Reactions of Hydroxymethyl Derivatives of Uric Acid with Oxiranes. I. Synthesis of Polyetherols with Purine Rings

IRMINA CISEK-CICIRKO, JACEK LUBCZAK

Rzeszów University of Technology, Faculty of Chemistry, 35-959 Rzeszów, Poland

ABSTRACT: Preliminary results on the utilization of uric acid in the synthesis of a new group of polyetherols with purine rings are presented. The polyetherols were prepared in a two-stage process. First, hydroxymethyl derivatives of uric acid were obtained from an uric acid and formaldehyde solution. This intermediate was then reacted with ethylene oxide or propylene oxide without any additional solvent. The structure of the intermediates and polyetherols and some of their physical properties were determined, and the possibilities of application of the polyetherols in manufacturing thermostable polyurethane foams were tested. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2667–2677, 2000

Key words: uric acid; formaldehyde; oxiranes; polyetherols; purine ring; thermostable polyurethane foams

INTRODUCTION

This work is related to improvement of the thermal stability of polyurethane foams. This can be done by

- Trimerization of diisocyanates during preparation of foams,[1] and
- Application of a component providing the improvement, such as polyetherols containing a heat-resistant heterocyclic ring, for example, an *s*-triazine ring.[2–5]

Polyetherols containing *s*-triazine rings are obtained in reactions of isocyanuric acid,[2] melamine,[3] or their derivatives[4,6] with oxiranes. The foams prepared from these polyetherols withstand temperatures of 180–200°C,[2] whereas the traditional foams start to decompose at 90–110°C.[1]

The foams obtained with diisocyanate trimerization are often too brittle. The *s*-triazine containing polyols, on the other hand, have the disadvantage of requiring a multistage chemical process[5] or the use of toxic highly boiling solvents which have to be removed from the products.[3–5] Cyanuric acid or melamine react with oxiranes in DMSO solutions. These compounds hardly dissolve in any other organic solvents. It is therefore of interest to seek a less complex method of preparation of polyetherols of a structure providing improved thermal stability of polyurethanes. Such a possibility seems to be offered by uric acid (**I**) which contains a purine ring system.

Uric acid decomposes at about 400°C,[7] that is, higher than the decomposition temperature of cyanuric acid (360°C) or melamine (350°C).[8] This suggests that polyols obtained from uric acid should also have good thermal stability. In this work, we studied the possibility of the utilization of uric acid in the synthesis of a purine ring containing polyetherols by reacting it with ethylene or propylene oxides.

EXPERIMENTAL

Chemicals

Uric acid (UA), pure (Loba Feinchemie, Fischamend, Germany), ethylene oxide (EO), and (±) propylene oxide (PO) pure (Fluka, Buchs, Switzerland), and formaldehyde, pure (POCh Gliwice City, Poland) were used.

Syntheses

Hydroxymethyl Derivatives of Uric Acid (HDUAs)

The reaction was carried out in a round-bottomed 250-cm^3 flask equipped with a mechanical stirrer, thermometer, and condenser. A mixture of 16.8 g (0.1 mol) of uric acid and 33.4 or 58.4 cm^3 of a 35 wt % formaldehyde solution (0.4 or 0.7 mol, respectively) was heated to 94–96°C while stirring until the acid dissolved (25 min) and then for another 6 h if a precipitate appeared 15–20 min after dissolution or for another 30 min if no precipitate was formed. The reaction mixture was then cooled and water distilled off under reduced pressure (20–27 hPa; vapor temperature 32–33°C).

Polyetherols with Purine Rings

To a round-bottomed 500-cm^3 flask equipped with a mechanical stirrer, thermometer, and condenser, 378 g of the product of the reaction of UA with formaldehyde (molar ratio 1 : 7), 19 g of water (5 wt %), and 50 cm^3 of a triethylamine catalyst were introduced. The contents were heated to 70°C and stirred vigorously to obtain a homogeneous mixture and then cooled to room temperature. It was placed in an autoclave of a 250-cm^3 volume in an amount to ensure that the sample contained 0.6 mol of an UA–formaldehyde (1 : 7) adduct. Then, 211.2 g (4.8 mol), 316.8 g (7.2 mol), or 422.4 g (9.6 mol) of EO or 278.4 g (4.8 mol), 417.6 g (7.2 mol), or 556.8 g (9.6 mol) of PO was added. The reactor was sealed tightly and its contents mixed and heated to 65–70°C until the components had reacted. The catalyst was distilled off under reduced pressure (16–21 hPa; vapor temperature 20–32°C).

Analytical Methods

The extent of the reaction was followed by measuring the epoxy number of the reaction mixture by titration with hydrochloric acid in dioxane.[9] The products of the reaction of HMUAs with oxiranes were characterized by determining the hydroxyl number by using the method of Glinka and Majewska,[10] the refractive index, the density in a pycnometer,[11] the viscosity in a Höppler viscometer, and the surface tension by the ring-detachment method. The GLC analysis was made on a Hewlett–Packard 5890 chromatograph [capillary column HP-FFAP, 10-m length and 0.53-mm diameter; layer thickness: 0.1 μm; temperature: 20–220°C (20°C/min) and 5 min at 240°C; injector and detector: 220°C; carrier gas (He) rate: 18.3 cm^3/min; sample: 0.2 μL]. Calibration curves were used as described in the literature.[12–14] The IR spectra were recorded on a Specord 71 IR (Zeiss, capillary film). ^{1}H-NMR spectra were recorded on an 80-MHz Tesla BS 487C spectrometer (Czechoslovakia) in a DMSO-d_6 solution with HMDS as the internal standard. The thermal stability was assessed using a derivatograph (Paulik–Paulik–Erdey system, MOM, Hungary).

Foam Preparation

The foams were prepared in 250-cm^3 paper cups at room temperature. Ten grams of polyetherol was well mixed with 0.1 g of a surfactant (Silicone 5340), the triethylamine catalyst (1–3 wt %), and water (2–3 wt %) with respect to polyetherol. A calculated portion of 4,4′-diphenyl methyl diisocyanate (MDI) was then added and all stirred vigorously until the contents were creamed. Test samples were cut out from the foams thus obtained.

Preliminary Foam Tests

The following properties of the foam samples were determined: apparent density,[15] water uptake,[16] linear shrinkage[17] as the change of the linear dimension of the sample heated for 4 h at 100°C, thermal stability as the weight lost at 175 and 200°C, and flammability.[18]

RESULTS AND DISCUSSION

Intermediates

The easiest method of preparation of polyetherols with a purine ring would be the reaction of UA with oxiranes:

$$(1)$$
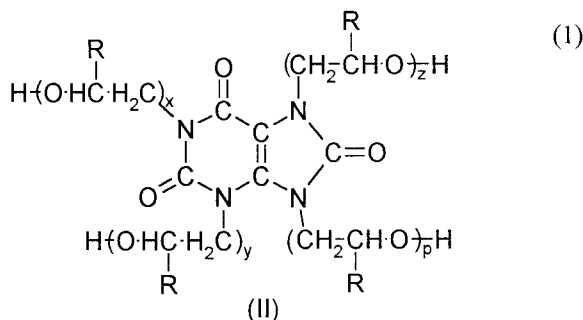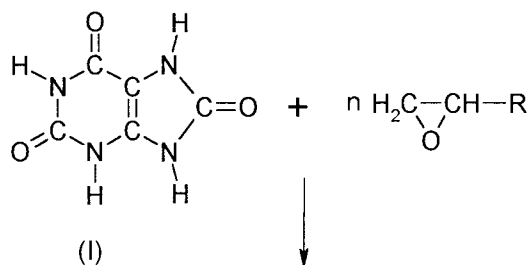
where $x + y + z + p = n$.

We have found, however, no information on such a reaction. The reason might be the lack of suitable solvents of UA in which the reaction could be carried out. This acid is insoluble even in DMSO or DMF and this solubility in water is only 0.5 g/dm^3 at 99°C.[19] This problem has been overcome by preparing HMUAs. It dissolves readily in formalin and the dissolution is accompanied by the formation of *N*-hydroxymethyl derivatives (**III**)[20]:


$$(2)$$
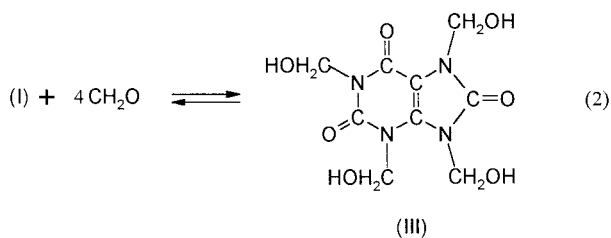
The final product is the *N,N',N'',N'''*-tetrakis(hydroxymethyl)ureate (**III**). It is a solid well soluble in water, DMSO, and DMF. In aqueous solutions, *N*-hydroxymethyl groups are unstable and dissociate as free formaldehyde. The acidic character of imide groups of UA reappear. The amount of released formaldehyde was found to be 41.9% [calculated for (**III**): 41.7%] and the acid number was 225.7 mg KOH/g. Apparently, just one imide group in compound (**III**) has an acidic character.

Compound (**III**) should react with oxiranes to yield the expected polyetherols. The appropriate reaction at the hydroxymethyl fragment of the molecule can be written as follows:

$$(3)$$
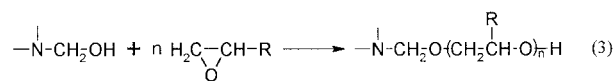
The synthesis of polyetherols from *N,N',N'',N'''*-tetrakis(hydroxymethyl)ureate and oxiranes requires some water, DMSO, or DMF. The use of these solvents has certain disadvantages:

- In the case of water, these are the reactions leading to diols and their subsequent products, which are difficult to eliminate in a way simple enough to apply on an industrial scale, for example:

$$(4)$$
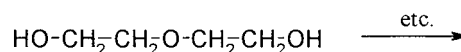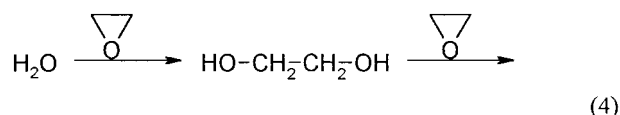
- In the case of other solvents, their toxicity and the need to distill them off despite high boiling points.

These were the reasons why we chose the following preparative route: In the first stage, the reaction of 1 mol of UA with 7 mol of formaldehyde was carried out. After the reaction was completed and the water distilled off, the molar ratio of the components in the product was, indeed, 1 : 7, as follows from, for example, ^{1}H-NMR spectra and the analysis of unbound formaldehyde. The extra three formaldehyde molecules over those in compound (**III**) form hemiacetals (cf. Fig. 1 and Table I). The product had the form of a solid resin which readily mixed with water. In aqueous solutions, it had a slightly acidic character; the acidic number was 147.6 mg KOH/g, which suggested that formaldehyde might disassociate in the solution [cf. reaction (5)].

Addition of 5 wt % water to the product of the reaction modified it into a semisolid resin (it liquefied at 50°C). An even better result was obtained by introducing to the system the catalyst of the reaction, that is, triethylamine. It became liquid at room temperature and mixed readily with oxiranes.

Synthesis of Polyetherols

To obtain polyetherols with purine rings, a liquid system was first introduced to the reactor. The
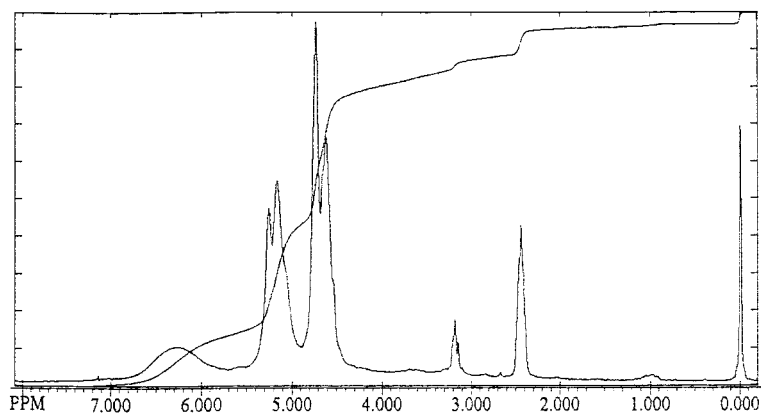
Figure 1 ^{1}H-NMR spectrum of the product of reaction of 1 mol of UA with 7 mol of formaldehyde.

liquid consisted of the product of the reaction of UA with 7 mol of formaldehyde, 5 wt % of water, and triethylamine. Then, the calculated amount of EO or PO was introduced and the contents of the reactor heated to 65–70°C while stirring until the reaction was completed (Table II). Products having the molar ratio of the HMUA to oxirane equal to 1 : 8, 1 : 12, or 1 : 16 formed according to eqs. (5) and (6), below.

The products obtained at the ratio lower than 1 : 8 were found to have some amount (0.6–12.2 wt %) of unbound formaldehyde (in the form of

O-hydroxymethyl groups). All this formaldehyde can be distilled off after the reaction, provided its content does not exceed about 0.6%. Otherwise, some of it stays in the product.

Certain physical properties of the polyetherols obtained at optimal conditions (cf. Table II) were measured at various temperatures. They are listed in Table III. The viscosity, density, and surface tension all decreased with an increasing number of oxirane molecules per molecule of the HMUA. Furthermore, these properties depended on the temperature in the typical way:
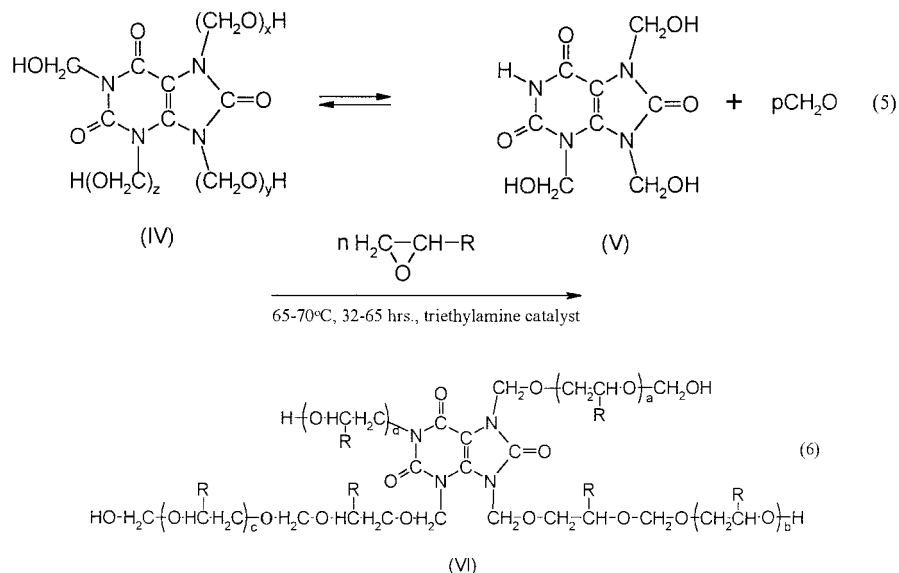
where $x + y + z = 6$, $1 \leq x, y, z \leq 3$; $1 \leq p \leq 4$; $a + b + c + d = n - 2$, R=H, CH$_3$.

Spectral and Thermal Analysis of the Products

The structure of product (**VI**) was confirmed by ^{1}H-NMR (Table I), IR spectra, and the analysis of

Table I ^{1}H-NMR Chemical Shifts of Functional Group Protons in HMUAs and the Products of Their Reaction of with Oxiranes

Compound	Functional Group or Substituent	Chemical Shift δ (ppm)
HMUA	—OH	6.25
	—N—CH$_2$—O—	5.0–5.3
	—O—<u>CH$_2$</u>—OH	4.5–4.7
	—N—CH$_2$—O—CH$_2$—N	4.6
Products of reaction of EO with HMUA	—N—CH$_2$—O—CH$_2$—N	4.6
	—OH	4.5
	—CH$_2$—	3.3–3.6
Products of reaction of PO with HMUA	—OH	4.5
	—CH—	3.8
	—CH$_2$—	3.3
	—CH$_3$	1.1

unbound CH$_2$O. In the ^{1}H-NMR spectrum of the product of the reaction of 1 mol of UA and 7 mol of formaldehyde, one can observe signals at 6.25 ppm of hydroxyl protons and at the range 5.0–5.3 ppm from protons of methylene groups in —N—<u>CH$_2$</u>OH (which are similar to those present in the spectra of hydroxymethyl derivatives of melamine or cyanuric acid[21,22]) as well as at 4.5–4.7 ppm from the protons in hemiacetal methylene groups formed by the addition of formaldehyde to hydroxymethyl groups (cf. Fig. 1). A weak signal appears at 4.6 ppm due to possible condensation of N-hydroxymethyl groups.[23] A proof of the origin of the signal at 6.25 ascribed to —OH protons is that it disappears when heavy water is added to the system. In the products of the reaction of oxiranes with hydroxymethyl derivatives (Figs. 2 and 3), the signals at 5.0–5.3 ppm vanish, confirming that, indeed, oxiranes react with hydroxymethyl groups. In the spectra of poly-etherols obtained from EO, the characteristic signal from methylene groups at 3.3–3.6 ppm can be observed as well as the OH signal at 4.5 ppm covering that from N—CH$_2$OCH$_2$—N groups (4.6 ppm) [cf. Fig. 2(a,b)]. One can estimate that the fraction of the latter does not exceed about 0.8 mol

Table II Conditions of Synthesis of Polyetherols

Stage	Reaction No.	No Mol of CH$_2$O or Oxirane per Mol of UA	Reaction Conditions Tempera-ture (°C)	Time (h)	In Crude Product wt%.	In Crude Product mol/mol UA	After Catalyst and Volatiles Distillation wt%	After Catalyst and Volatiles Distillation mol/mol UA	Acid No. Calcd. (mg KOH/g)	Acid No. Found (mg KOH/g)	OH No. (mg KOH/g)
Hydroxy-methylation	1	4	95–98	5.5	41.9	4	—	—	195.8	225.7	—
	2	7	95–98	1.0	55.5	7	—	—	148.5	147.6	—
EO addition	1	8	65	20	12.2	3.2	6.0	1.5	0.0	0.0	—
	2	12	65	28	7.4	2.4	1.0	0.3	0.0	0.0	267
	3	16	65	33	3.1	1.2	0.7	0.25	0.0	0.0	249
PO addition	1	8	70	45	8.2	2.5	8.2	2.4	0.0	0.0	—
	2	12	70	50	0.6	0.2	0.0	0.0	0.0	0.0	147.3
	3	16	70	65	0.0	0.0	0.0	0.0	0.0	0.0	126.1

The product with a molar ratio UA : CH$_2$O equal 1 : 7 was used in the reactions with oxiranes.

Table III   Some Physical Properties of Polyetherols

Oxirane	Molar Ratio of HMUA : Oxirane in Product	Temperature (°C)	Refractive Index n_D^{25}	Density (g/cm^3)	Viscosity $(N\ s^{-1}\ m^{-2}) \times 10^3$	Surface Tension $(N/m) \times 10^3$
EO	1 : 8	20	1.5141	1.2903	21,191	42.74
		30	1.5126	1.2823	8015	37.92
		40	1.5094	1.2703	3534	36.06
		50	1.5058	1.2635	1540	35.29
		60	1.5033	1.2562	768	33.10
		70	1.5004	1.2487	425	32.88
		80	1.4978	1.2417	26.0	31.89
	1 : 12	20	1.5013	1.2495	6330	39.35
		30	1.4994	1.2421	2520	37.04
		40	1.4961	2.2358	1116	35.95
		50	1.4934	1.2285	571	35.29
		60	1.4901	1.2215	306	33.54
		70	1.4875	1.2135	196	32.44
		80	1.4848	1.2074	125	31.78
	1 : 16	20	1.4959	1.2361	3604	38.36
		30	1.4936	1.2198	1036	36.94
		40	1.4906	1.2139	708	35.95
		50	1.4878	1.2069	384	33.54
		60	1.4847	1.2000	235	32.44
		70	1.4816	1.1931	197	32.00
		80	1.4788	1.1868	93	31.35
PO	1 : 8	20	1.4914	1.1815	11,699	37.04
		30	1.4882	1.1738	4103	33.10
		40	1.4857	1.1661	1583	32.77
		50	1.4834	1.1590	685	32.33
		60	1.4801	1.1511	324	29.70
		70	1.4769	1.1439	167	28.17
		80	1.4729	1.1361	97.8	26.52
	1 : 12	20	1.4810	1.1414	5022	36.61
		30	1.4780	1.1335	1773	35.51
		40	1.4749	1.1259	699	34.30
		50	1.4720	1.1184	332	29.59
		60	1.4680	1.1103	169	27.62
		70	1.4649	1.1022	93.3	25.87
		80	1.4612	1.0943	56.9	25.21
	1 : 16	20	1.4771	1.1254	3248	35.29
		30	1.4748	1.1163	673	33.76
		40	1.4746	1.1084	471	32.00
		50	1.4683	1.1003	236	29.15
		60	1.4653	1.0912	124	26.52
		70	1.4610	1.0828	73.1	24.99
		80	1.4572	1.0739	44.1	24.22

per mol of hydroxymethyl derivatives in the case of EO or not more than about 0.4 mol per mol in the case of PO. In the spectra of polyetherols obtained with PO, the signals from methyl, methylene, and methine group protons are at 1.0, 3.3, and 3.8 ppm, respectively. The ratio of areas under these signals is 3 : 2 : 1, as it should be.

The structure of intermediates and products was also confirmed by IR spectra (Figs. 4–6). In the product of the addition of 7 mol of formalde-
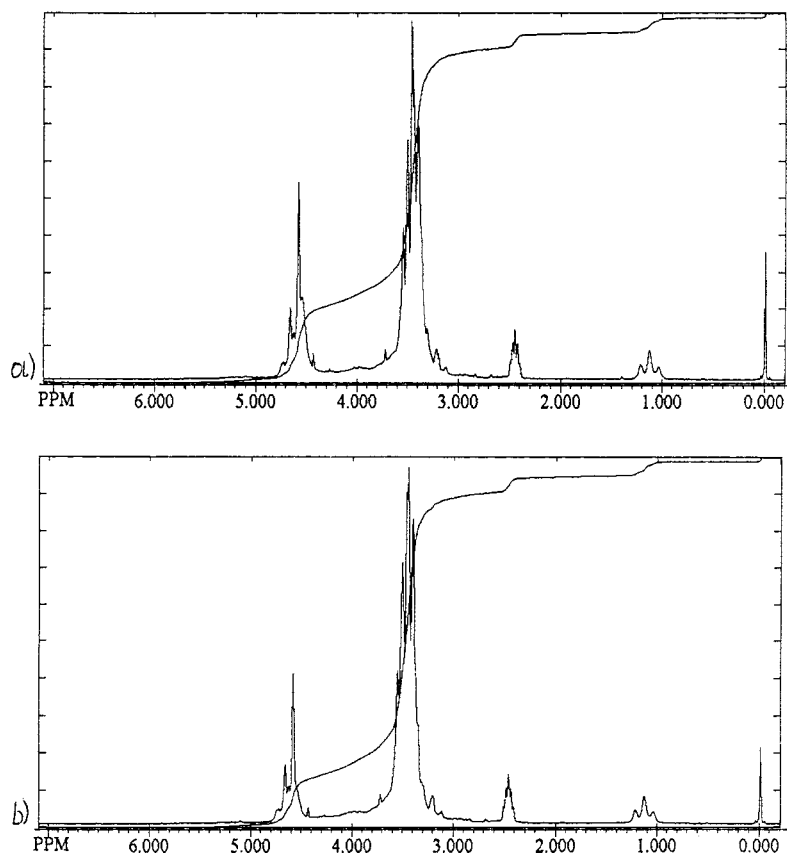
Figure 2   (a) ^{1}H-NMR spectra of the product of reaction of 1 mol of HMUA (UA : CH$_2$O = 1 : 7) with 16 mol of EO; (b) the same after introducing few drops of D$_2$O.

hyde per mol of uric acid, a characteristic broad band at about 3356 cm^{-1} is observed due to associated hydroxyl groups. The deformational vibrations of this group are at 1000 cm^{-1} and are superimposed on vibrations of C—O—C grouping. The C=O band of high intensity at 1646 cm^{-1} indicates that formaldehyde forms a link with the —NH group in the keto, not enolic, form of UA. As the number of moles of oxirane added to the HMUA increases, the intensity of the band at 1000 cm^{-1} also increases, indicating that more and more ether links are formed.
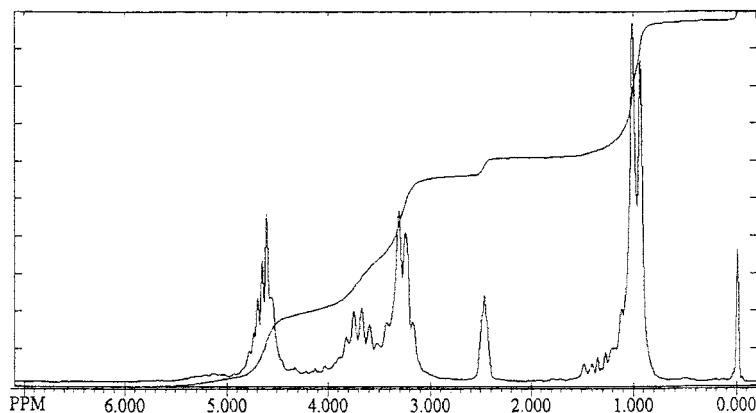

Figure 3 ^{1}H-NMR spectrum of the product of reaction of 1 mol of HMUA (UA : CH$_2$O = 1 : 7) with 12 mol of PO.
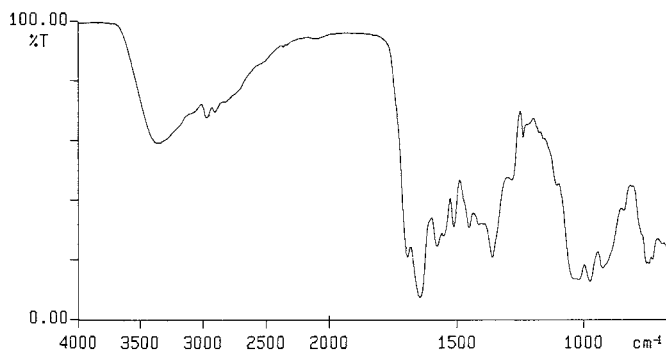
Figure 4 IR spectrum of the product of reaction of 1 mol of UA with 7 mol of formaldehyde.

Information on the thermal stability of poly-etherols, particularly on formaldehyde elimination, provides its thermal analysis. Decomposition of pure UA starts as high as at 400°C (Fig. 7). The maximum of endotherm lies at 420°C. HMUAs release formaldehyde already at 100°C. It is clearly seen on the derivatogram (Fig. 8) that formaldehyde molecules release at different temperatures depending on their position. The thermal stability of polyetherols depends on the starting molar ratio of the UA derivative to oxirane used in the synthesis. In the derivatograms of polyetherols obtained with the ratio 1 : 6, there are two endothermic peaks, one at 100–120°C due to decomposition of *O*-hydroxymethyl groups and a second at about 400°C, when the purine ring starts to decompose (Fig. 9). The size of the first peak decreases gradually as the excess of oxirane increases. For example, the product where the molar ratio of UA to formaldehyde and to PO was 1 : 7 : 12 had the maximum of decomposition at 200°C. The derivatographic analysis helped to select polyetherols suitable for prepara-

tion of polyurethane foams of improved thermal stability. These were the products where formaldehyde was fully or nearly completely blocked by oxirane, that is, the products of the reaction of the hydroxymethyl derivative with oxirane at the molar ratio 1 : 12 or 1 : 16.

Analysis of Side Products

The products obtained in the reactions of hydroxymethyl derivatives with oxiranes were analyzed by GC in order to determine the content of diols and the subsequent products formed by side reactions of oxiranes with water present in the system. The analysis was carried out after the catalyst had been removed. To identify all the peaks in the chromatograms due to the products of oxirane with water, chromatograms were analyzed using data in the literature.[12–14] The chromatograms contain mainly peaks corresponding to respective glycols and a few subsequent products of addition of oxiranes to these glycols (Table IV). The amount of glycols and their subsequent
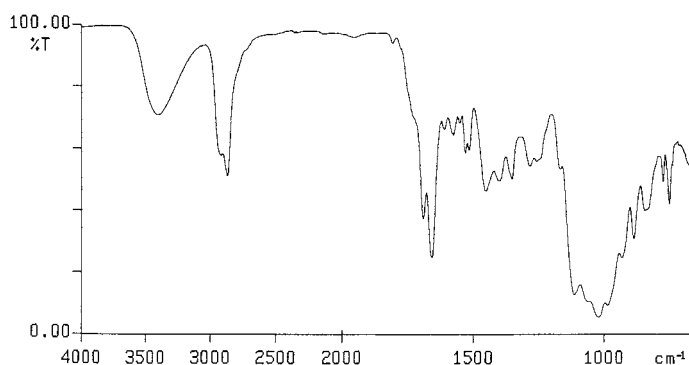

Figure 5 IR spectrum of the product of reaction of 1 mol of HMUA (UA : CH_2O = 1 : 7) with 16 mol of EO.
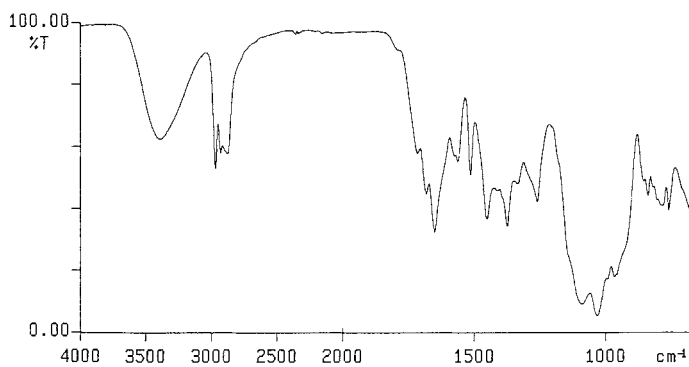
Figure 6   IR spectrum of the product of reaction of 1 mol of HMUA (UA : CH_2O = 1 : 7) with 12 mol of PO.

products was found in the polyethers to be relatively small. In the case of PO, the amount of diols does not exceed 1.2 wt % of the final product. For

EO, it depends on the starting molar ratio of the reagents. EO is more reactive than is PO and easily reacts with water, yielding more glycol and
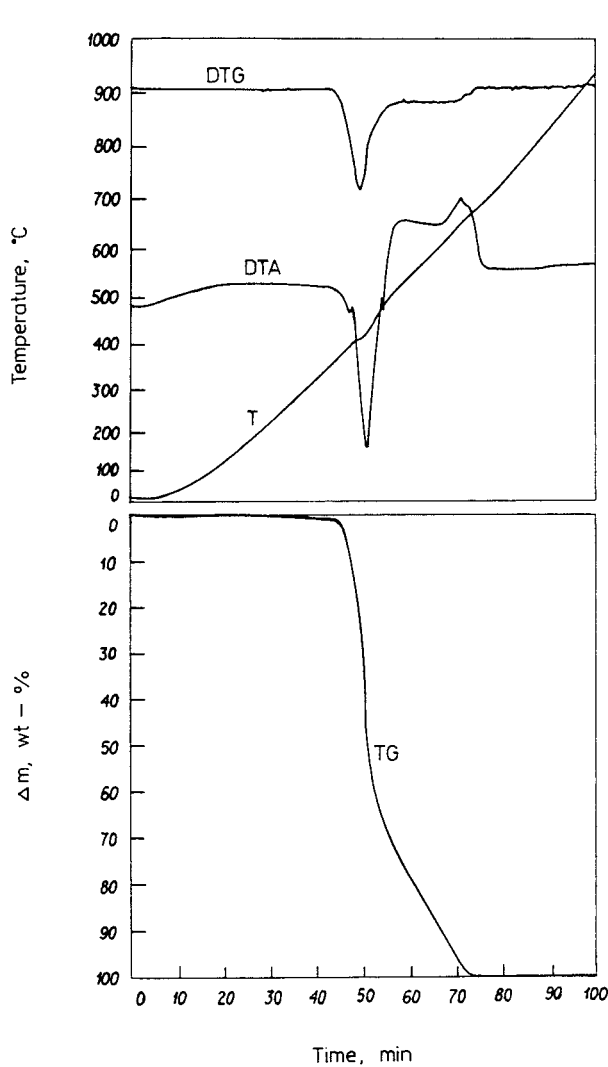

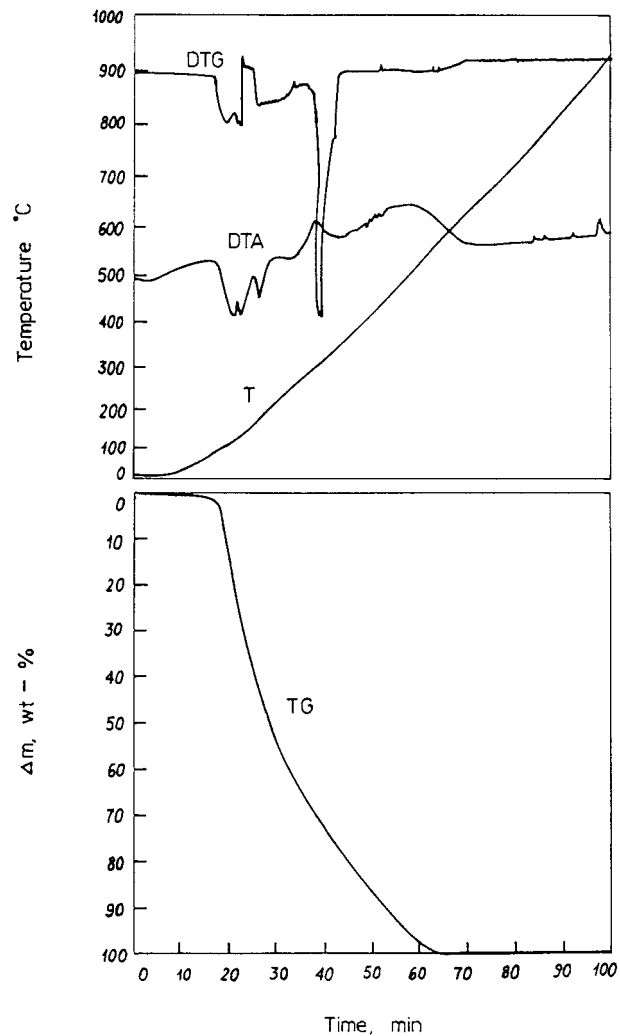**Figure 7**   Results of thermal analysis of UA.

Figure 8   Results of thermal analysis of the product of reaction of 1 mol of UA with 7 mol of formaldehyde.
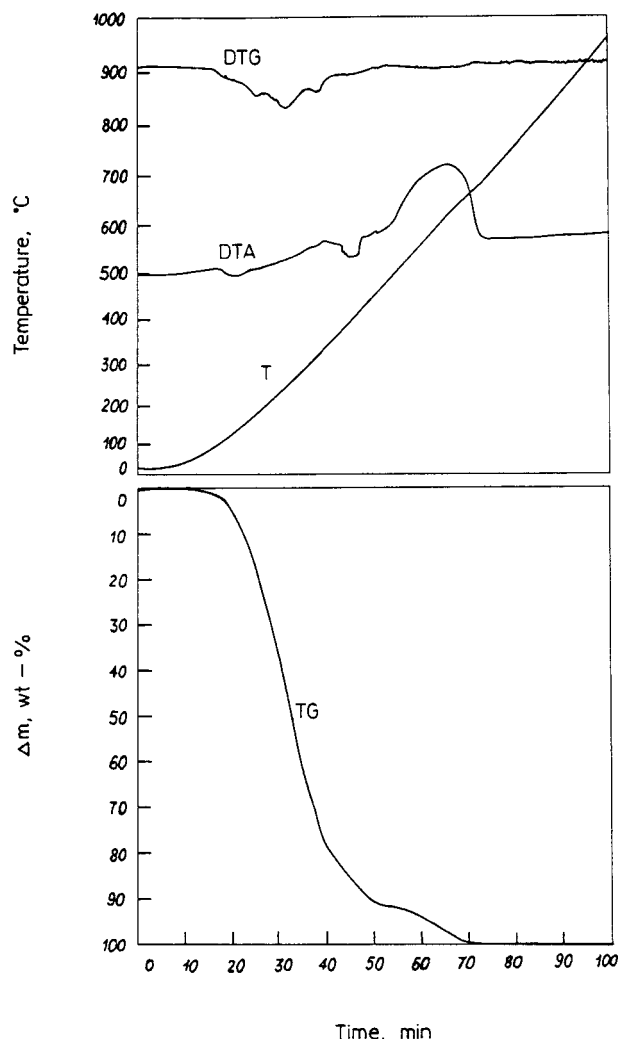
Figure 9 Results of thermal analysis of the product of reaction of 1 mol of HMUA (UA : CH$_2$O = 1 : 7) with 8 mol of PO.

subsequent products; at the molar ratio of UA : CH$_2$O : EO = 1 : 7 : 8, as much as 23.5 wt % of ethylene glycol was formed, whereas the fraction of subsequent products was only 0.6%. As the excess of EO increased, the amount of ethylene glycol decreased, and at the ratio 1 : 7 : 16, ethylene glycol was practically absent and the amount of diethylene glycol did not exceed 0.6 wt %. In this last case, the yield of polyetherols was the highest, close to 100%. It was noticed that as the excess of oxirane increased the amount of glycols formed decreased, sometimes in expense of their subsequent products since glycols relatively easily react with the excess of oxirane. The amount of these subsequent products, however, was never very large.

Preparation of Polyurethane Foams

The polyetherols based on UA were used to prepare polyurethane foams on a laboratory scale. The foams prepared were semirigid and turned into stiff foams after thermal treatment at 120°C. All foams were flammable. Their apparent density was in the range 50–70 kg/m^3 (Table V), that is, slightly higher than the density of thermostable foams based on isocyanuric acid.[2] The water uptake by the foams was exceptionally small when compared with the foams containing s-triazine rings. It was in the range 1.6–2.2%, whereas those prepared from cyanuric acid had, on average, the uptake of 3–8% of water. The foams containing a high amount of oxirane had the lowest uptake. They also had the lowest linear shrinkage (0.0–0.4%). The thermal stability tests of the foam samples were carried out at 175 and 200°C, measuring the loss of their weight and mechanical stability. The samples were heated

Table IV Side Products Formed in the Reaction of HMUAs with Oxiranes

Oxirane	HMUA : Oxirane Molar Ratio	Products of Reaction of Oxiranes with Water (wt %)				Polyetherol (wt %)
		I	**II**	**III**	**Σ %**	
EO	1 : 8	23.5	0.6	0.0	24.1	75.9
	1 : 12	9.9	0.9	0.0	10.8	89.2
	1 : 16	0.0	0.6	0.1	0.7	99.3
PO	1 : 8	0.8	0.4	0.0	1.2	98.8
	1 : 12	0.3	0.0	0.0	0.3	99.7
	1 : 16	0.1	1.1	0.0	1.2	98.9

I, II, III: the subsequent products of reaction of oxirane with water; Σ %: total percentage of side products in reactions of oxiranes with water.

Table V   Some Properties of Polyurethane Foams Prepared Using Polyetherols Obtained in Reaction of HMUAs with PO; HMUA : PO Ratio = 1 : 16

Composition no.	Composition (g/100 g Polyetherols)			Apparent Density (kg/m^3)	Water Uptake (wt %)	Linear Shrinkage (%)	Thermal Stability Measured as the Weight Loss at Plateau at Temperature (wt %)		Compressive Strength (N/m^2) $\times 10^{-5}$		
	Isocyanate	Water	Catalyst						Before exposure	After Exposure at	
							175°C	200°C		175°C	200°C
1	94	2	2.7	65.0	1.8	0.4	39	52	1.88	7.11	3.33
2	94	2	3.2	60.7	2.2	4.4	23	52	5.84	10.32	3.04
3	94	3	3.2	50.0	1.6	0.0	39	51	2.94	5.82	2.40

for nearly 1 month. The samples were losing their weight during the whole experiment, with the largest weight loss recorded on the first day of treatment. One should notice that all samples became more and more rigid during thermal treatment and, in most cases, had a higher compression strength (Table V). A more detailed study of the properties of polyurethane foams based on purine ring-containing polyetherols will be presented in a separate article.

SUMMARY

A simple method of preparing a novel group of polyetherols with a purine ring by reacting HMUAs with oxiranes, such as EO or PO. The advantage of the method compared to the methods known so far is that the reaction does not require organic solvents since it takes place in the oxirane solution.

The polyetherols are suitable for the preparation of polyurethane foams. Their properties are similar to those of classical foams, except that they have much better thermal stability.

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