Polyetherols Obtained from 6-Aminouracil and Ethylene Carbonate

Elżbieta Chmiel-Szukiewicz

Department of Organic Chemistry, Faculty of Chemistry, Rzeszów University of Technology, Powstańców Warszawy 6, 35-959 Rzeszów, Poland

ABSTRACT: The reactions of 6-aminouracil with ethylene carbonate were investigated. Potassium carbonate or 1,4-diazabicyclo[2.2.2]octane was used as a catalyst. An excess of ethylene carbonate was applied in the syntheses. In this way, polyetherols with 1,3-pyrimidine rings in their structure were prepared. The structure of the products was analyzed with infrared, proton nuclear magnetic resonance, and matrix-assisted laser desorption/ionization time-of-flight techniques. Some physical properties and the thermal stability of the prepared polyetherols were investigated. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3703–3709, 2007

Key words: ring-opening polymerization; heteroatom-containing polymers; NMR; MALDI; thermal properties

INTRODUCTION

1,3-Dioxolan-2-one [i.e., ethylene carbonate (EC or **I**)] is a cyclic organic ester of carbonic acid:

(I)
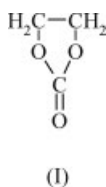
EC is a colorless solid with a melting point of 37°C and a boiling point of 248.2°C. It is a nontoxic, non-hygroscopic, and noncorrosive substance with a high ignition temperature. It dissolves many organic and inorganic compounds well.[1] EC reacts with compounds containing active hydrogen atoms, such as alcohols, phenols, thiols,[2] carboxylic acids,[3] and amines[4]; the products are hydroxyalkyl derivatives of these compounds. The reactions are commonly conducted at 100–200°C in the presence of catalysts such as potassium carbonate,[5,6] tertiary amines,[2,7] and quaternary ammonium salts.[7] Because EC has many advantages (it is nontoxic and is a good solvent), the substitution of ethylene oxide (EO) for EC to obtain polyetherols from isocyanuric acid,[8] uric acid,[9] parabanic acid,[10] or melamine[11] seems useful. Preliminary tests have shown that EC reacts with 6-aminouracil (6-AU), giving hydroxyalkyl derivatives.[12,13] Here the results of investigations of the reactions of 6-AU with EC to obtain polyetherols with 1,3-pyrimidine rings are described.

EXPERIMENTAL

Reaction of 6-AU with EC

To a round-bottom flask (100 or 250 cm³) equipped with a reflux condenser, thermometer, and stirrer, 12.7 g (0.1 mol) of 6-AU (pure; Sigma–Aldrich, Steinheim, Germany), 35.2 (0.4 mol), 52.8 (0.6 mol), 70.4 g (0.8 mol), or 105.6 g (1.2 mol) of EC (pure; Fluka, Buchs, Switzerland), and 0.4 g of potassium carbonate (pure; PPH POCh, Gliwice, Poland) or 0.4 g of 1,4-diazabicyclo[2.2.2]octane (DABCO; pure, Avocado Research and Development, Karlsruhe, Germany) as a catalyst were added. The mixtures were heated to 160°C with continuous stirring. The reaction was conducted for 5.5–15.5 h at this temperature. The reaction course was controlled by the determination of the amount of unreacted EC.

Analytical methods

The amount of unreacted EC was determined by a reaction with barium hydroxide.[11] The acid number was determined through the titration of a sample dissolved in 20 cm³ of H₂O with 0.1M NaOH.[14] The infrared (IR) spectra were recorded on a Fourier transform IR Paragon 1000 spectrometer (Perkin-Elmer Corp., Norwalk, CT). The samples for IR analysis were prepared as capillary films or KBr tablets. The proton nuclear magnetic resonance (^{1}H-NMR) spectra of the products were recorded on a BS-586A

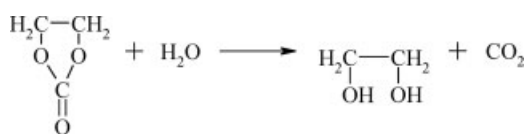*Correspondence to:* E. Chmiel-Szukiewicz (szukela@prz.rzeszow.pl).

TABLE I
Conditions of the Synthesis of Polyetherols from 6-AU with EC

Initial molar ratio (6-AU : EC)	Catalyst	Amount of the catalyst (g/mol of 6-AU)	Reaction conditions		
			Temperature (°C)	Dissolution time for 6-AU (min)	Reaction time (h)
1 : 4	K_2CO_3	4	160	25	5.5
1 : 6	K_2CO_3	4	160	25	8.0
1 : 8	K_2CO_3	4	160	20	9.0
1 : 8	DABCO	4	160	20	9.0
1 : 12	K_2CO_3	4	160	10	15.5

80-MHz spectrometer (Tesla, Brno, Czechoslovakia). The solvent was deuterated dimethyl sulfoxide with hexamethyldisiloxane as an internal standard. The products were also analyzed by gas chromatography with a Hewlett–Packard 5890 instrument (Wald-bronn, Germany) equipped with a flame ionization detector. From chromatograms, the amounts of the diols and the subsequent products of reactions of oxirane with water were determined. The gas chromatography conditions were as follows: HP-FFAP capillary column (nitroterephthalic acid modified polyethylene glycol), 10 m long and 0.53 mm in diameter; layer thickness, 0.5 μm; temperature profile, 50–220°C (20°C/min) and 6 min at 220°C; temperature of the injection chamber, 220°C; rate of the carrier gas (He), 18.3 cm^3/min; and sample volume, 0.2 μdm^3. The calibration was performed with cyclohexanone as an internal standard. The data are presented in Table I in ref. 15.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectra were obtained on a Voyager-Elite Perseptive Biosystems (Framingham, MA) mass spectrometer working in a linear mode with delayed ion extraction and equipped with a nitrogen laser working at 337 nm. The method of laser desorption from the matrix was used with 2,5-dihydroxybenzoic acid in tetrahydrofuran at a 10 mg/cm^3 concentration. The samples were diluted with methanol to 1 mg/cm^3, and this was followed by the addition of 10 mg/cm^3 NaI in acetone. Therefore, in some cases, the molecular ion masses were increased by the mass of Na^+ and CH_3OH.

The thermal analysis of the products was carried out with a derivatograph (MOM, Budapest, Hungary) in a nitrogen atmosphere. Each sample (100 mg) was heated in a china crucible over the temperature range of 20–1000°C. The sensitivity of the instrument was 1/10 for differential thermal analysis and 1/10 for differential thermogravimetry. Some other properties of the products were evaluated in the temperature range of 20–80°C, such as the refractive index, density (pycnometrically), viscosity (with a Höpler viscometer VEB MLW Prüfgerate-Werk, Medingen, Germany), and surface tension, with the torsion balance method.

RESULTS AND DISCUSSION

The reactions of 6-AU with EC were conducted on the basis of formerly described experiments.[12,13] 6-AU was dissolved in a proper amount of hot EC with 4 g of potassium carbonate per mole of 6-AU as a catalyst. A comparative synthesis in the presence of DABCO as a catalyst was also conducted. Initially, reactions were run under heterogeneous conditions, and then, when 6-AU was dissolved completely, they were in a homogeneous system. The reactions were conducted for 5.5–15.5 h at 160°C (Table I). The characteristic feature of the reaction course was the production of carbon dioxide, which caused foaming of the reaction mixture. When the production of carbon dioxide stopped, the amount of unreacted EC was determined to establish the end of the process. Dark brown resin products were obtained. Their consistency depended on the amount of substituted EC.

Scheme 1 Formation of ethane-1,2-diol.
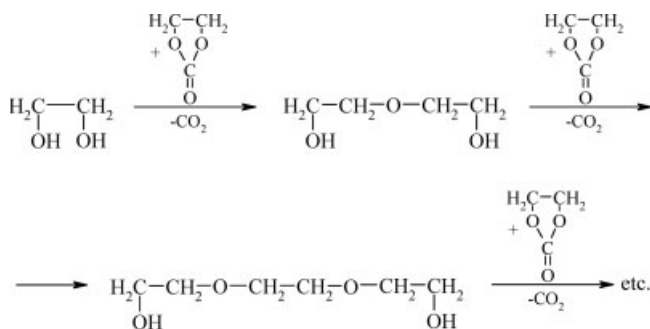
Scheme 2 Formation of polyglycols.

TABLE II
Percentages of the Byproducts in the Reaction of 6-AU with EC

| Initial molar ratio (6-AU : EC) | Byproduct (wt %) | | | | | Amount of EC reacted with 6-AU (mol) |
	Ethylene glycol	Diethylene glycol	Triethylene glycol	Tetraethylene glycol	Σ (%)	
1 : 4	16.45	4.77	3.26	0.00	24.48	3.0
1 : 6	8.57	11.62	7.49	6.00	34.12	4.0
1 : 8	4.47	13.48	13.42	10.75	42.12	4.6
1 : 8[a]	4.78	12.12	12.01	9.60	38.51	5.0
1 : 12	0.28	5.59	12.33	12.75	30.95	8.3

[a] With DABCO as a catalyst.
Σ(%), total amount of glycols (%).

The structure of the products was studied with gas chromatography, IR, ^{1}H-NMR, and MALDI-TOF spectroscopy. The amounts of ethane-1,2-diol (a product of a side reaction of EC with water; Scheme 1) and the products of its consecutive reactions with EC (Scheme 2) were estimated by chromatographic analysis.

The percentages of ethane-1,2-diol and polyglycols were calculated on the basis of calibration curves presented previously.[15] The maximum amounts of the byproducts appeared in the reaction of 1 mol of 6-AU with 8 mol of EC (42.12%; Table II). The more EC was added, the more successive polyglycols were formed. This resulted from the facile reaction between the formed diol and unreacted EC. The substitution of a potassium carbonate catalyst for DABCO resulted in the quenching of side reactions (Table II). When the amounts of ethane-1,2-diol and polyglycols in the products were known, the moles of EC that reacted with 6-AU could be estimated (Table II). That value was substantially smaller than the initial molar ratio of 6-AU to EC.

The IR spectra of the reaction products of 6-AU with EC (Fig. 1) and the reaction products of 6-AU with EO (Fig. 1 in ref. 15) are similar. Small differences are visible in the ^{1}H-NMR spectra of these products. In the ^{1}H-NMR spectra of polyetherols obtained from 6-AU and EO, in addition to signals of methylene and hydroxyl group protons and H—C= protons, a small signal at approximately 6 ppm has been observed and attributed to protons of an amine group [Fig. 2(b) in ref. [15]]. In ^{1}H-NMR spectra of the products of the reaction of 6-AU with EC (Fig. 2), this signal has not been observed, and this indicates that all the amine groups reacted completely. This suggests the following structure of the polyetherols:
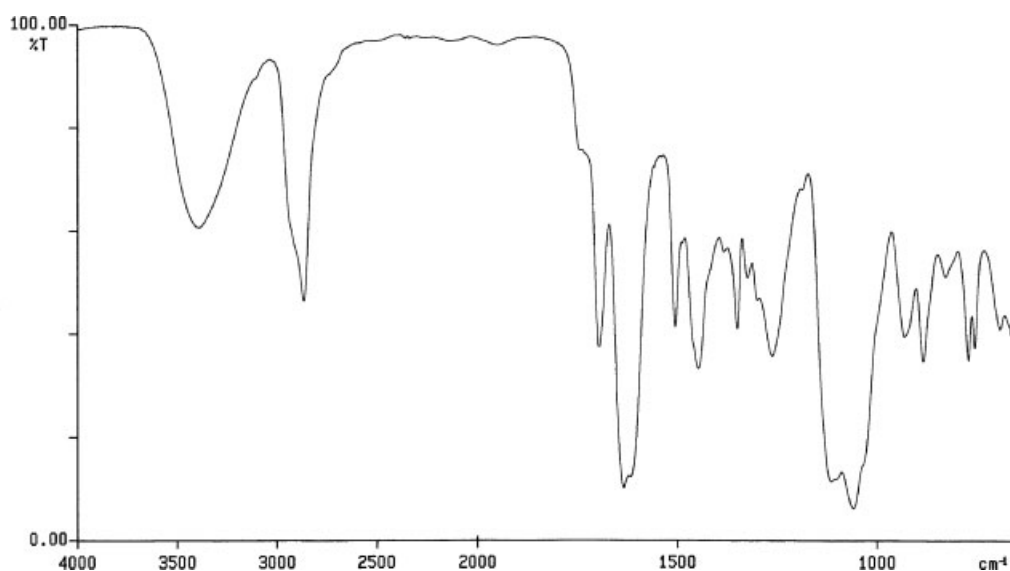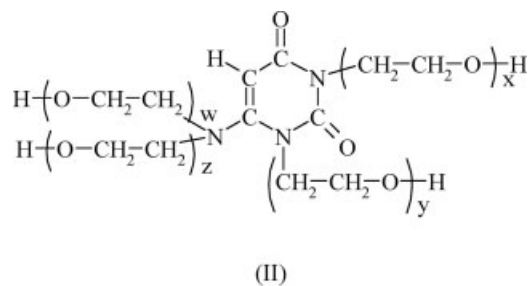

(II)

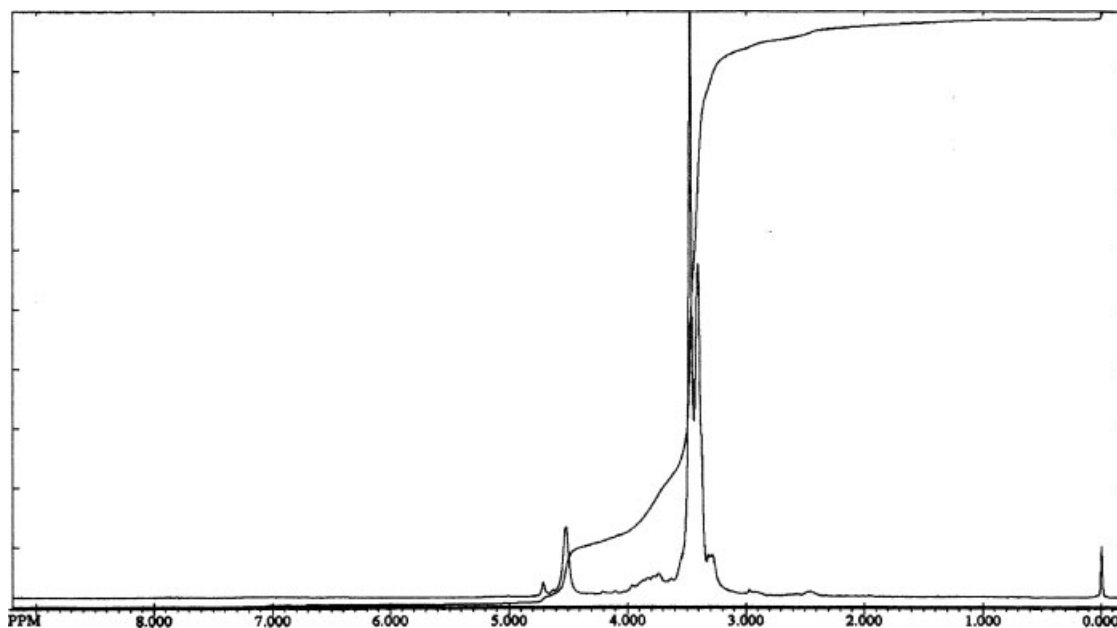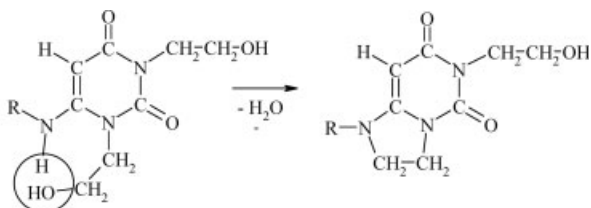**Figure 1** IR spectrum of the product of the reaction of 1 mol of 6-AU with 12 mol of EC.

Figure 2 ^{1}H-NMR spectrum of the product of the reaction of 1 mol of 6-AU with 12 mol of EC.

where $w + x + y + z$ is the number of moles of attached EC.

However, a chromatography analysis shows, for example, that in a reaction of 1 mol of 6-AU and 4 mol of EC, only 3 mol of EC reacted with 6-AU (Table II). Obviously, some other reactions of the amine groups took place. These were cyclization (Scheme 3), condensation (Scheme 4), and cyclization with condensation (Scheme 5).

The reactions required a high temperature (160°C) and/or a prolonged time of synthesis. They did not lead to crosslinking of the products, and neither gelation nor even an increase in the density of the reaction mixture was observed. The fact that the aforementioned reactions occurred was confirmed by MALDI-TOF spectroscopy of the obtained polyetherols. In the spectra, we found the peaks of molecular ions originating from the products of these reactions (Table III, nos. 3, 4, 6, 8, 9, 11–24, 26, 28, 29, and 31). These peaks were absent in the spectra of polyetherols obtained in the reactions of 6-AU with EO (Table IV).

In the spectra of products of the reaction of 6-AU and EC with potassium carbonate as a catalyst, the molecular ions of potassium-attached molecular ions were observed. Moreover, in the spectra were observed series of molecular ions differing by $m/z = 44$, the fragment that corresponds to oxyethylene subunits. These observations suggest that the length of the oxyalkylene chains was variable in the products.

Some physical properties of the polyetherols were determined, such as the refractive index (Fig. 3), density (Fig. 4), viscosity (Fig. 5), and surface tension (Fig. 6). The directions of the changes in these properties were as expected. They decreased with an increasing amount of EC.

The thermal stability of the products was determined by thermal analysis (Table V). The thermal stability of the polyetherols obtained from 6-AU and

where R= -H, -CH₂CH₂OH

Scheme 3 Cyclization.
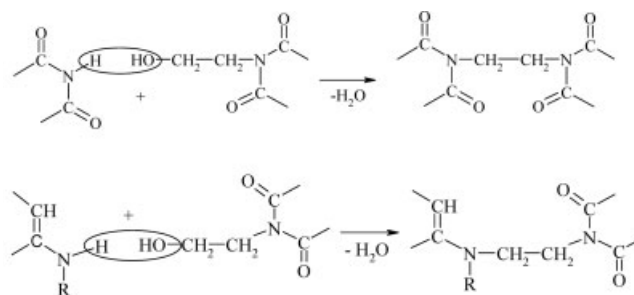
where R= -H, -CH₂CH₂OH

Scheme 4 Condensation.
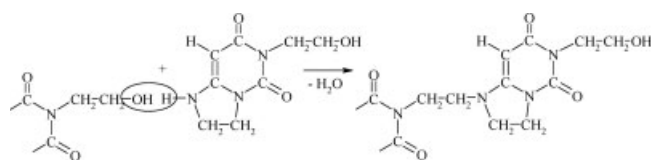
Scheme 5 Cyclization with condensation.

EC was comparable to the thermal stability of those obtained from 6-AU and EO.[15] Ethylene glycol and polyglycols, included in the products, did not reduce their thermal stability. Initial tests of the foaming of the obtained products showed that these polyetherols could be used as components of polyurethane foams of improved thermal stability. The polyetherols were comprehensively resistant to thermal treatments.
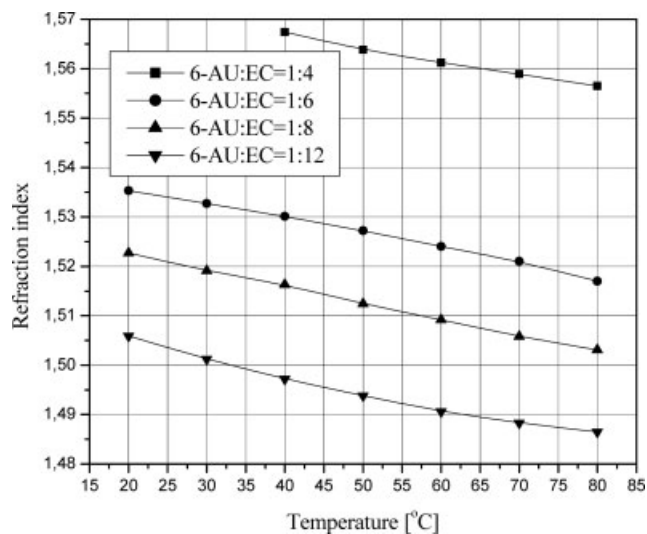

Figure 3 Refraction index of the products of the reaction of 6-AU with EC.

TABLE III
Interpretation of the MALDI-TOF Spectrum of the Product of the Reaction of 1 mol of 6-AU with 12 mol of EC

Run	Signal position	Signal intensity (%)	Probable structure of the molecular ion[a]	Calculated molecular weight (g/mol)
1	137.1	100	2,5-Dihydroxybenzoic acid $-$ H_2O + H^+	137.1
2	138.2	17.3	Diethylene glycol + CH_3OH	138.2
3	154.1	32.7	AU + EO $-$ H_2O + H^+	154.1
4	176.2	8.5	AU + EO $-$ H_2O + Na^+	176.1
5	194.8	7.2	Tetraethylene glycol	194.2
6	220.3	12.6	AU + 2EO $-$ H_2O + Na^+	220.1
7	238.8	9.4	AU + 2EO + Na^+	238.3
8	268.3	28.3	AU + 4EO $-$ $2H_2O$+ H^+	268.3
9	273.2	24.2	AU + 3EO $-$ H_2O + CH_3OH	273.2
10	277.1	7.9	AU + 3EO + H_2O	277.3
11	312.4	22.3	AU + 5EO $-$ $2H_2O$+ H^+	312.3
12	330.3	20.4	AU + 5EO $-$ H_2O + H^+	330.3
13	355.3	8.2	AU + 6EO $-$ $2H_2O$	355.4
14	356.4	17.0	AU + 6EO $-$ $2H_2O$+ H^+	356.4
15	374.3	25.8	AU + 6EO $-$ H_2O + H^+	374.4
16	399.3	14.1	AU + 7EO $-$ $2H_2O$	399.4
17	418.3	19.5	AU + 7EO $-$ H_2O + H^+	418.4
18	443.4	20.9	AU + 8EO $-$ $2H_2O$	443.5
19	462.4	9.6	AU + 8EO $-$ H_2O + H^+	462.5
20	487.4	22.2	AU + 9EO $-$ $2H_2O$	487.5
21	509.5	9.7	2(AU) + 5EO $-$ $2H_2O$ + CH_3OH + K^+	509.4
22	531.6	13.8	AU + 10EO $-$ $2H_2O$	531.6
23	553.4	16.7	2(AU) + 6EO $-$ $2H_2O$ + CH_3OH + K^+	553.5
24	574.9	10.3	AU + 11EO $-$ $2H_2O$	575.6
25	578.4	8.8	AU + 9EO + CH_3OH + Na^+	578.6
26	597.4	13.2	2(AU) + 7EO $-$ $2H_2O$ + CH_3OH + K^+	597.5
27	622.5	11.4	AU + 10EO + CH_3OH + Na^+	622.6
28	623.5	6.0	3(AU) + 6EO $-$ $3H_2O$ + CH_3OH	623.6
29	631.4	7.7	3(AU) + 6EO $-$ $3H_2O$ + K^+	630.6
30	666.4	11.3	AU + 11EO + CH_3OH + Na^+	666.7
31	684.7	5.3	3(AU) + 7EO $-$ $2H_2O$ + CH_3OH	685.6
32	710.3	8.2	AU + 12EO + CH_3OH + Na^+	710.7
33	732.9	5.7	AU + 13EO + CH_3OH + H^+	732.8
34	754.6	5.3	AU + 13EO + CH_3OH + Na^+	754.8
35	775.9	6.6	AU + 14EO + CH_3OH	775.8

[a] AU is a fragmentation product of 6-AU, EO is an oxyethylene group, and the number preceding the symbol indicates the number of 6-AU molecules or EOs in a structure.

TABLE IV
Interpretation of the MALDI-TOF Spectrum of the Product of the Reaction of 1 mol of 6-AU with 12 mol of EO

Run	Signal position	Signal intensity (%)	Probable structure of the molecular ion[a]	Calculated molecular weight (g/mol)
1	190.3	62.3	$AU + EO + H_2O + H^+$	190.2
2	234.3	100	$AU + 2EO + H_2O + H^+$	234.2
3	235.3	47.8	$AU + EO + 2CH_3OH$	235.2
4	236.3	15.7	$AU + EO + 2CH_3OH + H^+$	236.2
5	278.3	92.5	$AU + 3EO + H_2O + H^+$	278.3
6	279.3	51.3	$AU + 2EO + 2CH_3OH$	279.3
7	280.3	17.6	$AU + 2EO + 2CH_3OH + H^+$	280.3
8	281.3	6.6	$AU + 3EO + Na^+$	282.3
9	322.4	73.6	$AU + 4EO + H_2O + H^+$	322.4
10	323.4	36.5	$AU + 3EO + 2CH_3OH$	323.3
11	324.3	11.3	$AU + 3EO + 2CH_3OH + H^+$	324.3
12	325.3	6.9	$AU + 4EO + Na^+$	326.3
13	365.4	20.8	$AU + 5EO + H_2O$	365.4
14	366.4	48.7	$AU + 5EO + H_2O + H^+$	366.4
15	367.4	100	$AU + 4EO + 2CH_3OH$	367.4
16	409.4	26.6	$AU + 6EO + H_2O$	409.5
17	410.4	62.2	$AU + 6EO + H_2O + H^+$	410.4
18	411.4	8.5	$AU + 5EO + 2CH_3OH$	411.5
19	453.4	28.9	$AU + 7EO + H_2O$	453.5
20	454.5	19.2	$AU + 7EO + H_2O + H^+$	454.5
21	495.5	6.6	$AU + 8EO - H_2O + CH_3OH + H^+$	494.5
22	497.5	28.9	$AU + 8EO + H_2O$	497.5
23	498.5	12.9	$AU + 8EO + H_2O + H^+$	498.5
24	539.5	6.6	$AU + 9EO - H_2O + CH_3OH + H^+$	538.5
25	541.5	9.4	$AU + 9EO + H_2O$	541.6
26	542.6	5.0	$AU + 9EO + H_2O + H^+$	542.6
27	583.6	2.8	$AU + 10EO - H_2O + CH_3OH + H^+$	582.6
28	585.6	7.5	$AU + 10EO + H_2O$	585.6
29	629.6	3.8	$AU + 11EO + H_2O$	629.7
30	678.6	3.8	$AU + 12EO + Na^+$	678.7
31	723.7	2.8	$AU + 13EO + Na^+$	722.8

[a] AU is a fragmentation product of 6-AU, EO is an oxyethylene group, and the number preceding the symbol indicates the number of 6-AU molecules or EOs in a structure.
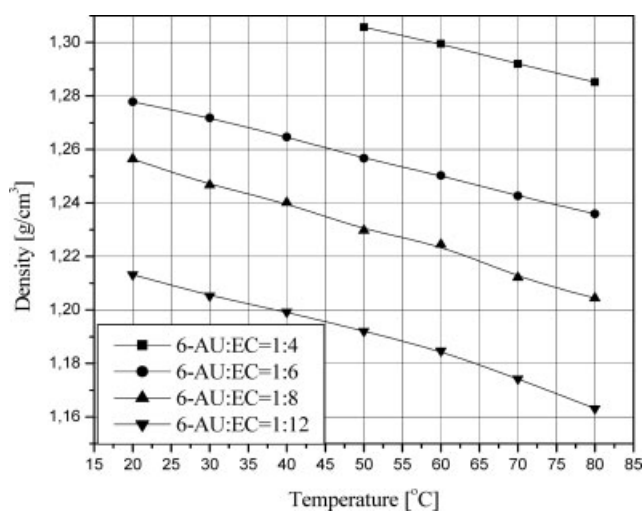

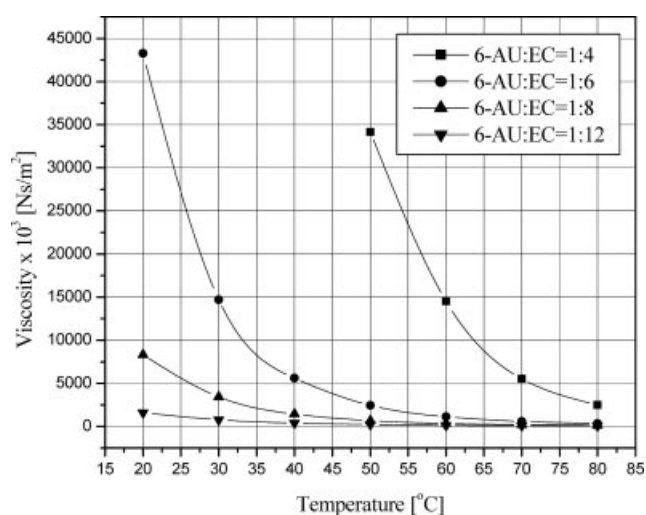**Figure 4** Density of the products of the reaction of 6-AU with EC.

Figure 5 Viscosity of the products of the reaction of 6-AU with EC.

TABLE V
Thermal Resistance of the Products Based on a Thermal Analysis

Initial molar ratio (6-AU : EC)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{25\%}$ (°C)	$T_{50\%}$ (°C)	Temperature of maximum decomposition (°C)
1 : 6	100	130	190	290	400
1 : 8	130	160	210	280	400
1 : 8[a]	120	140	210	290	410
1 : 12	100	130	210	280	400

$T_{5\%}$, $T_{10\%}$, $T_{25\%}$, and $T_{50\%}$ are the temperatures of 5, 10, 25, and 50% weight losses, respectively.
[a] With DABCO as a catalyst.

CONCLUSIONS

6-AU reacted with an excess of EC without any solvent in the presence of potassium carbonate or DABCO as a catalyst. Resin products were obtained and were mixtures of hydroxyethyl derivatives of 6-AU, products of condensation, ethylene glycol, and polyglycols.

The obtained products could be used as components of polyurethane foams of improved thermal stability.
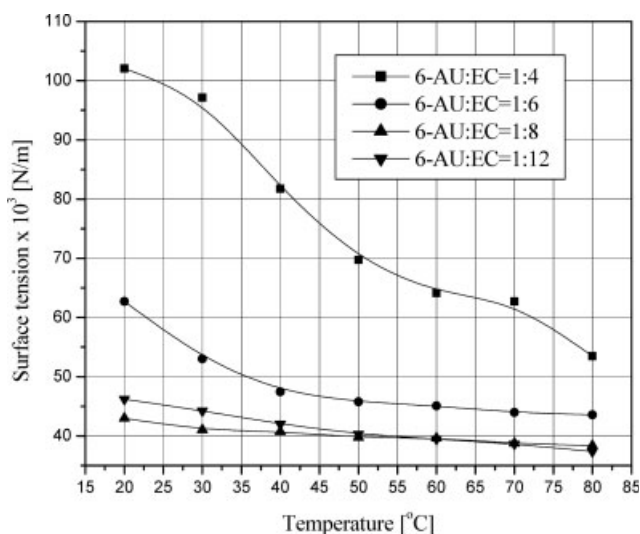

Figure 6 Surface tension of the products of the reaction of 6-AU with EC.

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