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## INVESTIGATION OF FUNCTIONAL CARBOXY-CONTAINING OLIGOMERS BY IR AND NMR SPECTROSCOPY

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**Abstract.** New functional oligomers have been synthesized *via* interreaction of epoxy oligomers with carboxylic ones or with dibasic carboxy acids. In some cases synthesis was accompanied by ROP-polymerization of DGEBA, initiated by carboxylic oligomer. The structure of obtained products was investigated by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

**Keywords:** IR spectroscopy, NMR spectroscopy, dianic epoxy resin, carboxyl group, hydroxyl group, peroxy fragment.

### 1. Introduction

The most common representatives of epoxy resins are products of Bisphenol A with epichlorohydrin reaction [1]. They are characterized by high mechanical and adhesive strength, hardness, thermal and chemical stability [2, 3]. Besides that, the chemical modification by both low [4, 5] and high molecular [6-8] compounds is used to expand branches of their application. Such modification of epoxy resins gives the opportunity to incorporate into their structure carboxy, isocyanate, alcohol or phenol hydroxy groups, peroxy fragments, polymerization active double bonds, esteric fragments, *etc.* This not only allows to regulate the properties of materials based on epoxy resins within a wide range but also to formulate three-dimensional network in their structure while crosslinking.

We have synthesized new oligomers with carboxy, epoxy, secondary hydroxy and peroxy esteric functional groups based on epoxy resins [9-13]. The initial compounds for oligomers synthesis were diglycidyl ether of Bisphenol A (DGEBA), ED-24 and ED-20 dianic epoxy resins, peroxy oligomer (the peroxy derivative of

ED-24 epoxy resin), carboxy-containing oligomers based on pyromellitic dianhydride, polyethylene glycol (PEG) and *tert*-butyl hydroperoxide or 1-butanol, dicarboxylic acids – adipic, maleic, terephthalic.

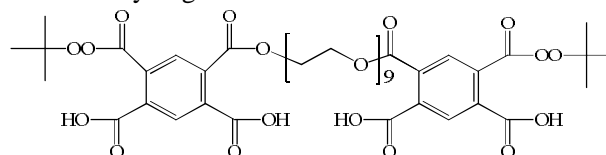
Chemical reactions being the basis of modification process very often do not give the possibility to interpret the structure of synthesized products clearly. Therefore, the present article is dedicated to investigation of structure of synthesized oligomers by IR, <sup>1</sup>H and <sup>13</sup>C spectroscopy.

### 2. Experimental

#### 2.1. Materials

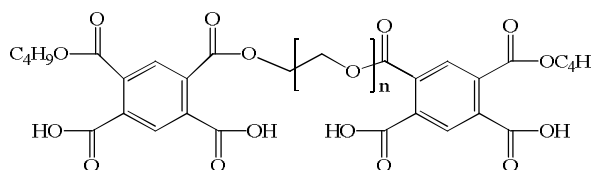
Diglycidyl ether of Bisphenol A (Sigma Aldrich) with epoxy groups content (*[E]*) 24 %; ED-20 dianic epoxy resin (Sigma Aldrich) with average molecular mass (*M<sub>n</sub>*) 430 g/mol and *[E]* equal to 20 % were used without additional purification.

Peroxy oligomer COPE with the formula:

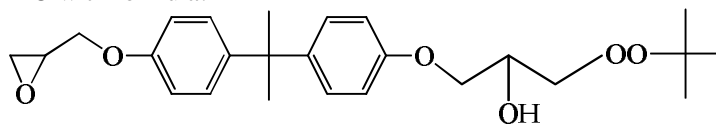


was obtained due to the method [14]; *M<sub>n</sub>* 900 g/mol, acid number (*[A.n.]*) 223.1 mgKOH/g, active oxygen content (*[O<sub>act.</sub>]*) 2.9 %.

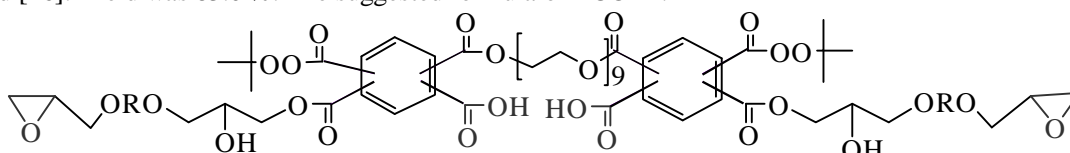
Oligomer COS with the formula:



was synthesized in accordance to the method [9];  $M_n$  980 g/mol,  $[A.n.]$  213.2 mgKOH/g, saponification number ( $[S.n.]$ ) 458.1 mgKOH/g. Oligomer PO with formula:



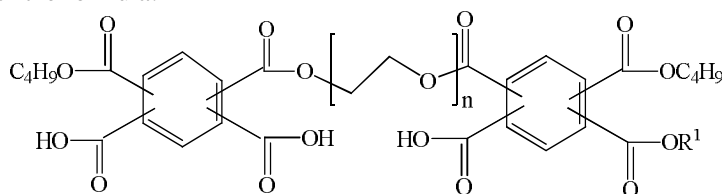
was synthesized due to the method [15];  $M_n$  420 g/mol,  $[E]$  9.0 %,  $[O_{act.}]$  2.9 %. Oligomer ECOPE was synthesized by the interaction of carboxy-containing peroxy-esteric oligomer COPE with DGEBA at molar ratio 1:2, according to the method [16]. Yield was 83.0 %. The suggested formula of ECOPE:



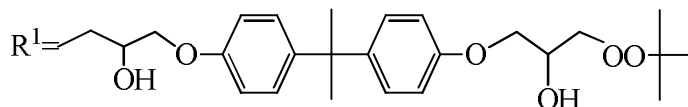
where R –

$M_n$  1800 g/mol,  $[A.n.]$  44.8 mgKOH/g,  $[E]$  5.2 %,  $[O_{act.}]$  1.4 %.

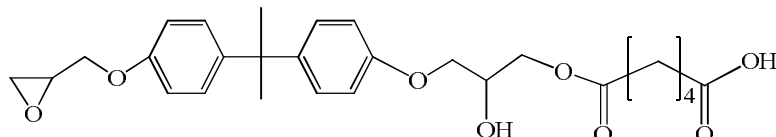
Oligomer PCOS with the formula:



where

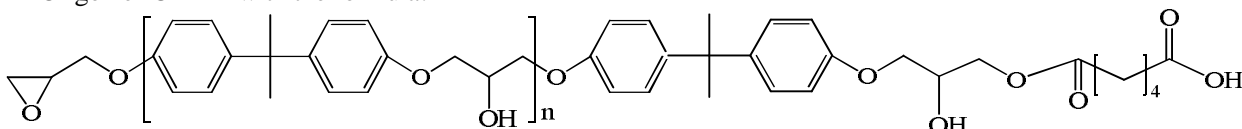


was synthesized with the yield 89.3 % according to the method [16] by the interaction of carboxy-containing oligomer COS with peroxy oligomer PO. Obtained product PCOS was characterized by  $M_n$  1890 g/mol,  $[A.n.]$  80.9 mgKOH/g,  $[E]$  0 %,  $[O_{act.}]$  1.4 %. Oligomer CHE I with the formula:



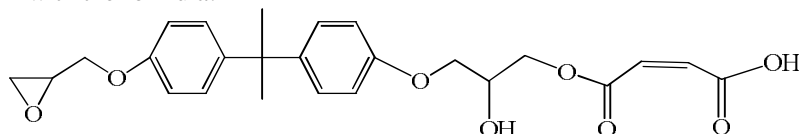
is a product of GDEBA chemical modification by adipic acid (AA) [16];  $M_n$  450 g/mol,  $[A.n.]$  107.1 mgKOH/g,  $[E]$  7.9 %. Yield of CHE I was 85.7 %.

Oligomer CHE II with the formula:



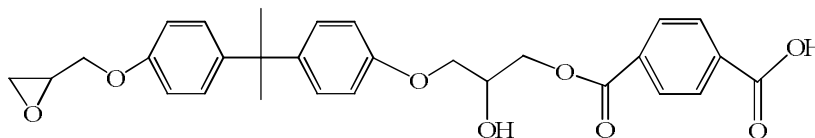
was obtained by the reaction of ED-20 epoxy resin with AA [13].  $M_n$  570 g/mol,  $[A.n.]$  95.9 mgKOH/g,  $[E]$  7.5 %. Yield of CHE II was 88.6 %.

Oligomer CHE III with the formula:



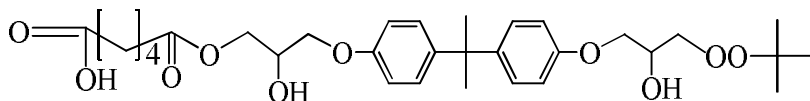
was synthesized by the reaction of ED-24 epoxy resin with maleic acid (MA) [13].  $M_n$  480 g/mol, [A.n.] 104.6 mg KOH/g, [E] 9.5 %. Yield of CHE III was 96.0 %.

Oligomer CHE IV was synthesized by the chemical interaction of ED-24 epoxy resin with terephthalic acid (TA) [13]. CHE IV probably has the next formula:



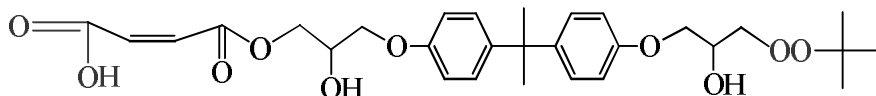
$M_n$  500 g/mol, [A.n.] 115.8 mgKOH/g, [E] 8.6 %. Yield of CHE IV was 97.0 %.

Oligomer CPO I with the formula:



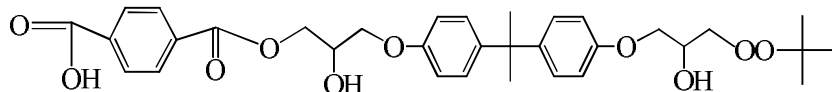
was obtained by chemical interaction of PO with AA [12].  $M_n$  560 g/mol, [A.n.] 109.6 mgKOH/g, [E] 0 %, [O<sub>act.</sub>] 2.0 %. Yield of oligomer was 94.2 %.

Oligomer CPO II with the formula:



was synthesized though the interaction of PO with MA [12]. Yield of CPO II was 86.0 %.  $M_n$  530 g/mol, [A.n.] 104.6 mgKOH/g, [E] 0 %, [O<sub>act.</sub>] 2.8 %. Yield was 86.0 %.

Oligomer CPO III with the formula:



was synthesized due to the interaction of PO with TA.  $M_n$  580 g/mol, [A.n.] 93.4 mgKOH/g, [E] 0 %, [O<sub>act.</sub>] 2.0 %. Yield of CPO II was 90.0 %.

## 2.2. Methods of Analysis

Molecular mass of synthesized oligomers was determined by a cryoscopic method, using 1,4-dioxane as a solvent [17]. Carboxy and epoxy groups content were determined according to the method [18], carboxy number due to [16], and active oxygen content according to [19].

## 2.3. Spectral Methods

### 2.3.1. IR spectroscopy

IR spectra of oligomers were recorded with "Specord-80" device with the relevant absorbance range of 4000–400  $\text{cm}^{-1}$ . Oligomers samples for investigation were dissolved in chloroform (10 % of oligomer). Obtained solutions were applied over the plate with KBr and dried.

### 2.3.2. NMR spectroscopy

NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectra were obtained using BrukerAvance II 400 device (Poland) in deuterated chloroform solution at room temperature. The frequency of magnetic field of  $^1\text{H}$  spectrum was 400 MHz, and of  $^{13}\text{C}$  – 100 MHz. Chemical shifts are presented in million parts (ppm) relatively to tetra methyl silane proton signal.

## 3. Results and Discussion

### 3.1. IR and $^1\text{H}$ NMR spectroscopy

IR and NMR spectroscopy of synthesized oligomers was accomplished according to the methods given in Subsections 2.3.1 and 2.3.2. The results are represented in Figs. 1-4 and Tables 1-3. Analysis of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of initial oligomers COPE and DGEBA showed that they do not contain impurities. The correlation of integral intensity of  $^1\text{H}$  signals in NMR spectra is corresponding to above presented oligomers formulas.

The IR spectrum of oligomer ECOPE (Fig. 1b), synthesized on the base of derivative of pyromellitic dianhydride (COPE) and DGEBA shows the absorbance band at 912  $\text{cm}^{-1}$ , indicating stretching vibration of epoxy ring. The presence of residual carboxy groups, peroxy esteric and esteric fragments in ECOPE molecule is a reason that their characteristic the absorbance bands are not divided but appear as one wide band at 1720–1780  $\text{cm}^{-1}$ . At the same time, the absorbance bands at 1250 and 1040  $\text{cm}^{-1}$  in  $-\text{C}(\text{O})-\text{O}-\text{C}-$  chain of esteric fragments are enhanced.

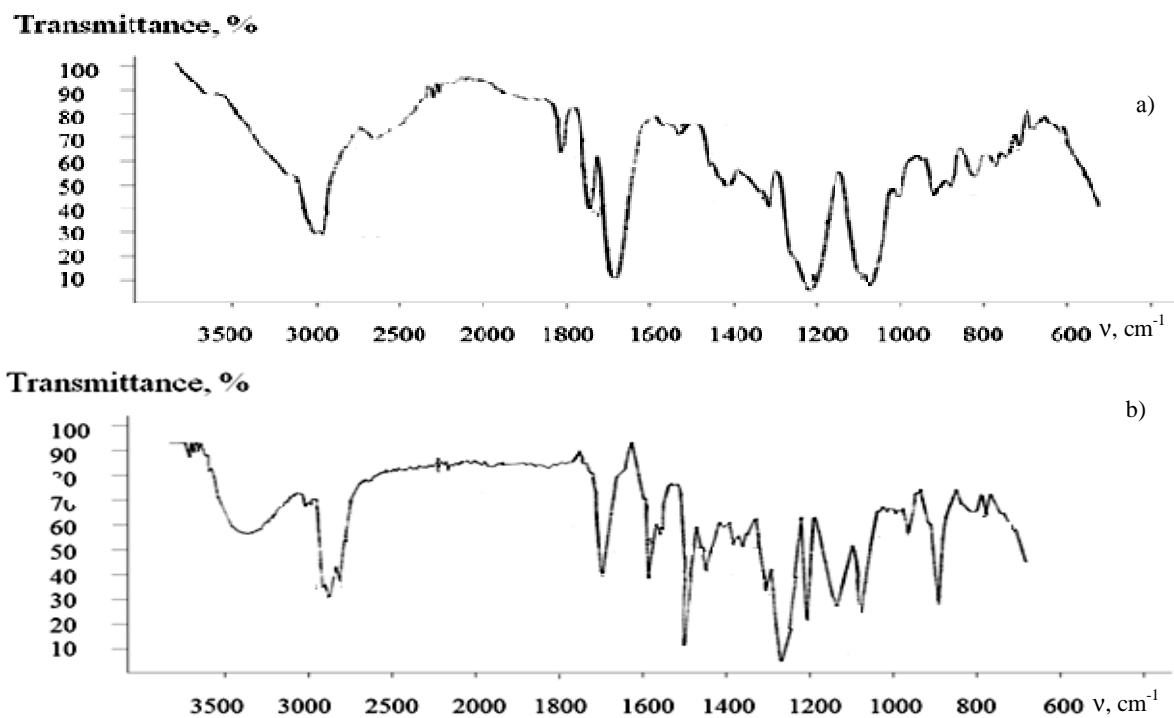

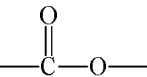

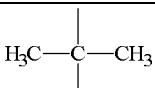


Fig. 1. IR spectra of oligomers COPE (a) and ECOPE (b)

Table 1

IR characteristics of initial and synthesized functional oligomers

Oligomer	Absorbance band, $\text{cm}^{-1}$							
	-OH,					-O-O-		
	$\nu(\text{OH})$	$\nu_{\text{sym}}(\text{epoxide})$	$\nu(\text{C-O-C})_{\text{as}}$	$\nu(\text{C-O-C})_{\text{sym}}$	$\nu(\text{C=O})$	$\delta(\text{C}(\text{CH}_3)_3)_{\text{sym}}$		$\nu(\text{benzene})$
COPE	3450	-	1250	1040	1735* 1760** 1805***	1380, 1360	-	1500
ECOPE	3376	912	1248	1040	1732	1380, 1360	-	1608, 1504
COS	3410	-	1250	1020	1732	-	-	1600, 1500
PCOS	3432	-	1248	1040	1728	1360, 1380	-	1612, 1512
CHE I	3456	912	1256	1048	1732	-	1384, 1360	1608, 1512
CHE II	3448	912	1248	1040	1736	-	1384, 1360	1608, 1512
CHE III	3320	915	1248	1040	1730	-	1384, 1360	1610, 1505
CHE IV	3440	910	1248	1044	1724	-	1384, 1360	1608, 1512
CPO I	3400	-	1248	1040	1724	1380, 1360		1605, 1510
CPO II	3416	-	1250	1044	1724	1384, 1360		1608, 1512
CPO III	3392	-	1248	1040	1720	1380, 1360		1608, 1512
PO	3400	910	-	-	-	1360, 1384	-	1600, 1508

Notes: \* in carboxy group; \*\* in ester fragment; \*\*\* in peroxyester fragment.

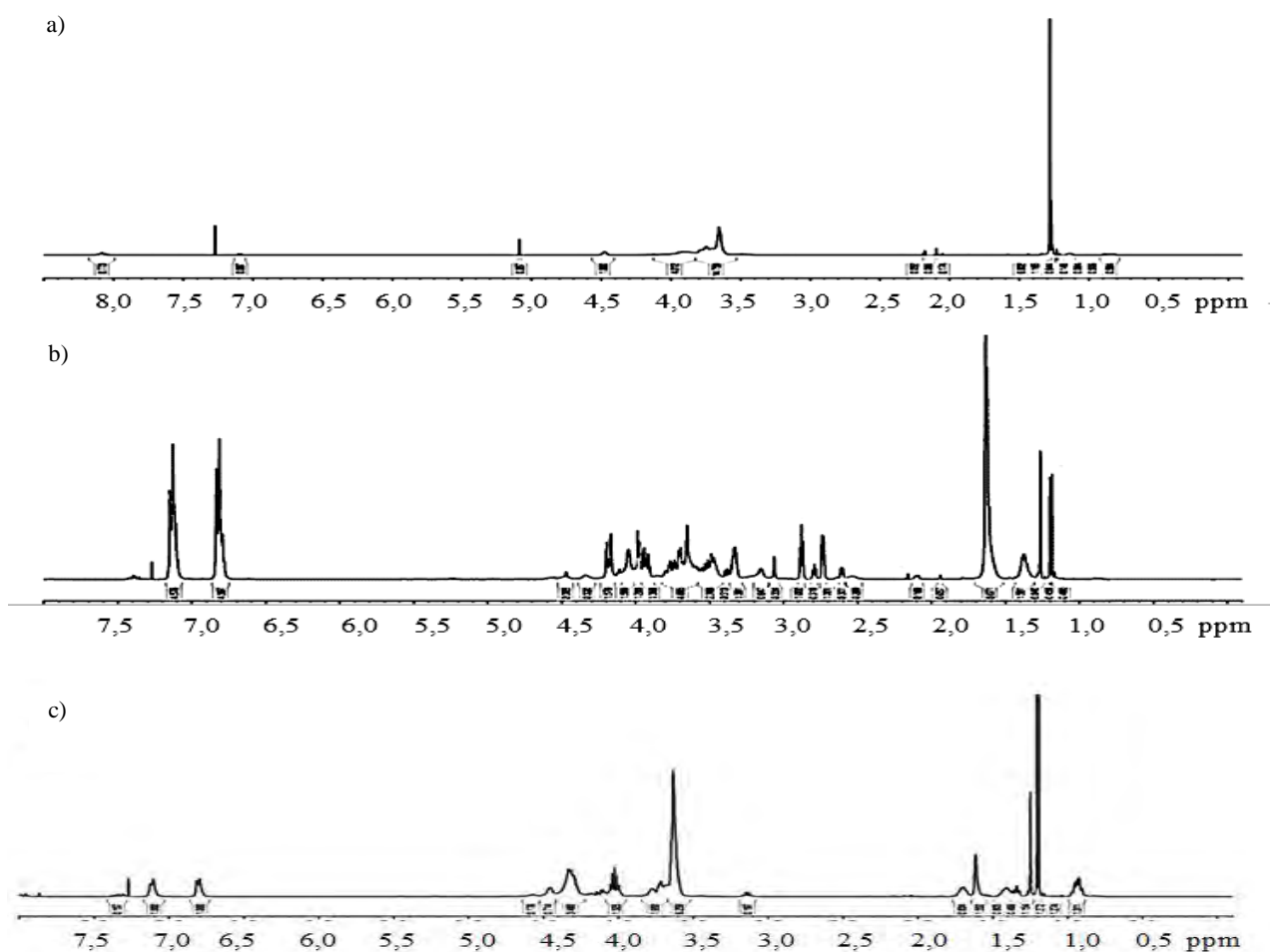
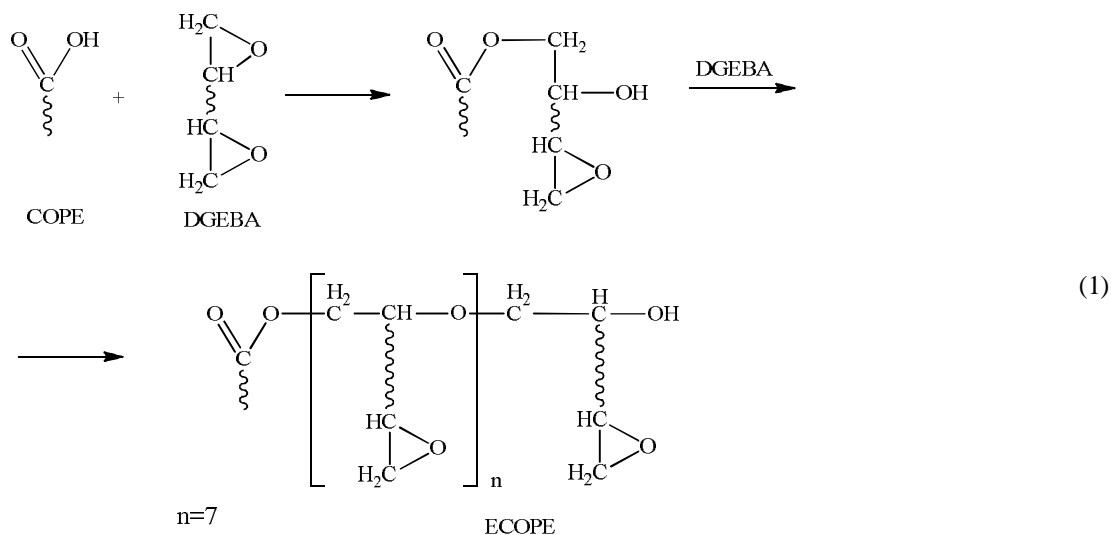


Fig. 2.  $^1\text{H}$  NMR spectra of COPE (a), ECOPE (b) and PCOS (c) oligomers

The interaction between COPE carboxy groups with DGEBA epoxy groups leads to secondary hydroxy groups formation. These groups appear in IR spectra as a wide absorbance band at  $3376\text{--}3450\text{ cm}^{-1}$ , which is probably imposed with bands of hydroxyl in carboxy groups. The presence of peroxy groups in a synthesized product is confirmed by deformation vibrations of  $(\text{CH}_3)_3\text{C}$ -group at  $1380$  and  $1360\text{ cm}^{-1}$ . The aromatic fragments are confirmed by the absorbance bands at  $1608$  and  $1504\text{ cm}^{-1}$ , which are typical for stretching vibrations of C–C bonds in replaced benzene rings.

Investigation of ECOPE by  $^1\text{H}$  NMR spectroscopy gives the opportunity to identify its structure more clearly. The content of residual epoxy rings in DGEBA fragments was determined as an integral intensity ratio of two magnetically nonequivalent methylene protons of epoxy ring (signals at  $2.72\text{--}2.88\text{ ppm}$  with integral intensity  $2.001$ ) and hem-dimethyl protons –  $1.6\text{ ppm}$  (6 protons, integral intensity  $8.071$ ) (table 2). The calculation gives the result  $2.001/2:8.071/6 = 1:1.34 = 0.75$ . The same calculation of integral intensity ratio of methylene protons of epoxy rings

signals and 8 aromatic protons with chemical shift  $6.82\text{--}7.12\text{ ppm}$  (integral intensity  $9.173$ ) gives the result:  $1:9.137/8 = 1:1.15 = 0.87$ . The average content of residual epoxy groups in DGEBA fragment is  $0.81$ . Thereby  $60\%$  epoxy groups of DGEBA react with COPE and  $40\%$  stay unchanged. In return, to determine fragments ratio for COPE and DGEBA it is necessary to select signals in IR spectra, matching separate protons in COPE fragment. Accordingly, multiplet signals with chemical shifts of  $4.32$  and  $4.46\text{ ppm}$  correspond to four methylene protons –  $\text{C}(\text{O})\text{--O--CH}_2\text{--}$  in PEG fragment. Their integral intensity is equal to  $0.625$ , which in recalculation for 1 COPE fragment is  $0.625/4 = 0.156$ . Other 32 methylene protons of PEG form a number of signals with chemical shift  $3.55\text{--}3.85\text{ ppm}$  and total intensity  $4.695$  ( $4.695/32 = 0.146$  in account for 1 COPE fragment). The calculated ratio of DGEBA and COPE fragments in ECOPE molecule is:  $(1.34+1.15):(0.156+0.146) = 8.2$ . This fact can be explained by ROP-polymerization of DGEBA, initiated by COPE. Thereby, interaction between COPE and DGEBA occurs according to the scheme:



Signal intensity of 18 protons at two *tert*-butyl groups at 1.25 ppm indicates degradation of 70 % of peroxy groups of ECOPE during a synthesis process. This is confirmed by much lower active oxygen content in ECOPE to compare with the calculated one. Furthermore, determined acid number of oligomer indicates the presence of three carboxy groups in each molecule of ECOPE.

Oligomer PCOS, synthesized *via* interaction of COS with PO, in contradistinction to ECOPE, does not contain epoxy groups in its structure, since the absorbance bands at 900–930  $\text{cm}^{-1}$  are absent at its IR spectrum. The presence of secondary hydroxy groups was confirmed by the absorbance band at 3432  $\text{cm}^{-1}$ . The PCOS oligomer contains esteric fragments in its structure, indicated by the absorbance bands at 1728, 1248 and 1040  $\text{cm}^{-1}$ . The presence in PCOS molecule of peroxy fragments was confirmed by the absorbance bands at 1380 and 1360  $\text{cm}^{-1}$ , matching deformation stretching vibrations of  $(\text{CH}_3)_3\text{C}$ -group, which is the part of peroxy fragment. These absorbance bands are absent at IR spectrum of the initial COS molecule (Fig. 2a). As in abovementioned oligomer ECOPE, in PCOS spectrum the absorbance bands at 1612 and 1512  $\text{cm}^{-1}$  appeared. This matches the stretching vibration of double bonds in substituted benzene rings.

The investigation of PCOS structure by  $^1\text{H}$ NMR spectroscopy (Fig. 2c, Table 2) confirmed the absence of epoxy groups and showed the following ratio of peroxy groups amount (signal of 9 protons with the chemical shift 1.20 ppm and integral intensity 2.546),  $>\text{C}(\text{CH}_3)_2$  groups – 1.6 ppm (6 protons, integral intensity 1.552) and aromatic rings (signals with the chemical shift 6.82–7.12 ppm and integral intensity 3.999) in PO fragment is  $2.546/9:1.552/6:3.999/4 = 0.268:0.258:0.5 = 1:1:2$ . This ratio indicates saving of peroxy groups during synthesis due to higher thermal stability of primary-tertiary dialkylperoxy groups in PO to compare with peroxyesteric groups in

ECOPE molecule. An average intensity of signal matching one proton in PO fragment is equal to 0.256.

The intensity calculation, indicating one proton in COS fragment by the signals of butyl fragment gives the results as follows:

Shift, ppm	1.70	1.39	0.92
Intensity	0.834	0.805	1.311
Intensity per 1 proton	0.209	0.201	0.218

Total signals of 32 methylene protons in PEG fragment  $-\text{C}(\text{O})-\text{O}-\text{CH}_2-(\text{CH}_2-\text{O}-\text{CH}_2)_8-\text{CH}_2-\text{O}-(\text{O})\text{C}-$ : with chemical shifts 3.55–3.84 ppm and intensity 6.259 gives intensity in account for 1 proton  $6.259/32 = 0.195$ . An average, intensity of signals from one proton in COS fragment is equal to 0.206. The correlation of PO and COS fragments amount is  $0.256/0.206 = 1.24$ . Thus, the structure of PCOS corresponds to the formula given above.

The structure of PCOS oligomer is also confirmed by the results of acid number and active oxygen content determination. Therefore, during PCOS formulation, despite ECOPE, ROP-polymerization of PO does not occur, but in both cases only one out of four carboxy groups of carboxy-containing oligomer takes part in the reaction with epoxy groups of PO, giving functional oligomer able to further transformation. Oligomers CHE I–IV were synthesized by the interaction of different epoxy resins with dicarboxylic acids. In their IR spectra (Table 1) the absorbance bands at 910–915  $\text{cm}^{-1}$  were found, indicating the presence of residual epoxy groups. The presence of carboxy groups and esteric fragments was confirmed by the absorbance bands at 1736–1724, 1256–1248 and 1048–1040  $\text{cm}^{-1}$ . Moreover, the carbonyl groups in esters and carboxy groups appear as one band at

1736–1724  $\text{cm}^{-1}$ , and secondary hydroxyl groups – as wide bands at 3456 and 3320  $\text{cm}^{-1}$ . The epoxy resin fragments formulate the absorbance bands at 1384 and 1360  $\text{cm}^{-1}$ , indicated by stretching vibrations of  $-\text{C}(\text{CH}_3)_2$  group. The benzene rings content is confirmed by the absorbance bands at 1610–1600 and 1512–1505  $\text{cm}^{-1}$ . Fragment of maleic acid in CHE III oligomer is confirmed by stretching vibrations of double bonds at 1650  $\text{cm}^{-1}$  (Table 1).

CHE I oligomer, obtained by DGEBA reaction with adipic acid, contains free epoxy groups in its structure, indicated by the presence in its NMR spectrum

of proton signals at 2.70–3.32 ppm (Table 2). Singlet signal of hem-dimethyl protons in DGEBA fragment with chemical shift 1.52–1.63 ppm and triplet of methylene protons  $\text{C}(\text{O})\text{CH}_2$  in adipic acid overlap each other. Other four methylene protons of adipic acid formulate triplet signal at 2.33 ppm. The ratio of adipic acid and DGEBA fragments in CHE I molecule calculated from ratio of signals intensities of four protons in adipic acid and eight aromatic protons of DGEBA is equal to:  $0.883/4:1.990/8 = 0.22:0.25 \approx 0.9$ . This calculation confirms the proposed CHE I oligomer formula.

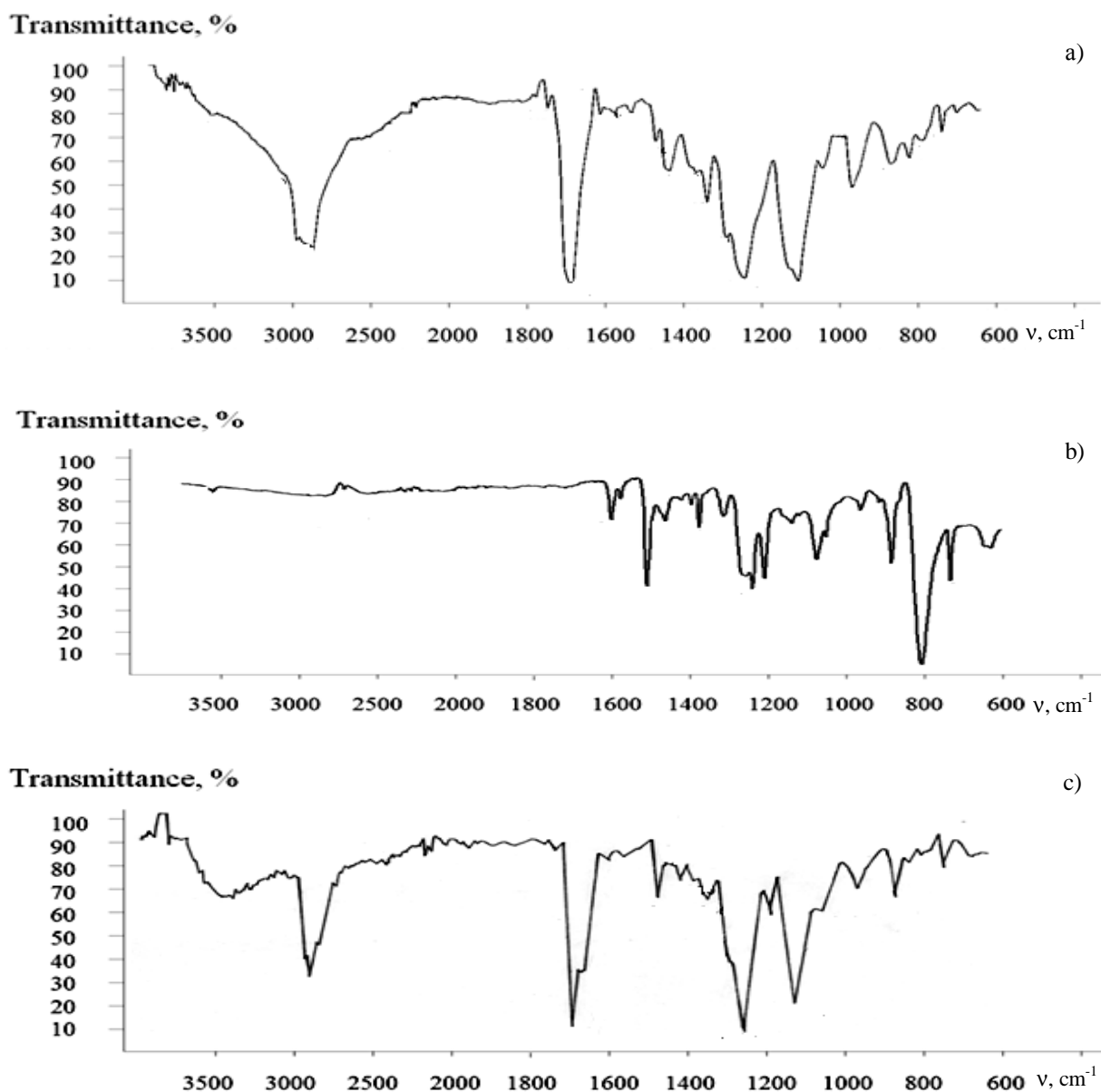
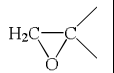
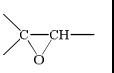
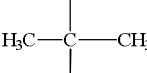


Fig. 3. IR spectra of KOS (a), PO (b) and PCOS (c)

<sup>1</sup>H NMR characteristic of initial and synthesized oligomers

Oligomer	Chemical shift, ppm								
			Ar-		-CH <sub>2</sub> -O, >CHO-	(CH <sub>3</sub> ) <sub>3</sub> COO-		-OH	-CH <sub>2</sub> -
			C <sub>6</sub> H <sub>2</sub> X <sub>4</sub>	C <sub>6</sub> H <sub>4</sub> X <sub>2</sub>					
COPE	-	-	7.28	-	3.65	1.25	-	3.80	-
ECOPE	2.63	3.30	7.20	6.82	3.65-4.20	1.22	1.60	4.00	-
PCOS	-	3.12	7.10	6.80	3.60-4.10	1.20	1.60	4.00	-
PO	2.70	3.35	-	6.85	3.90-4.30	1.30	1.62	4.00	-
CHE I	2.70	3.32	-	6.80-7.10	3.70-4.32	-	1.62	4.00	1.20
CPO I	-	-	-	6.80-7.10	3.70-4.30	1.30	1.63	4.10	1.20
DGEBA	2.72	3.34	-	6.80-7.15	3.90-4.00	-	1.62	-	1.15

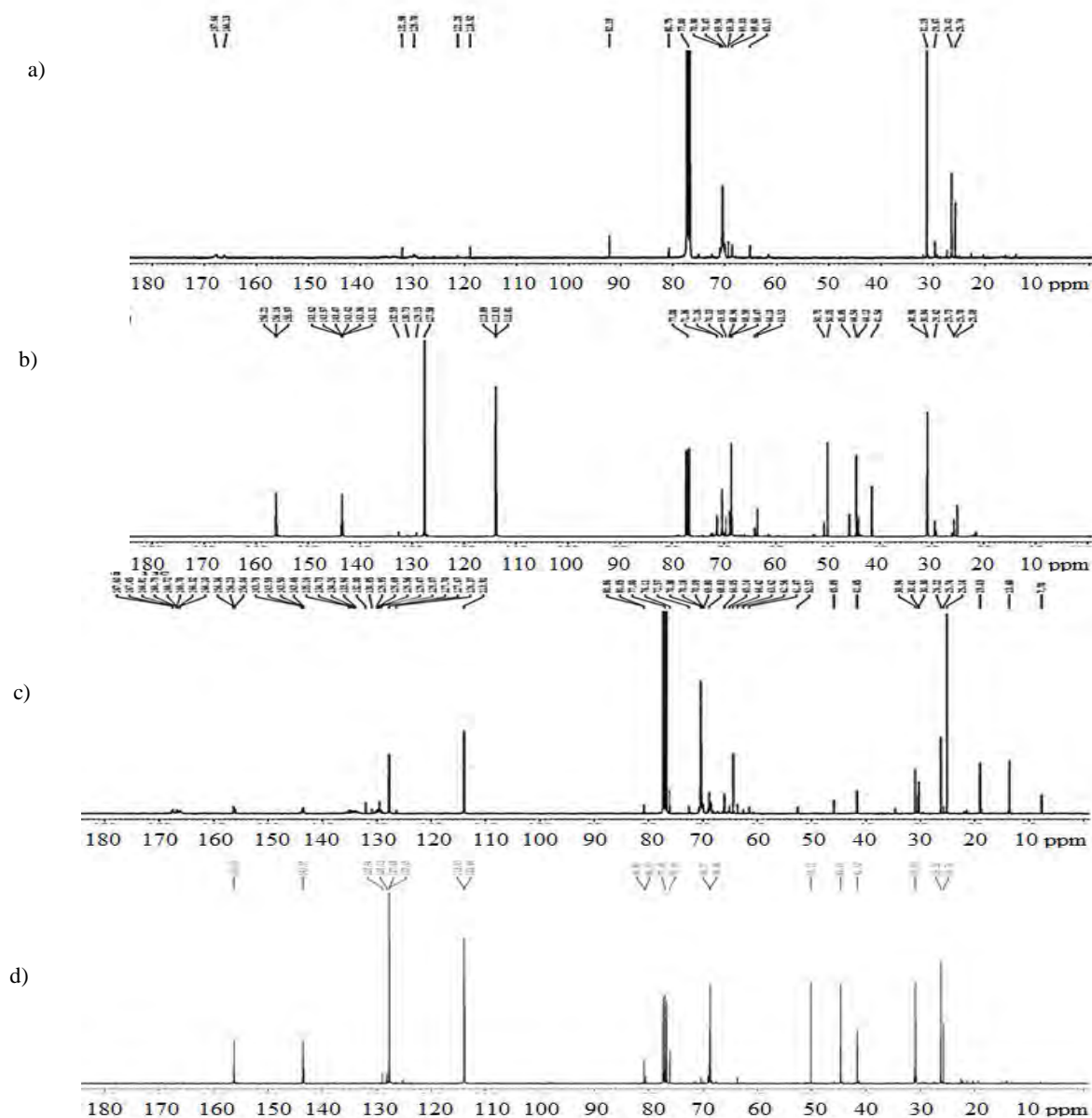

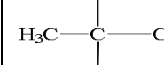
Fig. 4. <sup>13</sup>C NMR spectra of COPE (a), ECOPE (b), PCOS (c) and PO (d) oligomers



Table 3

<sup>13</sup>C NMR characteristic of initial and synthesized oligomers

Oligomer	Chemical shift, ppm						
		Ar-	-CH <sub>2</sub> O-, >CHO-	(CH <sub>3</sub> ) <sub>3</sub> COO-		>C-O-	-CH <sub>2</sub> -C-
	-CH <sub>2</sub> O-			CH <sub>3</sub> -C	CH <sub>3</sub> -C-		
COPE	–	119, 132	62, 65	27, 31	–	76–78	25–26
ECOPE	46	114, 128	63–64	31	25	76–78	25–26
PCOS	–	114, 128	70	42	25–26	76–78	31
PO	50	114, 128	69	42	26–27	76–78	31
CHE I	46	114, 128	65–69	–	24, 25	76–78	25
CPO I	–	114, 128	64–66	31	24–26	76–78	25
DGEBA	50	114, 128	69	–	31	76–78	–

The results of IR spectroscopy investigation of CPO I–III oligomers are present in Table 1. Analysis of spectra indicates the absence of the absorbance bands at 910 cm<sup>-1</sup> in CPO I–III IR spectra. This is the result of total exhaustion of epoxy groups in the synthesis process. The presence of peroxy fragments in CPO I–III is confirmed by stretching vibration of (CH<sub>3</sub>)<sub>3</sub>C-group at 1380 and 1360 cm<sup>-1</sup>. The esteric fragments, formulated by PO with dicarboxylic acids interaction appear as intensive bands of carbonyl absorbance at 1724–1720 cm<sup>-1</sup> and the absorbance bands of C–O bonds at 1250–1248 and 1044–1040 cm<sup>-1</sup>. The aromatic rings formulate the absorbance bands at 1608–1605, 1512–1510 cm<sup>-1</sup>. The band at 1640 cm<sup>-1</sup> indicates stretching vibration of double C=C bond in a maleic acid fragment in CPO II molecule (Table 1).

The absence of epoxy groups in CPO I structure is also confirmed by NMR spectroscopy. Simultaneously, singlet signal of methyl protons at 1.25 ppm (Table 2) appears, matching the presence of peroxy fragment.

### 3.2. <sup>13</sup>C NMR Spectroscopy

<sup>13</sup>C NMR spectroscopy investigations, as above mentioned IR and <sup>1</sup>H spectroscopy were used for confirmation of synthesized oligomers structure. Some of spectrums are represented in Fig. 4 and their interpretation is given in Table 3. The presence of epoxy groups in ECOPE, PO, CHE I and DGEBA oligomers structure was confirmed by signals with chemical shift 46 and 50 ppm, which corresponds to –CH<sub>2</sub>O– group in the epoxy ring. Signals <sup>13</sup>C at 31–42 ppm were found in all oligomers spectrums besides DGEBA and CHE I, which indicates the peroxy fragment (CH<sub>3</sub>)<sub>3</sub>COO– presence. C atoms in benzene rings produce signals at 114–119 and 128–132 ppm. The presence of secondary hydroxyl groups and esteric fragment was confirmed by signals at 76–79 ppm. The presence of DGEBA fragment in all derivatives was confirmed by the following signals: gem-

dimethyl group, –CH<sub>2</sub>O– and –CHO– fragments at 24–31 ppm, and 62–70 ppm respectively, –CH<sub>2</sub>C– fragments at 25–26 ppm (Fig. 4).

## 4. Conclusions

The structure of functional carboxy-containing oligomers based on derivatives of pyromellitic dianhydride or dibasic acids and epoxy oligomers was confirmed by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The predicted structure as well as the presence of various functional groups in synthesized oligomers (namely: carboxy, secondary hydroxyl, epoxy, esteric and peroxy groups) was confirmed.

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### ДОСЛІДЖЕННЯ СТРУКТУРИ ФУНКЦІЙНИХ КАРБОКСИЛВМІСНИХ ОЛІГОМЕРІВ МЕТОДАМИ ІЧ ТА ЯМР СПЕКТРОСКОПІЇ

**Анотація.** Одержані нові функційні олігомери взаємодією епоксидовмісних олігомерів з карбоксилвмісними або з двоосновними карбоновими кислотами. В окремих випадках процес їх одержання супроводжувався ROP-полімеризацією дигліциділового етеру бісфенолу А, ініційованою карбоксилвмісним олігомером. Структуру синтезованих олігомерів підтверджено методами ІЧ, <sup>1</sup>H та <sup>13</sup>C ЯМР спектроскопії.

**Ключові слова:** ІЧ спектроскопія, ЯМР спектроскопія, діанова епоксидна смола, карбоксильна група, гідроксильна група, пероксидний фрагмент.