{act}}]) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP 1.0 KOH 0.2</td>
<td>4.0</td>
<td>0.8</td>
</tr>
<tr>
<td>EP 1.0 KOH 1.0</td>
<td>3.5</td>
<td>2.0</td>
</tr>
<tr>
<td>EP 1.0 KOH 1.0</td>
<td>4.5</td>
<td>2.7</td>
</tr>
<tr>
<td>EP 1.2 KOH 1.0</td>
<td>3.5</td>
<td>2.1</td>
</tr>
<tr>
<td>EP 1.5 KOH 1.0</td>
<td>2.5</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Note: The reaction temperature is 318 K, reaction medium is 90% solution of tert-butyl alcohol. The molecular mass of starting PFR340

We can see from Table 3 that the highest content of active oxygen in the oligomer is achieved at the stohiometric amount of EP and potassium hydroxide. At the same time the reaction time also affects the content of peroxy groups in such compounds. The increase of the reaction time decreases the active oxygen content due to the partial decomposition of peroxy groups in the presence of alkali under such conditions.

No peroxy oligomers have been obtained using etherate of boron trifluoride as the catalyst. Products with three-dimensional crosslinked structure have been recovered out of reacting mixture. The waterless benzene has been the solvent.

Taking into consideration the obtained results the procedure for the PO-IV oligomer synthesis based on EP and EP has been suggested (see Subsection 3.4.2). The oligomer characteristics are represented in Table 5. Oligomer V is a viscous light-yellow product, soluble in the benzene, acetone, chloroform and other organic solvents.

3.3. Obtaining of Peroxy Oligomers via Polycondensation between DP and EP

DP molecule synthesized on the basis of Bisphenol A and EP (see Subsection 2.1) contains active centers in orto-position towards the phenol group. Hence, it can be used for obtaining of peroxy phenol-formaldehyde oligomers via polycondensation between DP and formaldehyde (F):

\[
\begin{align*}
\text{OH} & + \text{CH}_2\text{O} \\
\text{H}_3\text{C} = \text{C} - \text{CH}_3 & \quad \text{H}_3\text{C} = \text{C} - \text{CH}_3 \\
\text{OR} & \quad \text{OR}
\end{align*}
\]

\[
\text{HOH}_2\text{C} - \text{CH}_2 - \text{C} = \text{OOC(CH}_3)_3 \quad \text{OH} \\
\text{H}_3\text{C} = \text{OOC(CH}_3)_3
\]

here \( R = \text{CH}_3\text{CH}_2\text{OOC(CH}_3)_3 \)  

\( n = 0 \text{-} 2 \)
### Table 4
The polycondensation conditions and characteristics of oligomers based on DP and F

<table>
<thead>
<tr>
<th>Content of components, mol</th>
<th>Reaction temperature K</th>
<th>Time, h</th>
<th>Catalyst</th>
<th>Catalyst amount, %</th>
<th>Oligomer characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP</td>
<td>F</td>
<td></td>
<td></td>
<td></td>
<td>M_n</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>2</td>
<td>HCl</td>
<td>18</td>
<td>530</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>2</td>
<td>HCl</td>
<td>6</td>
<td>470</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>2</td>
<td>HCl</td>
<td>6</td>
<td>500</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>2</td>
<td>NH_{2}OH</td>
<td>12</td>
<td>450</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>2</td>
<td>HCl</td>
<td>6</td>
<td>480</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>2</td>
<td>NH_{2}OH</td>
<td>4</td>
<td>420</td>
</tr>
<tr>
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<td>2</td>
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<td>6</td>
<td>390</td>
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<tr>
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<td>8</td>
<td>3</td>
<td>NH_{2}OH</td>
<td>4</td>
<td>390</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>4</td>
<td>NH_{2}OH</td>
<td>4</td>
<td>410</td>
</tr>
<tr>
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<td>3</td>
<td>HCl</td>
<td>6</td>
<td>520</td>
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<td>HCl</td>
<td>6</td>
<td>530</td>
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<td>2</td>
<td>HCl</td>
<td>6</td>
<td>440</td>
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<td>NH_{2}OH</td>
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<td>310</td>
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<td>8</td>
<td>2</td>
<td>NH_{2}OH</td>
<td>18</td>
<td>400</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>2</td>
<td>NH_{2}OH</td>
<td>20</td>
<td>460</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>2</td>
<td>NH_{2}OH</td>
<td>18</td>
<td>500</td>
</tr>
</tbody>
</table>
Hydrochloric acid and ammonium hydroxide were used as catalysts.

The reaction was investigated by the procedure described in Subsection 2.4.3 in the range of 333–363 K during 2–4 h. The content of F was 1–12 mol of DP.

The effect of a catalyst nature on the characteristic of peroxy oligomer was examined using hydrochloric acid (37%-aqueous solution) and ammonium hydroxide (25%-aqueous solution) by the amount of 2–20 % depending on the starting DP mass. The results are presented in Table 4.

We can see from Table 4 that optimal conditions for the peroxy oligomers synthesis are: ratio DP:F = 1:8 mol, HCl = 18 % or NH₄OH = 12 % to calculate for DP mass. The polycondensation temperature is 353 K, reaction time is 2 h.

The increase of F content in the reacting mixture above 8 mol per 1 mol of DP insignificantly increases the molecular mass and active oxygen content in the oligomers. At the same time the decrease of F content (for example till 2 mol) considerably retards the polycondensation due to the improper solubility of DP in water.

We can see from Table 4 that NH₄OH as a catalyst reduces the molecular masses of the products and increases the content of –O–O– group in them. The increase of molecular masses of synthesized oligomers can be achieved using HCl as a catalyst.

The reaction temperature above 353 K is undesirable because of the partial decomposition of peroxy groups. The reduction of active oxygen content in the oligomers indicates to this fact. At the same time the temperature reduction till 333 K retards the oligomers synthesis.

Peroxy oligomer, to be called PO-VI (see Subsection 3.4.3), synthesized in the presence of hydrochloric acid (50%-aqueous solution) was added at 323 K. Then mixture consisting of 0.125 mol of DGEEG and 0.3125 mol of EP was added dropwise. The reacting mass was sustained for 5 h, cooled to the room temperature, then dissolved in benzene and neutralized by 30% solution of acetic acid. The organic phase was washed with water and then volatile products were distilled off at 323 K and residual pressure 1–2 gPa till the mass became constant.

PO-II oligomer was synthesized in an analogous way as PO-I using 0.125 mol of DGEEG, 0.25 mol of Bisphenol A and 0.3125 mol of EP.

PO-III oligomer was obtained in an analogous way as PO-I and PO-II using 0.125 mol of DGEEG, 0.25 mol of EG and 0.3125 mol of EP.

3.4.2. Synthesis via chemical modification of phenol-formaldehyde resin by EP

PO-IV oligomer was synthesized at 318–323 K during 4 h using 20.2 g of novolac phenol-formaldehyde resin, 7.0 ml of 40%-aqueous solution of potassium hydroxide and 0.19 mol of EP dissolved in tert-butyl alcohol. Purification and extraction of the main product has been carried out in an analogous way as PO-I oligomer.

PO-V oligomer was synthesized analogously to PO-IV using 16.6 g of DMPEPMFR, 0.1 mol of EP and 0.2 ml of etherate of boron trifluoride dissolved in waterless benzene. The process has been carried out at 288–295 K during 1.5–2 h.

3.4.3. Synthesis using peroxy derivative of Bisphenol A (DP)

PO-VI oligomer was synthesized in a three-necked reactor equipped with a mechanical stirrer and reflux condenser. 0.1 mol of DP, 75 g of formalin as a 32%-aqueous solution of formaldehyde and 6.73 g of hydrochloric acid (37%-aqueous solution) were loaded into a flask. The mixture was sustained at 353 K during 2 h, then cooled to the room temperature and washed with water until neutral reaction. The oligomer purification was carried out...
carried out by triple precipitation with water of acetone solution.

PO-VII oligomer was synthesized analogously to PO-I, using 0.1 mol of DP, 75 g of formalin and 4.5 g of ammonium hydroxide (25%-aqueous solution). Characteristics of thus synthesized PO-I–PO-VII oligomers are presented in Table 5.

4. Conclusions

1,2-Epoxy-3-tert-butylperoxypropane containing two reactive groups (epoxy and peroxy) in its molecule can be used for the synthesis of peroxy oligomers via telomerization, modification and polycondensation. Synthesized peroxy oligomers have –O–O– bonds at the ends of molecule or in the side chains.

It is necessary to carry out the synthesis of peroxy oligomers at the temperatures below 323 K to preserve the labile –O–O– bonds.

References