Analysis of the Reaction Course of Oxamide and N,N′-bis(2-hydroxypropyl)Oxamide with Propylene Carbonate

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ABSTRACT: Studies on obtaining and hydroxypropyl properties of oxamide (OD) derivatives with contribution of OD and N,N′-bis(2-hydroxypropyl)oxamide (BHPOD) were carried out. As a hydroxyalkylating agent, the propylene carbonate (PC) was used. Hydroxypropylating with OD proceeds with a partial preservation of carbonate groups in the structure of products, and during the reaction, a partial dimerization of hydroxypropoxylene derivatives of OD occurs. The obtained hydroxypropoxy derivatives of OD are distinguished by an increased thermal stability. Hydroxypropoxy derivatives of OD are expected to find application as polyol components for the manufacture of thermally stable foamed polyurethane plastics. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1624–1633, 2011

Key words: oxamide; N,N′-bis(2-hydroxypropyl)oxamide; propylene carbonate; structure of product; thermal properties

INTRODUCTION

Oxamide (OD) is an oxalic acid diamide. It is a crystal substance, sparingly soluble in water, and ethanol. It can be obtained by means of a glow electrolysis of formamide,[1] anode oxylation of HCN, or cyanide ions in an alkaline environment.[2] OD was also obtained through a pyrolysis of ammonium oxalate at 180–200°C in the ammonia atmosphere.[3] Another method of synthesis consists in alkaline[4] or acidic[5] hydrolysis of dicyan. A recent method consists in catalytic oxidation of hydrogen cyanide.[6]

OD found application as an ammonium fertilizer,[7,8] in cosmetic industry,[9] as well as in polymer chemistry. OD was used for stabilization of formaldehyde polymers, as an antidepolymerizing agent.[10] Furthermore, OD and its high-melting and sparingly volatile derivatives were used to increase the inhibiting effect of activity of copper(II) ions on thermal oxidation of polypropylene.[11] Moreover, the presence of OD arrangement in the structure of polymers, obtained in the reactions of dialkyl oxalates with polymethylenediamines, is responsible for the increased strength of fibers and a better light resistance compared to traditional polyamides.[12,13]

In this study, a synthesis of hydroxypropoxy derivatives of OD in reactions of OD and N,N′-bis(2-hydroxypropyl)oxamide (BHPOD) with propylene carbonate (PC) was attempted to obtain polyols.

Such reactions in these studies have been carried out for the first time. The literature does not reveal any data on obtaining hydroxyalkyl derivatives of OD, except for synthesis of BHPOD.[14] As a hydroxyalkylation agent, the PC was used, which is nontoxic, nonflammable, and ecofriendly. The obtained hydroxyalkyl derivatives of OD were used as polyol components for polyurethane foams of the enhanced thermal stability. The literature reveals that BHPOD was used as the ingredient of flame resistant polyurethane foams,[15] hence a similar effect should be expected when using other hydroxyalkyl derivatives of OD.

Grounds for the set forth expectations regarding properties and a possible application of hydroxyalkylation products of OD with PC can be confirmed by the example of properties of hydroxyalkylation products of parabanic acid.[16,17] In the structure of parabanic acid, a structure of OD can be distinguished and the reaction products of parabanic acid with alkylene carbonates featured by a high-thermal stability have found application as ingredients of thermally stable polyurethane foams.[18]

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EXPERIMENTAL

Synthesis

Synthesis of BHPOD
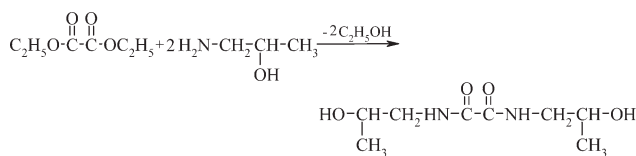
In a 1000-cm³ three-necked round-bottomed flask equipped with reflux condenser, thermometer, and dropping funnel, 67.8 cm³ (73 g, 0.5 mol) of diethyl oxalate (pure, Avocado, Germany) was placed. Oxalate was magnetically stirred and cooled to 0–5°C and 60.3 cm³ (61 g, 1 mol) 1-aminopropan-2-ol (pure, Fluka, Switzerland) and added slowly at such rate that the reaction temperature did not exceed 10°C. During reaction, with crystalline solid precipitated and due to difficulties with stirring, about 60 cm³ ethyl alcohol was added to reaction mixture. The reaction mass was dissolved in 600 cm³ of boiling ethyl alcohol and cooled until BHPOD crystallized. The precipitate was filtered off, separated, and dried in vacuum drier at 60°C under 0.09 MPa pressure. Melting point was 119°C.[14]

): IR (KBr), $\nu = 3448$ (s, O—H valence), $\nu = 3297$ (s, N—H valence), 2977 (w, —CH₃, asym. valence), 2937 (w, —CH₂—, asym. valence), 2884 (w, —CH₂— and —CH₃, sym. valence), 1642 (w, C=O, valence), 1538 (w, C—N and N—H, deform.), 1459 (s, —CH₂—, scissoring), 1091 (w, C—O—H, valence), [cm⁻¹]; ^{1}H NMR (500 MHz, d_6-DMSO), $\delta = 1.02$ (3 H, d, CH_3—, $J_{4,3} = 6.3$ Hz), 3.10 (2 H, —C_2H_2—, system AB, $J_{AB} = 14.0$ Hz, $\nu_A = 3.05$, $\nu_B = 3.15$, $J_{A3} = 5.6$ Hz, $J_{B3} = 6.3$ Hz), 3.75 (1 H, sept., —CH—, $J = 6.2$ Hz), 4.78 (1 H, d, —OH, $J = 4.9$Hz), 8.5 (1 H, t, —NH—, $J = 5.8$ Hz); [ppm]; ^{13}C NMR (d_6-DMSO), $\delta = 159.9$ (C₁), 64.6 (C₃), 46.5 (C₂), 20.9 (C₄) [ppm]; MS, $m/z = 198$ (35%), 167 (22%), 137 (12%), 120 (100%), 91 (46%), 59 (18%).

Reactions of OD or BHPOD with PC
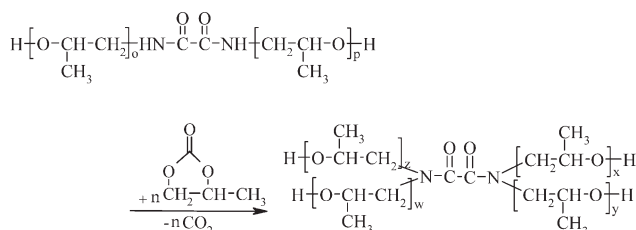
where $o = p = 0 - OD$, $o = p = 1 - BHPOD$, $z + w + x + y = n + o + p$.

In a 100-cm³ three-necked round-bottomed flask, 4.4 g (0.05 mol) OD (pure, POCH, Gliwice, Poland) or 10.2 g (0.05 mol) BHPOD and the appropriate amount of PC (pure, Fluka, Switzerland) were placed to reach the molar ratio of reagents of 1 : 2–1 : 12 and 0.42–0.62-g potassium carbonate (8.28–12.42 g/mol OD or BHPOD, 0.06–0.09 mol/mol OD or BHPOD) or 0.34–0.78 g dizabicyclo[2.2.2]octane (DABCO) (6.72–15.68 g/mol OD or BHPOD, 0.06–0.14 mol/mol OD or BHPOD) was added. The reaction mixture was protected from moisture and stirred mechanically at 160 or 180°C with monitoring of progress of the reaction by determination of unreacted PC.[19]

Synthesis of 3–(2-hydroxypropyl)-5-methyloxazolidinone

IPOX was synthesized similar to 3-(2-hydroxyethyl)oxazolidinone.[20]
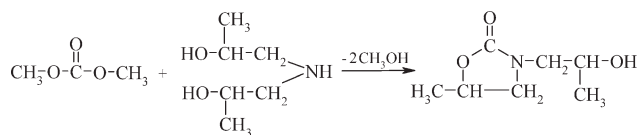
In a 250-cm³ three-necked round-bottomed flask equipped with reflux condenser, thermometer and magnetic stirrer 44.4 g (0.3 mol) diisopropanoloamine and 56.5 cm³ (0.6 mol) dimethyl carbonate were placed. The reaction mixture was stirred and heated to 90°C (at this temperature the solution becomes homogeneous) and reflux began. During this reaction, the temperature of the vapor decreased to 70°C. The reaction was completed after 24 h. Methanol was removed from the product mixture under reduced pressure, and the remaining was 3-(2-hydroxypropyl)-5-methyloxazolidinone (IPOX), which was characterized by spectral methods.

IR (KBr), $\nu = 3420$ (w, O—H valenc.), 2922 (w, —CH₂—, asym. valenc.), 2883 (w, —CH₂—, sym. valenc.), 1714 (w, C=O, valenc.), 1486 and 1436 (s, —CH₂—, scissoring), 1042 (w, C—O—H, valenc.), [cm⁻¹]; ^{1}H NMR (500 MHz, d_6-DMSO), $\delta = 1.05$ (3 H, d., HO—CH(CH₃) —, $J_{6,5} = 6.2$ Hz), 1.30 (3 H, d., —O—CH(CH₃)—, $J_{1,3} = 6.3$ Hz), 3.05 (2H, m, HO—CH(CH₃) —CH₂—, $J_{5,4} = 5.4$ Hz), 6.30 (2H, m, —O—CH(CH₃)—CH₂—, $J_{2,1} = 6.2$ Hz), 3.80 (H, s, HO—CH(CH₃)—, $J_{2,1} = 5.3$ Hz), 6.40 (H, s, —O—CH(CH₃)—, $J_{2,1} = 7.5$ Hz), 4.78 (1 H, s, HO—) [ppm].

Analytical Methods

^{1}H NMR spectra of products were recorded with 500 MHz spectrometer (Bruker, Germany) in d_6-

TABLE I
Reaction Conditions of OD With PC

Run	Initial Molar Ratio	Amount of catalyst (mol/mol OD)		Temp. (°C)	Time of reaction (h)	Molar ratio OD : x in postreaction mixture (from mass balance)	Percentage of ester group (mol %)
1	1 : 4	K_2CO_3	0.09	160	17	1 : 3.90	–
2	1 : 4		0.12	160	15	1 : 4.00	25
3	1 : 4		0.09	180	4.5	1 : 3.79	26
4	1 : 4	DABCO	0.09	160	28	1 : 4.00	–
5	1 : 4		0.09	180	6	1 : 3.82	20
6	1 : 6		0.09	180	6	1 : 5.72	21
7	1 : 8		0.09	180	6	1 : 7.14	–
8	1 : 8		0.12	180	6	1 : 7.45	19
9	1 : 12		0.12	180	7	1 : 9.24	14

x, oxypropylene unit.

DMSO and HMDS reference. IR spectra were taken for films with PARAGON 1000 FTIR spectrophotometer (PerkinElmer, Wellesley, MA).

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

Chromatographic analysis of side products, that is, propylene glycol (PG) and products of its consecutive reactions with PC (DPG and TRIPG) and IPOX were performed with gas chromatograph HP 4890A (Hewlett–Packard, Ringoes, NJ) with FID detector and HP1 30 m × 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, and detector temperature: 300°C. The samples were dissolved in methanol (0.01M). Internal reference was cyclohexanone. Percentage of diols and polyols was calculated according to calibration curves as described in Ref. 17.

MALDI ToF spectra of reaction products of OD or BHPOD with PC were obtained on Voyager–Elite Perseptive Biosystems (US) mass spectrometer working at a linear mode with delayed ion extraction, equipped with nitrogen laser working at 337 nm. The matrix was 2,5-hydroxybenzoic acid and α-cyanocinnamic 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^{+}, H^{+}, and CH_3OH.

Thermal analyses (DTG and TG) of hydroxypropyl derivatives of OD were performed at temperature range of 20–600°C, on ~ 2 mg sample, under nitrogen atmosphere with Termowaga TGA/DSC 1 derivatograph (Mettler).

RESULTS AND DISCUSSION

To obtain hydroxypropyl derivatives of OD, reactions of OD(I) with PC at the temperature of 160–180°C were carried out, initially in the presence of potassium carbonate and then DABCO as a catalyst (Table I). In the presence of potassium carbonate in the postreaction mixture, obtained with a 4M excess of PC, a sediment of BHPOD was precipitated, which was not the case while using DABCO for this reaction.

It was noticed that with a 4M excess of PC, there is still a certain amount of unreacted secondary amide groups in the product. Spectral analysis showed the presence of a signal at 8.5 ppm from protons of the secondary amide groups in ^{1}H NMR spectrum of the product (Fig. 1), similarly as in the spectrum of BHPOD (see Experimental section). Furthermore, in IR spectrum of the product (Fig. 2), the first and the second amide bands of the secondary amide at 1667 and 1516 cm^{-1} may be observed.

The mass balance indicates however a minimum decomposition of PC[21] (mass losses are near or equal to zero, Table I, syntheses 1–5). The presence of free amide groups means therefore that successive reactions of 2-hydroxypropyl groups occur more readily than those of secondary amide groups with PC and the products (II) are formed, where $x = 0$ and $y > 1$.

$$(1)$$
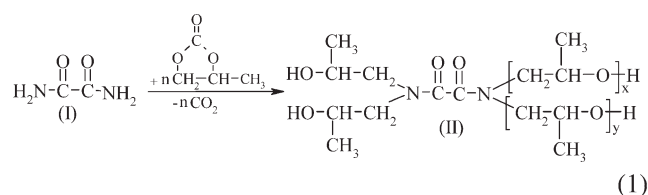
where $x \geq 0$, $y \geq 1$, and $n = 4$.

Formation of ether groups is confirmed by IR spectrum of the product (Fig. 2) in which a band specific for valence vibrations C—O—C at 1090 cm^{-1} occurs.
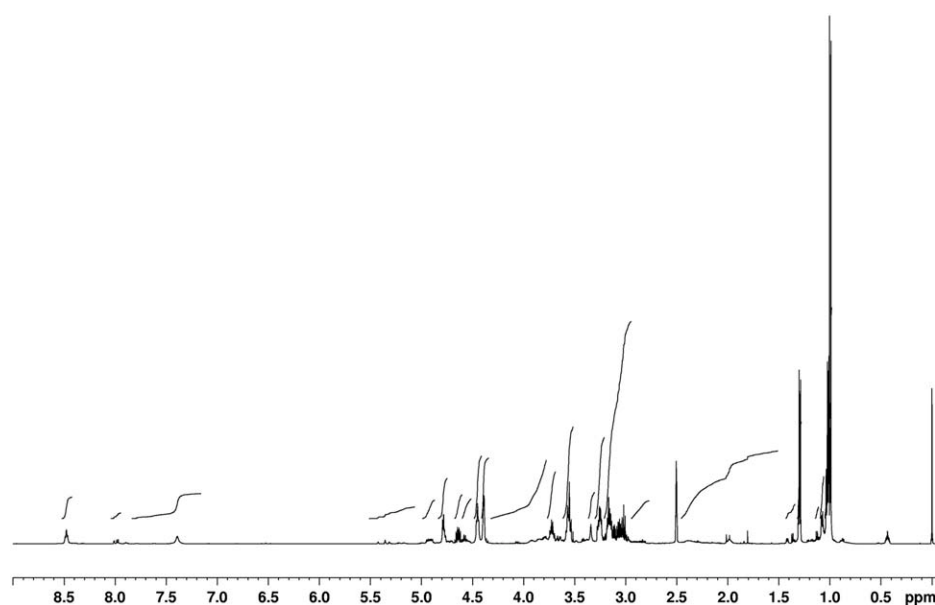
Figure 1 ^{1}H NMR spectrum of the reaction product of OD : PC at the initial molar ratio 1 : 4 in the presence of 0.12 mol DABCO/mol OD at 180°C.

In ^{1}H NMR spectrum of the product (Fig. 1), two mutliplets at 4.55 and 4.65 ppm from protons of methine groups at ester arrangement were observed. The signal at 4.55 ppm results from the presence of ester groups, which are formed by building up of the carbonate groups into the product's structure (III):

$$(2)$$
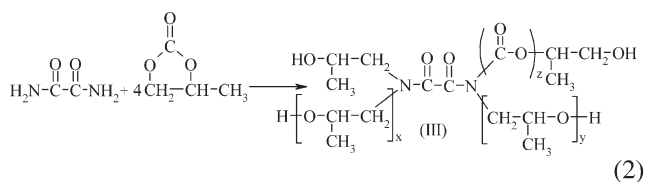
where $x, z \geq 0$, and $y \geq 1$.

The second signal at 4.65 comes from methine groups of OD ester, which indicates the occurrence of dimerization of OD hydroxypropyl derivatives while forming the product (IV):

$$(3)$$
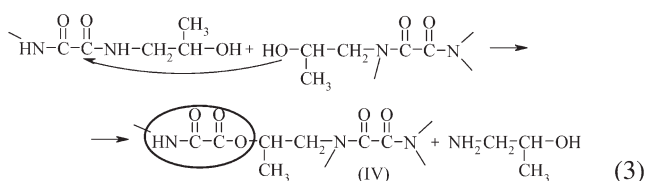
The presence of carbonate groups is confirmed by the signal observed at ^{1}H NMR spectrum of the product (Fig. 1) at 7.4 ppm from the secondary protons of amide groups in the structure (III), where x = 0. The dimerization is confirmed by the signal at 8.0 ppm from the secondary protons of amide groups of OD ester (IV).[22]

Furthermore, in IR spectra of the products, a band from valence vibrations of ester carbonyl groups at 1728 cm^{-1} as well as the band at 1246 and 1134 cm^{-1} from asymmetric and symmetric valence vibrations of ester's C—O bond were observed (Fig. 2).

It was noticed that an increase of the reaction temperature significantly reduces its duration (Table I, syntheses 4 and 5), whereas it does not influence the contribution of the a.m. processes (intensity ratios of the respective signals are the same). In turn, the change of the catalyst from potassium carbonate into DABCO (Table I, syntheses 1 and 4) makes the dimerization contribution distinctly decrease, which is indicated by the diminishing intensity of the signal at 4.65 ppm.

Similarly, when comparing intensity of signals at 1.0 and 1.25 ppm from protons of methyl groups of 2-hydroxypropyl groups and 2-hyxypropoxyl groups
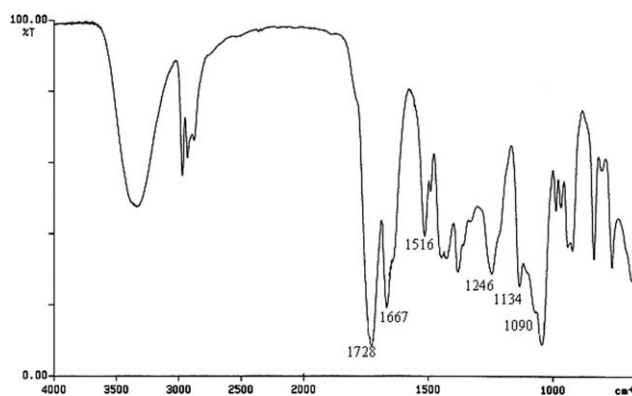

Figure 2 IR spectrum of the reaction product of OD : PC at the initial molar ratio 1 : 4 in the presence of 0.12 mol DABCO/mol OD at 180°C.
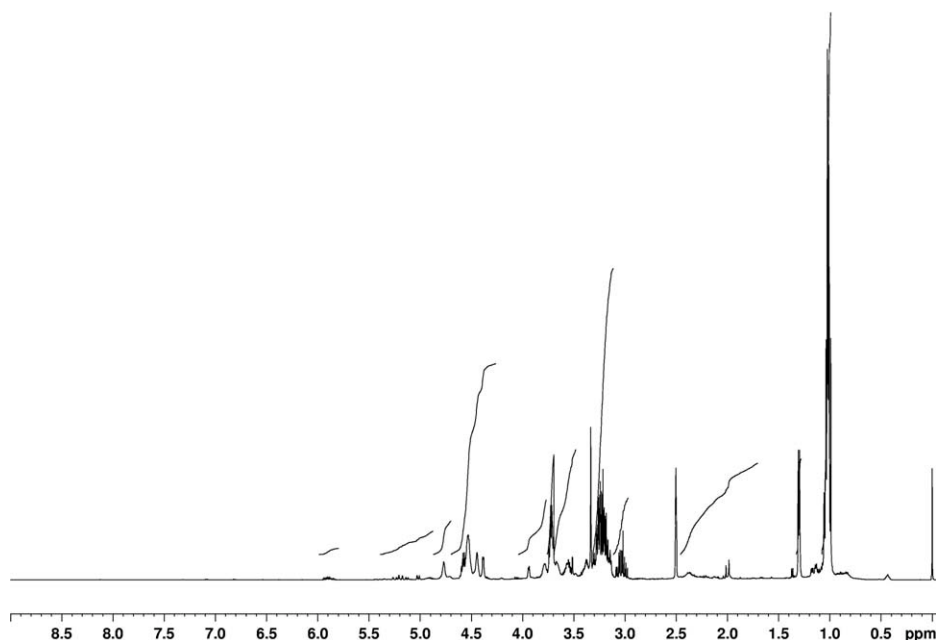
Figure 3 ¹H NMR spectrum of the reaction product of OD : PC at the initial molar ratio 1 : 12 in the presence of 0.12 mol DABCO/mol OD at 180°C.

as well as 2-hydroxypropyl groups contributing in the ester arrangement, diminishing contribution of ester groups may be noticed. The contribution of hydroxypropyl groups existing at the ester group in the products obtained using potassium carbonate as the catalyst amounts to 25 mol %, and when using DABCO to 20 mol %. The increase of PC excess makes the contribution of ester groups decrease to 14 mol % at a 12M excess of PC (Fig. 3, Table I).

Together with the increase of PC excess, the carbonate groups may build up into the product's structure joining not only the amide group (V, $x = 0$), but also hydroxyl group of hydroxyalkyl derivatives of OD while forming the product V ($x > 0$).
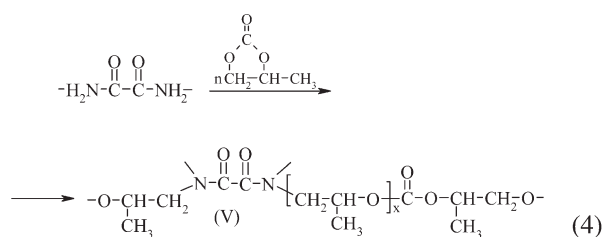
where $n \geq 6$.

Furthermore, together with the increase of PC excess, the signal disappears at 4.65 ppm, which means elimination of dimerization of the hydroxypropyl derivatives (Fig. 3).

MALDI ToF spectrography of the products obtained at a 6- and 10M PC excess (Fig. 4) did neither show any presence of dimmers. It confirmed, however, the presence of the carbonate groups in

the products. The products obtained at a 6- and 10M PC excess (Fig. 4) consist of oligomers containing up to 6 and 8 oxypropyl units per OD mole, respectively.

GC-MS analysis demonstrated the presence of IPOX (VI). IPOX is formed as the result of the reaction of 1-aminopropane-2-ol evolving by dimerization with PC:

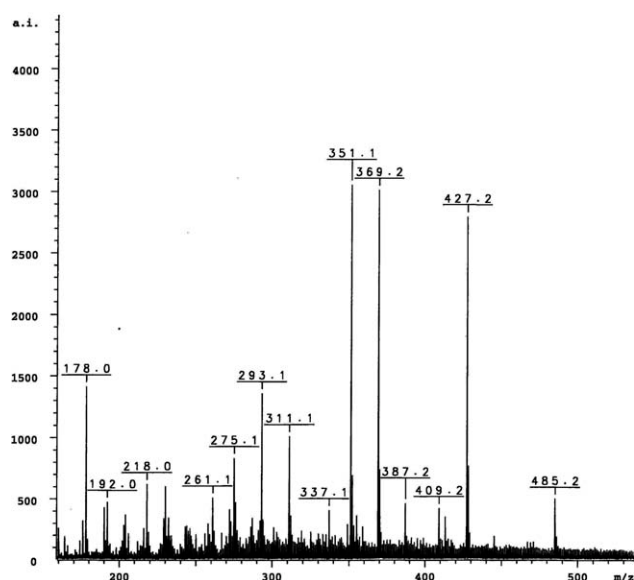**Figure 4** MALDI ToF spectrum of reaction product of OD : PC at the initial molar ratio 1 : 8 in the presence of 0.012 mol DABCO/mol OD at 180°C.

TABLE II
Percentage of By-Products in Reaction Products of OD with PC

Entry[a]	Percentage of glycols in postreaction mixtures (wt %)				Percentage of IPOX in postreaction mixtures (wt %)
	PG[c]	DGP[d]	TRIPG[e]	Σ	
1[b]	14.35	1.57	0.00	15.92	0.73
2[b]	16.31	1.68	0.00	17.99	1.12
3[b]	11.71	1.48	0.00	13.19	0.28
4	14.02	1.31	0.00	15.33	1.07
5	14.05	0.94	0.00	14.99	0.00
6	12.84	8.51	1.66	23.01	2.16
7	17.22	11.97	2.29	33.38	1.82
8	8.77	14.73	6.66	29.16	1.33
9	3.93	14.89	9.11	27.93	0.89

[a] Entry according to Table I.
[b] K_2CO_3 was used as catalyst.
[c] Propylene glycol.
[d] Dipropylene glycols.
[e] Tripropylene glycols.

$$(VI) \qquad (5)$$

The IPOX content determined by the GC method is small, not exceeding 2.2 wt %, and it does not depend on PC excess used in the reaction (Table II). The presence of IPOX indicates a minimum contribution of dimerization of OD hydroxypropyl derivatives.

The secondary amide groups disappear not earlier than at a $6M$ excess of PC. In this case, in the ^1H NMR spectra of the products, no signals above 6.0 ppm are observed, and in IR spectra, the band disappears at 1516 cm^{-1}, while the first amide band of tertiary amide displays at 1675 cm^{-1} (Fig. 5). In IR

spectra of the products obtained with larger and larger excess of PC, an increased intensity of the band at 1090 cm^{-1} from vibrations of —O—C—O— ether was noticed (see Figs. 2 and 5).

Furthermore, in ^1H NMR spectra of the products obtained with a $6M$ and higher excess of PC (Fig. 3), signals in the range 5–6 ppm specific for protons of allyl groups[23] were observed, which indicates dehydration of the ending hydroxypropyl groups:

$$(6)$$

A general structure of the products obtained from the reaction of OD with PC may be presented by the following formula (VII):

$$(VII)$$

where $0 \leq x, s, z, o \leq 1$.

The obtained products were analyzed by GC to identify any by-products, which may form in the reaction of PC with water, that is, PG and the products of its successive reactions with PC. It was noticed that the contribution of PG decreases together with an increase of PC excess used in the reaction, whereas the contribution of DPG and

TRIPG grows (Table II). Running the reaction at a $4M$ excess of PC in the presence of potassium carbonate or DABCO as a catalyst does not influence a contribution of glycols (Table II, entries 1–5). TRIPG are formed only when a $6M$ or higher PC excess was used (Table II, entries 6–9). A big excess of PC (a $6M$ and higher) makes that consecutive reactions of PG with PC occur; therefore, in the obtained
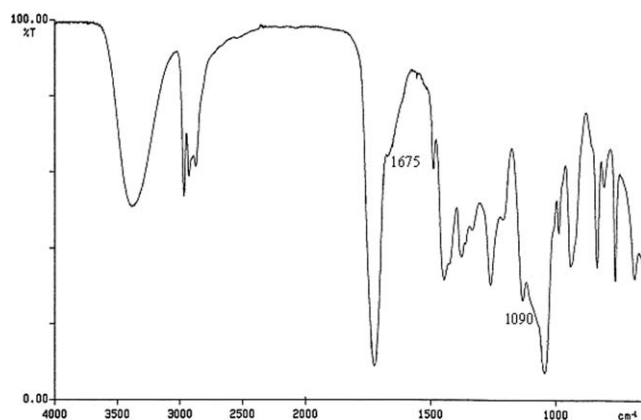
Figure 5 IR spectrum of the reaction product of OD : PC at the initial molar ratio 1 : 6 in the presence of 0.12 mol DABCO/mol OD at 180°C.
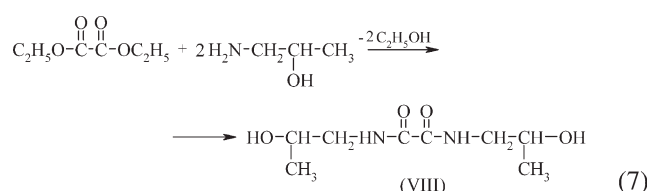
products, the contribution of PG decreases while the contribution of TRIPG increases.

Thermogravimetric studies demonstrated an enhanced thermal stability of the reaction products of OD with PC (Table III). On the DTG curve of the reaction product of OD with a 8M PC excess, two peaks are noticeable; the first one at 210°C indicates decomposition of the carbonate groups, and the second one at 290°C—a complete decomposition of the product, that is, decomposition of hydroxyalkyl and OD arrangements. The OD itself is subject to decomposition at 270°C (Table III, entry 1). Heating of the reaction product of OD with a 8M excess of PC at 200°C (decomposition conditions of the carbonate groups)[24,25] provides that the first peak with its maximum at 210°C on the DTG curve is decreased, which means decomposition of the carbonate groups. At a 12M excess of PC, one wide peak with the maximum at 290°C is observed on the DTG curve (Table III, entry 4), which indicates a lower

contribution of the carbonate groups in the product's structure.

In connection with the by-processes (building up of the carbonate group into the product's structure, dimerization of OD hydroxypropyl derivatives, and formation of propylene/poly/glycols), which accompany the reactions of OD with PC, it was decided to replace OD with BHPOD (VIII), expecting limitation on such processes.

BHPOD was obtained in a reaction analogous to the synthesis of N,N'-bis(2-hydroxyethyl)oxamide,[14] that is, in the reaction of diethyl oxalate with a 2M excess of 1-aminopropane-2-ol, upon suitable modification of synthesis conditions:

$$C_2H_5O-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OC_2H_5 + 2\,H_2N-CH_2\underset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow{-2\,C_2H_5OH}$$

$$\longrightarrow HO-\underset{CH_3}{\overset{|}{CH}}-CH_2-HN-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-NH-CH_2\underset{CH_3}{\overset{|}{CH}}-OH \quad (7)$$

$$\text{(VIII)}$$

BHPOD was subject to reactions with PC excess at 140–180°C temperature range, initially in the presence of potassium carbonate and then DABCO as a catalyst (Table IV). During the reaction of BHPOD with a 2M PC excess in the presence of potassium carbonate (Table IV, synthesis 1), a part of BHPOD remains unreacted in the postreaction mixture, similarly as in the reaction of OD with PC. Replacement of the catalyst for DABCO makes the reaction time longer (Table IV, syntheses 2 and 4 and 3 and 5), but BHPOD undergoes a complete reaction.

Similarly as during the reaction of OD with PC, the mass balance shows that a partial decomposition of PC occurred. The mass balance was made with the assumption that during the reaction of OD with PC, a complete separation of carbon dioxide occurs, hence with the completed reaction of PC with OD,

TABLE III
Thermal Stability of Reactions Products of OD or BHPOD with PC

Entry	Molar ratio of reagent	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	Temperature of max. decomposition (°C)
1	OD	215	235	250	270	270
2	OD : PC 1 : 8	130	160	190	260	210 and 290
3	OD : PC 1 : 8[a]	135	170	195	270	210 and 270
4	OD : PC 1 : 12	140	170	200	250	290
10[b]	BHPOD : PC 1 : 4	70	120	145	210	160 and 240
12[b]	BHPOD : PC 1 : 6	70	120	145	195	160 and 230
13[b]	BHPOD : PC 1 : 10	70	120	145	195	230

[a] After heating at 200°C.
[b] Entry according to Table IV.

TABLE IV
Reaction Conditions of BHPOD with PC

Run	Initial molar ratio	Amount of catalyst (mol/mol BHPOD)		Temp. (°C)	Time of reaction (h)	Molar ratio BHPOD : x in postreaction mixture (from mass balance)	Percentage of ester group (mol %)
1	1 : 2	K_2CO_3	0.09	140	27	1 : 1.86	24
2	1 : 2		0.06	160	15	1 : 1.79	–
3	1 : 2		0.09	160	10	1 : 1.54	–
4	1 : 2	DABCO	0.06	160	20	1 : 1.82	–
5	1 : 2		0.09	160	14	1 : 1.79	28
6	1 : 3		0.09	160	11	1 : 3.00	26
7	1 : 4		0.09	160	18	1 : 3.77	–
8	1 : 4		0.14	160	16	1 : 3.68	–
9	1 : 4		0.09	180	9	1 : 3.48	–
10	1 : 4		0.14	180	7	1 : 3.39	22
11	1 : 6		0.09	180	11	1 : 4.68	–
12	1 : 6		0.12	180	8	1 : 4.57	23
13	1 : 10		0.12	180	12	1 : 7.66	17

x-oxypropylene unit.

the ratio of hydroxypropylene groups to OD should correspond to the initial molar ratio OD : PC. The performed calculations show that it is lower, and so a partial decomposition of PC to propylene oxide and carbon dioxide occurs.[21] The spectral analysis proves the presence of ester groups in the structure of products, which means the contribution of carbonate and OD ester groups. The occurrence of dimerization (formation of OD ester groups) was confirmed by a GC-MS analysis for the obtained products, which indicated the presence of IPOX in their composition (Table V).

From the spectral analysis, it also appears that the contribution of ester groups in the structure of products decreases together with the increase of the PC excess used in the reaction and is subject to a change from 26 mol % at a 2M PC excess to 16 mol % at a 10M PC excess (Table IV).

A quantity analysis of IPOX in the reaction products of BHPOD with various molar excesses of PC showed the presence of a little amount of this compound, similarly to the reactions of OD with PC. The contribution of IPOX is within 0.26–3.38% wt % (Table V), and it is practically not related to the excess of PC used in the reaction; it is subject to a decrease together with an increase of catalyst's amount used in the reaction (Table V, entries 9 and 10 and 11 and 12). Thus, dimerization of hydroxypropyl derivatives of OD occurs only to a slight degree, irrespective of the PC's excess.

On the other hand, a MALDI ToF analysis of the products obtained at a 6- and 10M excess of PC

TABLE V
Percentage of By-Products in Reaction Products of BHPOD with PC

Entry[a]	Percentage of glycols in postreaction mixtures (wt %)				Percentage of IPOX in postreaction mixtures (wt %)
	PG[b]	DGP[c]	TRIPG[d]	Σ	
2	18.1	7.68	1.94	27.80	–
3	19.2	8.73	2.91	30.90	–
4	0	1.02	2.11	3.13	0
5	0	0.90	1.84	2.74	0
6	0	0.58	1.40	1.98	0.26
7	0	2.60	1.02	3.62	0.53
8	0	1.86	1.24	3.10	0.84
9	0	2.00	2.10	4.10	3.14
10	0	1.62	1.33	2.95	1.30
11	0	8.80	2.07	10.87	3.38
12	0	7.56	1.23	8.79	1.19
13	0	15.38	7.92	23.30	1.80

[a] Entry according to Table IV.
[b] Propylene glycol.
[c] Dipropylene glycol.
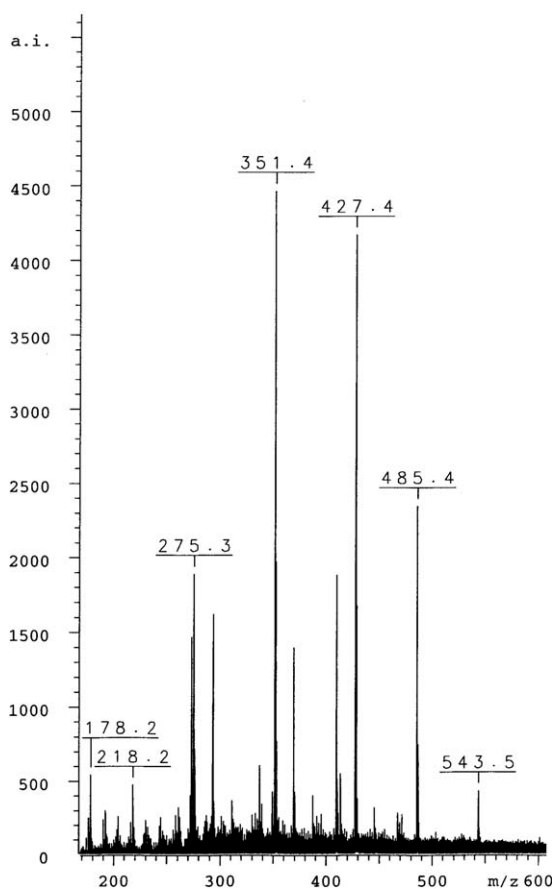[d] Tripropylene glycol.

Figure 6 MALDI ToF spectrum of the reaction product of BHPOD : PC at the initial molar ratio 1 : 6 in the presence of 0.012 mol DABCO/mol BHPOD at 180°C.

(Fig. 6), has not indicated a presence of dimmers in the reaction products of BHPOD with PC. However, it proved building up of the carbonate group into the structure of the products. From the MALDI ToF analysis, it results that the products obtained at a 6- and 10M PC excess consist of oligomers containing, respectively, up to 7 and 9 mol of oxypropylene units per OD mole, that is, by one oxypropylene unit more than the reaction products of OD with PC (see Figs. 4 and 6).

On the basis of the GC analysis, the content of by-products-/poly/propylene glycols in the reaction products of BHPOD with PC was investigated (Table V). It was noticed that using potassium carbonate as the catalyst promotes formation of by-products; a content of glycols being up to 30 wt % (Table V, entries 2 and 3). When DABCO and a 2–4M excess of PC are applied, DPG and TRIPG are formed in the amount of 2.0–4.1 wt % (Table V, entries 6–10). The contribution of by-products grows together with the increase of PC excess used in the reaction. When a 6 and 10M PC excess is used in the reaction with BHPOD, the resulting content of glycols is within 9–23 wt % (Table V, entries 11–13). It

should be noted that a temperature increase does not influence the amount of/poly/propylene glycols (Table V, entries 7 and 9 and 8 and 10), whereas an increase of the catalyst's amount results in a decreased content of glycols (Table V, entries 7 and 8, 9 and 10, and 11 and 12). The content of polyglycols in the reaction products of BHPOD with PC is distinctly lower compared to the reaction products of OD with PC (Tables II and V).

Thermogravimetric testing demonstrated an enhanced thermal stability of the reaction products of BHPOD with PC (Table III). On the DTG curve of the products (Fig. 7), two peaks are noticeable; the first one at 160°C comes from a decomposition of carbonate, and the second one at 240°C results from a decomposition of OD arrangements. The temperature exposure of the product obtained at a 4M PC excess in ratio to BHPOD at the temperature of 200°C (decomposition conditions of carbonate groups[24,25]) results in a distinct decrease of the first peak (Fig. 8). Together with the increase of PC
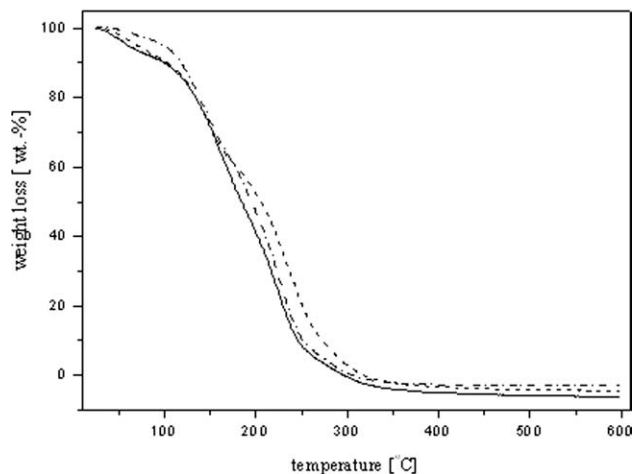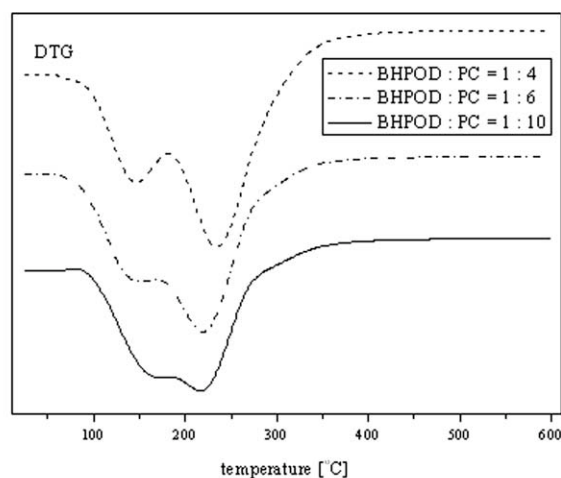

Figure 7 Thermal analysis of the reaction product of BHPOD : PC at the initial molar ratio: (a) 1 : 4, (b) 1 : 8, and (c) 1 : 12 in the presence of 0.12 mol DABCO/mol BHPOD at 180°C.
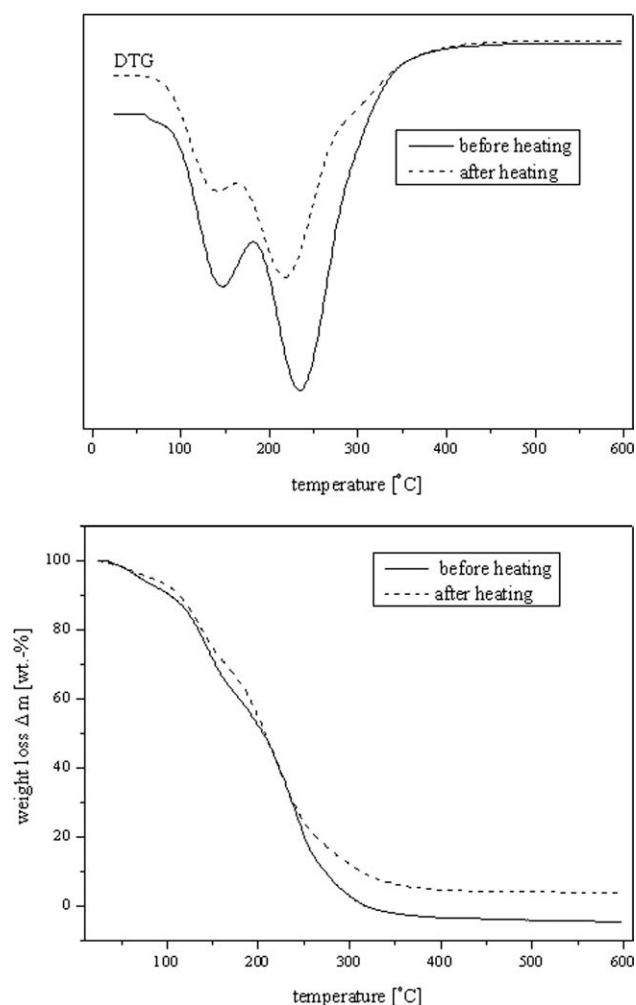
Figure 8 Thermal analysis of the reaction product of BHPOD : PC at the initial molar ratio:1 : 4 in the presence of 0.12 mol DABCO/mol BHPOD at 180°C.

excess used in the reaction, the peaks noted on DTG curve (Fig. 7) come closer, and at a 10*M* PC excess, practically one peak is observed. Hence, together with an increase of PC, excess building up of the carbonate group into the product's structure is subject to limitation.

CONCLUSIONS

In the reactions of OD with PC mainly hydroxypropoxy derivatives of OD are formed. During the reaction, condensation of these derivatives also occurs while the OD ester arrangement is being formed. Contribution of the condensation is limited to dime-

rization of the derivatives and is not dependent on the excess of PC used in the reaction. The obtained hydroxypropoxy derivatives of OD are distinguished by the enhanced thermal stability resulting from the presence of the OD group in their structure.

Using BHPOD in the reactions with PC instead of OD neither eliminates dimerization of hydroxypropyl derivatives of OD nor limits building up of the carbonate groups into the structure of the products, while it makes the contribution of by-products (polyglycols) firmly decrease.

Hydroxypropoxy derivatives of OD are expected to find application as polyol components for the manufacture of thermally stable foamed polyurethane plastics.[26]

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