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STUDY OF PHENOL-FORMALDEHYDE OLIGOMERS DERIVATIVES STRUCTURE BY IR- AND NMR-SPECTROSCOPY

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Abstract. Using IR-and NMR-spectroscopy (^{1}H and ^{13}C) the structure of functional oligomers based on novolac phenol-formaldehyde and polyglycidyl phenol-formaldehyde oligomers has been characterized. The structure of modified phenol-formaldehyde oligomers has been confirmed by the presence of absorption bands and proton shifts corresponding to furan ring, methacrylic fragment, peroxy, hydroxyl, and phenol groups.

Keywords: IR- and NMR-spectroscopy, phenol-formaldehyde oligomer, polyglycidyl phenol-formaldehyde oligomer, modification, methacrylate group, peroxide.

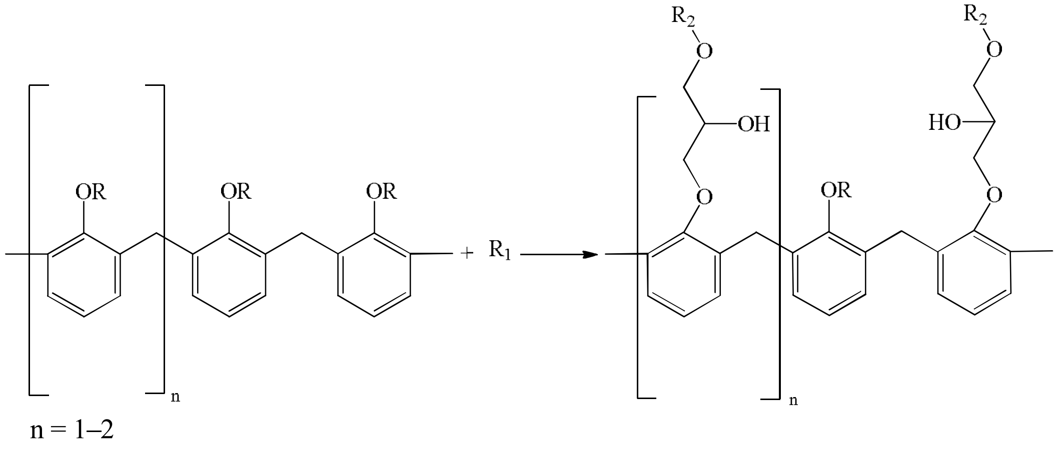
1. Introduction

Phenol-formaldehyde oligomers (PhFO) are synthetic products used for the production of glues, protective coatings, compounds, *etc.* [1, 2]. To improve the PhFO operational characteristics and to combine them with other polymeric materials, the oligomers are modified by different low- and high-molecular compounds [3-5]. PhFO may be modified both at the stage of chemical interaction with low-molecular compounds and at the stage of ware formation [6, 7]. The first variant is of special attention due to the possibility of obtaining compounds with reactive functional groups in the side branches allowing to control the properties of the final products.

Recently we have synthesized new modified PhFO with furan [8], unsaturated double bonds [9] and peroxy groups [10] in the side branches.

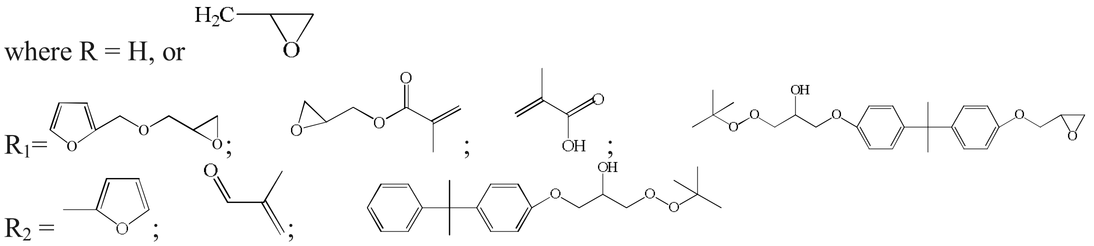
The initial compounds for the synthesis were novolac phenol-formaldehyde and polyglycidyl phenol-formaldehyde oligomers (PGPhFO). Furfurylglycide ether (FGE), glycidylmethacrylate (GMA), peroxy derivative of ED-24 epoxy resin (PO) and methacrylic acid (MAA) were the modifiers.

In general the synthesis of PhFO functional derivatives based on the above-mentioned compounds is carried out according to the following scheme:



n = 1–2

where R = H, or



The synthesized PhFO are used as active additives to epoxy-oligomeric mixtures to create protective coatings [10] and improve the petroleum bitumen properties [11]. At the same time the structures of the PhFO and PGPhFO modified by FGE, GMA, PO and MAA are examined insufficiently.

2. Experimental

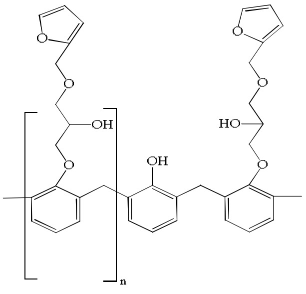
2.1. Materials

Oligomer **I** is synthesized *via* interaction between novolac PhFO and FGE according to the procedure described in [8]. Its molecular weight (M_n) is 460 g/mol. PhFO and GMA are used to synthesize oligomer **II** (the synthesis procedure is described in [9]). Its M_n is 640 g/mol, bromine number (*b.n.*) is 22.9 g Br_2/100 g product. Oligomer **III** is obtained using PGPhFO and MAA [12]. For this oligomer: M_n 590 g/mol, *b.n.* 28.1 g Br_2/100g product, epoxy number (*e.n.*) is 3.0 %. Oligomer **IV** is synthesized on the basis of novolac PhFO and PO [10]. Its M_n is 750 g/mol, active oxygen content is 1.6 %. The molecular weight of novolac PhFO [13] is 350 g/mol. The synthesized PGPhFO [13] has the molecular weight of 460 g/mol and *e.n.* 17 %.

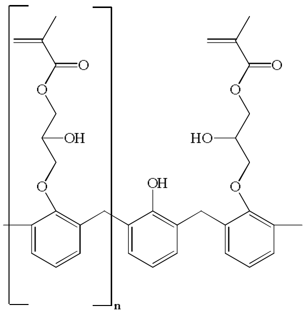
2.2. Spectral Methods

IR-spectra were recorded using Specord-80 spectrophotometer within the range of 4000–400 cm^{-1}. The investigated oligomers were as 10% solutions in chloroform.

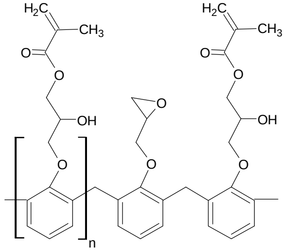
NMR (^1H and ^{13}C) spectra were recorded using Bruker Avance II 400 (Poland) at room temperature in deuterochloroform. The chemical shifts are represented in ppm.



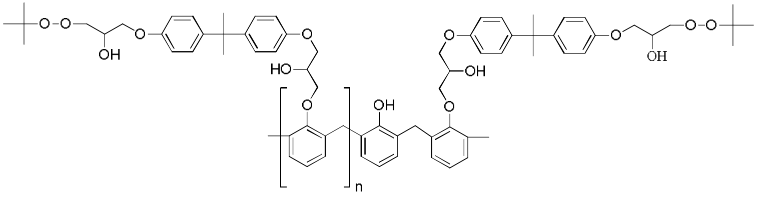
Oligomer **I**



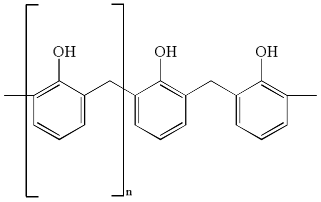
Oligomer **II**



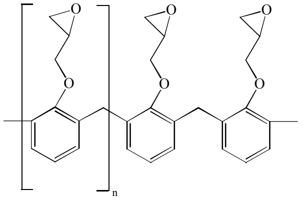
Oligomer **III**



Oligomer **IV**



PhFO



PGPhFO

3. Results and Discussion

3.1. IR Investigations

IR-spectroscopic investigations of the structures of the initial and synthesized PhFO and PGPhFO were carried out according to the procedure described in Subsection 2.2. The obtained results are represented in Figs. 1-2 and Table 1. The spectra of the initial oligomers were recorded for the comparison.

The results show that the spectra of the initial and modified oligomers are different. In the spectrum of oligomer **I** (Fig. 1b) the wide absorption band at 3306 cm^{-1} corresponding to phenol hydroxy groups is absent compared with that of the initial PhFO (Fig. 1a). At the same time the absorption band at 3400 cm^{-1} appears. This group corresponds to hydroxy groups formed due to the bonding of FGE molecule to PhFO. This fact is also confirmed by the appearance of band at 1041 cm^{-1} typical of ethers in alkyl fragments. Such band is absent in the initial PhFO (Fig. 1a). We assume that only part of phenol groups of the initial PhFO were substituted for FGE fragments and their absence in the spectrum may be explained by overlap of corresponding band by the band at 3400 cm^{-1} typical of secondary hydroxy groups.

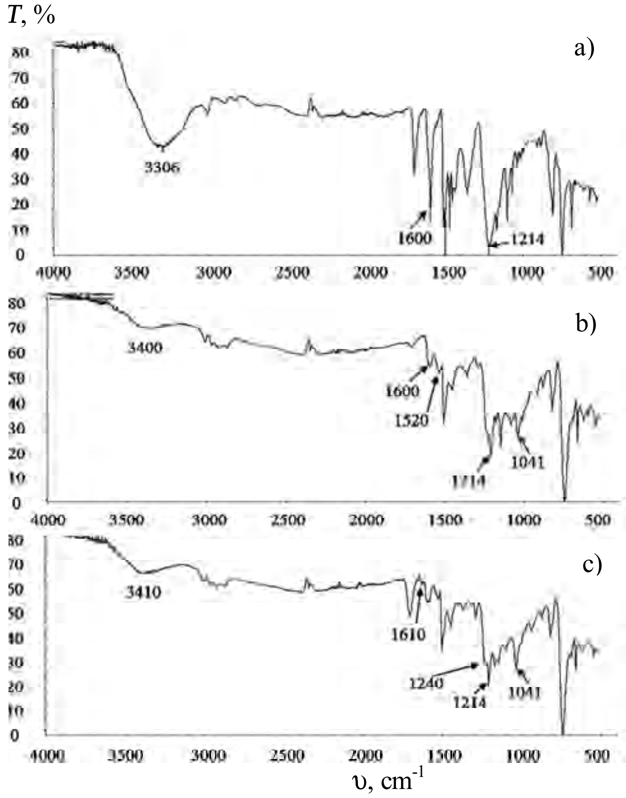
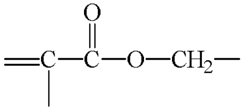


Fig. 1. IR-spectra of the initial PhFO (a), oligomer **I** (b) and oligomer **II** (c)

The absorption bands at 1214 cm^{-1} corresponding to the stretching vibrations of C–O group in ethers based on aromatic ring are confirmed in both initial and synthesized oligomer **I**. In contrast to the initial oligomer, in the oligomer **I** spectrum we observe the band at 1520 cm^{-1} typical of furan ring vibrations. Moreover, the absorption band at 910 cm^{-1} corresponding to the stretching vibrations of epoxy ring is not observed in the same spectrum. The obtained results show that oligomer **I** is formed as a result of FGE and PhFO bonding due to the opening of FGE epoxy ring and its interaction with PhFO phenol hydroxy group. The absence of epoxy groups in the spectrum of oligomer **I** and appearance of absorption bands typical of furan ring and secondary hydroxy groups indicate such interaction.

In the spectrum of oligomer **II** (Fig. 1c) obtained due to the interaction between PhFO and glycidylmethacrylate the absorption band at 3306 cm^{-1} is also absent. This band characterizes the stretching vibrations of hydroxy group in phenols. However, the absorption band at 3410 cm^{-1} typical of hydroxy group is observed. Moreover, we found the bands at 1240 and 1610 cm^{-1} corresponding to C–O–C bond in the fragment



$$=\underset{|}{C}-\overset{\overset{O}{\|}}{C}-O-CH_2-$$

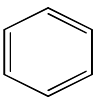
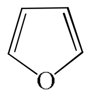
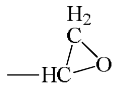
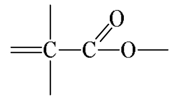
and double bond in the same fragment, respectively. The appearance of etheric bond at 1041 cm^{-1} testifies to adding of GMA molecules to PhFO molecules. The absence of absorption band at 910 cm^{-1} indicates the substitution of epoxy groups for etheric bond. The appearance of this bond and occurrence of bands at 1610 and 1240 cm^{-1} in the spectrum confirm the presence of GMA fragment in the molecule of oligomer **II**.

While analyzing the spectrum of initial PGPhFO (Fig. 2a) we observe the absence of absorption bands corresponding to hydroxy groups of both phenol and alcohol nature. At the same time there is the absorption band at 912 cm^{-1} typical of epoxy groups stretching vibrations. This confirms the presence of epoxy groups in the initial oligomer. The presence of etheric groups of aromatic and aliphatic nature is confirmed by the absorption bands at 1244 and 1036 cm^{-1}, respectively, and of the aromatic ring – at 1600 cm^{-1}.

The absorption band at 3430 cm^{-1} typical of secondary hydroxy group appears in the spectrum of oligomer **III** synthesized on the basis of PGPhFO (Fig. 2b). Such group may be formed due to the bonding of epoxide and compound with mobile hydrogen atom. In our case this compound is MAA. The decrease in intensity of absorption band at 912 cm^{-1} and appearance of bands typical of methacrylic fragments reveal MAA and PGPhFO molecules bonding. Thus, the carbonyl bond in the fragment is confirmed by the band at 1612 cm^{-1}, C–O–C bond – at 1296 cm^{-1} and double bond – at 1636 cm^{-1} (Table 1).

Table 1

IR-characteristics of the initial and synthesized oligomers

Oligomer	Absorption band, cm^{-1}										
	–OH			C–O							-O-O-
	$u_{\mathrm{OHph.}}$	$u_{\mathrm{OHal.}}$	$u_{\mathrm{ph.}}$	$u_{\mathrm{Ar\text{-}O.}}$	$u_{\mathrm{Alk\text{-}O}}$	$u_{\mathrm{furf.}}$	$u_{\mathrm{C\text{-}O\text{-}Cas.}}$	$u_{\mathrm{C=O}}$	$u_{\mathrm{C=C}}$	$u_{\mathrm{C\text{-}O\text{-}C}}$	$u_{\mathrm{O\text{-}O}}$
PhFO	3306	–	1600	1214	–	–	–	–	–	–	–
Oligomer **I**	–	3400	1600	1214	1041	1520	–	–	–	–	–
Oligomer **II**	–	3410	1600	1214	1041	–	–	–	1610	1240	–
PGPhFO	–	–	1600	1214	1036	–	912	–	–	–	–
Oligomer **III**	–	3430	1600	1214	1044	–	–	1716	1636	1296	–
Oligomer **IV**	–	3360	1600	1214	1041	–	–	–	–	–	880

Oligomer **IV** is obtained on the basis of PhFO and PO oligomer. PO contains free epoxy and peroxy groups. As a result of PO and PhFO molecules bonding we record the decrease in the intensity of absorption band at 3306 cm^{-1} and its shift toward 3360 cm^{-1} (Fig. 2c). Moreover, we observe the absorption band at 1041 cm^{-1} typical of the stretching vibrations of etheric group in the alkyl fragment. The absorption band at 880 cm^{-1} of low intensity corresponding to peroxy group is observed as well. The introduction of PO fragment in the structure of PhFO is also confirmed by the appearance of doublet of hem-methyl deformation vibrations at 1380 and 1360 cm^{-1} typical of $(CH_3)_3C$-group. Such group is in the structure of PO molecule. So we can assert that PO molecules add to PhFO molecules due to the interaction between oligomer peroxy groups and so-called comb-polymers are formed.

3.2. NMR Investigations

NMR investigations were also carried out to confirm the structure of the synthesized oligomers. For this purpose NMR (^{1}H and ^{13}C) spectra were recorded according to the procedure described in Subsection 2.3. The obtained results are represented in Figs. 3-4 and Tables 2-3.

3.2.1. ^{1}H NMR Spectroscopy

Just like IR-spectra, NMR-spectra of the initial and synthesized oligomers are different. In PhFO and PGPhFO spectra (Figs. 3-4 and Table 2) the proton signals at 4.1 ppm corresponding to the secondary hydroxy groups are absent. At the same time they appear in oligomers **I-IV**; at heating to 323–333 K they shift toward high field (3.8 ppm). This fact confirms the chemical interaction between epoxy groups of FGE, GMA and PO molecules with PhFO phenol groups. Moreover, all oligomers, the same as the initial compounds, contain phenol groups at 7.3–7.4 ppm. It means that during chemical modification the phenol groups are substituted for etheric bonds incompletely. The formation of etheric bonds, as well as –CH–O group present in the initial PhFO is confirmed by proton signals in the area of 3.7–4.4 ppm and benzene rings – in the area of 6.6–7.2 ppm. The presence of methacrylic groups in oligomers **II** and **III** is confirmed by proton signals in the area of 5.6–6.1 ppm.

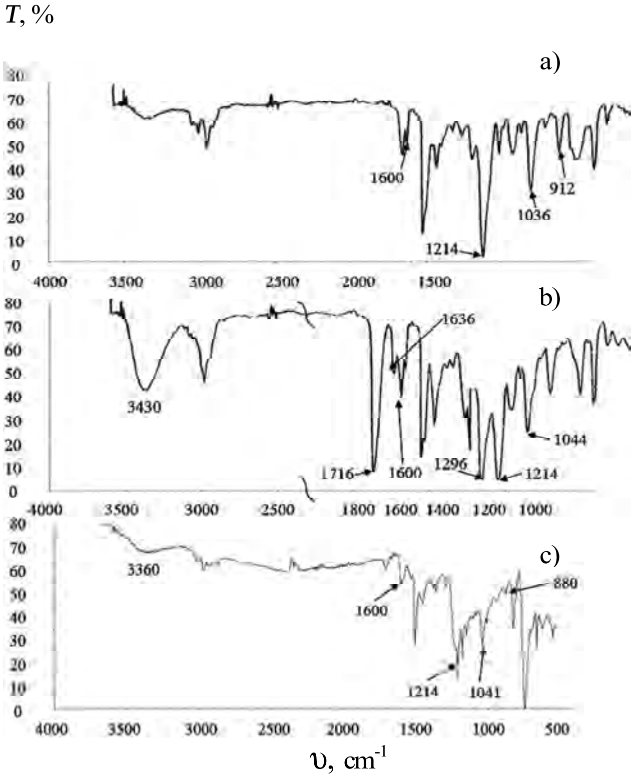


Fig. 2. IR-spectra of the initial PGPhFO (a), oligomer **III** (b) and oligomer **IV** (c)

The synthesized oligomer **III** based on PGPhFO has residual epoxy groups in its structure, just like the initial compound. The proton signals at 2.75 and 3.3 ppm confirm this fact.

The obtained results (similar to IR spectroscopic results, see Table 1) show that during PGPhFO chemical modification by methacrylic acid the complete substitution of epoxy groups for methacrylic fragments does not take place.

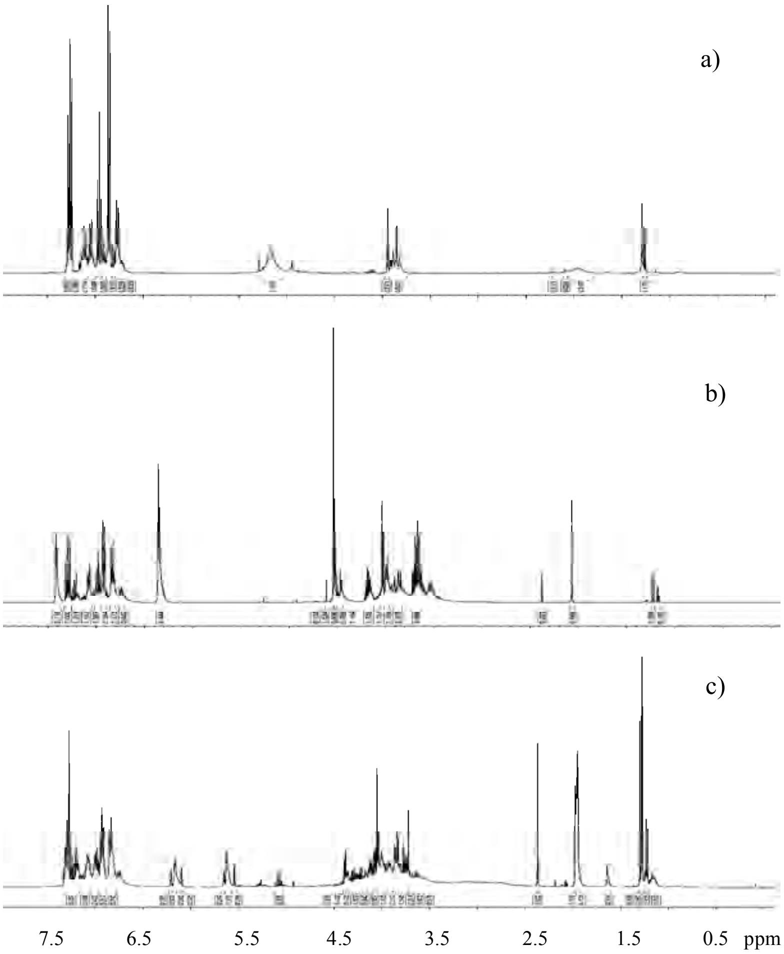
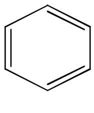
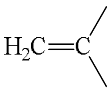
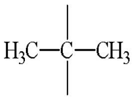
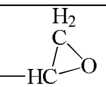
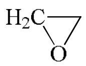
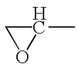


Fig. 3. ^{1}H NMR spectra of PhFO (a), oligomer **I** (b) and oligomer **II** (c)

Table 2

^{1}H NMR spectra of the initial and synthesized oligomers

Oligomer	Chemical shift *δ*, ppm							
	–OH			–CH_2O, CHO	 $H_2C{=}C\langle$	 $H_3C{-}C{-}CH_3$		
	$OH_{ph.}$	$OH_{al.}$						
PhFO	7.3	–	6.6–7.1	3.8–3.9	–	–	–	–
Oligomer **I**	7.3	4.1	6.6–7.0	3.8–4.0	–	–	–	–
Oligomer **II**	7.4	4.1	6.7–7.1	3.7–4.4	5.6–6.1	–	–	–
PGPhFO	7.4	–	6.7–7.1	3.8–4.2	–	–	2.75	3.30
Oligomer **III**	7.3	4.1	6.8–7.1	3.8–4.3	5.6–6.1	–	2.75	3.30
Oligomer **IV**	7.3	4.1	6.7–7.2	3.8–4.4	–	1.6	–	–

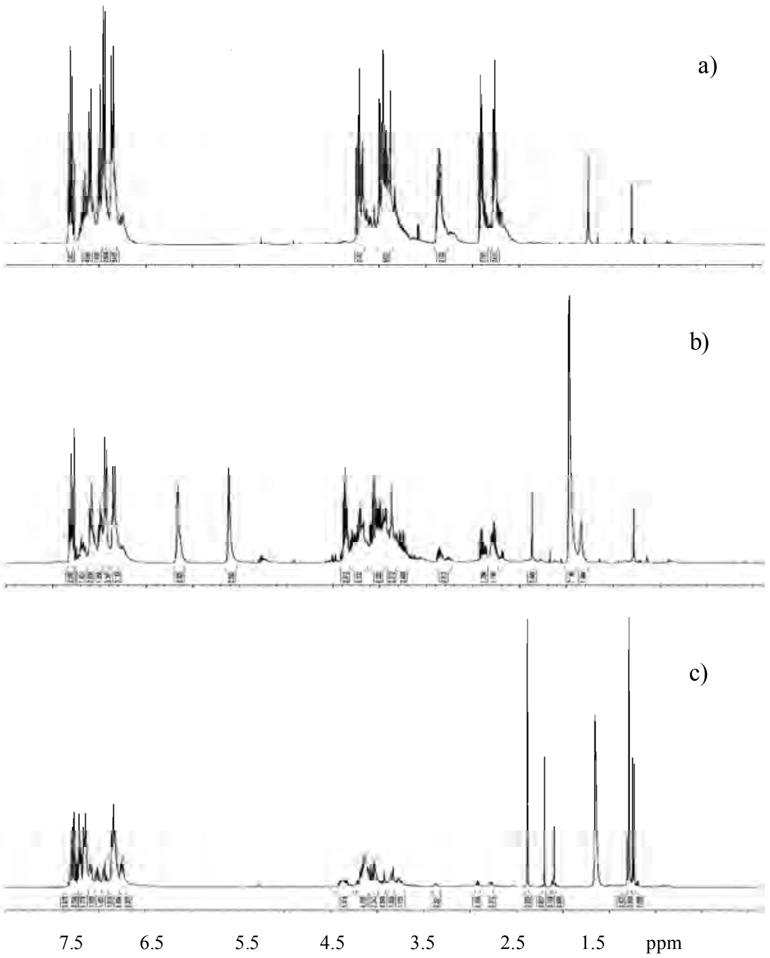
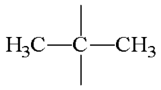
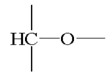
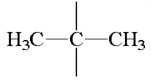
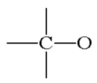


Fig. 4. ^{1}H NMR spectra of PGPhFO (a), oligomer **III** (b) and oligomer **IV** (c)

Oligomer **IV** as distinct from oligomers **I-III** is obtained *via* chemical modification between PhFO and PO molecules. PO is a peroxy derivative of ED-24 epoxy resin. On the other hand, it is known that quaternary carbon atom  $H_3C-\overset{|}{\underset{|}{C}}-CH_3$ is present in the PO structure. If PhFO is modified by PO, such group should be in the structure of the synthesized oligomer **IV**. The spectrum represented in Fig. 4c confirms that the above-mentioned fragment is in the structure of the oligomer and proton signal at 1.6 ppm corresponds to it.

3.2.2. ^{13}C NMR Spectroscopy

The structure of the above-mentioned compounds is confirmed by ^{13}C NMR spectroscopy (Figs. 5-6, Table 3). The secondary hydroxy group in oligomers **I-IV** is formed due to the chemical interaction between the initial compounds and compounds with mobile hydrogen atom. The presence of this group is confirmed by proton signals of  $H\overset{|}{\underset{|}{C}}-O-$ group in the area of 63.6–65.6 ppm. In all molecules we observe chemical shifts at 77.0 ppm proving the presence of benzene rings. The presence of $-CH_2-O$ group indicating the chemical interaction between the compounds with mobile hydrogen atom and PhFO phenol group is confirmed by the signals at 68.4–69.2 ppm. Methacrylic fragments in oligomers **II** and **III** are confirmed by the signals at 135.7–135.9 ppm; epoxy groups in oligomer **III** – by the signal at 50.1 ppm. Esteric bond in the methacrylic fragment is confirmed by the chemical shift at 167.1–167.6 ppm. The introduction of PO fragments into the structure of oligomer **IV** is confirmed by the signal at 20.3 ppm, corresponding to  $H_3C-\overset{|}{\underset{|}{C}}-CH_3$ group. The peroxy group in oligomer **IV** is confirmed by the signal at 31.1 ppm, corresponding to  $-\overset{|}{\underset{|}{C}}-O$ group, similar to the chemical analysis and IR-spectroscopy (Table 1).

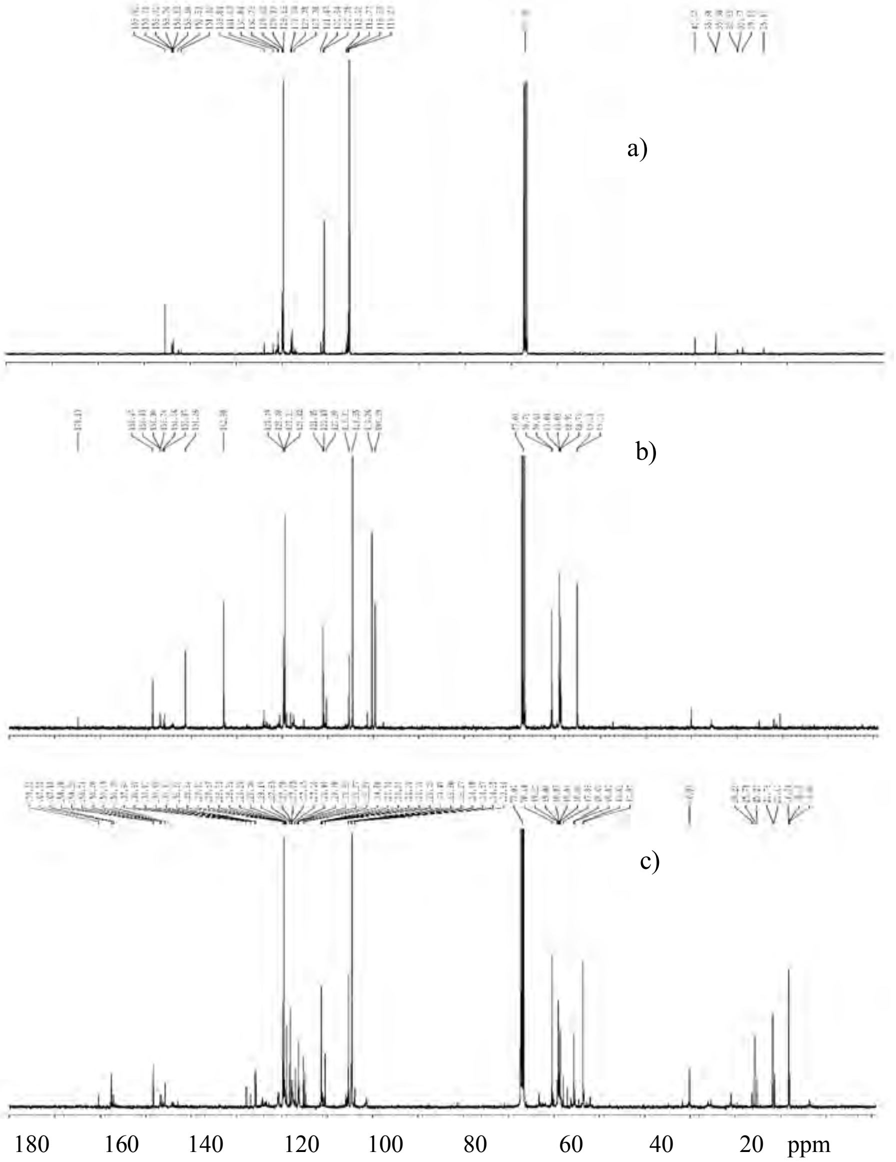
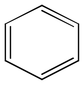
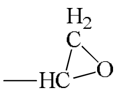


Fig. 5. ^{13}C NMR spectra of PhFO (a), oligomer **I** (b) and oligomer **II** (c)

Table 3

^{13}C NMR spectroscopic characteristics of the initial and synthesized oligomers

Oligomer	Chemical shift *δ*, ppm							
	OH-alcohol CH–O		–CH$_2$O, CHO	$H_2C{=}C\langle$	$H_3C{-}\overset{\vert}{\underset{\vert}{C}}{-}CH_3$		–CO(O)	$-\overset{\vert}{\underset{\vert}{C}}-O$
PhFO	–	77.0	–	–	–	–	–	–
Oligomer **I**	65.1–65.2	77.0	68.8–69.0	–	–	–	–	–
Oligomer **II**	65.5–65.6	77.0	68.0–69.2	135.7–135.9	–	–	167.1–167.6	–
PGPhFO	–	77.0	68.6–68.9	–	–	50.1–50.2	–	–
Oligomer **III**	65.4–65.6	77.0	68.4–69.8	135.8–135.9	–	50.1	167.1–167.5	–
Oligomer **IV**	63.6–64.7	77.0	68.7–69.1	–	20.3	–	–	31.1

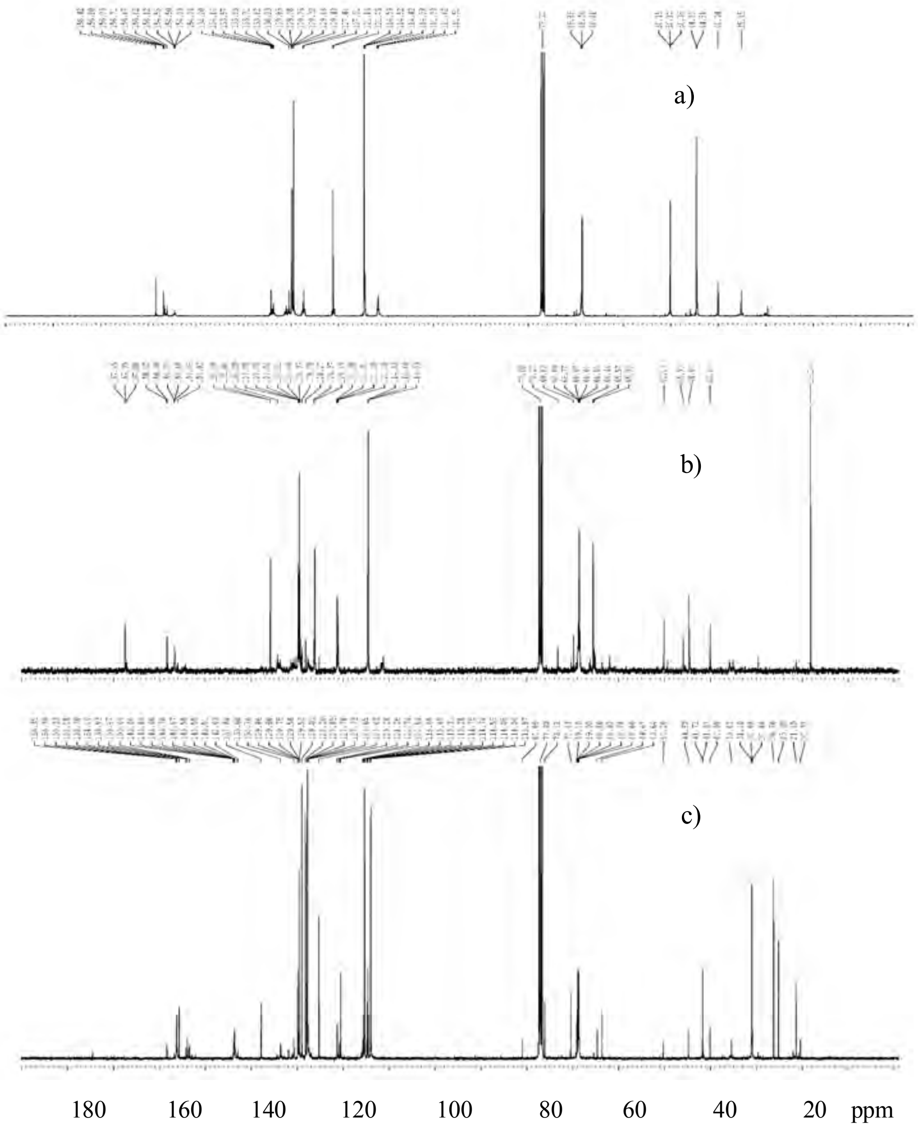


Fig. 6. ^{13}C NMR spectra of PGPhFO (a), oligomer **III** (b) and oligomer **IV** (c)

4. Conclusions

According to the results of IR- and NMR-spectroscopy it was established that the synthesized oligomers are multifunctional compounds. They contain phenol and furan or methacrylic or peroxy groups, as well as epoxy and methacrylic fragments in their structures. In all investigated modified oligomers the secondary hydroxy groups are formed due to the adding of furfurylglycide ether or glycidylmethacrylate or peroxy derivative of epoxy resin to methacrylic acid.

Acknowledgements

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References

[1] Gardziella A., Pilato L. and Knop A.: Phenolic Resins, Chemistry, Applications and Standardization, Safety and Ecology. 2nd edn. Springer-Verlag, Berlin 2000.
[2] Hirano K. and Asami M.: Reactive & Funct. Polymers, 2013, **73**, 256.
[3] Unnikrishnan K. and Thachil E.: Int. J. Polym. Mat., 2006, **55**, 385.
[4] Bazylyak L., Bratychak M. and Duchacek V.: Ukr. Khim. Zh., 2001, **67**, 61.

[5] Poljansek I., Sebenik U. and Krajnc M.: J. Appl. Polym. Sci., 2006, **99**, 2016.
[6] Bratychak M., Vostres V. and Puchin V.: Lakokrasochnye Mat. i ih Primenenie, 1987, **2**, 10.
[7] Fan D.-B., Li J.-Z. and Chang J.-M.: Eur. Pol. J., 2009, **45**, 2849.
[8] Strap G., Bratychak M. and Karateev A.: Visnyk Nats. Univ. "Lvivska Polytechnika", 2012, **726**, 458.
[9] Bratychak M., Strap G., Astakhova O. and Shyshchak O.: Chem.&Chem. Techn., 2013, **7**, 153.
[10] Bratychak M., Strap G. and Brzudziak P.: Ukr. Khim. Zh., 2014, **80**, 54.
[11] Strap G., Astakhova O. and Lazorko O. : Chem.&Chem. Techn., 2013, **7**, 279.
[12] Bratychak M., Strap G. and Shyshchak O.: Chem.&Chem. Techn., 2014, **8**, 157.
[13] Toroptseva A., Belogorodskaya K. and Bondarenko V.: Laboratornyi Praktikum po Khimii i Technologii Vysokomoleculyarnykh Soedineniy. Khimiya, Leningrad 1972.

ДОСЛІДЖЕННЯ БУДОВИ ПОХІДНИХ ФЕНОЛО-ФОРМАЛЬДЕГІДНИХ ОЛІГОМЕРІВ МЕТОДАМИ ІЧ- ТА ЯМР-СПЕКТРОСКОПІЇ

Анотація. *За допомогою ІЧ- та ЯМР (^{1}H та ^{13}C) спектроскопічних досліджень охарактеризовано будову функціональних олігомерів, отриманих на основі новолачного феноло-формальдегідного та полігліцидилфеноло-формальдегідного олігомерів. Структура модифікованих феноло-формальдегідних олігомерів доведена присутністю смуг поглинання та протонних зсувів, що віповідають фурановому кільцю, метакриловому фрагменту, пероксидним, гідроксильним та фенольним групам.*

Ключові слова: *ІЧ- та ЯМР спектроскопія, феноло-формальдегідний олігомер, полігліцидилфеноло-формальдегідний олігомер, модифікація, метакрилатна група, пероксид.*