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Preparation of polyetherols with pyrimidine rings by reaction of 6-aminouracil with excess of propylene carbonate

Summary — New method of synthesis of polyetherols with 1,3-pyrimidine rings by the reaction of 6-aminouracil (6-AU) with excess of propylene carbonate (PC) catalyzed by 1,4-diazabicyclo[2.2.2]octane and potassium carbonate is presented. The structures of products were analyzed by IR, ^{1}H NMR and MALDI ToF techniques. Some physical properties of prepared polyetherols were investigated. Among other things, they show improved thermal stability.

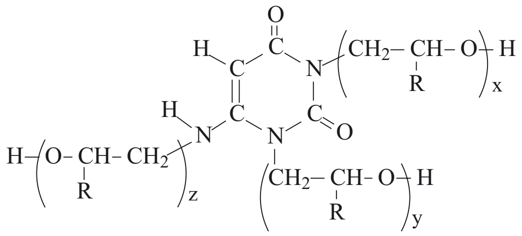
Key words: 6-aminouracil, propylene carbonate, polyetherols with 1,3-pyrimidine rings, polyurethanes, thermal stability.

OTRZYMYWANIE POLIETEROLI Z PIERSCIENIEM 1,3-PIRYMIDYNOWYM W REAKCJI 6-AMINOURACYLU Z NADMIAREM WĘGLANU PROPYLENU

Streszczenie — Przedstawiono nową metodę syntezy polieteroli z pierścieniem 1,3-pirymidynowym w wyniku reakcji katalizowanej przez 1,4-diazabicyklo[2.2.2.]oktan i węglan potasu (tabela 1). Polieterole otrzymuje się w postaci ciemnobrunatnych żywic, które w miarę wzrostu liczby grup oksypropylenowych stają się coraz bardziej płynne. Ich budowę oraz zawartość produktów ubocznych określono metodami IR, ^{1}H NMR i MALDI ToF i chromatografii gazowej (tabele 2—4, rys. 1—4) oraz scharakteryzowano na tej podstawie mechanizm syntezy. Zbadano niektóre właściwości fizykochemiczne polieteroli (współczynnik załamania światła, gęstość, lepkość i napięcie powierzchniowe — tabela 5). Określono także odporność termiczną produktów metodą analizy termicznej (tabela 6). Stwierdzono, że polieterole uzyskane z opisanej reakcji 6-aminouracylu (6-AU) z węglanem propylu (PC) charakteryzują się odpornością termiczną porównywalną z odpornością termiczną polieteroli uzyskanych uprzednio z 6-AU i tlenku propylenu (PO) [4]. Przeprowadzono też wstępne próby syntezy pianek poliuretanowych z wykorzystaniem opisanych polieteroli i 4,4'-diizocyjanianu difenylometanu (tabela 7) oraz zbadano niektóre użytkowe właściwości pianek (tabela 8).

Słowa kluczowe: 6-aminouracyl, węglan propylenu, polieterole z pierścieniem 1,3-pirymidynowym, poliuretany, odporność cieplna.

Polyetherols with 1,3-pyrimidine rings [Formula (I)] can be used to produce polyurethane foams of improved thermal stability [1]. So far these polyetherols were obtained in the reactions of 6-aminouracil (6-AU) with excess of oxiranes such as ethylene oxide (EO) or propylene oxide (PO) [2—4].



(I)

where: $R = -H, -CH_3$, and $3.0 \le x + y + z \le 10.7$

The method of synthesis of polyetherols from 6-AU and oxiranes has some drawbacks, namely (i) solvent and catalyst have to be distilled off at reduced pressure from the products after completion of the reaction and, (ii) time of synthesis is very long (78—110 h). Moreover the synthesis has to be conducted in pressure autoclaves, because oxiranes are volatile (b.p.: EO = 14 ^oC, PO = 35 ^oC), toxic and they form explosive mixtures with an air. Therefore, another way of synthesis of polyetherols with 1,3-pyrimidine rings was searched. Instead of oxiranes, non-flammable and non-toxic ethylene carbonate (EC) was used, which was both the solvent and reagent. It has been found recently, that EC reacts similarly to EO with formation of polyetherols, as in case of the reaction of 6-AU with EO [2—5]. It has also been demonstrated that PO in reactions with melamine [6], isocyanuric acid [7] or uric acid [8] can be replaced with propylene carbonate (PC) to obtain polyetherols, in which heterocyclic rings are connected with oxypropylene groups. The results of investigations of the reaction between 6-AU and PC [see Equation (2)] presented here are an extension of our studies on polyetherols with 1,3-pyrimidine rings.

EXPERIMENTAL

Reaction of 6-AU with PC

To a round-bottomed flask (100 cm^3 or 250 cm^3) equipped with a reflux condenser, thermometer, and stirrer, 12.7 g (0.1 mol) of 6-AU (pure; Sigma-Aldrich, Steinheim, Germany), and 40.8 g (0.4 mol) or 61.3 g (0.6 mol), or 81.7 g (0.8 mol), or 122.5 g (1.2 mol) of PC (pure; Fluka, Buchs, Switzerland), and 0.8 g of 1,4-diazabicyclo[2.2.2]octane (DABCO pure; Avocado Research and Development, Karlsruhe, Germany) as a catalyst were introduced. The mixture was heated to 180 °C with continuous stirring. When 6-AU have been dissolved, the 0.6 g of potassium carbonate (pure, PPH POCh, Gliwice, Poland) was added. The reaction was controlled by determination of amount of unreacted PC with barium hydroxide [6]. Mass balances of the syntheses were made. Reactions with potassium carbonate as a catalyst (amounts of catalyst: 0.4, 0.6, 0.8, 1.2, and 1.4 g/0.1 mol of 6-AU) or DABCO as a catalyst (amounts of catalyst: 0.4, 0.6, and 0.8 g/0.1 mol of 6-AU) have also been done.

Polyurethane foams preparation

The tests of foaming of polyetherols were carried out in small 250 cm^3 test cups at room temperature. 10 g of polyetherol, 0.08 g of surfactant (Silicon 5340, Houdry Hülls), 0.16 g of triethylamine (TEA pure, Fluka, Buchs, Switzerland) as a catalyst, and 0.2 g of water were mixed. After careful mixing of the components, a preweighed amount of 4,4′-diphenylmethane diisocyanate (pure, Merck, Germany) was added. Each composition was vigorously mixed until it started to cream. The samples for testing were cut out from the foams thus obtained after *ca*. 48 h.

Analytical methods

Polyetherols characterization

— The acid number was determined by titration of a sample dissolved in 20 cm^3 H_2O with 0.1 M NaOH [9].

— The infrared spectra were recorded using a Fourier transform IR PARAGON 1000 spectrometer (Perkin-Elmer Corp., Norwalk, CT). The samples for IR analyses were prepared in the form of capillary films. The ^{1}H NMR spectra of the products were recorded using 80 MHz BS-586A spectrometer (Tesla, Brno, Czechoslovakia). The solvent was d_6-DMSO with HMDSO internal standard. Before recording IR and ^{1}H NMR spectra, glycols were distilled off at reduced pressure (0.53 kPa, 180 °C) from polyetherols samples.

— MALDI ToF (*Matrix-Assisted Laser Desorption Ionization Time of Flight*) spectra were obtained using a Voyager-Elite Perseptive Biosystems (Framingham, MA, United States) mass spectrometer working at linear mode with delayed ion extraction, equipped with nitrogen laser working at 337 nm. The method of laser desorption from a matrix was used with 2,5-dihydroxybenzoic acid in THF at 10 mg/cm^3 concentration. The samples were diluted with methanol to 1 mg/cm^3, followed by addition of 10 mg/cm^3 of NaI in acetone. Therefore in some cases the molecular ion masses were increased by the mass of Na^+ and CH_3OH.

— Gas chromatography (GC) analysis was realized using a Hewlett-Packard 5890 instrument (Waldbronn, Germany) equipped with a flame ionization detector. From the chromatograms the amounts of diols and the subsequent products of reactions of PC with water were determined. The GC conditions were are follows: HP-FFAP capillary column (nitroterephthalic acid modified polyethylene glycol) of 10 m length and 0.53 mm diameter, layer thickness 0.5 μm, temperature profile 50—220 °C (20 deg/min), 6 min at 220 °C, temperature of injection chamber 220 °C, rate of carrier gas (He) 18.3 cm^3/min, sample volume 0.2 μdm^3. The calibration was made using cyclohexanone as an internal standard. The data are presented in Table 1 in ref. [4].

— The thermal analysis was carried out using a derivatograph (MOM, Budapest, Hungary) in nitrogen atmosphere. The sample (100 mg) was heated in a china crucible over the temperature range 20—1000 °C. The sensitivity of the instrument was 1/10 for DTA and 1/10 for DTG.

— Some other properties of the products were evaluated in the temperature range 20—80 °C, namely refractive index, density (pycnometrically), viscosity (using a Höpler viscometer, VEB MLW PRÜFGERÄTE-WERK, Medingen, Germany), and surface tension, by the torsion balance method.

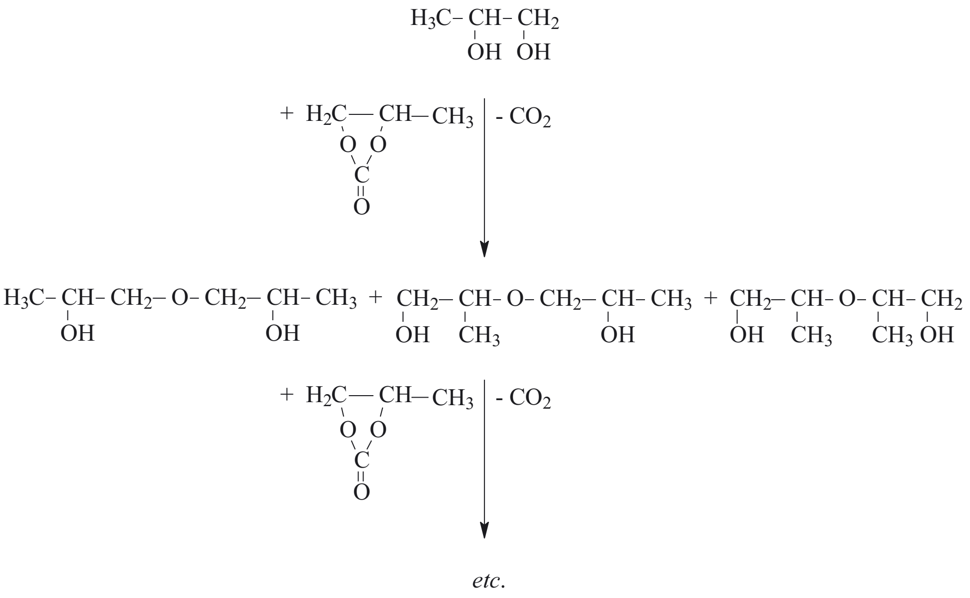
Foams characterization

The following properties of foams were determined: apparent density (PN-EN ISO 845:1995), water absorbtion capacity (PN-EN ISO 2896:1987), dimensional stability (PN-EN ISO 2796:1986), thermal stability as the weight loss after heating at 150 and 200 °C for a month, and the compression strength (PN-EN ISO 844:1978).

RESULTS AND DISCUSSION

Syntheses — conditions, mechanism, structures of products

An influence of the kind of the catalyst and its amount on reaction course was investigated for the initial molar ratio 6-AU:PC = 1:4. Initially potassium carbonate as a catalyst was used, because this compound had been successfully employed as a catalyst in reactions



(1)

Table 1. Conditions and results of the reactions of 1 mole of 6-AU with 4 moles of PC at temperature 180 °C — selection of kind and amount of catalyst

Type and amount of the catalyst, g/mol 6-AU	Reaction conditions		Amount of PC decomposed with release of CO_2 and PO, mol	Amount of by products, wt. %**)			
	dissolution time for 6-AU, h	reaction time, h		PD	OHD MOHD DMOPD OHEO MOHEO	MDODD 2,4-DMDOND 2,5-DMDOND TMDOOD MDODO DMDONEO	total amount of glycols
K_2CO_3, 4	5.25	12.50	0.66	—	—	—	—
K_2CO_3, 6	3.50	9.00	0.63	17.21	3.11	0	20.32
K_2CO_3, 8	4.75	9.50	0.63	16.55	2.56	0	19.11
K_2CO_3, 12	5.25	8.25	0.63	16.57	3.45	0	20.02
K_2CO_3, 16	6.25	11.50	0.86	—	—	—	—
DABCO, 4	3.75	17.25*)	—	—	—	—	—
DABCO, 6	2.50	19.00*)	—	—	—	—	—
DABCO, 8	1.75	14.25*)	—	—	—	—	—
DABCO, 8 + K_2CO_3, 6	1.75	7.00	0.63	15.57	2.66	0	18.23

*) Syntheses were finished when amount of PC in reaction mixture was approximately 3 %.

**) PD — propane-1,2-diol, OHD — 4-oxaheptane-2,6-diol, MOHD — 2-methyl-3-oxahexane-1,5-diol, DMOPD — 2,4-dimethyl-3-oxapentane--1,5-diol, OHEO — 4-oxahept-5-en-2-ol, MOHEO — 2-methyl-3-oxahex-4-en-1-ol, MDODD — 5-methyl-4,7-dioxadekane-2,9-diol, 2,4-DMDOND — 2,4-dimethyl-3,6-dioxsanonane-1,8-diol, 2,5-DMDOND — 2,5-dimethyl-3,6-dioxanonane-1,8-diol, TMDOOD — 2,4,7--trimethyl-3,6-dioxaoctane-1,8-diol, MDODEO — 5-methyl-4,7-dioxadec-8-en-2-ol, DMDONEO — 2,4-dimethyl-3,6-dioxanon-7-en-1-ol.

of 6-AU with EC [5]. Syntheses were conducted at 180 °C because of smaller reactivity of PC in comparison with EC, so the reactions with PC as a reagent [6—8] proceeded at higher temperature than those with EC [5, 10—12].

Optimal amount of catalyst was 6 g of K_2CO_3/mol of 6-AU; larger amounts of the catalyst resulted in formation of insoluble material, which was probably the potassium salt of 6-AU. Prolongation of the time of 6-AU dissolution is disadvantageous because of consecutive reactions of propane-1,2-diol with unreacted PC (formation of diols in reactions of alkylene carbonates with azacyclic compounds were shown by Lubczak [13, 14]).

When DABCO was used as a catalyst, the time of dissolution of 6-AU, in comparison with those for reactions catalyzed by potassium carbonate, was shorter (Table 1). The reaction did not proceed to the end (unreacted PC remained in the reaction mixture). On this basis one can assume that DABCO catalyzes mainly the first step of process, *i.e.* the reaction among nitrogen atoms in 6-AU ring and PC, and, in contrast to potassium carbonate, it does not catalyze further reactions of formed hydroxypropyl groups with PC. Thus we concluded that DABCO was a suitable catalyst for initial stage of the reaction, however, after 6-AU dissolution, potassium carbonate was better to use.

T a b l e 2. Effect of initial molar of 6-AU and PC on the courses of the syntheses of polyetherols*)

Initial molar ratio 6-AU:PC	Reaction conditions*)		Amount of PC decomposed with release of CO_2 and PO, mol	Oxypropylene group content in product mol	Amount of by products, wt. %**)				Amount of PC reacted with 6-AU mol
	dissolution time for 6-AU h	reaction time h			PD	OHD MOHD DMOPD OHEO MOHEO	MDODD 2,4-DMDOND 2,5-DMDOND TMDOOD MDODO DMDONEO	total amount of glycols	
1:4	2.25	10.75	0.52	3.48	18.65	2.52	0.00	21.17	2.55
1:6	2.00	11.50	0.81	5.19	12.54	10.08	2.34	24.96	3.68
1:8	1.75	14.75	1.55	6.45	7.30	14.88	5.99	28.17	4.39
1:12	1.50	14.00	2.91	9.09	2.54	15.38	13.50	31.42	5.99

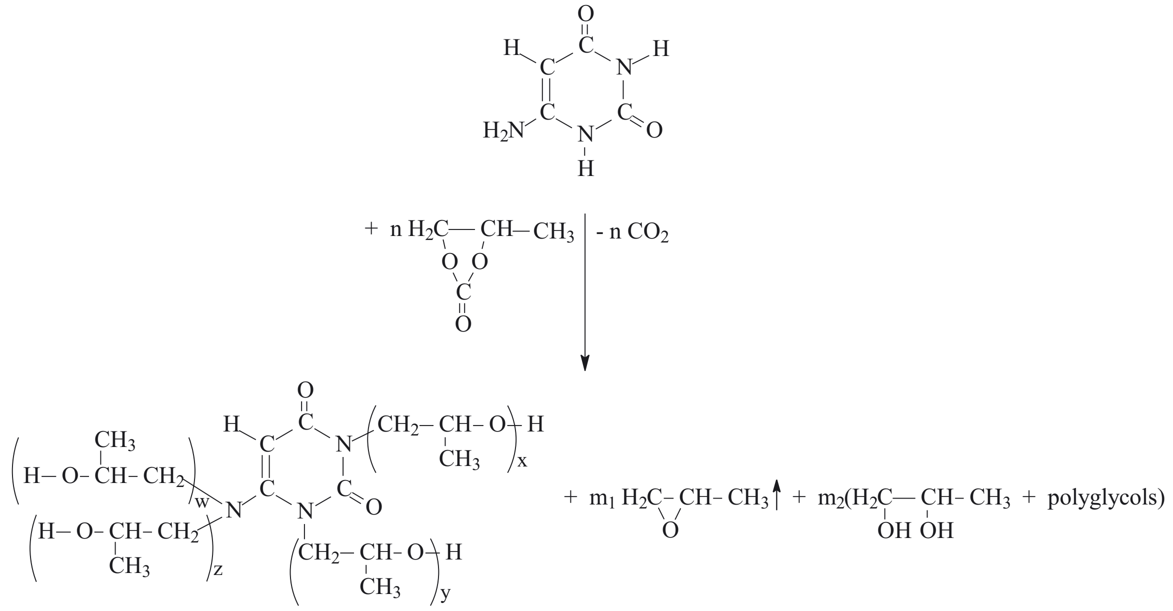
*) Temperature 180 °C, catalyst: (8 g DABCO + 6 g K_2CO_3)/mol 6-AU (K_2CO_3 added after 6-AU dissolving).

**) Symbols — see footnote in Table 1.

Therefore the reaction of 6-AU with PC (initial molar ratio = 1:4) was performed in the presence of 8 g of DABCO and 6 g of K_2CO_3 per mole of 6-AU. The potassium carbonate catalyst was added after dissolution of 6-AU. Using this procedure we achieved the shortest time of 6-AU dissolution and the shortest total time of the reaction (7 hours).

In order to estimate the percentage of propane-1,2--diol and consecutive products in the process, the chromatographic analyses of selected products of 6-AU and PC reaction were performed. Minor amount of side products was formed in the reaction catalyzed by 8 g of DABCO and 6 g of K_2CO_3/mol of 6-AU. This was optimized catalysts composition for further syntheses of hydroxypropyl derivatives of 6-AU.

Then, the series of syntheses at initial 6-AU:PC ratios 1:4, 1:6, 1:8 or 1:12 were done (Table 2). The analyses indicated that carbonate decomposes partially with release of CO_2 and PO [15]. Assuming that all PC has reacted, one can calculate the amount of oxypropylene groups in the reaction product. Chromatographic analyses of the products obtained in the reaction of 6-AU with PC revealed the absence of unreacted carbonate (missing peak at retention time 4.54 min). An estimation of the amount of propane-1,2-diol and consecutive products was done on the basis of chromatographic determinations, which varied in the range from 21 % to 31 %. The weight fraction of propane-1,2-diol was the highest (18.65 %) in the reaction of 1 mole of 6-AU with 4 moles of PC. When a number of PC moles increased the amount of diol decreased (until 2.54 % in a derivative 6-AU:PC = 1:12), while the amount of consecutive product increased due to the reaction between the formed diol and unreacted carbonate. The number of PC moles decomposed with formation of PO is known on the basis of mass balance and the amounts of propane-1,2-diol and polyglycols are found on the basis of chromatographic analyses. Hence one can approximate a number of PC moles which have been reacted with 6-AU. The data included in Table 2 show that it is approximately twice

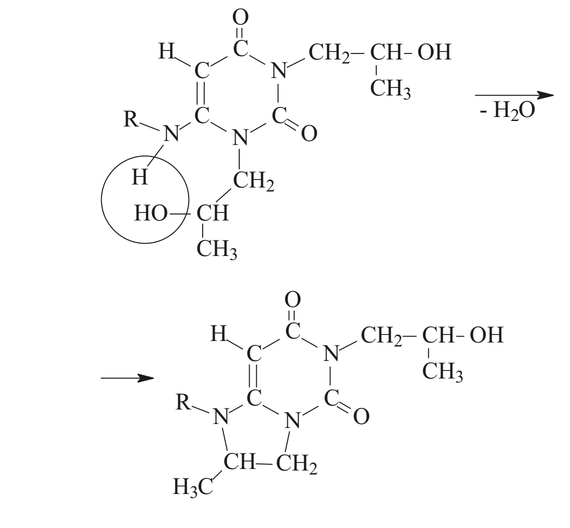


(II)

(2)

where: $4 \le n = x + y + z + w + m_1 + m_2 \le 12$ and $2.55 \le x + y + z + w \le 5.99$

smaller than those calculated according to Equation (2), from initial molar ratio of 6-AU and PC.



(3)

where: R = —H, —$CH_2CH(CH_3)OH$

Thus, in the ^1H NMR spectrum of the product of reaction of 1 mole of 6-AU with 6 moles of PC (Fig. 1) the resonance from unreacted amine group protons at 6.0 ppm should be present (nitrogen atoms in the ring react first [2—5]), which was not the case (similarly in the spectrum of the product of reaction of 1 mole of 6-AU with 4 moles PC). This resonance was observed clearly as separate signal together with that of hydroxyl group in the spectra of products of reaction 6-AU with excess of PO [4] (Fig. 2). Thus amine group had to be consumed in another way. The most likely reactions are: cyclization [Equation (3)], condensation [Equations (4a, b)] or cyclization with previous condensation [Equation (5)].

Due to high temperature (180 °C) and long time of syntheses these side reactions are able to proceed. They did not lead to crosslinking of the products, because neither gelation nor even an increase in density of the reaction mixture were observed. The fact that the afore-mentioned reactions occurred was confirmed by MALDI ToF spectroscopy of the polyetherols obtained.

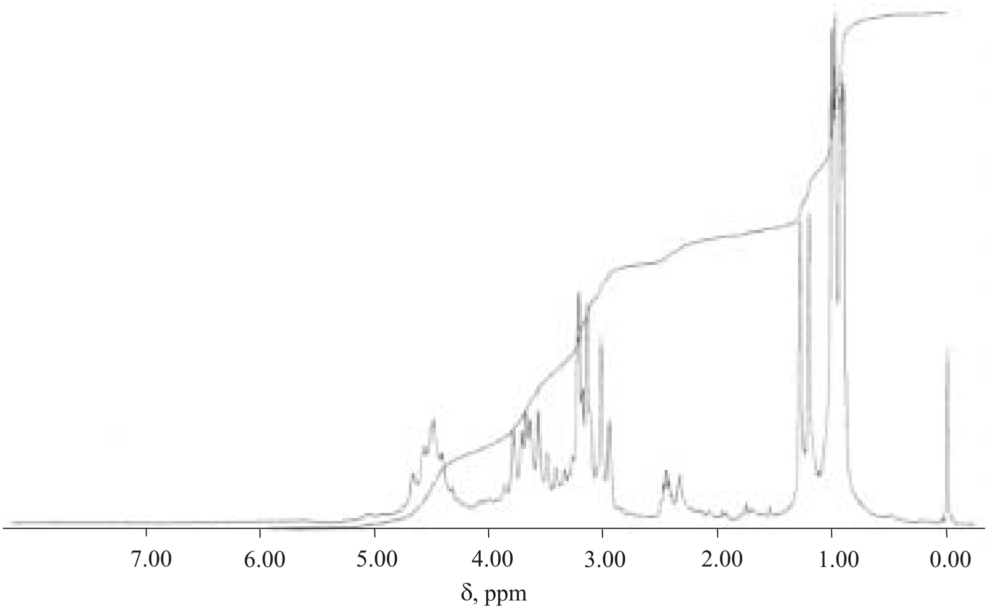


Fig. 1. ^1H NMR spectrum of the product of reaction of 1 mol of 6-AU with 6 moles of PC

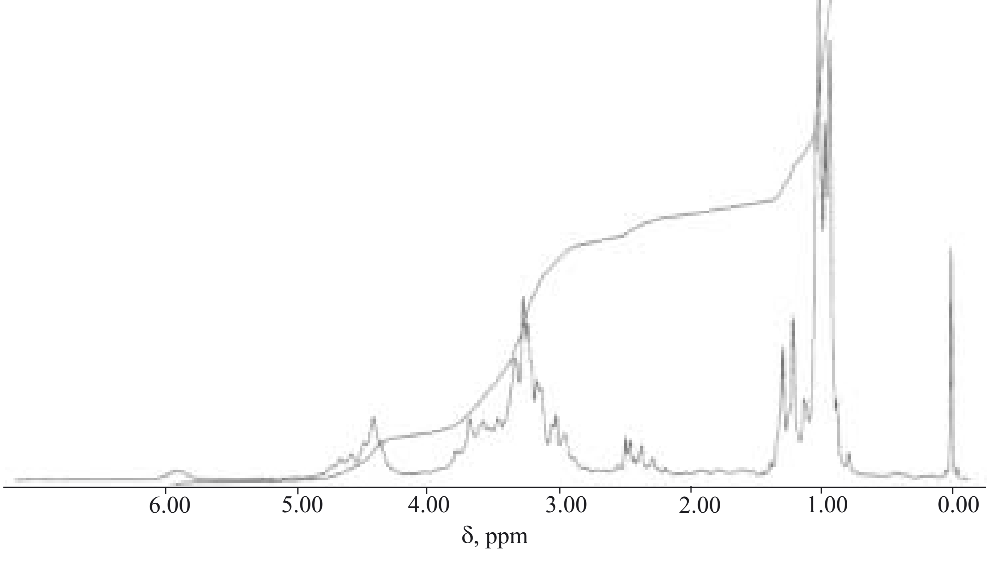
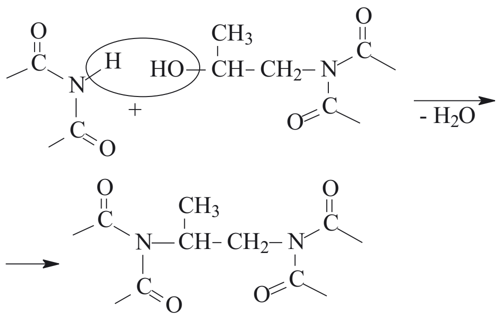
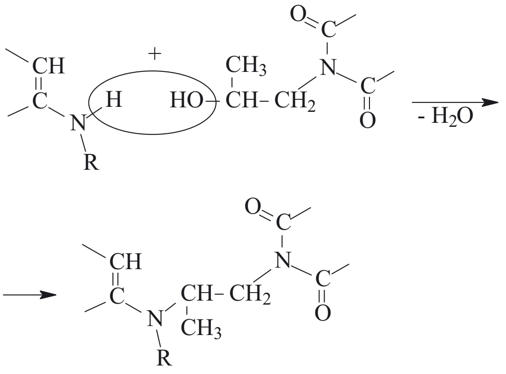


Fig. 2. ^1H NMR spectrum of the product of reaction of 1 mol of 6-AU with 12 moles of PO



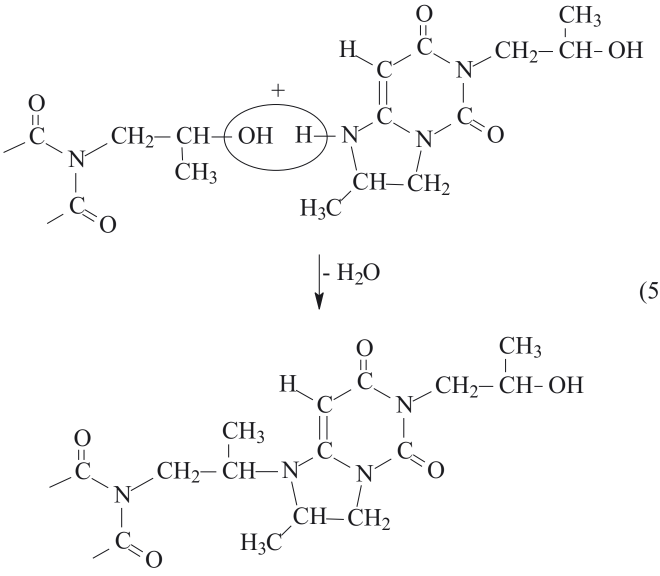
(4a)

and



(4b)

where: R = — H, — $CH_2CH(CH_3)OH$



(5)

T a b l e 3. Interpretation of MALDI ToF spectrum of the product of reaction of 1 mol of 6-AU with 8 moles of PC

No.	Signal position	Probable structure of molecular ion[*)]	Calculated molecular weight g/mol
1	192.3	Tripropylene glycol	192.3
2	198.8	6-AU + PO – H_2O + CH_3OH	199.1
3	203.3	6-AU + PO + H_2O	203.2
4	215.3	Tripropylene glycol + Na^+	215.2
5	216.3	6-AU + PO + CH_3OH	217.2
6	218.3	6-AU + PO + CH_3OH + H^+	218.2
7	221.3	6-AU + PO – H_2O + CH_3OH + Na^+	222.2
8	235.3	6-AU + PO + CH_3OH + H_2O	235.2
9	257.3	6-AU + 2 PO – H_2O + CH_3OH	257.3
10	261.4	6-AU + 2 PO + H_2O	261.3
11	266.3	6-AU + 2 PO + Na^+	266.3
12	273.3	Tetrapropylene glycol + Na^+	273.3
13	274.3	6-AU + 2 PO + CH_3OH	275.3
14	284.3	6-AU + 3 PO – H_2O + H^+	284.3
15	287.5	6-AU + 2 PO + -COO-	287.3
16	297.4	6-AU + 3 PO – 2 H_2O + CH_3OH	297.3
17	298.4	6-AU + 3 PO – 2 H_2O + CH_3OH + H^+	298.3
18	307.3	6-AU + 3 PO – H_2O + Na^+	306.3
19	319.3	6-AU + 3 PO + H_2O	319.4
20	320.3	6-AU + 3 PO – 2 H_2O + CH_3OH + Na^+	320.3
21	323.3	6-AU + 4 PO – 2H_2O	323.4
22	324.3	6-AU + 3 PO + Na^+	324.3
23	331.4	6-AU + 2 PO + 2 -COO-	331.3
24	335.4	2 (6-AU) + 2 PO – 2 H_2O + H^+	335.3
25	337.4	6-AU + 4 PO – 3 H_2O + CH_3OH	337.3
26	338.4	6-AU + 3 PO – H_2O + CH_3OH + Na^+	338.4
27	342.4	6-AU + 4 PO – H_2O + H^+	342.4
28	357.0	2 (6-AU) + 2 PO – 2 H_2O + Na^+	357.3
29	364.7	6-AU + 4 PO – H_2O + Na^+	364.4
30	378.7	6-AU + 4 PO – 2 H_2O + CH_3OH + Na^+	378.4
31	380.3	6-AU + 4 PO – H_2O + K^+	380.4
32	381.4	6-AU + 5 PO – 2H_2O	381.4
33	382.4	6-AU + 4 PO + Na^+	382.4
34	395.4	6-AU + 5 PO – 3 H_2O + CH_3OH	395.5
35	396.4	6-AU + 4 PO – H_2O + CH_3OH + Na^+	396.4
36	400.6	6-AU + 5 PO – H_2O + H^+	400.5
37	405.3	2 (6-AU) + 2 PO – 2 H_2O + CH_3OH + K^+	405.3
38	422.4	6-AU + 5 PO – H_2O + Na^+	422.5
39	438.4	6-AU + 5 PO – H_2O + K^+	438.5
40	439.4	6-AU + 6 PO – 2 H_2O	439.5
41	440.4	6-AU + 5 PO + Na^+	440.5
42	453.4	6-AU + 6 PO – 3 H_2O + CH_3OH	453.5
43	463.8	2 (6-AU) + 3 PO – 2 H_2O + CH_3OH + K^+	463.4
44	480.2	6-AU + 6 PO – H_2O + Na^+	480.6
45	497.5	6-AU + 7 PO – 2 H_2O	497.6
46	588.5	6-AU + 8 PO – 2 H_2O + CH_3OH + H^+	588.7

[*)] AU is a fragmentation product of 6-AU, PO is an oxypropylene group, and the number preceding the symbol indicates the number of 6-AU molecules or oxypropylene groups in a structure.

T a b l e 4. Interpretation of MALDI ToF spectrum of the product of reaction of 1 mol of 6-AU with 12 moles of PO

Run	Signal position	Probable structure of molecular ion[*)]	Calculated molecular weight, g/mol
1	192.2	Tripropylene glycol	192.2
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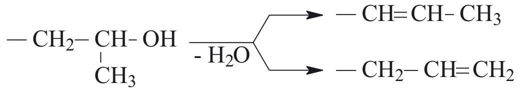
3	215.2	Tripropylene glycol + Na^+	215.2
4	218.3	6-AU + PO + CH_3OH + H^+	218.2
5	235.3	6-AU + PO + CH_3OH + H_2O	235.2
6	242.3	6-AU + 2 PO	243.3
7	248.6	6-AU + 2 PO – H_2O + Na^+	248.2
8	262.0	6-AU + 2 PO + H_2O + H^+	262.3
9	274.3	Tetrapropylene glycol + Na^+	273.3
10	276.3	6-AU + 2 PO + CH_3OH + H^+	276.3
11	293.4	6-AU + 2 PO + CH_3OH + H_2O	293.3
12	300.7	6-AU + 3 PO	301.4
13	334.4	6-AU + 3 PO + CH_3OH + H^+	334.4
14	351.3	6-AU + 3 PO + CH_3OH + H_2O	351.4
15	377.4	6-AU + 4 PO + H_2O	377.4
16	434.6	6-AU + 5 PO + H_2O	435.5

[*)] See footnote in Table 3.

In the spectra, the peaks of molecular ions originating from the product of the reaction of 1 mol of 6-AU with 8 moles of PC were observed (Table 3, No. 24, 28, 37, 43). These peaks were absent in the spectra of polyetherols obtained in the reactions of 1 mol of 6-AU with 12 moles of PO (Table 4).

In the ^{1}H NMR spectra of the products of reaction of 6-AU and PC (see Fig. 1) there are signals from protons of: methyl groups in the products of normal addition (1.0 ppm) and abnormal addition (1.25 ppm), methylene groups (2.8—4.1 ppm), hydroxyl and methine groups and proton at carbon atom with double bond H-C= in the ring of 6-AU (common signal at 4.3—4.8 ppm). Moreover, in the spectra the signals at 4.8—5.2 ppm are observed (they did not disappear after D_2O addition). These observations led to conclusion that unsaturated fragments were present in the product. They appear at the ends of chains as a result of elimination of water:



$$-CH_2-\underset{\displaystyle CH_3}{CH}-OH \xrightarrow{-H_2O} \begin{cases} -CH{=}CH-CH_3 \\ -CH_2-CH{=}CH_2 \end{cases} \quad (6)$$

The presence of unsaturated fragments was confirmed by MALDI ToF spectroscopy (Table 3). In the spectra of polyetherols we found the peaks of molecular ions differing by m/z = 58 (oxypropylene sub—units), what suggested that polyetherols with oxypropylene chains of variable length were formed (see Table 3, No. 11, 22, 33, 41 and No. 3, 10, 19). Moreover in the spectra of products of reaction 6-AU with PC potassium-attached molecular ions were observed (K^+ from catalyst — K_2CO_3). We found also small amount of structures containing ester groups ($-\overset{O}{\overset{\|}{C}}-O-$ groups attached to molecular ions; Table 3, No. 15, 23).

In ^{1}H NMR spectra of the products of reaction between 6-AU and PC the signals from methyl groups in

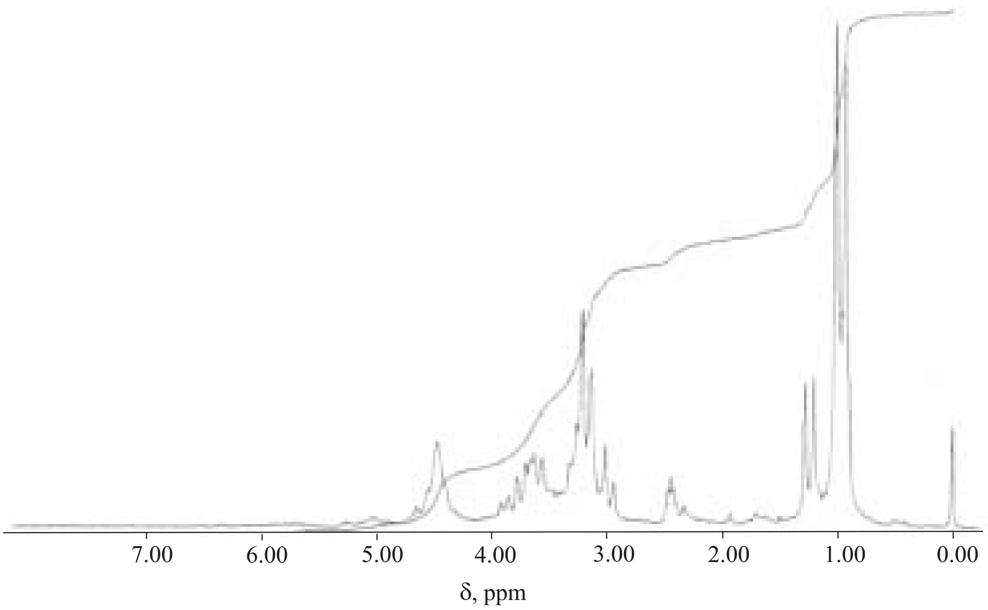


Fig. 3. ^{1}H NMR spectrum of the product of reaction of 1 mol of 6-AU with 12 moles of PC

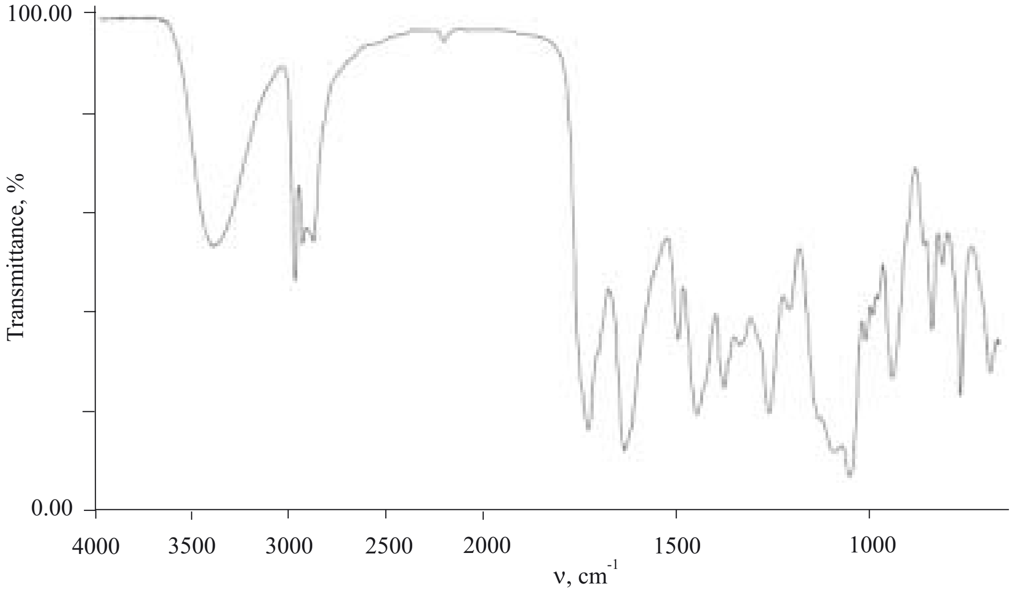
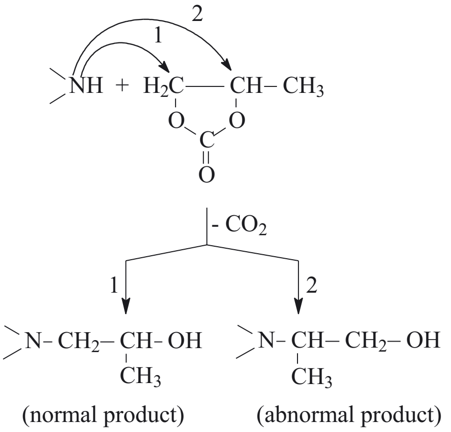


Fig. 4. IR spectrum of the product of reaction of 1 mol of 6-AU with 8 moles of PC

normal addition products and abnormal ones [Equation (7)] at chemical shift 1.0 and 1.25 ppm respectively were present (see Fig. 1); similar signals were observed in the spectra of products of reaction between 6-AU and PO (see Fig. 2).



(7)

Comparison of the intensities of the signals indicated that the amount of abnormal product is higher at lower initial molar ratio of 6-AU and PC (Figs. 1, 3). It shows that the highest amount of abnormal product is formed at the first stage of the reaction. It is due to acidity of 6-AU. As long as unreacted 6-AU is present, the way of carbonate ring opening is similar to the reaction of oxirane ring opening in the presence of acids. If both nitrogen atoms in 6-AU ring are substituted by hydroxypropyl groups then acidic character of 6-AU no longer persists, and opening of carbonate ring is continued in basic medium and therefore normal product is formed.

The structures of obtained polyetherols were confirmed by IR spectra, too. In the IR spectra of polyetherols (Fig. 4) the changes or disappearance of the bands at 3415—2700, 1530, 1290, and 1237 cm^{-1} in comparison with that of 6-AU (Fig. 1 in ref. [2]) were observed. The valence and deformation bands of hydroxyl groups (3340, 1410, 1250 cm^{-1}), methyl, methylene and methine groups (2875—2970, 1490, 1460, 1375, 1130 cm^{-1}), the valence band of C-O groups in primary and secondary alcohols (1050 and 1100 cm^{-1}) and the valence band of C-O-C group (at 1120 cm^{-1}) appear in the products. These changes indicate clearly the substitution of nitrogen-bound hydrogens with hydroxypropyl groups.

Properties of polyetherols and PUR foams on their bases

Some physical properties of polyetherols received with different initial molar ratios of 6-AU and PC were determined, namely refractive index, density, viscosity and surface tension (Table 5). Typical trends of changes of these properties with temperature were observed. The values of parameters decreased with an increase in initial molar ratio of 6-AU and PC.

Table 5. Some physical properties of the products of reactions of 6-AU with PC

Initial molar ratio 6-AU:PC	Temperature, °C	Refractive index	Density g/cm^3	Viscosity $\cdot 10^3$ Ns/m^2	Surface tension $\cdot 10^3$ N/m
1:4	20	1.5175	1.1810	—	51.52
	30	1.5144	1.1714	23318.71	48.44
	40	1.5107	1.1637	7062.90	46.90
	50	1.5076	1.1575	2473.18	44.80
	60	1.5041	1.1501	1026.18	41.86
	70	1.5007	1.1421	447.96	40.46
	80	1.4972	1.1349	116.00	39.20
1:6	20	1.5008	1.1443	7667.57	42.70
	30	1.4973	1.1348	2414.99	41.30
	40	1.4940	1.1274	928.34	37.80
	50	1.4903	1.1197	387.66	35.28
	60	1.4872	1.1121	183.30	33.18
	70	1.4842	1.1045	97.37	31.36
	80	1.4804	1.0972	57.64	28.70
1:8	20	1.4910	1.1187	3009.38	39.06
	30	1.4883	1.1110	1064.55	37.38
	40	1.4848	1.1034	404.32	35.28
	50	1.4813	1.0989	184.48	33.88
	60	1.4782	1.0876	94.50	32.20
	70	1.4743	1.0806	52.69	30.80
	80	1.4709	1.0709	32.44	28.98
1:12	20	1.4842	1.0895	851.51	32.48
	30	1.4783	1.0830	335.55	28.84
	40	1.4709	1.0761	153.83	26.74
	50	1.4675	1.0682	79.04	25.69
	60	1.4675	1.0618	43.73	22.30
	70	1.4631	1.0484	27.09	15.82
	80	1.4608	1.0385	17.20	13.30

Table 6. Thermal resistance of the products, based on thermal analyses

Initial molar ratio 6-AU:PC	$T_{5\%}$ °C	$T_{10\%}$ °C	$T_{25\%}$ °C	$T_{50\%}$ °C	Temperature of max decomposition, °C
1:6	130	150	200	260	350
1:8	130	160	210	260	360
1:12	140	160	210	260	370

The thermal stability of the products was determined by thermal analysis (Table 6). It was confirmed that thermal stability of polyetherols obtained in reaction of 6-AU with PC was comparable to the thermal stability of those obtained from 6-AU and PO [4]. Propylene glycol and polyglycols, included in products, did not reduce the thermal stability of polyetherols.

Polyetherol obtained in the reaction of 1 mol of 6-AU with 8 mol of PC was used to prepare polyurethane foams by a method described in Experimental Part. The data presented in Table 7 illustrate the effect of the amount of 4,4′-diphenylmethane diisocyanate on the course of foaming reaction of foams based on polyetherol prepared from the composition of 6-AU:PC = 1:8.

T a b l e 7. Influence of composition*) on foaming process (initial molar ratio 6-AU:PC = 1:8)

Composition number	Amount of isocyanate, g/100 g of polyetherol*)	Molar ratio OH:NCO	Foaming process**)			Characteristics of foams just prepared
			time of creaming, s	time of expanding, s	time of drying, s	
1	172	1.51	15	15	1	rigid
2	148	1.30	14	16	1	rigid

*) Amount of water 2 g per 100 g of polyetherol, amount of TEA 1.6 g per 100 g of polyetherol, amount of silicon 0.8 g per 100 g of polyetherol.
**) Mixing time of composition: 10 s; time of creaming — time elapsed from the moment of mixing to the start of volume expansion, time of expanding — time from the start of expansion to the moment of reaching the sample final volume, time of drying — time from reaching by the sample its final volume to the moment of loosing its surface adhesion to powdered substances.

Apparent density, water absorption, dimensional stability, compression strength and thermal stability of the foams were investigated (Table 8). The obtained foams show apparent density and water absorption smaller than those based on polyetherols obtained from 6-AU and PO [1]. Other given properties were related to the properties of foams obtained according to [1].

T a b l e 8. Some properties of polyurethane foams

Properties of foams		Composition number*)	
		1	2
Density, kg/m^3		31.75	31.05
Water absorption, wt. %	after 5 min	1.8	2.6
	after 3 h	2.4	3.7
	after 24 h	4.0	5.2
Linear dimensional stability at temperature 150 °C (after 20 h heating), %	length increase	0.12	-6.75
	width increase	1.07	-7.26
	depth increase	0.56	-6.57
Thermal stability expressed as the weight loss (wt. %) after 30 days heating in:	150 °C	7.0	15.1
	200 °C	39.8	42.5
Compression strength at 10 % strain, MPa	before heating	0.18	0.16
	after 30 days heating at 150 °C	0.14	0.20
	200 °C	0.24	0.17

*) See Table 7.

CONCLUSIONS

6-AU reacted with an excess of PC without any solvent in the presence of DABCO and potassium carbonate as catalysts. The resin products were obtained. With an increase in number of oxypropylene groups the resins became more fluid. Chromatographic analysis shows that apart from hydroxypropyl derivatives of 6-AU, propane-1,2-diol and polyglycols are formed. Initial tests of the foaming of obtained products showed that these compounds could be used as components of polyurethane foams of improved thermal stability.

REFERENCES

1. Chmiel-Szukiewicz E.: *J. Appl. Polym. Sci.* 2008, **109**, 1708.
2. Chmiel-Szukiewicz E.: *J. Appl. Polym. Sci.* 2006, **100**, 715.
3. Chmiel-Szukiewicz E.: *e-Polymers*, International Polymer Seminar Gliwice 2006, P_017, 1—6.
4. Chmiel-Szukiewicz E.: *J. Appl. Polym. Sci.* 2007, **103**, 1466.
5. Chmiel-Szukiewicz E.: *J. Appl. Polym. Sci.* 2007, **106**, 3703.
6. Kucharski M., Kijowska D.: *J. Appl. Polym. Sci.* 2001, **80**, 1776.
7. Węglowska E., Lubczak J.: *J. Appl. Polym. Sci.* 2005, **98**, 2130.
8. Lubczak J.: *J. Appl. Polym. Sci.* 2006, **101**, 2482.
9. Kastierina T., Kalinina L.: "Chemical Analysis of Plastics", WNT, Warsaw 1965, p. 141 (in polish).
10. Poplewska I., Węglowska E., Lubczak J.: *J. Appl. Polym. Sci.* 2004, **91**, 2750.
11. Lubczak J.: *Polimery* 2005, **50**, 15.
12. Zarzyka-Niemiec I., Naróg D., Lubczak J.: *J. Appl. Polym. Sci.* 2006, **100**, 1443.
13. Lubczak J., Węglowska E.: *Intern. J. Chem. Kinetics* 2009, **41**, 512.
14. Lubczak J., Węglowska E.: *Intern. J. Chem. Kinetics* 2009, **41**, 523.
15. *Pat. USA* 4 265 821 (1981).

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