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Reactions of oxamide with ethylene carbonate

Summary — Oxamide (OD) was hydroxyalkylated with ethylene carbonate (EC). An influence of initial molar ratio of OD:EC, quantity and type of a catalyst as well as temperature on the course of reaction was studied. A structure and composition of products was analyzed by means of IR, ^{1}H NMR, MALDI ToF, GC and GC-MS methods. Participation of by-products was assessed and thermal stability of the reaction products of OD with EC was investigated. Good thermal stability and some other physical properties of the obtained products indicate the possibility of their application in manufacturing of thermostable polyurethane foams.

Keywords: oxamide, ethylene carbonate, synthesis of hydroxyethoxy derivatives, structure of products, thermal stability, polyurethane foams.

REAKCJE OKSALAMIDU Z WĘGLANEM ETYLENU

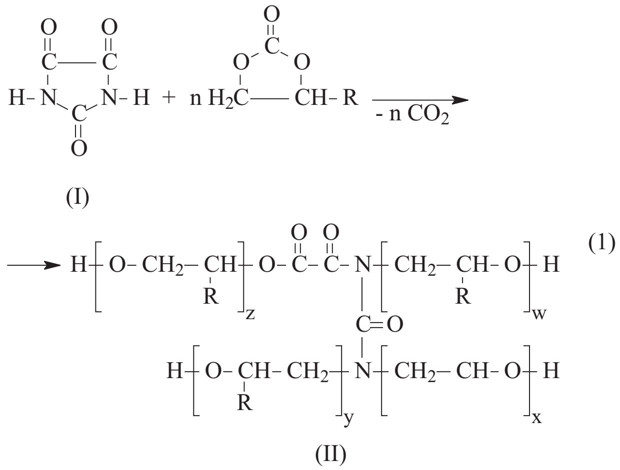
Streszczenie — Praca stanowi kontynuację wcześniejszych badań własnych dotyczących produktów reakcji kwasu parabanowego, kwasu oksamowego i mocznika z węglanem etylenu [1, 3, 5] i węglanem propylenu [2, 4, 6]. Charakteryzują się one zwiększoną odpornością termiczną, która wynika z obecności w ich strukturze (jednocześnie lub odrębnie) grupy oksalamidoestrowej i karbamidowej. W niniejszej publikacji przedstawiono wyniki badań dotyczących syntezy i właściwości hydroksyetylowych i hydroksyetoksylowych pochodnych oksalamidu (OA) powstających w wyniku jego reakcji z węglanem etylenu (EC) jako czynnikiem hydroksyalkilującym, w obecności węglanu potasu jako katalizatora (tabela 1). Metodami IR, ^{1}H NMR, MALDI ToF, GC i GC-MS (tabele 2 i 3, rys. 1—6) scharakteryzowano budowę i skład uzyskanych produktów, szacując przy tym udział substancji powstających ubocznie (tabela 4). Na tej podstawie szczegółowo omówiono wpływ warunków reakcji, mianowicie molowego stosunku substratów (OD:EC = 1:4—1:12), ilości i rodzaju katalizatora (K_2CO_3 lub DABCO w ilości 0,03—0,09 mola na mol OD) oraz temperatury (140—160 °C) na czas jej trwania i skład mieszaniny poreakcyjnej a także przedstawiono mechanizm procesu. Zwiększona odporność termiczna (rys. 7 i 8) oraz dobre właściwości fizyczne (rys. 9) uzyskanych z OA i EC pochodnych hydroksyetoksylowych wskazują na możliwość zastosowania ich do otrzymywania pianek poliuretanowych o zwiększonej odporności termicznej. Jak wykazały badania mikroskopowe, w piankach takich występują regularnie rozmieszczone pory o wymiarach 0,2—0,6 mm (rys. 10).

Słowa kluczowe: oksalamid, węglan etylenu, synteza pochodnych hydroksyetoksylowych, struktura produktu, odporność termiczna, pianki poliuretanowe.

During reaction of parabanic acid (I) with alkylene carbonates (AC), *i.e.* ethylene carbonate (EC) and/or propylene carbonate, products (II) characterized by enhanced thermal stability (temperature of their maximum decomposition is 250—290 °C) are obtained [1, 2]. It is caused by presence in the product of a structure (II) oxalamidoester and carbamide groups connected with an imide bond, which are formed after opening of acid ring [eq. (1)].

The above hypothesis was proved by studies of thermal stability of hydroxyalkoxy derivatives of oxamic acid and urea, each containing respectively and separately oxalamidoester and carbamide unit in their structures [3—6]. Reaction products of oxamic acid with AC (products with the oxalamidoester unit) exhibit enhanced thermal stability: temperature of their maximum decomposition is within 250—310 °C [3, 4]. Similarly, reaction products of urea with AC (products with the carbamide unit) show relatively high thermal stability 240—360 °C [5, 6].

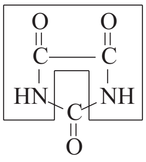
Products of hydroxyalkylation of parabanic acid, urea and oxamic acid with AC were used as polyol substrates for obtaining polyurethane foams. Such rigid polyurethane foams were characterized usually by a slight water

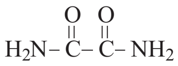

(1)

where: R = H—, CH$_3$—

uptake, good stability of dimensions and enhanced thermal stability [6—8].

In the structure of parabanic acid (I) a structural fragment of oxamide (OD, III) is present:


(I)


$$H_2N-C(=O)-C(=O)-NH_2$$
(III)

therefore it is assumed that hydroxyalkylation products of OD with AC should be characterized by an enhanced thermal stability, like same other products including oxalamide structure [9—13].

In this study, the mechanism of the reaction of OD with EC was studied, followed by investigation of composition and properties of the obtained products, in terms of any possibility of their application as polyol substrates for foamed polyurethane (PUR) plastics with enhanced thermal stability.

EXPERIMENTAL

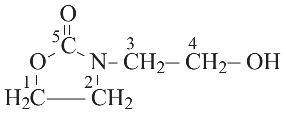
Synthesis

Reactions of OD with EC

In a 100 cm^3 three-necked round bottom flask 4.4 g (0.05 mole) of OD (pure, Aldrich, Germany) and the appropriate amounts of EC (pure, Fluka, Switzerland) were placed to reach the molar ratio of reagents of 1:4—1:12, than 0.21—0.62 g of potassium carbonate (4.14—12.42 g/mole OD, 0.03—0.09 mole/mole OD) or 0.28 g diazabicyclo[2.2.2]octane (DABCO) (7.6 g/mole OD, 0.06 mole/mole OD) was added. The reaction mixture was protected from moisture (by a tube filled with magnesium sulfate) and stirred mechanically at 140 or 160 °C while monitoring the progress of reaction by determination of an unreacted EC [14].

Synthesis of *N*-(2-hydroxyethyl)oxazolidinone

N-(2-hydroxyethyl)oxazolidinone was according [15] and was examined by spectral analysis:



IR (KBr), ν = 3407.5 (w, O-H valence), 2922 (w, -CH$_2$-, asym. valence), 2882.5 (w, -CH$_2$-, sym. valence), 1714 (w, C=O, valence), 1485.5 and 1435.8 (s, -CH$_2$-, scissoring), 1042 (w, C-O-H, valence) cm^{-1}; ^{1}H NMR (500 MHz, d$_6$-DMSO, ppm), δ = 3.19 (2H, t, -N-C**H**$_2$-, J$_{3.4}$ = 5.6 Hz), 3.51 (2H, t, -C**H**$_2$-OH, J$_{3.4}$ = 5.6 Hz), 3.58 (2H, t, -N-C**H**$_2$-, J$_{2.1}$ = 7.9 Hz), 4.23 (2H, t, -C**H**$_2$-O-, J$_{1.2}$ = 7.9 Hz), 4.78 (1H, s, -OH); ^{13}C NMR (d$_6$-DMSO, ppm), δ = 158.3 (C$_5$), 61.8 (C$_1$), 58.7 (C$_4$), 46.4 (C$_3$), 44.9 (C$_2$); MS, *m/z* = 131 (7.4 %), 115 (9.3 %), 100 (100 %), 56 (79.0 %).

PUR foams preparation

Attempts of foaming the reactions products of OD with EC were carried out in small 250 cm^3 test cups at room temperature. 5 g of hydroxyethoxy derivatives of OD, 0.1 g of surfactant (Silicon 5340, Houdry Hülls), 0.0—0.22 wt. % of triethylamine (TEA) catalyst (pure, Avocado, Germany), and 2 wt. % of water were. Carefully mixed and than a pre-weighed amount (calculated as described in [16]) of 4,4'-diphenylmethane diisocyanate (pure, Merck, Germany) was added. The amounts of diisocyanate and water were adjusted to produce the OH:NCO molar ratio varying from of 1:1.75 to 1:2.50. Each composition was vigorously mixed until it started to turn into cream. The samples for testing were cut out from the foam thus obtained after *ca.* 48 hrs.

Analytical methods

— ^{1}H and ^{13}C NMR spectra of OD and other products were recorded with 500 MHz spectrometer (Bruker, Germany) in deuterated dimethyl sulfoxide (d$_6$-DMSO), and hexamethyldisiloxane (HMDS) or tetramethylsilan (TMS) reference.

— IR spectra were recorded from a capillary film or KBr pellets on a PARAGON 1000 FT spectrometer (Perkin-Elmer).

— GC-MS experiments were conducted with Hewlett Packard 6890N chromatograph equipped with 5973 Network mass detector and HP-5MS 30 m x 0.25 mm column packed with film of 0.25 μm thickness. The samples were dissolved in acetononitrile.

— Chromatographic analysis of by-products, *i.e.* ethylene glycol (EG) and products of its consecutive reactions with EC were performed with gas chromatograph HP 4890A (Hewlett Packard, Ringoes, NJ, US) with flame ionization detector (FID) and HP1 30 m x 0.53 mm column packed with crosslinked methylsiloxane film of

1.5 μm 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 was calculated according to calibration curves as described in [1].

— MALDI ToF spectra of reaction products of OD with EC were obtained on Voyager-Elite Perseptive Biosystems (US) mass spectrometer working at linear mode with delayed ion extraction, equipped with nitrogen laser working at 337 nm. The matrix was 2,5-hydroxybenzoic acid. The samples were diluted with methanol to 1 mg/cm^3, followed by addition of 10 mg/cm^3 NaI in acetone. Therefore in some cases the molecular ion weights were increased by the mass of Na^+, K^+, H^+ and CH_3OH.

— Thermal analyses (DTG and TG) of hydroxyethyl derivatives of OD were performed in a ceramic crucible, at temperature range of 20—600 °C, on app. 2 mg sample, under a nitrogen atmosphere with Thermobalance TGA/DSC 1 derivatograph, Mettler.

The following properties of hydroxyethoxy derivatives of OD have been determined: pycnometer density [17], Höppler viscosity [18], and surface tension by ring detach method [19]. All measurements were made at the temperature range of 20—80 °C.

The following properties of foams were determined: apparent density [20], water uptake [21], stability of dimension [22], glass transition temperature (by DSC), thermal stability as the weight loss after heating at 150, 175 and 200 °C for a month.

The microscopic observations were performed with optical microscope Nikon Eclipse LV100 POL, camera Digital Sight DS-5Mc, 2.5 x L Plan lens. These measurements were performed in the Biophysical Laboratory of the Department of Physics at the Rzeszow University of Technology. The Laboratory has been established under the UE Polish Integrated Regional Operation Programme.

RESULTS AND DISCUSSION

Characterization of the products received in the reactions of oxamide with ethylene carbonate

OD (III) was subject to reactions with EC in the presence of potassium carbonate as a catalyst (Table 1). Also, DABCO was tested as a catalyst, however its presence elongates the reaction time significantly in comparison with potassium carbonate (Table 1, see runs 6 and 3).

Studies carried out with a 4-molar excess of EC (runs 1—5) had evidenced that reactions with OD should be held at the temperature of 160 °C, in the presence of 0.06 mole of K_2CO_3/mole of OD (runs 5). Then the reaction rate is the highest and a large number of oxyethylene units are kept in a structure of the product.

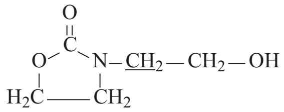
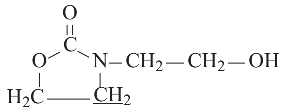
T a b l e 1. Conditions of OD with EC reaction

Run	Initial molar ratio	Amount of K_2CO_3 mole K_2CO_3/ mole OD	Temp. °C	Time of reaction h	Molar ratio OD:x*) in post-reaction mixture (from mass balance)
1	1:4	0.03	140	8.5	1:2.8
2	1:4	0.03	160	6	1:3.8
3	1:4	0.06	140	8	1:3.5
4	1:4	0.09	140	7	1:3.9
5	1:4	0.06	160	3.5	1:3.8
6	1:4	0.06**)	140	14	1:3.8
7	1:5	0.06	160	3	1:4.8
8	1:6	0.06	160	4	1:5.8
9	1:8	0.09	140	22	1:7.9
10	1:8	0.09	160	5	1:7.9
11	1:12	0.09	160	8	1:11.8

*) Oxyethylene unit.

**) DABCO was used as catalyst.

T a b l e 2. The ^{1}H NMR data (see Fig. 1)

Chemical shift, ppm	Signal originating
7.7 and 8.0	NH_2- in OD
8.5	-NH- in substituted OD
8.0	-NH- in oxalamidoester
4.25	-(CO)O-CH_2-
3.49	-CH_2-OH
3.52	-CH_2-O-CH_2-
3.2	
3.6	

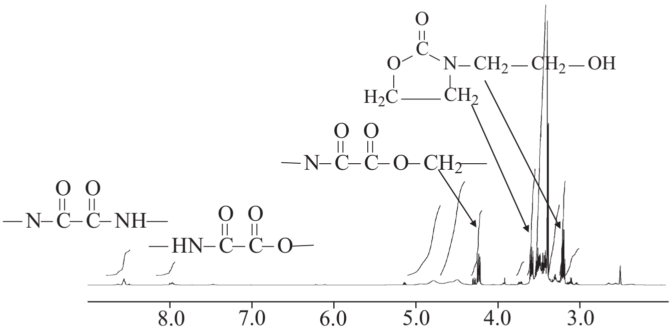


Fig. 1. ^{1}H NMR spectrum of the product of reaction of OD:EC = 1:4 received in the presence of 0.03 mole K_2CO_3/mole OD at 140 °C (run 1 in Table 1)

In ^{1}H NMR spectrum of OD two signals of chemical shift at 7.7 and 8.0 ppm (Fig. 1 and Table 2) are observed

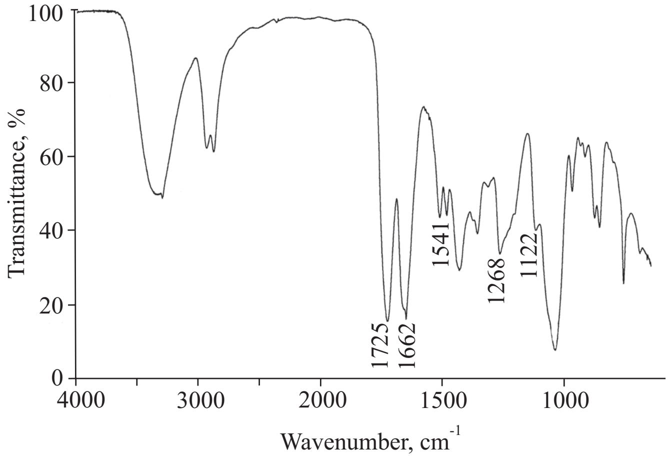


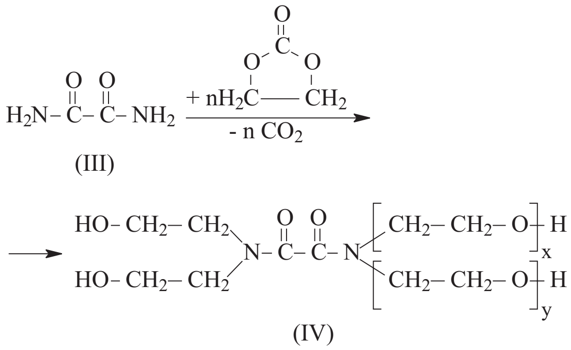
Fig. 2. IR spectrum of the product of reaction of OD:EC = 1:4 received in the presence of 0.03 mole K_2CO_3/mole OD at 140 °C

resulting from unequally valuable protons of amide groups, and in ^{13}C NMR spectrum one signal at 162.4 ppm. In IR spectrum at 1663 and 1610 cm^{-1} the first and second amide bands occur and at 3383 and 3192 cm^{-1} bands originating from vibration band of N-H bonds of secondary amides are present (Fig. 2, Table 3).

So, ^{1}H NMR analysis demonstrated that with a 4-molar excess of EC there are still unreacted secondary amide groups [Equation (2) (IV) where x = 0, y ≥ 1] in the product, as proved by the presence of a signal at 8.5 ppm (Fig. 1) from protons of secondary amide groups and the first and second amide bands of secondary amides at 1662 and 1541 cm^{-1} in IR spectrum (Fig. 2, Table 3).

Table 3. The IR data (see Fig. 2)

Frequency, cm^{-1}	Band originating
1663	first band of first amide
1610	second band of first amide
3383 and 3192	N-H of secondary amides
1662	first band of secondary amide
1541	second band of secondary amide
1122	C-O-C valence of ether
1725	C=O valence of ester
1268	C-O valence asymm. of ester



(2)

where: n = 4

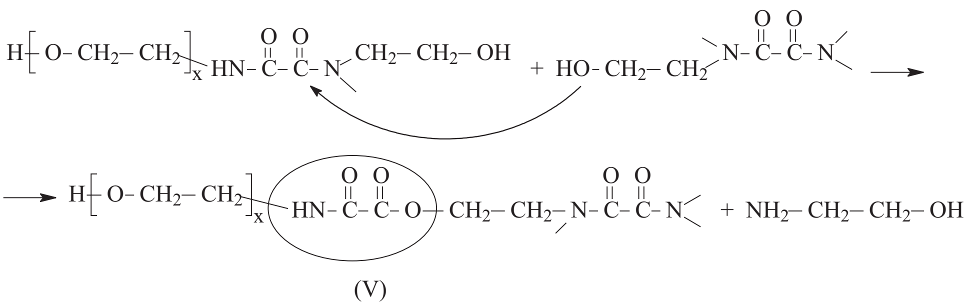
The secondary amide groups disappear only in the spectra of the reaction products obtained with a 6-molar excess of EC (Table 1, run 8).

The presence of the unreacted amide groups results from a partial decomposition of EC into carbon dioxide and ethylene oxide [23] in such conditions, which is evidenced by a mass balance (Table 1). Further, consecutive reactions of 2-hydroxyethylene groups with unreacted EC take place, where — apart from the product (IV), where x = 0 and y = 1 — the products (IV) are formed where x = 0 and y > 1. In IR spectrum of the product (Fig. 2) a band at 1122 cm^{-1} is noticeable which is specific for vibrations of C-O-C ethers (Table 3). It results from greater reactivity of hydroxyl groups than secondary amide groups during their reactions with EC.

In ^{1}H NMR spectrum of the product (Fig. 1) there is also a signal of chemical shift at 8.0 ppm originating from proton of amide groups of oxalamidoester (V) [4]. These groups are effected by condensation of the formed hydroxyethylene derivatives of OD [eq. (3)].

Confirmation of such course of the reaction is provided by the presence in ^{1}H NMR spectra of the products (Figs 1 and 3) signals at 3.2 and 3.6 ppm from protons of methylene groups at nitrogen atom of 2-hydroxyethylene group and in ring of *N*-(2-hydroxyethyl)oxazolidinone [see (VI) in Equation (4) and Table 2]. Their concentration decreases with the increase of excess of EC used for the reaction (Figs 1 and 3).

N-(2-hydroxyethyl)oxazolidinone (VI), identified under GC-MS analysis of the obtained products, is formed in the reaction of 2-aminoethanol (evolved during condensation) with EC:



(3)

where: x = 0 or 1

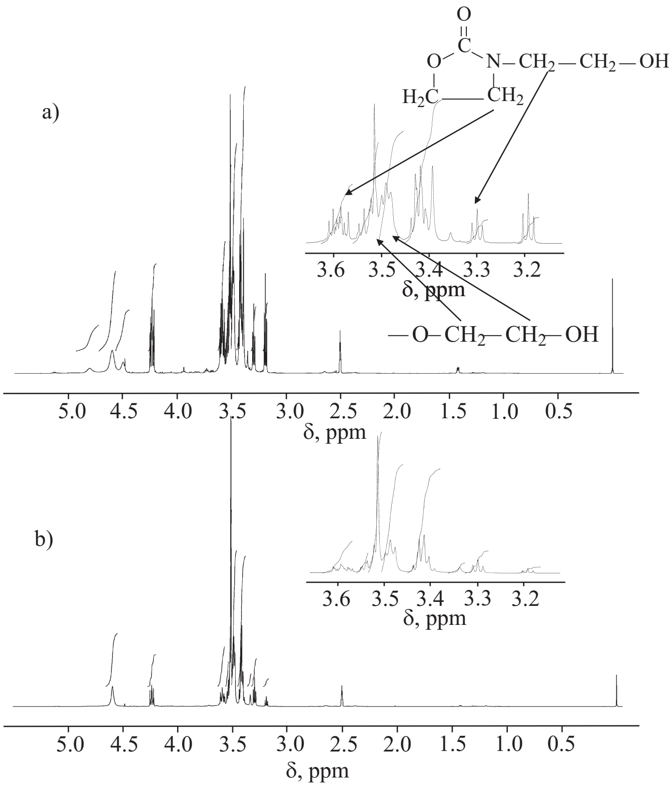


Fig. 3. ^{1}H NMR spectra of the product of reaction of OD:EC = a) 1:8 — run 10 in Table 1, b) 1:12 — run 11 in Table 1, received in the presence of 0.09 mole K_2CO_3/mole OD at 160 °C

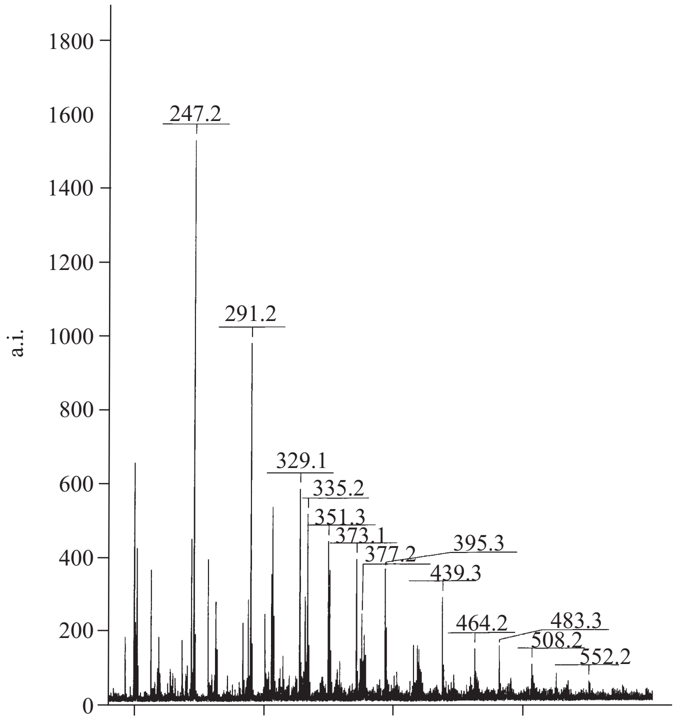
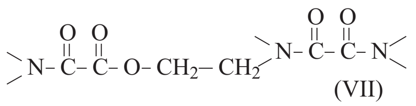


Fig. 4. MALDI ToF spectrum of product of reaction of OD:EC = 1:8 received in the presence of 0.09 mole K_2CO_3/mole at 160 °C



$$>N-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-N<\;\; >N-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-N<$$

(VII)

The occurrence of the condensation is confirmed by MALDI ToF analysis indicating the presence of hydroxyethylene derivatives of dimers (VII) (Figs 4 and 5).

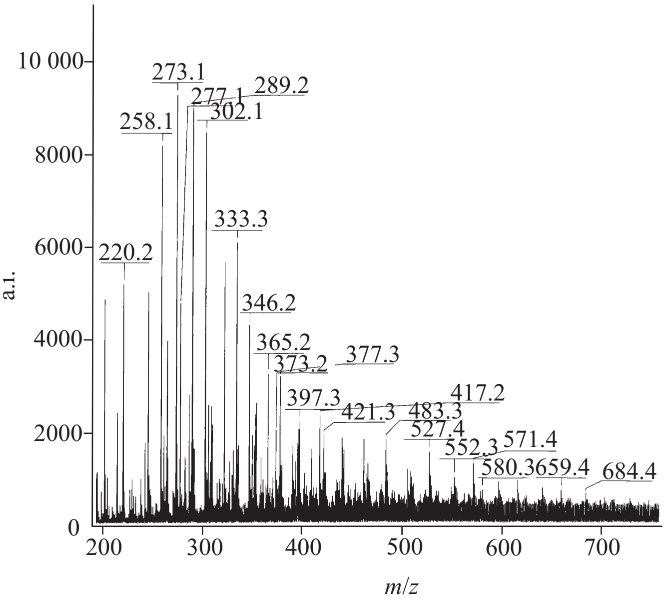
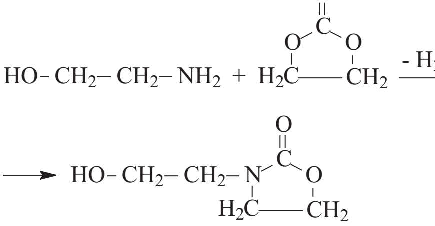


Fig. 5. MALDI ToF spectrum of product of reaction of OD:EC = 1:12 received in the presence of 0.09 mole K_2CO_3/mole at 160 °C

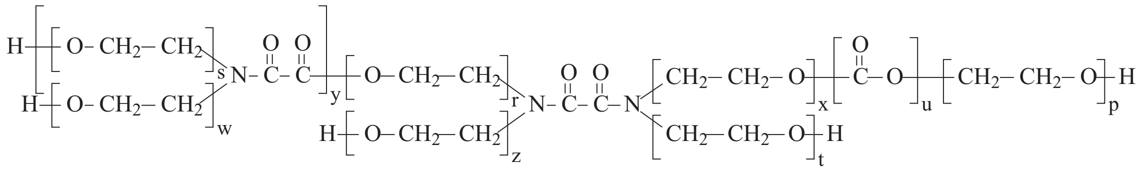
Analysis of MALDI ToF spectra shows that the products obtained with 8- and 12-molar excess of EC comprise oligomers containing respectively up to 10 and 13 of oxyethylene units per mole of OD or its dimer (VII).



(VI)

(4)

Contribution of the condensation was estimated by determination of GC content of *N*-(2-hydroxyethyl)oxazolidinone in the obtained products (Table 4). Together with the increase of EC excess used for the reaction (runs 1 → 11), the content of *N*-(2-hydroxyethyl)oxazolidinone decreases and at 12-molar excess of EC it is already only 3.8 wt. %. Similarly, it decreases together with an increase of the reaction temperature (runs 1 and 2, 9 and 10) or increase of catalyst's amount at a given temperature (runs 1 and 3, 3 and 4, 2 and 5). It is also seen in ^{1}H NMR spectra of the products obtained in reactions



where: y, u ≥ 0, s + w + r + z + x + t + p ≤ 12 (VIII)

with growing excess of EC, where decreasing signals from protons of methylene groups at nitrogen atom (3.2 and 3.6 ppm) are noticeable (Fig. 3).

T a b l e 4. Percentage of by-products in reaction products of OD with EC

Run*)	Percentage of *N*-(2-hydroxyethyl)oxazolidinone in post-reaction mixtures, wt. %	Percentage of glycols in post-reaction mixtures, wt. %	
		TRIEG**)	TETRAEG**)
1	27.6	0	0
2	16.8	0	0
3	23.1	0	0
4	17.0	0	0
5	13.6	0	0
7	9.3	0	0
8	11.5	0	0
9	7.2	6.4	5.8
10	5.3	0	7.1
11	3.8	0	10.4

*) Run according to Table 1.

**) TRIEG — triethylene glycol, TETRAEG — tetraethylene glycol.

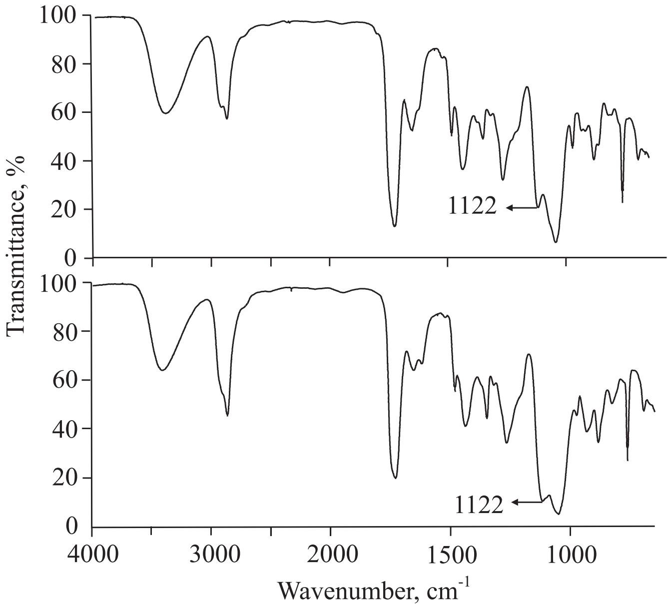


Fig. 6. IR spectra of the product of reaction of OD:EC = a) 1:8, b) 1:12, received in the presence of 0.09 mole K_2CO_3/mole OD at 160 °C

In ^{1}H NMR spectrum a signal at 4.25 ppm is also noticeable, which is typical for protons of methylene groups adjoining to ester unit *e.g.* of *N*-(2-hydroxyethyl)oxazolidinone or of the product (V). Further, during the reaction of OD with EC the carbonate groups may be built-in the product's structure [see (VIII)], therefore this signal may also originate from methylene groups present at the carbonate group.

The presence of ester groups in structure of the obtained products is confirmed by their IR spectra (Fig. 2) in which there are bands at 1725 and 1268 cm^{-1} from C=O and -O-(CO) vibration bands of ester respectively (Table 3).

Together with the increase of EC excess (Table 1, runs 7—11), in ^{1}H NMR spectra of the products (Fig. 3) the signal at 3.54 ppm originating from methylene groups at hydroxyl group splits into 2 signals of chemical shifts at 3.49 and 3.52 ppm originating from protons of the methy-

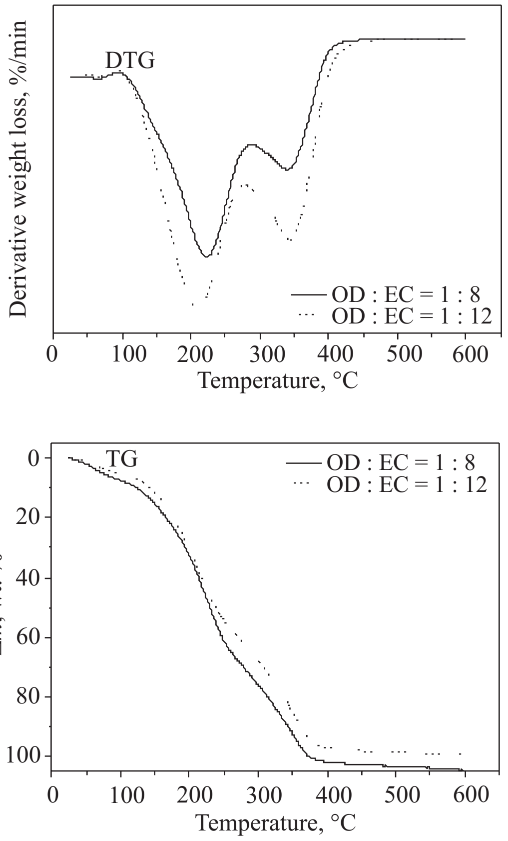


Fig. 7. Thermal analysis of the product of reaction of OD:EC = 1:8 or 1:12, received in the presence of 0.09 mole K_2CO_3/mole OD at 160 °C

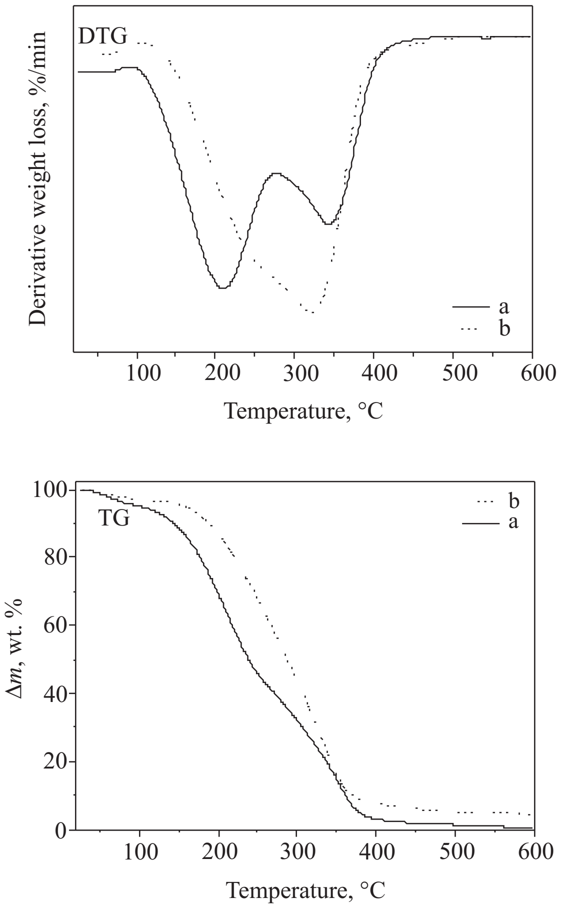


Fig. 8. Thermal analysis of the product of reaction of OD:EC = 1:12 received in the presence of 0.09 mole K_2CO_3/mole OD at 160 °C: — before heating, ···· after heating at 200 °C for 4 h

lene groups at hydroxyl group and in the ether unit (Figs 3a and 3b, Table 2) respectively; intensity of the latter signal increases together with the increase of EC excess. Also, a distinct increase of intensity of a band at 1122 cm^{-1} sourced from -O-C-O- vibrations of ethers in IR spectra of the products (Fig. 6) has been observed.

GC analysis showed that the reaction products of OD with 8- and 12-molar excess of EC also includes other by-products, *i.e.* TRIEG and TETRAEG (Table 4, runs 9—11).

Thermogravimetric studies demonstrated enhanced thermal stability of the obtained hydroxyethoxy derivatives of OD. The thermogram of the product obtained at 8- or 12-molar excess of EC shows two peaks at temperature *ca*. 230 and 350 °C (Fig. 7). The first of them results from decomposition of carbonate groups while the second one from decomposition of oxalamide and oxalamidoester groups [3, 4]. Heating up of the product obtained at 12-molar excess of EC at 200 °C, *i.e.* in decomposition conditions of the carbonate groups [24, 25], results in a practical disappearance of the peak at 230 °C, with only one peak left with the maximum at temperature of 330 °C (Fig. 8).

Some selected physical properties of the obtained derivatives of OD, namely density, viscosity and surface tension (Fig. 9) have been examined. It was found that together with a temperature increase, density and surface tension decrease linearly and the viscosity in exponential mode. Therefore, they are subject to change in temperature function, similarly to properties of typical polyols used for obtaining polyurethane foams [25]. These physical properties together with increased thermal stability, cause that hydroxyethoxy derivatives of OD will be suitable for obtaining foamed polyurethane plastics with enhanced thermal stability.

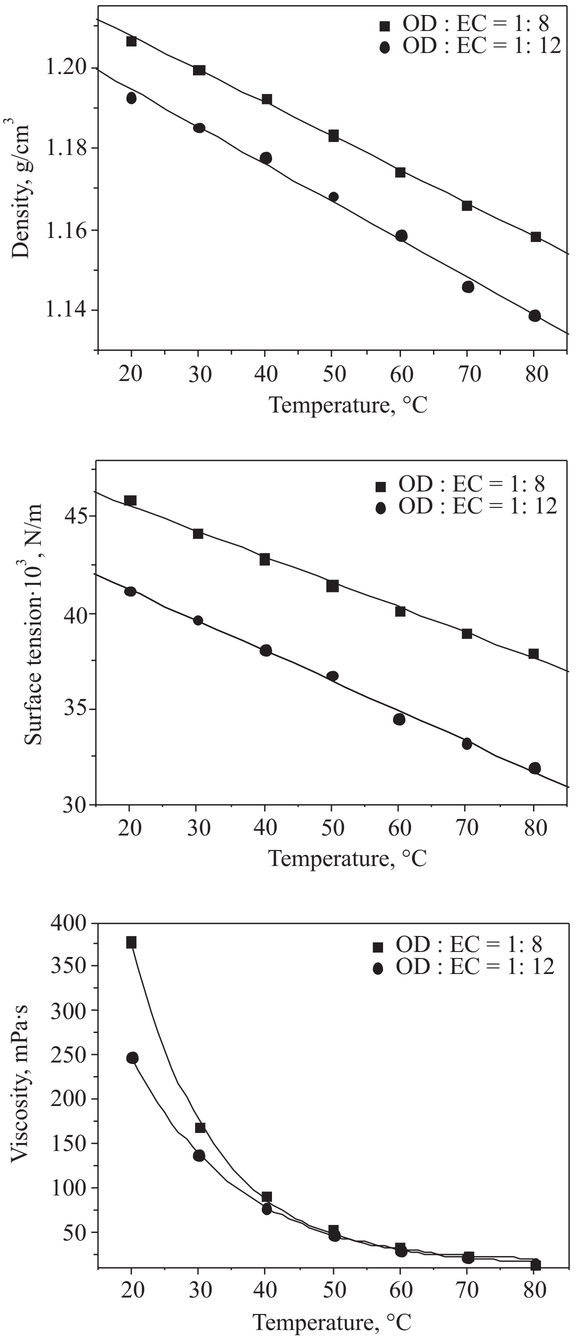


Fig. 9. Some physical properties of reactions products of OD with EC in function of temperature

Foams

Hydroxyethoxy derivatives of OD of variable percentage of ethoxy groups were foamed with diphenylmethane diisocyanate (MDI) and water. The optimized water amount was 2 wt. % related to polyol and *ca.* 1.21 g TEA/100 g of polyol as catalyst. The best foams were obtained with the use of 2.0-molar excess of isocyanate groups in relation to number of hydroxyl groups.

As it was stated before, the following relevant properties of polyurethane foams were studied: apparent density, water uptake, stability of dimension, thermal stability and glass transition temperature.

The apparent density of obtained foams falls within the 23—33 kg/m^3 region. Water uptake for the obtained foams was not more than 10 wt. % after 24-hour exposition.

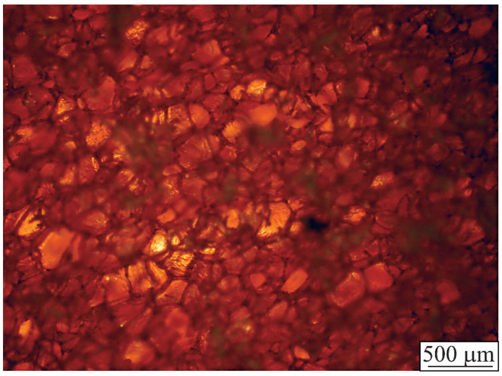


Fig. 10. Morphology of foam on the basis of the polyols obtained as the product of reaction of OD:EC = 1:8 (magnification 25×)

The optical microscope photography of obtained polyurethane foam displays morphology, namely the size and distribution of the pores. The foams have closed, regularly distributed pores of 0.2—0.6 mm size (Fig. 10) and good stability of dimension: the linear distortions are less than 5 linear %.

Glass transition temperature of foams generally exceeds ambient temperature. Thus, the products fall into category of rigid foams [25].

The prolonged heating tests (30 days at 150, 175 or 200 °C) indicated that constant mass of samples was achieved after 10—15 days. The lowest mass loss was observed for the foam on the basis of polyols obtained with using molar excess of EC equal to 8. It reached 19, 28 or 37 wt. % at selected temperatures, respectively.

CONCLUSIONS

In the reaction of oxamide with ethylene carbonate mainly hydroxyethoxy derivatives are formed. Condensation of these derivatives also takes place during the reaction while generating the oxamidoester unit. Contribution of the condensation is limited to dimerization of the derivatives and decreases together with an increase of excess of ethylene carbonate used for the reaction. The obtained hydroxyethoxy derivatives are characterized by the enhanced thermal stability, which results mainly from the presence of oxamide group in their structures. They can be advantageously used as polyols in synthesis of polyurethane foams with increased thermostability.

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