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SYNTHESIS OF PEROXY OLIGOMERS ON THE BASIS OF EPOXY COMPOUNDS IN PRESENCE OF *TERT*-BUTYLPEROXYMETHANOL

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Abstract. We have studied the possibility of peroxy oligomers synthesis by chemical modification of epoxy resins with *tert*-butylperoxymethanol or diepoxy compounds telomerization with glycols in the presence of trifluorine boron using *tert*-butylperoxymethanol as telogen. The reaction conditions have been determined and synthesis procedures have been developed. The structures of synthesized products were proved by chemical, IR- and PMR-spectroscopic investigations.

Keywords: chemical modification, telomerization, peroxide, oligomer, resin.

1. Introduction

Oligomeric products containing labile –O–O– bonds in their structure are sources of free radicals. That is why they are used as initiators of polymerization reactions, as well as cross-linking agents of polymeric mixtures [1]. The advantage of peroxy oligomers (PO) over compounds with low molecular masses and –O–O– bonds is higher safety while storing or application [2]. At the same time PO may be used as initiating and cross-linking agents [1]. The problem of PO formation on the basis of polycondensation resins is considered in the monograph [3] and several scientific reports [4-6]. Epoxy resins are starting compounds for PO synthesis. Aliphatic, aromatic and alkylaromatic hydroperoxides are used as modifies of epoxy resins. Inorganic hydroxides, Lewis acids, quaternary ammonium salts and Crown-ethers are catalysts of PO synthesis [3, 7].

We have studied the possibility of PO synthesis with *tert*-butylperoxymethanol (TBPM). Its chemical formula is given below:

$$HOCH_2OOC(CH_3)_3$$

Two reactive groups: –O–O– bond and primary hydroxyl group are present in TBPM molecule. Taking into consideration that TBPM has primary hydroxyl group in its structure, it may react with epoxy compounds [8] saving peroxy group. It is useful for PO synthesis, which can proceed by following reactions:

– chemical modification of epoxy resins with TBPM;

– telomerization of diepoxy compounds with glycols using TBPM as telogen.

2. Experimental

2.1. Initial reagents and their purification

TBPM was synthesized according to the following scheme:

$$(CH_3)_3COOH + CH_2O \longrightarrow (CH_3)_3COOCH_2OH$$
(TBPM)

38% aqueous solution of formalin (79.0 g), *tert*-butylhydroperoxide (90.1 g) and zinc oxide (0.51 g) were loaded into a three-neck reactor equipped with mechanical stirrer, reflux condenser and thermometer. The mixture was kept at room temperature for 1 hour and transported to the separating funnel. Next, the water layer was separated and organic layer was washed with water and dried with magnesium sulphate. After distillation at 320 K and residual pressure 10 gPa TBPM (102.2 g) was obtained. TBPM had following characteristics: yield 85.2 %, $n_d^{20} = 1.4128$; $d_4^{20} = 0.9684$; molecular refraction (MR=30.92; calculated MR=30.79).

ED-20 epoxy resin is condensation product of 4,4'-dihydroxy-2,2-diphenylpropane (diphenylpropane, Bisphenol A or DPhP) with epichlorohydrin. MEG-1, DEG-1 and TEG-1 resins are products obtained on the basis of epichlorohydrin, ethyleneglycol (MEG), diethyleneglycol (DEG) and triethyleneglycol (TEG), correspondingly. ED-20, MEG-1, DEG-1 and TEG-1 are of industrial production.

MEG, DEG and TEG were purified by distillation under vacuum. The main fraction of the product was dried with sodium sulphate and distilled again. Physico-chemical constants of used products agreed with literature data [9].

DPhP was purified by toluene recrystallization. DPhP melting temperature (T_m) was 429 K (T_m = 429-430 K in literature [9]).

2,2-Di-[4-(2,3-epoxy-1-propoxy)phenyl]propane (DGEDPP) was synthesized via procedure described in

[10]. After distillation at 433 R/1 Pa it had following characteristics: $n_d^{25} = 1.5690$ (literature data [10] $n_d^{25} = 1.5690$), epoxy number e.n. = 25.30 % (theoretical e.n. = 25,29 %).

1,2-Di-(2,3-epoxy-1-propoxy)ethane (DGEEG) was synthesized via procedure described in [11]. Its characteristics: $n_d^{30} = 1.4498$, e.n. = 49.40 %. Obtained characteristics were similar to the literature data [11].

Trifluorine boron etherate бору [$BF_3(C_2H_5)_2O$] was purified via distillation. $T_{boil.}$ = 428 K [9].

Tin tetrachloride ($SnCl_4$) was of heightened purity. Organic solvents were purified via procedures described in [9] and their characteristics were similar to the literature data.

2.2. Analytical determinations

Average molecular mass (M_n) of oligomers were determined by cryoscopy. The active oxygen content ([$O_{act.}$]) for the compounds or oligomers was determined by iodometry. The epoxy number was determined by back titration of acetone solution of hydrochloric acid by 0.1N alkali solution. Methylol groups (–CH_2OH) and free formaldehyde were determined by the procedure described in [12].

2.3. Spectral methods

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

Proton magnetic resonance ^{1}H-NMR spectra have been recorded on the BS-487c spectrometer of the Tesla company, Brno, Czech Republic, at the frequency n=80 MHz in carbon tetrachloride. Hexamethyldisiloxane has been used as internal standard. The chemical displacements of group signals have been determined by evaluating positions of centers of symmetry of these signals.

2.4. Investigation procedure

2.4.1. PO synthesis via chemical modification

PO synthesis via chemical modification was examined in reactor, equipped with mechanical stirrer, thermometer and reflux condenser with tube filled with calcium chloride. Epoxy resin, TBPM and anhydrous benzene were loaded into reactor. The amounts of components were calculated in so manner that epoxy groups concentrations were in the range 0.4-0.6 g-eq/l. Reaction mass was thermostated till necessary temperature (303, 313 or 323 K) and trifluorine boron etherate was added under stirring. In some equal period of time the sample of 0.5 ml was taken and catalyst was neutralized by 1 ml of 0.1N solution of sodium hydroxide. Acetone solution (10 ml) was added to the sample. The solution was prepared using 40 ml of acetone and 1 ml of hydrochloric acid. Blank sample without reaction mixture was prepared in the same way. The catalyst concentration was determined by sample titration with 0.1N solution of NaOH. Solutions were kept at room temperature for 2 hours. Concentrations of epoxy groups (mol/l) were calculated according to the following formula:

$$[C]_{en} = \frac{\left[V_x - (V_p + 1) - V_k\right] \cdot N \cdot K}{V_{np}} \quad (1)$$

where V_x –volume of 0.1N sodium hydroxide, necessary for the titration of blank sample, ml;

V_p – volume of 0.1N sodium hydroxide, necessary for the titration of reaction sample, ml;

V_k – volume of 0.1N sodium hydroxide, necessary for the titration of catalyst, ml;

N –normality of sodium hydroxide (0.1N);

K – correction factor of 0.1N sodium hydroxide;

V_{np} – volume of sample (0.5 ml)

2.4.2. PO synthesis via telomerization

Oligomer synthesis was carried out in a three-neck reactor equipped with a mechanical stirrer, thermometer and drop funnel. Ethyleneglycol, TBPM, anhydrous chloroform and catalyst were loaded into reactor. First, solution of 1,2-di(2,3-epoxy-1-propoxy)ethane in anhydrous chloroform was added by drops for 1-4 hours to the mixture, previously heated to 293-323 K. Next, the reaction mass was kept for 10-30 minutes, cooled to room temperature and neutralized by 5% solution of alkali. The organic layer was washed out and the product was dried in vacuum thermostat at 323-328 K under residual pressure 1-2 gPa, till its mass became constant. Then the resin molecular mass and content of epoxy and peroxy groups were determined. Functionality (f) of the compounds was calculated by the formula:

$$f = \frac{M}{M_{eq}} \quad (2)$$

here M_{eq} – equivalent molecular mass calculated by formula: $M_{eq} = M_{fg} \cdot 100 / C_{fg}$

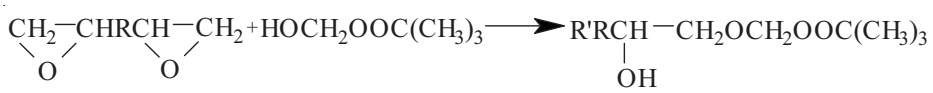
M *and* M_{fg} – molecular masses of chemical compound and functional group, correspondingly;

C_{fg} – concentration of functional groups in the compound (mass %)

3. Results and discussion

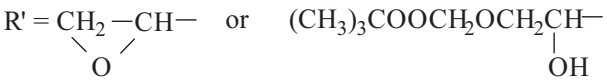
3.1. PO synthesis via chemical modification

PO synthesis was carried out according to the following scheme:



(3)

where R – structural fragment of ED-20, MEG-1, DEG-1 or TEG-1;



In order to establish main kinetic regularities of PO synthesis we investigated the effect of ratio between starting reagents, temperature and catalyst amount on the proceeding of the reaction (3).

The reaction was studied at 303, 313 and 323 K using ED-20 resin in anhydrous benzene. The TBPM amount was 0.5, 1.3 and 4.0 moles calculated relatively to the one epoxy group. Catalyst concentration was $3.80 \cdot 10^{-4}$; $5.63 \cdot 10^{-4}$ and $16.90 \cdot 10^{-4}$ mol/l. We controlled the reaction rate by determination of epoxy group concentration using formula (1). The procedure of investigations was described in Subsection 2.4.1. The results are presented in Figs. 1-3.

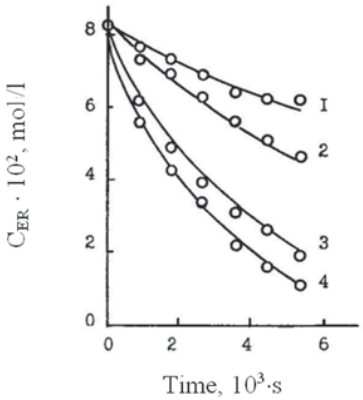


Fig. 1. Kinetic curves of concentration change of epoxy groups upon reaction time for the reaction between ED-20 epoxy resin and TBPM at 313 K and initial concentrations: $[ER]_0 = 8.5 \cdot 10^{-2}$ mol/l, $[TBPM]_0 = 54.7 \cdot 10^{-2}$ mol/l, $[catalyst]_0 = 11.3 \cdot 10^{-4}$ mol/l. Temperatures: 303 (1), 313 (2) i 323 (3) K

As can be seen from Fig. 1, the increase of concentration of trifluorine boron etherate ([catalyst]) from $2.8 \cdot 10^{-4}$ to $16.9 \cdot 10^{-4}$ mol/l increases the reaction rate. At the same time, at concentration of the catalyst higher than $11.3 \cdot 10^{-4}$ mol/l, the partial polymerization takes place resulting in the evolving of polymeric products from reaction mass.

The increase of TBPM concentration from $13.2 \cdot 10^{-2}$ to $67.6 \cdot 10^{-2}$ mol/l also increases the reaction rate (Fig. 2). Actually, the increase of concentration from $54.7 \cdot 10^{-2}$ till $67.6 \cdot 10^{-2}$ mol/l does not change the concentration of epoxy groups. Hence, the effect of temperature on the reaction proceeding was examined at the TBPM concentration $54.7 \cdot 10^{-2}$ mol/l. As it was expected, the reaction rate increases with temperature growth. The optimal temperature is 313 K.

Taking into consideration above-mentioned results, we established the optimal conditions for PO synthesis via chemical modification: the temperature is 313 K, reaction time is 2 hours, TBPM amount is 6 moles and catalyst amount is 1.8·10-02- moles calculated relatively to the one epoxy group of initial resin.

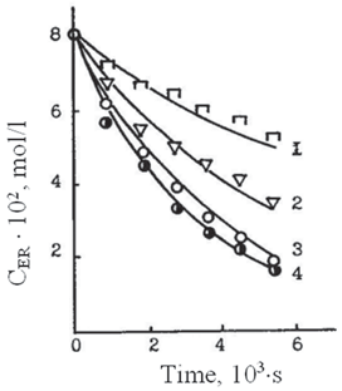


Fig. 2. Kinetic curves of concentration change of epoxy groups upon reaction time for the reaction between ED-20 epoxy resin and TBPM at 313 K and initial concentrations: $[ER]_0 = 8.5 \cdot 10^{-2}$ mol/l, $[catalyst]_0 = 11.3 \cdot 10^{-4}$ mol/l, $[TBPM]_0 = 13.2 \cdot 10^{-2}$ (1), $35.3 \cdot 10^{-2}$ (2), $54.7 \cdot 10^{-2}$ (3) and $67.6 \cdot 10^{-2}$ (4) mol/l

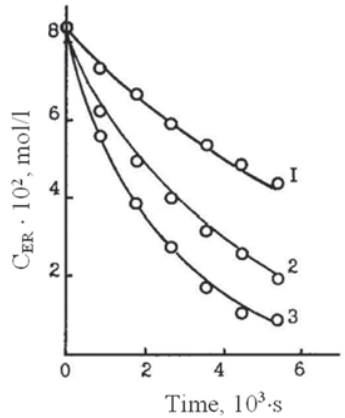


Fig. 3. Kinetic curves of concentration change of epoxy groups upon reaction time for the reaction between ED-20 epoxy resin and TBPM at initial concentrations: $[KR]_0 = 8.5 \cdot 10^{-2}$ mol/l, $[TBPM]_0 = 54.7 \cdot 10^{-2}$ mol/l, $[catalyst]_0 = 11.3 \cdot 10^{-4}$ mol/l. Temperatures: 303 (1), 313 (2) i 323 (3) K

Obtained results were used for the development of procedure for the synthesis of peroxy oligomers PO-I – PO-IV (*vide* Subsection 3.3.1). The characteristics of PO-I, PO-II, PO-III and PO-IV oligomers are represented in Table 1.

Table 1

Characteristics of initial epoxy resins and PO on their bases, synthesized via chemical modification

Initial epoxy resin			PO symbol	PO characteristics		
Resin symbol	M_n	e.n., %		M_n	$[O_{act}]$, %	Yield, %
ED-20	390	20.7	PO-I	520	2.7	86.5
DEG-1	290	26.8	PO-II	390	3.2	89.0
MEG-1	240	26.5	PO-III	340	3.7	88.5
TEG-1	370	19.8	PO-IV	440	3.4	88.0

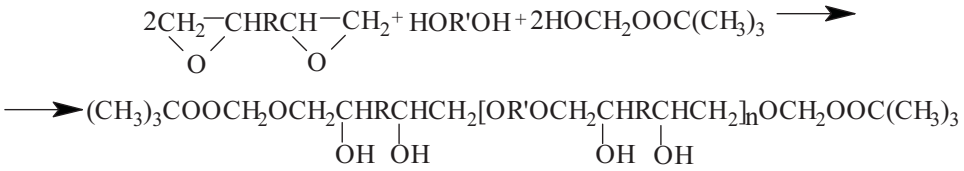
Note: epoxy groups are absent in synthesized PO.

Above-mentioned oligomers are viscous light-yellow compounds, stable, soluble in acetone, dioxane, chloroform and other organic solvents. The structures of synthesized oligomers were confirmed with IR- and PMR-spectral investigations. Absorption bands around 910 cm^{-1} were absent in the IR-spectra of these oligomers. This fact indicates the absence of epoxy groups in the compounds, what is adjusted with the results presented in Table 1. Data of PMR-spectroscopy also indicate the absence of epoxy groups. Protons signals in the area of 2.75-3.30 ppm were not presented in the PMR-spectra of synthesized oligomers. At the same time there were weak absorption bands around 880-830 cm^{-1} in the IR-spectra, typical for the stretching vibrations of –O–O– bonds, also there is 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 oligomer molecules.

The presence of –O–O– bonds in the compounds is also confirmed with PMR-spectroscopy. Protons signals of $(CH_3)_3C$– group introduced into oligomer molecule with TBPM have been detected in the area of 1.13-1.15 ppm. The presence of hydroxyl groups formed by the opening of epoxy ring in the epoxy resins has been confirmed by the IR- and PMR-spectroscopy. The wide adsorption band around 3400-3300 cm^{-1} was detected in the IR-spectra and proton signals at 3.8-4.0 ppm – in PMR-spectra, which are able to move towards more powerful field at the heating to 313 K. The presence of etheric bonds is confirmed by the proton signals in the area of 3.7-4.3 ppm and absorption band in the IR-spectra around 1100 cm^{-1}.

3.2. PO synthesis via telomerization

PO synthesis via telomerization and TBPM as telogen, was carried out by the following scheme:



(4)

where

$R = -CH_2OCH_2CH_2OCH_2-$ or $-CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2-$

$R' = -CH_2CH_2-$, $-CH_2CH_2OCH_2CH_2-$, $-CH_2CH_2OCH_2CH_2OCH_2CH_2-$

or $-C_6H_4C(CH_3)_2C_6H_4-$

$n = 0\text{-}3$

DGEEG, DGEDPP, MEG, DEG and TEG were initial reagents for PO synthesis. The determination of synthesis optimal conditions was realized via reaction between DGEEG and MEG. Also the effect of ratio between initial components, catalyst nature and amount, reaction temperature and time on the characteristics of obtained compounds was examined. Synthesis was carried out at 293, 303, 313 and 323 K and molar ratio DGEEG:MEG:TBPM = 2:1:(1.5-4), correspondingly, in the presence of 10 mass % of the catalyst (calculated relatively to the TBPM mass) in the medium of anhydrous chloroform.

The procedure of investigation is described in Subsection 2.4.2, and results are presented in Tables 2 and 3 and Figs. 4 and 5.

Table 2

Characteristics of PO synthesized by chemical modification

Temperature, K	M_n	$[O_{act}]$, %	e.n., %	Functionality, f
293	920	2.5	13.4	1.4
303	1100	2.3	5.0	1.5
313	1400	2.3	absent	2.0
323	960	2.8	absent	1.7

Notes:
1. ratio DGEEG:MEG:TBPM = 2:1:2 moles, correspondingly
2. $BF_3(C_2H_5)_2O$ content was 10 mass % calculated relatively to TBPM amount
3. molecular mass was determined by cryoscopy in the dioxane

Table 3

Dependence of functional group content in PO upon catalyst nature and amount

Catalyst	Catalyst amount, % relatively to TBPM	$[O_{act}]$, %	e.n., %
$BF_3(C_2H_5)_2O$	5	2.2	1.4
$BF_3(C_2H_5)_2O$	10	2.3	absent
$SnCl_4$	10	1.8	15.0
$BF_3(C_2H_5)_2O$	15	2.2	absent
$BF_3(C_2H_5)_2O$	20	2.3	absent
$SnCl_4$	20	1.7	5.0

Notes:
1. ratio DGEEG:MEG:TBPM = 2:1:2 moles, correspondingly
2. reaction temperature was 313 K, reaction time was 1 hour.

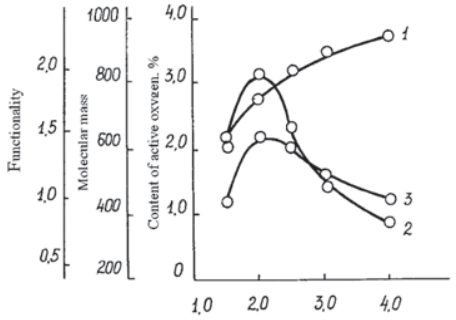


Fig. 4. Dependence of active oxygen content (1), molecular mass (2) and functionality (3) of oligomers upon TBPM content in the initial mixture at 303 K and reaction time of 1.5 hours

One can see from Fig.4 that the highest functionality was obtained with molar ratio DGEEG:MEG:TBPM = 2:1:2. The further increase of TBPM amount decreases PO functionality, in spite of general increase of active oxygen content.

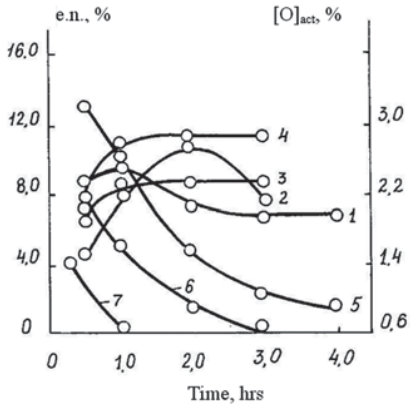


Fig. 5. Dependence of active oxygen content (1-4) and epoxy groups (5-7) upon reaction time at 293 (1, 5), 303 (2,6), 313 (3,7) i 323 (4) K

Comparing the results from Table 2 and Fig. 5, one can see that oligomeric chains are formed for 4 hours at 293 K and for 3 hours at 303 K. Apparently, temperature rising prior 313 K and higher increases considerably the reaction rate. This fact is confirmed by absence of epoxy groups in PO synthesized for 1 hour. At the same time for PO synthesized for 0.5 hours, epoxy group content is 0.74 % at 313 K and 0.49 % at 323 K. The constant content of peroxy group in oligomers demonstrates the finishing of oligomeric molecule formation (*vide* Fig. 5).

One can see from Table 2 that bifunctional compounds may be obtained at 313 K. The increase of temperature prior to 323 K decreases functionality as a result of side reactions, *viz*. polymerization reaction of epoxy groups in the presence of trifluorine boron etherate. Such reaction disturbs ratio between functional groups participated in PO synthesis and increases the number of hydroxyl groups in the mixture resulting in the decrease of PO molecular mass, as well as its functionality (*vide* Fig. 4).

Comparing the results from Table 3, one can see that trifluorine boron etherate in amount of 10 mass % calculated relatively to TBPM mass has the highest catalytic activity.

Taking into consideration above-mentioned results, we established the optimal conditions for PO synthesis via telomerization: the temperature is 313 K, reaction time is 1 hour, molar ratio DGEEG:MEG:TBPM = 2:1:2, amount of trifluorine boron etherate is 10 mass % calculated relatively to TBPM mass.

Obtained results were used for the development of procedure for the synthesis of peroxy oligomers (*vide* Subsection 3.3.2). The characteristics of PO-V – PO-X oligomers are represented in Table 4.

Table 4

Characteristics of PO synthesized via telomerization reaction

Initial compounds		PO symbol	PO characteristics			
Epoxy resin	Monomer		M_n	$[O_{act}]$, %	f	Yield, %
DGEEG	MEG	PO-V	1400	2.3	2.0	91
DGEEG	DPhP	PO-VI	770	1.8	0.9	85
DGEDPP	MEG	PO-VII	880	2.4	1.3	89
DGEDPP	DPhP	PO-VIII	930	2.0	1.1	83
DGEEG	DEG	PO-IX	1600	1.8	1.9	90
DGEEG	TEG	PO-X	1000	1.9	1.2	87

Notes:
1. epoxy groups in PO were absent;
2. molecular mass was determined by cryoscopy in the dioxane

Above-mentioned oligomers are viscous colorless compounds, stable and soluble in organic solvents. PO-V – PO-X oligomers have not epoxy groups in their structures, similar to PO-I – PO-IV oligomers. Absence of absorption band around 910 cm^{-1} in the IR-spectra and proton signals in the area of 2.3-31 ppm in PMR-spectra

confirms this fact. The presence of peroxy groups is shown by adsorption bands around 870-880 cm^{-1} and duplet of gel-dimethyl vibrations around 1380 and 1360 cm^{-1}, indicating the presence of $(CH_3)_3C$-group. In PMR-spectra the presence of –O–O– bonds is confirmed with protons signals of $(CH_3)_3C$– group introduced into oligomer molecule with TBPM. Proton signals around 3.52-3.88 ppm and absorption band at 1110 cm^{-1} indicate the presence of etheric bonds. The wide absorption band around 3400-3350 cm^{-1} in the IR-spectrum and and proton signals around 4.88-5.55 ppm able to move towards more powerful field at the heating to 313 K in the PMR-spectrum confirm the presence of hydroxyl groups formed due to the opening of epoxy ring.

3.3. Synthesis procedures

3.3.1. Synthesis via chemical modification

PO-I was obtained in three-necked reactor equipped with mechanical stirrer, thermometer and drop funnel. Trifluorine boron etherate (2.0 ml) was added to the mixture consisting of TBPM (40.5 g or 0.33 moles) and anhydrous benzene (75 ml) while intensive stirring. Next, solution of ED-20 epoxy resin (22.0 g) and anhydrous benzene (65 ml) was added by drops at 313 K for 1.5 hours. Reaction mixture was kept 0.5 hours and then washed with 5% aqueous solution of sodium hydroxide and water. Solvent was poured out and product was dried in a vacuum thermostat at 333-338 K under residual pressure of 1-3 gPa till the mass became constant. The amount of PO-I was 30 g.

PO-II was synthesized in analogous way, using TBPM (19.0 g or 0.158 moles), catalyst (1.2 ml) and DEG-1 epoxy resin (9.0 g). The amount of PO-II was 14 g.

PO-III was synthesized using TBPM (18.0 g or 0.15 moles), catalyst (1.2 ml) and MEG-1 epoxy resin (10.0 g). The amount of PO-III was 15.4 g.

PO-IV was synthesized in analogous way, using TBPM (21.6 g or 0.18 moles), catalyst (1.4 ml) and TEG-1 epoxy resin (12.0 g). The amount of PO-IV was 16.4 g.

3.3.2. Synthesis via telomerization

PO-V was obtained in the reactor equipped with mechanical stirrer, thermometer and drop funnel. MEG (7.8 g or 0.125 moles), TBPM (30.0 g or 0.25 moles), anhydrous chloroform (250 ml) and triofluorine botron etherate (3.0 g) were loaded into the reactor. Next, DGEEG (43.5 g or 0.25 moles) and anhydrous chloroform (125 ml) was added by drops under intensive stirring at 313 K for 1.0 hour. After the reaction the mixture was kept for 10 minutes, then cooled to the room temperature and washed with 5% aqueous solution of alkali. Solvent was poured out and product was dried in vacuum thermostat at 323-328 K under residual pressure of 1-2 gPa till the mass became constant.

PO-VI was synthesized in analogous way, using DPhP (28.5 g or 0.125 moles) instead of MEG.

PO-VII was synthesized in the same manner as PO-V, using DGEDPP (85.0 g or 0.25 moles) instead of DGEEG.

PO-VIII was synthesized in the same manner as PO-V – PO-VII, using DGEDPP (85.0 g or 0.25 moles) and DPhP (28.5 g or 0.125 moles) as monomer.

PO-IX was synthesized using DGEEG (43.5 g or 0.25 moles) as diepoxy component and DEG as monomer (13.3 g or 0.125 moles).

PO-X was synthesized in analogous way, using DGEEG (43.5 g or 0.25 moles) and TEG (18.8 g or 0.125 moles).

4. Conclusions

1. The presence of primary hydroxyl group and labile peroxy group in the molecule allows using *tert*-butylperoxymethanol as an active compound for the production of oligomers with –O–O– bonds.

2. T*ert*-butylperoxymethanol may be a modifier of epoxy resins via their chemical modification for the synthesis of peroxy oligomers. On the other side, it may be telogen at cationic telomerization of diepoxy compounds with compounds containing primary hydroxyl groups.

3. Trifluorine boron etherate is the catalyst of the reaction so that epoxy groups would be substituted for peroxy ones. The reaction temperature is 313 K, the reaction time is 1.0-1.5 hours.

References

[1] Bratychak M., Brostow W.: Polym.Eng.&Sci., 1999, **39**, 1541.
[2] Abdel Azim A.: Polym.Eng.&Sci., 1996, **36**, 2973.
[3] Bratychak M., Bratychak Mich.Mich. Peroxydni pohidni epoksydnyh smol.Lviv 2003.
[4] Bazylyak L., Bratychak M., Brostow W.: Mater. Res. Innovat., 1999, **3**, 132.
[5] Bazylyak L., Bratychak M., Brostow W.: Mater. Res.Innovat., 2000, **3**, 218.
[6] Bratychak M., Bratychak M. (junior), Brostow W., Shyshchak O.: Mater.Res.Innovat., 2002, **6**, 24.
[7] Bratychak M., Chervinskii T., Gagin M., Gevus O., Kinash N.: Ukr. Khim. Jurnal, 2005, **71**, 50.
[8] Ells B.: Chemistry and Technology of Epoxy Resins. London 1993.
[9] Khimicheskiy encyklopedicheskiy slovar (pod red. I. Knunyanca). Moskva 1983.
[10] Cohen S., Haas H.: J.Amer.Chem.Soc., 1953, **75**, 1733.
[11] Paken A.: Epoksidnye soedineniya i epoksidnye smoly. Leningrad 1962.
[12] Suhanova N., Shuvalova L.: Lakokrasochnye materialy i ih primenenie, 1981, **4**, 47.

СИНТЕЗ ПЕРОКСИДНИХ ОЛІГОМЕРІВ НА ОСНОВІ ЕПОКСИДНИХ СПОЛУК У ПРИСУТНОСТІ ТРЕТ-БУТИЛПЕРОКСИМЕТАНОЛУ

Анотація. *Вивчена можливість використання трет-бутилпероксиметанолу для одержання пероксидних олігомерів хімічною модифікацією епоксидних смол або теломеризацією діепоксидних сполук з гліколями в присутності етерату трифтористого бору. Встановлені умови реакцій одержання пероксидних олігомерів та запропоновані методики їх синтезу. Структура синтезованих продуктів підтверджена хімічними та ІЧ- і ПМР-спектроскопічними дослідженнями.*

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