

Hydroxyalkylation of Barbituric Acid. II. Synthesis of Polyetherols with Pyrimidine Ring

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ABSTRACT: The route of synthesis of new polyetherols with pyrimidine ring from barbituric acid (BA) was presented. The polyetherols were obtained in two steps: synthesis of hydroxymethyl derivative of BA followed by reaction of the latter with neat ethylene or propylene oxides. Physical properties of the products and preliminary

application for fabrication of thermal stability polyurethane foams were determined. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4067–4074, 2007

Key words: barbituric acid; oxiranes; addition polymerization; oligomers; polyurethanes

INTRODUCTION

Pyrimidine ring of barbituric acid (BA) decomposes upon heating to about 280°C.¹ Therefore, the increase of thermal stability of polymers, such as polyurethanes and polyesters, with the ring of BA may be anticipated. The synthetic routes to such polymers were unknown to date. Recently we have demonstrated² that tetrafunctional polyetherols with pyrimidine ring can be obtained by the reaction of hydroxymethyl derivatives of BA with oxirane in excess. The hydroxymethyl derivative of BA was obtained by reaction of BA with at 1 : 6M ratio. The product of the latter reaction could be used as oxirane-soluble substrate for the synthesis of polyetherols, provided that trace water and catalyst (triethylamine) were introduced into the system. Here we describe the details on the synthesis and properties of polyetherols obtained from hydroxymethyl derivative of BA with ethylene (EO) and propylene (PO) oxides and their potential applicability to form the thermally resistant foams.

EXPERIMENTAL

Syntheses

Preparation of hydroxymethyl derivative of BA (HMBA)

To the round-bottomed three-necked 250 cm³ flask, equipped with mechanical stirrer, thermometer, and

reflux condenser, 12.8 g (0.1 mol) of BA (pure, BDH, Laboratory Supplies, Poole, UK) and 50 g 36% formaline (0.6 mol CH₂O) (pure, POCH, Gliwice City, Poland) were introduced. The mixture was heated to reflux (96°C) for 2 h. Then the reaction mixture was cooled to room temperature, and water was partially removed under reduced pressure ($p = 13.33$ hPa, $t = 20$ –60°C). The resin-like, straw-colored product was obtained.

Synthesis of polyetherols with pyrimidine ring

To the round-bottomed three-necked 500 cm³ flask, equipped with mechanical stirrer, thermometer, and reflux condenser, 287 g HMBA (1 mol), 14.4 g H₂O (5% w/w related to a product mass) and 40 cm³ triethylamine (TEA, pure, Fluka, Buchs, Switzerland) were introduced. The HMBA used at this reaction contained 5.3 HCHO bound per 1 mol of BA. The mixture was stirred and heated at 70°C until mixture became homogeneous, then cooled and the halt of it (containing 0.5 mol of HMBA) was placed at high pressure reactor of 750 cm³ capacity. Then, 396 g (9 mol) of ethylene oxide (EO) or 290 g (5 mol), 348 g (6 mol), or 522 g (9 mol) of propylene oxide (PO; pure, Fluka, Buchs, Switzerland) were added to the reactor. The reactor was firmly closed and the mixture was heated and stirred magnetically at 65–70°C. Then, the catalyst was removed by distillation under reduced pressure ($p = 16$ –21 hPa; 12–14 mmHg) at 20–100°C temperature range.

Analytical methods

The progress of reactions were monitored by the determination of epoxide number using hydrochloric

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TABLE I
Conditions of Synthesis of Polyetherols

Synthetic step	Run no.	No moles of CH ₂ O or oxirane per mole of BA	Reaction conditions		Characteristics of Products					
					CH ₂ O content after catalyst and volatiles distillation		Acidic no [mg KOH/g]		Hydroxylic no [mg KOH/g]	
					Temperature (°C)	Time (h)	wt %	mol/mol BA	Calc.	Found
Hydroxymethylation	1.	6	50	2	55.3	5.3	195.5	132.5	–	–
EO addition	1.	18	60	48	1.8	0.6	0.0	0.0	208	201
PO addition	1.	10	70–75	28	3.6	1.0	0.0	0.0	259	184
	2.	12	70–75	32	1.8	0.6	0.0	0.0	228	173
	3.	18	70–75	60	1.5	0.6	0.0	0.0	169	135

in dioxane method.³ In products of reaction of HMBA with oxiranes, the hydroxyl number was determined according to Glinka and Majewska method.⁴ The refraction index was determined with Abbe refractometer, the density was estimated picnometrically,⁵ the viscosity was obtained with Höppler viscosimeter, and surface tension was determined by the method of ring drawing. The IR spectra were recorded with Specord 71 IR, Carl Zeiss spectrophotometer in capillary film, the ¹H NMR spectra were recorded at 80 MHz, BS 487C Tesla spectrometer in *d*₆-DMSO, with HMDS internal reference. The thermal analysis of polyetherols was conducted with F. Paulik, J. Paulik, L. Erdey (MOM, Hungary) derivatograph. The gas chromatographic studies were done with Hewlett-Packard, type 5890 with FID, while the identification of side products were performed using: capillary HP-FFAP column of 10 m length and 0.53 mm diameter; 0.1 μm thickness; within the 50–220°C temperature range and 20°/min gradient, followed by 5 min heating at 240°C temperature; injector and detector temperature 220°C; 18.3 cm³/min helium flow rate; sample volume 0.2 μdm.³ The calibration curves were used as before.^{6,7} MALDI ToF (Matrix-Assisted Laser Desorption Ionization Time of Flight) were obtained on Voyager-Elite Perseptive Biosystems (USA) mass spectrometer working at linear mode with delayed ion extraction, equipped with nitrogen laser working at 337 nm. The method of laser desorption from matrix was used with 2,5-hydroxybenzoic acid in THF at mg/cm³ concentration. The samples were diluted with methanol to 1 mg/cm³, followed by addition of 10 mg/cm³ NaI in acetone. Therefore, in some cases, the molecular ion masses were increased by the mass of Na⁺ and CH₃OH.

Foam preparation

Foaming tests were conducted on a laboratory scale in 250 cm³ paper cups at room temperature. In details polyetherol (10 g) was mixed with 0.1 g of

Silicone 5340 as surfactant, the TEA catalyst (1–3 wt %) and water (2–3 wt %) with respect to polyetherols. A calculated portion of diphenylmethane 4,4'-diisocyanate (MDI, pure, Merck, Darmstadt, Germany) was then added and the mixture was vigorously stirred until the contents were creamed. Test samples were cut out from the foams thus obtained.

Preliminary studies of foams

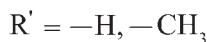
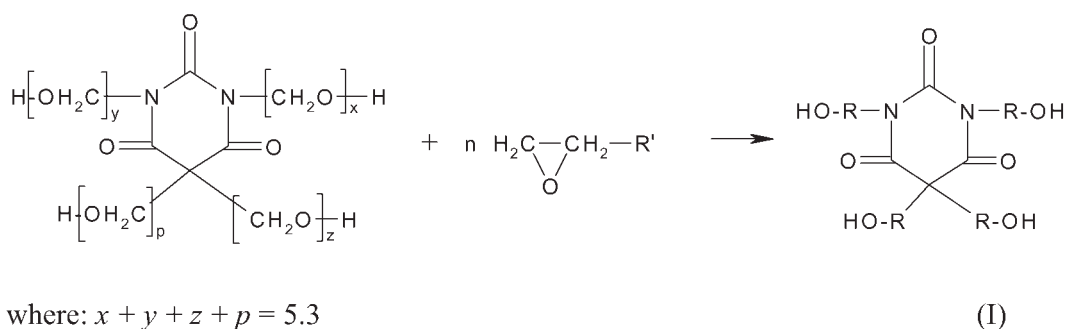
The following properties of foams were studied: apparent density,⁸ water uptake,⁹ linear shrinkage estimated on the basis of the change of linear dimension of the sample heated for 4 h at 100°C,¹⁰ thermal stability as the weight loss at 150, 175, and 200°C, flammability,¹¹ and compressive strength before and after thermal exposure.¹²

RESULTS AND DISCUSSION

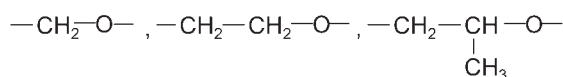
The product of reaction of 1 equiv. of BA with 6 equiv. of HCHO is water-miscible solid resin (HMBA). The percentage of weakly bound formaldehyde in this HMBA was 55.3% CH₂O, indicating that BA : CH₂O ratio in the product was 1 : 5.3. HMBA is slightly acidic in aqueous solution; the acidic number is 132.5 mg KOH (Table I). This can be caused by splitting of formaldehyde from N-hydroxymethyl groups and restoring of imide group. When 5% w/w of water and TEA are added to HMBA, it becomes liquid and miscible with oxiranes at room temperature.

Synthesis of polyetherols

To obtain polyetherols with pyrimidine ring it was necessary to perform the reaction between HMBA, preliminarily conditioned with water and TEA, then heat it with EO or PO at 60–75°C in high pressure reactor with continuous stirring. The conditions of the syntheses are collected in Table I. The products were obtained using 10–18 oxirane excess in relation to HMBA. The reaction can be shown by the scheme:



R – stands for oxyalkylene groups:



It has been found that products obtained at low excess of oxirane related to HMBA (1 : 10, 1 : 12) contain some amount (1.5–3.6%) of weakly bound formaldehyde (as O-hydroxymethyl groups). This formaldehyde can be removed after synthesis by distillation together with the catalyst. Physical properties of obtained polyetherols were examined in function of temperature (Table II). The decrease of viscosity, density, and surface tension of polyetherols with increasing number of oxirane equivalents used for the synthesis was observed together with typical temperature dependence. These results clearly show that the polyetherols with pyrimidine rings can be successfully used for obtaining polyurethane foams, especially considering the values of surface tension (0.033–0.040 N/m), viscosity (0.3–1.1 N s/m²) in 20°C, and their temperature dependence.

Spectral and thermal analysis of products

Structure of obtained polyetherols can be shown by general formula (I). It is well defined by the ¹H NMR spectra (Table III), IR spectra, and the results on determination of weakly bound formaldehyde. In the ¹H NMR spectrum of HMBA the resonances at the 5.0–5.3 ppm region were attributed to methylene group protons in $-N-CH_2OH$ and hydroxyl group protons.² In the spectra of products formed upon addition of oxirane to HMBA (Figs. 1 and 2) these resonance collapse, indicating the reactivity of hydroxymethyl groups with oxiranes. The intensity of resonances from C₅–CH₂OH protons (2.1 ppm) also diminishes upon reaction due to hydroxyl reactivity. Instead, in the spectra of the products of reaction between HMBA and EO (Fig. 1) the new resonances at 3.4 ppm attributed to methylene group protons and at 4.7 ppm from hydroxyl protons, overlapped

with signal from $N-CH_2O-CH_2-N$ methylene group protons (at 4.6 ppm). The latter groups are formed upon mutual condensation of hydroxymethyl groups of HMBA.² Moreover, in the spectra of polyetherols obtained from PO, the resonances attributed to methyl group protons at 0.9–1.2 ppm and multiplet from methine group at 3.8–3.9 ppm appear. The integral intensity ratio of those resonances is as 3 : 2 : 1 consistently with structure of polyetherols formed.

The IR spectra are consistent with described reaction pathway (Figs. 3 and 4). In the IR spectrum of the HMBA (with 5.3 equiv. of CH₂O per BA) the characteristic band at 3400 cm⁻¹ from hydroxyl group is present, while the deformation mode band of this group is placed at about 1100 cm⁻¹ and overlapped with C–O–C absorption.² During the attachment of consecutive oxirane equivalents the intensity of latter band increases. The intensity of the band centered at 2830 cm⁻¹ from valence stretching of methylene groups also increases in comparison with that of ν(OH) band, which is consistent with increasing number of attached oxyalkylene units. The skeleton vibration at 935 cm⁻¹ of pyrimidine ring is present at spectra of the products, indicating the pyrimidine ring remains preserved in the products.

Thermal stability of polyetherols was studied by thermal analysis. It has been found that thermal resistance of polyetherols depends on initial HMBA : oxirane molar ratio. For the products with small amount of oxirane units attached to HMBA (less than 10 mol/mol HMBA), two partially overlapped peaks at 160 and 280°C appear at DTG curves, corresponding to the release of formaldehyde from unstable semiacetal groups and decomposition of pyrimidine ring (Fig. 5). At the DTG curves of polyetherols

TABLE II
Some Physical Properties of Polyetherols and Regression Equations Describing Their Dependence on Temperature, in the Range of 20–80°C

Molar ratio HMBA : oxirane	Surface tension τ (Nm) $\times 10^3$			Refractive index n (-)			Viscosity η [N s/m ²] $\times 10^3$			Density d [g/cm ³]		
	$\tau = aT + b$			$n = aT + b$			$\eta = A + be^{-T/c}$			$d = aT + b$		
	A	b	r	a $\times 10^4$	b	r	A	b	r	a $\times 10^4$	b	r
HMBA : EO 1 : 18	-0.1656	39.858	0.9932	-3.027	1.4869	0.9999	43.805	4698.82	12.81	-7.24	1.2078	0.9999
HMBA : PO 1 : 10 ^a	32.64	18.41	0.9904	-3.23	1.4744	0.999	7.1473	4312.17	14.62	-7.49	1.1087	0.9999
HMBA : PO 1 : 12	-0.0626	35.92	0.9997	-3.44	1.4736	0.9998	22.960	4375.42	11.83	-7.34	1.1052	0.9998
HMBA : PO 1 : 18	-0.1211	39.805	0.9978	-3.74	1.4660	0.9996	8.033	1311.76	13.64	-8.54	1.0863	0.9978

r, correlation coefficient.

^aThe equation describing the changes of surface tension in function of temperature is $\tau = a + be^{-T/c}$.

TABLE III
¹H NMR Chemical Shift of Protons in HMBA and the Products of Its Reaction with Oxiranes

Compound	Functional group or substituent	Chemical shift δ (ppm)
HMBA	-NH-	12.0–11.3
	CH ₂ O (free)	8.1
	-N-CH ₂ -OH	6.0
	-N-CH ₂ -O-	5.1
	-N-CH ₂ -O-CH ₂ -N-	4.5
	-N-CH ₂ -N-	4.4
	-C-CH ₂ -O-CH ₂ -C-	4.45
Products of reactions of EO with HMBA	-C _{ring} -CH ₂ -	2.1
	-O-CH ₂ -CH ₂ -O-	3.1–3.8
	-C _{ring} -CH ₂ -	3,4
	-N-CH ₂ -CH ₂ -O-	3.6–3.9
Products of reactions of PO with HMBA	-OH	4.6
	-OH	5.1–5.2
	-CH-	3.8–3.9
	-CH ₃	0.9–1.2

with permanently blocked formaldehyde, only one endothermic peak is observed (at 270–280°C), corresponding to the cleavage of pyrimidine ring (Fig. 6). Thermal analysis was also useful for selection of polyetherol substrates for the formation of polyurethane foams. The best selection was the product of addition, in which the formaldehyde was almost totally blocked with oxirane, i.e., the product(s) of reaction between HMBA and oxirane in large excess (higher than 10-fold).

Structures of products were confirmed by their MALDI-ToF spectra. In the spectra of products of reaction with HMBA with oxiranes the series of peaks were observed attributed to molecular ions differing of $M/z = 30$ each to other (Table IV, e.g., No 9,14 and 17). This difference corresponds to the mass of formaldehyde. According to the analysis the obtained polyetherols contain variable amount of formaldehyde units (1–5). The observed pattern indicates that formaldehyde split off from semiacetal groups upon removal of the catalyst by distillation after the synthesis. Also observed are the series of molecular ions differing of $M/z = 44$ (for the products obtained from EO, Table IV, e.g., Nos. 23, 24, 25, and 26), the fragment that corresponds to oxyethylene subunits. In another spectra (recorded for the products obtained from PO), the series of molecular peaks differing of $M/z = 58$ were found, which correspond to variable amount of oxypropylene groups attached in the product. These observations suggest that the length of oxyalkylene chains is variable in products. Furthermore, the peaks from glycols and polyglycols were found; the latter form in the reaction between substrate oxiranes and water introduced into the system at the beginning of synthesis (Table IV, cf. Nos. 1, 2, 6, and 10). The highest molecular weight glycols observed were tetraethy-

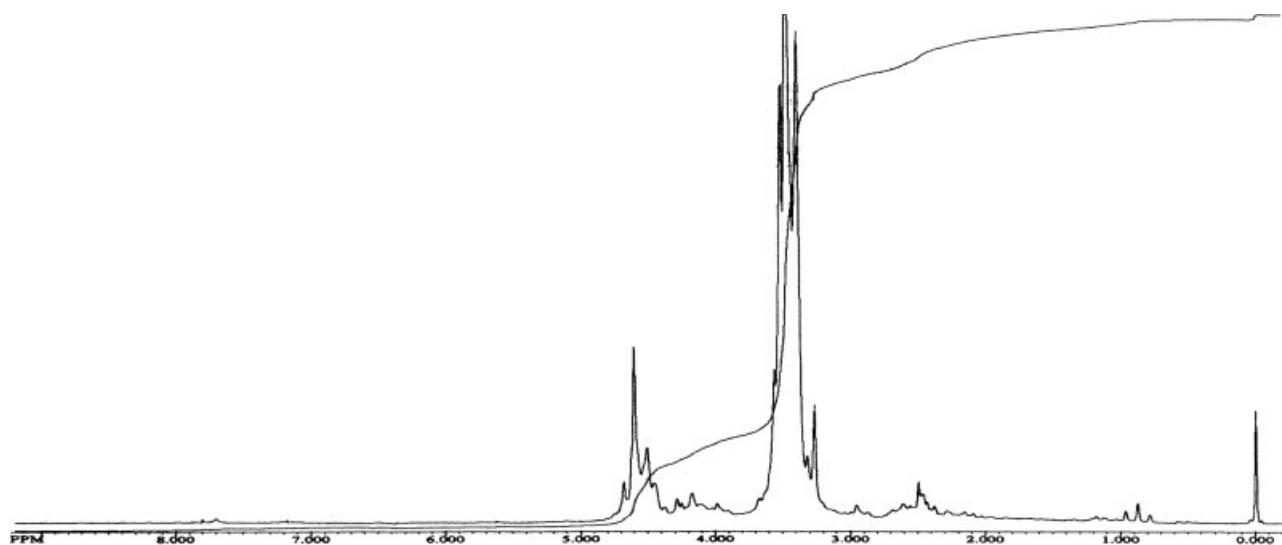


Figure 1 ¹H NMR spectrum of the product of reaction obtained from HMBA : EO = 1 : 18 substrate mixture.

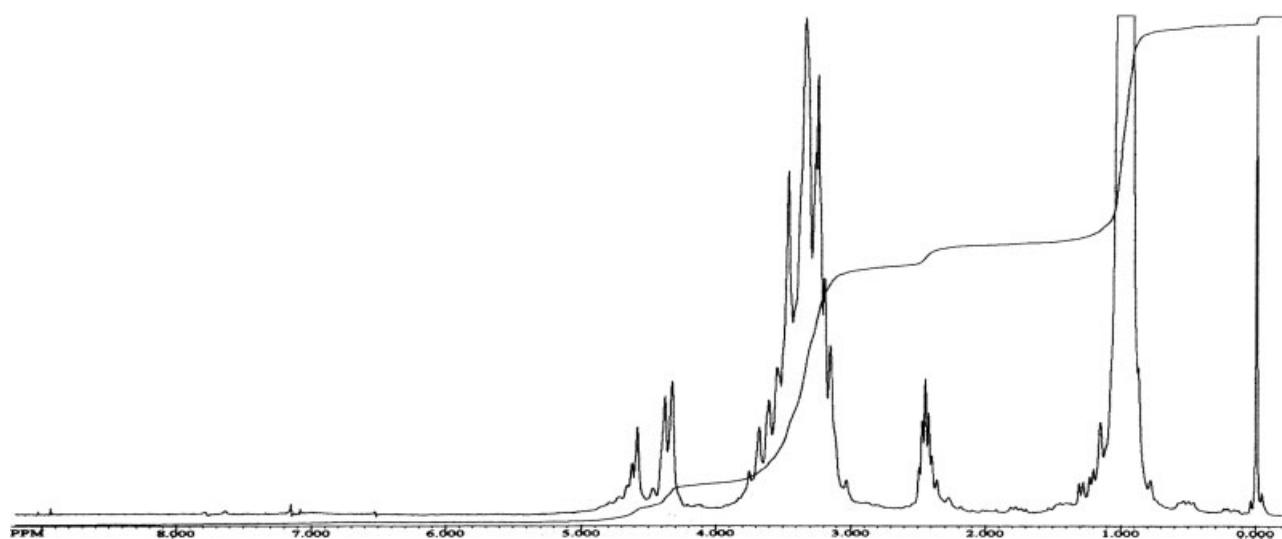


Figure 2 ¹H NMR spectrum of the product of reaction obtained from HMBA : PO = 1 : 18 substrate mixture.

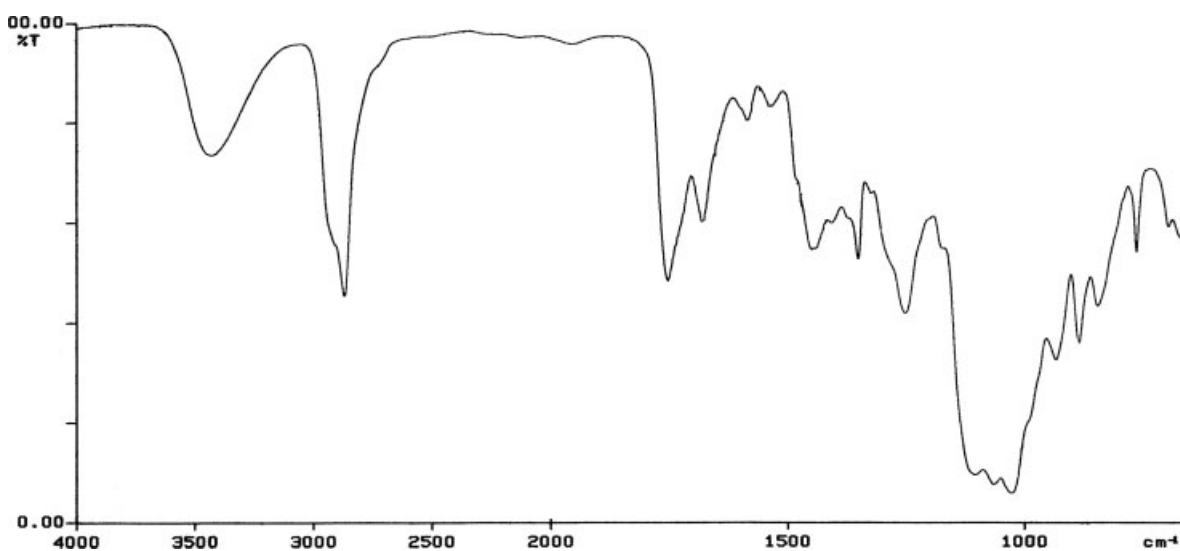


Figure 3 IR spectrum of the product of reaction obtained from HMBA : EO = 1 : 18 substrate mixture.

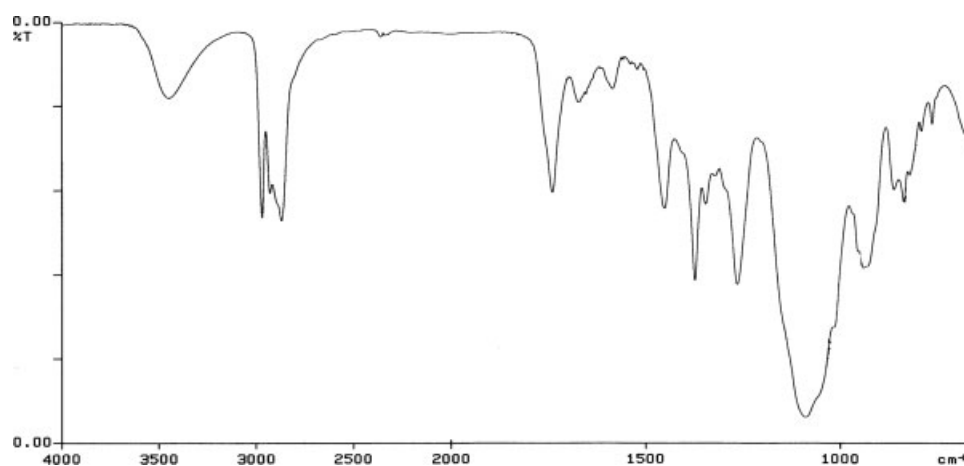


Figure 4 IR spectrum of the product of reaction obtained from HMBA : PO = 1 : 18 substrate mixture.

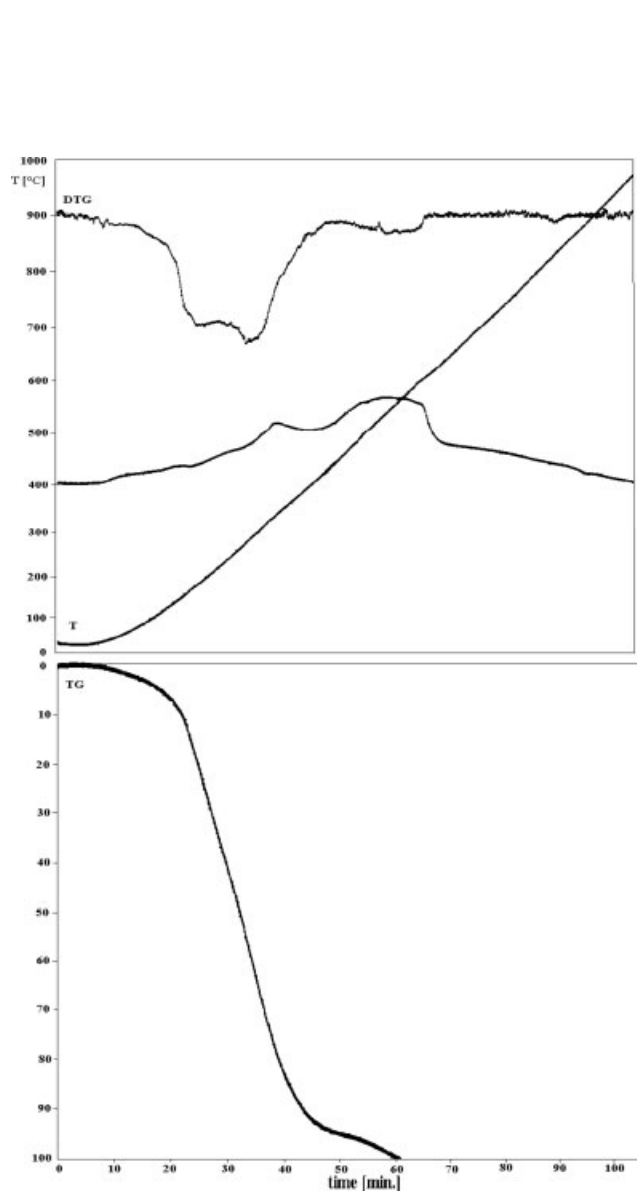


Figure 5 Thermal analysis of the product of reaction obtained from HMBA : EO = 1 : 10 substrate mixture.

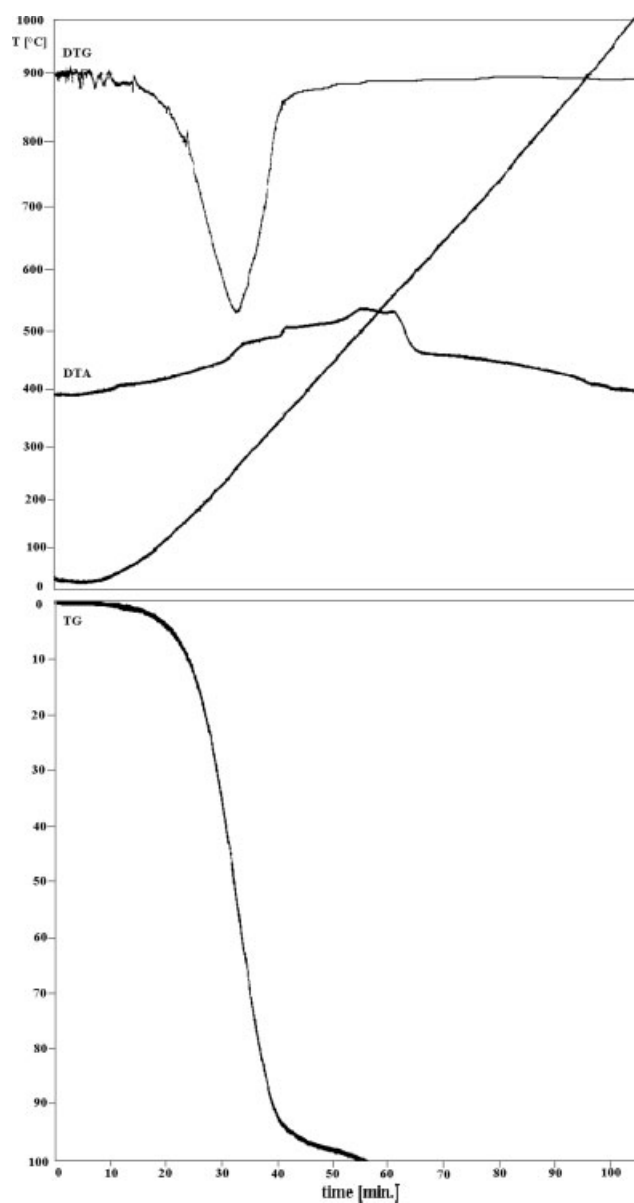


Figure 6 Thermal analysis of the product of reaction obtained from HMBA : EO = 1 : 18 substrate mixture.

TABLE IV
Interpretation of MALDI ToF Spectrum of Reaction Product Obtained from 1 mole of HMKB and 10 moles of EO

No.	Signal position M/z	Relative intensity of signal [%]	The molecular ion structure	Calc. molecular weight (g/mol)
1.	85.2	< 5	EG+Na ⁺	85.1
2.	137.1	10	DEG+CH ₃ OH	138.2
3.	163.1	< 5	DEG+CH ₃ OH+Na ⁺	161.2
4.	190.2	100	BA+CH ₂ O+CH ₃ OH	190.2
5.	191.2	20	BA+CH ₂ O+CH ₃ OH+H ⁺	191.2
6.	206.2	10	TEG+CH ₃ OH+Na ⁺	205.2
7.	220.3	58	BA+2CH ₂ O+CH ₃ OH	220.2
8.	234.3	65	BA+CH ₂ O+EO+CH ₃ OH	234.2
9.	247.1	< 5	BA+CH ₂ O+2 EO	246.2
10.	250.3	20	TeEG+CH ₃ OH+Na ⁺	249.2
11.	264.3	40	BA+3CH ₂ O+EO	262.2
13.	265.3	10	BA+2CH ₂ O+EO+H ⁺ +CH ₃ OH	265.2
14.	278.3	18	BA+2CH ₂ O+2 EO	276.2
15.	279.3	5	BA+4CH ₂ O+CH ₃ OH	280.2
16.	294.3	25	BA+3CH ₂ O+EO+CH ₃ OH	294.3
17.	308.4	18	BA+3CH ₂ O+2 EO	306.3
18.	309.3	< 5	BA+CH ₂ O+3 EO+CH ₃ OH	310.3
19.	324.4	5	BA+CH ₂ O+4 EO	322.3
20.	338.4	15	BA+3CH ₂ O+2 EO+CH ₃ OH	338.3
21.	352.4	< 5	BA+2CH ₂ O+3 EO+CH ₃ OH	352.3
22.	368.4	5	BA+5CH ₂ O+2 EO+H ⁺	367.3
23.	382.4	< 5	BA+4CH ₂ O+3 EO	380.4
24.	422.3	< 5	BA+4CH ₂ O+4 EO	424.4
25.	468.5	< 5	BA+4CH ₂ O+5 EO	468.5
26.	513.4	< 5	BA+4CH ₂ O+6 EO	512.5
27.	550.8	< 5	BA+3CH ₂ O+7 EO+Na ⁺	549.5
28.	668.8	8	BA+4CH ₂ O+9 EO+Na ⁺	667.7
29.	696.8	< 5	BA+5CH ₂ O+9 EO+Na ⁺	697.7

EG, ethylene glycol; DEG, diethylene glycol; TEG, triethylene glycol; TeEG, tetraethylene glycol; EO, oxyethylene unit; CH₂O, oxymethylene unit.

lene glycol (for the system with EO) and tripropylene glycol (for the system with PO).

Analysis of side products

Products obtained in the reactions between HMBA and oxiranes were analyzed using gas chromatography to determine diols (glycols) content and products of consecutive reaction products with water (polyglycols). Determination was performed after initial removal of TEA from postreaction mixtures. The results are collected in Table V. It has

been found that diol and consecutive side-products percentages in case of the polyetherols obtained from EO was lower than 12 wt %, while in case of PO it was lower than 18.5 wt %. The percentage of side-products increased significantly upon increase of PO equivalents from 10 to 12. Further increase of number of equivalents of PO did not influence the side-product or diols. Consistently the presence of glycols and polyglycols led to diminished hydroxyl numbers of polyetherols in comparison with that calculated based upon initial mass of reactants (cf. Table I).

TABLE V
Side Products Formed in the Reaction of HMBA with Oxiranes

Oxirane	HMBA : oxirane molar ratio	Products of reaction of oxiranes with water (wt %)					Polyetherols (wt %)
		I	II	III	IV	Σ%	
EO	1 : 18	1.0	2.2	3.4	6.0	11.6	88.4
PO	1 : 10	4.0	3.1	7.0		14.1	85.9
	1 : 12	3.7	4.8	10.0		18.5	81.5
	1 : 18	2.9	3.1	11.3		17.3	82.7

I, II, III, IV, the subsequent products of reaction of oxiranes with water; Σ%, total percentage of side products obtained in reaction between oxiranes and water.

TABLE VI
Some Properties of Polyurethane Foams Prepared from Polyetherols Obtained in Reaction of HMBA with PO

Molar ratio HMBA : PO in polyetherol	Composition No.	Amount of cosubstrate ^a (g/100 g polyetherol)		Apparent density (kg/m ³)	Water uptake (wt%)	Linear shrinkage (%)	Thermal stability measured as the weight loss (wt %) at plateau temperature after month			Compressive strength (MPa)			
		Isocyanate	Water				Catalyst	150°C	175°C	200°C	Before exposure	After Exposure at: 150°C	175°C
1 : 10	1.	108	2	0.8	8.76	2.1	2.66	2.57	9.43	0.1200	0.1468	0.1486	0.2338
	2.	120	2	0.8	8.97	10.2	29.0	40.3	47.4	0.1053	0.1398	0.1285	0.1428
1 : 12	3.	98	2	1.0	9.07	4.8	36.5	45.1	51.8	0.1669	0.1465	0.2569	0.1036
	4.	112	2	1.0	8.48	4.6	31.3	41.4	48.8	0.1414	0.1731	0.1989	0.2206
1 : 18	5.	102	2	1.6	7.83	4.2	31.0	41.8	49.6	0.1750	0.2380	0.2070	0.2074

^a The surfactant SILIKON 5340 was introduced into the reaction mixture at the level of 1 g/100 g polyetherol at the beginning of synthesis.

Preparation of polyurethane foams

The polyetherols based on HMBA were used to prepare polyurethane foams on a laboratory scale. It has been found that stiff polyurethane foams were obtained from polyetherols and PO, while semirigid foams were obtained from polyetherols synthesized from HMBA and EO, which was slightly surprising. The latter foams became elastic at temperature above 100°C. All foams were flammable. The apparent density of stiff foams falls into 44–48 kg/m³ (Table VI). Water uptake of those products is comparable with that of foams containing 1,3,5-triazine rings and falls into the region of 7.8–9.1 wt %.¹³ Thermal stability of products was studied at 150, 175, and 200°C temperatures by measurements of mass loss with simultaneous determination of mechanical properties. The foams were heated for 1 month. The continuous mass loss was observed during this period of time. One should notice that all samples became more rigid after thermal treatment and in most cases, had a higher compression strength (Table VI).

CONCLUSIONS

Simple method of synthesis of polyetherols with pyrimidine ring is based on reaction of HMBA with oxiranes, like EO or PO. The reaction proceeds in neat oxirane. Thus the synthetic protocol allowed to avoid organic solvents. The polyetherols with pyrimidine ring are useful substrates for formation of polyurethane foams of enhanced thermal stability.

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