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SYNTHESIS AND CROSS-LINKING PROPERTIES OF MELAMINE FORMALDEHYDE OLIGOMERS WITH PEROXY GROUPS

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Abstract. Melamine formaldehyde oligomers with peroxy groups (MFOP) have been synthesized based on melamine or urea and melamine in the presence of *tert*-butyl peroxymethanol or *tert*-butyl hydroperoxide. Zinc oxide was used as a catalyst. The effect of peroxide nature, ratio of the starting components and process time on the characteristics and yield of MFOP has been studied. The structure of the synthesized MFOP was confirmed by IR- and PMR-spectroscopy. The chemistry of the cross-linked structures formation was studied. The possibility of using such oligomers as a cross-linking agent for the mixtures based on TGM-3 oligoesteracrylate is shown.

Keywords: melamine, urea, formaldehyde, oligoesteracrylate, zinc oxide, peroxide, hydroperoxide, melamine formaldehyde oligomers, IR- and PMR spectroscopy, cross-linking.

1. Introduction

Nowadays the creation of oligomers and polymers containing peroxy and other functional groups in their structure is of great attention. These compounds may be used for the production of new polymer materials or as a cross-linking agent for different composites [1-10]. To synthesize oligomers with –O–O– bonds in the structure the known commercial products are used, namely epoxy resins [11-14] and phenol-formaldehyde oligomers [15, 16].

The choice of above-mentioned compounds relates to the presence of reactive epoxy groups in their structure allowing to modify them *via* the reaction of epoxy group and compound containing mobile hydrogen atom [17-21]. Moreover, the products based on epoxy resins are characterized by good mechanical and dielectric properties, as well as high chemical stability and adhesion [18-20].

The introduction of peroxy groups into phenol-formaldehyde oligomers gives the possibility not only to extend the application area but to improve some operational properties due to the compatibility with other polymers [15, 16, 22]. The peroxy groups are introduced *via* the reaction of phenol hydroxyl groups with epoxy groups of peroxy-containing compound [15].

Apart from phenol formaldehyde oligomers, urea formaldehyde compounds are also of great interest, especially melamine formaldehyde oligomers, which are used to produce various polymeric materials [23, 24]. At the same time, they have low solubility in organic solvents and cannot be combined with majority of polymers, with oligoesteracrylate, in particular.

This work deals with the synthesis of melamine formaldehyde oligomers containing both free methylol and peroxy groups in their structure. This will allow to obtain products without the catalysts and to combine them with other polymers, namely with oligoesteracrylate.

2. Experimental

2.1. Materials

Melamine (2,4,6-triamino-1,3,5-triazine) of analytical grade was used without additional purification (mp 625.3; lit. mp 624-627 K [25]). Urea of pure grade was used without additional purification (mp 405.1 K; lit. mp 405.7 K [25]). Technical formaldehyde (methanal) was used as 38-40% aqueous solution [25].

tert-Butyl peroxy methanol (TBPM) was synthesized according to the procedure described in [26]. TBPM characteristics: $n_D^{20} = 1.4128, d_4^{20} = 0.9684$.

tert-Butyl hydroperoxide (TBHP) was synthesized according to the procedure described in [27]. After vacuum distillation at 308-310 K and residual pressure of 13-14 kPa a product with the following characteristics was obtained: $n_D^{20} = 1.4128, d_4^{20} = 0.9684$ (lit. data bp 310 K/13 kPa; $n_D^{20} = 1.4006, d_4^{20} = 0.8960$.

Zinc oxide of analytical grade was used without additional purification.

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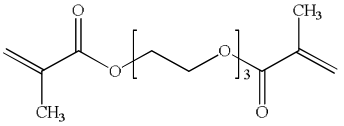
Oligoesteracrylate TGM-3 of the formula  was used as received.

2.2. Methods of Analyses

Content of active oxygen ($[O]_{act}$, %) was determined by the iodometric method [28], the content of methylol groups – by the method described in [29], molecular weight – by the isopiestic method [30].

IR spectra were measures by means of the Nicolet 8700 spectrometer (Thermo Scientific, Waltham, MA) equipped with the GoldenGate ATR accessory (Specac Ltd., Orpington, Great Britain). A single-reflection diamond crystal was used as internal reflection element of the accessory. For each spectrum 256 scans were taken with the resolution of 4 cm^{-1}. The temperature was set at 28 K with using an electronic temperature controller (Specac Ltd., Orpington, Great Britain). All spectra were collected and analyzed using the commercially available software: OMNIC (Thermo Scientific, Waltham, MA), Matlab (MathWorks, Natic, MA).

NMR spectra were recorded at 400 MHz, using Bruker Avance II 400 spectrometer (Poland) in deuterochloroform at room temperature.

2.3. Kinetic Studies

The process was studied in a three-necked reactor, which was loaded with melamine or urea and melamine, formalin, peroxide or hydroperoxide and zinc oxide. The reaction was controlled according to the consumption of one of the components of the reaction mixture. The oligomer yield was calculated in g per 100 g of starting compound.

2.4. Methods of MFOP Synthesis

Oligomer I was synthesized in a three-necked reactor, equipped with a mechanical stirrer, thermometer and backflow condenser. The reactor was loaded with 6.31 g (0.05 moles) of melamine, 45.1 g of formalin (40 % aqueous solution containing 18.0 g (0.6 moles) of formaldehyde), 36.0 g (0.3 moles) of TBPM and 0.044 g ($5.43 \cdot 10^{-4}$ moles) of zinc oxide. The reaction mixture was sustained at 343 K for 3 h and filtered. A filtrate was vaccumized for 2 h at 328–333 K and residual pressure of 1–3 hPa. 21.4 g of the product were obtained.

Oligomer II was synthesized the same as oligomer I. The reactor was loaded with 6.31 g (0.05 moles) of melamine, 47.4 g of formalin (38 % aqueous solution containing 18.0 g (0.6 moles) of formaldehyde), 36.1 g (0.4 moles) of TBHP and 0.00631 g ($7.75 \cdot 10^{-5}$ moles) of zinc oxide. 19.4 g of the product were obtained.

Oligomer III was synthesized the same as oligomer I. The reactor was loaded with 3.0 g (0.05 moles) of urea, 1.26 g (0.01 moles) of melamine, 26.25 g of formalin (40% aqueous solution containing 10.5 g (0.35 moles) of formaldehyde), 24 g (0.2 moles) of TBPM and 0.03 g ($3.69 \cdot 10^{-4}$ moles) of zinc oxide. 19.3 g of the product were obtained.

Oligomer IV was synthesized the same as oligomer I. The reactor was loaded with 3.0 g (0.05 moles) of urea, 1.26 g (0.01 moles) of melamine, 31.6 g of formalin (38 % aqueous solution containing 12.0 g (0.25 moles) of formaldehyde), 22.54 g (0.25 moles) of TBHP and 0.00426 g ($5.23 \cdot 10^{-5}$ moles) of zinc oxide. 15.7 g of the product were obtained.

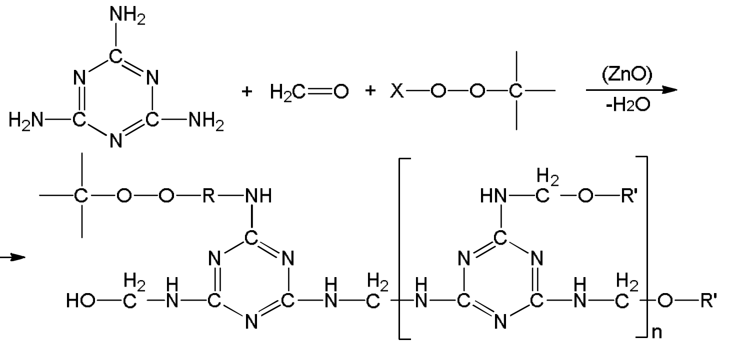
3.Results and Discussion

3.1. MFOP Synthesis

The introduction of peroxy groups into the structure of melamine formaldehyde oligomers will allow to use them for the production of composites without additional introduction of initiating additives.

Melamine formaldehyde oligomers with peroxy groups (MFOP), similar to urea formaldehyde oligomers with peroxy groups, can be obtained using *tert*-butyl peroxymethanol (TBPM) and *tert*-butyl hydroperoxide (TBHP).

The MFOP synthesis can be represented by the following equation:



(1)

where X = –H, $HOCH_2$– ; R = –CH_2–, –CH_2–O–CH_2– ; R' = –H, –$OC(CH_3)_3$, –$CH_2OOC(CH_3)_3$; n = 0–2

To determine the optimal conditions for MFOP synthesis, the effect of the nature of peroxy compound as a modifier, the starting reagents ratio and reaction time on the characteristics of the obtained oligomers, their yield and solubility in organic solvents was studied.

The research methodology is given in Experimental section.

3.1.1. MFOP synthesis in the presence of TBPM

The reaction according to Eq. (1) was studied for the melamine (M) : formaldehyde (F) : TBPM molar ratio equal to 1 : (8-18) : (4-8) for 1–5 h. The amount of zinc oxide as a catalyst was 0.7 wt% relative to the melamine content. The results are shown in Figs. 1-3.

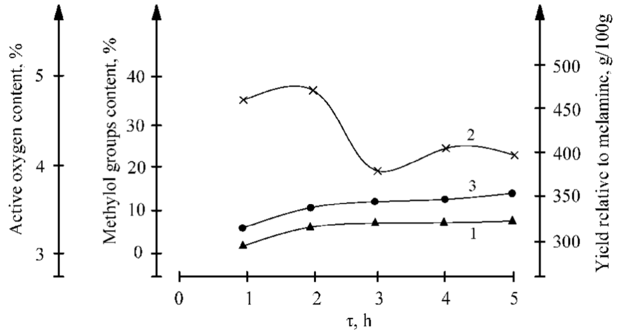


Fig. 1. Active oxygen content (1), methylol groups content (2) and oligomer yield (3) *vs.* the reaction time; M : F : TBPM molar ratio is 1 : 12 : 6; temperature is 343 K

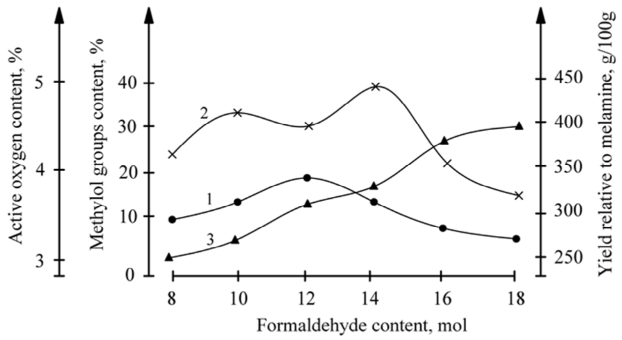


Fig. 2. Active oxygen content (1), methylol groups content (2) and oligomer yield (3) *vs.* the formaldehyde amount; M : TBPM molar ratio is 1 : 6; temperature is 343 K; reaction time is 3 h

Is obvious from Fig. 1 that oligomers synthesized at a temperature of 343 K for 3–5 h have the highest value of active oxygen content. At the same time the increase in the process time (more than 3 h) leads to a slight increase in the content of peroxide groups in the oligomer. Along with this, the yield of oligomers remains virtually unchanged. Based on this, further study of the MFOP formation reaction in the presence of TBPM was carried out for 3 h.

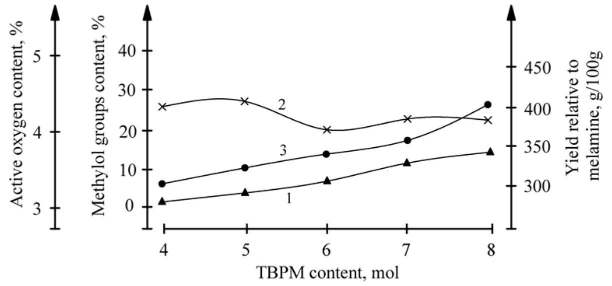


Fig. 3. Active oxygen content (1), methylol groups content (2) and oligomer yield (3) vs. the TBPM amount; M : F molar ratio is 1 : 12; temperature is 343 K; reaction time is 3 h

Analyzing the results shown in Fig. 2, we find that the increase in the formaldehyde amount from 12 to 18 moles, decreases the active oxygen content from 3.4 to 2.8 %. The results obtained can be explained based on the following considerations. The increase in the formaldehyde amount in the reaction mixture reduces the initial concentration of melamine, and this leads to a decrease in the formation rate of methylol derivatives of melamine [31]. Reducing the content of methylol groups, in turn, leads to a decrease in the content of peroxide groups that are introduced into the oligomer structure, due to the interaction of TBPM with methylol derivatives of melamine. At the same time, it should be noted that despite the increased yield of peroxide oligomers with increasing formaldehyde content in the reaction mixture, the solubility of the synthesized products in organic solvents deteriorates. This makes it possible to assume that under the studied conditions, the optimal amount of formaldehyde in the reaction mixture is 12 moles per mole of melamine.

Fig. 3 shows that an increase in the TBPM content from 4 to 8 moles leads to an increase in the active oxygen content from 3.1 to 3.7 %. But this increase is insignificant if compared to the amount of TBPM introduced into the reaction mixture. Moreover, the content of methylol groups in the oligomers indicates the achievement of the equilibrium for the reaction of TBPM and methylol derivatives of melamine. The yield of peroxide oligomers also increases by a small value. Thus, we assume that the optimal number of TBPM is 6 moles per mole of melamine.

The above results make it possible to propose the following conditions for the MFOP synthesis using TBPM:

– the M : F : TBPM molar ratio is 1 : 12 : 6;
– the temperature is 343 K;
– the process time is 3 h;

– the amount of zinc oxide is 0.7 wt% relative to the melamine content.

The synthesis procedure is described in subsection 2.4 and its characteristics is given in Table 1.

3.1.2. MFOP synthesis in the presence of TBHP

When the synthesis procedure according to Eq. (1) was developed, we took into account all regularities established for the reaction of TBHP and urea formaldehyde oligomer [26].

The synthesis was carried out at a temperature of 343 K for 3 h and M : F : TBHP molar ratio equal to 1 : 12 : 8. The amount of zinc oxide as a catalyst was 0.1 wt% relative to the melamine content. The synthesis procedure is described in subsection 2.4 and its characteristics is given in Table 1.

The usage of urea formaldehyde resins based on melamine are restricted due to their high cost. The introduction of urea fragments into oligomers allows to improve some properties of the resulting products and make cheaper their production.

Table 1

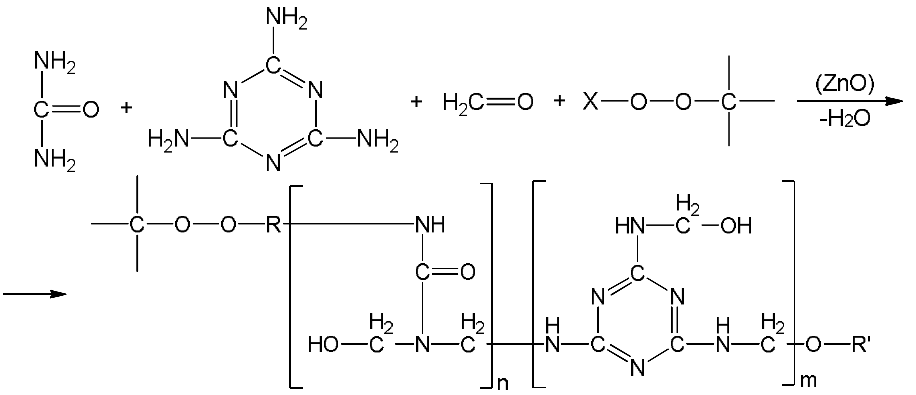
Characteristics of MFOP

Oligomer	Peroxide	Characteristics			
		$\overline{M_n}$, g/mol	$[O]_{act}$, %	Methylol groups content, %	Yield, g/100 g melamine
Oligomer I	TBPM	510	3.8	15.4	340
Oligomer II	TBHP	450	5.6	11.3	310

Notes: Oligomer I and II are solid compounds stable during storage and soluble in acetone, chloroform, benzene and other organic solvents

3.1.3. Synthesis of urea melamine formaldehyde oligomers with peroxy groups

The urea melamine formaldehyde oligomers with peroxy groups (UMFOP) are synthesized according to Eq. (2):



(2)

where X = –H, $HOCH_2$– ; R = –CH_2–, –CH_2–O–CH_2– ; R' = –H, –$OC(CH_3)_3$, –$CH_2OOC(CH_3)_3$; n = 0–3, m = 0–2

UMFOP are synthesized in one stage due to the reaction of urea, melamine and formaldehyde with TBPM or TBHP in the presence of zinc oxide.

When TBPM is used (Oligomer III), the amount of the catalyst is 0.7 wt% relative to the total amount of aminocompound, temperature is 343 K, process time is 3 h. The characteristics of the resulting oligomers at different ratios of the starting components are represented in Table 2.

The highest amount of peroxy groups is observed for Oligomer III synthesized according to the procedure described in subsection 2.4 with U : M : F : TBHP molar ratio equal to 1 : 0.2 : 7 : 4. Its characteristics is represented in Table 3.

When TBHP is used (Oligomer IV), the amount of the catalyst is 0.1 wt% relative to the total amount of aminocompound, temperature is 343 K, process time is 3 h. Oligomer IV synthesized according to the procedure described in subsection 2.4 with U : M : F : TBHP molar ratio equal to 1 : 0.2 : 8 : 5. Its characteristics is represented in Table 3.

Table 2

UMFOP characteristics depending on starting reagents ratio

Oligomer	Starting reagents, moles				Characteristics			
	U	M	F	TBPM	$[O]_{act}$, %	Methylol groups content, %	$\overline{M_n}$, g/mol	Yield, g/100 g
Oligomer III	1	0.2	7	4	5.4	24.1	490	453
Oligomer IIIa	1	0.2	10	6	4.9	32.6	470	364
Oligomer IIIb	1	0.5	16	6	3.6	33.8	440	517

Notes: U is urea; M is melamine; F is formaldehyde

Table 3

UMFOP characteristics

Oligomer	Initial peroxide	Characteristics			
		$\overline{M_n}$, g/mol	$[O]_{act}$, %	Methylol groups content, %	Yield, g/100 g
Oligomer III	TBPM	490	5.4	24.1	453
Oligomer IV	TBHP	520	5.8	13.6	370

Notes: Oligomer III and IV are viscous compounds soluble in acetone, chloroform, benzene and capable of compatibility with unsaturated oligoesters

Table 4

IR- and PMR-spectroscopic characteristics of oligomers

Oligomer	IR spectrum, cm^{-1}							ПМР-спектр, δ, м.ч.		
	—OH —NH—CO—NH—			–COC– –COH	$(CH_3)_3COO$–			$(CH_3)_3COO$–	$–NCH_2N–$ $–NCH_2O–$	–OH –(NH)–
	ν_{OH}	Amide I ν_{CO}	Amide II $\delta_{NH} + \nu_{CN}$	ν_{CO}	$\delta_{(CH_3)_3C-}$	ν_{CO} –COOC–	ν –O–O–			
Oligomer I	3300	1660	1540	1260 1115	1380 1360	1190	845	1.14	4.50–5.50	6.8–6.9
Oligomer II	3350	1660	1540	1260 1015	1385 1365	1190	850	1.13	4.70–5.50	6.95
Oligomer III	3350	1660	1540	1260 1000	1385 1365	1190	850	1.15	4.75–5.15	6.95
Oligomer IV	3400	1660	1540	1260 1000	1385 1365	1190	870	1.15	4.75–5.15	6.8–6.95

So, using TBPM or TBHP it is possible to synthesize oligomers with free –O–O– bonds and methylol groups in the structure (see Eqs. 1 and 2). Moreover, when using TBPM it is possible to increase the content of peroxy groups in oligomer and to decrease the necessary amount of the catalyst.

3.2. MFOP Structure

To confirm the structure of the synthesized oligomers, IR- and PMR-spectroscopy was used. Interpretation of the recorded spectra is represented in Table 4.

The weak absorption bands at 845 cm^{-1} in the spectrum of Oligomer I, the band at 870–850 cm^{-1} in the spectra of Oligomers II-IV, doublet of deformational vibrations $(CH_3)_3C$ groups at 1385–1360 cm^{-1} (Oligomers I-IV), as well as ν_{CO} (COOC) at 1190 cm^{-1} indicate the presence of peroxy fragments in the synthesized oligomers.

The structure is also confirmed by absorption bands Amide I (1660 cm^{-1}) and Amide II (1540 cm^{-1}); stretching vibrations of methylol groups at 3400–3300 cm^{-1} (ν_{OH}) and 1260–1000 cm^{-1} (ν_{COC}). The etheric bond is confirmed by the band at 1150–1060 cm^{-1}.

PMR-spectra confirm the presence of peroxy fragments in the synthesized oligomers. Narrow signal (singlet) in the area of 1.13–1.15 ppm which belong to the protons of $(CH_3)_3C$ group reveals this fact. The signal in the area of 4.5–5.5 ppm indicates the presence of $-NCH_2O-$ and $-NCH_2N-$ groups in the oligomers. But we failed to identify proton signals in –NH and HO– groups due to the fast exchange of protons. The signals at 6.80–6.95 ppm corresponding to HO– group were recorded due to their shift toward high field (6.75 ppm) during heating to 333 K. Position of HO– group in a weak field instead of usual arrangement is explained by the formation of strong intermolecular hydrogen bonds of –OH…N type.

The ratio of integral intensities of proton signals of $(CH_3)_3COO-$ group and the sum of proton signals of $-NCH_2O-$ and $-NCH_2N-$ groups was calculated to confirm the structure of the synthesized oligomers. The calculation results are in agreement with the results represented in Table 4.

3.3. Cross-Linking Properties of MFOP

The synthesized MFOP contain labile peroxy groups allowing to use them as a source of free radicals while heating. This property may be used for the production of oligoesteric compositions. Non-modified melamine formaldehyde oligomers have not peroxy groups in their structure and cannot be used to form cross-linked films with the participation of oligoesters [31].

The possibility of MFOP usage for the production of oligoesteric compositions was studied by the example of Oligomer I and TGM-3 oligoesteracrylate, the formula of which is represented in subsection 2.1.

Oligoesteric mixtures containing Oligomer I and TGM-3 with the ratio of 1 : 3 (w/w) were prepared due to the dissolution of mentioned compounds in chloroform till 5% solution was obtained.

To establish the chemistry of the process of films formation we used IR-spectroscopy. For this purpose, the solutions were applied over KBr plates, the solvent (chloroform) was evaporated and the plates were heated stepwise for 1 h at the temperatures of 363, 383, 403 and 423 K. After this the IR-spectra were recorded. The spectra of pure Oligomer I were recorded for the comparison. The results obtained are represented in Figs. 4 and 5.

MFOP spectra before and after heating are non-identical (Fig. 4). During heating the changes in the intensity of bands at 1445, 1385, 1365, 1200, 1000 and 875 cm^{-1} are observed, as well as the formation of new absorption band at 1705 cm^{-1}. The decrease in the intensity of absorption band at 1000 cm^{-1} corresponding to stretching vibrations of C–O– bond of methylol groups $-CH_2OH$ indicates the interaction of the mentioned groups resulting in the formation of three-dimensional structures and the increased molecular weight of MFOP. Moreover, the band at 1000 cm^{-1} (Fig. 4) does not disappear even at a temperature of 423 K, indicating the possibility of condensation processes proceeding in the oligomer. The formation of dimethylene esteric bonds due to methylol groups condensation is impossible to be controlled because the bonds are accumulated and destroyed with the release of free formaldehyde [31]. This is also indicated by the decrease of absorption band at 1445 cm^{-1} corresponding to the vibrations of $-CH_2$ group and its following disappearance at high temperatures. The experimental results are in agreement with the literature data [31] obtained for melamine formaldehyde oligomers without peroxy groups.

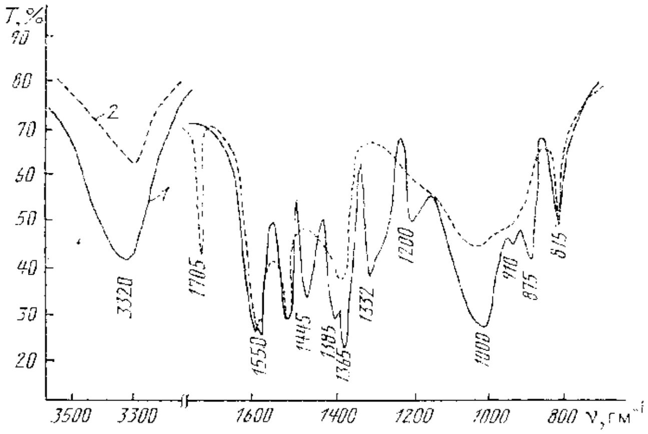


Fig. 4. IR-spectra of Oligomer I at 293 K (1) and 423 K (2)

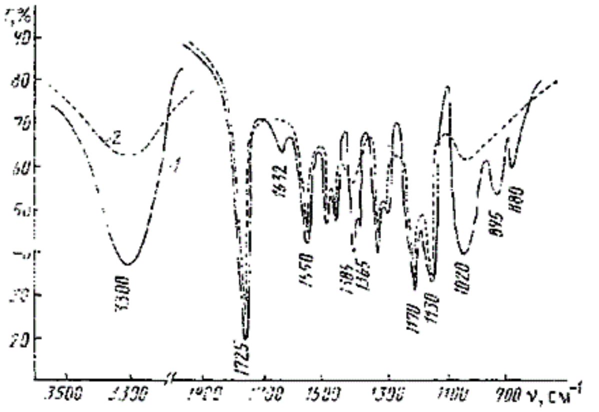
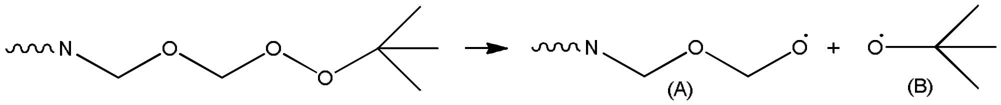


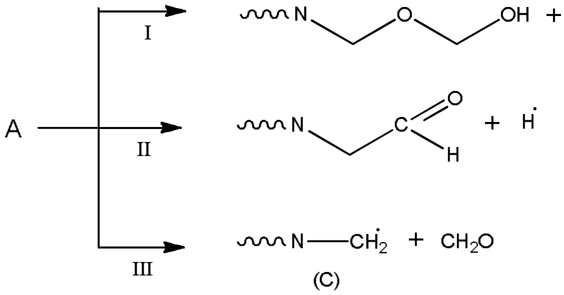
Fig. 5. IR-spectra of oligoesteric composition (Oligomer I:TGM-3 = 1:3, w/w) at 293 K (1) and 423 K (2)

While heating we also observed the decrease and following disappearance of the absorbance band at 875 cm^{-1} corresponding to $(CH_3)_3COO$– group, as well as doublet of deformational vibrations at 1385 and 1365 cm^{-1} typical of $(CH_3)C$– group. Moreover, the absorption band at 1705 cm^{-1} is observed, corresponding to the stretching vibrations of carbonyl C=O group (Fig. 4, *curve* 2).

The obtained results show the participance of labile –O–O– bonds in the cross-linking process and allow to propose the following scheme of peroxy groups decomposition:



(3)



(4)

The transformation of radical B occurs according to the known scheme [27] with the formation of *tert*-butyl alcohol and acetone, which are evaporated under the cross-linking conditions and thus cannot participate in the formation of cross-linked structure. Macroradical A (Eq. 4) is a source for producing new radical B, as well as compounds with hydroxy and aldehyde groups. Recombination of A and B results in the formation of cross-linked products (Table 5). The proceeding of the reaction II (see Eq. 4) is confirmed by the appearance and following increase of the absorption band at 1705 cm^{-1} (Fig. 6).

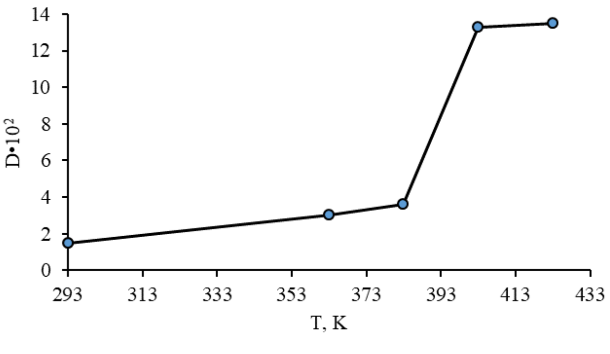


Fig. 6. Change of band optical density of the carbonyl group (ν_{CO}) of Oligomer I during cross-linking

The proceeding of the reaction I (Eq. 4) is hard to prove by IR-spectroscopy because hydroxy groups formed due to the decomposition of –O–O– bonds can interact with each other and form dimethylene esteric groups, which further convert into methylene ones.

The results represented in Fig. 4 and Table 5 allow to assert that cross-linked products are formed at the temperature of 403 K. Further light increase in gel-fraction content (Table 5) is provided by the condensation processes.

Table 5

Gel-fraction content during cross-linking of Oligomer I

Cross-linking time, h	Gel-fraction content, % at		
	383 K	403 K	423 K
0.5	89.6	94.7	97.4
1.0	93.7	95.2	97.8
2.0	96.2	96.4	98.0
3.0	96.7	96.8	98.2

Note: Gel-fraction content was determined by extraction with acetone for 10 h using Soxhlet apparatus

For oligoesteric compositions (Fig. 5) we found at 403 K the decrease and disappearance of the absorption band at 880 cm^{-1} and doublet of deformational vibrations at 1385 and 1365 cm^{-1} corresponding to Oligomer I. At the same time, we observed a decrease of the band at 1020 cm^{-1}, typical of methylol group in Oligomer I; the disappearance of absorption bands at 1632 and 895 cm^{-1}, which are characteristic of the stretching vibrations of double bond $\nu_{C=C}$ and deformational vibrations δ_{CH2} of $RR_1C=CH_2$ fragment, respectively. The obtained results indicate that oligoesteric composition are formed *via* both radical and condensation mechanisms.

4. Conclusions

Melamine formaldehyde oligomers with peroxy groups have been synthesized based on melamine or urea and melamine in the presence of *tert*-butyl peroxymethanol (TBPM) or *tert*-butyl hydroperoxide (TBHP). Zinc oxide was used as a catalyst. The highest content of peroxy groups was found for the oligomer synthesized at 343 K for 3 h in the presence of TBPM, with melamine : formaldehyde : TBPM molar ratio of 1:12:6. Oxide zinc amount was 0.7 wt% relative to melamine content. When TBHP was used, the melamine: formaldehyde : TBHP molar ratio was 1:12:8.

When urea and melamine were the starting materials, the synthesis conditions in the presence of TBPM were: temperature 343 K, time 3 h, urea : melamine : formaldehyde : TBPM molar ratio 1:0.2:7:4, catalyst amount 0.7 wt% relative to total amount of amino-compounds. When TBHP was used, the urea : melamine : formaldehyde : TBHP molar ratio was 1:0.2:8:5.

IR- and PMR spectroscopic investigations proved the presence of free peroxy and methylol groups in the synthesized oligomers. The chemistry of peroxy groups decomposition was proposed. By means of IR-spectroscopy it was confirmed that formation of cross-linked structures of peroxy oligomer and oligoesteric compositions occurs *via* both radical and condensation mechanisms.

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СИНТЕЗ ТА СТРУКТУРУЮЧІ ВЛАСТИВОСТІ МЕЛАМІНО-ФОРМАЛЬДЕГІДНИХ ОЛІГОМЕРІВ З ПЕРОКСИДНИМИ ГРУПАМИ

Анотація. *Синтезовані на основі меламіну або сечовини й меламіну в присутності трет.-бутилпероксиметанолу або трет.-бутилгідропероксиду меламіно-формальдегідні олігомери з пероксидними групами (МФОП). Як каталізатор реакції використаний оксид цинку. Вивчений вплив природи пероксидної сполуки, співвідношення вихідних компонентів суміші та тривалості процесу на характеристику та вихід МФОП. Наведені методики одержання МФОП та підтверджена їх структура з використанням ІЧ- і ПМР-спектроскопічних досліджень. Вивчено хімізм формування просторово-зшитих структур на основі МФОП та показано можливість використання таких олігомерів як структуруючих агентів сумішей на основі олігоестерактилату ТГМ-3.*

Ключові слова: *меламін, сечовина, формальдегід, олігоестеракрилат, оксид цинку, пероксид, гідропероксид, меламіно-формальдегідні олігомери, ІЧ- і ПМР-дослідження, структурування.*