Hydroxyalkylation of Parabanic Acid. III. Polymers from Parabanic Acid and Ethylene Carbonate

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ABSTRACT: The influence of initial molar ratio of reagents, amount of catalyst, and temperature of reaction between parabanic acid and ethylene carbonate on structure of product was studied. The reaction led to the opening of the trioxoimidazolidine ring, resulting in formation of thermally resistant linear polymeric products constructed of urea and oxoamidoester subunits linked via imide bond. The percentage of side products was estimated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1443–1449, 2006

Key words: parabanic acid; ethylene carbonate; hydroxylkylation; ring-opening polymerization; structure; thermal stability

INTRODUCTION

Polymers with parabanic acid (PA, I) included in polymeric chain are mechanically[1,2] and thermally resistant.[2–4] Previously, they were obtained by closure of parabanic ring in the course of polyreaction, for example, by polymerization of cyanoformamidyl isocyanates.[5–8] Another route was based on the build-in of PA ring on the preformed polymers, for example, polyurea[9,10] or polycarbodiimides.[11,12] Quite recently the 4,4'-(hexamethylene-1,6-diyl)bis(2,4,5-trioxoimidazolidine-1,3-diyl)dibenzyl dichloride containing trioxoimidazolidine ring was explored as monomer to produce polyesters in reaction of the former with bisphenols.[13]

Another monomer with trioxoimidazolidine ring are hydroxyalkyl derivatives of PA (*N,N'*-bis(hydroxyalkyl) derivatives, BHAP) obtainable from PA and formaldehyde[14–16] or PA and oxiranes; ethylene oxide (EO), propylene oxide (PO), or epichlorhydrin of glycerol. On the other hand, the reaction of PA with oxiranes, apart from low-molecular weight hydroxyalkyl derivatives (II, III), the polymeric products that resulted from PA ring opening (IV)[17–19]:
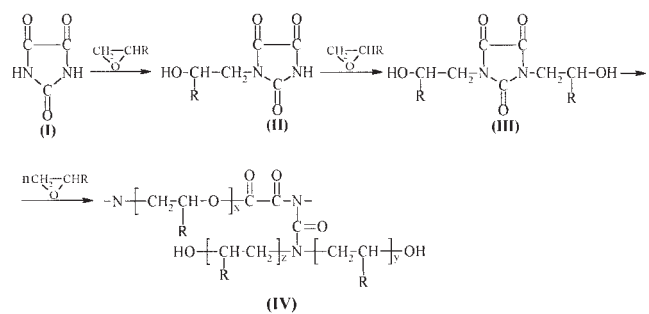
$$(1)$$

where R=H— and $x + y = 3$, $z = 0$; R=CH$_3$—, ClCH$_2$— and $x + y + z = 3:8$.

The BHAP (III) were then used to produce polyester resins,[20] polyurethanes, polyacrylates, and polymethacrylates[21,22] of high thermal stability and heat resistance.[20,22]

On the other hand, the trioxoimidazolidine ring remained untouched in reaction between PA with formaldehyde,[16] regardless the reaction conditions and molar ratio of reagents. In case of oxiranes as coreagents for PA, the trioxoimidazolidine ring was preserved only when 1–2 mol of oxirane per mole of PA were reacted at temperature below 40°C in presence of triethylamine (TEA) catalyst (at the level of 0.03 mol/mol PA).[17,19]

Alkylene carbonates, like ethylene carbonate (EC) or propylene carbonate (PC), were recently used as hydroxyalkylation reagents.[23] Hydroxyalkylation is conducted at 100–200°C temperature range in presence of

basic catalysts like potassium carbonate,[24,25] tertiary amines,[23] or quaternary ammonium salts.[26] These prompted us to use alkylene carbonates for hydroxyalkylation of PA, thus avoiding formation of polymeric products without trioxoimidazolidine rings. Here, we studied this issue for the reaction of PA with EC.

EXPERIMENTAL

Syntheses

PA was obtained according to procedure described in Murray.[27]

Reactions of PA with EC

In a 100 cm[3] three-necked round bottom flask, 5.7 g (0.05 mol) PA and the appropriate amount of EC (pure, Fluka, Switzerland) were mixed to reach the molar ratio of reagents of 1:1–1:12 and 0.000–1.242 g potassium carbonate (0.00–24.84 g/mol PA; 0.00–0.18 mol/mol PA) was added. The reaction mixture was protected from moisture and stirred mechanically at 100°C–160°C to dissolve PA in EC and maintained at 160°C, with monitoring the progress of reaction by the determination of unreacted EC.

Analytical methods

The reaction was monitored by determination of EC[28] and by IR spectral measurements of aliquots. Products were analyzed by determination of acidic number (AN) by alkacymetric titration (with $0.1M$ KOH(aq)) as previously in Kastierina and Kalinina.[29] ^{1}H NMR spectra of products were recorded with BS-586A 80 MHz spectrometer (Tesla, Brno, Czechoslovakia) in d_6-DMSO, and HMDS reference. IR spectra were taken for films with PARAGON 1000 FTIR spectrophotometer (Perkin–Elmer, Wellensley, MA).

Chromatographic analysis of side-products, for example, ethylene glycol (EG) and products of its consecutive reactions with EC were performed with gas chromatograph HP 4890A (Hewlett–Packard, Ringoes, NJ, US) with FID detector and HP1 30 mm × 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 was 6 min, loader temperature 250°C, detector temperature 300°C. The samples were dissolved in methanol ($0.01M$). Internal reference was cyclohexanone.

RESULTS AND DISCUSSION

In the reaction of 1 mol of PA with 1 mol of EC the low-melting solid was obtained. The product con-

tained 0.6 mol of incorporated oxyethylene units per mole of PA (Table I, run 1). Thus, PA remained partially unreacted. However, the value of AN indicated the presence of low content of trioxoimidazolidine rings in product (about 2.3 mol %) determined by the procedure described previously.[19] This value suggested that consecutive reactions of hydroxyalkyl derivatives of PA (II or III) with still available PA took place with trioxoimidazolidine ring opening. As it was found recently,[19,30] the ring opening results from the attack of hydroxyl groups from derivatives of PA on carbonyl carbon in other PA molecule:

(2)
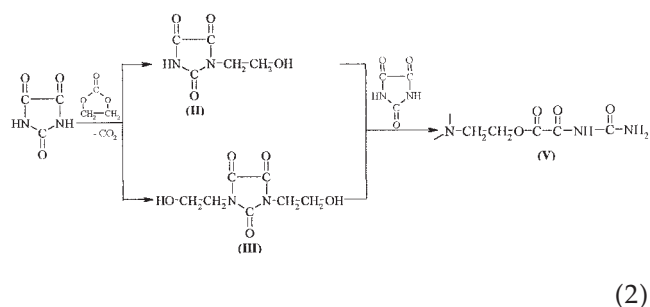
Also, the hydroxyethyl derivatives of PA (II) instead of PA itself can be involved in those reactions; in such a case, the attack of hydroxyl group on trioxoimidazolidine ring can occur from both sides of unsymmetrical derivative of PA leading to products (VI) and (VII):


(3)
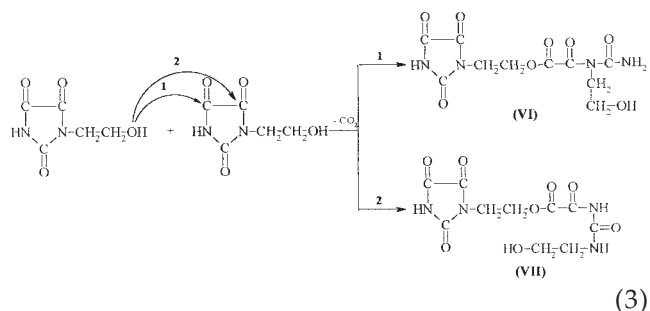
Analysis of ^{1}H NMR spectra (Fig. 1) of the product indicated the presence of the primary and secondary amide hydrogens and imide hydrogens by resonances at 6.5, 7.1–8.2, and 8.3–9.1 ppm, respectively. The resonance at 6.5 ppm is identical to those of —NH$_2$ in the ^{1}H NMR spectra of urea derivatives: X—NHCO—NH$_2$, where X is accepting group.[31] The resonances at 7.1–8.2 and 8.3–9.1 ppm are present in the ^{1}H NMR spectra of products of reaction between PA and EO formed upon PA ring opening.[19] Moreover, in the IR spectrum, the bands assigned to valence vibrations of imide carbonyl at 1740 cm^{-1} and bands I, II, and III secondary amide bands at 1639,

TABLE I
Condition of Reaction between PA and EC and Characterization of Obtained Products

Entry	Starting molar ratio	Amount of K_2CO_3 (mol/mol PA)	Temp. (C°)	Time (h)	Molar ratio x:y in post-reaction mixture (from mass balance)	Percentage of glycols in postreaction mixtures (wt %) EG	DEG	TIEG	TAEG	Sum	Number of moles of EC converted into diols (mol/mol PA)	Molar ratio x:y in polymeric product	AN (mg KOH/g) Calculated	Determined	Number of PA rings preserved in product (mol %)
-1-	-2-	-3-	-4-	-5-	-6-	-7-	-8-	-9-	-10-	-11-	-12-	-13-	-14-	-15-	-16-
1	1:1	—	120		1:0.60	1.2	0	0	0	1.2	0.03	1:0.57	400.0	9.2	2.3
2	1:2	—	120	0	—	—	—	—	—	—	—	—	—	—	—
3	1:2	—	140	10	—	—	—	—	—	—	—	—	—	—	—
4	1:2	—	160	6.5	—	—	—	—	—	—	—	—	—	—	—
5	1:2	0.18	100	50	—	—	—	—	—	—	—	—	—	—	—
6	1:2	0.06	110	19	1:1.73	0	0	0	0	0	0	1:1.73	324.3	109.6	33.8
7	1:2	0.06	120	7	1:1.26	1.12	0	0	0	1.12	0.03	1:1.23	363.0	120.7	32.8
8	1:2	0.06	130	5.5	1:1.04	0	0	0	0	0	0	1:1.04	351.8	11.2	3.2
9	1:2	0.03	140	4.75	1:0.98	1.78	0	0	0	1.78	0.045	1:0.935	364.7	9.3	2.6
10	1:2	0.06	140	3.5	1:0.95	1.03	0	0	0	1.03	0.03	1:0.92	362.7	129.5	35.7
11	1:2	0.09	140	2	1:1.12	0	0	0	0	0	0	1:1.12	343.6	8.8	2.6
12	1:2	0.06	150	2.5	1:1.12	0	0	0	0	0	0	1:1.12	343.6	4.7	1.4
13	1:2	0.06	160	2	1:0.95	1.36	0	0	0	1.36	0.03	1:0.92	363.6	11.1	3.0
14	1:3	0.06	120	29	1:2.05	1.52	0	0	0	1.52	0.03	1:2.02	278.0	8.5	3.0
15	1:3	0.06	140	8.5	1:1.90	1.27	0	0	0	1.27	0.04	1:1.86	286.5	8.7	3.0
16	1:4	0.06	140	10.5	1:2.94	4.03	0	0	0	4.03	0.16	1:2.78	237.5	12.9	5.4
17	1:4	0.06	160	4	1:2.50	0.82	0	0	0	0.82	0.03	1:2.47	251.7	7.35	2.9
18	1:2[a]	0.06	40	6.5	1:2.94	1.70	2.61	0	0	4.31	0.19	1:2.75	238.7	20.4	8.6
19	1:8	0.12	140	22	1:7.08	1.56	3.74	3.92	5.10	14.32	1.19	1:5.89	140.4	11.1	7.4
20	1:8	0.12	160	4	1:6.82	0	5.07	5.19	7.33	17.58	1.45	1:5.37	154.4	34.9	21.3
21	1:12	0.12	160	5	1:10.93	0	3.77	4.59	7.02	14.37	1.72	1:9.21	108.0	19.3	17.9

[a] N,N'-bis(2-hydroxyethyl)parabanate was used instead of PA.

x, number of moles of moieties obtained from PA; y, number of moles of oxyethylene units.
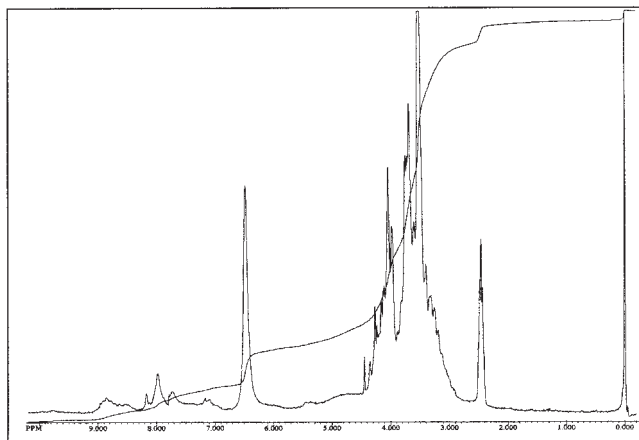
Figure 1 ^{1}H NMR spectrum of product of reaction of PA:EC 1:1 at 120°C.

1536.9, and 1337 cm^{-1}, respectively, and band III of primary amide at 1413 cm^{-1}, analogous to that in urea, were found.[31]

In the structure of products described by formulae (VI) and (VII), there are ester bonds present, which were detected by the presence of resonance at 4.1 ppm from methylene group in —CH$_2$—O— (CO)— at the ^{1}H NMR spectrum (Fig. 1), observed previously in the product of reaction between PA with EO, which formed upon trioxoimidazolidine ring opening[19] as well as in the spectra of esters obtained from *N,N'*-bis(2-hydroxyethyl)parabanate (BHEP) and organic acids.[21] On the other hand in the IR spectra, the bands assigned to asymmetric and symmetric vibrations in —O—C(CO)— at 1224 and 1181 cm^{-1} were observed, while characteristic stretching vibration band of ester C=O was overlapped with C=O imide band (1740 cm^{-1}).

It was not possible to follow the reaction between PA and EC exclusively by determination of unreacted EC, that is, on the way previously used for the reactions between melamine or isocyanuric acid with EC,[32,33] because Ba(OH)$_2$ showed extra reactivity toward the trioxoimidazolidine rings preserved in the products, inducing their decomposition. Thus, IR spectra were used to determine unreacted EC through valence bands of carbonyl group (at 1800 and 1767 cm^{-1}). The corresponding bands of PA (at 1832, 1785, and 1745 cm^{-1}) and products of reaction (1730 cm^{-1}) do not overlap with those from unreacted EC. Therefore, following the decrease of absorption band at 1800 cm^{-1} in reaction mixture, we were able to determine the end of reaction [Figs. 2(a)–(d)].
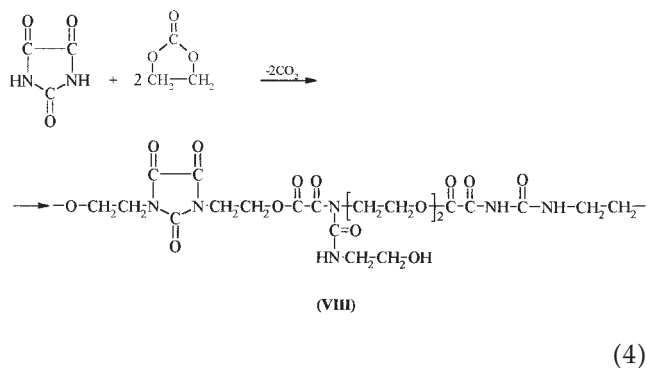
Reaction between 1 mol of PA with 2 mol of EC required the use of the catalyst; the attempted changes of reaction conditions (time and temperature; Table I, run 2–4) resulted in gelation, while EC still remained unreacted. Typical catalyst for alky-
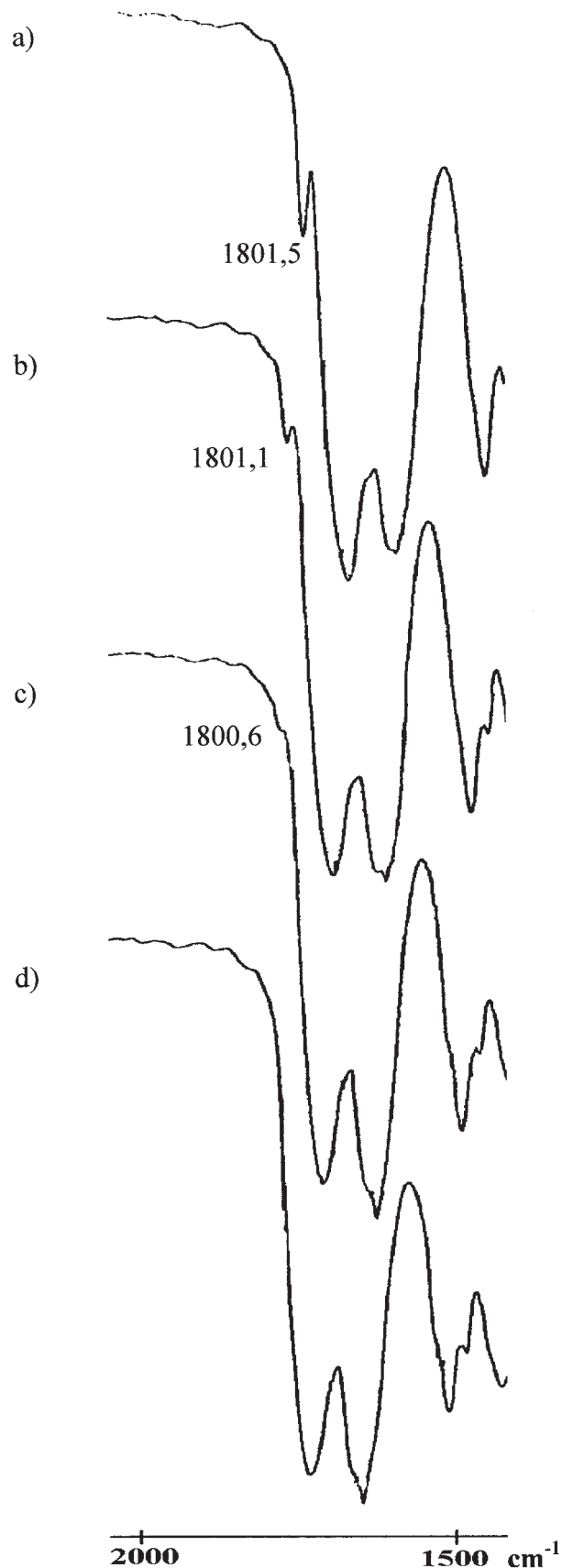
Figure 2 Relevant fragments of IR spectra of products obtained from PA:EC 1:2, at the presence of 0.03 mole K$_2$CO$_3$/mole PA, at 140°C obtained after (a) 2, (b) 3, (c) 4, (d) 4.75 h of reaction.
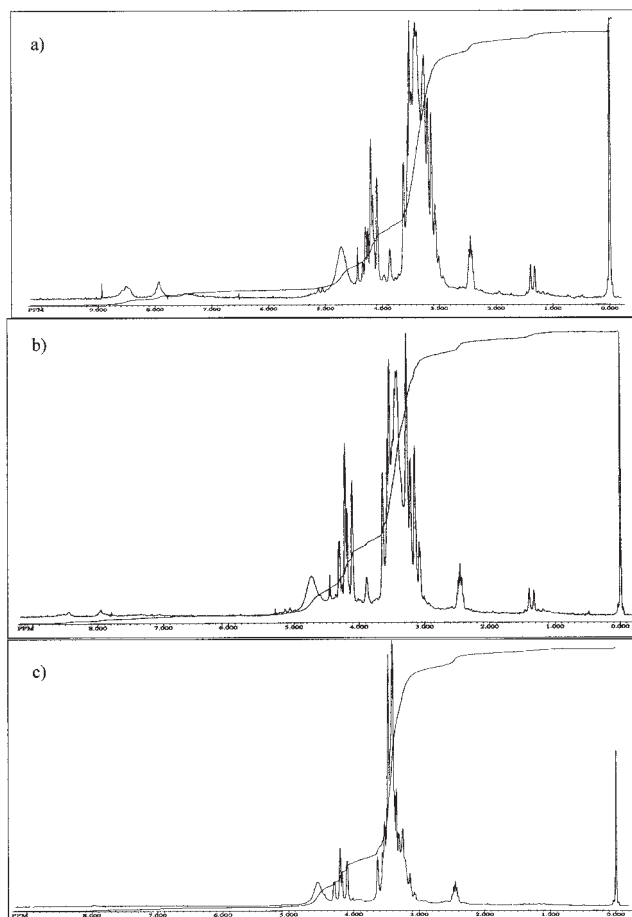
lene carbonates,[24,25] potassium carbonate was used (Table I, run 5–13). It has been practiced that reactions should be performed at temperatures higher than 100°C (Table I, run 5–8, 10, 12, and 13). Even though, 50 h heating at this temperature in presence of vast amount of catalyst (0.18 mol K_2CO_3/mol PA; Table I, run 5) caused incomplete dissolving of PA in EC, at higher temperatures, the reaction was completed within 19 h at 110°C and in 2 h at 160°C (Table I, run 6–8, 10, 12, and 13). The smallest loss of EC from reaction mixture resulted from its decomposition into EO and CO_2[23] occurred at 110°C (Table I, run 6), while it was substantial at higher temperatures (Table I, run 7, 8, 10, 12, and 13).

^{1}H NMR spectra of products obtained from PA:EC 1:2 showed the presence of primary and secondary amides, similarly, as it was the case for PA:EC 1:1 system. High intensity resonances at 7.1–8.2 and 8.3–9.2 ppm regions in comparison with those at 6.5 ppm indicated the domination of secondary amide and imide groups in products:

(4)

Figure 3 ^{1}H NMR spectra of products obtained from PA : EC (a) 1 : 3 and (b) 1 : 4 in the presence of 0.06 mole K_2CO_3/ mole PA catalyst at 140°C, and (c) 1 : 8 in presence of 0.15 mole K_2CO_3/mole PA at 140°C.

Chromatographic analysis evidenced the presence of EG side-product at the level of 1.8 wt % (Table I, run 6–13). It has been noticed that depending on reaction temperature, it was possible to obtain exclusively polymeric products without side-products (Table I, run 6, 8, 11, and 12).

Previously, we have established[19] that percentage of PA rings preserved in polymeric product in reactions between PA with excess of oxirane could be estimated on the basis of titration procedure to give AN; PA rings in polymer decompose upon titration, while the number of PA rings could be calculated providing that all PA rings are incorporated into polymer. Thus, comparing the experimental AN with calculated ones we have found that only slight incorporation of trioxoimidazolidine rings into polymers took place depending on reaction temperature (Table I, run 6–8, 10, 12, and 13) and the amount of catalyst (Table I, run 9–11). The products obtained at 110 and 120°C (Table I, run 6 and 7)

contain the most preserved PA rings (33–34%). Further increase of the temperature to 130°C (Table I, run 8) resulted in decrease of PA ring percentage to 3.2%, surprisingly further increase of temperature of 10°C induces again increase of PA ring percentage increase up to 35% (Table I, run 10). It has also been found that at 140°C, the change of catalyst content from 0.06 mol to 0.03 mol or to 0.09 mol K_2CO_3 resulted drastic decrease of PA rings percentage in products (Table I, run 9–11). Similar changes were found at higher temperatures (Table I, run 12 and 13), and in presence of 0.06 mol K_2CO_3/mol PA.

Reactions between PA and 3–8-fold excess EC (Table I, run 14–21) led to formation of products without primary amide groups. It has been found that increase of starting amount of EC, the intensity of resonances from secondary amide and imide protons in ^{1}H NMR spectra was diminished [Figs. 3(a) and (b)] up to total disappearance at PA to EC 1:8 ratio [Fig. 3(c)]. Structure of products can be expressed as (IX):
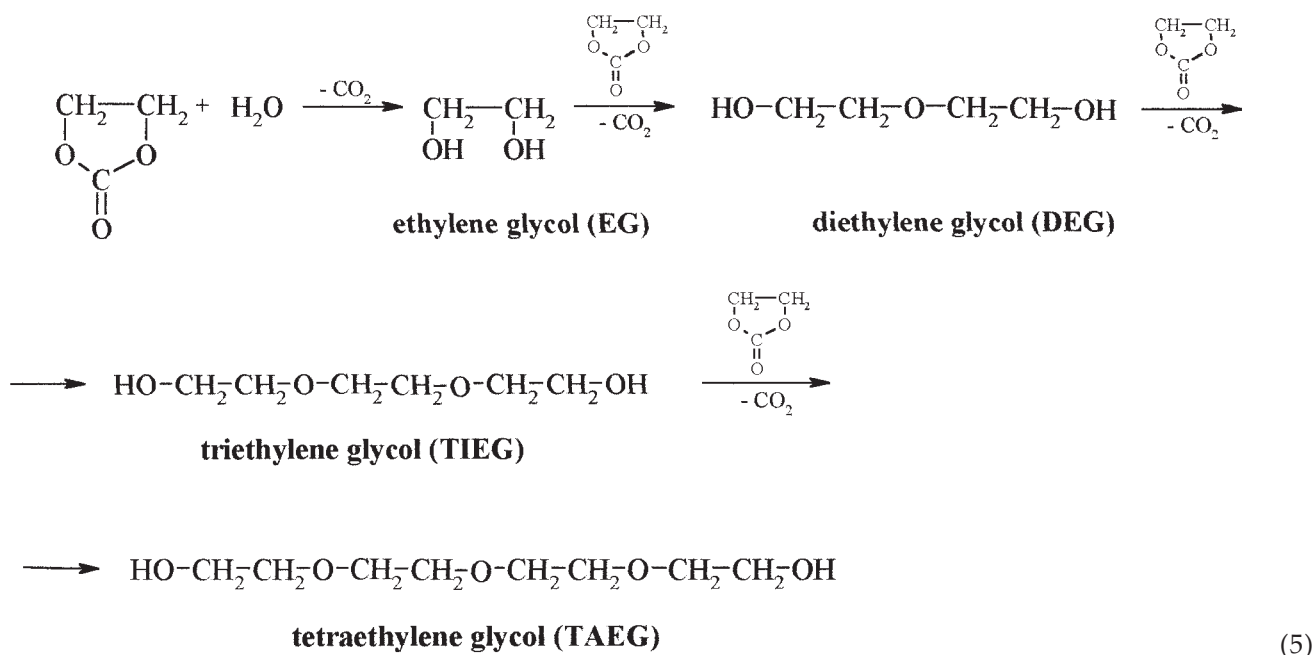
TABLE II
Thermal Resistance of Products Based on Thermal Analysis

Run no. as in Table I	Temperature (°C)				Temperature of max decomposition (°C)
	5% of mass loss	10% of mass loss	30% of mass loss	50% of mass loss	
7				260	250
10	170	200	220	265	250
12	110	170	200	250	240
15	170	200	230	260	245
17	135	170	210	250	240
20	150	180	220	270	250

(IX)
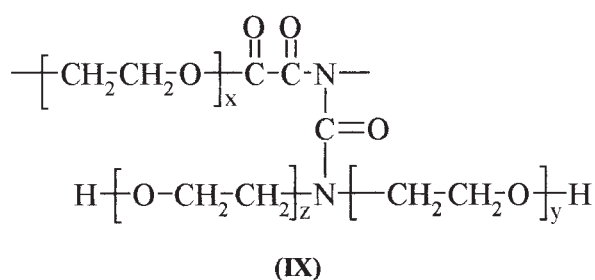
where $0 < z < n - (x + y)$, $x + y + z = n$, $n = 3{:}12$.

During the reaction of PA with excess of EC (3–4 mol/mol PA), the EG is still formed as a side-product and its content slightly increases upon addition of EC to starting mixture (Table I, run 14 and 16). When BHEP is used instead of PA at the reaction of 1 mol PA with 2 mol of BHEP, the side product was obtained as the product of reaction between EG and unreacted EC (Table I, run 18). When higher excess of EC was used, other side products appear, which result from the consecutive reaction of EG with EC. Their total content increases up to 18 wt % (Table I, run 19–21):


ethylene glycol (EG)　　　diethylene glycol (DEG)

triethylene glycol (TIEG)

tetraethylene glycol (TAEG)

(5)

From the analysis of percentage of trioxoimidazolidine rings in products, one can see the increase of ring percentage upon increasing amount of EC in reaction mixtures (Table I, run 15, 16, and 19).

Thermal analysis studies of polymeric products indicated their high thermal stability. They are characterized by temperature of maximum de-

composition in the range of 240–250°C (Table II). Based on AN of products (Table I, run 7, 10, 12, 15, 17, and 20) and using the data in Table II it is easy to conclude that ring percentage has no influence of thermal stability of products. The products with 30% preserved PA rings (Table II, run 7, 10, and 20) have merely 5–10°C higher thermal stability from

those with 3–5% of the rings (Table II, run 12, 15, and 17). Thus, rather the ester-amidoimidotetraol (X) structure of polymers is responsible for high thermal stability than presence of PA rings.

(X)
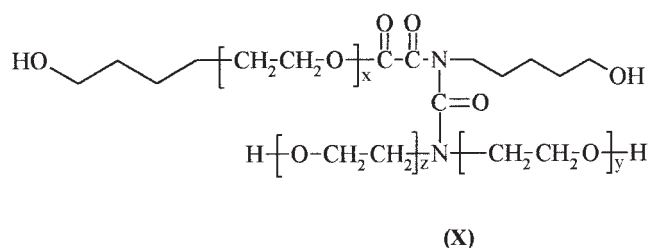
Obtained products can be used for production of thermally resistant polymers despite the fact that trioxoimidazolidine rings percentage is low. This observation will be the matter of separate communication.

CONCLUSIONS

1. Reactions of PA with EC lead to trioxoimidazolidine rings openings and formation of linear polymeric products.
2. Depending on the reaction conditions (amount of catalyst, temperature) and molar ratio of reagents, part of PA rings can be preserved in polymer products. The highest ring percentage can be obtained at $1:2M$ ratio at $140°C$ in presence of 0.02 mol K_2CO_3/mol PA.
3. At high excess of EC, the secondary amide groups formed upon ring opening, react with excess of carbonate to give products with ternary amide groups.
4. Ring opening reaction are accompanied by side-reactions, leading to EG and consecutive products of its reaction with EC. The side-product percentage depends on molar ratio of reagents, temperature of reaction, and amount of catalyst.
5. Products formed during hydroxyalkylation of PA with EC possess high thermal resistance, which is not related to preservation of trioxoimidazolidine rings.

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