

AN OLIGOMER WITH TERMINAL UNSATURATED DOUBLE BONDS  
BASED ON EPIDIAN 5 AND ETHYLACRYLIC ACIDOlena Astakhova<sup>1, ✉</sup>, Mykhailo Bratychak Jr<sup>2</sup>, Ananiy Kohut<sup>3</sup>, Taras Chervinsky<sup>1</sup><https://doi.org/10.23939/chcht17.01.070>

**Abstract.** An oligomer with terminal unsaturated double bonds (unsaturated oligomer, UO) has been synthesized from epoxy resin Epidian 5 and ethylacrylic acid. The impact of the catalyst nature, temperature, and reaction duration on the progress of the reaction between the resin and the acid has been studied. A synthetic technique is proposed for producing the UO. The UO has been characterized by chemical and FTIR-spectroscopic analyses. The UO has been examined in the cross-linking processes with oligoesteracrylates TGM-3 and MGP-9 as well as unsaturated polyester PE-246. In order to prepare structurally colored films, unsaturated azo dyes have been additionally used. A mixture of cumene hydroperoxide and cobalt naphthenate dissolved in styrene has been utilized as an initiating system for the cross-linking of the formulations. By using FTIR-spectroscopy, the chemistry of the development of the cross-linked structures of the oligoester mixtures in the presence of the UO has been revealed.

**Keywords:** Epidian 5, ethylacrylic acid, catalysts, unsaturated oligomer, oligoesteracrylates, oligomeric mixtures, FTIR-spectroscopy.

## 1. Introduction

Low molecular weight polymers (*i.e.*, oligomers) having different functional groups in their structure are widely applied as modifiers and initiators for polymer blends.<sup>1–7</sup> Recently, epoxy resins have been used to synthesize the functional oligomers.<sup>8,9</sup> The choice of epoxy resins for the synthesis of oligomers with functional groups stems from the fact that the resins contain reactive epoxy groups in their structure, which can easily react with active hydrogen compounds of a low molecular weight.

For example, oligomers with reactive peroxide groups in their structure have been prepared *via* the chemical modification of epoxy resins with hydroperoxides. Such oligomers are usually synthesized at a temperature of 333–343 K that allows preserving the labile peroxide groups.<sup>10</sup> Benzyltriethylammonium chloride (BTEAC) is the most common catalyst of the reaction. The oligomers synthesized from epoxy resins and hydroperoxides serve as cross-linkers and initiators for oligoesteracrylates and rubbers.<sup>3,11</sup>

Oligomers with ester bonds and free terminal carboxyl groups in their structure have been produced upon the reaction of epoxy resins and saturated dicarboxylic acids.<sup>12</sup> The synthesis of these oligomers has been conducted in an isopropyl alcohol medium at a temperature of 343 K for 2.5 h using BTEAC as a catalyst. The oligomers formed are applied as cross-linkers for oligoesteracrylate-based polymer blends.<sup>13</sup>

Oligomers with terminal hydroxyl groups have been synthesized through the interaction between epoxy resins and diols.<sup>14</sup> The reaction has been carried out at a temperature of 333 K for 30 min using a catalytic mixture of BTEAC and KOH. The reaction product has contained residual epoxy groups and free primary hydroxyl groups in its structure.

The presence of free primary and secondary hydroxyl groups in the molecule of the synthesized oligomer enables the latter to be used as an additive for the formation of polymer films based on Epidian 5 and a diisocyanate. In this case, 4,4'-diphenylmethane diisocyanate has been utilized as a diisocyanate.<sup>14</sup>

On the other hand, oligomers based on epoxy resins and unsaturated acids have recently attracted much attention. Acrylic and methacrylic acids are typically used as the unsaturated acids. The esterification of the resins with the unsaturated acids is carried out at an equimolar ratio of the reactants at a temperature of 323–423 K under an inert gas blanket in the presence of polymerization inhibitors. Tertiary amines, quaternary ammonium salts,

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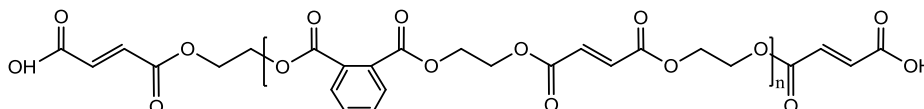
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pyridine, alkalis, *etc.*, are utilized as catalysts for these reactions.<sup>15,16</sup> The presence of the reactive terminal acrylic groups in the oligomers allows using them both individually and as additives to other polymer systems in order to form various items.

Quite interesting is the chemical modification of epoxy resins with methacrylic acid in order to preserve the epoxy group.<sup>17</sup> The reaction is carried out at a temperature of 373 K for 17 h in an inert medium using BTEAC as a catalyst. Monosubstituted reaction products synthesized in such a way serve as oligomeric monomers. In the copolymerization reaction, styrene is used as a comonomer.<sup>18</sup>

Acrylic and methacrylic acids applied for the preparation of the unsaturated oligomers are capable of homopolymerization<sup>19</sup> and the substances based thereon are unstable during storage. Therefore, this study aims at investigating the possibility of using ethylacrylic acid (EAA) as an acid component for the synthesis of oligomers with terminal unsaturated groups. According to the literature,<sup>20</sup> ethylacrylic acid is less capable of homopolymerization. This could allow synthesizing a reactive oligomer more stable during storage using ethylacrylic acid as a reactant.

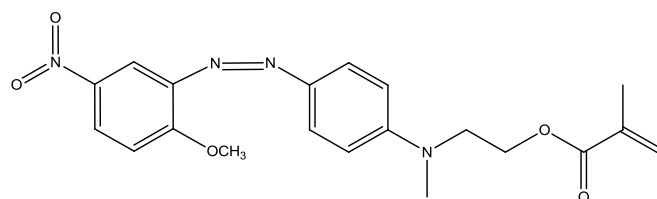
Polyester PE-246 of the formula



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

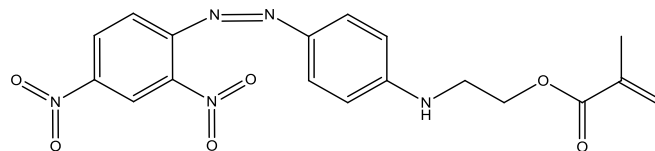
Azo dyes:

- N-methyl-N-[4-(2-methoxy-5-nitrophenyl)-azophenyl]-2-aminoethyl methacrylate



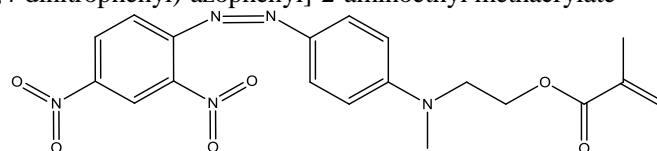
(D-1)

- N-[4-(2,4-dinitrophenyl)-azophenyl]-2-aminoethyl methacrylate



(D-2)

- N-methyl-N-[4-(2,4-dinitrophenyl)-azophenyl]-2-aminoethyl methacrylate



(D-3)

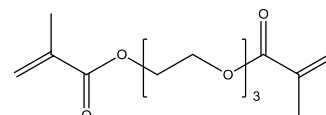
## 2. Experimental

### 2.1. Materials

Epidian<sup>®</sup>-5 (Sarzyna-Ciech) was used as an initial epoxy resin. Its molecular weight ( $M_n$ ) is 390 g/mol and content of epoxy groups (CEG) is 20.0 %.

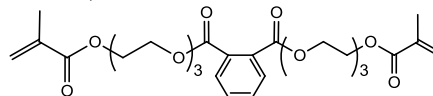
Ethylacrylic acid was synthesized according to the technique described elsewhere,<sup>21</sup> b.p. 453 K,  $n_D^{20} = 1.4375$ ,  $d_4^{20} = 1.0106$ .

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



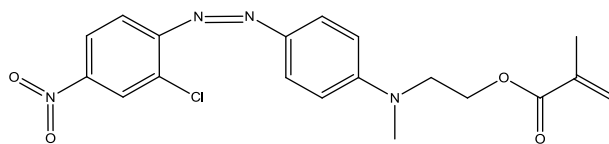
of technical grade was used without further purification (Ukraine).

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



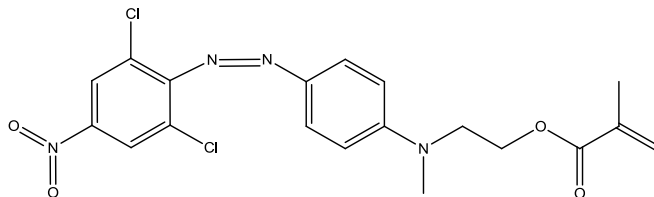
of technical grade was used as received (Ukraine).

- N-methyl-N-[4-(2-chloro-4-nitrophenyl)-azophenyl]-2-aminoethyl methacrylate



(D-4)

- N-methyl-N-[4-(2,6-dichloro-4-nitrophenyl)-azophenyl]-2-aminoethyl methacrylate



(D-5).

The azo dyes were synthesized in the laboratories at Lviv Polytechnic National University. The characteristics of the azo dyes are given in Table 1.

**Table 1.** Characteristics of the azo dyes

Azo dye	Melting point, K	Color	Characteristics of solutions	
			$\lambda_{\max}$ (toluene), nm	$\lg \varepsilon_{\max}$
D-1	392-395	Yellow	275; 429	4.08; 4.33
D-2	421-423	Red-purple	284; 513	3.99; 4.46
D-3	419-421	Red-purple	288; 505	3.94; 4.41
D-4	348-351	Ruby	284; 489	3.98; 4.44
D-5	415-418	Reddish-brown	270; 429	3.95; 4.28

Cobalt naphthenate and cumene hydroperoxide (CHP, 85 %) of technical grade were used.

Triethylamine was dried over solid sodium hydroxide and distilled. Its characteristics: boiling point 362 K (literature value 362.5 K),<sup>22</sup>  $n_D^{20} = 1.4000$  (literature value 1.4009).<sup>22</sup>

Benzyltriethylammonium chloride (BTEAC) was used as received without additional purification (Sigma-Aldrich, Germany).

Sodium hydroxide (NaOH) was used as received without additional purification (Sigma-Aldrich, Germany).

Styrene was dried before the experiments with a solid alkali and purified by distillation at 323 K under residual pressure of 300–400 Pa. Its characteristics: refractive index  $n_D^{20} = 1.5471$  (literature value  $n_D^{20} = 1.5468$ ); density  $d_4^{20} = 0.9063$  (literature value  $d_4^{20} = 0.9060$ ).<sup>23</sup>

Toluene was purchased from Aldrich. The petroleum ether was a fraction with a boiling range of 313–343 K,  $d_4^{20} = 0.650$ .

## 2.2. Analytical Methods

The iodine value (g I<sub>2</sub>/100 g) was determined as described elsewhere.<sup>24,25</sup>

The number-average molecular mass of the synthesized products were determined by cryoscopy using benzene or dioxane as a solvent.

FTIR-spectroscopic study. The FTIR-spectra of the synthesized UO were recorded using a Thermo Electron Corporation-Nicolet 8700 instrument at the spectroscopic laboratory of Gdansk University of Technology. The instrument is equipped with a Specac Golden Gate adapter and diamond crystal ATR.

To study the structural properties of the UO, the oligoester blends were applied in a thin layer over KBr plates and FTIR-spectra were recorded. Then, the plates were placed in a desiccator, held for 24 h at room temperature before more FTIR-spectra were recorded. Afterwards, the blends were heated to the corresponding temperature for a certain time. FTIR-spectra were recorded after every heating step.

Film hardness ( $H$ , rel. units) was measured by an M-3 pendulum device at room temperature according to the standard. Gel-fraction content ( $G$ , %) was determined *via* extraction of grinded samples by acetone in a Soxhlet apparatus for 12 h.<sup>26</sup>

## 2.3. Research Methods

### 2.3.1. Kinetic Study of the Reaction of Epidian 5 and EAA

Epidian 5, EAA, and a solvent were charged into a flask equipped with a mechanical stirrer, thermometer, and reflux condenser. The reaction mixture was heated to

a needed temperature and a catalyst was added under agitation. The reaction was conducted at a stoichiometric ratio of the initial reactants in a toluene medium in the presence of the catalyst (5 mol. %). After charging the catalyst, portions of the reaction mixture (1 mL) were taken at certain time intervals to determine the content of carboxyl groups by Eq. (1):

$$C_c = \frac{W_{KOH} \cdot N \cdot K}{V_s} \quad (1)$$

where  $V_{KOH}$  is the volume of a 0.1 N KOH solution expended for the sample titration, mL;  $V_s$  is a sample volume, mL;  $N$  is the normality of the KOH solution;  $K$  is a correction factor for titer of the 0.1 N KOH solution.

From the obtained data, the kinetic parameters of the interaction between Epidian 5 and EAA were calculated.

### 2.3.2. Synthetic Technique for the UO

Epidian 5 (100 g), EAA (50 g, 0.5 mol), and toluene (150 mL) were charged into a three-necked flask. Under agitation, the reaction mixture was heated to a temperature of 373 K and a BTEAC catalyst (6 g) was added. The reaction mixture was hold at 373 K for 3.5 hours, cooled to room temperature, washed with a 5 % alkali solution, and then with water until a neutral reaction. Afterwards, the solvent was distilled out and the oligomer formed was dried at 343 K and a residual pressure of 132-266 Pa until a constant weight. 140 g of the UO was obtained.

### 2.3.3. Technique for the Study of Cross-Linking Activity of the UO

The UO and an unsaturated oligoester were dissolved in styrene. CHP and a 10 % cobalt naphthenate

solution in styrene were added to the mixture of the UO and the unsaturated oligoester prior to beginning the cross-linking. The formed mixture was applied onto glass plates and subjected to heating in an air thermostat. After cross-linking, the samples were crushed and their gel fraction content, hardness, and chemical resistance were determined according to the techniques given in Subsection 2.2.

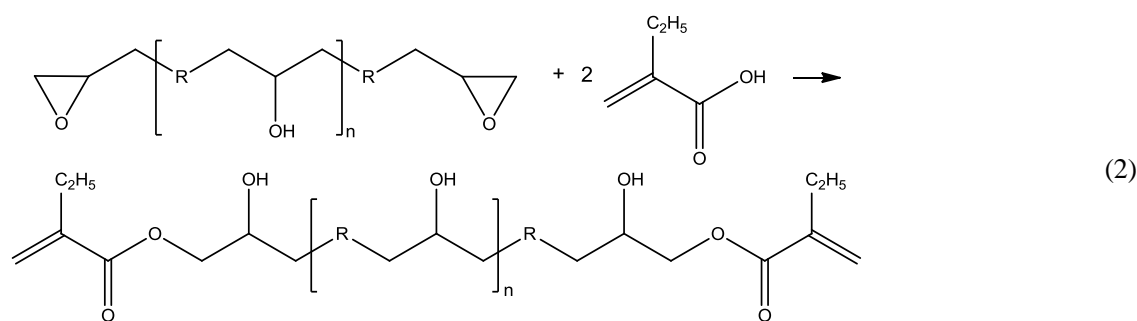
To determine the physico-chemical characteristics, the mixtures in the form of a styrene solution were applied onto steel plates. The films formed upon drying at room temperature in vacuum to a constant weight, were subjected to heat treatment in an air thermostat.

## 3. Results and Discussion

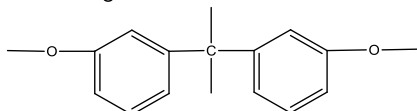
As it has been already mentioned above, both acrylic and methacrylic acids are used for the preparation of epoxy-based oligomers with unsaturated double bonds. In this work, ethylacrylic acid (EAA) is suggested as a modifier of an epoxy resin.

The choice of EAA for the synthesis of unsaturated oligomers with double bonds (UO) stems from the fact that, according to the literature,<sup>20</sup> ethylacrylic acid, unlike acrylic and methacrylic acids, is less capable of homopolymerization. This allows producing the UO in the presence of atmospheric oxygen without the use of radical polymerization inhibitors to completely replace the epoxy groups of an initial resin by the unsaturated fragments.

The reaction of the UO synthesis through the modification of the epoxy resin with EAA can be represented by Eq. (2):



where R =



Epidian 5 has been utilized as an initial epoxy resin.

In order to find out the conditions for the synthesis of the UO based on Epidian 5 and EAA, the effect of va-

rious factors on the UO yield has been studied, *i.e.*, temperature, the catalyst nature and amount, the ratio of initial reactants, and the reaction time.

### 3.1. Kinetic Features

To explore the impact of the catalyst nature, the reaction of Epidian 5 with EAA has been studied at a stoichiometric ratio of the initial reactants in a toluene medium using triethylamine (TEA), pyridine, powdered sodium hydroxide, and benzyltriethylammonium chloride (BTEAC) as a catalyst. A catalyst was added in the amount of 5 mol. % of the quantity of the initial EAA. The synthesis has been carried out at a constant temperature of 363, 373, and 383 K. The obtained results are given in Figs. 1-3 and Table 2.

The study of the effect of the catalyst nature on the rate of UO formation has revealed (Fig. 1) that sodium hydroxide is an inefficient catalyst while BTEAC is the most efficient one. The  $K_{\text{BTEAC}} : K_{\text{NaOH}}$  ratio is 9.67.

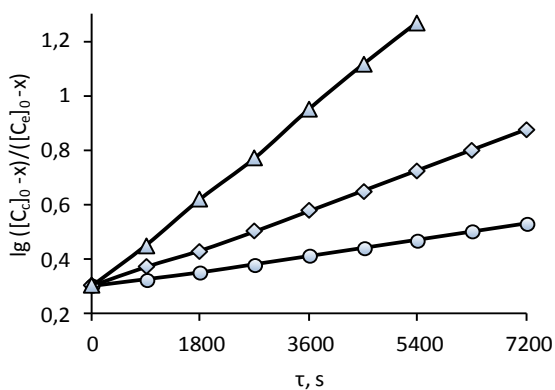
Some of the effective rate constants for the reaction of Epidian 5 with EAA in the presence of different catalysts are summarized in Table 2.

**Table 2.** Effective rate constants for the reaction of Epidian 5 with EAA in the presence of different catalysts

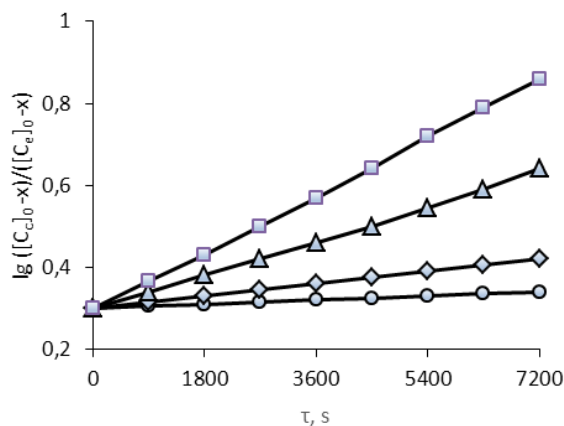
Catalyst	Temperature, K	$K \cdot 10^4, \text{L}/(\text{mol} \cdot \text{s})$
TEA	373	0.98
Pyridine	373	2.12
NaOH	373	0.43
BTEAC	363	1.58
BTEAC	373	3.49
BTEAC	383	8.21

Note: the accuracy of determining  $K$  is  $\pm 0.05 \cdot 10^{-4} \text{L}/(\text{mol} \cdot \text{s})$

The study of the effect of temperature on the reaction has shown (Fig. 2) that, with increasing temperature, a rise in the rate of the reaction of Epidian 5 with EAA has been observed. It is clearly seen from Fig. 2 that 373 K is an optimal and sufficient temperature for the process since energy consumption increases at higher temperatures.

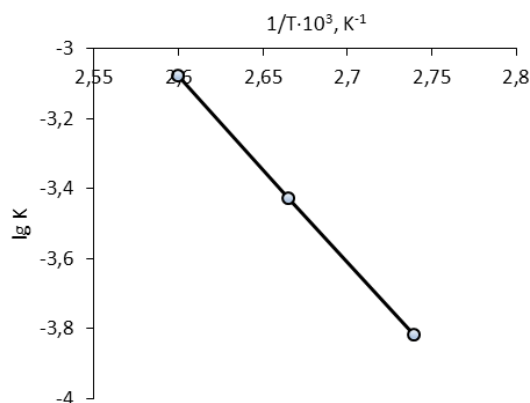


**Fig. 2.** Semi-logarithmic anamorphoses of the interaction between Epidian 5 and EAA at a temperature of 363 (○), 373 (◇), and 383 (▲) K in the presence of 5 mol. % of BTEAC of the quantity of EAA in a toluene medium



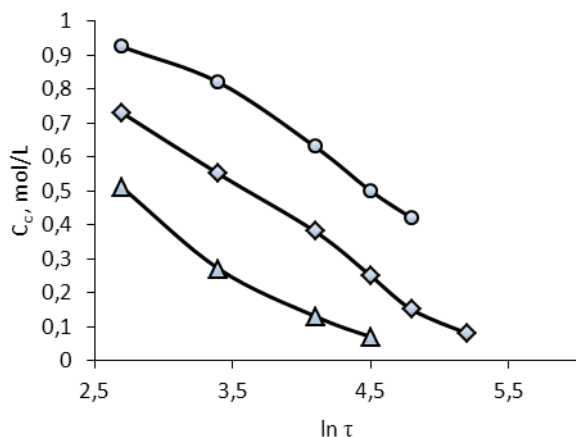
**Fig. 1.** Semi-logarithmic anamorphoses of the interaction between Epidian 5 and EAA at a temperature of 373 K in the presence of NaOH (○), TEA (◇), pyridine (▲), and BTEAC (□) as a catalyst in the amount of 5 mol. % of the quantity of EAA in a toluene medium

The interpretation of the values of the reaction rate constants in Arrhenius coordinates (Fig. 3) has allowed determining the effective activation energy of the interaction between Epidian 5 and EAA in the presence of BTEAC in a toluene medium. Its value has been found to be 95.8 kJ/mol.



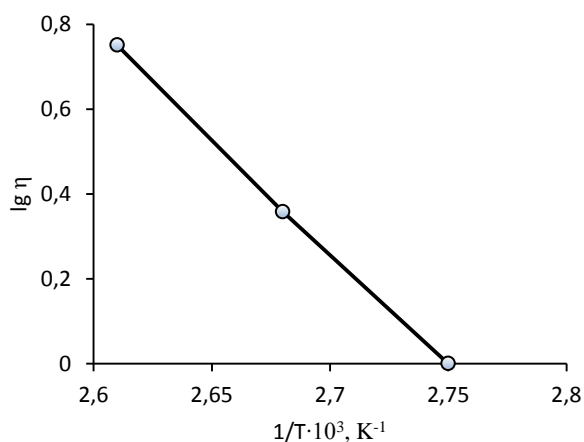
**Fig. 3.**  $\lg K$  vs.  $1/T$  for the reaction of Epidian 5 with EAA in toluene at the content of BTEAC of 5 mol. % of the quantity of EAA

In order to verify these findings, the transformation method has been applied. The dependencies obtained by using the transformation method are shown in Figs. 4-6. The results in  $C_c - \ln \tau$  coordinates given in Fig. 4 have enabled to calculate transformation coefficients ( $\eta$ ).



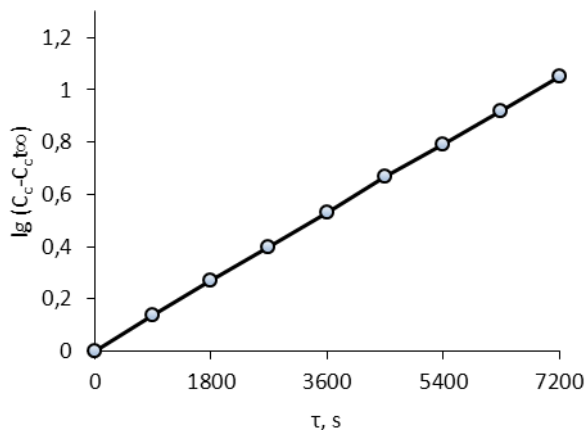
**Fig. 4.** Dependence of the carboxylic group content change on  $\ln \tau$  at a temperature of 363 ( $\circ$ ), 373 ( $\diamond$ ), and 383 ( $\blacktriangle$ ) K in a toluene medium at a molar ratio of Epidian 5 : EAA as 1 : 2 and a BTEAC concentration of 5 mol. % of the quantity of EAA ( $\tau$  [min])

The linear dependence of  $\lg \eta$  on  $1/T$  (Fig. 5) indicates that the effective activation energy of the process is constant in the studied temperature range (363-383 K). The effective activation energy determined from Fig. 5 is 98.8 kJ/mol. This value is very close to the value of the effective activation energy calculated from Fig. 3 (95.8 kJ/mol).



**Fig. 5.** Dependence of  $\lg \eta$  on  $1/T$  for the reaction of Epidian 5 with EAA in toluene at the content of BTEAC of 5 mol. % of the quantity of EAA

From the findings shown in Fig. 6, it can be concluded that the reaction of Epidian 5 with EAA is characterized by the first order in respect to the acid.



**Fig. 6.** Dependence of  $\lg (C_c - C_c(\infty))$  on  $\tau$  at a temperature of 373 K in toluene at a molar ratio of Epidian 5 : EAA as 1 : 2 and a BTEAC concentration of 5 mol. % of the quantity of EAA

The obtained kinetic findings have been used to develop a synthetic technique for producing the UO based on Epidian 5 and EAC. The technique for synthesis of the UO is given in Subsection 2.3.2. The synthesized UO has a molecular weight of 540 g/mol as determined cryoscopically in benzene, an iodine number of 94.27 g  $I_2/100$  g of the product, and a saponification number of 198.28 mg KOH/g of the product.

The UO is a light yellow viscous substance soluble in acetone, benzene, and other organic solvents. The absence of free epoxy and carboxyl groups in the oligomer structure has been proven by chemical methods of analysis. The UO is shelf-stable.

### 3.2. FTIR-Spectroscopic Characteristics of the UO

In the FTIR-spectrum of the UO (data not shown), there is an absorption band at  $1620 \text{ cm}^{-1}$  corresponding to the  $C=C$  stretching vibrations. The absence of an absorption band at  $910 \text{ cm}^{-1}$  indicates complete replacement of the epoxy groups by the unsaturated fragments. Moreover, an absorption band at  $1175 \text{ cm}^{-1}$  corresponding to the  $C-O$  group has been also found in the spectrum. The presence of the carbonyl group ( $C=O$ ) has been confirmed by an absorption band at  $1710 \text{ cm}^{-1}$  which implies that the UO structure contains ester groups. The formation of secondary hydroxyl groups as well as the presence of these groups in the initial Epidian 5 has been proven by the presence of a broad absorption band at  $3360 \text{ cm}^{-1}$  in the spectrum.

### 3.3. Oligomer Mixtures

Epoxy resin-based items are known to exhibit high physical and mechanical properties along with resistance

to aggressive environments.<sup>26</sup> Combining epoxy resins with various polymers (oligomers) allows improving the properties of the latter. Mixtures based on epoxy resins with unsaturated oligomers have recently attracted much attention. In order to develop items with satisfactory physical and mechanical properties as well as chemical resistance to aggressive environments, all ingredients of the mixture are needed to be chemically linked together into a single three-dimensional polymer. In this regard, epoxy resins are modified with unsaturated acids, in particular acrylic and methacrylic acids.<sup>26</sup> The developed epoxy acrylates are characterized by higher elasticity, lower brittleness, enhanced strength, heat resistance, and adhesion as compared with the native epoxy resins. Modification of epoxy resins with unsaturated acids enables the formation of items through the three-dimensional polymerization of the double bonds of the epoxy acrylate and unsaturated compounds. Various hydroperoxides are utilized as initiators of such processes. In order to reduce the temperature of three-dimensional polymerization, the salts of metals with variable valence are usually added.

Similarly to epoxy acrylates, the synthesized UO contains unsaturated double bonds in its structure. This allows using the UO for formation of items by combining the UO with industrial oligoesters.

In order to prepare oligoester mixtures, unsaturated oligoesters PE-246, MGP-9, and TGM-3 have been used besides the UO. The oligoester characteristics are given in Section 2. A mixture of cumene hydroperoxide (CHP) and a 10 % cobalt naphthenate solution in styrene has been utilized as an initiator for the development of cross-linked structures. The composition of the oligoester mixtures is given in Table 3.

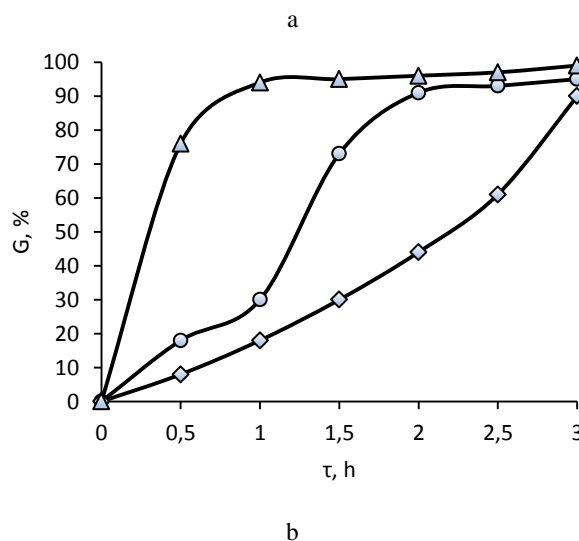
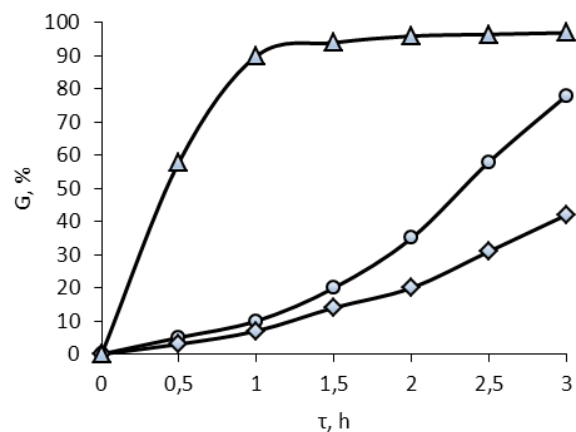
**Table 3.** Composition of the oligoester mixtures

Ingredients	Ingredient content, weight parts		
	I	II	III
UO	30	30	30
MGP-9	30		
TGM 3		30	
PE-246			30
Styrene	30	30	30
Cumene hydroperoxide	2.7	2.7	2.7
Cobalt naphthenate	7.3	7.3	7.3

The cross-linking of the mixtures has been studied at temperatures of 333, 343, 353, and 363 K. The kinetics of the cross-linked structure formation has been monitored through the gel-fraction content. The research technique is described in Subsection 2.2. The results obtained at particular temperatures are shown in Fig. 7.

The study has revealed that the maximum gel fraction content has been reached with an increase in tempera-

ture, in particular at 363 K. However, a rapid decomposition of the CHP hydroperoxide groups has occurred thereat, thus leading to foaming of the mixture. Lowering the temperature to 333 K practically has not affected the gel fraction content in mixture III; however, in all other mixtures, the content of insoluble products has not exceeded 33 % after cross-linking for 3 hours. Increasing the temperature to 343 and 353 K (Fig. 7) has resulted in the higher gel fraction content in the mixtures based on oligoesteracrylates TGM-3 and MGP-9 (mixtures II and I, respectively).



**Fig. 7.** Dependence of the gel-fraction content (%) on the mixture composition and cross-linking time at 343 K (a) and 353 K (b): mixture I (○), mixture II (◇), and mixture III (▲)

In order to clarify the chemistry of the cross-linked structure formation in the mixtures, FTIR-spectra have been recorded for mixture II (composition is given in Table 2). Control over structural changes has been carried out by monitoring the absorption band at  $1635\text{ cm}^{-1}$ , which corresponds to the double bond stretching vibra-

tions, and the absorption band at  $940\text{ cm}^{-1}$ , which characterizes the CH deformation vibrations in the *trans*-HC=CH- group.

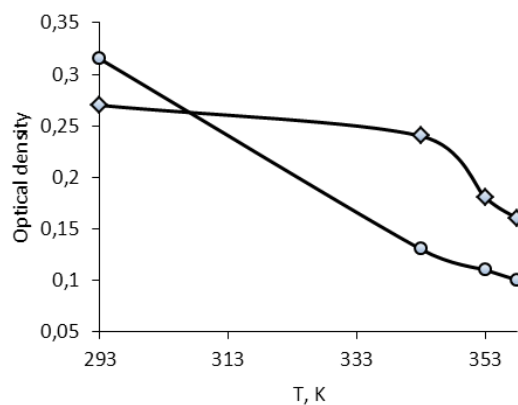
A comparison of the FTIR-spectra of mixture II at 293 K and after heating to 358 K has shown that they are not identical (Fig. 8). It has been found that, after heating the mixture to 358 K for 1.5 hours, a significant decrease in the intensity of the absorption bands corresponding to stretching and deformation vibrations of the carbon-carbon double bonds has been observed. It is clearly seen from Fig. 9 that, after heating the mixture to a temperature of 343 K for 4.5 hours, the absorption band at  $1635\text{ cm}^{-1}$  has almost completely disappeared. This implies the disappearance of the double bonds due to their reaction leading to the formation of cross-linked products as also evidenced by Fig. 8.

This confirms that the double bonds of the oligoester mixture ingredients react to form cross-linked structures.

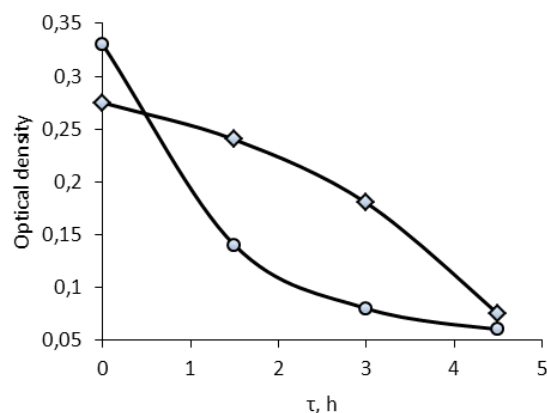
From these findings, it has been concluded that the cross-linking of the mixtures, the composition of which is given in Table 2, should be first conducted at room temperature for 24 hours, and then at a temperature of 353 K for 2.5 hours.

Some characteristics of the films formed from the studied mixtures are given in Table 4.

The data in Table 4 indicate the possibility of using the synthesized UO as an active additive of oligoester mixtures containing unsaturated polymer PE-246 and oligoesteracrylates TGM-3 and MGP-9. The polymer films formed with utilizing the UO exhibit satisfactory physical and mechanical properties along with chemical resistance to aggressive environments.



**Fig. 8.** Dependence of the optical density of the absorption bands  $\nu_{C=C}$  at  $1635\text{ cm}^{-1}$  (○) and  $\delta_{CH}$  at  $940\text{ cm}^{-1}$  (◇) in mixture II on temperature at cross-linking time of 1.5 hours



**Fig. 9.** Dependence of the optical density of the absorption bands  $\nu_{C=C}$  at  $1635\text{ cm}^{-1}$  (○) and  $\delta_{CH}$  at  $940\text{ cm}^{-1}$  (◇) in mixture II on cross-linking time at a temperature of 343 K

**Table 4.** Physical and mechanical characteristics and chemical stability of the films based the oligoester mixtures

Mixture number from Table 3	Cross-linking degree, %	Hardness by M-3, rel. units	Strength		Chemical stability (days) in a medium			
			bending, mm	impact, J	5 % NaOH solution	3 % CH <sub>3</sub> COOH solution	3 % NaCl solution	H <sub>2</sub> O
I	93.2	0.88	1	5	10	10	10	10
II	99.8	0.81	1	5	10	10	10	10
III	97.2	0.97	1	5	2, peeling	10	10	10

### 3.4. Structurally Colored Mixtures

For coloring items based on epoxy resins and epoxy acrylates, azo compounds D-1–D-5 have been used as dyes. The dye's characteristics are given in Subsection 2.1.

When utilized in the development of items based on common polymers, these azo dyes are not chemically included into the structure of the polymeric items. This leads to deterioration of their color during operation.

In order to enhance the item color, it has been suggested to explore the possibility of using the synthesized UO and industrial oligoesters for the chemical bonding of the azo dyes. Similarly to the oligoester mixtures, a cross-linking system based on TGM-3 and MGP-9 has been applied. Styrene has been used to dilute the mixture. CHP has been utilized as a polymerization initiator. Cobalt naphthenate (CN) in the form of a 10 % styrene solution served as an accelerator of the cross-linking process. The composition of the mixtures is given in Table 5.



**Table 5.** Composition of the colored mixtures

Ingredients	Ingredient content, weight parts									
	I	II	III	IV	V	VI	VII	VIII	IX	X
UO	30	30	30	30	30	30	30	30	30	30
TGM-3	30	30	30	30	30					
MGP-9						30	30	30	30	30
Styrene	30	30	30	30	30	30	30	30	30	30
CHP	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
CN	7.3	7.3	7.3	7.3	7.3	7.3	7.3	7.3	7.3	7.3
D-1	0.1					0.1				
D-2		0.1					0.1			
D-3			0.1					0.1		
D-4				0.1					0.1	
D-5					0.1					0.1

**Table 6.** Gel fraction content in the colored oligoester mixtures (wt. %)

Cross-linking temperature, K	Cross-linking time, hours	Formulation number from Table 5	
		II	VII
343	0.5	8.4	12.4
	1.0	11.3	19.7
	1.5	14.2	24.3
	2.0	23.3	29.6
	2.5	34.3	36.5
	3.0	48.9	41.4
353	0.5	12.1	14.9
	1.0	23.5	25.7
	1.5	35.8	38.3
	2.0	55.7	43.7
	2.5	70.8	50.6
	3.0	92.6	55.8

**Table 7.** Physical and mechanical characteristics and chemical stability of the coatings based on the colored oligoester mixtures

Mixture number from Table 5	Cross-linking degree, %	Hardness by M-3, rel. units	Bending strength, mm	Chemical stability (days) in 5 % NaOH solution	Coating color
I	99.0	0.89	1	15	Yellow
II	99.8	0.84	1	15	Red
III	99.7	0.86	1	15	Red
IV	99.5	0.79	1	15	Ruby
V	99.8	0.90	1	15	Reddish-brown
VI	94.7	0.85	3	15	Yellow
VII	94.6	0.84	3	15	Red
VIII	93.0	0.88	3	15	Red
IX	94.5	0.83	3	15	Ruby
X	93.6	0.80	3	15	Reddish-brown

The colored mixtures have been prepared by dissolving the UO, an unsaturated oligoesteracrylate, and a dye in styrene. CHP and CN have been charged into the system prior to the start of cross-linking. The gel fraction content in the cross-linked samples has been determined by extraction with acetone in a Soxhlet apparatus for 14 hours.

While exploring the effect of temperature on the gel fraction content in the structurally colored mixtures, it has been found that, at temperatures of 293–396 K, the gel fraction content has not exceeded 16.2–18.1; 22.5–24.3, and 40.7–44.6 wt. % in 24, 48, and 72 hours, respectively. An increase in temperature (Table 6) leads to an increase in the gel fraction content in the mixtures.

These findings indicate that the cross-linking of the mixtures should be carried out in stages: first at room temperature for 24 hours and then at 353 K for 2.5 hours. The characteristics of the varnish coatings developed under the above conditions are given in Table 7.

While exploring the effect of the azo dye nature on the amount of the gel fraction, it has been found that the dye nature has virtually no impact on the content of insoluble products (Table 7). However, it should be noted that the mixture color intensity is achieved at an azo dye concentration of at least 0.1 wt. %. The coatings exhibit satisfactory physical and mechanical properties along with chemical resistance to aggressive environments.

The cross-linked films remained colored even after extraction with boiling acetone whereas the solvent itself was colorless. This indicates a chemical bond between the dye molecules, which contained unsaturated bonds, with the mixture ingredients.

These outcomes indicate that the application of the UO in oligoester mixtures containing TGM-3 and MGF-9 allows producing structurally colored coatings with satisfactory physicochemical properties and chemical resistance to aggressive environments. The formation of colored films occurs due to three-dimensional polymerization involving the molecules of the UO, oligoester acrylate, styrene, and the azo dye.

## 4. Conclusions

An oligomer with terminal unsaturated groups (unsaturated oligomer, UO) has been synthesized through the reaction of the industrial epoxy resin Epidian 5 with ethylacrylic acid (EAA). The study of the kinetic features of the reaction of Epidian 5 with EAA has revealed that benzyltriethylammonium chloride (BTEAC) is the most efficient catalyst whereas sodium hydroxide is the least efficient one. From the kinetic studies, the effective activation energy of the interaction between Epidian 5 and EAA in the presence of BTEAC in a toluene medium has been determined to be 95.8 kJ/mol. In order to verify the obtained kinetic findings, the transformation method has been applied. The obtained linear dependence of  $\lg \eta$  on  $1/T$  indicates that the effective activation energy of the process is constant in the temperature range of 363–383 K and its value of 98.8 kJ/mol is very close to the experimentally found effective activation energy (95.8 kJ/mol). The conducted chemical and FTIR-spectral analyses imply that the synthesized UO does not contain residual epoxy groups in its structure and is, hence, a product with unsaturated double bonds only.

While studying the oligoester mixtures comprising of 30 weight parts of the synthesized oligomer, 30 weight parts of oligoesteracrylate (MGP-9 or TGM-3) or unsatu-

rated oligomer PE-246, 30 weight parts of styrene, 2.7 weight parts of cumene hydroperoxide as a polymerization initiator, and 7.3 weight parts of a 10 % cobalt naphthenate solution in styrene as a polymerization accelerator, film with the following characteristics have been prepared: the content of insoluble products of 93.2–99.8 %, pendulum hardness of 0.81–0.97 rel. units, bending strength of 1 mm, and impact strength of 5 J. The chemical stability of the prepared films in aggressive environments exceeded 10 days. Similar results have been obtained for the cross-linking of the above-mentioned mixtures containing an unsaturated azo dye. The chemical stability of the cross-linked azo colored coatings in aggressive environments has been found to be 15 days. Furthermore, the coatings have retained the azo dye color even after extraction with hot acetone for 14 hours. This indicates the incorporation of the azo dye molecules into the structure of the formed coating. The FTIR-spectroscopic study has confirmed that the double bonds of the polymer mixture ingredients react to form a cross-linked structure.

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### ОЛІГОМЕР З КІНЦЕВИМИ НЕНАСИЧЕНИМИ ПОДВІЙНИМИ ЗВ'ЯЗКАМИ НА ОСНОВІ EPIDIAN 5 ТА ЕТИЛАКРИЛОВОЇ КИСЛОТИ

**Анотація.** З використанням епоксидної смоли Epidian 5 та етилакрилової кислоти отримано олігомер з кінцевими ненасиченими подвійними зв'язками (ненасичений олігомер, НО). Вивчено вплив природи каталізатора, температури та тривалості процесу на перебіг реакції між смолою та кислотою. Запропоновано методику синтезу НО. НО охарактеризовано хімічним та ІЧ-спектроскопічним методами дослідження. НО вивчено в процесах структурування з олігоестеракрилатами ГТМ-3 й МГФ-9 та ненасиченим поліестром ПЕ-246. З метою одержання структурно забарвлених плівок додатково використані ненасичені азобарвники. Як ініціувальну систему в процесі структурування таких сумішей використано суміш гідропероксиду кумолу та нафтенату кобальту, розчиненого в стирені. З використанням ІЧ-спектроскопії визначено хімізм процесу формування просторовозитих структур олігоестерних сумішей в присутності НО.

**Ключові слова:** Epidian 5, етилакрилова кислота, каталізатори, ненасичений олігомер, олігоестеракрилати, олігомерні суміші, ІЧ-спектроскопія.