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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.

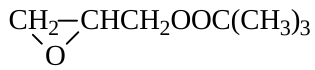
1. Introduction

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 [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:



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;

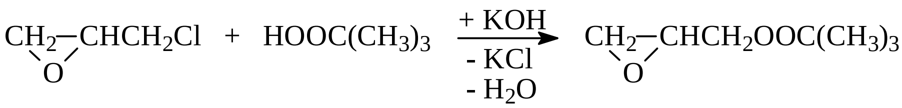
– modification of the existing phenol-formaldehyde resins by EP;

– polycondensation between the formaldehyde and peroxy monomer synthesized from the phenol and EP.

2. Experimental

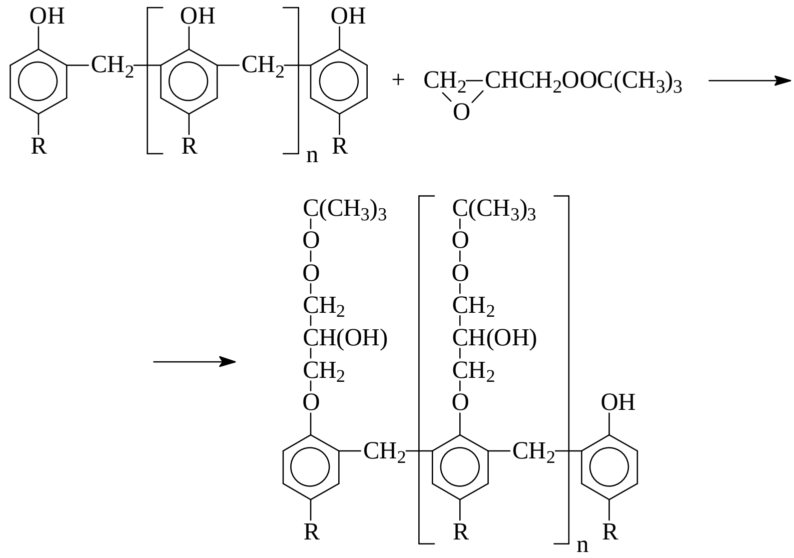
2.1. Starting Reagents and their Purification

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 Na_2SO_4. 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 $[O]_{act}$ 10.8 % (theoretical $[O]_{act}$ 10.96 %).

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



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 $[O]_{act}$ 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. Physico-chemical constants were in agreement with those reported in literature.

Diglycydil ether of Bisphenol A (DGEBP) was obtained *via* the procedure described in [12]. After distillation at 433 K and 1 Pa the component had following characteristics: n_D^{25} 1.5690 (lit. n_D^{25} 1.5690 [12]), *e.n* 25.3 % (the theoretical one is 25.29 %).

Diglycydil 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^{30} was 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.

Dimethylvinylethynyl-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 $[O]_{act}$ 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 (–CH_2OH 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 ^{1}H-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 ($[O]_{act}$) 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 $M_{eq} = M_{pg} \cdot 100 / C_{pg}$; M and M_{pg} are the molecular masses of peroxy oligomer and peroxy group, correspondingly; C_{pg} 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:

$$\underset{\backslash O /}{CH_2{-}CH}\ R\ \underset{\backslash O /}{CH{-}CH_2} + 2\ HO\ R'\ OH + 2\ \underset{\backslash O /}{CH_2{-}CH}CH_2OOC(CH_3)_3 \longrightarrow \quad (1)$$

$$\longrightarrow (CH_3)_3COOCH_2\underset{OH}{CH}CH_2O\ R'\ O\left[CH_2\underset{OH}{CH}\ R\ \underset{OH}{CH}CH_2O\ R'\ O\right]_n CH_2\underset{OH}{CH}CH_2OOC(CH_3)_3$$

here R = $–CH_2OCH_2CH_2OCH_2–$ or $–CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2–$; R' = $–C_6H_4(CH_3)_2C_6H_4–$ or $–CH_2CH_2–$; 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.

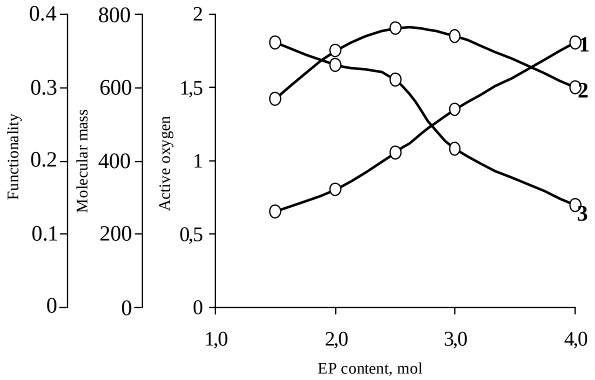


Fig. 1. The dependence of active oxygen content (1), molecular mass (2) and oligomer functionality (3) upon the EP content in the starting mixture. The reaction temperature is 313 K, time is 4 h, catalyst amount is 28 mol % to calculate for EP content.

From Fig. 1 we can see that the highest functionality of the oligomer (to calculate for the peroxy groups content in the compounds) is achieved at the Bisphenol A : DGEEG : EP molar ratio equal to 2:1:2.5. The further increase of EP content in the reacting mixture decreases the oligomer functionality in spite of the increase of the active oxygen total amount.

The effect of a catalyst nature and amount on the formation of peroxy oligomers is represented in Table 1. We can see from the Table that potassium hydroxide has the highest catalytic activity by the amount of 28 mol % per 1 mol of EP. The increase of potassium hydroxide concentration from 28 till 56 mol % actually does not effect the increase of active oxygen content for oligomers.

Using potassium isopropylate as the catalyst for the given reaction we obtained the same results. But taking into account the availability of the alkali, later on we used KOH as the catalyst.

During the study of the effect of temperature and reaction duration on the characteristics of obtained oligomers we determined (see Fig. 2 and Table 2) the optimal temperature. The temperature is 323 K. The increase of the temperature till 333 K increases the rate of side reactions despite the increase of peroxy groups content and decrease of epoxy groups amount. The darkening of reacting mixture and formation of three-dimensional cross-linked products illustrate this fact.

Table 1

The effect of catalyst nature and amount on the content of functional groups in the peroxy oligomers

Catalyst	Catalyst amount, depending on EP content, mol %	$[O]_{act}$,%	*e.n.*, %
KOH	14	0.85	5.0
KOH	28	1.00	1.8
KOH	42	1.05	–
KOH	56	1.00	–
NaOH	28	0.80	5.5
Potassium izopropylate	28	0.95	1.9
Sodium izopropylate	28	0.77	6.2

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 2

The characteristics of peroxy oligomers

Reaction time, h	Molecular mass, M_n	$[O]_{act}$, %	Functionality, *f*
1	380	0.81	0.19
2	490	1.05	0.32
3	550	1.25	0.43
4	640	1.25	0.50
5	800	1.10	0.55
6	940	1.03	0.60

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

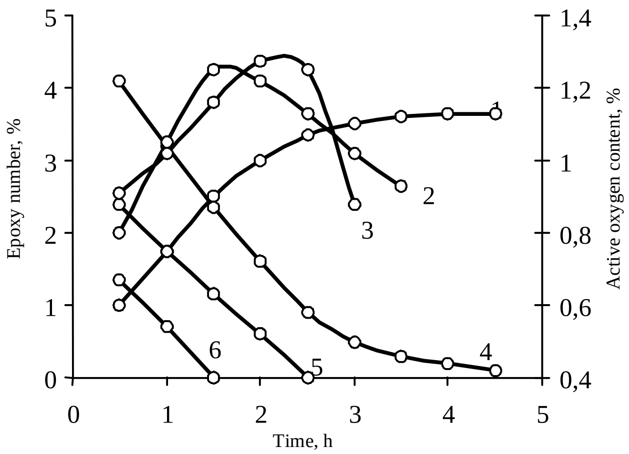


Fig. 2. The dependence of active oxygen content (1-3) and epoxy groups content (4-6) upon the reaction time at 313 K (1, 4), 323 K (2, 5) and 333 K (3, 6)

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.

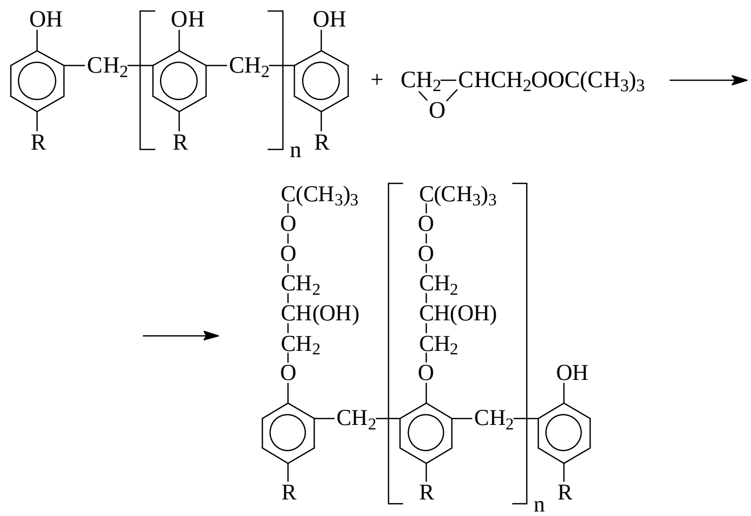
PO-I, PO-II and PO-III oligomers are stable, soluble in the acetone, benzene, chloroform and other organic solvents, viscous and light-yellow compounds. The structures of synthesized oligomers are confirmed by IR- and PMR-spectroscopy. Absorption bands at 910 cm^{-1} are absent in the IR-spectra of these 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 $(CH_3)_3C$-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 $(CH_3)_3C$-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 $CH_3{-}\overset{|}{\underset{|}{C}}{-}CH_3$ 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:



(2)

here R = H or $–C(CH_3)_2–Ca"C–CH=CH_2$

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 ($[O]_{act}$) in the oligomer on the reaction time and amount of EP and catalyst

Content (in moles) per one phenol group		Time, h	$[O]_{act}$, %
EP	KOH		
1.0	0.2	4.0	0.8
1.0	1.0	3.5	2.0
1.0	1.0	4.5	2.7
1.2	1.0	3.5	2.1
1.5	1.0	2.5	1.9

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 PhFR and EP has been suggested (see Subsection 3.4.2). The oligomer characteristics are represented in Table 5.

The PO-IV oligomer is a solid light-yellow compound, soluble in ketones, alcohols and other organic solvents.

The absorption band at 910 cm^{-1}, which is typical for stretching vibrations of epoxy ring, is absent in the PO-IV oligomer. At the same time, the intensity of absorption band at 3340 cm^{-1} increases (to compare with the IR-spectrum of the starting PFR) and band at 1082 cm^{-1} appears, related to the secondary hydroxyl group. The presence of peroxy groups in the oligomer is confirmed by the absorption bands at 876 cm^{-1} typical for the stretching vibrations of –O–O– bond and absorption bands at 1380 and 1360 cm^{-1} corresponding to the $(CH_3)_3C$-groups.

DMEPMFR contains double unsaturated bonds besides the free phenol groups to compare with PhFR. In this connection DMEPMFR, in the case of its introduction into the peroxy group structure, is interesting on the one hand as a compound able to self-structurization and combining with unsaturated compounds. On the other hand, DMEPMFR permits to clarify the possibility of the introduction of –O–O– bonds into the molecule in unsaturated compounds.

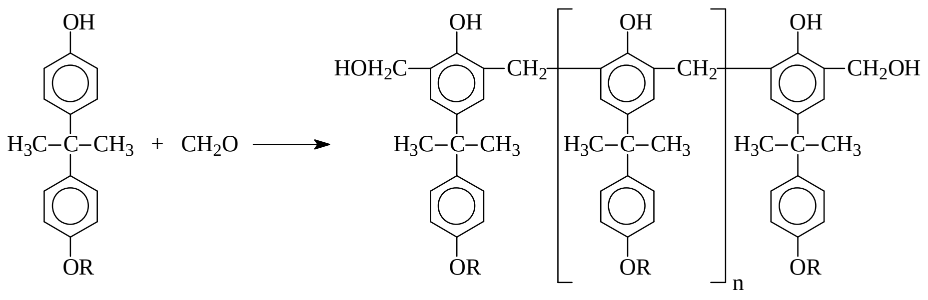
The synthesis of peroxy oligomers on the base of DMEPMFR and EP may be described by Eq. (2). The potassium hydroxide and etherate of boron trifluoride were examined as reaction catalysts. It was established that alkali as a catalyst does not permit to obtain peroxy oligomers. Therefore, the etherate of boron trifluoride was used for the following investigations by amount of 0.1 % depending on the mass of a starting resin. The reaction has been studied in the range of temperatures 288–323 K in the medium of waterless benzene during 2–4 h.

It had been established that it was necessary to carry out this reaction at the temperatures below 298 K during 1.5–2 h. The formation of tree-dimensional polymerization products was observed with the increase of the temperature and process duration.

The procedure of synthesis of peroxy oligomer based on DMEPMFR and EP, to be called oligomer V, is described in Subsection 2.4.2. Its characteristic is 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):



(3)

here $R = -CH_2CH(OH)CH_2OOC(CH_3)_3$ n = 0-2

Table 4

The polycondensation conditions and characteristics of oligomers based on DP and F

Content of components, mol		Reaction temperature, K	Time, h	Catalyst	Catalyst amount, %	Oligomer characteristics			
DP	F					M_n	[O_{act}], %	Methylol groups, %	Free formaldehyde, %
1	8	353	2	HCl	18	630	3.9	22.0	0.02
1	2	353	2	HCl	6	470	3.8	23.0	0.02
1	8	353	2	HCl	6	500	3.8	29.0	0.03
1	8	353	2	NH_4OH	12	450	4.1	3.9	0.05
1	4	353	2	HCl	6	480	4.1	22.0	0.04
1	8	353	2	NH_4OH	4	420	3.7	31.5	0.04
1	8	343	3	HCl	6	390	3.9	30.8	0.04
1	8	342	3	NH_4OH	4	390	3.8	25.0	0.02
1	8	333	4	NH_4OH	4	410	4.1	21.5	0.02
1	10	353	2	HCl	6	520	3.8	30.2	0.06
1	12	353	2	HCl	6	530	3.7	31.4	0.05
1	1	353	2	HCl	6	440	3.4	18.6	0.02
1	2	363	2	HCl	6	310	2.6	18.0	0.02
1	8	353	2	NH_4OH	2	400	3.2	30.2	0.05
1	8	353	2	NH_4OH	18	460	4.0	32.3	0.06
1	8	353	2	NH_4OH	20	500	4.0	33.0	0.06

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 NH_4OH = 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 NH_4OH 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 HCl (18 % for the DP mass, ratio DP:F = 1:8 mol), is a solid product. PO-VII (see Subsection 3.4.3), synthesized in the presence of ammonium hydroxide (12 % for the DP mass, ratio DP:F = 1:8 mol), is a viscous product. PO-VI and PO-VII are stable and soluble in ketones, dioxane and other organic solvents.

The presence of absorption bands at 870–876 and 1380, 1360 cm^{-1} in IR-spectra confirms the presence of peroxy groups in PO-VI and PO-VII.

The presence of –O–O– labile bonds in PO-I – PO-VII oligomers allow to use them as active curing agents for polymeric compositions.

3.4. Synthesis of Peroxy Oligomers

3.4.1. Synthesis *via* telomerization

The oligomer synthesis based on DGEEG and Bishpenol A (PO-I). PO-I was synthesized in a three-necked reactor equipped with a mechanical stirrer, thermometer and funnel. 0.25 mol of Bisphenol A were solved in 150 ml of isopropanol. 10.0 g of potassium hydroxide (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 DGEBP, 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 DMEPMFR, 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

Table 5

The characteristics of peroxy oligomers

Oligomer symbol	M_n	$[O_{act}]$	Hydroxy number, mg KOH/g	Iodine number, g/100 g of products	Functionality
PO-I	800	1.1	–	–	0.55
PO-II	370	2.4	–	–	0.55
PO-III	640	1.2	–	–	0.48
PO-IV	470	2.7	45.0	–	–
PO-V	720	4.5	12.5	143.0	–
PO-VI	630	3.9	22.0	–	–
PO-VII	450	4.1	30.9	–	–

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.

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СИНТЕЗ ПЕРОКСИДНИХ ОЛІГОМЕРІВ З ВИКОРИСТАННЯМ 1,2-ЕПОКСИ-3-*ТРЕТ*-БУТИЛ ПЕРОКСИПРОПАНУ

Анотація. *Вивчена можливість синтезу пероксидних олігомерів трьома методами: теломеризацією діепоксидних похідних етиленгліколю або бісфенолу А з використанням 1,2-епокси-3-трет-бутил пероксипропану як телогену, модифікацією фенол-формальдегідних смол 1,2-епокси-3-трет-бутил пероксипропаном та поліконденсацією фенолу, що містить –О–О– зв'язки, з формальдегідом. Встановлено оптимальні умови одержання пероксидних олігомерів та синтезовано 7 нових олігомерів. Структуру синтезованих олігомерів підтверджено хімічними та спектральними методами досліджень.*

Ключові слова: *поліконденсація, теломеризація, модифікація, пероксид, олігомер, смола.*