

# Polyurethane Foams with 1,3-Pyrimidine Ring

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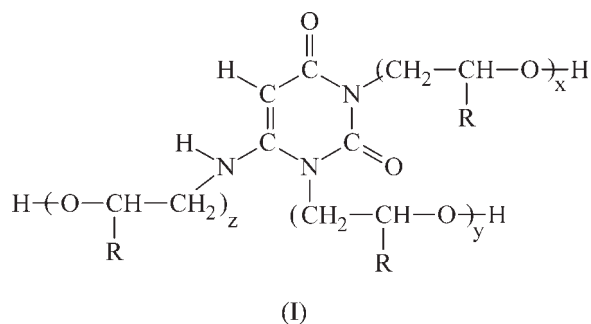
**ABSTRACT:** Attempts of obtaining of polyurethane foams using polyetherols with 1,3-pyrimidine ring (obtained in reactions of 6-aminouracil with oxiranes) are reported. Properties of the foams are investigated, especially their thermal stability. The foams show an improved

thermal stability up to 200°C for a long time. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1708–1713, 2008

**Key words:** heteroatom-containing polymers; polyurethanes; thermal properties; mechanical properties

## INTRODUCTION

The typical polyurethane foams show thermal stability up to 120°C (a temperature range below which their properties do not yet deteriorate is typically 90–110°C).<sup>1–3</sup> For some applications such thermal stability is not sufficient, for instance in thermal insulation of heating pipelines. Foams of improved thermal stability can be obtained by using a polyetherols component containing some heterocyclic ring, such as, perhydro-1,3,5-triazine,<sup>4–7</sup> 1,3,5-triazine,<sup>8–11</sup> or purine.<sup>12</sup> Polyetherols containing 1,3-pyrimidine ring (I) can also be used for the foams of improved thermal stability.<sup>13</sup>



where: R = -H, -CH<sub>3</sub>, and 3.0 ≤ x + y + z ≤ 10.4.

In this work, attempts of obtaining of polyurethane foams with improved thermal stability with the use of polyetherols obtained from 6-aminouracil (6-AU) and oxiranes are described.

## EXPERIMENTAL

### Synthesis of polyetherols with 1,3-pyrimidine ring

Polyetherols with 1,3-pyrimidine ring were obtained in reactions of 6-AU (pure; Sigma-Aldrich, Steinheim, Germany) with 8 or 12 moles ethylene oxide (EO; pure; Fluka, Buchs, Switzerland) or propylene oxide (PO; pure; Fluka, Buchs, Switzerland) according to the procedure described in Ref. 13.

### Foams preparation

Attempts of foaming of polyetherols were carried out in small 250 cm<sup>3</sup> test cups at room temperature. To 10 g of a polyetherol the 0.1 g of surfactant (Silicon 5340, Houdry Hüls) was added, 0.2 g of water, and 0.5–1.6 g of triethylamine (TEA; pure; Fluka, Buchs, Switzerland) catalyst were added. After careful mixing of the components, a preweighed amount of 4,4'-diphenylmethane diisocyanate (Merck-Schuchardt, Hohenbrunn, Germany) was added. The mixture was vigorously stirred until it started creaming. The amount of diisocyanate was adjusted to OH : NCO molar ratio of 1 : 0.84–1.5. From the foams thus obtained samples for testing were cut out after ca. 48 h.

### Analytical methods

The following properties of foams were determined: apparent density,<sup>14</sup> water absorbing capacity,<sup>15</sup> stability of dimensions,<sup>16</sup> thermal stability as the mass loss after heating at 150, 175, and 200°C for month, and compression strength.<sup>17</sup> The thermal analysis of products was carried out using a derivatograph (thermogravimetric analysis apparatus; MOM, Hungary) working under nitrogen atmosphere regime. Sample (100 mg) was heated in a china crucible over

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**TABLE I**  
The Influence of Composition on Foaming Process

	Content of oxyalkylene groups in product	Composition number	Composition <sup>a</sup> (g/100 g of polyetherol)			Foaming process <sup>b</sup>			Characteristics of foams just prepared
			Isocyanate	TEA	Molar ratio OH : NCO	Time of creaming (s)	Time of expanding (s)	Time of drying (s)	
Polyetherol obtained in reaction of 6-AU with EO	7.8	1	100	0.5	0.84	18	35	8	not fully cured <sup>c</sup> rigid rigid rigid rigid rigid rigid, large pores rigid rigid
		2	176	1.1	1.47	23	47	146	
		3	148	1.6	1.23	16	20	16	
	12	4	150	1.6	1.25	18	29	27	
		5	140	1.6	1.16	18	43	15	
		6	128	1.6	1.42	6	5	5	
		7	128	1.3	1.42	6	8	5	
		8	110	1.3	1.22	6	4	5	
		9	136	1.6	1.50	10	5	5	
Polyetherol obtained in reaction of 6-AU with PO	7.4	10	156	1.6	1.50	9	53	16	
		11	152	1.3	1.46	8	38	7	
	11.6	12	112	1.6	1.47	7	35	25	
		13	114	1.6	1.50	4	43	8	
		14	110	1.3	1.45	5	35	17	
		15	108	1.6	1.42	5	21	40	

<sup>a</sup> Amount of surfactant; 1 g per 100 g of polyetherol; amount of water; 2g per 100 g of polyetherol.

<sup>b</sup> Mixing time of composition: 10 s.

<sup>c</sup> Sample was not used for later investigations.

Time of creaming, the time elapsed from the moment of mixing to the start of volume expansion; time of expanding, the time from the start of expansion to the moment of reaching the sample final volume; time of drying, the time from reaching by the sample its final volume to the moment of loosing its surface adhesion to powdered substances.

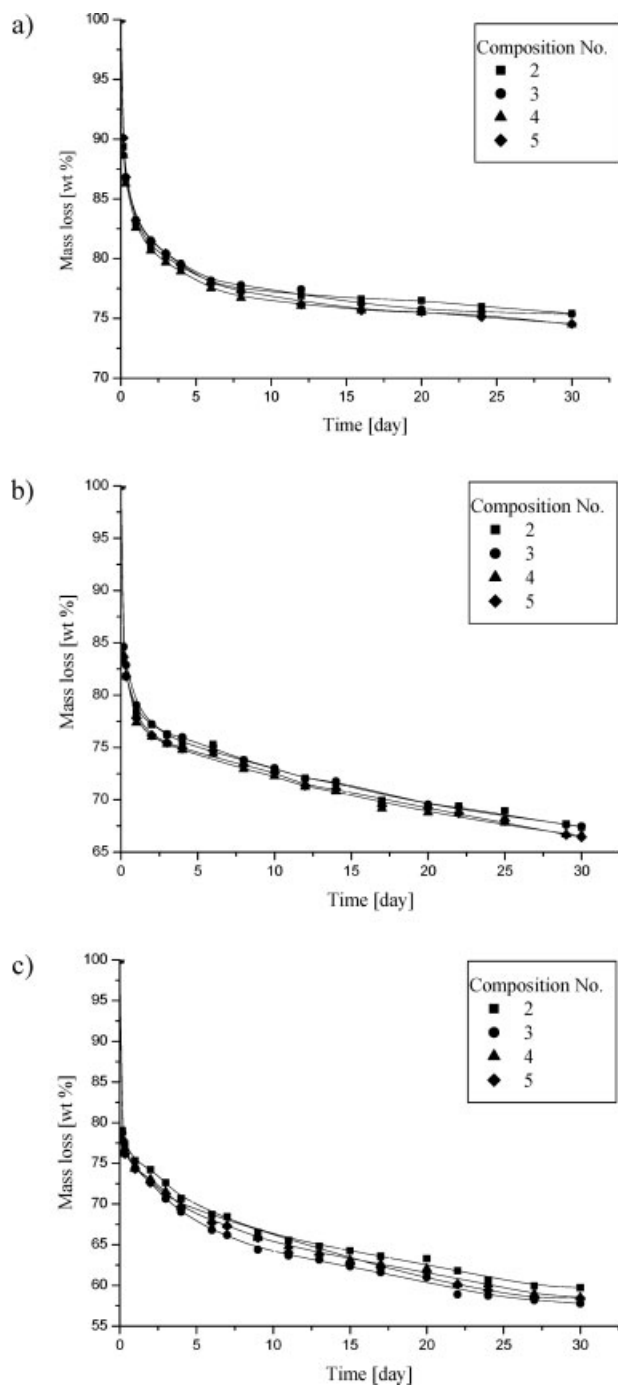
the temperature range of 20–1000°C. The sensitivity of the instrument was 1/10 for DTA and 1/10 for DTG. Thermal investigations<sup>18</sup> of the foams were made using differential calorimeter DSC type 822<sup>e</sup> with the software Stare<sup>e</sup> system (Mettler Toledo, Spain). Recording conditions were as follows: sample weight 10–20 mg, temperature range 0–200°C, heating velocity 10–20°C/min., flow rate 30 cm<sup>3</sup>/min., nitrogen atmosphere).

## RESULTS AND DISCUSSION

Polyetherols, obtained in reactions of 6-AU (1 mol) with EO or PO (8 and 12 mol)<sup>13</sup> were used to prepare polyurethane foams. Foaming was carried out in small scale. Influence of catalyst (TEA) amount, optimal amount of isocyanate (4,4'-diphenylmethane diisocyanate), amount of a foaming agent (water), and length of polyether chain on the foaming course

**TABLE II**  
Some Properties of Polyurethane Foams

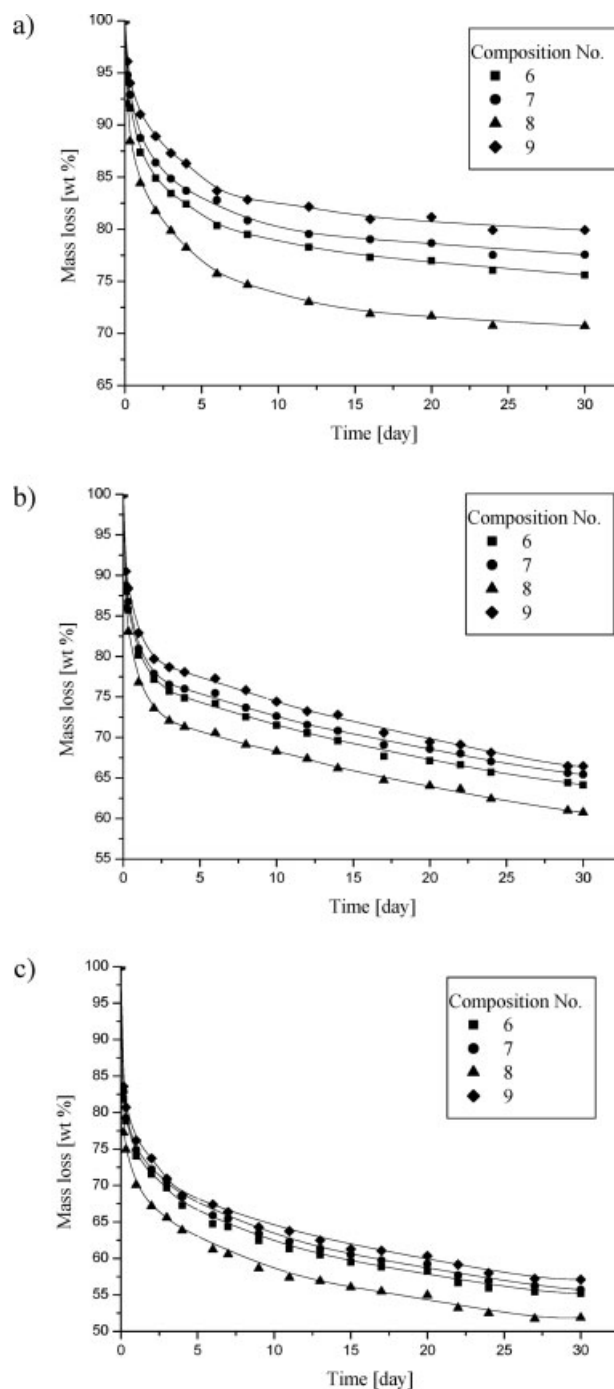
	Content of oxyalkylene groups in product	Composition number	Density (kg/m <sup>3</sup> )	Absorbtion of water (wt %)			Linear dimensions stability at temperature 150°C					
				After 5 min	After 3 h	After 24 h	Length increase (%)		Width increase (%)		Depth increase (%)	
				After 5 min	After 3 h	After 24 h	After 20 h	After 40 h	After 20 h	After 40 h	After 20 h	After 40 h
Polyetherol obtained in reaction of 6-AU with EO	7.8	2	73.50	12.8	19.3	32.5	-2.23	-2.18	-0.22	-0.77	1.83	-1.27
		3	60.88	7.3	9.6	15.3	-6.47	-8.15	-1.83	-2.75	-8.43	-9.64
		4	66.75	11.3	13.8	23.6	-8.37	-9.80	-8.46	-10.22	-0.14	-3.08
	12	5	50.96	10.9	12.0	17.8	-9.81	-11.59	-11.27	-13.58	-5.66	-8.06
		6	44.42	8.7	10.1	12.4	-4.11	-5.16	-2.21	-5.22	-3.88	-5.25
		7	55.32	8.4	10.7	11.3	-2.06	-2.36	-2.42	-2.72	-3.27	-4.07
		8	48.60	12.4	14.1	15.4	-5.30	-7.23	-7.42	-8.59	-6.82	-7.51
		9	47.18	6.5	8.8	10.1	-2.22	-2.96	-2.70	-3.47	-1.97	-3.29
		10	53.91	2.7	4.4	5.8	-4.42	-4.42	-3.23	-2.76	0	-0.56
Polyetherol obtained in reaction of 6-AU with PO	7.4	11	45.92	2.6	4.0	6.2	0.71	0.57	0.77	0.67	-1.46	-1.66
		12	50.93	4.6	5.9	10.4	8.57	7.14	8.73	9.13	12.94	12.94
	11.6	13	43.64	3.8	5.1	9.8	6.49	5.68	12.11	11.90	8.78	8.13
		14	42.12	3.8	5.1	8.4	6.55	3.97	11.39	9.86	13.99	12.13
		15	40.65	3.2	4.3	8.3	5.70	3.47	8.74	7.73	0.04	-3.26



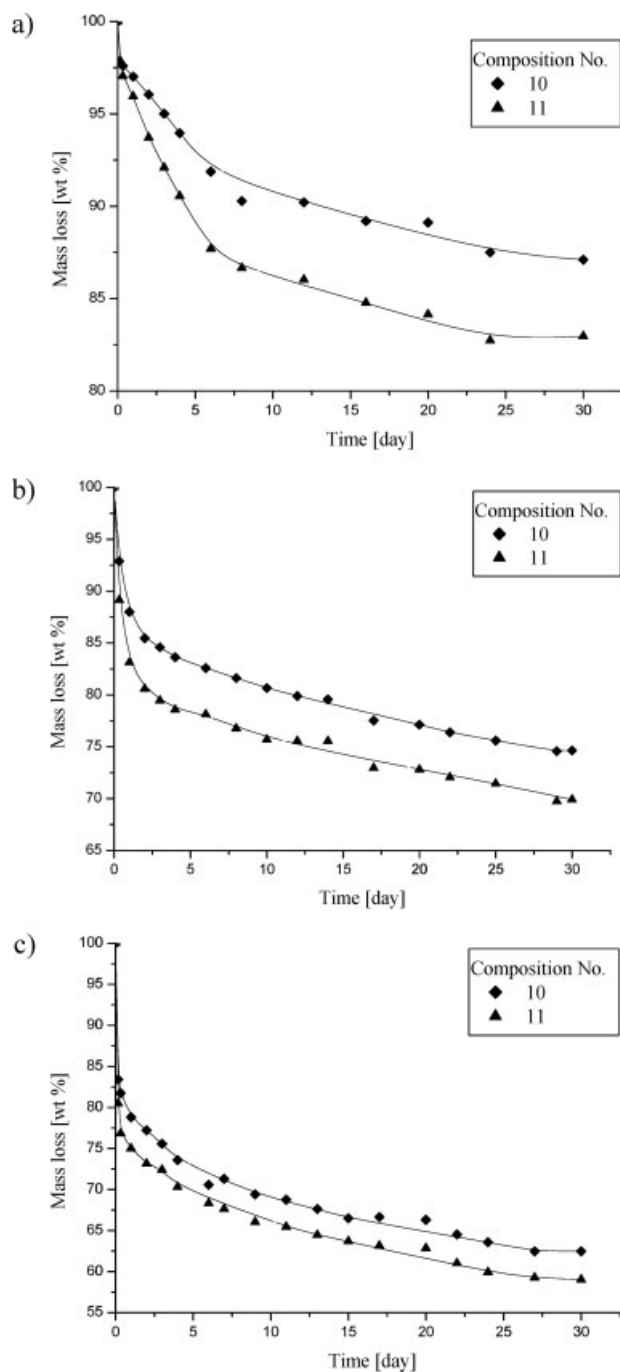
**Figure 1** Thermal stability of the polyurethane foams obtained from polyetherols 6-AU : EO = 1 : 7.8 expressed as the mass loss after heating at (a) 150, (b) 175, (c) 200°C.

were determined. It has been found that the best results are obtained using such an amount of 4,4'-diphenylmethane diisocyanate, for which the molar ratio of hydroxy to isocyanate groups in the former mixture was within the range of 1 : 1.2 ÷ 1 : 1.5. If amount of isocyanate groups was smaller than optimal the foams will be too soft (composition no. 1, Table I). It has been also found that the optimal

amount of water is 2 wt % with respect to the mass of polyetherol. The amount of catalyst (TEA) was in the range of 1.1 ÷ 1.6 g per 100 g polyetherol. For the polyetherol containing 7.8 mol oxyethylene groups per 1 mol 6-AU mixing of a composition was difficult due to high density of this polyetherol. Creaming times of these compositions were longer (16–23 s.) than those obtained for compositions con-



**Figure 2** Thermal stability of the polyurethane foams obtained from polyetherols 6-AU : EO = 1 : 12 expressed as the mass loss after heating at (a) 150, (b) 175, (c) 200°C.

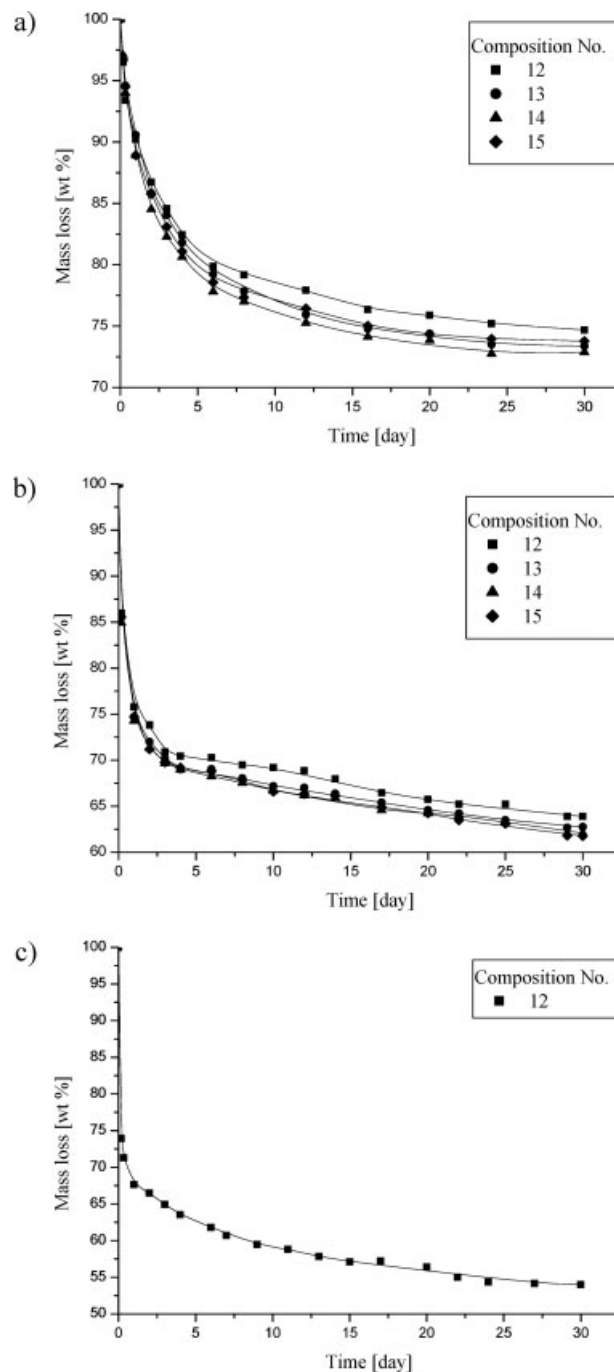


**Figure 3** Thermal stability of the polyurethane foams obtained from polyetherols 6-AU : PO = 1 : 7.4 expressed as the mass loss after heating at (a) 150, (b) 175, (c) 200°C.

taining 12 mol oxyethylene groups or 7.4 and 11.6 mol oxypropylene groups per 1 mol 6-AU (4–10 s., Table I). The shortest foaming time characterizes foams obtained from polyetherol containing 12 mol oxyethylene groups per 1 mol 6-AU.

All foams are rigid. Their apparent density was found in the range of 40–70 kg/m<sup>3</sup> (Table II) and it can be compared with density of the foams based on isocyanuric acid<sup>7</sup> or uric acid.<sup>12</sup>

Absorption of water significantly varies. The foams obtained from polyetherols based on 6-AU and PO show the smallest absorption (5.8–10.4 wt % after 24 h of exposition, Table II). Large absorption of water (up to 32.5 wt %) show the foams based on polyetherol containing 7.8 mol oxyethylene groups per 1 mol 6-AU. Results of stability dimensions measurements were diverse (Table II). Polyurethane foams based on polyetherol containing 11.6 mol



**Figure 4** Thermal stability of the polyurethane foams obtained from polyetherols 6-AU : PO = 1 : 11.6 expressed as the mass loss after heating at (a) 150, (b) 175, (c) 200°C.

**TABLE III**  
**Thermal Resistance and Heat Stability of Some Polyurethane Foams Based on Thermal Analysis and DSC**

	Content of oxyalkylene groups in product	Composition number	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{25\%}$ (°C)	$T_{50\%}$ (°C)	$T_g$ (°C)
Polyetherol obtained in reaction of 6-AU with TE	7.8	2	180	210	280	500	77
	12	6	200	240	290	460	96
		7	210	240	290	470	100
		9	200	240	290	480	108
Polyetherol obtained in reaction of 6-AU with TP	7.4	10	200	220	260	490	144
		11	200	220	260	470	146

oxypropylene groups per 1 mol 6-AU have positive dimension change after thermal treatment at temperature 150°C (a volume of a sample grows). In remaining cases dimension changes are negative. The smallest dimension changes show foams obtained from polyetherol containing 7.4 mol oxypropylene groups per 1 mol of 6-AU (composition No 11, Table II).

The thermal stability measurements of polyurethane foams were performed at temperatures 150, 175, and 200°C by registering the loss of mass (Figs. 1–4). The samples were exposed to the thermal treatment for one month. The gradual loss of mass has been observed. The highest loss of mass was always observed after the first day of exposition. Stabilization of mass at temperature 150°C was reached after 10 days, at temperature 175°C, after 20 days and, finally, at temperature 200°C, after 25 days. Polyurethane foams based on polyetherol containing 11.6 mol oxypropylene groups per 1 mol 6-AU (except of Composition No. 12) show small distortion of their

shape after 4–6 days of thermal treatment at temperature 150°C and after 1–2 days of thermal treatment at temperature 175°C. It was a reason that they were not heated at temperature 200°C. The foams obtained from polyetherol containing oxyethylene groups show small distortion after 1 day of thermal treatment at temperature 175°C (the only exception was composition No. 8). Heated polyurethane foams based on polyetherol containing 7.4 mol oxypropylene groups per 1 mol 6-AU did not change their shape (Composition Nos. 10 and 11, Fig. 3). These foams show the lowest loss of mass. In other cases the loss of mass was much bigger – even up to 48% at temperature 200°C [Composition No. 8, Fig. 2(c)].

Thermal analysis of some polyurethane foams with the lowest loss of mass show that 5% mass loss occurred at temperature 200°C while it was 50% at temperature about 480°C (Table III). These investigations confirm improved thermal resistance of obtained foams. Determined by the DSC method glass transition of some polyurethane foams are included

**TABLE IV**  
**Compression Strength of Polyurethane Foams**

	Content of oxyalkylene groups in product	Composition number	Before exposition $\bar{\sigma}_{10}$ (MPa)	After exposition			Increase of compressive strength (%)		
				150°C $\bar{\sigma}_{10}$ (MPa)	175°C $\bar{\sigma}_{10}$ (MPa)	200°C $\bar{\sigma}_{10}$ (MPa)	150°C	175°C	200°C
Polyetherol obtained in reaction of 6-AU with TE	7.8	2	0.05	0.28	0.32	0.66	460	540	1220
		3	0.11	0.36	– <sup>a</sup>	– <sup>a</sup>	227	– <sup>a</sup>	– <sup>a</sup>
		4	0.12	0.51	0.67	1.78	325	458	1383
	12	5	0.18	0.24	0.59	– <sup>a</sup>	33.3	228	– <sup>a</sup>
		6	0.14	0.26	0.38	0.63	85.7	171	350
		7	0.18	0.25	0.38	0.52	38.9	111	189
		8	0.13	0.41	0.57	0.67	215	338	415
		9	0.11	0.23	0.37	0.35	109	236	218
		10	0.24	0.32	0.28	0.33	33.3	16.7	37.5
Polyetherol obtained in reaction of 6-AU with TP	7.4	11	0.15	0.22	0.23	0.28	46.7	53.3	86.7
		12	0.19	–	0.14	–	–	–26.3	–

$\bar{\sigma}_{10}$ , Compression strength at 10% strain.

<sup>a</sup> Sample deformed.

in the range 77–146°C (Table III) what shows that the obtained foams are rigid.

Foams based on polyetherols containing 1,3-pyrimidine ring show slightly better thermal stability than those based on polyetherols containing perhydro-1,3,5-triazine,<sup>7</sup> 1,3,5-triazine,<sup>10</sup> or purine ring.<sup>12</sup>

Thermal conductivity coefficient of obtained foams is equal to 0.036 (J/m s K) and its value is comparable with heat conduction coefficients of classic polyurethane foams (0.025–0.03 [J/m s K]).<sup>1,3</sup>

Mechanical properties were evaluated on the basis of compression strength measurements (Table IV). The compression strength was tested for some compositions before and after thermal exposure. Before the thermal treatment compression strength at 10% deformation strain of the foams was in the range of 0.05–0.24 MPa. Composition No. 10 shows the largest compression strength; it was obtained from the polyetherol containing 7.4 mol oxypropylene groups (Table IV). It has been observed, that one month long thermal treatment at temperature 150, 175, and 200°C resulted in higher compression strength (exception: Composition No. 12, Table IV). After thermal exposition at temperature 200°C foams have shown the highest compression strength. Compression strength of the 6-AU and EO based polyetherols compositions increased as much as 1380% (Composition No 4, Table IV).

## CONCLUSIONS

The polyetherols obtained in reactions of 6-AU with oxiranes can be utilized for synthesis of polyur-

ethane foams. Apparent density, water absorption, dimension stability, compression strength, and thermal conductivity of the foams are related to the properties of classical polyurethane foams, but their thermal stability is significantly higher.<sup>1,3</sup> Their thermal stability is also higher than that of the foams containing perhydro-1,3,5-triazine,<sup>7</sup> 1,3,5-triazine,<sup>10</sup> or purine rings.<sup>12</sup>

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