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Oligomers from parabanic acid and propylene carbonate rings' opening

Summary — Reactions of parabanic acid with propylene carbonate in the presence of 1,4-diazabicyclo[2.2.2]octane as catalyst were studied. During the reactions parabanic acid rings undergo opening and linear oligomeric products are formed. They are built from oxyisopropylene units formed in normal way of propylene carbonate ring opening. The oligomers discussed are characterized with higher thermal stability than parabanic acid and they can be used to produce thermally stable polyurethane foams. The chemical structures of the products obtained were characterized using IR, ^{1}H NMR and MALDI TOF methods. On the basis of these analytical results the mechanisms of the processes leading to the products' formation were interpreted in detail.
Key words: parabanic acid, propylene carbonate, hydroxyalkylation, ring-opening polymerization, chemical structures of products, thermal stability.

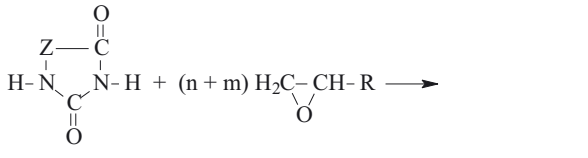
OLIGOMERY POWSTAJĄCE W WYNIKU OTWARCIA PIERŚCIENIA KWASU PARABANOWEGO I WĘGLANU PROPYLENU

Streszczenie — Przeprowadzono reakcje kwasu parabanowego (PA) z węglanem propylenu (PC) w warunkach różnych wyjściowych stosunków molowych PA:PC (mieszczących się w przedziale od 1:1 do 1:12) w obecności różnych ilości diazabicyklo[2.2.2]oktanu (DABCO) lub mieszaniny DABCO + K_2CO_3 jako katalizatorów w temp. 140 ^oC, 160 ^oC lub 180 ^oC (tabela 1). W tych warunkach pierścień PA otwiera się z wytworzeniem struktury liniowej zbudowanej z fragmentu mocznikowego i oksalamidoestrowego połączonych wspólnie mostkiem imidowym. Otwiera się także pierścień PC, ugrupowanie węglanowe rozkłada się z wydzieleniem CO_2 i do jednostki strukturalnej PA przyłączają się głównie grupy 2-hydroksypropylenowe. Tworzą się produkty oligomeryczne zawierające w swoich cząsteczkach różną liczbę grup 2-hydroksypropylenowych oraz jednostek strukturalnych PA. Budowę chemiczną powstających produktów scharakteryzowano szczegółowo metodami ^{1}H NMR (rys. 1 i 3), IR (rys. 2) oraz MALDI TOF (tabela 2), uwzględniając przy tym wpływ warunków syntezy (molowy stosunek substratów, temperatura, stężenie DABCO) na jej mechanizm i wyniki, m.in. na udział produktów ubocznych (glikoli propylenowego, dipropylenowego oraz tripropylenowego) a także na stopień rozkładu PC do CO_2 w toku reakcji. Analiza derywatograficzna uzyskanych oligomerów wykazała ich zwiększoną (w porównaniu z PA) odporność termiczną (tabela 3). Mianowicie, ich maksymalny rozkład następuje (w zależności od wyjściowego stosunku PA:PC) dopiero w temp. 270—295 ^oC. Zgodnie z wynikami wstępnych badań, uzyskane oligomeryczne produkty hydroksyalkilowania PA mogą być stosowane do otrzymywania pianek poliuretanowych o zwiększonej odporności termicznej.
Słowa kluczowe: kwas parabanowy, węglan propylenu, hydroksyalkilowanie, polimeryzacja z otwarciem pierścienia, budowa chemiczna produktów, odporność termiczna.

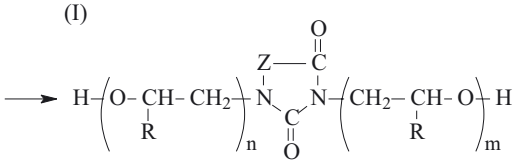
METHODS OF PARABANIC ACID HYDROXYALKYLATION

N-hydroxyalkylation of heterocyclic compounds similar to parabanic acid (PA) [1—5], like barbituric acid, uracil, dihydrouracil, hydantoine and their derivatives of the general formula (I), with ethylene oxide (EO) or propylene oxide (PO) results in formation of alcohols and diols (II) (eq. 1).

Reactions can be performed in *N*,*N*-dimethylformamide [5], *N*,*N*-dimethylacetamide, dioxane, or halogenated hydrocarbons [3], at slight oxirane excess in relation to number of NH groups in the substrate. Tetraethylammonium chloride, ternary amines, alkali metal halogenates (LiCl, NaCl) or Lewis acids ($AlCl_3$, $SbCl_5$, $SnCl_4$, $FeCl_3$, $ZnCl_2$, BF_3) are used as catalysts [3—5]. For syntheses of derivatives (II), where n + m > 2, the diols with heterocyclic ring (II), where n = m = 1, were used in reaction with oxirane resulting in consecutive addition of oxirane to terminal hydroxyl groups. Thus formed derivatives (II) were useful precursors for syntheses of polyesters and polyurethanes for glues, coatings or laminates [3—5].



(I) (1)



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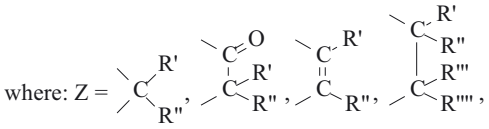
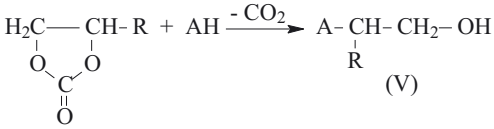


R', R'', R''', R'''' = H-, alkyl, cycloalkyl, substituted phenyl;
R = H-, CH_3-

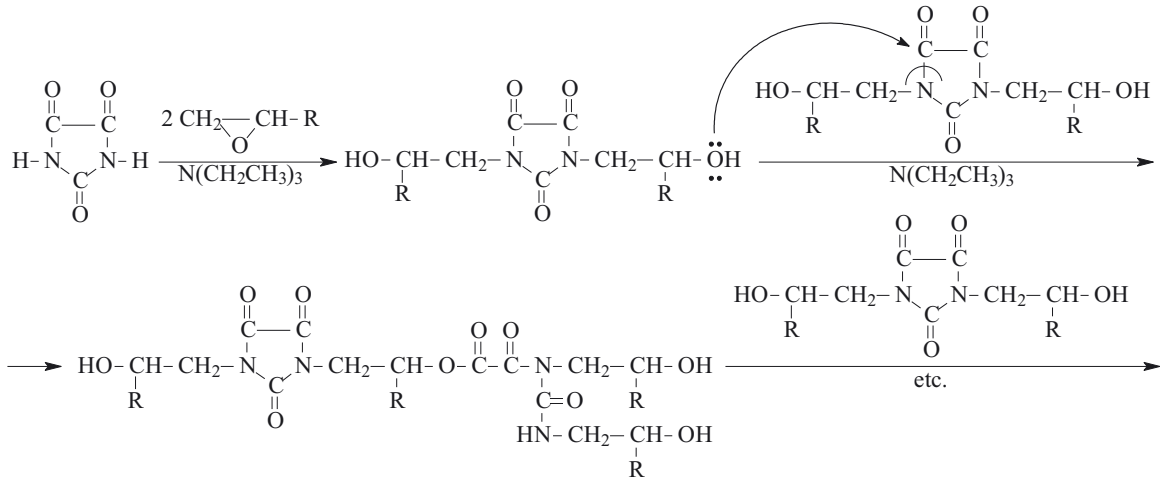
Alkylene carbonate were proved to be also suitable for hydroxyalkylation of azacyclic compounds with labile hydrogen atoms (AH) like PA. Formation of products was accompanied by carbon dioxide release or formation of carbonate group in the product [7—11] (eq. 3).

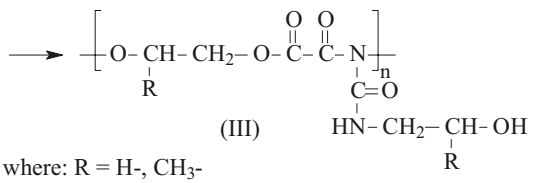
The route of the reaction depends on temperature and kind of catalyst [7—9]. In the reactions with CO_2 evolution, the normal (IV) or abnormal (V) products can be formed:



(V) (4)

Another reaction course concerns the reaction of PA with excess of ethylene carbonate (EC). The reaction pathway was described in [12]. Namely, mostly the

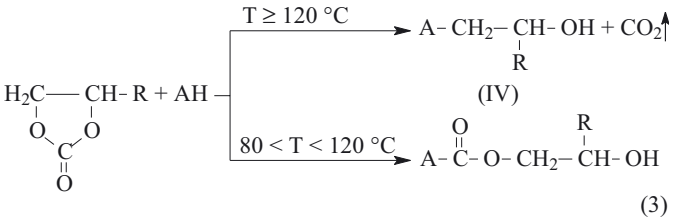




(III) (2)

where: R = H-, CH_3-

The reaction between PA and oxiranes can go differently, dependently on reaction conditions [6]. In the reaction of PA with 1 or 2 equivalents of oxirane in the presence of triethylamine (TEA) as catalyst at <0.03 mole/mole PA concentration, the *N*-(hydroxyalkyl)- and *N,N'*-bis(hydroxyalkyl)- derivatives are formed. In the presence of larger amount of catalyst or larger excess of oxirane, the polymeric products (III) are formed with linear fragments originated from PA ring opening (eq. 2).



(IV) (3)

where: R = H-, CH_3-

opening of the trioxoimidazolidine and EC rings occurs, resulting in formation of thermally stable linear polymeric products built from urea and oxamidester. Minor amount of PA rings was preserved in the products (max. 20 % mol.). Continuing the research we studied the reaction course of PA with propylene carbonate (PC) and characterized the products obtained.

EXPERIMENTAL

Reactions of PA with PC

In a 100 cm^3 three-necked round bottom flask 5.7 g (0.05 mole) of PA (obtained according to the procedure described in [13]) and the appropriate amount of PC (pure, Fluka, Switzerland) were placed to reach the molar ratio of reagents in the range 1:1—1:12, and 0.38—0.78 g of 1,4-diazabicyclo[2.2.2]octane (DABCO)

Table 1. Conditions of PA with PC reactions and characterization of products obtained

Sample	Initial molar ratio PA:PC	Amount of DABCO mole/mole PA	Reaction conditions		Molar ratio x:y in post-reaction mixtures[**] (from mass balance)	Percentage of side-products (glycols) in post-reaction mixtures, weight %[***]				Number of moles of PC reacted into diols mole/mole PA	Molar ratio x:y in oligomeric product	AN, mg KOH/g		Number of PA rings preserved in product mole %
			temp. °C	time h		PG	DGP1	TRIPG2	Σ			calculated	experimental	
1.	1:1	0.068	140	6	1:0.33	—	—	—	—	—	—	421.4	27.6	6.6
2.	1:2	0.028[*] + 0.055[*]	140	41	—	—	—	—	—	—	—	—	8.7	—
3.	1:2	0.055[*] + 0.055	140	24.25	—	—	—	—	—	—	—	—	6.6	—
4.	1:2	0.068	140	22.5	1:1.11	4.09	1.99	0.98	7.06	0.16	1:1.09	330.4	7.7	2.3
5.	1:2	0.068	160	20	1:1.11	2.83	4.03	0.96	7.82	0.18	1:0.94	329.9	6.6	2.0
6.	1:2	0.068	180	3	1:0.91	3.02	1.57	0.83	5.42	0.12	1:0.79	351.2	7.3	2.1
7.	1:2	0.095	160	12	1:1.18	3.78	1.40	1.03	6.21	0.13	1:1.05	320.7	9.3	2.9
8.	1:3	0.095	160	10	1:1.78	8.72	4.18	1.48	14.38	0.44	1:1.34	293.0	14.5	4.9
9.	1:3	0.095	180	6.5	1:1.71	5.44	0.85	1.17	7.46	0.22	1:1.49	280.3	4.5	1.6
10.	1:4	0.095	160	20	1:2.63	6.37	2.91	1.03	10.30	0.39	1:2.24	230.0	12.6	5.5
11.	1:4	0.095	180	5	1:2.43	6.84	1.68	1.12	9.63	0.34	1:2.09	238.7	5.4	2.3
12.	1:8	0.140	160	53	1:4.27	14.75	5.88	1.62	22.26	1.12	1:3.15	189.1	13.5	7.2
13.	1:8	0.140	180	11	1:3.81	8.89	4.07	1.53	14.49	0.78	1:3.03	189.1	14.2	7.5
14.	1:10	0.140	180	12.5	1:6.21	7.6	6.98	4.55	19.14	1.18	1:5.03	156.9	11.0	8.3
15.	1:12	0.140	180	22.5	1:9.70	0.53	9.91	12.78	23.22	2.37	1:7.33	104.1	0	0

[*] K_2CO_3 was used as catalyst. [**] x — number of moles of structures obtained from PA, y — number of moles of oxyisopropylene units. [***] 1 — dipropylene glycols, 2 — tripropylene glycols.

(pure, Avocado, Germany) (7.47—15.68 g DABCO/mole PBA, 0.068—0.140 mole/mole PA) was added; in some cases potassium carbonate (0.028 or 0.055 mole/mole PA) was also added. The reaction mixture was protected from moisture and stirred mechanically at 140—180 °C to dissolve PA in PC with monitoring of reaction progress by determination of unreacted PC.

Analytical methods

— Analogous standard analytical procedures as in [12] were used (acid number, ^{1}H NMR, thermal analysis).

— Molecular weights [number-average ($\overline{M}_n$), weight-average ($\overline{M}_w$), z-average ($\overline{M}_z$) ones] and molecular weight distribution of esteramidoimidotetraols were determined using "Viscotec T60A" gel chromatograph equipped with three detectors systems: RI (refractive index), LS (light scattering detector) and DV (viscometer detector). Particles separation was performed using two columns PSS SDV (7.8 mm × 300 mm with TSK bed of 100 and 1000 Å pore diameter gel), using the following recording parameters: temperature 25 ± 0.1 °C, volume flow of eluent 1 cm^3/min, the injection loop volume of 20 μdm^3, concentration of polymer solution 4—5 mg/cm^3, analysis time 30 min, eluent — THF (distilled over sodium prior to use), calibration based on the common polystyrene references.

— MALDI ToF (Matrix-Assisted Laser Desorption Ionization Time of Flight) spectra were obtained using "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/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^+ and CH_3OH.

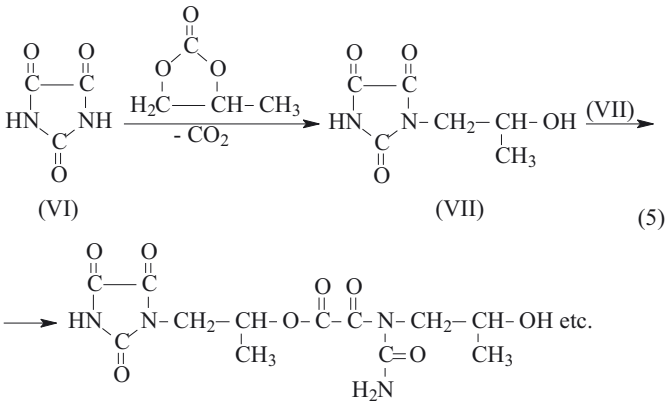
— Number average molecular weights of the products of reaction between PA and PC were determined by cryoscopic method using dioxane as a solvent.

RESULTS AND DISCUSSION

Structures of the products

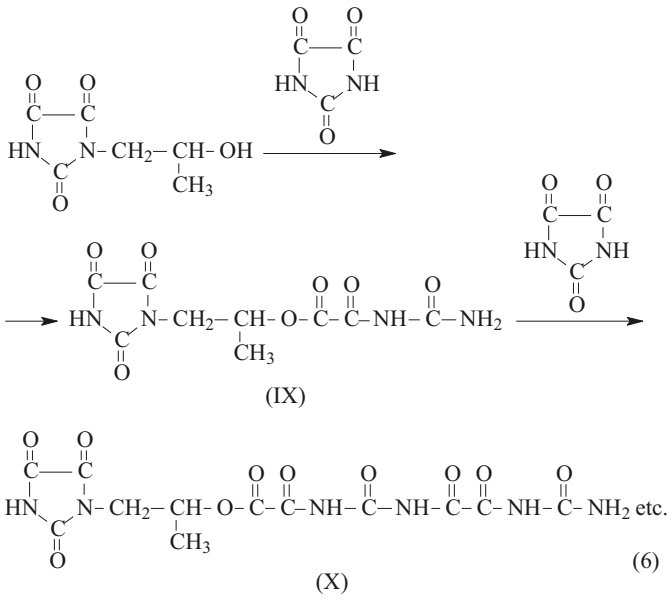
In the reaction performed at PA (VI) to PC 1:1 molar ratio the product with acid number (*AN*) of 27.6 mg KOH/g (Table 1, sample 1)

was obtained. The *AN* shows the value of 6.6 % mole of preserved trioxoimidazolidine rings (the way of calculating the percentage of preserved trioxoimidazolidine rings according to *AN* was described in [6]). This suggested that products of hydroxypropylation (VII) could subsequently react with simultaneous cleavage of trioxoimidazolidine ring:



The ^{1}H NMR spectrum of the product (Fig. 1) showed primary and secondary amide groups by vibration at 6.4 ppm from primary amine protons interacting with accepting groups [14] and 7.2—8.8 ppm from secondary amide and imide [15]. The latter have the same chemical shifts as products of reaction between PA and EO or PO [6], and EC [12]. The intensity of vibration concerning secondary amide protons and imide protons is higher than that of primary amide protons. The intensity ratio indicates that product of hydroxypropylation (VII) can react with PA with generation of more imide groups in (X) (eq. 6).

The presence of mentioned structural fragments in the product is corroborated by its IR spectrum (Fig. 2). I and II amide bands from secondary amide at 1670 and 1516 cm^{-1} as well as 1720 cm^{-1} band from valence vibrations of C=O in imides and esters are observed. The III amide bands at 1410 and 1300 cm^{-1} from primary and secondary amide are also present. In the 3000—3500 cm^{-1} region the valence vibrations from primary and secondary amide, imide and hydroxyl groups are visible. The bands at 1240 and 1070 cm^{-1}, characteristic for ester CO-O and secondary alcohol C-OH groups are also found.



Moreover, in the ^{1}H NMR spectrum (Fig. 1) there are signals centered at 0.95 and 1.25 ppm, which were supposed initially to origin from methyl group protons of the product obtained by normal (XI) or abnormal (XII) PC ring opening (eq. 7).

However, in the presence of abnormal product (XII) and its consecutive reaction with PA the resonance at about 4.2 ppm from -**CH$_2$**-O-(CO) group protons should be observed (eq. 8).

This resonance was observed in the spectra of acrylates and methacrylates obtained from *N,N'*-bis(2-hy-

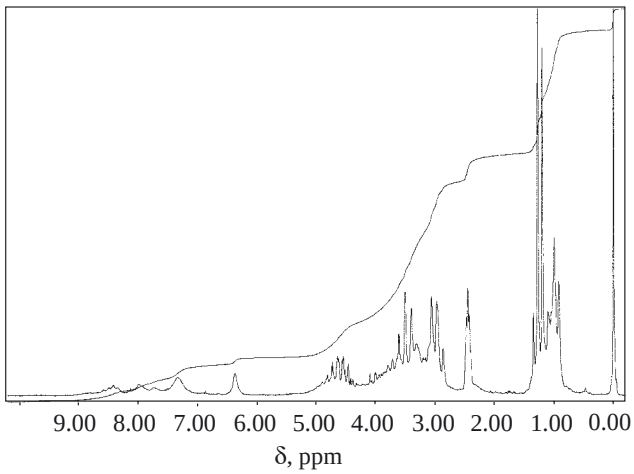


Fig. 1. ^{1}H NMR spectrum of reaction product for PA:PC = 1:1 mole (reaction conditions — see Table 1, sample 1)

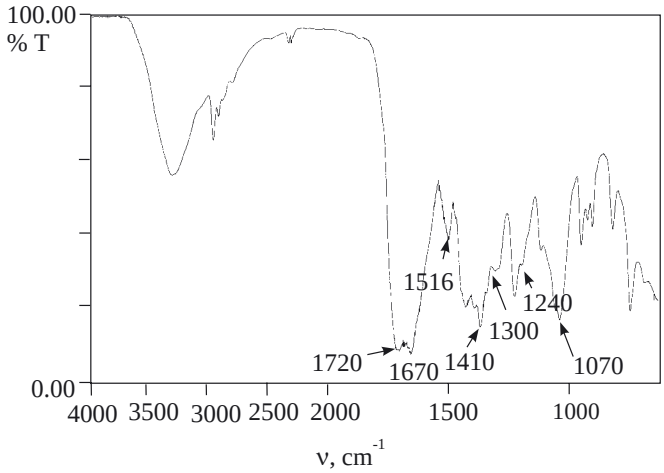
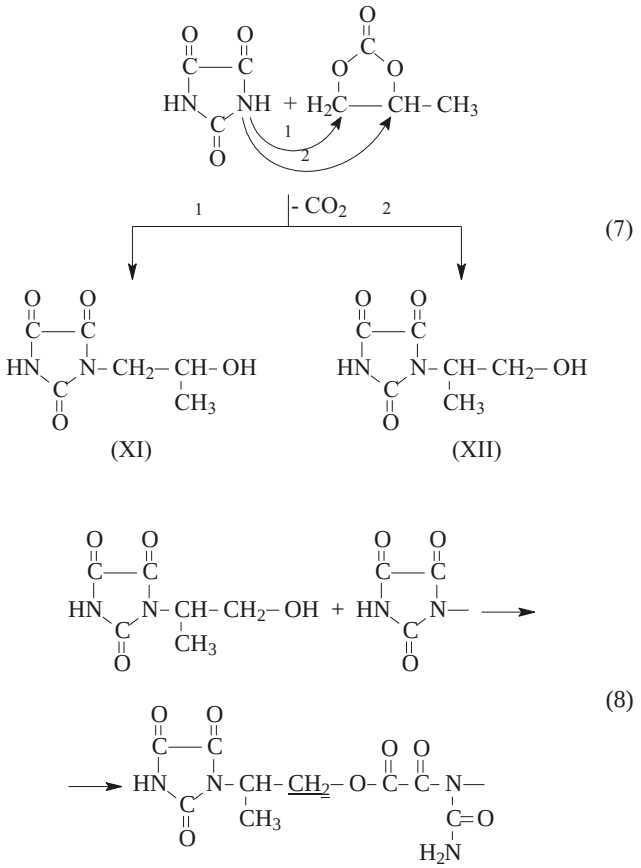


Fig. 2. IR spectrum of reaction product for PA:PC = 1:1 (sample 1)



(7)

(8)

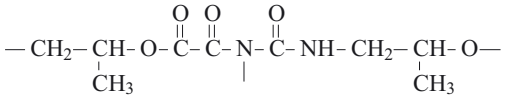
droxyethyl) parabanate [16], products of reaction of PA with EO [6] or EC [12] occurring at trioxoimidazolidine ring opening. In case of the sample 1 (Fig. 1) this resonance was not observed; instead a multiplet at *ca* 4.6 ppm from methine protons of -**CH**-O-(CO)- group (IX) was found. However, the resonance at 4.6 ppm was found also in the spectra of products of reaction between PA with PO [6], as well as of acrylates and methacrylates obtained from *N*,*N*'-bis(2-hydroxypropyl) parabanate [16].

We conclude that in the reaction between PA and PC the abnormal product (XII) is not formed. The resonances at 0.95 and 1.25 ppm are related to the engagement of hydroxyl groups of normal product (XI) in the interaction with PA with formation of ester bond. This renders protons of methyl groups from oxyisopropylene groups to appear at the spectrum ^{1}H NMR (Fig. 1) at lower field (1.25 ppm) in comparison with free 2-hydroxylpropyl protons (0.95 ppm) [16, 17].

Reactions between PA and PC at 1:2 molar ratio have to be performed in the presence of DABCO catalyst. The use of potassium carbonate or its mixture with DABCO needs the prolonged reaction time (Table 1, samples 2 and 3). The shortest reaction time was reached by temperature increasing from 140 °C to 180 °C (Table 1, samples 4—6).

The increase in amount of catalyst at fixed temperature (Table 1, samples 5 and 7) resulted in formation of ester groups in the products, detected by increase in the resonance centered at 1.25 ppm in comparison with that at 0.95 ppm in ^{1}H NMR spectra of corresponding products. Thus, we conclude that increase in the amount of catalyst induces trioxoimidazolidine ring opening reaction.

As the analysis of the ^{1}H NMR spectra of products of reaction between PA and PC indicated that free primary amide groups from normal or abnormal products of addition of PC to PA were not present, so only the products of the formula (XIII) were formed:



(XIII)

Reactions of PA with PC at higher molar part of PC (1:3—1:10) lead to the products containing only tertiary amide groups. In the ^{1}H NMR spectrum of the product obtained from PA:PC 1:3 reagents system (Fig. 3a) the diminishing resonance from secondary amide group protons (7.2—8.8 ppm) is observed in comparison with the product obtained from the 1:2 system and eventually the disappearance of this resonance was observed at 1:4 reaction system (Fig. 3b). Structure of the products can be then shown as (XIV) (eq. 9).

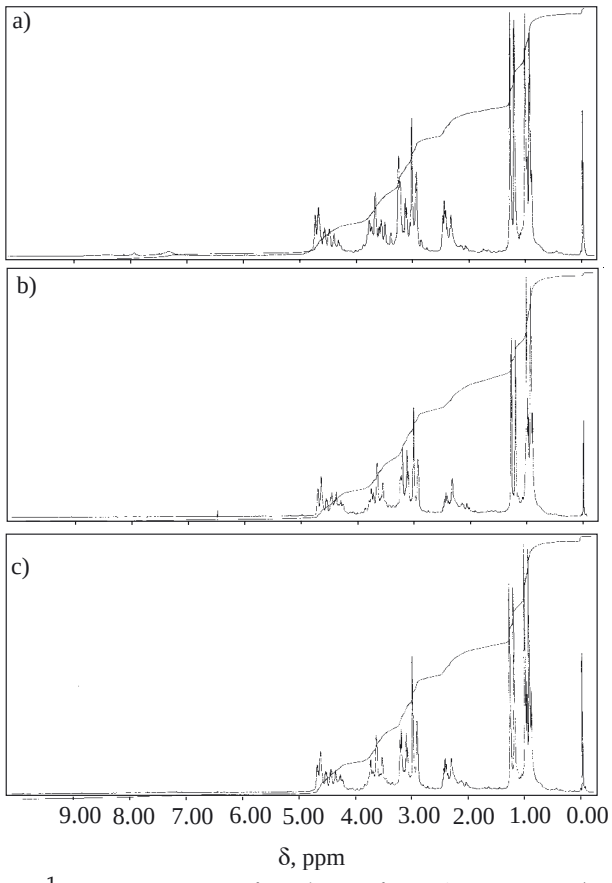
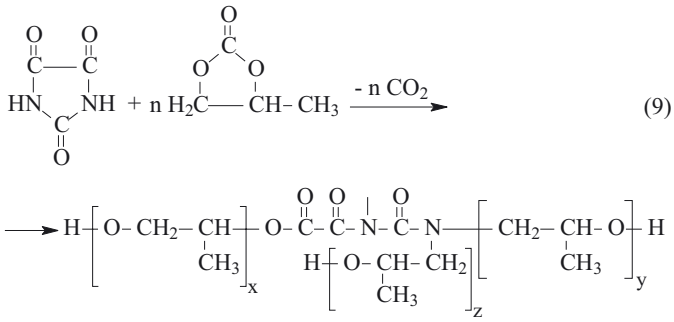


Fig. 3. ^{1}H NMR spectra of products of reaction PA:PC: a) 1:3, b) 1:4, c) 1:8; for reaction conditions see: a) — sample 9, b) — sample 11, c) — sample 13 in Table 1



(9)

where: x + y + z = n, n = 3—10, 0 ≤ z < n - (x + y)

Also the intensity ratio of the resonances from methyl group protons [in free 2-hydroxypropyl groups and oxyisopropylene groups (at 0.95 ppm)] and methyl group protons in ester groups (at 1.25 ppm) changes considerably. In ^{1}H NMR spectrum of the product obtained from 1:3 system the intensity of the resonance at 1.25 ppm drops down, what evidences that less 2-hydroxypropyl groups are engaged in the formation of ester groups in comparison with total amount of oxyisopropyl units present in the product (Fig. 3a—c).

Simultaneously in the IR spectra of products obtained in excess PC the substantial increase in -C-O-C- valence bands is observed. The determination of AN provided information on preservation of PA rings in the products irrespective of the temperature or kind and amount of catalyst added (Table 1, samples 2—7).

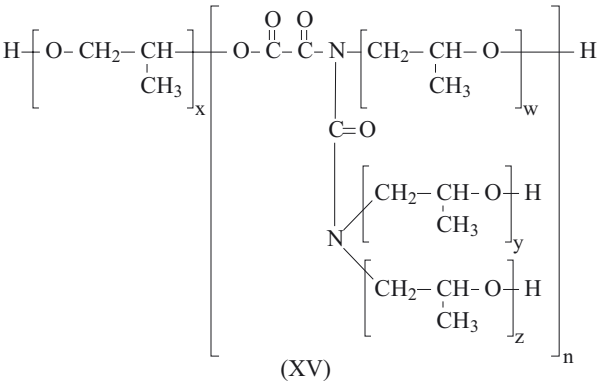
Mass balance indicates the loss of PC in the course of reaction due to its decomposition and eventually the lower ratio between oxyisopropylene groups and PA in products is found than that expected on the basis of initial ratio of reactants (Table 1, samples 4—15). The processes conducted at higher temperature induce larger loss of PC (Table 1, samples 4—13); this can be partially reduced by addition of larger amount of catalyst to the reaction mixture (Table 1, samples 5 and 7).

It has been found that the change of reaction conditions did not influence substantially the amount of side-products (PG, DGP, TRIPG — Table 1, samples 4—15). The side-products are formed because hydroxypropylation reaction is accompanied by the reaction of PC with trace water leading to PG and consecutive products of reaction of PG with PC. It has been found that products obtained at 1:2 molar ratio of substrates contained 5.5—8 wt. % of propylene glycol and polyglycols (Table 1, samples 2, 4—7) and percentage of the side-products exceeded 20 weight % with increasing number of excessive moles of PC (Table 1, samples 8—15).

The *AN* values of products of hydroxyalkylation of PA with excess of PC indicate that the percentage of trioxoimidazolidine rings increases slightly with number of excess moles of PC (Table 1). The maximum percentage of PA rings in products (obtained from PA:PC 1:10 system) does not exceed 9 mole % (Table 1, sample 14).

Based on the gel chromatographic analysis we found that the products obtained from the systems with 8—12 molar PC excess could contain maximum two structural units deriving from PA ring opening. Mostly the products with one such fragment are formed, which have variable number of attached oxyisopropylene units.

The MALDI ToF analysis indicated that products of reaction between PA and 8- or 12-fold excess of PC contained 1—4 units formed in ring opening of PA (XV),



(XV)

where: n = 1, 2 or 4

but the oligomers with 2 and especially with 1 units were the major products (Table 2).

T a b l e 2. Results of MALDI ToF analysis of the products obtained for PA:PC = 1:8 at temp. 180 °C (Table 1, sample 13)

Signal position	Signal intensity, %	Probable structure of molecular ion*)
190.3	27.5	DPG + CH_3OH + Na^+
203.3	25.0	PA + PO + CH_3OH + H^+
216.3	22.5	PA + PO + CO_2 + H^+
229.3	30.6	PA + PO + CH_3OH + Na^+
230.3	62.5	PA + 2PO + H^+
261.4	31.9	PA + 2PO + CH_3OH + H^+
275.4	68.1	PA + 2PO + CO_2 + H^+
287.4	31.9	PA + 3PO + H^+
296.4	45.0	PA + 2PO + CO_2 + Na^+
311.4	36.2	PA + 3PO + Na^+
333.4	16.8	PA + 3PO + CO_2 + H^+
337.4	24.4	2PA + PO + CH_3OH + Na^+
351.4	100	PA + 3PO + CO_2 + Na^+
369.5	62.2	PA + 4PO + Na^+
379.5	11.2	PA + 4PO + CH_3OH + H^+
387.5	15.6	PA + 3PO + CO_2 + CH_3OH +Na^+
427.5	89.4	PA + 5PO + Na^+
467.5	12.5	2PA + 3PO + CO + Na^+
485.6	59.4	PA + 6PO + Na^+
504.7	18.1	PA + 5PO + CO_2 + CH_3OH + Na^+
543.7	10	PA + 7PO + Na^+
573.7	6.9	2PA + 5PO + CH_3OH + Na^+
671.8	5.6	PA + 9PO + CH_3OH + H^+
704.8	5.6	PA + 9PO + CO_2 + Na^+
754.9	5.0	4PA + 4PO + CO_2 + Na^+

*) PO — the unit formed at cleavage of PC ring and CO_2 evolution, PA — stands for preserved unit of PA or the linear product of its ring opening, CO_2 — carbonate unit.

Despite on high temperature of syntheses (180 °C) the products still contain preserved carbonate groups (O-CO-), usually one per molecule of a product. Based upon this spectral results one can see, that for application of 8- and 12-molar excess of PC the similar products are obtained. The number average molecular weights equal 394 and 453, indicate that average 4 or 6 oxyalkylene fragments are formed in PC ring decomposition per one unit of linear fragment formed by ring opening of PA.

Products thermal stability

Thermal analyses of products have shown that the products of hydroxyalkylation of PA with PC were remarkably thermally stable (Table 3). As it was mentioned, the products from PA:PC = 1:2 reaction system contained barely 2.5 % trioxoimidazolidine rings (Table 1, samples 4—7) and their temperature of maximum decomposition was 270—280 °C (Table 3). The highest temperature of PA decomposition is 230 °C (Table 3, sample 16). Thus, the thermal stability of polymeric products does not depend on the presence of trioxoimidazolidine rings but originates from the presence of oxamidester and urea groups linked together *via* imide bond in (XIV).

T a b l e 3. Thermal stability of the products based on thermal analyses results[*)]

Sample (according Table 1)	$T_{5\,\%}$ °C	$T_{10\,\%}$ °C	$T_{20\,\%}$ °C	$T_{50\,\%}$ °C	T_{max} °C
4.	180	210	235	270	270
5.	190	210	240	270	280
6.	170	205	230	270	270
7.	180	210	230	270	280
15.	120	150	195	250	295
16.[**)]	200	205	210	220	230

[*)] $T_{5\,\%}$, $T_{10\,\%}$, $T_{20\,\%}$, $T_{50\,\%}$ — temperatures of 5 %, 10 %, 20 % or 50 % weight loss, respectively, T_{max} — temperature of maximum decomposition.
[**)] Results of thermal analysis of PA.

So, the products obtained in the reactions of PA with PC can be used for preparation of plastics of high thermal stability. Preliminary studies indicated that polyurethane foams based on them had indeed such properties. This will be reported separately.

CONCLUSIONS

— Reactions of parabanic acid with propylene carbonate occur with trioxoimidazolidine ring opening independently on molar ratio of reagents and reaction conditions.

— At low PA and PC ratio (1:1 and 1:2) the products contain primary, secondary and tertiary amide groups and oxamidester groups, while at 1: >3 molar ratio only tertiary amide and substituted imide groups are present.

— In the reaction of PA with 8-fold or higher excess of PC, the products formed contain one or two preserved PA units or one or two fragments of PA ring opening.

— Reaction between PA and PC is accompanied by carbon dioxide release with partial preservation of carbonate groups in the product.

— At higher excess of PC the percentage of side-products (propylene, dipropylene and tripropylene glycols) increases, but higher temperature causes lowering of their percentages.

— Products of hydroxyalkylation of PA with PC are remarkably thermally stable.

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