

Hydroxyalkylation of Oxamic Acid with Propylene Carbonate: Synthesis, Composition, and Properties of Products

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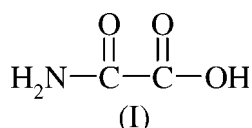
ABSTRACT: The work aimed at synthesis of hydroxypropoxy compounds containing oxalamidoester group from oxamic acid (OA) and propylene carbonate (PC) substrates. The thermal stability of obtained products was tested to estimate their usefulness for formation of polyurethane foams. The influence of initial molar ratio of reagents, amount of catalyst and temperature of reaction between OA and PC on structure of product was studied. The Matrix-Assisted Laser Desorption Ionization Time of Flight (MALDI ToF) analysis

of products evidenced that in the conditions used the formation of hydroxypropoxy derivatives of OA was accompanied by homocondensation of OA, which became minor process in presence of excess of PC. The physicochemical and thermal properties of products were studied. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 66–75, 2008

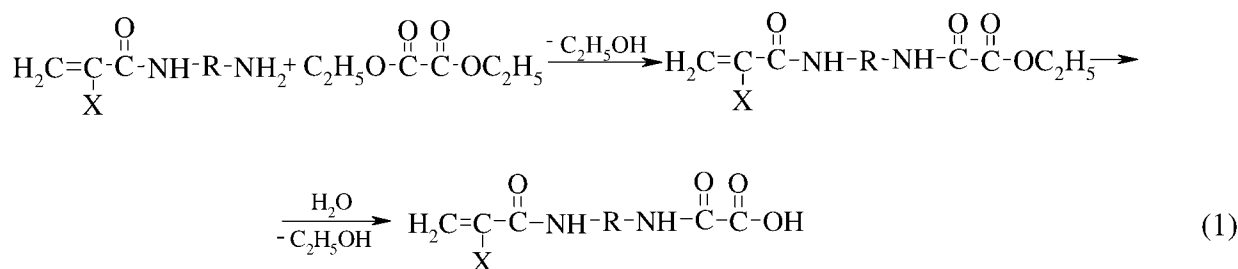
Key words: oxamic acid; propylene carbonate; structure of product; thermal properties

INTRODUCTION

Oxamic acid (I) is useful substrate for modification of structure and properties of polymers.^{1–6}



Introducing OA to acrylic, polyester, polyamide, epoxide, and polyethyleneimine resins renders the polymers more soluble in water, enhances their dispersity, and improves the stability of emulsions.^{1,2} The OA-based monomers which were applied for those purposes were obtained from dialkyl oxalate and unsaturated amine, and the semi product was further hydrolyzed according to the scheme:

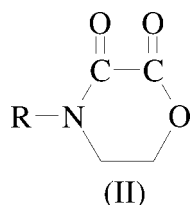


The high molecular weight products were then obtained in the free radical polymerization. The products were still reactive and at the same time resistant to water. They are used as varnishes, glues, and reactive resins.^{1,2} Another route to introduce OA

into polymer is served by reaction of dialkyl oxalates with resins containing primary and/or secondary amine groups. These nongel composites are used as crosslinking agents for resins with free amine groups or as semi products for nonflammable coatings.³ Furthermore, the incorporating of dialkyl oxalates into thermoplastic resins containing free amine groups leads to their fast crosslinking at ambient temperature with formation of thermally crosslinking coatings.⁴

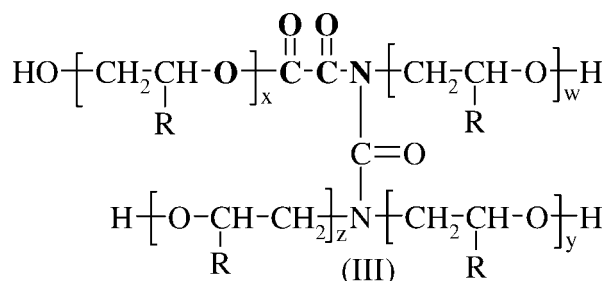
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The structural motif is present in morpholine-2,3-dione (II), which upon reaction with polyoxypropylenediamine or polyoxypropylenetriamine and next with ethylene oxide leads to dioxalamidotetraols. The latter can be successfully used for synthesis of polyurethanes, polyisocyanurates applicable as glues, laminates, or coatings.^{5,6}



where R=H—, alkyl, hydroxyalkyl, cyanoalkyl group.

Thus, the OA unit (oxalamidoester unit) was usually incorporated to polymer chains as ester or morpholino-2,3-dione. Here we present the attempts to synthesize hydroxypropyl- and hydroxypropoxy-derivatives with oxalamidoester unit starting from OA itself. Products were expected to possess enhanced thermal stability by analogy with the products obtained from parabanic acid and alkylene carbonates (III), in which the oxalamidoester group was formed as a result of parabanate ring opening.^{7,8} The products of the general formula:



where R=CH₃—, H— revealed high thermal stability,^{7,8} which rendered them useful substrates for obtaining thermally stable polyurethane foams.⁹ The temperature range within which the typical polyurethane foams can operate is 90–110°C,^{10,11} whereas the foams obtained on the basis of the products of hydroxyalkylation of parabanic acid are thermally stable up to 180°C.⁹

In this article OA was subjected to hydroxyalkylation with PC. The thermal stability of products obtained from OA and PC was studied in the aspect of their further application to synthesis of thermally stable polyurethanes.

EXPERIMENTAL

Reactions of OA with PC

In a 100 cm³ three-necked round bottom flask 3.5 g (0.04 mol) OA (pure, Avocado, Great Britain) and

the appropriate amount of PC (pure, Fluka, Switzerland), were placed to reach the molar ratio of reagents of 1 : 1-1 : 15 and 0.266–0.350 g diazabicyclo[2.2.2]octane (DABCO) (6.83–15.58 g/mol OA, 0.06–0.140 mol/mol OA) or 0.328 g potassium carbonate (8.42 g/mol OA, 0.060 mol/mol OA) was added. The reaction mixture was protected from moisture with tube filled with magnesium sulfate mounted on top of reflux condenser and stirred mechanically at 160–180°C to dissolve OA in PC. Progress of reaction was followed by determination of unreacted PC.¹²

Analytical methods

The acid number (AN) of derivatives of OA was determined by titration with 0.1M potassium hydroxide solution in presence of phenolphthalein.¹³ ¹H NMR spectra of products were recorded with BS-586A 80 MHz spectrometer (Tesla, Brno, Czechoslovakia) in deuterated dimethyl sulfoxide (d₆-DMSO), and hexamethyldisiloxane (HMDS) reference. IR spectra were taken for films with PARAGON 1000 FTIR spectrophotometer (Perkin-Elmer, Wellesley, MA).

Chromatographic analysis of by-products, i.e., propylene glycol (PG) and products of its consecutive reactions with PC 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 was 20°C/min, end temperature was 220°C, time of heating at 220°C was 6 min, loader temperature was 250°C, detector temperature was 300°C. The samples were dissolved in methanol (0.01M). Internal reference was cyclohexanone. Percentage of diols and polyols were calculated according to calibration curves what was described in article.⁷

MALDI ToF spectra of reaction products of OA with PC were obtained on Voyager-Elite Perseptive Biosystems (USA) 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/cm³, followed by addition of 10 mg/cm³ NaI in acetone. Therefore in some cases the molecular ion weights were increased by the mass of Na⁺, H⁺, and CH₃OH.

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

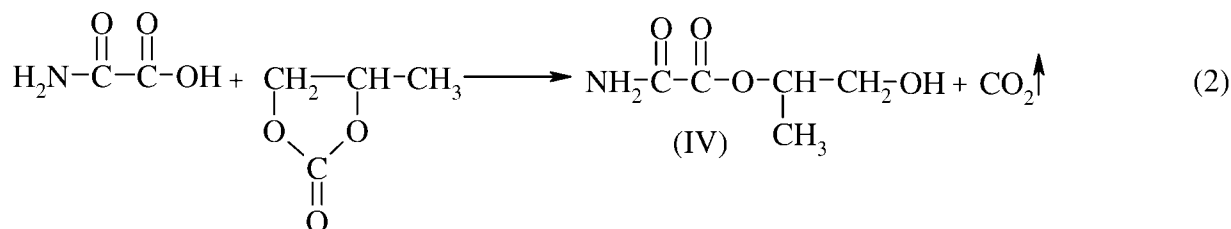
The following properties of esteramidoimidotetraols have been determined: pycnometer density,¹⁴

refractive index (with Abbe's refractometer), Höppler viscosity,¹⁵ and surface tension by ring detach method.¹⁶ All measurements were made in temperature range 20–80°C.

RESULTS AND DISCUSSION

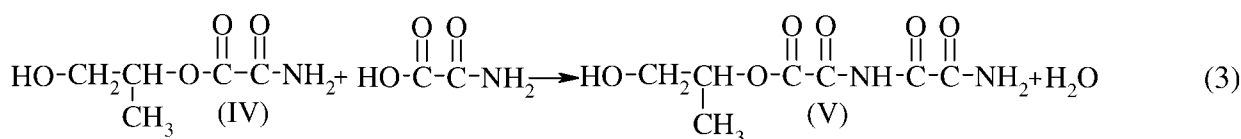
Based upon previous literature data the basic catalysts: potassium carbonate and DABCO were used for the reaction between OA and PC.^{17,18}

The reactivity of acidic carboxyl group and amphoteric amide groups of OA is different. The reaction between OA and PC at 1 : 1M ratio results in formation of product without free carboxyl groups as determined on the basis of IR spectrum [the acid-amide bands at 2400–2600, 1889, and 985 cm⁻¹, Fig. 1(a,b)]. The found AN of the product is very small, ~ 10 mg KOH/g (calculated AN is 313 mg KOH/g). Accordingly, PC reacts preferentially with carboxyl group of OA to give product IV:

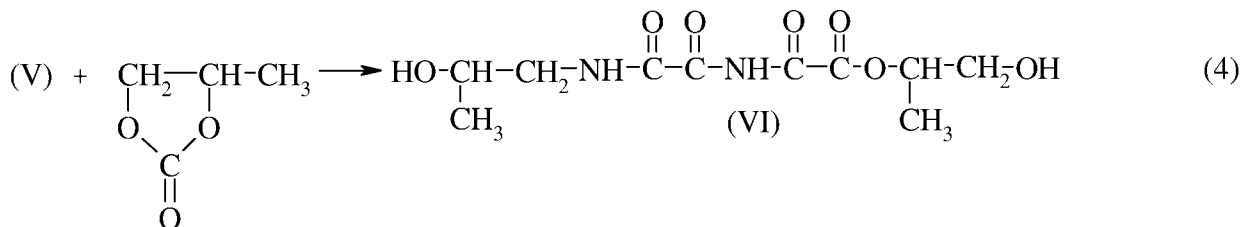


On the other hand, the mass balance evidences that in the product formally only 0.38 oxypropylene unit per one OA unit is present (Table I, run 1). Thus, the rest of OA (0.62 mol) is involved in other reaction

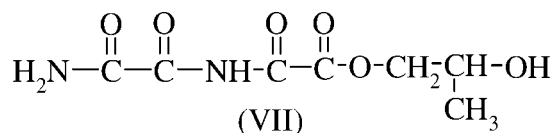
which is condensation of IV with next OA and formation of imide bond in V. This product was identified on the basis on the ¹H NMR [Fig. 2(a)] spectrum by the resonance of imide group proton at 8.5 ppm.¹⁹



Then the product V reacts further with PC with formation of amide group in VI:



Furthermore, the presence of the resonance from $-(\text{CO})-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2-$ centered at 4.6 ppm indicates the abnormal attack of PC on carboxyl group of OA. The pure resonance of that proton becomes cleared upon deuteration of hydroxyl group protons, which otherwise overlap with the former signal [Fig. 2(a,b)]. It is noticeable, that abnormal product VII does not form which can be deduced from the absence of the methylene group proton resonance at 4 ppm in $-(\text{CO})-\text{O}-\text{CH}_2-$.



Previously we have identified the abnormal product in the reaction between *N,N'*-bis(2-hydroxyethyl) parabanate and carboxylic acids.²⁰ Moreover, the absence of the resonance at 4.0 ppm precludes the involvement of carboxyl groups of OA in the reaction:

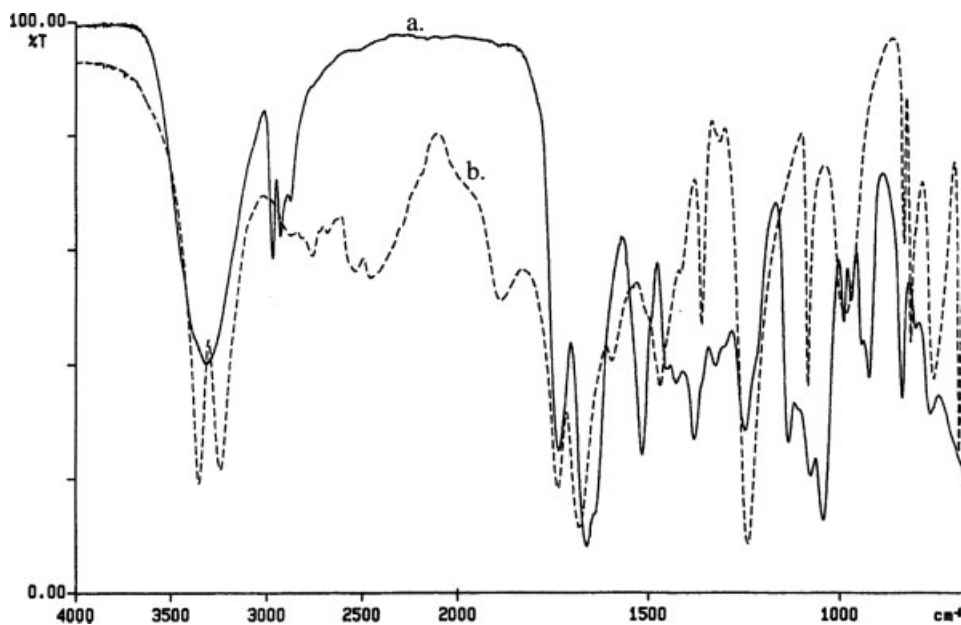


Figure 1 IR spectra of (a) product from OA : PC 1 : 1 in the presence of 0.06 mol K_2CO_3 /mol OA at temperature 160°C, (b) OA.

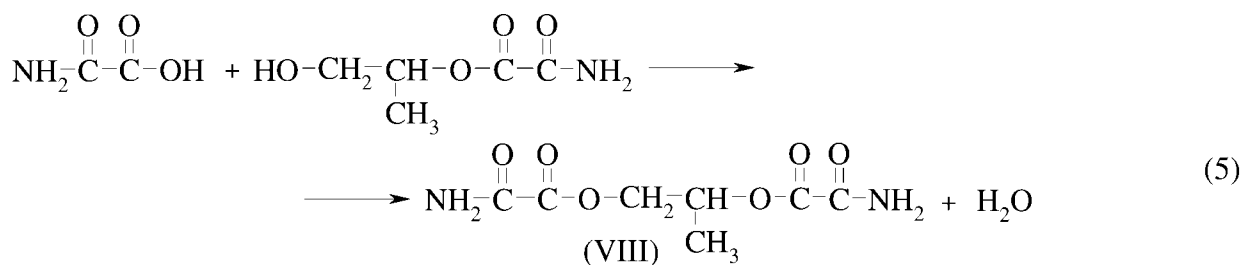


TABLE I
Reaction Conditions of OA with PC

Run	Initial molar ratio	Amount of DABCO (mole/mole OA)	Temp. (°C)	Time of reaction (h)	Molar ratio : x in postreaction mixture (from mass balance)	Mass loss of PC (wt %)
1	1 : 1	0.06 ^a	160	8.5	1 : 0.38	26.0
2	1 : 2	0.06 ^a	160	7.5	1 : 1.34	33.0
3	1 : 3	0.06 ^a	160	16	1 : 2.43	19.0
4	1 : 3	0.06 ^a	180	4	1 : 2.04	32.0
5	1 : 3	0.06	160	26	1 : 2.63	37.0
6	1 : 3	0.06	180	6	1 : 2.34	22.0
7	1 : 3	0.09	160	7	1 : 2.54	15.0
8	1 : 4	0.09	180	5	1 : 3.16	21.0
9	1 : 6	0.09	180	8.5	1 : 4.37	27.2
10	1 : 9	0.09	180	10	1 : 4.99	44.5
11	1 : 9	0.11	180	9	1 : 5.37	40.0
12	1 : 9	0.14	180	9	1 : 6.06	32.7
13	1 : 12	0.09	180	13	1 : 5.61	53.2
14	1 : 12	0.11	180	12	1 : 6.44	46.0
15	1 : 12	0.14	180	12	1 : 7.14	40.5
16	1 : 15	0.14	180	20	1 : 8.20	52.8

^a K_2CO_3 was used as catalyst, x, oxypropylene unit.

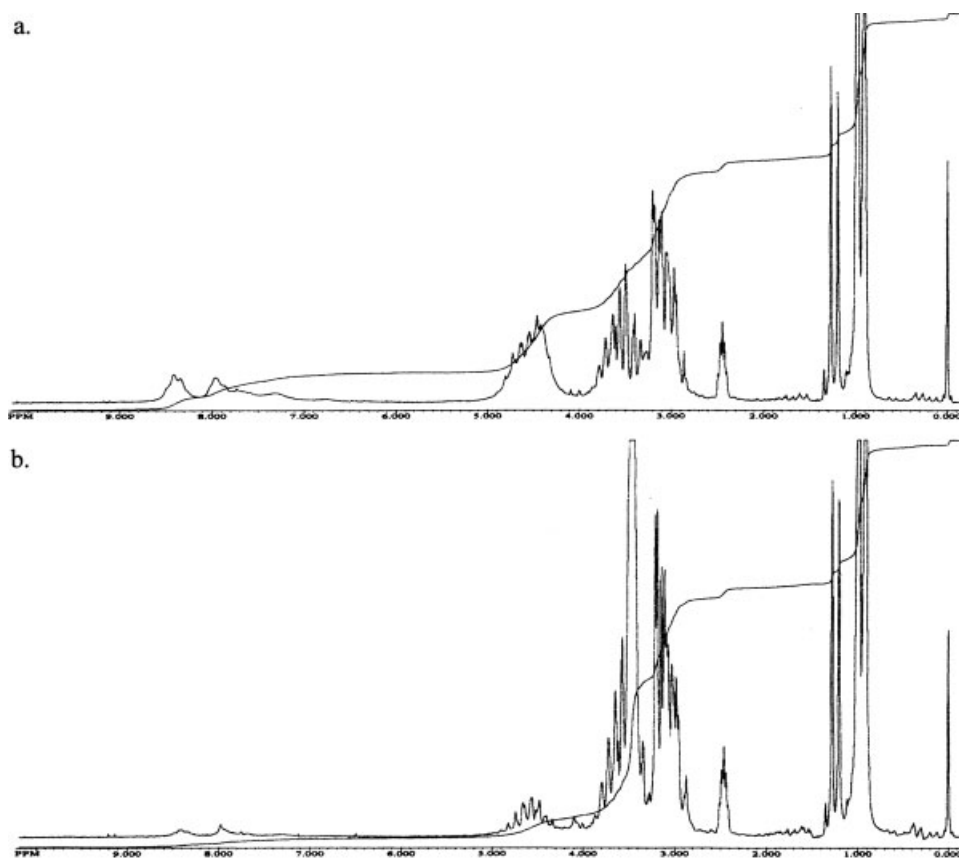
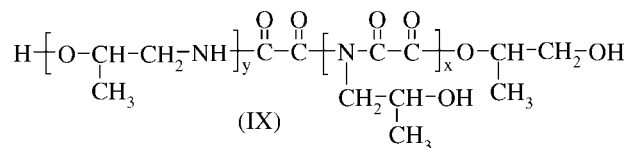


Figure 2 ^1H NMR spectrum of product from OA : PC 1 : 1 in the presence of 0.06 mol K_2CO_3 /mol OA at temperature 160°C (a) without D_2O , (b) with D_2O .

The presence of ester bond was confirmed by the bands at 1745 and 1247 cm^{-1} in the IR spectrum of product, assigned as valence bands of $\text{C}=\text{O}$ and $\text{C}-\text{O}(\text{CO})$ [Fig. 1(a)].

Two doublets at 0.95 and 1.25 ppm in the ^1H NMR spectrum (Fig. 2) were attributed to: $(\text{CO})\text{NH}-\text{CH}_2-\text{CH}(\text{CH}_3)-$ and $(\text{CO})-\text{O}-\text{CH}(\text{CH}_3)$, respectively.¹⁹ The integral intensity ratio is 8:1, i.e., eight $\text{N}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{OH}$ groups per one $(\text{CO})-\text{O}-\text{CH}(\text{CH}_3)-\text{CH}_2\text{OH}$ group are present totally in amide and imide fragments. This observation leads to conclusion that OA condenses with hydroxypropyl derivative of OA with formation not only dimeric structures, but also further oligomers. There is one imide group per one amide group in dimeric product, whereas in oligomers the number of imide groups per one amide group increases. Amide and imide groups form product IX upon further reaction with PC resulting in number of N -(2-hydroxypropyl) groups in comparison with the number of O -(2-hydroxypropyl) ones.



where $y < 1$.

Thus, it can be concluded that at the OA : PC 1 : 1 system (Table I, synthesis 1) the mixture of products is formed by condensation of O -(2-hydroxypropyl) derivatives of OA with OA and then upon reaction of imide and amide groups with PC.

In the ^1H NMR spectrum of product of reaction between OA and PC at 1:2M ratio (Table I, synthesis 2) the resonances from secondary amide and imide protons are still present, though their integral intensity is lower than before. Also the relative intensity ratio of resonances at 0.95 and 1.25 ppm from methyl protons on amide (or imide) and ester changes; about 25% mol of oxypropylene groups become involved in formation of ester. The products obtained from 1 : 3 OA : PC system (Table I, synthesis 3-7) have no free imide groups and amide groups disappear totally when fourfold excess of PC is used. In the products obtained from 1 : 3 and 1 : 4 systems there are about 33 and 20% mol oxypropylene groups in the ester fragment, respectively.

The characteristic feature of IR spectrum of the product obtained from OA : PC 1 : 2 system is the presence of 1080 cm^{-1} stretching $\text{C}-\text{O}-\text{C}$ ether vibration which demonstrates the consecutive reaction of hydroxypropyl groups with PC [Fig. 3(a)].

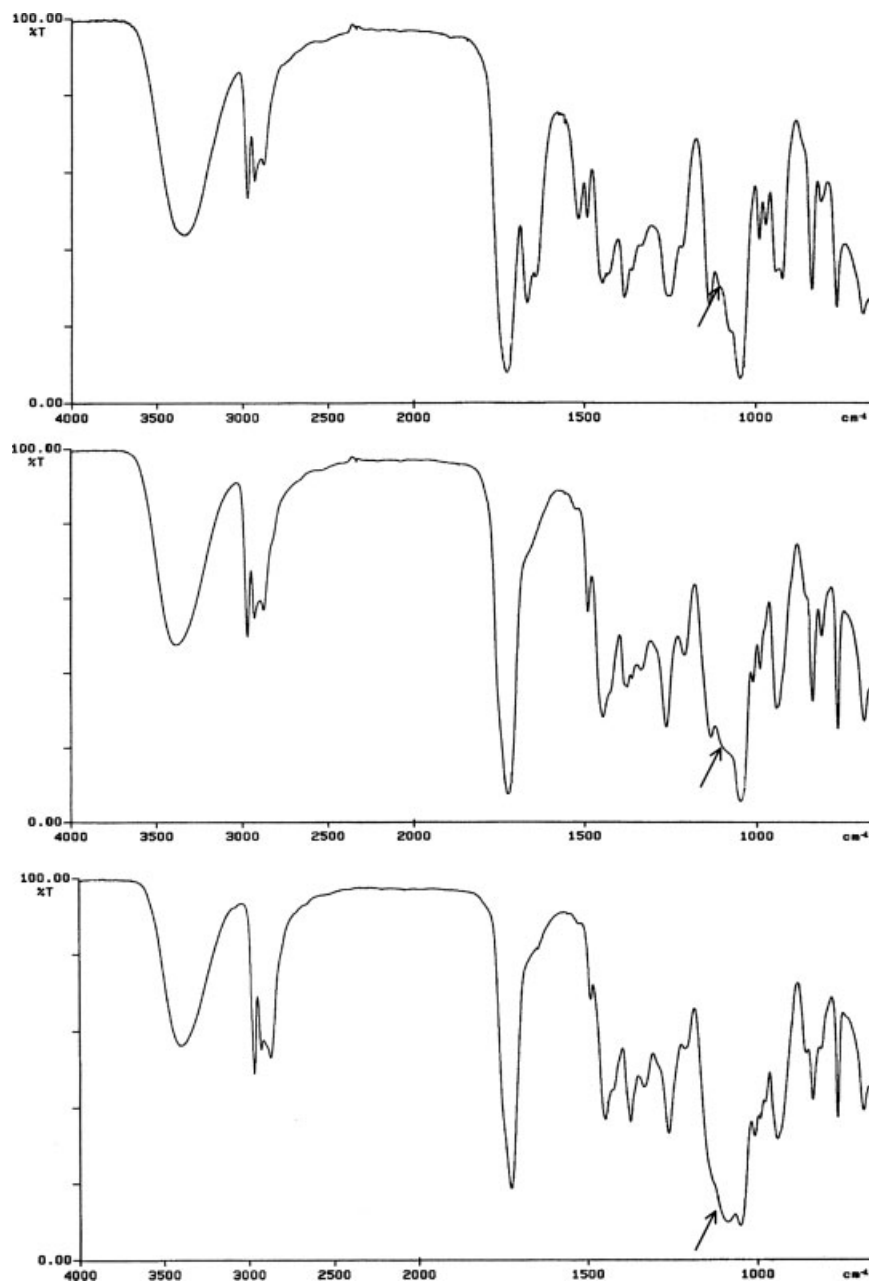


Figure 3 IR spectra of products of reaction OA : PC (a) 1 : 2 in the presence of 0.06 mol DABCO/mol OA at 160°C, (b) 1 : 4, (c) 1 : 12, in the presence of 0.09 mol DABCO/mol OA at 180°C.

The intensity of this band increases upon excessive amount of PC used in reactions [Fig. 3(a-c)].

Mass balance and relatively low intensity of resonances at 1.25 and 4.6 ppm (attributed to methyl and methine group protons in CO—O—CH(CH₃—

—CH₂OH) and the lack of the resonance at 4.0 ppm in the ¹H NMR spectra of products obtained from OA and PC clearly evidence the release of CO₂ without any incorporation of carbonate into product:

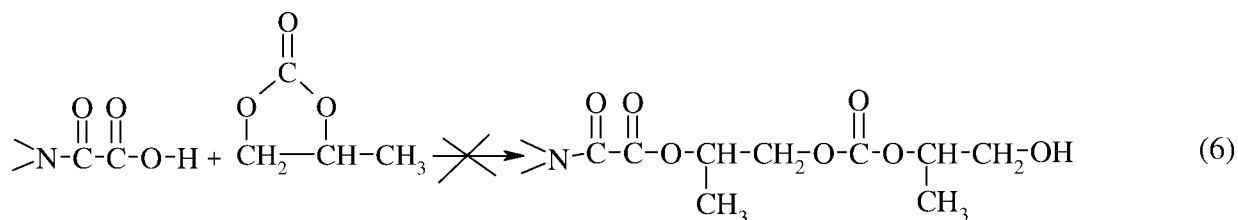


TABLE II
Results of MALDI ToF Determination of Product from
OA : PC 1 : 3 in the Presence of 0.06 Mole DABCO/Mole
at 160°C

Signal position	Probable structure of molecular ion
136.2	DPG + H ⁺
150.2	OA + PO + H ⁺
192.3	OA + PO + CO ₂ + H ⁺
202.2	OA + PO + CH ₃ OH + Na ⁺
206.3	OA + 2PO + H ⁺
218.3	2OA-H ₂ O + PO + H ⁺
227.3	OA + 2PO + Na ⁺
237.3	OA + 2PO + CH ₃ OH + H ⁺
261.3	OA + 2PO + CH ₃ OH + Na ⁺
286.4	OA + 3PO + Na ⁺
296.0	OA + 3PO + CH ₃ OH + H ⁺
300.3	OA + 3PO + CH ₃ OH + Na ⁺ - H ₂ O
319.4	OA + 3PO + CH ₃ OH + Na ⁺
330.4	OA + 3PO + CO ₂ + Na ⁺
344.4	OA + 4PO + Na ⁺
355.4	OA + 4PO + CH ₃ OH + H ⁺
369.4	OA + 4PO + CO ₂ + Na ⁺ - H ₂ O
380.4	OA + 5PO + H ⁺
388.4	OA + 4PO + CO ₂ + Na ⁺
398.4	OA + 4PO + CO ₂ + CH ₃ OH + H ⁺
421.4	OA + 4PO + CO ₂ + CH ₃ OH + Na ⁺
481.5	OA + 6PO + CO ₂ + H ⁺
515.5	2OA-H ₂ O + 5PO + CO ₂ + Na ⁺
554.6	OA + 8PO + H ⁺
578.6	OA + 8PO + CO ₂ + H ⁺ - H ₂ O

PO, oxypropylene unit; CO₂, carbonate unit.

Small amount of water-insoluble precipitates were obtained upon reaction of OA and PC at 1 : 3M ratio in presence of potassium carbonate catalyst at 160–180°C (1.3 and 1.9 wt %). They melt at about 400°C with decomposition. This product was not observed in case the DABCO was used as catalyst. The structure of main product only slightly changes; in the latter case the product contains more oxypropylene units (Table I, synthesis 3 and 5), which means that PC decomposes into propylene oxide and CO₂ to lesser extent.²¹ The synthesis in presence of DABCO instead of K₂CO₃ at 160°C (Table I, synthesis 3 and 5) take about 10 h longer but number of oxypropylene units is slightly larger. When larger amount of DABCO catalyst is used at 160°C (Table I, synthesis 7) the time of synthesis shortens without involvement on number of preserved oxypropylene groups remains unchanged. Upon increase of temperature to 180°C (Table I, synthesis 3 and 4; 5 and 6) the time of synthesis drops down fourfold in presence of any catalyst of two. However the number of preserved oxypropylene units in case of DABCO catalyst remains always larger.

The mass loss during the synthesis in the 1 : 3, 1 : 4, and 1 : 6 systems in comparable conditions (Table I, synthesis 6, 8, and 9) is similar and equal about 20 wt %. When larger excess of PC is used the higher

mass loss is observed due to its decomposition (Table I, synthesis 10–16). It also has been noticed that increase of amount of catalyst results in smaller carbonate loss from reaction mixture, i.e., the increase of amount of catalyst from 0.09 to 0.14 mol/mol OA in falls about 12 wt % down. (Table I, synthesis 10–12 and 13–15).

Estimation of number of OA units in products was provided from MALDI ToF measurement. The spectrum of the product obtained from OA : PC 1 : 3 system indicated that OA underwent dimerization process in the conditions used. Also is has been noticed that despite of high temperature of the synthesis (180°C) carbonate groups remain partially in the product which was demonstrated by series of peaks separated of 44 Daltons (Table II). However, only one carbonate group per molecule is present. The increase of excess of PC does not involve the formation of dimers (Table III). The molecules constructed of one OA and 4 (or 5) PO units with preserved (or not) carbonate have the highest contribution in the product.

TABLE III
Results of MALDI ToF Determination of Product from
OA : PC 1 : 12 in the Presence of 0.09 Mole DABCO/
Mole at 180°C

Signal position	Probable structure of molecular ion
150.5	OA + PO + H ⁺
170.5	OA + PO + Na ⁺
190.6	OA + PO + CO ₂ + H ⁺
206.6	OA + 2PO + H ⁺
217.6	2OA-H ₂ O + PO + H ⁺
230.6	OA + 2PO + CO ₂ + H ⁺ - H ₂ O
261.6	OA + 2PO + CH ₃ OH + Na ⁺
275.7	2OA-H ₂ O + 2PO + H ⁺
287.6	OA + 3PO + Na ⁺
292.7	2OA-H ₂ O + PO + CO ₂ + CH ₃ OH + H ⁺
301.7	OA + 3PO + Na ⁺ + CH ₃ OH - H ₂ O
319.7	OA + 3PO + CH ₃ OH + Na ⁺
345.7	OA + 4PO + Na ⁺
351.7	OA + 4PO + CH ₃ OH + H ⁺
364.7	OA + 4PO + CO ₂ + H ⁺
377.8	OA + 5PO + H ⁺
388.5	OA + 4PO + CO ₂ + Na ⁺
402.8	OA + 5PO + Na ⁺
405.8	OA + 5PO + CO ₂ + H ⁺ - H ₂ O
421.8	OA + 6PO + H ⁺ - H ₂ O
436.8	OA + 6PO + H ⁺
446.8	OA + 5PO + CO ₂ - H ₂ O + Na ⁺
458.8	OA + 6PO + Na ⁺
471.8	OA + 6PO + CH ₃ OH + H ⁺
485.9	OA + 6PO + CO ₂ + Na ⁺
504.8	OA + 6PO + CO ₂ + Na ⁺
518.8	OA + 7PO + Na ⁺
529.9	OA + 7PO + CH ₃ OH + H ⁺
562.9	OA + 7PO + CO ₂ + Na ⁺
595.9	OA + 7PO + CO ₂ + CH ₃ OH + Na ⁺
769.0	OA + 10PO + CO ₂ + CH ₃ OH + Na ⁺

PO, oxypropylene unit; CO₂, carbonate unit.

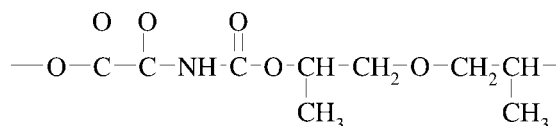
TABLE IV
Percentage of By-Products in Reaction Products of OA with PC

Entry ^a	Initial molar ratio	Percentage of glycols in postreaction mixtures (wt %)				Number of moles of PC reacted into Diols (mole/mole OA)	Molar ratio OA : x in polymeric product
		PG	DPG	TRIPG	Σ		
1	1 : 1	0	1.9	0	1.9	0.03	1 : 0.35
2	1 : 2	0	9.06	0	9.06	0.23	1 : 1.11
3	1 : 3	0	0.56	1.11	1.67	0.06	1 : 2.37
4	1 : 3	0	1.37	1.04	2.41	0.08	1 : 1.96
5	1 : 3	0	1.29	1.31	2.60	0.10	1 : 2.53
6	1 : 3	0	1.39	1.19	2.58	0.09	1 : 2.25
7	1 : 3	0	1.90	1.77	3.67	0.11	1 : 2.43
8	1 : 4	0	0.70	2.60	3.30	0.10	1 : 3.06
9	1 : 6	0	10.35	5.47	15.82	0.73	1 : 3.64
10	1 : 9	0	9.66	5.69	15.35	0.88	1 : 4.11
11	1 : 9	0	4.29	7.76	12.05	0.66	1 : 4.71
12	1 : 9	0	6.33	7.88	14.21	0.94	1 : 5.12
13	1 : 12	0	7.05	3.72	10.77	0.55	1 : 5.06
14	1 : 12	0	9.61	13.36	22.97	1.46	1 : 4.98
15	1 : 12	0	7.28	8.91	16.19	1.23	1 : 5.91
16	1 : 15	0	10.74	17.51	28.25	2.38	5 : 8.20

X, oxypropylene unit.

^a Entry according to Table I.

According to MALDI ToF, mass balance and ¹H NMR results the contribution of (CO)—O—CH₂—CH(CH₃)— was excluded and the presence of carbonate was attributed to the straightforward addition carbonate to nitrogen with formation of the structural fragment:



Reactions of PC are accompanied by its side-reaction with water resulting in formation of PG and the products of its consecutive reactions. Chromatographic analysis of products evidenced that small amount of by-products are formed (Table IV). The formation of products obtained from OA: PC 1 : 1 and 1 : 2 systems is accompanied by formation of dipropylene glycols (DPG), while in the products obtained from 1 : 3 and higher system the DPG and tripropylene glycols (TRIPG, Table IV) are present. The amount of catalyst does not change the percentage of by-products (Table IV, entries 10 ÷ 12 and 13 ÷ 15). For the OA : PC 1 : 9 system the mean by-products percentage is 15.35 wt %. The increase of amount of catalyst initially causes the decrease of amount of by-products, while further increase of catalyst concentration causes rapid increase of amount of by-products (Table IV, entries 10 ÷ 12). Products obtained from 1 : 12 and 1 : 15 systems are accompanied by large amount of by-products (Table IV, entries 13 ÷ 16).

The product obtained from 1 : 6 system contains yet another by-product, namely allyl alcohol, which

forms upon dehydration of PG. In the ¹H NMR spectrum of that product (Fig. 4) the characteristic allylic group multiplets at 4.8–6.1 ppm are observed.¹⁹ Allyl alcohol accompanies also the product obtained from 1 : 9 system; its percentage is in this case 10 wt %. It can be distilled off under reduced pressure. In the presence of 12 and 15M excess of PC the allyl alcohol is not present.

In the product obtained from 1 : 9 system both the allyl alcohol and PG are present. In case when 12M excess of PC is used, the PG undergoes the consecutive reaction with PC. It has been demonstrated before,²² that allyl alcohol has formed upon reaction of melamine with PC. Thus, during the reaction of PC with amine or imide groups there are the proper conditions to form allyl alcohol. This was not observed in the reaction between parabanic acid and PC.⁸

The products of reaction between OA and PC were analyzed thermogravimetrically (Table V). The products are well thermally stable. The maximal decomposition temperature products of reaction OA with PC was about 290°C. Thermogravimetric analysis of the products obtained from OA and 4-, 6-, and ninefold molar excess of PC revealed the 20 wt % mass loss within the 160–180°C temperature range (Table V). In case of products obtained from OA and 6- and ninefold molar excess of PC the mass loss is mainly due to the presence of by-products in the postreaction mixture (Table IV, entries 9–12) while in products obtained at fourfold molar excess of PC the mass loss is related not only to by-products (Table IV, entry 8) but also mainly to low-molecular weight products of reaction of 1 mol of OA with 1 or 2 mol of PC. The formation of the latter was indicated by

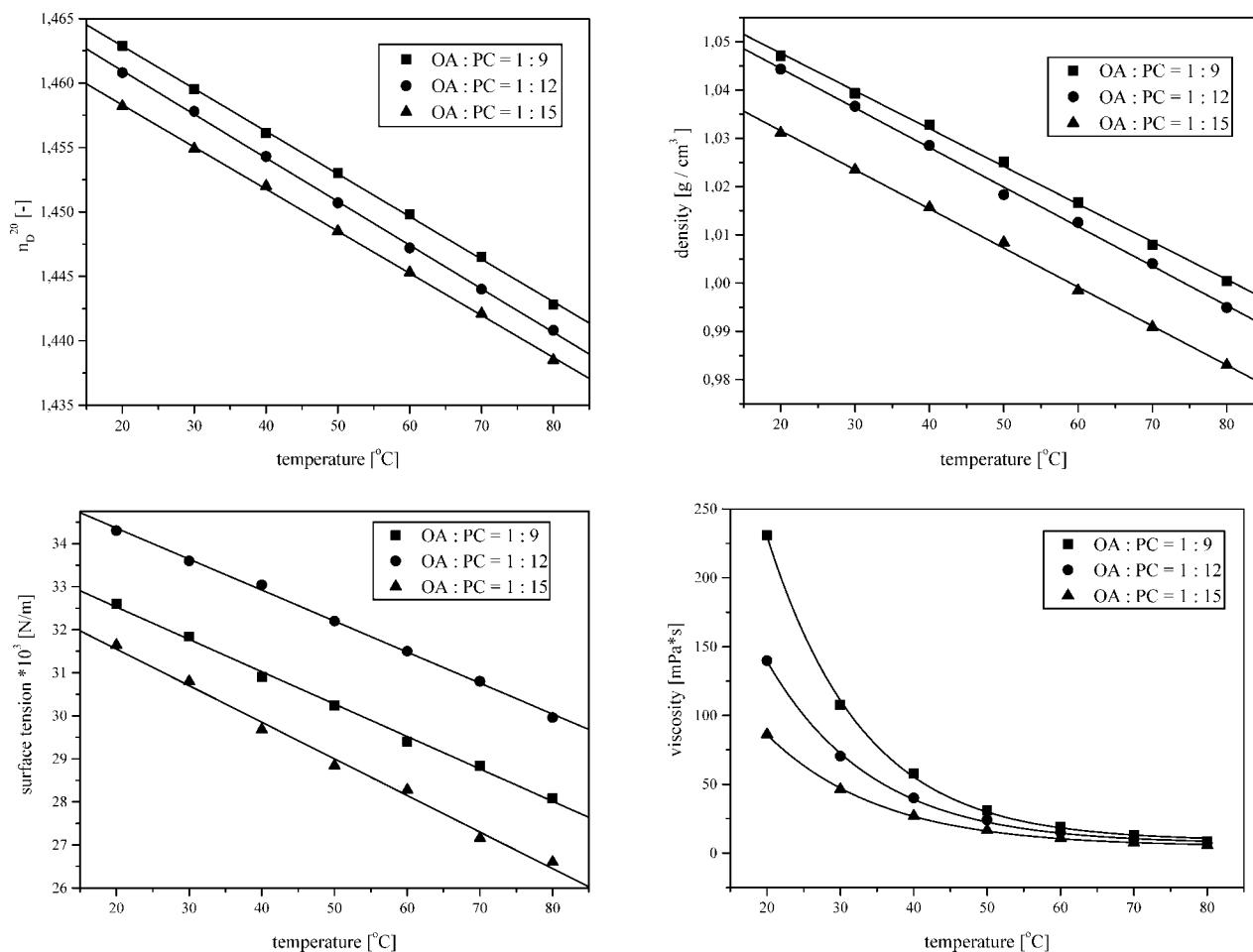


Figure 5 Physical properties of reactions products of OA with PC in function of temperature.

CONCLUSIONS

Hydroxypropoxy derivatives with oxalamidoester were obtained in straightforward reaction between oxamic acid with propylene carbonate. The reaction was optimized at 180°C using 6M or less excess of propylene carbonate in presence of 0.09 mol DABCO catalyst per mole of oxamic acid or 9M or larger excess of propylene carbonate and 0.14 mol DABCO/mol OA. The reaction is accompanied by condensation of oxamic acid, partial incorporation of carbonate groups in the product and minor formation of by-products. The obtained products have high thermal stability and good physical properties suggest that these products of hydroxyalkylation of oxamic acid with propylene carbonate can be effectively use for obtaining polyurethane foams of enhanced thermal stability in comparison with traditional polyurethanes.

References

- Shinsuke, S.; Kazunori, K.; Mitsuo, Y.; Satoshi, U.; Kei, A. Eur. Pat. 371,640 (1989).
- Shinsuke, S.; Kazunori, K.; Mitsuo, Y. U.S. Pat. 5,663,262 (1997).
- Schimmel, K.; Word, T.; Seiner, J. U.S. Pat. 4,684,710 (1987).
- Constanza, J.; Trapasso, L. U.S. Pat. 4,414,250 (1983).
- Klein, H. U.S. Pat. 4,118,422 (1978).
- Klein, H. U.S. Pat. 4,184,024 (1980).
- Lubczak, J.; Naróg, D.; Zarzyka-Niemiec, I. J Appl Polym Sci 2006, 100, 1443.
- Zarzyka-Niemiec, I. Polimery (Warsaw) 2008, 53, 33.
- Zarzyka-Niemiec, I. Polym Int 2007, 562, 1499.
- Koztowski, K.; Szczepkowski, L.; Hernacki, S.; Papinski, J.; Mastowski, H. Pol. Pat. 94,421 (1977).
- Wirpsza, Z. Poliuretany; WNT: Warszawa, 1991 (in Polish).
- Kucharski, M.; Kijowska, D. J Appl Polym Sci 2001, 80, 1776.
- Kastierina, T.; Kalinina, L. Chem Analysis of Plastics; WNT: Warsaw, 1965 (in Polish).
- Kowalski, P. Laboratory of Organic Chemistry; WNT: Warsaw, 2004 (in Polish).
- Kocot-Bónczak, D. Laboratory Experiments in Physical Chemistry; PZWL: Warsaw, 1977 (in Polish).
- Drýnski, T. Laboratory Experiments in Physic; PWN: Warsaw, 1967 (in Polish).
- Osamu, K.; Masaya, Y. Jpn. Pat. 296,545 (1990), CA: 113, 77906j (1990).
- Nariyuki, H.; Miyuki, T. Jpn. Pat. 352,838 (1991), CA: 115, 71109w (1991).
- Pauchert, C. H.; Behnke, J. The Aldrich Library of ¹³C and ¹H-NMR Spectra; Aldrich Chemical: Milwaukee, 1993; Vol. 1.
- Zarzyka-Niemiec, I.; Lubczak, J. Heterocycl Comm 2005, 11, 13.
- Clements, J. H. Reactive Applications of Cyclic Alkylene Carbonates. <http://www.huntsman.com/index.cfm?PageID=1201>.
- Kijowska, D.; Kucharski, M. J Appl Polym Sci 2003, 89, 104.