

## INITIATING AND CROSS-LINKING PROPERTIES OF UREA-FORMALDEHYDE OLIGOMERS WITH PEROXIDE GROUPS

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**Abstract.** The initiating properties of urea-formaldehyde oligomers with peroxide groups have been studied. For comparison, the initiating activity has been examined for the polymerization of styrene by the peroxide oligomer based on the epoxy oligomer Epidian-5 and *tert*-butyl hydroperoxide. The cross-linking properties of the urea-formaldehyde oligomers with peroxide groups have been investigated using unsaturated oligoesters as a model. The chemistry of the formation of the substances with a cross-linked structure has been studied using IR spectroscopy.

**Keywords:** urea-formaldehyde oligomers, peroxide, styrene, unsaturated oligoesters, Epidian-5, initiating and cross-linking properties, EPR method, IR spectroscopy.

### 1. Introduction

Oligomeric substances having different functional groups in their structure can serve as active additives for the development of tailor-made materials.<sup>1–4</sup> Such functional groups may be epoxy, carboxyl, and primary hydroxyl ones as well as unsaturated acrylate moieties.<sup>5–8</sup> But at the same time, oligomers with a labile peroxide group and another functional group have recently attracted much attention.<sup>9–11</sup> These substances can serve as cross-linkers and initiators for polymer blends enabling the formation of an item from different polymers.<sup>9,12,13</sup> Epoxy<sup>11,14,15</sup> and phenol-formaldehyde resins<sup>16,17</sup> are most often used to prepare oligomers with a peroxide group in their structure. Application of these resins stems from the fact that they contain either a reactive epoxy group (in the case of epoxy resins) or a phenolic hydroxyl group (while using phenol-formaldehyde resins) in their structure. This

allows introducing different additional functional groups into the structure of the above-mentioned resins *via* oligomer reactions.

In recent years, the synthesis of amino-formaldehyde oligomers with peroxide groups has been reported.<sup>18,19</sup> These oligomers contain nitrogen atoms in their structure unlike materials synthesized from either epoxy or phenol-formaldehyde resins. As evidenced by the literature,<sup>20</sup> the presence of nitrogen atoms in the peroxide oligomers results in the decomposition of labile –O–O– bonds at much lower temperatures. This allows forming items with good performance characteristics at moderate temperatures. Another difference between the amino-formaldehyde oligomers with peroxide groups and the peroxide materials based on epoxy or phenol-formaldehyde resins is that the former are synthesized in one stage.<sup>18,19</sup> The starting materials for the synthesis of the amino-formaldehyde oligomers with peroxide groups are urea or melamine. *tert*-Butyl hydroperoxide or *tert*-butyl peroxyethanol are the reactants responsible for introducing labile –O–O– bonds into the oligomer structure.<sup>18,19</sup>

Synthesis of urea-based amino-formaldehyde oligomers has been reported in our previous work.<sup>18</sup> This study aims at investigating the initiating and cross-linking properties of the urea-formaldehyde oligomers with peroxide groups.

### 2. Experimental

#### 2.1. Materials

A urea-formaldehyde oligomer based on urea, formaldehyde, and *tert*-butyl peroxyethanol (Oligomer I) was synthesized as reported earlier.<sup>18</sup> For Oligomer I, it was found: molecular weight ( $M_n$ ) of 280 g/mol, content of active oxygen of 5.6 %, and content of methylol groups of 31.2 %.

A urea-formaldehyde oligomer based on urea, formaldehyde, and *tert*-butyl hydroperoxide (Oligomer II) was synthesized using the same technique as for Oligomer I.<sup>18</sup> For Oligomer II, it was found:  $M_n$  of 370 g/mol, content

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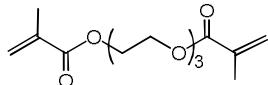
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of active oxygen of 7.1 %, and content of methylol groups of 19.8 %.

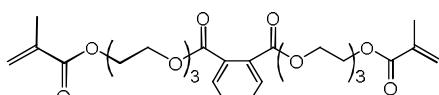
Oligomer III which does not contain nitrogen atoms in its structure was studied for comparison with the properties of Oligomers I and II. Oligomer III was synthesized from the epoxy resin Epidian-5 ( $M_n$  of 390 g/mol, epoxy groups content of 20.0 %) and *tert*-butyl hydroperoxide ( $n_D^{20} = 1.4006$ ,  $n_4^{20} = 0.8961$ ). 12.6 g (0.14 mol) of *tert*-butyl hydroperoxide and 25 mL of anhydrous benzene were loaded in a three-necked reactor equipped with a mechanical stirrer, a thermometer and an addition funnel. The mixture was cooled to 274–278 K and 0.06 g ( $4.2 \cdot 10^{-4}$  mol) of boron trifluoride etherate was added at vigorous stirring. To the resulting mixture, a solution of 10 g of the epoxy resin Epidian-5 in 30 mL of anhydrous benzene was added dropwise at 313 K for 1.5 hours. The reaction mixture was agitated at this temperature for additional 0.5 hours and then washed with an aqueous solution of sodium hydroxide and water. The solvents were distilled off and the residue formed was kept in vacuum at 333–338 K and residual pressure of 1–3 hPa until a constant weight. 13.9 g of Oligomer III was obtained (yield 93.7 %). For Oligomer III, it was found:  $M_n$  of 680 g/mol, content of active oxygen of 4.5 %.

Oligoesteracrylate TGM-3 (triethylene glycol dimethacrylate) of the formula



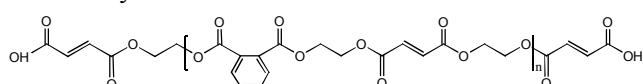
of technical grade was used without further purification.

Oligoester MGP-9 ( $\alpha,\omega$ -methacryl(bis-triethylene glycol) phthalate) of the formula



of technical grade was used as received.

Polyester PE-246 of the formula



had  $M_n$  of 1400 g/mol and acid value of 39.7 mg KOH/g.

Styrene was purified by vacuum distillation at 322–323 K and residual pressure of 1–3 hPa.

## 2.2. Methods

**EPR-method.** EPR-spectra were recorded using a RadioPANSE/x-2543 spectrometer (Poland) with a working frequency of 9500 MHz.

A solution containing an oligomer with peroxide groups, styrene, and 2,2,6,6-tetramethylpyridine-1-oxyl was loaded into an ampoule with a diameter of 4 mm, degassed with argon, vacuumized, sealed, and put into a thermostated resonator of an EPR spectrometer. The rate

of nitroxyl radical consumption was calculated by the method of least squares using corresponding software.

### Cross-linking properties.

Mixtures consisting of an oligomer with peroxide groups and an unsaturated oligoester were prepared by dissolving in acetone to a concentration of 30 %. The mixtures were vacuumized and heated up to a corresponding temperature. The formed samples were ground and extracted with acetone in a Soxhlet apparatus for 20 hours.

### 2.3. Spectral method

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

## 3. Results and Discussion

As shown above, oligomeric substances with labile –O–O– bonds in their structure can serve as a source of free radicals at certain temperatures. Therefore, such substances can be applied as initiators in polymerization of monomers or as cross-linkers of mixtures containing unsaturated polymers. Moreover, the characteristic feature of the oligomers with peroxide groups is that free radicals formed upon the decomposition of the –O–O– bonds contain structural moieties of the initial oligomer and, thus, they can affect the properties of the final items (polymers) through the initiation and cross-linking processes.

The urea-formaldehyde oligomers synthesized via the condensation reaction of urea with formaldehyde and *tert*-butyl peroxymethanol (Oligomer I) and urea, formaldehyde and *tert*-butyl hydroperoxide (Oligomer II) contain labile –O–O– bonds in their structure. Moreover, unlike the known phenol-formaldehyde oligomers<sup>16,17</sup> and epoxy resin-based oligomers with peroxide groups,<sup>11</sup> the molecules of Oligomers I and II contain nitrogen atoms in their structure, which can affect the thermal stability of –O–O– bonds in these structures.

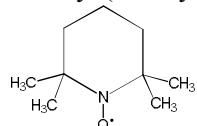
### 3.1. Initiating properties

Initiating properties of the urea-formaldehyde oligomers with peroxide groups have been studied by the case of Oligomer II using styrene as a monomer. In order to clarify the impact of nitrogen atoms in Oligomer II on its initiating activity, we have also examined initiating activity of the oligomer with peroxide groups which does not contain nitrogen atoms in its structure (Oligomer III) in the polymerization of styrene.

Initiating properties of the above-mentioned oligomers have been explored by electronic paramagnetic resonance (EPR), which allows detecting free radicals in

amounts up to  $10^{-12}$  mol/L<sup>21</sup> according to the technique described in subsection 2.2.

The method of radical accentuation has been used to determine the rates of initiation and decomposition of peroxide groups. A stable nitroxyl radical 2,2,6,6-tetramethylpiperidine-1-oxyl (nitroxyl) of the formula

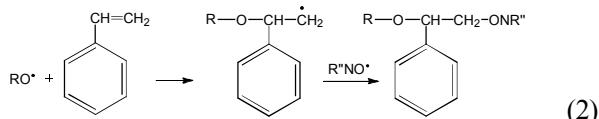


has served as a radical acceptor.

A peroxide group is known to decompose upon heating to form two alkoxyl radicals:<sup>20</sup>



The nitroxyl radicals do not react directly with the alkoxyl radicals formed in Eq. (1). The former can only react with alkyl radicals formed by the addition of the free radicals to double bonds in the monomer molecules.<sup>20,21</sup>



Under the experimental conditions, all alkoxyl radicals are consumed in formation of alkyl radicals. Hence, it can be assumed that the consumption rate of the nitroxyl radicals ( $V_{NO}$ ) should be equal to the initiation rate ( $V_{in}$ ).<sup>20,21</sup>

$$V_{NO} = V_{in} \quad (3)$$

When the concentration of the nitroxyl radicals is sufficiently high, their consumption rate does not depend on their concentration. The consumption rate is only determined by the decomposition rate of the oligomer with

**Table 1.** Effective rate constants and activation energy for the initiation and the decomposition of the oligomers with peroxide groups

Oligomer	Temperature, K	$\frac{V_{in}(V_d) \cdot 10^7}{K_{ef} \cdot 10^7, \text{s}^{-1}}$ , L/mol·s		$K_{av} \cdot 10^7, \text{s}^{-1}$	$E_a, \text{kJ/mol}$
		at the peroxide group concentration, mol/L 0.1	0.2		
II	333	<u>0.458</u> 4.58	<u>0.853</u> 4.30	4.44	95.6
	343	<u>1.09</u> 10.9	<u>2.90</u> 14.50	12.70	
	353	<u>6.78</u> 67.8	<u>15.2</u> 76.0	71.90	
	363	<u>16.8</u> 168.0	<u>37.3</u> 186.5	177.25	
III	343	<u>0.278</u> 2.78	<u>0.607</u> 3.04	2.91	99.7
	353	<u>0.929</u> 9.29	<u>1.65</u> 8.25	8.77	
	363	<u>3.43</u> 34.3	<u>5.67</u> 28.4	31.35	
	373	<u>8.17</u> 81.7	<u>13.71</u> 68.6	75.15	

peroxide groups ( $V_d$ ). In the experimental curve of the nitroxyl radical consumption, this corresponds to a straight line segment, from the slope of which one can determine the consumption rate of the nitroxyl radicals.

Taking into account<sup>22</sup> that the value of the cage effect does not change upon entering the oligomer with peroxide groups into the formed polystyrene macromolecules and assuming that the consumption rate of the nitroxyl radicals should be twice as high as the decomposition rate of the peroxide groups – as it can be seen from Eqs. (1) and (2) – one obtain:

$$V_d = V_{NO} / (2 \cdot K) = V_{vo} \quad (4)$$

where K is the coefficient of diffusion out of the cage equal to 0.5.

Based on Eq. (4), it can be assumed that, under the process conditions, the consumption rate of the nitroxyl radicals is equal to the initiation rate and the decomposition rate of the peroxide groups.

Analysis of the obtained data has revealed that the change in the nitroxyl radical consumption occurs with a constant rate. The slope of the experimental lines has allowed determining the consumption rate of the nitroxyl radicals, which corresponds to the initiation rate and the decomposition rate. The obtained results are summarized in Table 1.

Using the obtained results, the constants of the initiation (decomposition) rate of Oligomers II and III have been calculated at a corresponding concentration (Table 1) from Eq. (5):<sup>21</sup>

$$V = K \cdot [A]^n \quad (5)$$

where n is the reaction order with respect to substance A.

Analysis of the results in Table 1 has revealed that the presence of nitrogen atoms in the molecules of Oligomer II enhances the initiating properties when compared with Oligomer III which does not contain such atoms.

### 3.2. Cross-linking properties

Cross-linking properties of the urea-formaldehyde oligomers with peroxide groups have been examined by the case of unsaturated oligoesters. Oligomers I and II have been applied in this study. Polyesters TGM-3, MGP-9, and PE-246 have served as substances with unsaturated double bonds.

The development of three-dimensional structures has been monitored through the gel-fraction content. The results obtained are given in Figs. 1 and 2 and in Table 2.

It is clearly seen from Figs. 1 and 2 that the content of insoluble substances in the cross-linked samples depends on the ratio of the initial ingredients, temperature, duration of the cross-linking process, and the oligoester nature. The highest content of insoluble substances has been achieved by using TGM-3 and MGP-9 oligoesters.

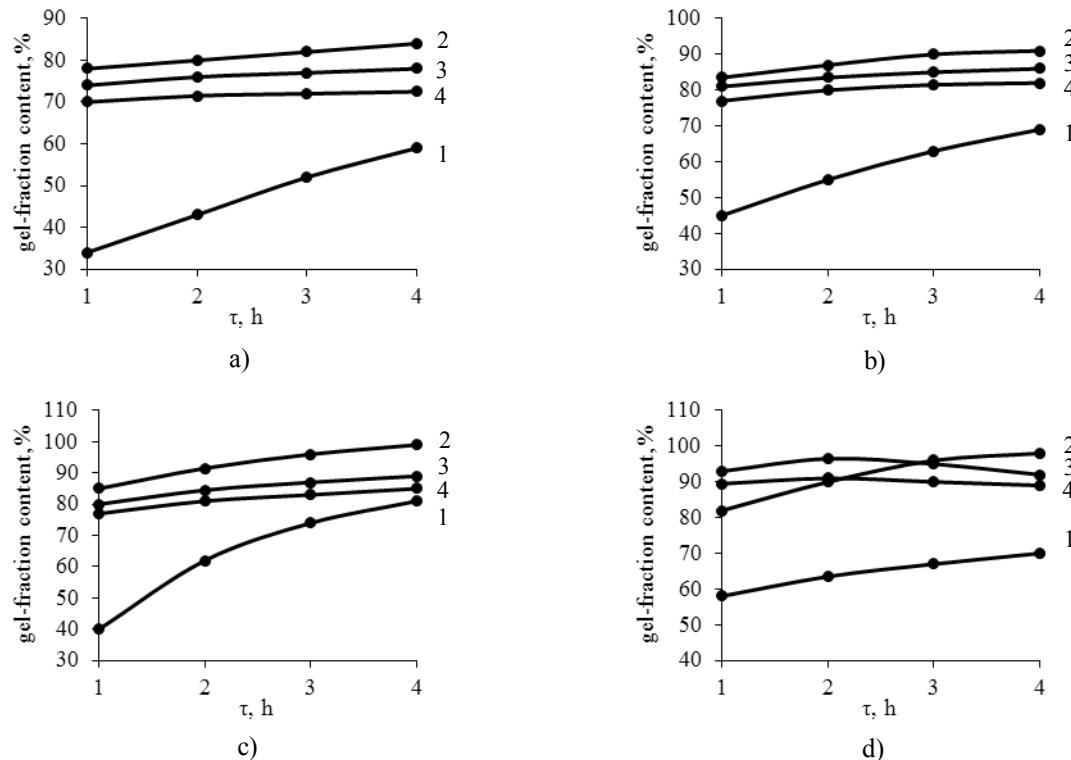
IR spectroscopic studies of both pure Oligomer I and mixtures consisting of Oligomer I and the oligoesters have been conducted in order to clarify the chemistry of

the development of the substances with a cross-linked structure (Figs. 3 and 4).

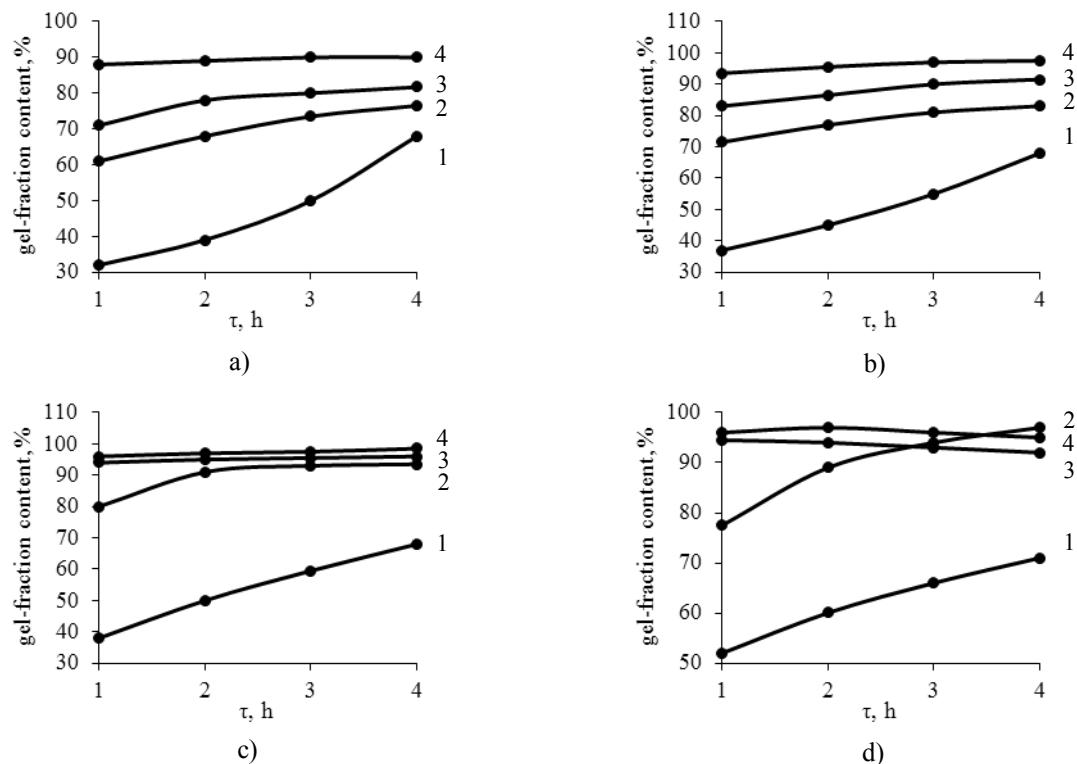
Monitoring of the structural changes has been carried out using the absorption bands at  $840\text{ cm}^{-1}$  ( $\nu_{OO}$ ),  $1190\text{ cm}^{-1}$  ( $\nu_{CO}$ ),  $1385$ ,  $1365\text{ cm}^{-1}$  ( $\delta_{(CH_3)_3C}$ ), Amide I, Amide II,  $3300\text{ cm}^{-1}$  ( $\nu_{OH}$ ), and  $1015$ – $1000\text{ cm}^{-1}$  ( $\nu_{CO}$ ) which are characteristic for the urea-formaldehyde oligomers with peroxide groups. In our case, monitoring of the double bonds of the oligoesters at  $1650$ – $1640\text{ cm}^{-1}$  is complicated due to the overlap with the absorption band of the tertiary amide, which is formed by the interaction between the  $-\text{NH}$  and  $-\text{CH}_2\text{OH}$  groups at heating. To this end, the changes in the double bond content during cross-linking has been analyzed using the absorption band at  $985$ – $980\text{ cm}^{-1}$  which corresponds to the out-of-plane bending vibrations of the  $-\text{CH}$  group in a *trans*– $-\text{CH}=\text{CH}-$  bond.

The obtained results have indicated that, at  $413\text{ K}$ , the absorption bands at  $840$ ,  $1190$  and  $1385$ ,  $1365\text{ cm}^{-1}$  attributed to the  $-\text{O}-\text{O}-$  group completely disappear in the spectrum of the oligomer with peroxide groups.

In addition, we have observed a change in the intensity of the absorption bands of Amide I ( $1660\text{ cm}^{-1}$ ), Amide II ( $1540\text{ cm}^{-1}$ ), and the methylol groups ( $1015$ – $1000\text{ cm}^{-1}$ ) which implies the interaction between the primary and secondary amino groups and the methylol derivatives in the oligomer molecules (Fig. 3).



**Fig. 1.** Kinetic curves of the cross-linking of the mixtures based on Oligomer I and oligoester TGM-3 at  $373$  (1),  $393$  (2),  $413$  K (3), and  $433$  K (4) and a content of Oligomer I in the initial mixture of  $10$  (a),  $25$  (b),  $50$  (c), and  $75$  wt % (d)



**Fig. 2.** Kinetic curves of the cross-linking of the mixtures based on Oligomer I and oligoester PE-246 at 373 (1), 393 (2), 413 (3), and 433 K (4) and a content of Oligomer I in the initial mixture of 10 (a), 25 (b), 50 (c), and 75 wt % (d)

**Table 2.** Gel-fraction content in the mixtures based on Oligomer II

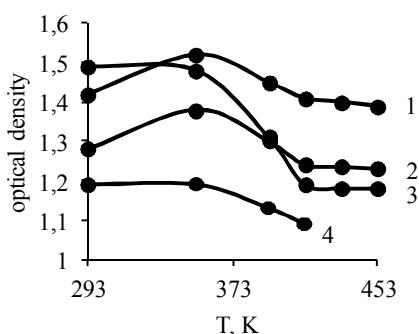
Cross-linking temperature, K	Time, hours	Oligomer II : TGM-3, mass parts			Oligomer II : MGP-9, mass parts			Oligomer II : PE-246, mass parts		
		5 : 95	10 : 90	20 : 80	5 : 95	10 : 90	20 : 80	5 : 95	10 : 90	20 : 80
373	0.5	80.4	84.6	83.7	86.9	79.3	77.6	0	18.0	10.7
	1.0	94.9	96.7	87.1	89.7	88.5	81.3	0	26.2	28.3
	1.5	95.5	97.1	90.0	88.9	88.9	82.6	0	30.8	34.0
	2.0	97.0	98.3	90.4	90.2	90.3	84.1	15.1	41.6	38.2
	3.0	99.9	99.8	90.6	90.7	90.6	86.5	36.7	46.5	51.5
383	0.5	87.5	85.8	84.1	85.6	86.8	80.1	10.5	22.6	12.3
	1.0	90.3	92.8	85.2	91.0	88.1	83.2	23.8	33.6	36.2
	1.5	95.8	98.5	86.1	91.8	89.6	85.8	35.9	40.4	56.8
	2.0	99.6	99.1	86.2	94.6	91.5	87.4	42.7	53.0	60.1
	3.0	99.8	99.7	86.8	97.7	91.8	93.8	50.5	60.9	62.8
393	0.5	97.4	81.3	83.0	93.6	81.4	77.7	39.2	51.0	48.5
	1.0	99.0	81.5	86.1	94.0	87.3	78.5	47.9	52.6	51.6
	1.5	99.7	88.0	86.9	95.2	92.9	79.6	53.4	55.1	52.3
	2.0	99.8	92.4	87.7	96.8	93.2	82.4	57.8	58.6	61.7
	3.0	99.8	96.8	87.9	96.8	94.0	86.1	61.1	67.3	69.6

These findings allow us to conclude that the cross-linking of the urea-formaldehyde oligomers with peroxide groups occurs due to both the decomposition of the labile  $-O-O-$  bonds and various condensation reactions occurring between the functional groups of the oligomer.

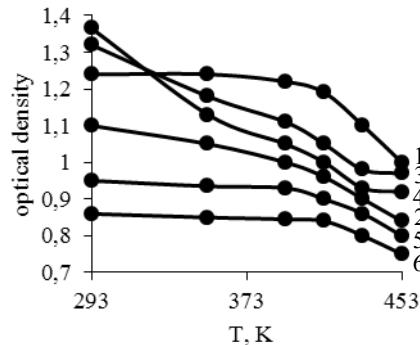
In the case of the cross-linking of the mixtures based on urea-formaldehyde oligomers with peroxide groups (Fig. 4), we have observed a significant decrease in the intensity of the absorption bands at  $985\text{-}980\text{ cm}^{-1}$  attributed to the bending vibrations of the double bonds in

the oligoesters along with the above-mentioned changes characterizing the decomposition of the  $-O-O-$  groups.

This leads to the formation of the substances having a three-dimensional structure (the data are given in Table 2).



**Fig. 3.** Optical density of the absorption bands Amide I (1), Amide (II),  $\nu_{CO}$  of the methylol groups (3), and  $\nu_{CO}$  in the COOC groups (4) of Oligomer I vs. temperature



**Fig. 4.** Optical density of the absorption bands Amide I (1), Amide II (2),  $\nu_{CO}$  of the methylol groups (3), and out-of-plane bending  $\delta_{CH}$  in *trans*-RCH=CHR' (4) of the mixtures based on Oligomer I and PE-246 as well as the absorption bands Amide I (5), Amide II (6) of the mixtures based on Oligomer I and TGM-3 vs. temperature

## 4. Conclusions

The presence of nitrogen atoms in the molecules of the urea-formaldehyde oligomers with peroxide groups enhances their initiating activity in comparison with the oligomers with peroxide groups based on Epidian-5 which do not contain such atoms.

The urea-formaldehyde oligomers are able to undergo cross-linking both themselves and in the presence of unsaturated oligoesters. Moreover, in the case of the oligoester application, the highest content of insoluble substances is achieved for TGM-3 and MGP-9 oligoesters.

The IR-studies have revealed that the cross-linking occurs due to both the decomposition of the labile bonds in the oligomers with peroxide groups and condensation reactions occurring between the functional groups of the compound containing the  $-O-O-$  bonds. In the case of the mixtures containing the oligomer with peroxide groups and the oligoester, the cross-linking occurs due to the decomposition of the labile  $-O-O-$  groups, the polymerization of the unsaturated bonds in the oligoesters initiated by the formed free radicals, and the condensation reactions between the functional groups of the mixture ingredients.

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## ІНІЦІЮЧІ ТА СТРУКТУРУЮЧІ ВЛАСТИВОСТІ СЕЧОВИНО-ФОРМАЛЬДЕГІДНИХ ОЛІГОМЕРІВ З ПЕРОКСИДНИМИ ГРУПАМИ

**Анотація.** Вивчені ініціючі властивості пероксидних сечовино-формальдегідних олігомерів. Для порівняння вивчено ініціючу активність у процесі полімеризації стирену пероксидним олігомером на основі епоксидного олігомеру *Epidian-5* та трет.-бутилгідропероксиду. Структуруючі властивості сечовино-формальдегідних олігомерів з пероксидними групами вивчені на прикладі ненасичених олігоестерів. Хімізм процесу утворення продуктів просторово-зашитої будови досліджено з використанням  $^{13}\text{C}$ -спектроскопії.

**Ключові слова:** сечовино-формальдегідні олігомери, пероксид, стирен, ненасичені олігоестери, *Epidian-5*, ініціючі та структуруючі властивості, ЕПР-метод,  $^{13}\text{C}$ -спектроскопія.