

# Polyetherols Obtained from 6-Aminouracil and Oxiranes

Elżbieta Chmiel-Szukiewicz

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

Received 9 February 2006; accepted 28 April 2006

DOI 10.1002/app.25100

Published online in Wiley InterScience (www.interscience.wiley.com).

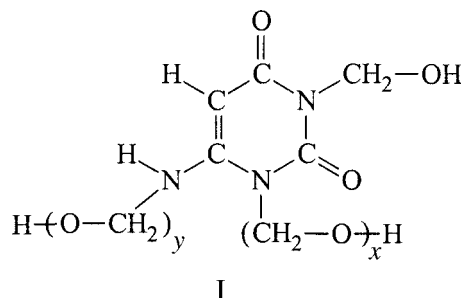
**ABSTRACT:** Reactions of 6-aminouracil with an excess of oxiranes (ethylene oxide and propylene oxide) in dimethylsulfoxide in the presence of triethylamine as a catalyst leads to polyetherols with a 1,3-pyrimidine ring. The products are analyzed using IR and  $^1\text{H-NMR}$  spectroscopies. The physical properties and ther-

mal stability of the prepared polyetherols are investigated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1466–1472, 2007

**Key words:** 6-aminouracil; oxiranes; heteroatom-containing polymers; catalysts; NMR

## INTRODUCTION

We previously reported preliminary results of the hydroxyalkylation of 6-aminouracil (6-AU).<sup>1,2</sup> We identified the products of the reaction between 6-AU and formaldehyde as hydroxymethyl derivatives of structure:



where  $x = 1$ ,  $y = 0$ , or  $x + y = 3$ . Those investigations also showed that 6-AU reacts with excess oxiranes [ethylene oxide (EO) and propylene oxide (PO)] in dimethylsulfoxide (DMSO) solution in the presence of triethylamine (TEA) as a catalyst, yielding the appropriate hydroxyalkyl derivatives.<sup>1,2</sup> Hydroxyethyl derivatives can be produced in reactions of 6-AU with ethylene carbonate as well. 6-AU in the presence of potassium carbonate or 1,4-diazabicyclo[2,2,2]octane dissolves in hot ethylene carbonate (160°C) and reacts with this reagent. The compounds that were obtained have improved thermal stability. They can be utilized to produce thermally resistant polyurethane foams similar to other polyetherols with a heterocyclic ring, for example, perhydro-1,3,5-triazine,<sup>3</sup> s-triazine,<sup>4–8</sup> or purine.<sup>9</sup> The present work presents the details of the reactions of 6-AU with oxiranes.

## EXPERIMENTAL

### Reaction of 6-AU with oxiranes

To a 500-cm<sup>3</sup> autoclave reactor equipped with a stirrer were added 12.7 g (0.1 mol) of pure 6-AU (Sigma–Aldrich, Steinheim, Germany), 50 cm<sup>3</sup> of pure DMSO (Sigma–Aldrich), pure TEA (Fluka, Buchs, Switzerland) catalyst, and pure EO (Fluka) or pure PO (Fluka). Oxirane was added in such an amount that the molar ratios of 6-AU/oxirane were 1 : 4, 1 : 6, 1 : 8, or 1 : 12. The amounts of EO were 17.6 (0.4 mol), 26.4 (0.6 mol), 35.2 (0.8 mol), and 52.8 (1.2 mol); for PO the amounts were 23.2 (0.4 mol), 34.8 (0.6 mol), 46.4 (0.8 mol), and 69.6 g (1.2 mol). The amount of catalyst varied from 2 to 4 cm<sup>3</sup> for the reactions with EO or 4 to 8 cm<sup>3</sup> for the reactions with PO. The mixture was stirred and heated to 50–60°C for the reaction with EO (78–110 h) or 60–70°C for the reaction with PO (124–194 h). 6-AU gradually dissolved during the course of the reaction and the reaction mixture became brown. The end of the reaction was established by determining the epoxy number of the reaction mixture. Then, the solvent and catalyst were distilled off at reduced pressure (0.93 kPa) and the resin product was obtained.

### Analytical methods

The epoxy number was determined by titrating a sample with a dioxane solution of hydrochloric acid.<sup>10</sup> The acid number was determined by titrating a sample dissolved in 20 cm<sup>3</sup> of DMSO and 5 cm<sup>3</sup> of H<sub>2</sub>O with 0.1M NaOH. The IR spectra were recorded on a Fourier transform IR PARAGON 1000 spectrometer (PerkinElmer Corp., Norwalk, CT). The samples for IR analysis were prepared in the form of capillary films or KBr pellets. The  $^1\text{H-NMR}$  spectra of the products were recorded on a BS-586A spectrometer at

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

TABLE I  
Diols Used for Calibration of Gas Chromatography

Formula	Name	Best line coefficients		Correlation coefficients	Retention time (min)
		Slope	Intercept		
HOCH <sub>2</sub> CH <sub>2</sub> OH	Ethane-1,2-diol (ED)	0.3421 ± 0.0035	-0.0430 ± 0.0054	0.999	3.33
HOCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	3-Oxapentane-1,5-diol (OPD)	0.3185 ± 0.0029	-0.1469 ± 0.0082	0.999	5.20
HOCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	3,6-Dioxaoctane-1,8-diol (DOOD)	0.2129 ± 0.0079	-0.1911 ± 0.0323	0.997	6.87
HOCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	3,6,9-Trioxaundecane-1,11-diol (TOUD)	0.0985 ± 0.0055	-0.1374 ± 0.0022	0.997	8.47
HOCH <sub>2</sub> CH(OH)CH <sub>3</sub>	Propane-1,2-diol (PD)	0.4208 ± 0.0084	-0.0444 ± 0.0166	0.999	3.11
CH <sub>3</sub> CH(OH)CH <sub>2</sub> OCH <sub>2</sub> CH(OH)CH <sub>3</sub>	4-Oxaheptane-2,6-diol (OHD)	0.4876 ± 0.0119	-0.0650 ± 0.0414	0.999	4.45
HOCH <sub>2</sub> CH(CH <sub>3</sub> )OCH <sub>2</sub> CH(OH)CH <sub>3</sub>	2-Methyl-3-oxahexane-1,5-diol (MOHD)				4.72
HOCH <sub>2</sub> CH(CH <sub>3</sub> )OCH(CH <sub>3</sub> )CH <sub>2</sub> OH	2,4-Dimethyl-3-oxapentane-1,5-diol (DMOPD)				4.76
CH <sub>3</sub> CH(OH)CH <sub>2</sub> OCHCHCH <sub>3</sub>	4-Oxahept-5-en-2-ol (OHEO)				4.86
HOCH <sub>2</sub> CH(CH <sub>3</sub> )OCHCHCH <sub>3</sub>	2-Methyl-3-oxahex-4-en-1-ol (MOHEO)				5.13
CH <sub>3</sub> CH(OH)CH <sub>2</sub> OCH(CH <sub>3</sub> )CH <sub>2</sub> OCH <sub>2</sub> CH(OH)CH <sub>3</sub>	5-Methyl-4,7-dioxadecane-2,9-diol (MDODD)	0.4139 ± 0.0099	-0.1108 ± 0.0518	0.999	5.81
CH <sub>2</sub> (OH)CH(CH <sub>3</sub> )OCH(CH <sub>3</sub> )CH <sub>2</sub> OCH <sub>2</sub> CH(OH)CH <sub>3</sub>	2,4-Dimethyl-3,6-dioxanonane-1,8-diol (2,4-DMDOND)				5.86
CH <sub>2</sub> (OH)CH(CH <sub>3</sub> )OCH <sub>2</sub> CH(CH <sub>3</sub> )OCH <sub>2</sub> CH(OH)CH <sub>3</sub>	2,5-Dimethyl-3,6-dioxanonane-1,8-diol (2,5-DMDOND)				5.99
CH <sub>2</sub> (OH)CH(CH <sub>3</sub> )OCH(CH <sub>3</sub> )CH <sub>2</sub> OCH(CH <sub>3</sub> )CH <sub>2</sub> OH	2,4,7-Trimethyl-3,6-dioxaoktane-1,8-diol (TMDOOD)				6.08
CH <sub>3</sub> CH(OH)CH <sub>2</sub> OCH(CH <sub>3</sub> )CH <sub>2</sub> OCHCHCH <sub>3</sub>	5-Methyl-4,7-dioxadec-8-en-2-ol (MDODEO)				6.21
CH <sub>2</sub> (OH)CH(CH <sub>3</sub> )OCH(CH <sub>3</sub> )CH <sub>2</sub> OCHCHCH <sub>3</sub>	2,4-Dimethyl-3,6-dioxanon-7-en-1-ol (DMDONEO)				6.41

80 MHz (Tesla) in *d*<sub>6</sub>-DMSO solution and hexamethyldisiloxane as the internal standard. The products were also analyzed by gas chromatography with a Hewlett Packard 5890 instrument equipped with a flame ionization detector. From the chromatograms the amounts of diols and the subsequent products of the reactions of oxirane with water were determined. The gas chromatography conditions were the following: a capillary column (HP-FFAP) with a 10-m length and 0.53-mm diameter, a layer thickness of 0.5 μm, a

temperature profile of 50–220°C (20 deg/min) and 6 min at 220°C, an injection chamber temperature of 220°C, a carrier gas (He) rate of 18.3 cm<sup>3</sup>/min, and a sample volume of 0.2 μm<sup>3</sup>. The calibration was made by using cyclohexanone as the internal standard. The data are presented in Table I.

The thermal analysis of the products was carried out using a derivatograph (MOM) working in a nitrogen atmosphere regime. A 100-mg sample was heated in a china crucible over a temperature range

TABLE II  
Conditions of Synthesis of Polyetherols from 6-AU with Oxiranes

Oxirane	Initial molar ratio of 6-AU/oxirane	Reaction conditions			Oxyalkylene group content in product	
		Amounts of TEA (mol/mol 6-AU)	Temp. (°C)	Time of 6-AU dissolution (h)		
EO	1 : 4	0.14	50–60	50	109	3.7
	1 : 6	0.28	50–60	75	100	5.6
	1 : 8	0.28	50–60	64	102	7.8
	1 : 12	0.28	50–60	44	78	12
PO	1 : 4	0.28	60–70	102	136	3.7
	1 : 6	0.57	60–70	57	124	5.3
	1 : 8	0.57	60–70	54	146	7.4
	1 : 12	0.57	60–70	69	194	11.6



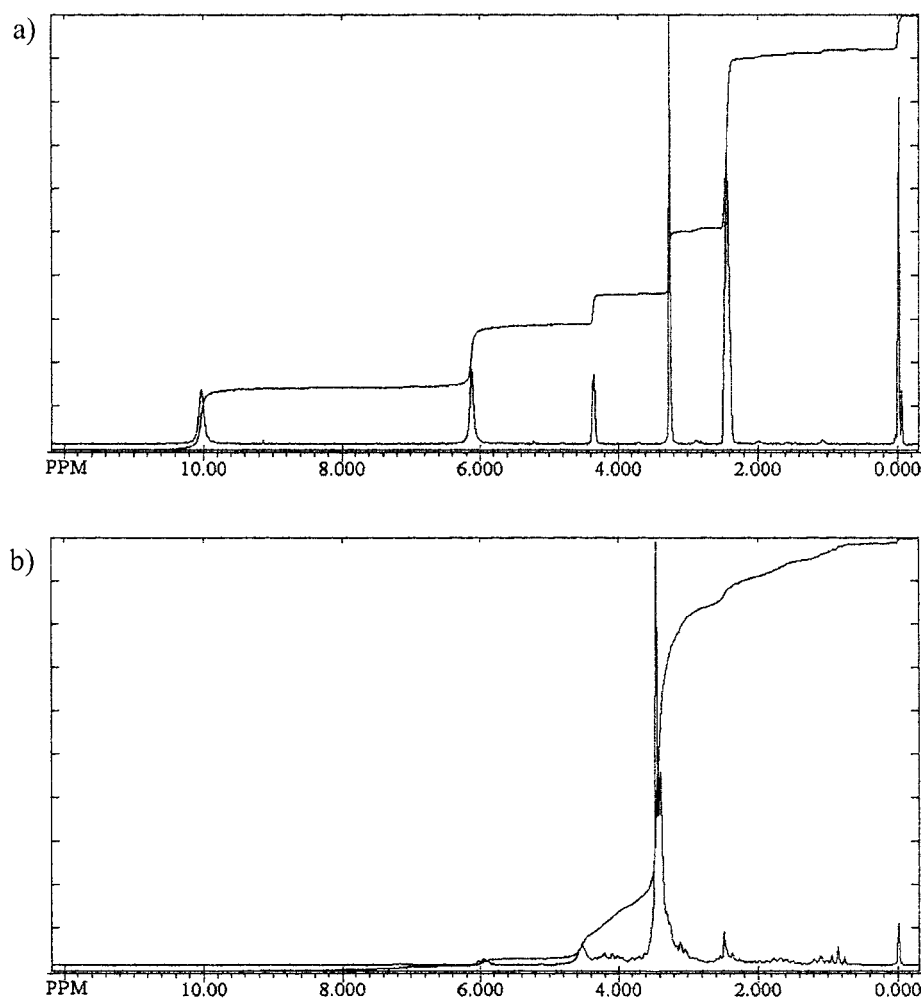


Figure 2  $^1\text{H-NMR}$  spectra of (a) 6-AU and (b) the product of the reaction of 1 mol 6-AU with 12 mol EO.

mass was higher than that calculated exclusively from the mass balance. This is related to the formation of glycols and polyglycols (in the presence of a trace amount of water) in the reactions in Scheme 1, in which R represents  $-\text{H}$  or  $-\text{CH}_3$ . They are par-

tially distilled off under reduced pressure together with DMSO and TEA.<sup>2</sup> This is the reason why the content of oxyalkylene groups is smaller than that resulting only from the initial molar ratio of the substrates (Table II).

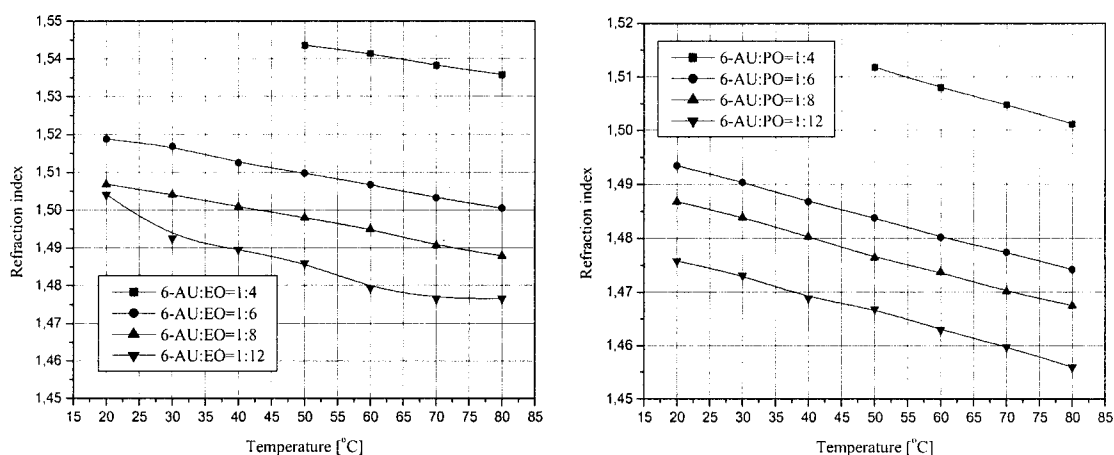
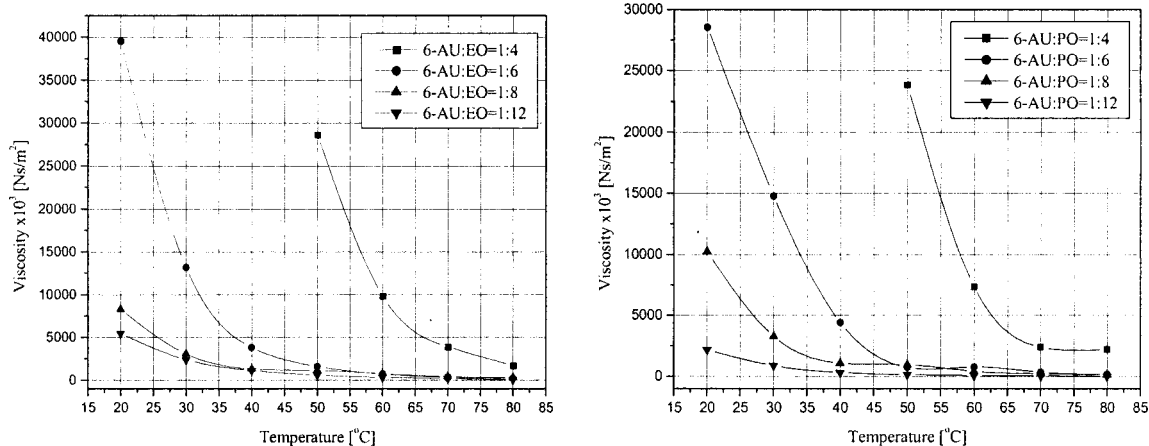


Figure 3 The refraction index of the products of the reaction of 6-AU with EO and PO.

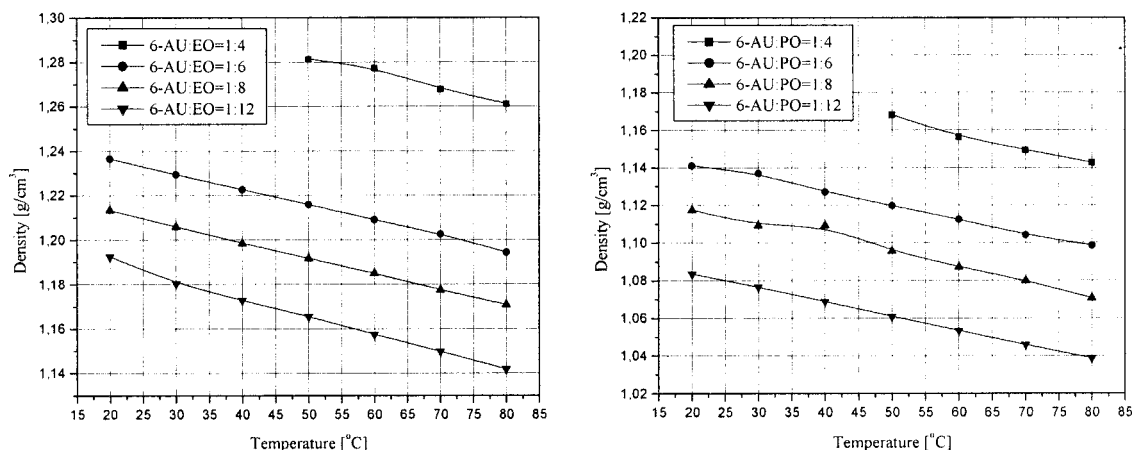


**Figure 4** The viscosity of the products of the reaction of 6-AU with EO and PO.

The amount of glycols and polyglycols was estimated chromatographically. The analysis was performed after the solvent and catalyst were removed from reaction mixture. The standard diols and the products of consecutive reactions were used for comparison (Table I). An analysis of post-reaction mixtures indicated that the amount of glycols and polyglycols in the products of the reaction of 6-AU with oxiranes was within the 1.52 and 11.98% limits, respectively (Tables III, IV). A larger amount of by-products was observed in polyetherols obtained from 6-AU and EO. Because EO is more reactive, it reacts easier with water and the amount of subsequent products is larger. Small amounts of glycols (<1%) in polyetherols from 6-AU and EO and their absence in polyetherols obtained from 6-AU and PO are the result of partial removal of glycols by distillation at reduced pressure. It was observed that the amount of polyglycols increased upon the increase of the amount

of oxirane in the reaction system. This results from the reaction between diols that are formed and unreacted oxirane. Knowing the amount of glycols and polyglycols in postreaction mixtures and taking into account the molar ratio of reagents used, the number of moles of oxirane that reacted with 6-AU were calculated (Tables III, IV). This number was smaller than estimated from the initial molar ratio of 6-AU to oxirane.

The structure of the obtained polyetherols was deduced from IR and  $^1\text{H-NMR}$  spectra. In the IR spectra of the polyetherols the changes of the bands at  $3400\text{--}2700\text{ cm}^{-1}$  and disappearance of shifts of the bands at  $1530$ ,  $1290$ , and  $1237\text{ cm}^{-1}$  in comparison with that of 6-AU (Fig. 1) were a diagnostic method. The valence and deformation bands from hydroxyl groups at  $3330$ ,  $1410$ , and  $1250\text{ cm}^{-1}$ ; from methylene groups at  $2920$ ,  $2875$ , and  $1480\text{ cm}^{-1}$ ; from methyl groups (present only in the spectra of products of the reaction between 6-AU and PO) at  $2870\text{--}$



**Figure 5** The density of the products of the reaction of 6-AU with EO and PO.

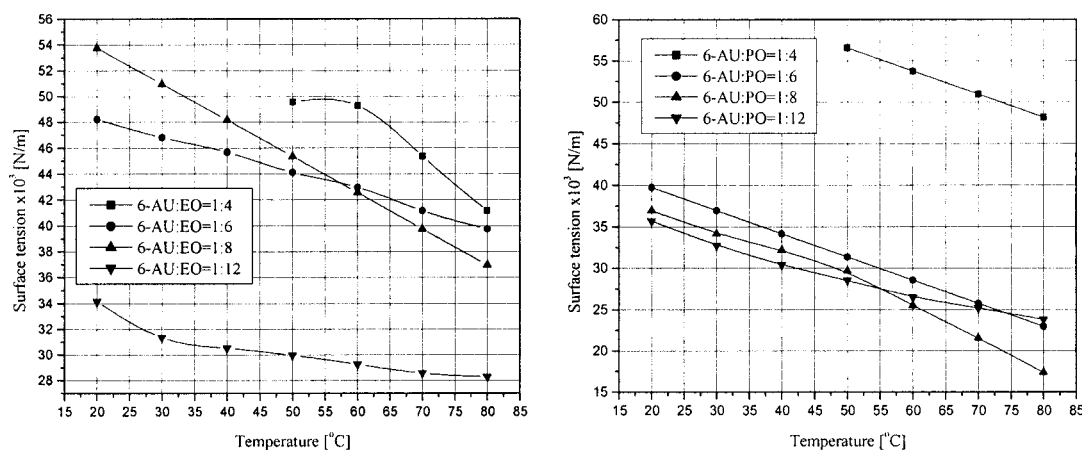
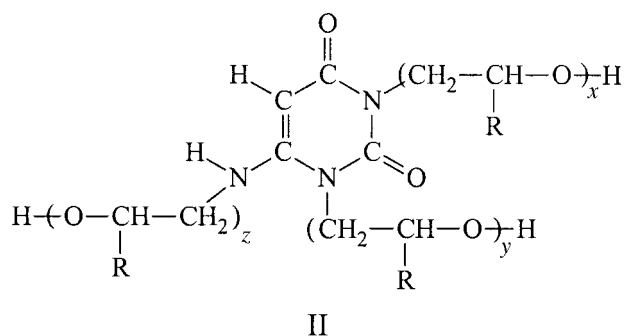


Figure 6 The surface tension of the products of the reaction of 6-AU with EO and PO.

2970, 1450, and 1375  $\text{cm}^{-1}$ ; and the valence band from the C—O—C group at 1120  $\text{cm}^{-1}$  appear in the products. These changes clearly indicate the substitution of nitrogen-bound hydrogens with hydroxyalkyl groups. The IR spectra provide good corroboration of the  $^1\text{H-NMR}$  spectral observation; in the spectra of the products between 6-AU and oxiranes the resonance at 10 ppm (Fig. 2) disappears, indicating the hydrogen replacement with hydroxyalkyl groups. In the spectra of products obtained from 6-AU and EO, resonances at 3.0–3.7 ppm from methylene protons, resonances at 4.1–4.4 ppm attributed to H—C=, and peaks at 4.4–4.8 ppm from hydroxyl protons are present [Fig. 2(b)]. In the spectra of products obtained from 6-AU and PO, the resonances at 0.9–1.4 ppm from methyl protons and resonances from methine protons overlapped with those from hydroxyl protons and H—C= protons (at 4.2–5.0 ppm) are visible. Moreover, in the  $^1\text{H-NMR}$  spectra of hydroxyalkyl derivatives of 6-AU, the small resonance from amine protons at 6 ppm appears [Fig. 2(b)]. The estimations based upon integration of resonances indicated the presence of one unsubstituted proton attached to nitrogen in the products. Another observation was the presence of a trace amount of TEA by the characteristic peak at 1.1 ppm [Fig. 2(b)].

The structure of the obtained hydroxyalkyl derivatives of 6-AU is



where R represents —H or —CH<sub>3</sub> and  $3.0 \leq x + y + z \leq 10.4$ .

Some physical properties of prepared polyetherols as a function of temperature were determined (Figs. 3–6). The density (Fig. 4), viscosity (Fig. 5), and surface tension (Fig. 6) of the polyetherols decreased with increasing amounts of oxirane used in the syntheses.

The thermal stability of polyetherols was determined by thermal analysis (Table 5). Polyetherols obtained from 6-AU and EO were characterized by the slightly larger thermal stability than polyetherols obtained from 6-AU and PO. The 12% content of by-products did not reduce the thermal stability. Initial tests on foaming of the obtained products showed that these polyetherols can be used as components of polyurethane foams with improved thermal stability.

TABLE V  
Thermal Resistance of Products Based on Thermal Analysis

Oxirane	Initial molar ratio 6-AU/oxirane	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{25\%}$ (°C)	$T_{50\%}$ (°C)	Temp. max decomp. (°C)
EO	1 : 8	170	200	230	300	420
	1 : 12	180	210	260	320	420
PO	1 : 8	160	180	210	260	280
	1 : 12	180	200	230	270	300

## CONCLUSIONS

6-AU was reacted with an excess of EO or PO in DMSO with TEA used as the catalyst, and polyetherols containing a 1,3-pyrimidine ring were obtained. Glycols and polyglycols were the by-products of the reaction. The amount of oxyalkylene groups in the products was smaller than that calculated from the initial molar ratio of the reagents. Initial tests on the foaming of the obtained products demonstrated that these polyetherols can be used as components of polyurethane foams with improved thermal stability.

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