Reaction Pathway and Product Analysis for Hydroxyalkylation of Urea and N,N-Bis(2-hydroxypropyl)urea with Propylene Carbonate

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ABSTRACT: The hydroxyalkylation of urea and N,N'-bis(2-hydroxypropyl)urea (BHPU) with propylene carbonate (PC) was studied by spectral analysis of oligomeric products using ^{1}H-NMR, IR and MALDI ToF methods. During the hydroxypropylation the carbonate groups in a product are partially preserved. Additionally, the hydroxypropyl groups of urea derivatives undergo partially dimerization to give carbamate groups. The obtained derivatives posses enhanced thermal stability. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3917–3925, 2008

Key words: urea; propylene carbonate; structure of product; thermal properties

INTRODUCTION

Hydroxyalkylation of parabanic acid (PA, I) with excess alkylene carbonates (ACs) occurs with preferential opening of trioxoimidazolidine ring of PA and formation of esteramidoimidotetraols (II)[1–3]:
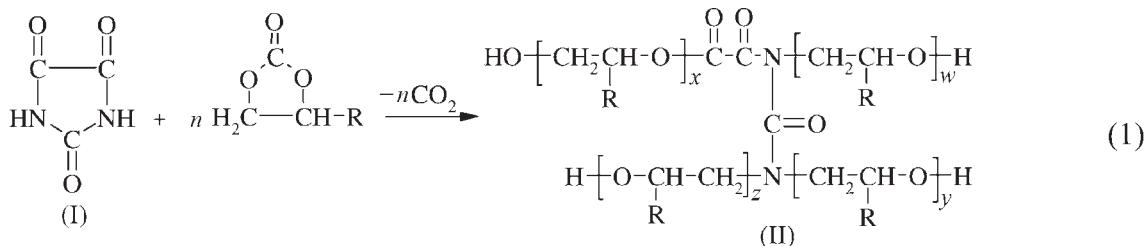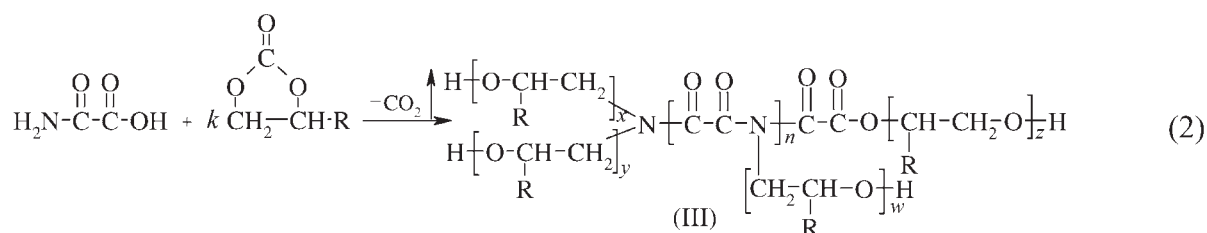

where, R = H—, CH$_3$—, $x + y + z + w \leq n = 8$–12.

The oligomers obtained in this way have higher thermal stability. For instance the products obtained with excess ethylene carbonate have at most 20 mol % of preserved trioxoimidazolidine rings and reveal the temperature of maximum thermal decomposition of 250°C.[2] Hydroxyalkylation of PA with excess PC occurs with total disappearance of trioxoimidazolidine rings and products are even more thermally stable; their temperature of maximum decomposition is about 280°C.[3] Their thermal stability is comparable with that of the polyurethanes derived from N,N'-bis(2-hydroxyalkyl)parabanates.[4] This feature was attributed to the presence of oxalamidoester and/or carbamide groups linked together via imide bond.[2,3] Also the hydroxyalcoxy derivatives containing separated oxalamidoester and carbamide groups are expected to be thermally stable.

Temperature of maximum decomposition for the products of hydroxyalkylation of oxamic acid with excess ethylene carbonate or PC (the products with oxalamidoester groups, III) was 315 and 290°C, respectively.[5,6]

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$$H_2N\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-OH} \;+\; k\,\overset{\displaystyle \overset{O}{\overset{\|}{C}}}{CH_2\text{---}CH\cdot R} \xrightarrow{-CO_2}$$

$$\begin{array}{c} H\!\!\left[O\text{-}CH\text{-}CH_2\right]_{\!x}\\[-2pt] \qquad R \\ H\!\!\left[O\text{-}CH\text{-}CH_2\right]_{\!y}\\[-2pt] \qquad R \end{array} N\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}N\!\!\left[\,\right]_{n}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-O}\!\!\left[CH\text{-}CH_2\text{-}O\right]_{z}\!\!H \qquad (2)$$

$$(III) \qquad \begin{array}{c}\left[CH_2\text{-}CH\text{-}O\right]_w H\\ R\end{array}$$

where, R = H—, CH₃—, $n = 0$ or 1, $k = 9$, 12, or 15.

In the line with those studies here the hydroxyalkyl derivatives containing carbamide groups were obtained from urea or BHPU and PC and their thermal stability was studied.

EXPERIMENTAL

Synthesis

Reactions of urea or BHPU WITH PC

In a 100-cm³-three-necked round bottom flask 3 g (0.05 mol) urea (pure, POCH, Gliwice, Poland) or 4.5 g (0.025 mol) BHPU[7] and the appropriate amount of PC (pure, Fluka, Switzerland), were placed to reach the molar ratio of reagents of 1 : 1–1 : 12 and 0.42–0.98 g potassium carbonate (0.84–19.56 g/mol urea or BHPU, 0.06–0.14 mol/mol urea or BHPU) or 0.38 g diazabicyclo[2.2.2]octane (DABCO) (7.6 g/mol urea, 0.06 mol/mol urea) was added. The reaction mixture was protected from moisture by tube filled with magnesium sulfate, and stirred mechanically at 140 or 160°C with monitoring of progress of reaction by determination of unreacted PC.[8]

Analytical methods

^{1}H-NMR spectra of products were recorded with BS-586A 80 MHz spectrometer (Tesla, Brno, Czechoslovakia) or with 500 MHz spectrometer (Bruker, Germany) 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 (DPG, TRIPG) 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, detector temperature: 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 as described in Ref. 2.

MALDI ToF spectra of reaction products of BHPU with PC were obtained on Voyager-Elite Perseptive Biosystems (Framingham, MA) 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⁺, K⁺, H⁺, and CH₃OH.

Thermal analyses (DTA, DTG, and TG) of hydroxypropyl derivatives of urea were performed in ceramic crucible at 20–1000°C temperature ranges, with 100 min registration time, 200 mg sample, under air atmosphere with Paulik-Paulik-Erdey derivatograph, MOM, Hungary.
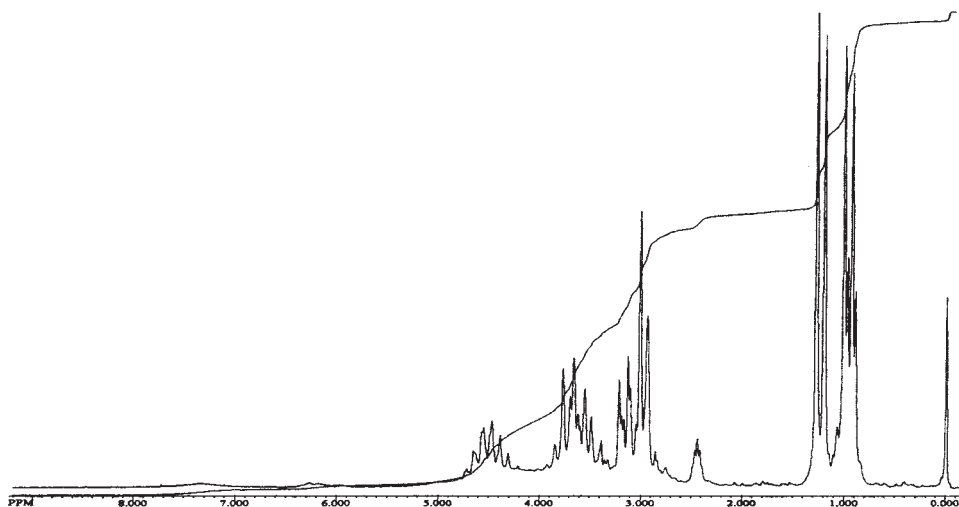
The following properties of reactions products of BHPU with PC have been determined: pycnometer density,[9] Höppler viscosity,[10] and surface tension by ring detach method.[11] All measurements were made in temperature range 20–80°C.

RESULTS AND DISCUSSION

Reaction pathway of urea with PC—structure of products

To obtain N-hydroxypropyl derivatives with carbamide group the reaction between urea and PC was performed in the presence potassium carbonate as catalyst. Formerly, it has been shown that reaction of substrates bearing replaceable hydrogen atoms with ACs at temperatures above 120°C give rise to total release of carbon dioxide.[12–17] Mass balance and spectral analysis of the products of reaction between urea and PC at 140 and 160°C indicated (Table I) the presence of carbonate group in the products. Specifically, the mass of products was larger than that for the product with lost all carbonate groups. Thus, for the crude product obtained from 1 : 2 reaction mixture at 140°C (Table I, Synthesis 1) suggested the formation mainly the compound with 2-hydroxypropyl groups (Formula IV) and ca 11 mol % carbonate groups (Formula V):

$$
\begin{gathered}
\text{(3)}
\end{gathered}
$$

The ^{1}H-NMR (Fig. 1) of the mixture indicated the presence of imide group and secondary amide group protons of V by resonance at 7.1–7.6 ppm region,[18] which confirm incorporation of carbonate groups into product.

Thus, in the ^{1}H-NMR spectrum of the product obtained from 1 : 2 system two doublets at 0.95 and 1.25 ppm from methyl group protons of —CH(CH_3)OH (IV) and —CH(CH_3)OCO— (V), re-spectively, were present (Fig. 1). Integration of these two resonances revealed that ca 40 mol % of carbonate groups were incorporated into the product.

The product containing carbonate group was formed upon the attack of urea nitrogen on carbonylic carbon of PC, while the carbonate ring opening could occur on both sides of carbonyl group (Pathway 1 or 2) according to the scheme:

$$
\begin{gathered}
\text{(4)}
\end{gathered}
$$

TABLE I
Reaction Conditions of Urea with PC and Percentage of By-Products

Entry	Initial molar ratio	Amount of K_2CO_3 (mole/mole urea)	Temp. (°C)	Time of reaction (h)	Percentage of glycols in post-reaction mixtures (wt %)			
					PG	DPG	TRIPG	Σ
1	1 : 2	0.06	140	13.5	–	–	–	–
2	1 : 2	0.06	160	6.5	0	3.08	0	3.08
3	1 : 2	0.09	160	3	–	–	–	–
4	1 : 2	0.06[a]	140	35[b]	–	–	–	–
5	1 : 4	0.06	160	7	0	1.47	0	1.47
6	1 : 6	0.06	160	18.5	0	1.12	5.02	6.14
7	1 : 6	0.06	140	21[c]	–	–	–	–
8	1 : 12	0.14	160	10	0	0.87	9.07	9.94

[a] DABCO was used as catalyst.
[b] PC was unreacted.
[c] About 20 wt % PC was unreacted.

Figure 1 ^{1}H-NMR spectrum of the product of reaction of urea : PC 1 : 2 in the presence of 0.06 mol K_2CO_3/mol urea at 140°C.

The presence of the doublet at 1.25 ppm and a multiplet resonance at 4.5 ppm from methyl and methine protons in VI evidenced that ring opening occurred at the less hindered side (Path 1). The same resonances were found previously in the ^{1}H-NMR spectra of the products obtained from PA and PC[3,19] or propylene oxide[20] with simultaneous trioxoimidazolidine ring opening. It should be noted that in case of the presence of VII as resulting from ring opening according to Path 2 the resonance from $-(CO)-O-CH_2-C$ proton at ca 4.2 ppm should be observed,[18] which was absent in the products obtained from urea and PC (Fig. 1).

Furthermore, in the ^{1}H-NMR spectrum (Fig. 1) the resonance at 6.2 ppm from secondary amide group protons of IV was present. Doublets at 2.95 and 3.15 ppm belong to methylene protons in the structures of $-CH_2-NH-(CO)-NH-CH_2-$ (IV) and $-CH_2-NH-(CO)-NH-(CO)O-$ (V), respectively. Multiplet resonance at 3,6 was attributed to protons of methine group $-CH-CH_2-NH-(CO)-NH-CH_2-CH-$ (IV) and of methylene group $-NH-(CO)-NH-(CO)O-CH_2-$ (V).

It has been noticed that upon increase of the temperature of the reaction from 140 to 160°C at the 1 : 2 urea: PC system in presence of K_2CO_3 catalyst (Table I, Synthesis 1 and 2) the white ammonium carbamate was formed, which sublimed in the reflux condenser. This product was formed in the reaction between urea and water in vast amount and depending on molar ratio of reagents and reached as much as 25 wt % of starting urea.

In was noticed earlier that depending on the reaction conditions, part of N,N'-disubstituted urea derivatives underwent dehydration into carbodiimide[21] which could be identified based upon the presence of the valence vibrations of N=C=N group at 2158 cm^{-1} in the IR spectrum (Fig. 2).

Here, this product was identified only in the products obtained from 1 : 2 system. When excess of PC was applied, the substituted urea formed was higher and carbodiimide was no longer observed. However, when 2M excess of PC was used, even the change of the catalyst from K_2CO_3 into DABCO did not eliminate the formation of both carbodiimide and ammonium carbamate; instead the reaction proceeded slower (Table I, Synthesis 1 and 4). When 4- or 6M excess of PC was used (Table I, Synthesis 5 and 6), the ammonium carbamate was still formed; a lowering of reaction temperature into 140°C caused only the increase of the reaction time (Table I, Synthesis 7).

The products obtained at four and higher molar excess of PC did not contain free amide or imide groups; no resonances at higher chemical shift than 6 ppm were observed in the ^{1}H-NMR spectra of products. Thus, the formula of the product in these cases can be represented by VIII:
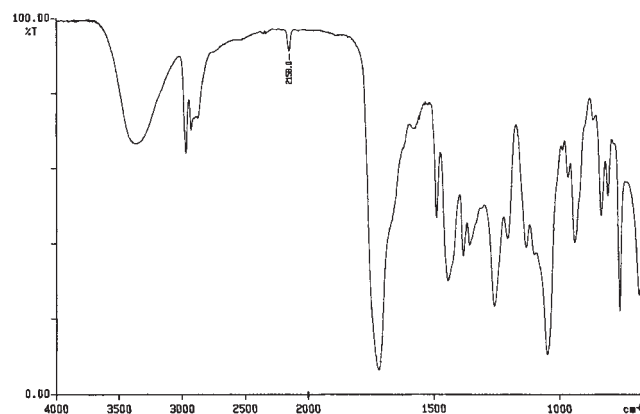
Figure 2 IR spectrum of the product of reaction urea: PC 1 : 2 in the presence of 0.06 mol K_2CO_3/mol urea at 160°C.
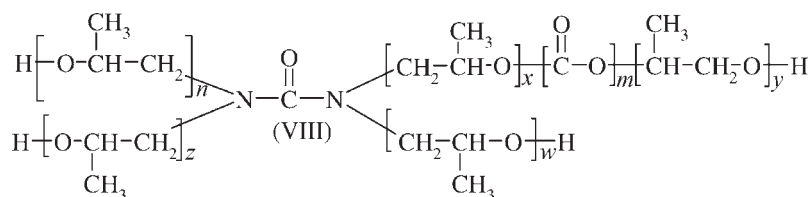
where: $z + w + n + x + y = 4$–12, $0 \leq m \leq 1$, $x \geq 0$.

In such circumstances, carbonate groups can attach not only straight to amide groups of urea, but also can incorporate into oxypropylene chain (Formula VIII, $x \geq 1$). The carbonate ring still opens from less substituted side which was concluded by the absence of the resonance at 4.2 ppm in the ^{1}H-NMR spectra.

From the integral intensity of the resonances centered at 1.25 and 0.95 ppm, it could be estimated that ca 33 and 27 mol % of oxypropylene groups in the products obtained from 1 : 4 and 1 : 6 systems, respectively, was present near ester group. Further

increase of excess of PC caused the decrease of oxypropylene groups next to ester group; at twelvefold molar excess of PC it was ca 17 mol % (Table I, Synthesis 8). If, however, the insertion of carbonate groups occurs according to the reaction (5), the number of oxypropylene groups next to ester bond does not correspond to number of incorporated carbonate groups; instead it is lower.

Thus, the question arises is the resonance centered at 1.25 ppm attributed only methyl group protons in 2-hydroxypropyl groups attached ester (like in VIII) or the consecutive condensation of hydroxypropyl groups according to the scheme presented below takes place:


(5)
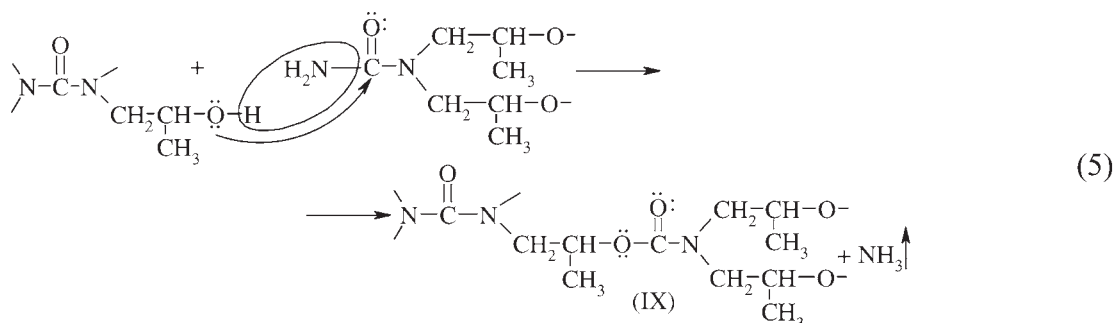
In such a case the carbamate groups would be formed and the resonance of the methyl group proton in —N—(CO)O—CH(CH_3)—CH$_2$— would be also present at 1.25 ppm in the ^{1}H-NMR spectrum, as it was observed before.[18]

To recognize this issue, the product obtained in the reaction between urea and twelvefold molar excess of PC was further heated at 200°C (at this temperature the decomposition of carbamate groups occurs[22]). The ^{1}H-NMR spectra of this product before and after thermal

conversion were compared [Fig. 3(a,b)]. The ^{1}H-NMR spectrum of the product heated for 4 h [Fig. 3(b)] the appearance of additional signal catered at 2.4 ppm was observed which was attributed to the protons of methylene group attached to amine nitrogen atom. Furthermore, the resonance at 1.25 ppm decreases and the resonance at 0.95 ppm increases [Fig. 3(a,b)]. Hence, the carbamate groups which are present in the consecutive condensation reaction were decomposed with formation of tertiary amine according to the scheme:

(6)
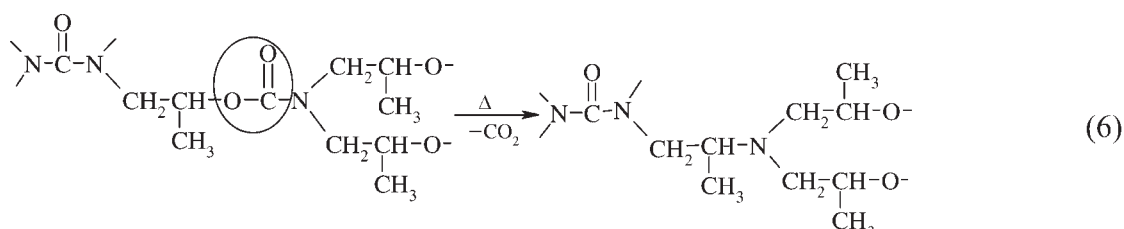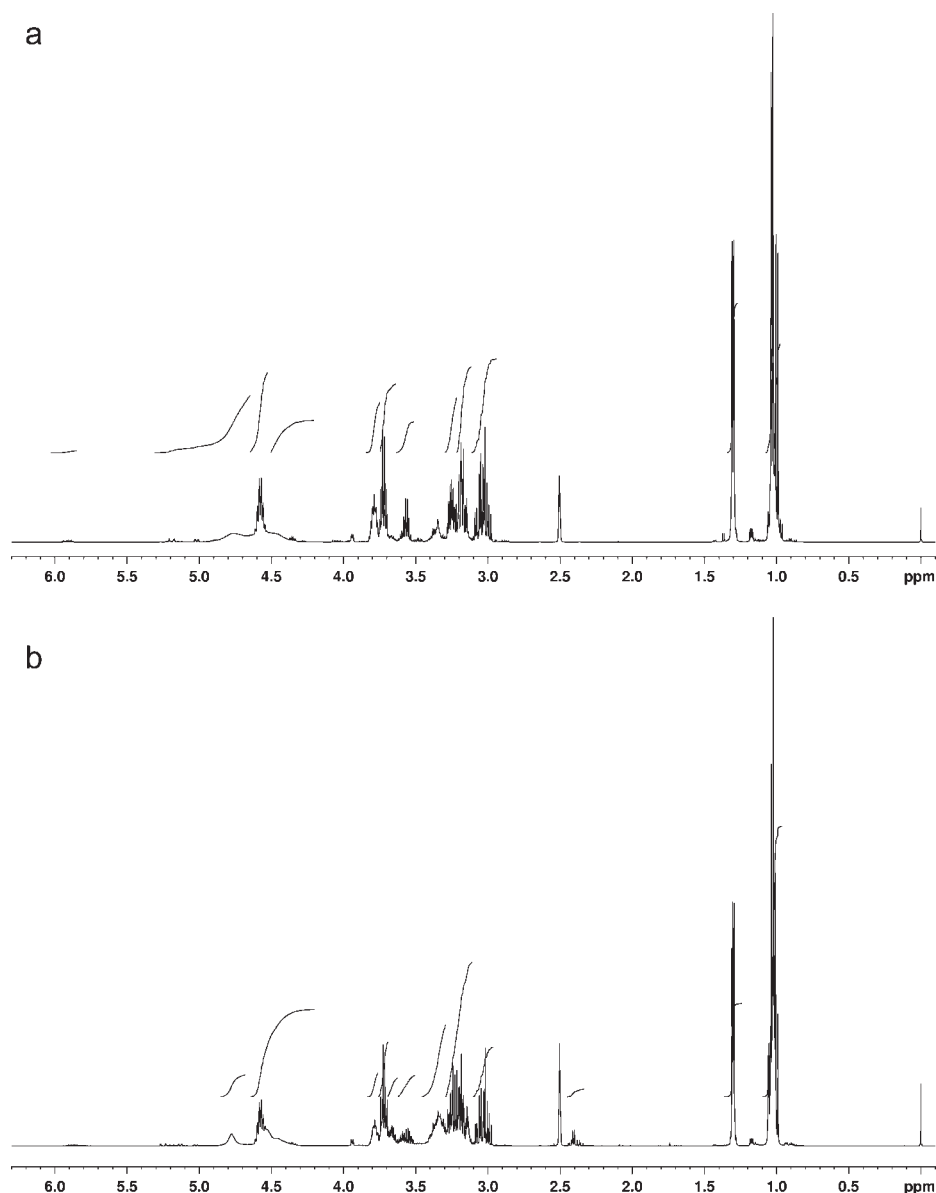
Figure 3 ^{1}H-NMR spectra of product of reaction of urea: PC 1 : 12 in the presence of 0.09 mol K_2CO_3/mol urea at 160°C: (a) before heating at 200°C; (b) after heating at 200°C for 4 h.

Analysis of side-products

It has been found previously that the reactions of substrates with labile hydrogen with PC are accompanied by competitive reaction between carbonate with water leading to the formation of PG as well as by consecutive reaction of PG with PC[12–17] giving di- and tripropylene glycols (DPG and TRIPG). Here in the products obtained from urea : PC 1 : 2 and 1 : 4 systems DPG were present at 3 wt % (Table I, Syn-thesis 2 and 5). When sixfold molar excess of PC was used, the TRIPG formed too, but total amount of gly-cols did not exceed 10 wt % (Table I, Synthesis 6 and 8). Moreover, in the ^{1}H-NMR spectra of products obtained from 1 : 6 system the appearance of new resonances at 4.8–6.1 ppm region was observed, which are diagnostic for allylic group protons.[18] The latter were formed upon dehydration of end hydroxy-propyl groups according to the scheme:
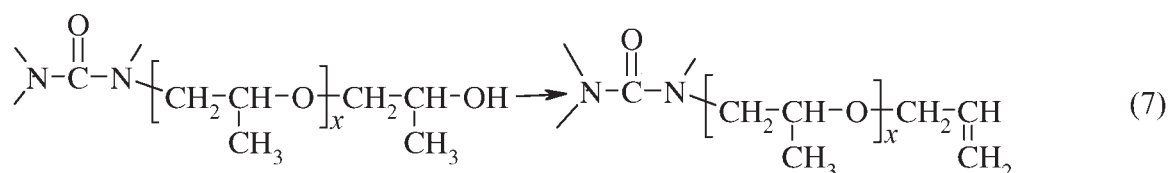

(7)

TABLE II
Thermal Stability of Reaction Products of Urea or BHPU with PC

Entry	Initial molar ratio of x : PC	x	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	T_{max} (°C)
1	1 : 6	Urea	140	170	200	240	260
2	1 : 6	BHPU	140	160	200	240	270
3	1 : 8	BHPU	140	180	200	240	300

$T_{y\%}$, temperature at which the weight loss is y%.

Similar phenomenon was observed previously for the reaction of melamine with PC.[8] Because allylic groups were not formed at the system with large excess of PC in relation to PA[3] it follows that rather presence of amine groups is necessary.

Thermal properties of reaction products of urea with PC

The derivatographic analysis of the products of reaction between urea and PC showed their enhanced thermal stability. Only one peak was observed on DTG curve assigned to simultaneous decomposition of carbonate, carbamate, and carbamide groups. The temperature of maximum decomposition of the product obtained from 1:6 system was 260°C (Table II, entry 1).

Reaction pathway of BHPU with PC and its comparison with reaction pathway of urea with PC

As it was mentioned earlier, the products contain carbonate and carbamate groups. Moreover, side reactions lead to ammonium carbamate, carbodiimide, propylene polyglycols, and allylic groups in main product. To clarify the picture the PC was reacted with BHPU (Table III). The elimination or restriction of some of those processes was expected. The mass balance and spectral analysis of products indicated that carbonate groups were still incorporated into products. In the ^{1}H-NMR spectrum of product obtained from BHPU with twofold excess PC (Fig. 4) besides the resonances at 1.0, 3.0, and 3.55 ppm belonging to methyl, methylene, and methine protons, analogically as in the spectrum of

BHPU,[7] new resonances were found at 1.25, 3.7, 3.8, and 4.65 ppm of the same group protons in the product containing incorporated carbonate, i.e., —CH$_2$—(CH$_3$)CH—O—(CO)—. The resonances at 3.15 and 3.25 ppm belong to protons of methylene group in structure —CH$_2$—NH—(CO)—NH—(CO)O—. The presence of the resonance at 7.4 ppm assigned to secondary amide group evidenced the incorporation of carbonate groups next to nitrogen atom of BHPU (Formula VIII, x, n = 0).

Spectral analysis indicate that the number of oxypropylene groups next to ester bond is comparable in products obtained in reaction of urea with PC and BHPU with PC.

In the course of reaction between BHPU and PC the condensation of hydroxypropyl derivatives of urea with formation of carbamates also occurred. This can be concluded based upon analysis of the ^{1}H-NMR spectrum of the product obtained from BHPU and sixfold molar excess of PC (Table III, Synthesis 4) converted thermally at 200°C in analogous manner as before for the product obtained from urea and twelvefold molar excess of PC.

Reaction products of BHPU with PC and its thermal properties

Condensation of hydroxypropyl derivatives of urea with formation of carbamates was provided from MALDI ToF measurement too (Table IV). The spectrum of the product obtained from BHPU : PC 1 : 6 system indicated that derivatives of urea underwent partially dimerization process in the conditions used. Also it has been noticed that despite high temperature of the Synthesis (160°C) carbonate groups

TABLE III
Reaction Conditions of BHPU with PC and Percentage of By-Products

Entry	Initial molar ratio	Amount of K$_2$CO$_3$ (mole/mole BHPU)	Temp. (°C)	Time of reaction (h)	Percentage of glycols in post-reaction mixtures (wt %)			
					PG	DPG	TRIPG	Σ
1	1 : 2	0.06	140	9	0	1.45	0	1.45
2	1 : 2	0.09	140	8	0	0	0	0
3	1 : 4	0.09	160	10	0	3.84	5.03	5.87
4	1 : 6	0.09	160	19	0	3.56	3.22	6.88
5	1 : 8	0.09	160	24	0	4.77	2.74	7.51
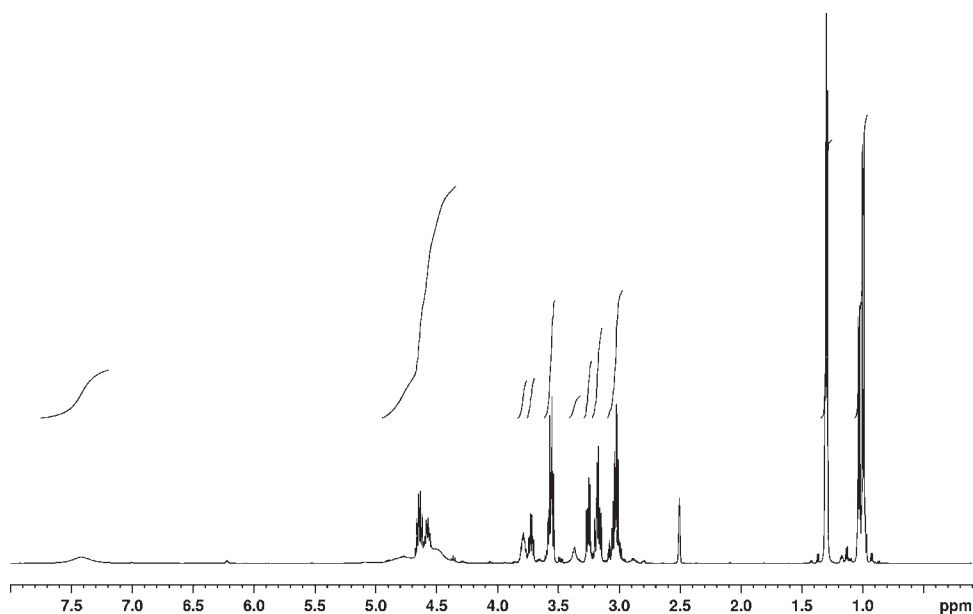
Figure 4 ^{1}H-NMR spectrum of the product of reaction BHPU : PC 1 : 2 in the presence of 0.06 mol K_2CO_3/mol BHPU at 140°C.

remain partially in the product (Table IV). However, only one carbonate group per molecule is present. Moreover, MALDI ToF measurement indicated the presence of allylic group in the products of reaction of BHPU with PC (Table IV).

Propylene polyglycols were also formed in the reaction between BHPU and PC. At the 1 : 2 system glycols were present at 1.5 wt % level (Table III, Synthesis 1), while larger excess of PC led to products contaminated by 7.5 wt % of glycols (Table III, Synthesis 3–5). Thermogravimetric analysis of these products indicated a bit higher thermal stability of products obtained from BPHU and PC as that of the products obtained from urea itself and PC. Temperature of maximum decomposition occurred at 270°C or 300°C for the products prepared from the systems with sixfold and eightfold molar excess of PC (Table II, Entry 2 and 3). It is known that carbonate and carbamate groups undergo decomposition at about 200°C,[12,13,22] thus it can be concluded that enhanced thermal stability of the products obtained here is due to the presence of carbamide group.

Prospects of hydroxypropoxy derivatives of urea in polymer chemistry

Physical properties of hydroxypropyl derivatives of urea obtained from BHPU and PC, i.e., density, surface tension, and viscosity (Fig. 5) depend typically from temperature resembling those of polyols used for Synthesis of polyurethane foams[22] (the density, and surface tension decreased linearly with temperature and the viscosity decreased somewhat faster). Their enhanced thermal stability and physical pa-

rameters renders these hydroxypropoxy derivatives of urea especially valuable substrates for polyurethane foams of higher thermal stability, similarly as those obtained from PA and PC.[23] The results on those studies will be the matter of separate report.

CONCLUSIONS

Reactions of urea and N,N′-bis(2-hydroxypropyl)urea with propylene carbonate occur with partial incorporation of carbonate groups into product.

In the course of these reactions the partially dimerization of hydroxypropyl derivatives of urea takes place with formation of carbamate.

The reaction between urea and propylene carbonate are accompanied by the formation of ammonium

TABLE IV
Results of MALDI ToF Determination of Product from BHPU : PC 1 : 6 in the Presence

Signal position	Probable structure of molecular ion
256.2	U + 3 PO + Na$^+$
266.0	U + 3 PO + CH$_3$OH + H$^+$
314.3	U + 4 PO + Na$^+$
409.1	U + 6 PO + H$^+$
423.0	U + 6 PO + CH$_3$OH −H$_2$O + H$^+$
450.4	U + 5 PO + CH$_3$OH + CO$_2$ + Na$^+$
493.1	U + Carb + 6PO + Na$^+$
601.0	U + 8 PO + CO$_2$ +CH$_3$OH + H$^+$
615.0	U + Carb + 8PO + CH$_3$OH + Na$^+$
719.6	U + 11 PO + Na$^+$

PO, oxypropylene unit; U, urea unit; Carb, carbamic acid unit; CO$_2$, carbonate unit; H$_2$O, indicate the presence of allyl group
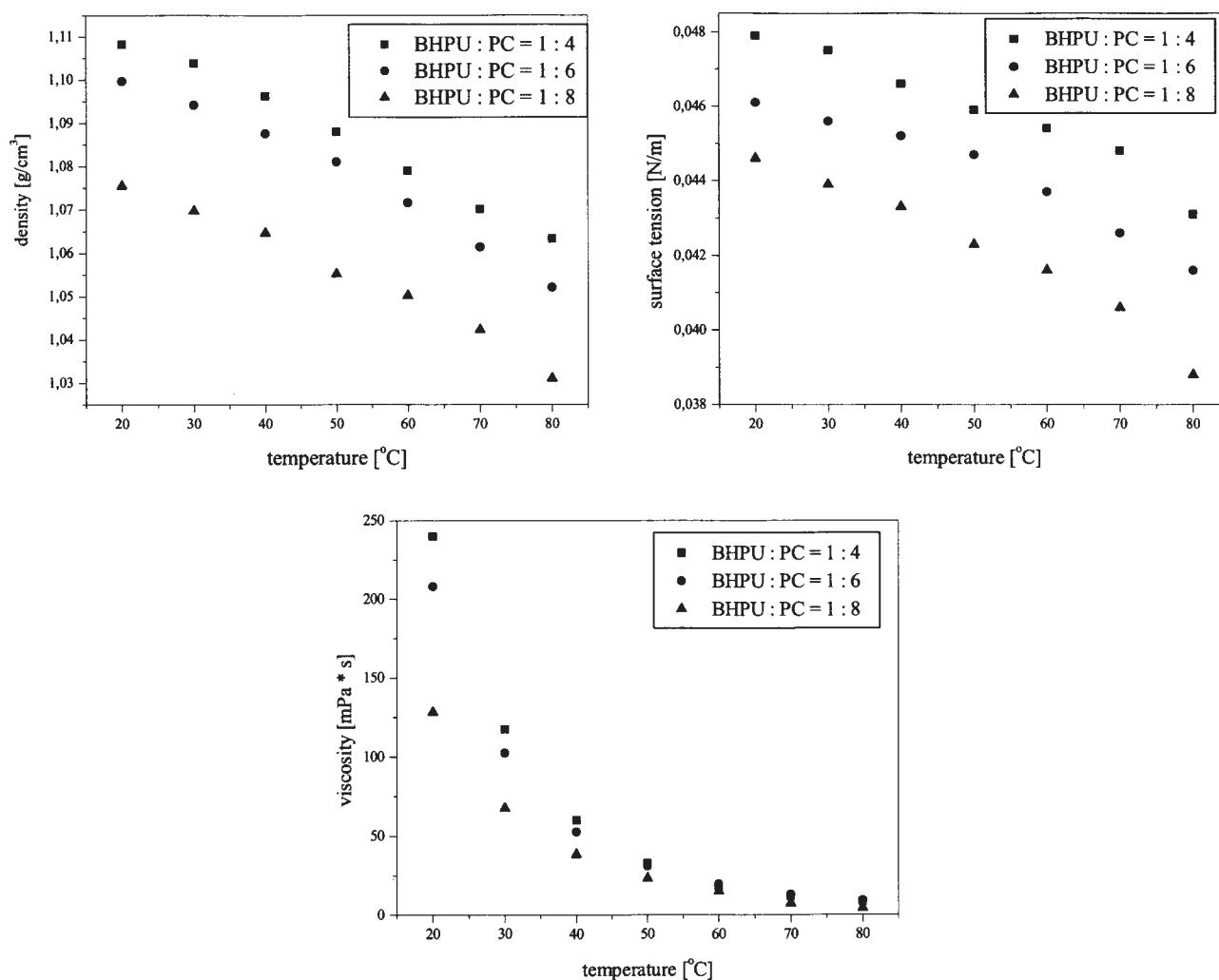
Figure 5 Physical properties of reactions products of BHPU with PC in function of temperature.

carbamate, carbodiimide, propylene polyglycols by-products and allylic groups in the product.

The replacement of urea with its *N,N'*-bis (2-hydroxypropyl) derivative as substrate for the reaction with propylene carbonate excludes the formation of ammonium carbamate and carbodiimide and suppresses the formation of polyglycols.

Hydroxypropoxy derivatives of urea obtained from urea or *N,N'*-bis(2-hydroxypropyl)urea with propylene carbonate show enhanced thermal stability, which is due to the presence of carbamide group.

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