

# STUDY OF THE PHYSICAL AND CHEMICAL PROPERTIES AND CHEMICAL STRUCTURE OF THE OLIGOMER SYNTHESIZED IN THE RATIO OF 80:1 mol/mol OF PHENOL ALCOHOL AND DIETHYLENEGLYCOLADIPINATOLS

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**Abstract.** *In this study, the effect of synthesis time on the physicochemical properties of thermosetting high molecular weight phenol-formaldehyde oligomers synthesised in the ratio of phenolic alcohol and diethyleneglycoladipinats (80:1 mol/mol) was investigated. The synthesis of diethyleneglycoladipinats (DEGA), phenolic alcohol (PhA) and the structure of the final oligomers were studied by IR spectroscopy and NMR<sup>1</sup>H, NMR<sup>13</sup>C spectroscopy.*

**Keywords:** *phenol, formaldehyde, adipic acid, diethyleneglycol, phenolic alcohol, diethyleneglycoladipinats, amount of hydroxyl group, number average molecular mass, weight average molecular mass, turbidimetry, IR spectrum, NMR<sup>1</sup>H, NMR<sup>13</sup>C.*

**Introduction.** Phenol-formaldehyde resins are increasingly being used in various fields due to their properties such as high heat resistance[1], high binding properties[2], resistance to mechanical forces[3], low toxicity of smoke when burnt and ability to blend with polymers[4]. For example, they are widely used in automotive parts and electrical switches due to their high heat resistance[5]. Low thermal conductivity makes phenol-formaldehyde resins suitable for use in insulation materials[6].

In the automotive and construction industries, phenol-formaldehyde resins are employed in a variety of applications, including brake surfaces [7], insulating foams, casting binders and composites [8], due to their high thermal stability and fire resistance. The properties of phenol-formaldehyde resins can be modified to suit any desired property by changing the catalysts used in the manufacturing process[8].

Furthermore, the synthesis of phenol-formaldehyde resins [10-11], the partial substitution of phenol in the synthesis process with substitutes [12], and the synthesis processes with the participation of various catalysts have been the subject of several scientific research studies [13-14]. In particular, in order to reduce the curing time, the synthesis of a high ortho-phenol-formaldehyde oligomer was carried out in the presence of a cocatalyst, sodium carbonate. Ether and carbamate accelerators were employed to enhance the hardening speed, and the physico-chemical properties of the resulting resin and the hardening mechanism were investigated [15].

The formation mechanisms of thermosetting phenol-formaldehyde oligomers with high molecular mass were investigated in [16]. The physical-chemical properties of the monomer polyether polyols used in synthesis were examined in [17-18]. The synthesis of oligomers with

high molecular mass as a result of changing the molar ratio of phenolic alcohol to polyether polyol was explored in [19-20].

The purpose of the research. The synthesis of a high molecular weight thermosetting phenol-formaldehyde oligomer was undertaken. Then the physical-chemical properties of the synthesized oligomer and its structure were studied.

**Research object and methods.** The following substances were employed in the conduct of scientific research: Phenol, formalin, adipic acid, diethylene glycol, maleic anhydride. Phenol was removed under vacuum at 100-110°C before use. The extracted phenol exhibited a refractive index of  $D_n^{20}=1.54027$ . A 37% solution of formaldehyde in water (formalin) was employed. Diethylene glycol was extracted under vacuum (0.90-0.97 kg/sm<sup>2</sup>) at a temperature of 133-145°C. The refractive index of the extracted diethylene glycol was  $D_n^{20}=1.4474$ .

The synthesis of a hydroxyl containing polyether polyol was conducted in a 1:1.1 mol/mol ratio of adipic acid and diethylene glycol for a period of six hours at a temperature of 195°C in an inert environment.

Phenolic alcohol (PhA) was synthesised in a 1:1.5 molar ratio of phenol to formaldehyde for 16 hours at a pH of 9 and a temperature of 56-60°C.

The synthesis of the two monomers, diethyleneglycoladipinatol and phenolic alcohol, was carried out by the process of copolycondensation in a 1:80 mol/mol ratio, with the addition of a catalyst (30% solution of maleic anhydride) under conditions of pH=3.

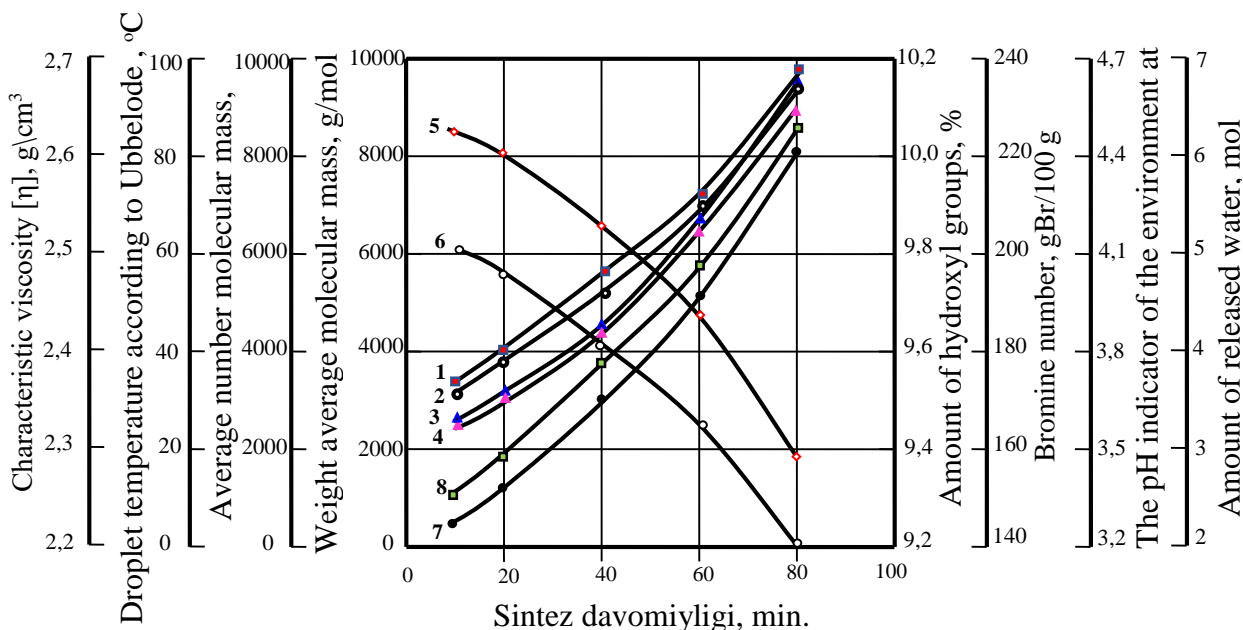
The physical-chemical properties of our synthesised oligomers and monomers were studied using a range of analytical techniques, including the determination of the number of hydroxyl groups (%), viscosity of oligomers, number of bromine (gBr/100g), Ubellode's drop temperature, average number molecular mass and average weight molecular mass. The turbidimetric analysis of the synthesised monomers and oligomers was conducted in accordance ISO standarts, utilising an optical spectrophotometer (KFK-3). In the turbidimetric titration, dimethylformamide was employed as the solvent, while distilled water served as the precipitant. The structure of the synthesized monomers and oligomers was elucidated through the acquisition of NMR <sup>1</sup>H and NMR <sup>13</sup>C spectra on a JNM-ECZ600R spectrometer (JEOL, Japan) operating at 600 MHz in a deuterated methanol (CD<sub>3</sub>OD) solution. IR spectra were obtained on an "IR Tracer-100" (SHIMADZU CORP., Japan, 2017) spectrometer.

**Results and analysis.** The study of the physico-chemical properties of high molecular mass thermosetting phenol-formaldehyde oligomers synthesised with a 1:80 mol/mol ratio of diethyleneglycoladipinatol and phenolic alcohol will play a pivotal role in the future production and utilisation of the oligomers as binders.

The impact of the synthesis duration of diethyleneglycoladipinatol and phenolic alcohol in a ratio of 1:80 mol/mol on the physicochemical properties of the final oligomers was investigated. The obtained results are presented in graphical form in Fig. 1.

In curve 1 of Figure 1 the characteristic viscosity of the oligomers increases from 2.37 to 2.69 when the synthesis is carried out from 10 to 80 minutes. This means that the oligomers become more solid than liquid state. We can see evidence of this in curve 2. In fact, the increase in synthesis time caused a sharp increase in the Ubellode drop temperature of the oligomers from 35°C to 95°C. It is therefore understandable that 1 mol of diethylene glycol dipinatol is added more than our phenolic alcohol monomer over time. This leads to very high molecular weights. Curves 3 and 4 in Figure 1 show the number average molecular mass and the weight average molecular mass of the oligomers. According to our analysis above, increasing the synthesis time resulted in

an increase in molecular mass from 2500 g/mol to 9600 g/mol. The results were very close when



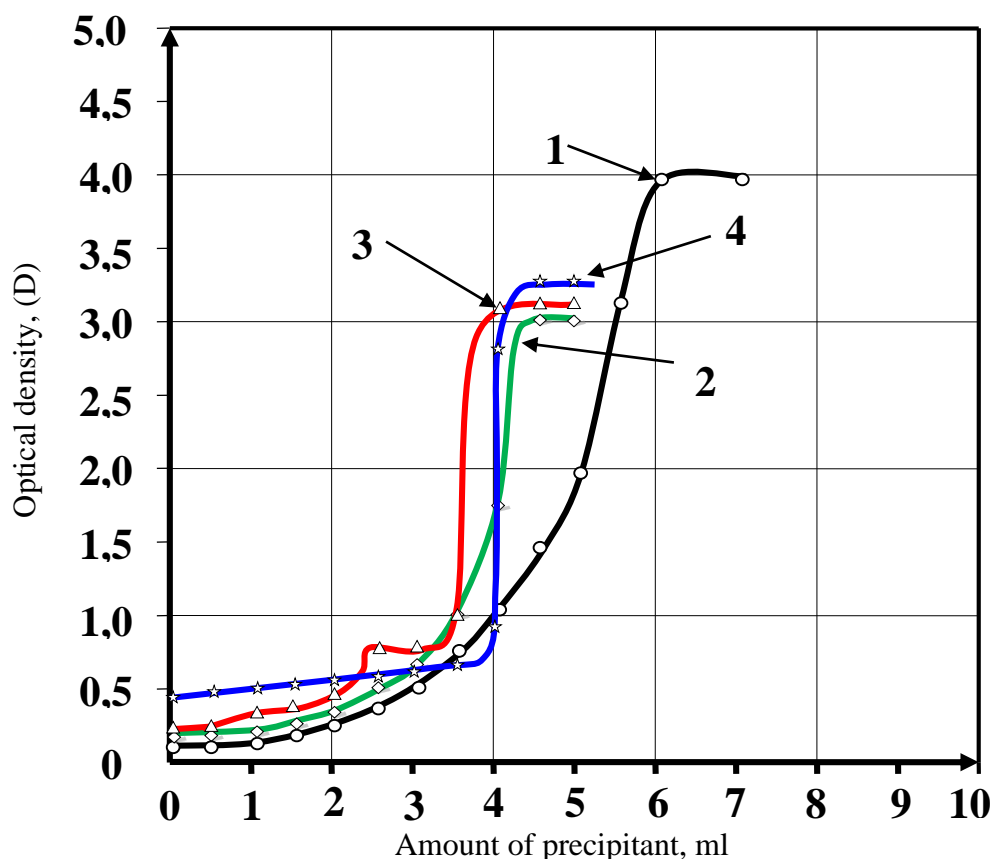
**Figure 1. Effect of reaction time on the formation of co-oligomers of phenolic alcohol and diethyleneglycoladipinatol (80:1 mol/mol)**

**1-Characteristic viscosity; 2-Droplet temperature according to Ubbelode; 3- Average number molecular mass; 4- Weight average molecular mass; 5- Amount of hydroxyl groups; 6- Bromine number; 7- Amount of released water; 8- The pH indicator of the environment at the end of the synthesis.**

cryoscopic and viscometric methods were used to determine that the molecular mass was indeed high. Typically, the molecular mass of traditional phenol-formaldehyde oligomers can be as high as 500-900 g/mol [24-26].

In order to find out which processes in the synthesised oligomers increase the length of the synthesis, we studied how functional groups in the main monomers, diethylene glycol dipinatol and phenolic alcohols, participate in the polycondensation process and influence the increase in molecular mass. The number of hydroxyl groups in the oligomers at the end of the synthesis is shown in curve 5 of Figure 1 and the number of bromine groups is shown in curve 6. As the synthesis time increases, it can be seen that both curves slope downwards. If the amount of hydroxide groups in the oligomer that took 10 minutes to synthesise is 10.05%, this indicator will decrease over time to 9.39%. Similarly, the number of bromines decreases from 200 gBr/100 g to 140 gBr/100 g. It can be concluded that the amount of functional groups in the monomers decreases, the macromolecule chain and the molecular weight increases.

Another hypothesis for the increase in molecular mass is that maleic anhydride, used as a catalyst, can participate as a monomer in the main chain and cause the molecular mass of the oligomer to increase. This assumption is supported by the change in the pH indicator of the medium at the end of the synthesis in curve 7 of Figure 1. Before synthesis, the reaction medium was at pH=3. As the duration of the synthesis increases, the pH indicator of the reaction medium increases from 3.25 to 4.41, which is a significant indicator. This means that maleic anhydride, used as a catalyst, is participating in the polycondensation reaction. The amount of maleic anhydride obtained for the synthesis is 5 times higher than the amount of our main monomer diethyleneglycoladipinatol, a certain amount of maleic anhydride is involved as a monomer. Curve 8 shows that the above analysis is correct and the molar amount of water separated during the



**Figure 2.** Optical density of 1% oligomer solutions as a function of the amount of precipitate. 1:80  
1)DEGA (diethyleneglycoladipinatol): solvent - dimethylformamide, precipitant - distilled water.  
2)Traditional simple phenol-formaldehyde oligomer (TSPFO) of the resol type synthesised on the basis of phenolic alcohol (phenol:formaldehyde 1:1.5 mol/mol): solvent - dimethylformamide, precipitant - distilled water.  
3)A mechanical mixture of diethyleneglycoladipinatol and phenolic alcohol (phenol:formaldehyde 1:1.5 mol/mol) in a ratio of 1:80 mol/mol: solvent - dimethylformamide, precipitant - distilled water.  
4)High molecular weight thermosetting phenol-formaldehyde co-oligomers of phenolic alcohol and diethyleneglycoladipinatol, synthesised in a ratio of 80:1 mol/mol: solvent - dimethylformamide, precipitant - distilled water.

polycondensation process. The more the amount of water formed during polycondensation, the more the molecular weight of the oligomers was obtained. When the synthesis time was increased from 10 to 80 minutes, the amount of water removed increased from 2.53 mol to 6.32 mol.

After studying the effects of high molecular weight thermosetting phenol-formaldehyde oligomers in a ratio of 1:80 mol/mol of diethylene glycol adipinatol and phenolic alcohol on the physico-chemical properties of the synthesis duration, it was checked by turbidimetry whether the synthesised oligomers were truly high molecular weight oligomers or a simple mixture. Based on the results obtained, the curves in Figure 2 were generated. The first curve in Fig. 2 is diethylene glycol adipinatol, the second curve is a traditional simple phenol-formaldehyde oligomer of the resol type synthesised on the basis of phenolic alcohol (phenol:formaldehyde 1:1.5 mol/mol), the third curve is a mixture of diethylene glycol adipinatol and phenolic alcohol (phenol:formaldehyde 1:1.5 mol/mol) in the ratio of 1:80 mol/mol) belongs to the mechanical mixture, the fourth curve is the high molecular weight thermosetting phenol-formaldehyde co-oligomer synthesised in the ratio of diethylene glycol adipinatol and phenolic alcohol 1:80 mol/mol.

Analysing the first curve in Figure 2, when 0.5 ml of distilled water was added to a 1% solution of diethyleneglycoladipinatol in dimethylformamide, the optical density of the system (characterising the turbidity of the solution) gradually increased. This increase continued until 1.5 ml of precipitating agent was added; the addition of 0.5 ml of precipitating agent to the solution resulted in a significant increase in optical density. This condition was maintained until 6 ml of precipitant was added. When 1.5 ml precipitant was added, the optical density of the system increased to 0.125 D. When 6 ml precipitant was added, this indicator reached 3.965 D. Further addition of precipitant did not change the optical density of the system. This means that precipitation of the oligomer from the solution is complete. A curve resembling an *S-shape* then appeared. And the *S-shape* of the turbidimetric titration curve indicates the sedimentation of molecules with the same structure but different molecular weights.

In the next second curve, up to 0.5 ml of precipitant was added to a 1% solution of resol-type phenol-formaldehyde oligomer synthesised from phenolic alcohol (phenol:formaldehyde 1:1.5 mol/mol). This resulted in a gradual increase in the optical density of the system. Further addition of precipitating agent significantly increased the optical density. This condition was maintained until 4 ml of precipitant was added and when the precipitant reached 4.5 ml, the turbidity of the solution did not change. In this case, when 0.5 ml of precipitant was added, the optical density of the system increased to 0.128 D and when 4.5 ml of precipitant was added, this indicator reached 3.0 D. In this case, the turbidimetric titration resembled an *S-shaped* curve, as in the first curve. This situation also showed the deposition of molecules with the same structure but different molecular mass.

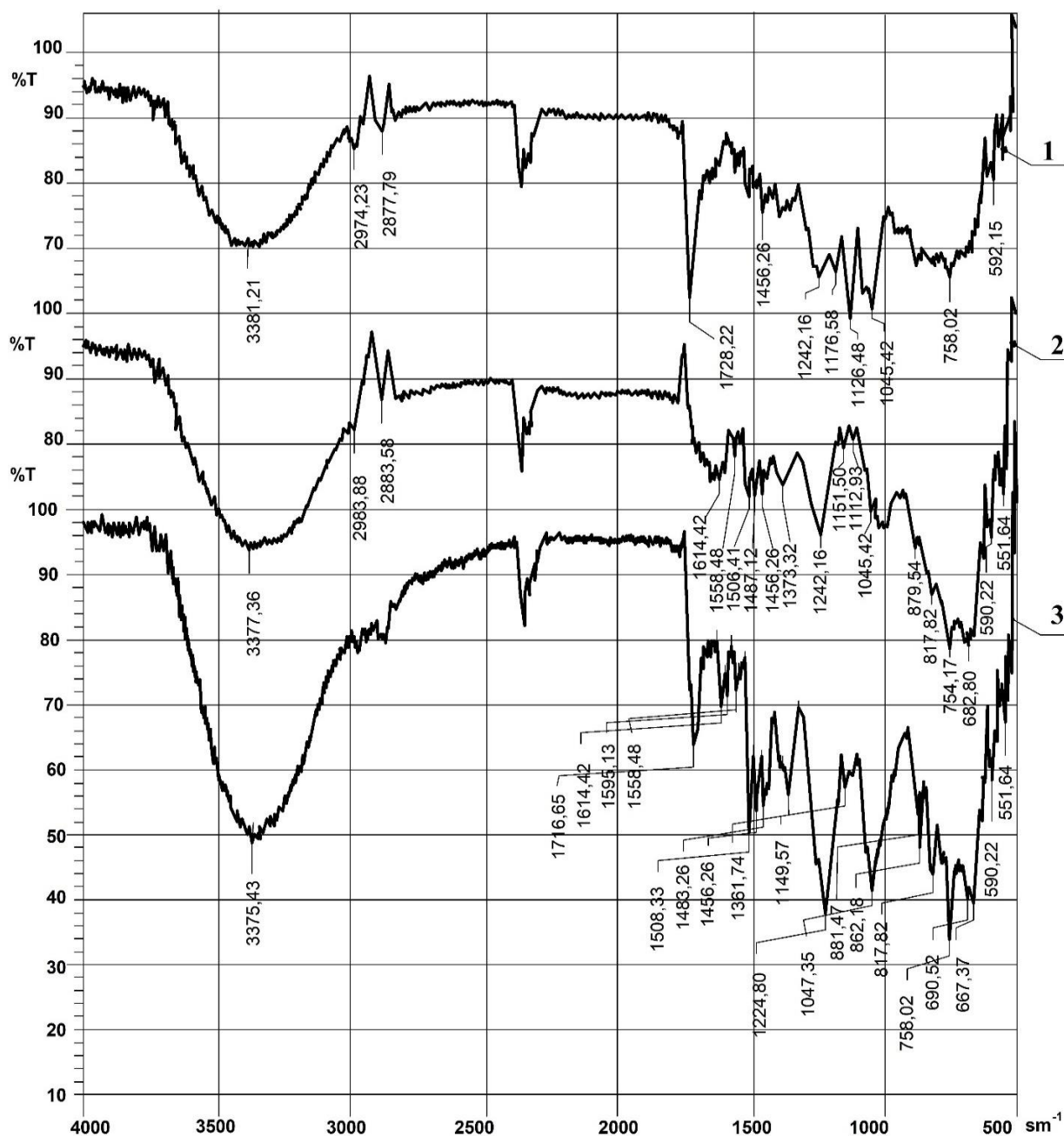
The third curve shows the turbidimetric titration analysis of a 1% solution of diethyleneglycoladipinatol and phenolic alcohol (phenol:formaldehyde 1:1.5 mol/mol) in a ratio of 1:80 mol/mol in dimethylformamide. When 0.5 ml to 2 ml of precipitant was added to the solution, the optical density gradually changed to 0.4-0.45 D. When 2.5 ml of precipitant was added to the solution, the optical density increased by 0.7 D and continued at this density until 3.7 ml of precipitant was added. When the amount of precipitant reached 4 ml, the optical density of the solution changed sharply by 3.2 D. The optical density of the solution remained unchanged at 3.2 D even when 5 ml of precipitant was added. Analysis of the variation of the third curve showed that this system also has two components, i.e. first the variation of the optical density has a single *S-shape*, indicating the degree of precipitation of the first component of the system, then the optical density remains constant, after which the second component of the system collapses with the formation of the second *S-shape*. Therefore, in this case too, we see two successive *S shapes*, characteristic of a mechanical mixture of two different oligomers.

The fourth curve in Figure 2 shows the turbidimetric shaking analysis of a solution of phenolic alcohol and diethyleneglycoladipinatol synthesised in a ratio of 80:1 mol/mol of thermosetting high molecular weight phenol-formaldehyde co-oligomers in 1% dimethylformamide. Also, when 3.5 ml of precipitant is added, the optical density of the solution gradually and uniformly increases to 0.45-0.52 D. If a further 0.5 ml of precipitant is then added, the optical density of the solution increases sharply by 3.25 D, after which this indicator does not change with further addition of precipitant. In this case, 1, 2, as well as the curves, indicate that it is an oligomer with the same chemical composition. Analysing Figure 2 in general, curves 1, 2 and 4 in this figure can be said to be characteristic of oligomers composed of macromolecules with a single chemical structure. Curve 3 is characteristic of two component systems and can be described as a mixture of two types of oligomers.



Further, the monomers used to synthesise and the structure of the final product synthesised were studied. In first, the IR spectra of the synthesised monomers and the final product were recorded using an IR Tracer-100 (SHIMADZU CORP., Japan, 2017) spectrometer. The samples were investigated in the range of the wave number scale - 4000 ÷ 400 cm<sup>-1</sup>. IR spectra of liquid samples were recorded from a thin film between two KBr plates, and solid samples were recorded on a plate pressed with KBr.

Transition peak 1 in Figure 3 corresponds to diethyleneglycoladipinitol synthesised in a 1:1.1 mol/mol ratio of ADK and DEG. The transition peaks in it were formed in Table 1 and the results obtained were analysed.



**Figure - 3. IR spectra of co-oligomers synthesised at a DEGA:FeS ratio of 1:80 mol/mol and of the monomers used for the synthesis.**

**1- Diethyleneglycoladipinatol; 2-Phenolalcohol; 3- High molecular mass thermosetting phenol-formaldehyde oligomer.**

**Transmission peaks of diethyleneglycoladipinatosol**

Groups	Transmission peak, cm <sup>-1</sup>		
	Current transfer peak, cm <sup>-1</sup>	The peak of the transmission given in the literature, cm <sup>-1</sup>	Intensity*
—OH Hydroxyl group	3381	3200-3400 3200-3750	$\nu(\text{O-H})$ , B, S
—CH <sub>2</sub> — Methylene group	2974	2926-2980	$\nu_s(\text{C-H})$ , M
	2877	2860-2926	$\nu_{as}(\text{C-H})$ , W
	1456	1445-1485	$d(\text{C-H})$ , M
$\begin{array}{c} \text{—C—O—} \\    \\ \text{O} \end{array}$ Ester group	1728	1650-1820 1725-1745	$\nu(\text{C=O})$ , S
—C—O—C— A simple ether group	1242	1275-1200	$\nu_{as}(\text{C-O-C})$ , W
	1176	1200-1040	$\nu_s(\text{C-O-C})$ , W
	1126	1150-1060	$\nu_s(\text{C-O-C})$ , S
—CH <sub>2</sub> OH Primary hydroxyl group	1045	1010-1075	$\nu(-\text{CH}_2-\text{OH})$ , S
—(CH <sub>2</sub> ) <sub>4</sub> —	758	770-720	$\nu_s(\text{C-H})$ , M

\*In the table:  $\nu$  - valence transfer;  $\nu_s$  and  $\nu_{as}$  - symmetric and asymmetric valence transfer;  $d$  - deformation transfer; B - has a broad intensity; S - has a strong intensity; M - has a medium intensity; V - has a variable intensity; W - has a weak intensity.


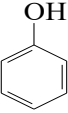
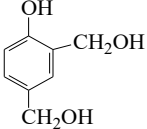
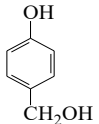
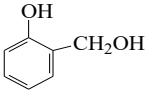
Analysing the data in Table 1, it was found the synthesised diethyleneglycoladipinatosol contains a hydroxyl group (-OH), a primary hydroxyl group (-CH<sub>2</sub>OH) and a methylene group (-CH<sub>2</sub>-). As a result of the synthesis, the carbonyl group of adipic acid and the primary hydroxyl

groups of diethylene glycol were formed as a result of ester groups ( $\begin{array}{c} \text{—C—O—} \\ || \\ \text{O} \end{array}$ ). After synthesis, diethyleneglycoladipinatosol was found to contain a simple ether group (-C-O-C-) belonging to diethyleneglycol and a methylene group -(CH<sub>2</sub>)<sub>4</sub>- belonging to adipic acid.


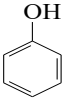
The second transmission peak in Figure 3 belongs to the IR spectra of phenolalcohol synthesised in a 1:1.5 mol/mol ratio of phenol and formaldehyde. The transmission peaks of the phenol alcohol were formed and analysed in Table 2.

**Transmission peaks of phenolalcohol**

Groups	Transmission peak, cm <sup>-1</sup>		
	Current transfer peak, cm <sup>-1</sup>	The peak of the transmission given in the literature, cm <sup>-1</sup>	Intensity*

—OH Hydroxyl group	3377	3200-3400 3200-3750	$\nu(\text{O-H})$ , B, S
—CH <sub>2</sub> — Methylene group	2983	2926-2980	$\nu_s(\text{C-H})$ , M
	2883	2860-2926	$\nu_{as}(\text{C-H})$ , W
	1456	1440-1480	$\nu(\text{C-H})$ , M
 The -C=C- group in the aromatic ring	1614	1590-1625	$d(\text{C=C})$ , M
	1558	1500-1600	$d(\text{C=C})$ , V
	1506		
	1487	1475-1525	$\nu(\text{C=C})$ , W
 The C-O group in phenol	1373	1310-1410	$d(\text{C-O})$ , S
	1242	1180-1260	
	1151	1140-1230	
	1112	1110-1120	$d(\text{C=C})$ , V
—CH <sub>2</sub> OH Primary hydroxyl group	1045	1010-1075	$\nu(-\text{CH}_2-\text{OH})$ , S
 C-H bonding in o,p- substituted phenol	879	830-880	$d(\text{C-H})$ , S-M
 The C-H bond in p- substituted phenol	817	815-835	$d(\text{C-H})$ , M
 The C-H bond in o- substituted phenol	754	720-790	$d(\text{C-H})$ , S

\*In the table:  $\nu$  - valence transfer;  $\nu_s$  and  $\nu_{as}$  - symmetric and asymmetric valence transfer;  $d$  - deformation transfer; B - has a broad intensity; S - has a strong intensity; M - has a medium intensity; V - has a variable intensity; W - has a weak intensity.

As can be seen from the data in Table 2, it was found the synthesised phenolic alcohol contains a hydroxyl group (-OH), a methylene group ( $-\text{CH}_2-$ ), an aromatic ring () and a C-O group in phenol (). We can also see that the methylol group attached to the aromatic ring

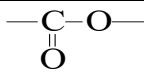

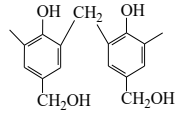

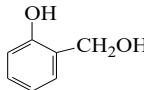
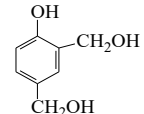


(-CH<sub>2</sub>OH) is attached to the o-, p-substituted aromatic ring, p-substituted aromatic ring and o-substituted aromatic ring. This shows that mono-, di- methylol phenols have been formed.

The third transfer peaks in Figure 3 belong to the IR spectra of the final product synthesised at a DEGA:FeS ratio of 1:80 mol/mol. The transfer peaks in Figure 3 were formed and analysed in Table 3.

*3 – table*

**Transmission peaks of the oligomer with DEGA:FeS ratio 1:80 mol/mol**

Groups	Transmission peak, cm <sup>-1</sup>		
	Current transfer peak, cm <sup>-1</sup>	The peak of the transmission given in the literature, cm <sup>-1</sup>	Intensity*
—OH Hydroxyl group	3375	3200-3750	<i>v</i> (O-H), b, S
 Complex ether group	1716	1730-1715	<i>v</i> (C=O), S
 The -C=C- group in the aromatic ring	1614	1590-1625	<i>d</i> (C=C), M
	1558	1500-1600	<i>d</i> (C=C), V
	1508		
	1483	1475-1525	<i>v</i> (C=C), W
Combined with -HC=CH- (C=O).	1595	1660-1580	<i>d</i> (C=C), S
 methylene bridge	1456	1440-1480	<i>d</i> (C-H), M
 C-O bond in phenol	1361	1310-1410	<i>d</i> (C-O), S
	1224	1180-1260	
—CH <sub>2</sub> —O—CH <sub>2</sub> — ordinary ether	1149	1150-1085	<i>v</i> <sub>as</sub> (C-O-C), S
—CH <sub>2</sub> OH Primary hydroxyl group	1047	1010-1075	<i>v</i> (—CH <sub>2</sub> —OH), S
 The C-H bond in o-substituted phenol	881	860-900	<i>d</i> (C-H), W-M
 The C-H bond in p-substituted phenol	862	830-880	<i>d</i> (C-H), S-M



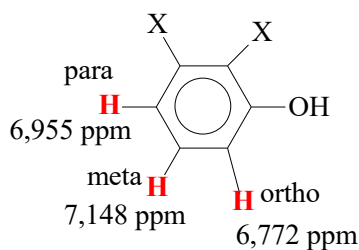


Figure 6. Location of protons in NMR <sup>1</sup>H chemical shift in

diethyleneglycoladipinatol (DEGA), which is a synthesis product of DEG and ADA in a 1.1:1 mol/mol ratio, can be expressed as follows:

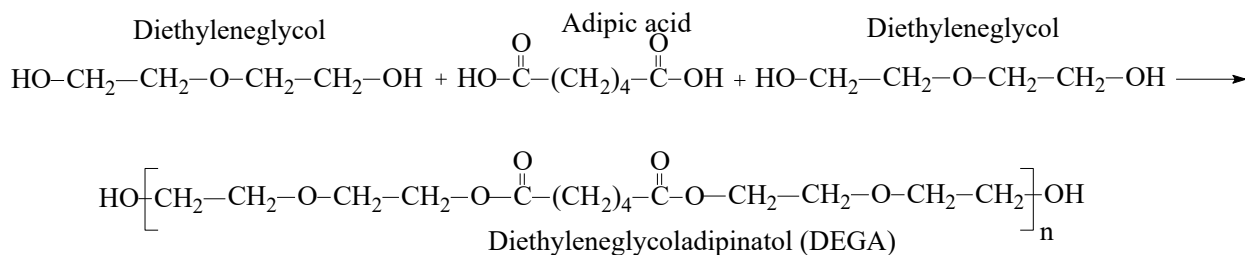


Figure 4 (b) shows the NMR <sup>1</sup>H chemical shifts of phenol alcohol (PA) synthesised in a 1:1.5 mol/mol ratio of phenol and formaldehyde. It was found that chemical shifts of 3.3-3.7 ppm belong

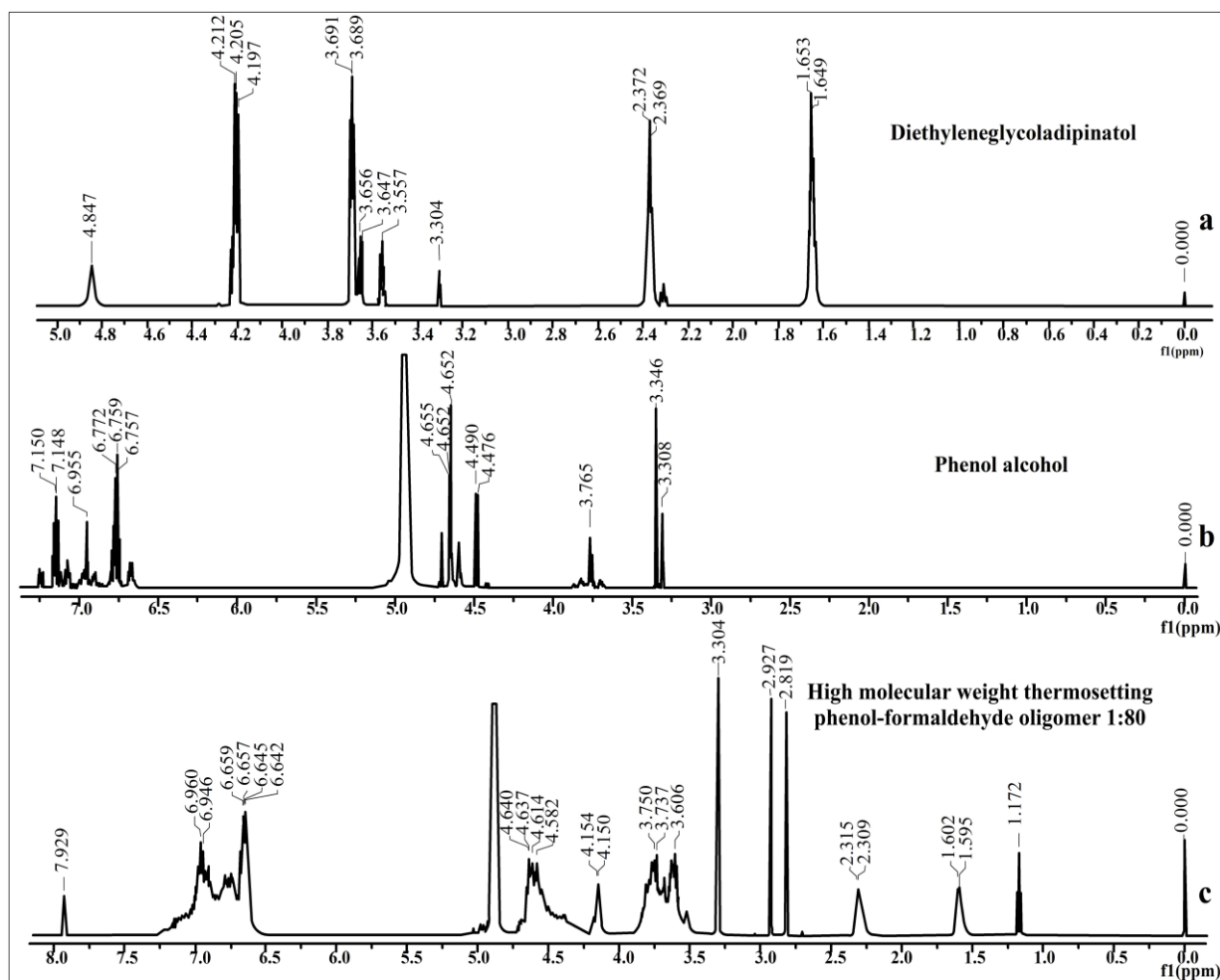
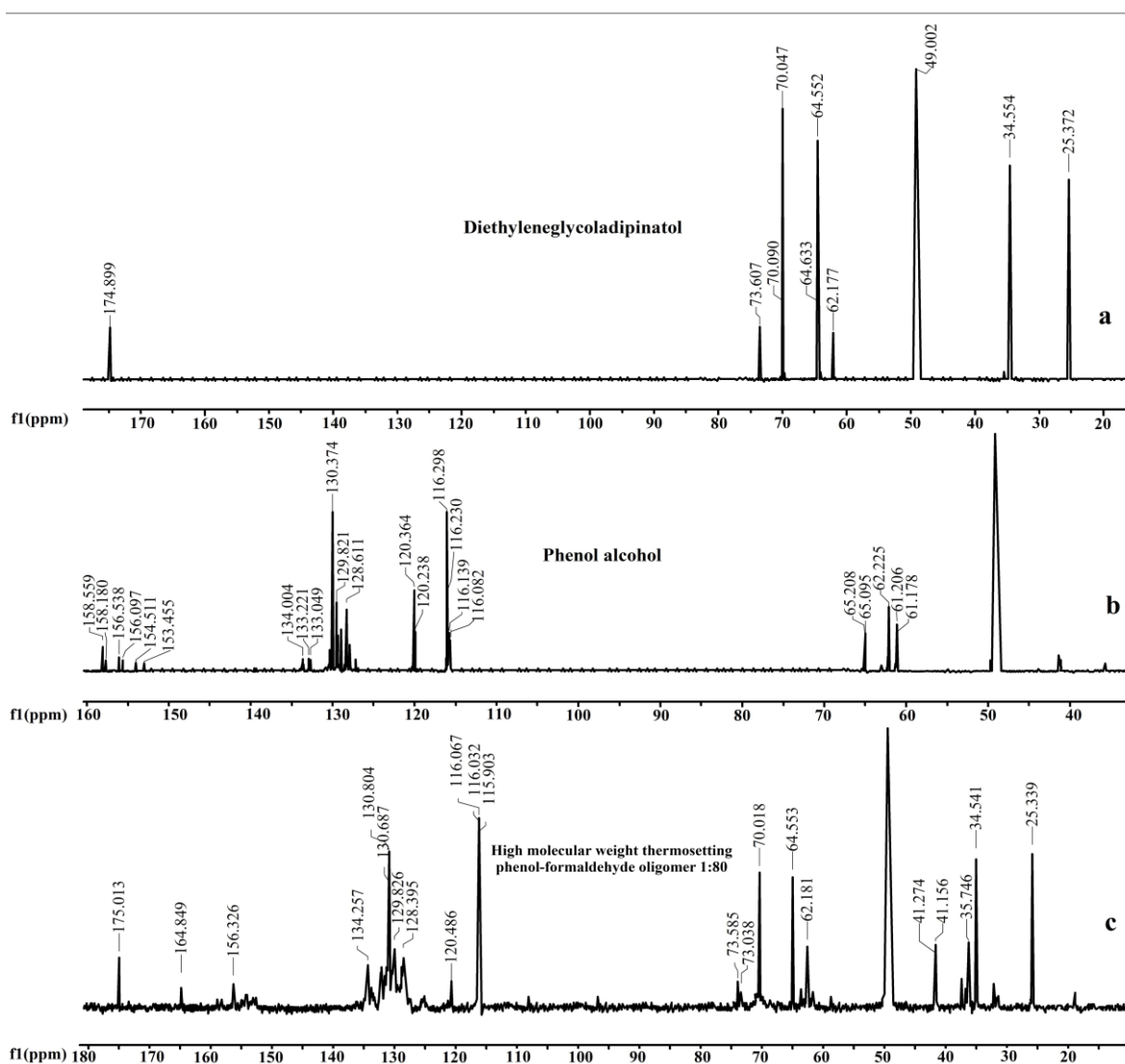


Figure 4. NMR <sup>1</sup>H spectra of synthesised monomers and high molecular weight thermosetting phenol-formaldehyde oligomer:

a-Diethyleneglycoladipinatol; b- Phenol alcohol; c- High molecular weight thermosetting phenol-formaldehyde oligomer 1:80

to protons in the methylol group (-CH<sub>2</sub>-OH) in methylene, and chemical shifts in the range of 4.4-5 ppm belong to protons in the hydroxyl group (-CH<sub>2</sub>-OH). It was also determined that the NMR <sup>1</sup>H chemical shifts in the range of 6.7-7.1 ppm in the spectrum of Figure 4 (b) belong to the protons in the aromatic ring. As shown in Figure 6, the position of the protons in the aromatic ring is determined from the literature [29-30] that 6.772 ppm belongs to the ortho-shifted proton, 6.955 ppm to the para-shifted proton and 7.148 ppm to the meta-shifted proton.

The spectrum in Figure 5(b) shows the NMR <sup>13</sup>C chemical shifts in phenol alcohol. It shows that the chemical shifts in the range 61.0-65.5 ppm belong to the carbon atom of the methylol groups located in the aromatic ring. The location of the methylol group attached to the carbon (C) atoms of the aromatic ring belongs to ortho-phenol-methylol with a chemical shift of 61.1-61.5 ppm and para-phenol-methylol with a chemical shift of 64.5-65.5 ppm and has the structure shown



**Figure 5. NMR <sup>13</sup>C spectra of synthesised monomers and high molecular weight thermosetting phenol-formaldehyde oligomer.**

a-Diethyleneglycoladipinatol; b- Phenol alcohol; c- High molecular weight thermosetting phenol-formaldehyde oligomer 1:80

in Figure 7a.

The ortho and para unsubstituted carbons in the phenol ring involved in the methylation reaction occur at chemical shifts of 116.0-117.1 and 119.5-121.4 ppm respectively [15]. In the

spectrum of Figure 5 (b), the chemical shift in the range 116.082-116.298 ppm belongs to the carbon in the ortho position, and the chemical shift in the range 120.238-120.364 ppm belongs to the carbon in the para position. Its chemical structure is shown in Figure 7b.

Also, the chemical shifts of 128.611-130.374 ppm belong to the carbon atoms para-exchanged with the methylol group, and the chemical shifts of 133.049-134.004 ppm belong to the carbon atoms ortho-exchanged with the methylol group. They were found to have the chemical structure shown in Figure 7c. Chemical shifts in the range 153.445-158.559 ppm belong to carbon atoms in phenol. This the chemical structure shown in Figure 7d.

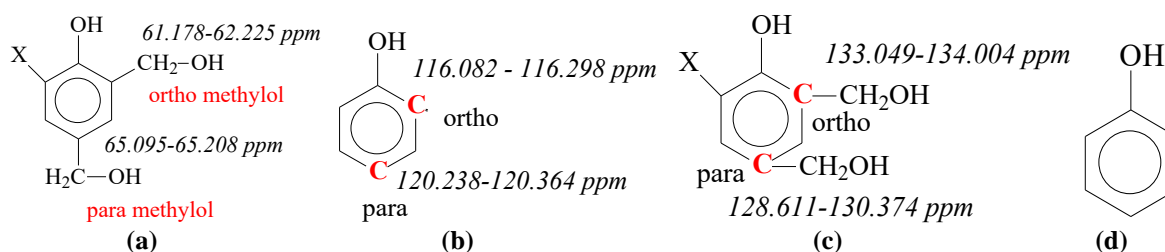
From the analysis of the NMR  $^{13}\text{C}$ ,  $^1\text{H}$  spectra of our DEGA and PA monomers discussed above, we will consider the analysis of the NMR  $^{13}\text{C}$ ,  $^1\text{H}$  spectra of final product high molecular weight thermosetting phenol-formaldehyde oligomer.

The spectrum in Figure 4(c) corresponds to the NMR  $^1\text{H}$  chemical shifts of the final high molecular weight thermosetting phenol-formaldehyde oligomer. The chemical shift of 1.17-1.60 ppm means that this group belongs to the proton in the (-CH=CH-) state and that maleic anhydride also participates in the copolycondensation process due to the increase in molecular mass. Short chemical shifts 2,309 ppm, long chemical shifts 2,819-3,304 ppm intervals (-CH<sub>2</sub>-) belong to the proton of methylene group, these chemical shifts were absent in NMR  $^1\text{H}$  spectra of monomers. Chemical shifts of 2.3-3.3 ppm belonging to the proton in the methylene group indicate the formation of methylene bridges (Ar-CH<sub>2</sub>-Ar).

3,606-3,750 ppm chemical shifts to protons in (-CH<sub>2</sub>-O-), 4,154 ppm chemical shifts to protons in (-O-C(O)-(CH<sub>2</sub>)<sub>4</sub>-C(O)-O), 4,582-4,640 ppm chemical shifts ether, it was determined from the literature [29] that the chemical shifts of 6,642-6,960 ppm belong to the protons in the (-CH<sub>2</sub>-O-CH<sub>2</sub>-) configuration and to the ortho and para unexchanged protons in the aromatic state.

The spectrum in Figure 5(c) corresponds to the  $^{13}\text{C}$  NMR chemical shifts of the final product. Also 25.339 ppm, 34.541 ppm, 41.274 ppm and 50.0 ppm NMR  $^{13}\text{C}$  belong to methylene bridges connecting radical to radical or aromatic ring to radical in (R-CH<sub>2</sub>-R) or (Ar-CH<sub>2</sub>-R) chemical shifts. It was determined that 62.181 ppm belongs to the carbon atom of the methylol group in the ortho position in the aromatic case, which was formed during methylolation and did not participate in the copolymerisation, and 64.553 ppm belongs to the carbon atom of the methylol group in the para position in the benzene case. Chemical shifts in the range 70.018-73.585 ppm belong to carbon atoms involved in methylene ether (-CH<sub>2</sub>-O-CH<sub>2</sub>-) bonds[16].

The chemical shifts of the carbon atoms not involved in the chemical reaction in the phenol ring are shown in the ranges 115.9-116.0 ppm and 120.4 ppm. It was found that the chemical shift of



**Figure 7. The structure of the aromatic ring and the carbon in the aromatic ring, the methylol group, in NMR  $^{13}\text{C}$  chemical shifts.**

130.804 ppm belongs to the carbon atom in the para position and the chemical shift of 134.257 ppm belongs to the carbon atom in the ortho position. It was also determined from the literature

that the chemical shift of 156.326 ppm belongs to the phenoxy group and the chemical shifts of 164.849 ppm and 175.013 ppm belong to (-C=O) carbonyl groups [30,31].

The conclusion. In conclusion, it can be stated DEGA:PA was synthesized in a 1:80 mol/mol ratio for 10, 20, 40 and 60 minutes and optimal conditions were selected for copolycondensation reactions carried out in the presence of maleic anhydride catalyst for 80 minutes. The effect of synthesis time on the physical and chemical properties of thermosetting phenol-formaldehyde oligomers of high molecular mass, synthesised according to different synthesis durations, was studied. An increase in the synthesis time resulted in a reduction in the number of bromine atoms per 100 grams and the amount of hydroxyl groups present. Consequently, the oligomer exhibited an increase in the number average molecular mass, weight average molecular mass, characteristic viscosity, and the amount of water (mol) released at the end of the synthesis. It was observed the thermosetting phenol-formaldehyde oligomer with the highest molecular mass was present in the oligomer with a synthesis time of 80 minutes.

Turbodimetric titration to determine whether the product is a simple mixture or a high molecular weight oligomer showed, that synthesised high molecular weight thermosetting phenol-formaldehyde oligomer exhibited an S-shaped curve, which is characteristic of the whole substance. Subsequently, the results of the IR spectrum and NMR <sup>1</sup>H, NMR <sup>13</sup>C spectra were found to be in agreement with regard to the structure of monomers and oligomers.

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