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Synthesis and application of oligomers obtained from oxamic acid and ethylene carbonate

Summary — The reaction between oxamic acid and ethylene carbonate in the presence of potassium carbonate catalyst was studied. The products were characterized by ^{1}H NMR, IR and MALDI ToF techniques. The hydroxyethoxy derivatives of the acid are remarkably thermally stable due to the presence of oxalamidoester group. They were used as components of thermally stable polyurethane foams.

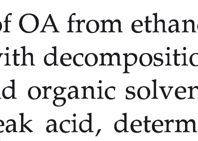
Key words: amidoacids, ethylene carbonate, hydroxyalkylation, oligomerization, chemical structure, thermal stability, polyurethane foams.

SYNTEZA I ZASTOSOWANIE OLIGOMERÓW OTRZYMYWANYCH W REAKCJI KWASU OKSAMOWEGO Z WĘGLANEM ETYLENU

Streszczenie — Praca stanowi kontynuację wcześniejszych badań produktów reakcji kwasu parabanowego z węglanem etylenu [4] i węglanem propylenu [6] charakteryzujących się zwiększoną odpornością termiczną, którą przypisano obecności w nich grup oksalamidoestrowej i mocznikowej połączonych mostkiem imidowym. W niniejszej pracy przedstawiono wyniki badań dotyczących syntezy i właściwości hydroksyetylowych i hydroksyetoksylowych pochodnych kwasu oksamowego (OA) zawierających ugrupowania oksalamidoestrowe, otrzymanych z udziałem węglanu etylenu (EC) jako czynnika hydroksyalkilującego oraz węglanu potasu jako katalizatora (tabela 1). Metodami analizy instrumentalnej (spektroskopii ^{1}H NMR, IR, MALDI ToF) określono budowę chemiczną powstających produktów (rys. 1—4, tabele 2 i 3). Stwierdzono, że otrzymane hydroksyetoksylowe pochodne UA charakteryzują się zwiększoną odpornością termiczną, którą warunkuje obecność ugrupowania oksalamidoestrowego (tabela 4). Określono fizyczne właściwości tych związków typu polioli (tabela 5), zbadano przebieg ich spieniania w układzie z diizocyjanianem 4,4′-difenylometanu (tabela 6) oraz scharakteryzowano właściwości użytkowe tak uzyskanych pianek poliuretanowych (tabela 7).

Słowa kluczowe: amidokwasy, węglan etylenu, hydroksyalkilowanie, oligomeryzacja, budowa chemiczna, odporność termiczna, pianki poliuretanowe.

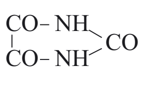
Oxamic acid [OA (I)] is the monoamide of oxalic acid obtained in the reaction between oxalic acid and excess of ammonia [1, 2].



$$H-O-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-N\begin{matrix}H\\H\end{matrix} \qquad (I)$$

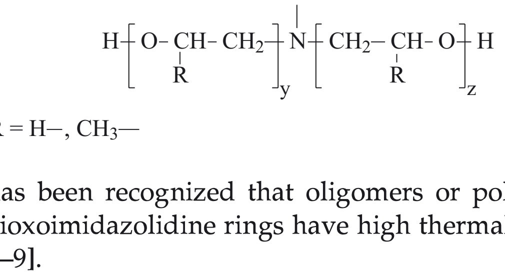
Crystallization of OA from ethanol gives the product melting at 218 °C with decomposition. It is only slightly soluble in water and organic solvents. The dissociation constant of this weak acid, determined potentiometrically, was $1.46 \cdot 10^{-2}$ [3].

The oxalamidocarboxylate group, present at OA was found to be formed also during the ring opening of trioxoimidazolidine ring of parabanic acid [PA (II)] upon its reaction with alkylene carbonates (AC) [4—6].



$$\begin{matrix}CO-NH\\ |\\ CO-NH\end{matrix}\!\!>CO \qquad (II)$$

In that process the esteramidoimidotetraols (III) containing oxalamidocarboxylate group are formed.



(III)

where: R = H—, CH$_3$—

It has been recognized that oligomers or polymers with trioxoimidazolidine rings have high thermal stability [7—9].

The percentage of preserved trioxoimidazolidine rings in (III) is rather small (0—20 % mol.), but despite of this fact, the obtained oligomers show higher thermal stability than PA (the temperature of maximum decomposition ranges within 250—280 °C) [4—6].

So not the presence of trioxoimidazolidine ring, but rather the product of its ring opening, *i.e.* the oxalamidoester and urea groups linked together *via* imide bond, is responsible for thermal stability of products obtained in hydroxyalkylation of PA with AC. Oligomers containing in their structures the oxalamidoester and urea groups separately should be characterized by higher thermal stability too.

In order to verify this hypothesis we have performed the synthesis of hydroxyalkyl and/or alkoxy derivatives of OA containing oxalamidoester and hydroxyalkyl and/or hydroxyalkoxy derivatives of urea fragments and tested their thermal stability. In the research described in this paper we studied the synthesis and properties of hydroxyethoxy derivatives of OA. We used the ethylene carbonate (EC) as hydroxyalkylating agent.

EXPERIMENTAL

Reactions of OA with EC

In a 100 cm^3 three-necked round bottom flask 3.5 g (0.04 mole) of OA (pure, Avocado, Great Britain) and the appropriate amount of EC (pure, Fluka, Switzerland), were placed to reach the molar ratio of reagents from 1:1 to 1:12 and 0.00—0.49 g of potassium carbonate (0.00—12.42 g/mole OA, 0.00—0.090 mole/mole OA) was added. The reaction mixture was protected from moisture and stirred mechanically at 140—160 °C to dissolve OA in EC with monitoring of reaction progress by determination of unreacted EC [4].

Polyurethane foam preparation

Foaming experiments were carried out in small 250 cm^3 test cups at room temperature. To 5 g of a polyol (product of reaction of OA with EC), 0.1 g of surfactant (Silicon 5340, Houdry Hülls), 0.21 wt. % of triethylamine (TEA) catalyst (pure, Avocado, Germany), and 2 wt. % of water were added. After careful mixing of the components, a pre-weighed amount of 4,4'-diphenylmethane diisocyanate (pure, Merck, Germany), calculated as described in was added [10]. The amounts of diisocyanate and water were adjusted to give OH:NCO molar ratio varying from of 1:1.78 to 1:2.08. Each composition was vigorously mixed until it started to cream. The samples for testing were cut out from the foams thus obtained after *ca.* 48 h.

Analytical methods

Products of reaction of OA and EC

— Determination of acid number (AN) was performed by alkacymetric titration [with 0.1 M KOH(aq)] [11].

— ^1H NMR spectra of products were recorded using BS-586A 80 MHz spectrometer (Tesla, Brno, Czechoslovakia) in d_6-DMSO, and HMDS reference.

— IR spectra were taken for the films using PARAGON 1000 FTIR spectrophotometer (Perkin Elmer, Wellesley, MA, US).

— MALDI ToF (Matrix-Assisted Laser Desorption/Ionization Time of Flight) spectra were obtained using Voyager-Elite Perseptive Biosystems (USA) mass spectrometer by the method described in [6]; similarly to [6] in some cases the molecular ion weights were increased by the weight of Na^+, K^+, H^+ and CH_3OH.

— Chromatographic analyses of by-products, *i.e.* ethylene glycol (EG) and products of its consecutive reactions with EC, were performed using gas chromatograph HP 4890A (Hewlett Packard, Ringoes, NJ, US) with FID detector and HP1 30 m × 0.53 mm column packed with crosslinked methylsiloxane film of 1.5 mm thickness. Initial temperature was 50 °C, heating rate 20 °C/min, end temperature 220 °C, time of heating at 220 °C 6 min, loader temperature 250 °C, detector temperature 300 °C. The samples were dissolved in methanol (0.01 M); internal reference was cyclohexanone. Percentage of diols and polyols were calculated according to calibration curves as described in [6].

— Thermal stability (DTA, DTG and TG) of hydroxyethoxy derivatives of OA were analyzed (using Paulik-Paulik-Erdey derivatograph, MOM, Hungary) in ceramic crucible at 20—1000 °C temperature range, with 100 min registration time, 200 mg sample, under air atmosphere.

Moreover, the following properties of reaction products of OA with 9- and 13-fold molar excess of EC have been determined: pycnometer density [13], refractive index, Höppler viscosity [14] and surface tension by ring detach method [15]. All measurements were made in temperature range 20—80 °C.

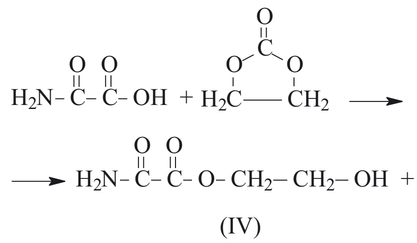
Foams

The following properties of foams were determined: apparent density (PN-EN ISO 845), water uptake (PN-EN ISO 2896), stability of dimension (PN-EN ISO 2796), glass transition temperature (by DSC), thermal stability.

The differential scanning calorimetry (DSC) measurements were made using a DSC822^e Mettler Toledo instrument, in 20—200 °C temperature range and 10 deg/min heating rate under nitrogen atmosphere. The results were recorded as heat flow in W/g *versus* temperature.

RESULTS AND DISCUSSION

According to higher reactivity of carboxylate group in comparison to that of amide one, we have anticipated that reaction between OA and EC at 1:1 molar ratio will lead to 2-hydroxyethyl oxamate (IV):



$$H_2N-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH + H_2C(-O-\overset{O}{\overset{\|}{C}}-O-)CH_2 \longrightarrow H_2N-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-OH + CO_2\uparrow \quad (1)$$

(IV)

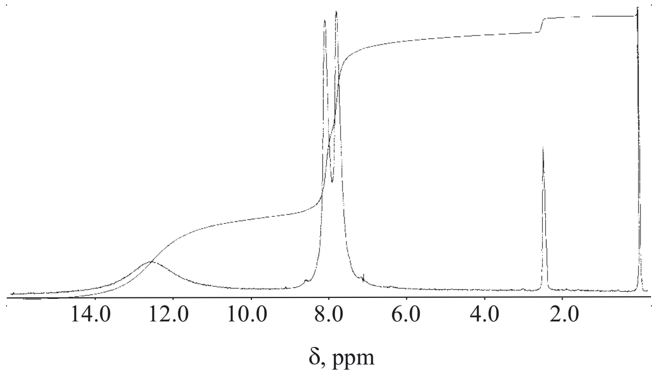


Fig. 1. ^{1}*H NMR spectrum of oxamic acid*

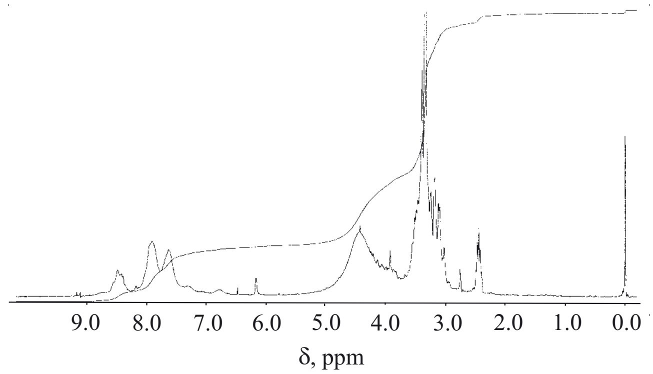


Fig. 2. ^{1}*H NMR spectrum of the product of reaction of OA:EC = 1:1 in the presence of 0.06 mole* K_2CO_3*/mole OA at 140* °*C*

Considering the possibility of formerly observed partial decomposition of EC to ethylene oxide and CO_2 [16] we also expected the presence of unreacted OA in the final product. In ^{1}H NMR spectrum of OA (Fig. 1) the resonances at 7.73 and 9.03 ppm were attributed to amide group protons, while the resonance at 12.3 ppm was assigned to carboxylic group proton. The latter was not observed in the spectrum of product which indicated that all carboxylic groups were consumed in the reaction between OA and EC. Formation of ester group was confirmed by the signal at 4.0 ppm related to methylene protons of $-CH_2-O-CO-$ group [17]. Furthermore, two resonances of amide protons (at 7.6 and 7.95 ppm) were present, however they had different integral intensities — the signal at 7.95 ppm was more intense (Fig. 2). Also new signal at 8.5 ppm appeared, which was assigned to imide protons in accordance to previous observation [17].

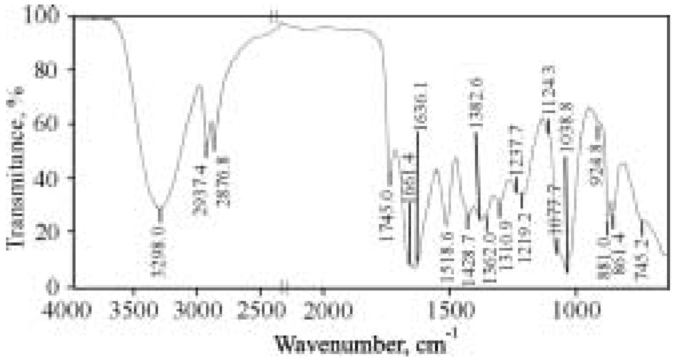


Fig. 3. IR spectrum of the product of reaction of OA:EC = 1:1 in the presence of 0.06 mole K_2CO_3*/mole OA at 140* °*C*

The absence of carboxylic groups in the product was confirmed by IR spectrum (Fig. 3) by absence of the bands at 1889 cm^{-1} or those in 2400—2600 cm^{-1} region, characteristic for amidoacids, and the band at 985 cm^{-1} from non-planar deformation mode of OH, similarly to the spectrum of OA itself.

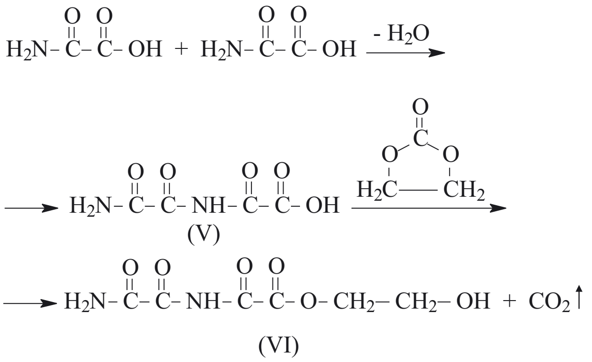
Mass balance of the performed reaction indicated that barely 0.72 moles of EC has reacted with OA. That indicated that remaining 0.28 moles of OA should be found in the product, while this was inconsistent with *AN* of product (Table 1, run 1) which evidenced much lower free OA amount than calculated one.

Table 1. Reaction conditions of OA with EC

Run	Initial molar ratio	Amount of K_2CO_3 mole/mole OA	Temp., °C	Time of reaction, h	Molar ratio OA:x in post-reaction mixture (from mass balance)*)	*AN*, mg KOH/g	
						Calculated	Found
1.	1:1	0.06	140	2	1:0.72	130	13
2.	1:2	0.06	160	1	1:1.47	122.5	8
3.	1:3	—	150	12	1:2.42	—	—
4.	1:3	0.06	140	12	1:2.54	—	—
5.	1:3	0.06	160	1.5	1:2.20	—	—
6.	1:4	0.06	160	1	1:3.26	—	—
7.	1:6	0.09	160	3.3	1:5.13	—	—
8.	1:9	0.09	160	5.75	1:8.07	—	—
9.	1:12	0.09	160	8.25	1:11.0	—	—

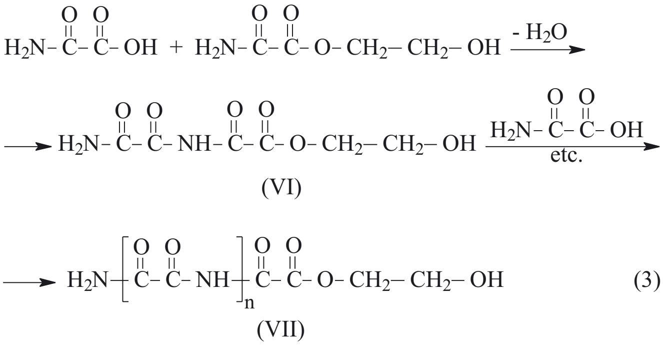
*) x — oxyethylene unit.

From outlined overall picture the conclusion can be drawn that during the high temperature process OA condenses with formation of amidoimidoacid (V), which consecutively reacts with EC to give a product (VI):



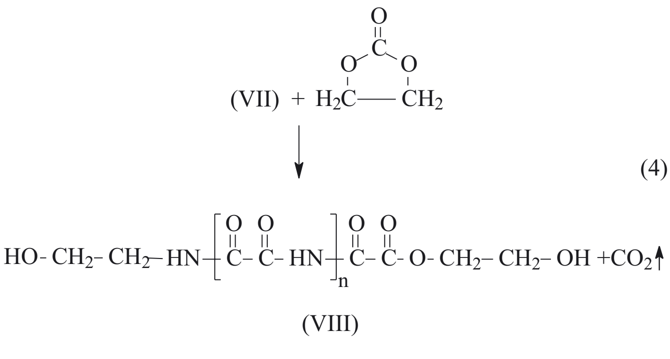
(2)

The formation of 2-hydroxyethyl oxamate, which reacts further with OA with formation of imide groups:



(3)

cannot be excluded either. The process of condensation is accompanied by the presence of the resonance at 8.5 ppm observed at ^{1}H NMR spectrum of the product, which was attributed to imide protons, as was previously found [17]. The product (VII) reacts with EC, still present in excess, to give (VIII), with secondary amide groups, with characteristic resonance centered at 7.95 ppm in ^{1}H NMR spectrum. This signal is actually due to two overlapping resonances from amide protons from (VII) and secondary amide protons of (VIII):

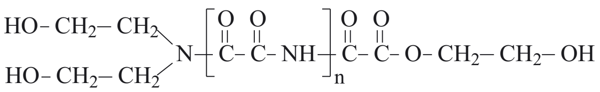


(4)

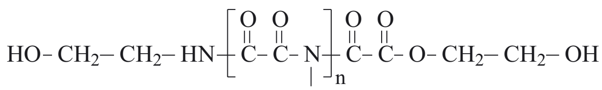
Similar spectra patterns were observed for the products of reaction between PA and ethylene oxide or EC, during which the trioxoimidazolidine ring opening occurred [4, 12].

The analysis of IR spectrum of the product (Fig. 3.) confirms the structure of (VIII). Within the 3200—3400 cm^{-1} region the broad valence band of overlapping -OH from alcohol, -NH of primary and secondary amide and imide groups are present. The valence band of carbonyl group from ester and imide is also visible at 1745 cm^{-1}. The presence of primary hydroxyl group is related to the band at 1040 cm^{-1}, characteristic for valence of C-OH, while ester valence asymmetric band is visualized by the band centered at 1237 cm^{-1}.

In IR spectrum of the product obtained from OA and EC at 1:2 molar ratio (Table 1, run 2), the character of the band above 3000 cm^{-1} changes more in comparison with those of OA and the product described previously. The valence band of primary amide N-H bond disappears and the shape of a band at 1650 cm^{-1} changes, indicating the absence of primary amine and consequently the possibility of ternary amide formation. The intensity of 1242 and 1040 cm^{-1} enlarges the evidence of increase in participation of ester and primary hydroxyl groups in the product. In ^{1}H NMR spectrum of the this product the resonances from imide and secondary amide group protons are observed at 8.5 and 7.95 ppm, respectively, which can be attributed to the product (VIII) and/or (IX) and (X):



(IX)



(X)

The intense resonance at 3.1—3.6 ppm from overlapping methylene protons makes the estimation of number of 2-hydroxyl groups attached to amide and imide function impossible. Mass balance of reaction and the intensity of the resonance of protons from methylene group attached to ester fragment (observed at 4.0 ppm) suggest that reaction between OA and EC is accompanied by release of carbon dioxide, without incorporation of carbonate into the product.

The products obtained from OA:EC = 1:3 system in the absence of catalyst (Table 1, run 3) still contain some percentage of secondary amide and imide groups. The IR spectrum of the product shows the II amide band (from secondary amide) while in ^{1}H NMR spectrum the low intensity resonances at 7.95 and 8.5 ppm are also present (Fig. 4a). The reaction of OA with 4-fold excess of EC in the presence of catalyst leads to a total disappearance of imide and primary amide groups, instead a small amount of secondary amide groups are still present (Fig. 4b, 7.95 ppm).

In the IR spectra of products obtained from OA and 3-fold or higher excess of EC systems the band at

1120 cm^{-1} appears assigned to -C-O-C- ether group, which proves that the consecutive reaction of hydroxyl groups with EC occurs. The band enlarges with the increase in excess of EC.

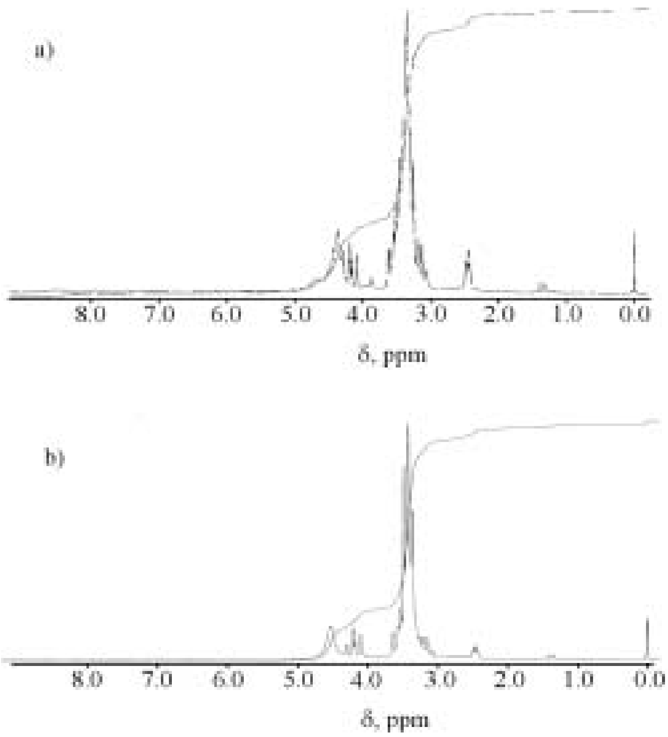
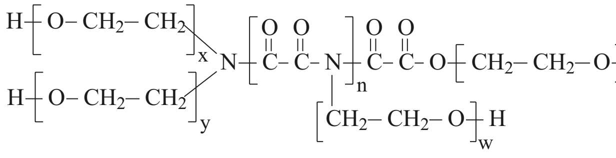


Fig. 4. ^{1}H NMR spectra of the products of reaction OA:EC: a) 1:3, without catalyst at 150 °C, b) 1:4, in the presence of 0.06 mole K_2CO_3/mole OA at 160 °C

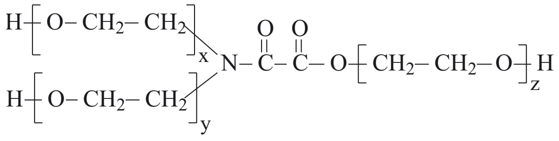
In ^{1}H NMR spectra of the products obtained from OA:EC = 1:4 (Table 1, run 6, Fig. 4b) the intensity ratio of resonances from methylene protons attached to ester and to hydroxyl groups is 1:2. This indicates the formation of product (XI), where n = 1-hydroxyethoxy derivatives of OA dimer:



$$\left.\begin{matrix}H\left[O-CH_2-CH_2\right]_x\\ H\left[O-CH_2-CH_2\right]_y\end{matrix}\right\rangle N\left[\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-\underset{\underset{\left[CH_2-CH_2-O\right]_w H}{|}}{N}\right]_n\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O\left[CH_2-CH_2-O\right]_z H \qquad (XI)$$

where: x + y + z + w = 4—12

The ^{1}H NMR spectrum obtained for OA and 12-fold excess of EC (Table 1, run 9) shows that the ratio of those groups is 2:3, which means that product (XII) is formed:



$$\left.\begin{matrix}H\left[O-CH_2-CH_2\right]_x\\ H\left[O-CH_2-CH_2\right]_y\end{matrix}\right\rangle N-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O\left[CH_2-CH_2-O\right]_z H \qquad (XII)$$

Table 2. Results of MALDI ToF determination of the product of OA:EC = 1:3 reaction in the presence of 0.06 mole K_2CO_3/mole OA at temperature 160 °C

Signal position	Probable structure of molecular ion*)
132.2	$OA + EO + H^+$
157.0	$OA + EO + Na^+$
159.2	$OA + K + CH_3OH + H^+$
203.2	$OA + 3\,EO + H^+ - H_2O$
220.2	$OA + 3\,EO + H^+$
226.2	$OA + 3\,EO + Na^+ - H_2O$
241.2	$OA + 2\,EO + CH_3OH + K^+$
247.2	$OA + 2\,EO + CH_3OH + K^+$
254.2	$OA + 3\,EO + CH_3OH + H^+$
263.3	$OA + 4\,EO + H^+$
274.3	$OA + 3\,EO + CH_3OH + K^+ - H_2O$
285.2	$OA + 3\,EO + CH_3OH + K^+$
291.3	$2\,OA - H_2O + 3\,EO + H^+$
289.4	$OA + 5\,EO + H^+ - H_2O$
307.4	$OA + 4\,EO + K^+$
316.3	$2\,OA - H_2O + 3\,EO + Na^+$
329.3	$OA + 5\,EO + K^+ - H_2O$
330.2	$OA + 5\,EO + Na^+$
351.4	$OA + 6\,EO + H^+$
356.6	$OA + 6\,EO + Na^+ - H_2O$
376.3	$OA + 6\,EO + Na^+$
395.5	$OA + 7\,EO + H^+$
419.4	$2\,OA - H_2O + 5\,EO + K^+$

*) EO — oxyethylene unit.

Table 3. Results of MALDI ToF determination of the product of OA:EC = 1:12 reaction in the presence of 0.09 mole K_2CO_3/mole OA at temperature 160 °C

Signal position	Probable structure of molecular ion
233.1	$OA + 2\,EO + CH_3OH + Na^+$
258.1	$OA + 3\,EO + K^+$
266.2	$OA + 4\,EO + H^+$
302.1	$OA + 4\,EO + CH_3OH + Na^+ - H_2O$
304.2	$OA + 4\,EO + K^+$
321.1	$OA + 4\,EO + CH_3OH + Na^+$
346.1	$OA + 5\,EO + K^+$
365.2	$OA + 5\,EO + CH_3OH + Na^+$
378.3	$OA + 6\,EO + Na^+$
409.2	$OA + 6\,EO + CH_3OH + Na^+$
446.2	$OA + 8\,EO + Na^+ - H_2O$
452.2	$OA + 7\,EO + CH_3OH + Na^+$
478.3	$OA + 8\,EO + K^+$
497.3	$OA + 8\,EO + CH_3OH + Na^+$
541.3	$OA + 9\,EO + CH_3OH + Na^+$
584.3	$OA + 10\,EO + CH_3OH + Na^+$

In order to estimate the number of OA units incorporated into the products, *i.e.* the number of OA molecules condensed, the MALDI ToF spectra of the products were taken. The results indicated that the product obtained from OA:EC = 1:3 system (Table 2, run 5 in Table 1) were hydroxyethyl and hydroxyethoxy derivatives composed of 1—6 ethoxy untis per one OA and dimeric OA containing 5 ethoxy groups per dimer. When 12-fold excess of EC was used (Table 3, run 9 in Table 1), the product contained up to 10 hydroxyethoxy groups per OA, and hydroxyethoxy derivatives of dimeric OA was absent. This leads to the conclusion that the higher excess of EC, the easier OA reacts with carbonate and condensation of hydroxyethyl derivatives with OA occurs in less extent.

Chromatographic analysis indicated the absence of by-products, which could be formed in the reaction of EC with water [16].

Table 4. Thermal stability of the products (T, °C)*)

Run from Table 1	Initial molar ratio OA:EC	$T_{5\%}$	$T_{10\%}$	$T_{20\%}$	$T_{50\%}$	$T_{max.}$
6.	1:4	140	165	200	250	240
7.	1:6	160	195	230	290	255
8.	1:9	170	200	235	290	315
9.	1:12	170	200	235	290	315

*) Subscripts at T symbols mean the respective weight basses of the samples, $T_{max.}$ corresponds to maximum decomposition temperature.

Thermogravimetric derivatographic analyses demonstrated (Table 4) that T_{max} values of the products obtained from 1:4 and 1:6 OA to EC systems — which constitute mixtures of esteramidotriols (XII) and esteramidoimidotetraols (XI) — are 240 °C and 255 °C, respectively. The products prepared from the systems with 9- and 12-fold excess of EC, containing mostly esteramidotriols show even higher maximal decomposition temperature, namely 315 °C. It is worth to note, that thermal stability of esteramidoimido-tetraols obtained previously from PA and EC does not depend on molar ratio of reagents used (1:4—1:12) and is in the range 240—260 °C [4].

Oligomers obtained in the reaction of OA and 9- or 12-fold molar excess of EC were used as starting polyols for polyurethane foams of increased thermal stability. The density, viscosity, surface tension and refractive index at 20 °C of these polyols are listed in Table 5.

Table 5. Physical properties (temp. 20 °C) of reaction products of OA and EC used as polyols in polyurethane foams syntheses

Entry in Table 1	Initial molar ratio OA:EC	Refractive index [-]	Density g/cm^3	Viscosity $\cdot 10^3$ N · s/m^2	Surface-tension $\cdot 10^2$, N/m
8.	1:9	1.4777	1.1802	262.50	4.889
9.	1:12	1.4762	1.1834	330.14	5.160

As it was mentioned in Experimental Part the foaming of polyols received by us was performed with 4,4′-diphenylmethane diisocyanate in the presence of triethylamine (TEA) as catalyst (Table 6).

The foams of the best thermal stability were obtained from polyol synthesized from OA and 9-fold molar excess of EC with isocyanate index 2.02 and in the presence of 0.21 wt. % of TEA (composition 1 in Table 6).

Apparent density of the foams obtained (Table 7), and their glass transition temperatures (74 °C and 68 °C) are the parameters characteristic for rigid foams [18].

The lowest water uptake (13.7 wt. %) after 24 h sinking at room temperature was observed for the foam obtained with EC9, while that of the foams obtained with

Table 6. Parameters of foaming process

Initial molar ratio OA:EC in polyol	Percentage of oxyethylene units in product mol/mol OA	Composition No.	Composition, g/100 g of polyol				Times of foaming process, s*)		
			4,4′-diphenyl-methane diisocyanate	water	triethyl-amine (catalyst)	molar ratio OH/NCO	creaming	expanding	drying
1:9	8.1	1	172	2	0.21	1:2.02	12.0	1.8	0
		2	150	2	0.21	1:1.78	11.2	1.3	0
1:12	11.0	3	136	2	0.21	1:2.08	10.0	1.2	0
		4	120	2	0.21	1:1.83	9.8	1.9	0

*) Time of creaming — time elapsed from the moment of mixing to the start of volume expansion; time of expanding — time from the start of expansion to the moment of reaching the sample final volume; time of drying — time from reaching by the sample its final volume to the moment of loosing its surface adhesion to powdered substances.

Table 7. Properties of polyurethan foams

Composition No. (see Table 6)	Apparent density, kg/m^3	Water uptake, wt. %			Linear dimension change after heating at 150 °C, %					
					length		width		thickness	
		after 5 min	after 3 h	after 24 h	after 20 h	after 40 h	after 20 h	after 40 h	after 20 h	after 40 h
1	64.94	10.05	13.09	13.66	6.87	7.25	9.77	9.77	8.51	9.57
2	65.97	11.33	17.18	33.36	9.14	9.9	10.1	13.13	10.17	15,25
3	53.13	10.07	11.81	15.47	12.46	15.22	11.96	18.48	26.51	26.51
4	53.80	20.83	31.06	36.88	12.1	—	30.00	—	51.61	—

EC12 was 15.5 wt. % (Table 7). The foams from polyols EC9 shrink during heating at 150 °C and the maximal change reaches linear 10 % (Table 7).

Derivatographic profiles of polyurethane foams confirm their higher thermal stability — the 5 % mass loss occurs at 180 °C and temperature of maximal decomposition equals 250 °C for the foam obtained from EC9.

CONCLUSIONS

— Reaction of oxamic acid with ethylene carbonate is accompanied by homocondensation of OA with formation of imide bond. The contribution of homocondensation process falls down when excess of EC is used. In case of 3-fold molar excess of EC only the products of OA dimer reaction with EC are formed, while higher excess of EC quenches this reaction.

— The oligomers obtained upon hydroxyethylation of OA with EC do not contain polyol by-products, namely ethylene glycol and polyethylene glycols.

— Hydroxyethoxy derivatives of OA have similar and higher thermal stability than the previously obtained products of the reaction between parabanic acid with EC, due to the presence of oxalamidoester group.

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