Application of Glycidol in Synthesis of Oligoetherols with Perhydro-1,3,5-Triazine Ring

Karina Cyzio, Jacek Lubczak

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

ABSTRACT: A new method of preparation of oligoetherols containing perhydro-1,3,5-triazine rings from isocyanuric acid and an excess of glycidol, alkylene carbonates, or oxiranes is presented. The course of reaction was studied at various molar ratios of glycidol to isocyanuric acid. The structure of the products was established, and some physical properties were measured. The oligoetherols were demonstrated to be useful substrates for polyurethane foams of enhanced thermal stability. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 417–426, 2011

Key words: heteroatom containing polymer; synthesis; oligomers; structure; polyurethanes

INTRODUCTION

In reactions of isocyanuric acid (IA) with an excess of oxirane, such as ethylene oxide (EO) or propylene oxide (PO), trifunctional oligoetherols containing perhydro-1,3,5-triazine rings can be obtained[1,2]
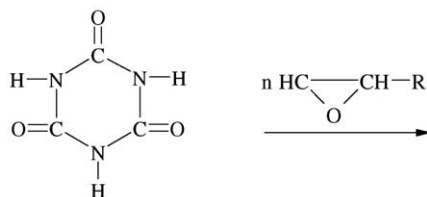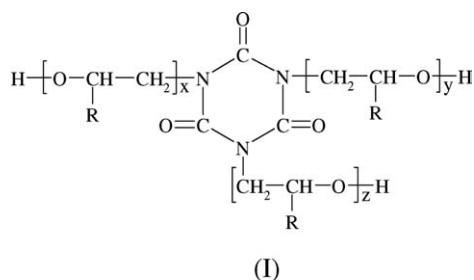

where: R = –H, –CH₃, –CH₂Cl

$$x + y + z = n$$

(I)

Compounds (I) are suitable reagents for isocyanates in preparation of polyurethane foams. The presence of perhydro-1,3,5-triazine rings substantially improves thermal stability of the resulting products.[3,4]

The main complication in the synthesis of oligoetherols (I) is the lack of feasible solvents providing sufficient solubility of IA. The latter is insoluble in most solvents, but in dimethylsulfoxide (DMSO) and water, it dissolves only slightly. For practical reasons, the reactions of IA with oxiranes are carried out in DMSO, since oxiranes readily react with water yielding respective glycols and polyglycols. Furthermore, the solvent has to be removed from final products by distillation. Distillation usually leads to partial decomposition of the high boiling solvent and hence contamination of oligoetherols with products of the decomposition that have unpleasant odor.

An alternative method of preparing polyetherols from IA was described in literature.[5,6] The method involves a reaction of the acid with formaldehyde to obtain N,N′,N″-tris(hydroxymethyl) isocyanurate (THMI). The latter dissolves well in oxiranes in the presence of a small amount of water and hence no additional solvents are needed. The reaction scheme can be represented as follows[5]:

Correspondence to: J. Lubczak (jml@prz.edu.pl).

where: $3n + 2w = 3$, $x + y + z = r$.　　　(II)
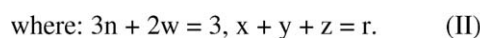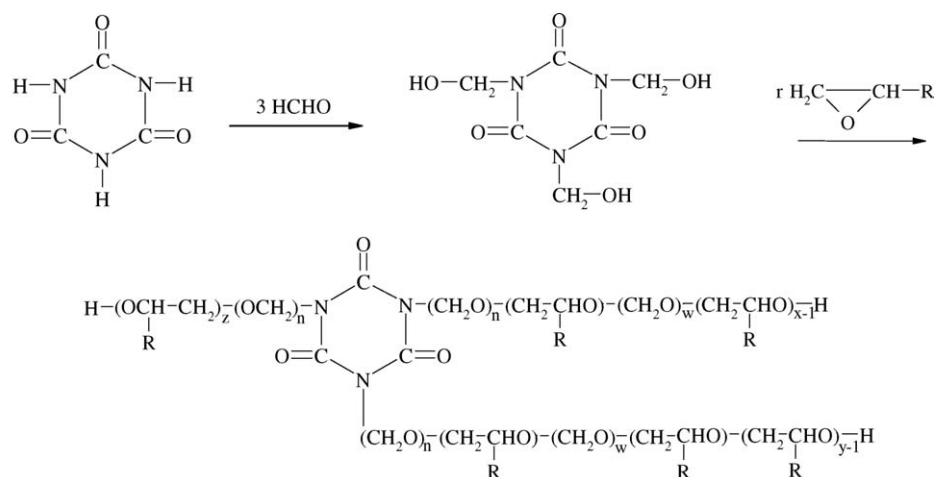
The disadvantage of the method is that hydroxymethyl groups blocked by just one hydroxyalkyl unit of oxirane tend to release formaldehyde. The latter then migrates to the end of etherol chain. Therefore, to prevent formaldehyde release, one has to use large excess of EO or PO rather than direct reaction of oxirane with unmodified IA.

Thus, the more convenient methods of synthesis of oligoetherols are still a target. The best choice would be a method excluding solvents, i.e., the protocol based on straightforward reaction of the acid and hydroxyalkylating agent. The reaction of IA with glycidol (GL) might have obeyed such a condition. There was not much information on the subject in literature.[7,8] It has been stated that the reaction of one equivalent of IA with three equivalents of GL led to product III (where $n = 3$ and $x = y = z = 1$):

(III)
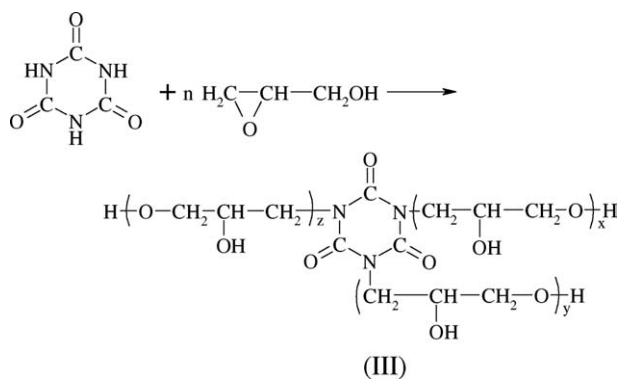
identified by elemental analytical results.[7]

Here the detailed studies on GL-based method of preparation of semiproducts containing perhydro-1,3,5-triazine ring as precursors for synthesis of oligoetherols useful substrates for foamed polyurethanes of enhanced thermal stability are presented.

EXPERIMENTAL

Syntheses

Reaction of isocyanuric acid with glycidol at $1 : 1 \div 1 : 4$ molar ratio

6.4 g (0.05 mol) of IA (pure, Fluka, Buchs, Switzerland) was placed together with 3.7 g (0.05 mol), 7.4 g (0.10 mol), 11.1 g (0.15 mol), or 14.8 g (0.02 mol) of GL (pure, ç-Aldrich, Steinheim, Germany) in a three-necked 250 cm^3 flask equipped with mechanical stirrer, thermometer, and reflux condenser. The mixture was heated to 145–150°C. In all cases, the exothermic effect caused initial increase of temperature to 190°C. Further, the process was conducted at 175°C up to disappearance of GL ($\sim$ 15 min). Then the reaction mixture was cooled down to 50°C, 40 cm^3 of water was added, and the mixture was heated shortly to boiling. The reaction mixture was cooled to room temperature resulting in precipitation of insoluble products (containing predominantly IA), which were filtered off, washed with acetone, and dried in vacuum to constant mass at 90°C. The removal of water from filtrates resulted in isolation of resin-like products from it. The acid number and epoxide number were determined in solid and resin products.

Reactions of isocyanuric acid with glycidol at $1 : \geq 4$ molar ratio

9.6 g (0.075 mol) of IA and appropriate amount of GL 22.2–55.5 g (0.30–0.75 mol) were placed in three-necked 100 cm^3 flask equipped with mechanical stirrer, reflux condenser, and thermometer, and the temperature of the mixture was gradually increased to 110°C. The temperature increased spontaneously to 150°C without further heating. The mixture was maintained at 150°C for 1.0–1.5 h with cooling system.

After the exothermic process ceased, the mixture was kept at 150°C for next 15 min up to completion of the reaction as determined by epoxide number.

Reactions of obtained semiproduct with oxiranes

28.05 g (0.05 mol) of semiproduct, in which the molar ratio IA : Gl was 1 : 6, 2 cm^3 triethylamine (pure, Fluka, Buchs, Switzerland) as catalyst, and 17.4 g (0.03 mol) of propylene oxide (pure, Fluka, Buchs, Switzerland) were placed in pressure reactor of 250-cm^3 capacity. The reactor was closed, the content was mixed, heated to 80°C, and maintained until completion of reaction (determined by epoxide number). After ca 20 h, the catalyst was removed under reduced pressure ($t = 120°C$, $p = 20–27$ hPa; 15–20 mmHg).

Remark: the similar protocol was used when EO was applied.

Reactions of obtained semiproduct with ethylene or propylene carbonates

42.9 g (0.075 mol) of product of reaction between IA and GL at IA : GL = 1 : 6 molar ratio, 39.6 g (0.45 mol) ethylene carbonate (EC, pure, Fluka, Buchs, Switzerland) or 45.9 g (0.45 mol) propylene carbonate (PC, pure, Fluka, Buchs, Switzerland), and 0.1 g or 0.3 g potassium carbonate (pure, POCH, Gliwice City, Poland) as catalyst were placed in three-necked 100 cm^3 flask equipped with mechanical stirrer, reflux condenser, and thermometer. The mixture was heated to 150°C and maintained in that temperature with stirring for 23 h. The reaction progress was monitored by determination of alkylene carbonate in the mixture.

Analytical methods

The course of reaction between IA and GL was followed by measuring the content of unreacted epoxide groups by hydrochloric acid method in dioxane.[9] The course of reaction between semiproduct and EC or PC was followed by measuring the content of unreacted alkylene carbonate. The sample was then treated with 2.5 cm^3 of 0.15M barium hydroxide, vigorously shaken, and the excess of barium hydroxide was titrated with 0.1M HCl solution.[10] In obtained products, the acid numbers were determined by titration with a standard potassium hydroxide solution. Elemental analysis for C, H, N were done with EA 1108, Carlo-Erba analyzer. The ^{1}H-NMR spectra of products were recorded at 500 MHz Bruker UltraShield in DMSO-d$_6$ with hexamethyldisiloxane as internal standard. IR spectra were registered on PARAGON 1000 FT IR Perkin–Elmer spectrometer in KBr pellets or ATR technique. MALDI ToF (Matrix-Assiated Laser Desorption Ioni-

zation Time of Flight) of oligoetherols were obtained on Voyager-Elite Perceptive Biosystems (US) 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/cm^3 concentration. The samples were diluted with methanol to 1 mg/cm^3, followed by 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$_3$OH.

Thermal analyses of oligoetherols and foams (DTA, DTG, and TG) were performed in ceramic crucible at 20–600°C temperature range, about 200-mg sample, under air atmosphere with Termowaga TGA/DSC 1 derivatograph, Mettler.

Physical properties of oligoetherols

Refraction index, density, viscosity, and surface tension of oligoetherols were determined with Abbe refractometer, picnometer, Höppler viscometer (typ BHZ, prod. Prüfgeratewerk, Germany) and by the detaching ring method, respectively.[11]

Foam preparation

Foaming tests were conducted on laboratory scale in 250-cm^3 paper cups at room temperature. In details, oligoetherol (10 g) was mixed with 0.1 g of Silicone 5340 (pure, Houdry Hüls, Marl, Germany) as surfactant, the triethylamine catalyst (1–3 wt %), and water (2–3 wt %) with respect to oligoetherols. Diphenylmethane 4,4'-diisocyanate (MDI, pure, Merck, Darmstadt, Germany; containing 30% of trifunctional isocyanates) 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 foam

The following properties of foam were studied: apparent density,[12] water uptake,[13] linear shrinkage estimated on the basis of the change of linear dimension of the sample heated for 4 h at 100°C,[14] flammability, thermal stability as the weight loss at 150, 175, and 200°C within one month, and compression strength.[15]

RESULTS AND DISCUSSION

Reaction of isocyanuric acid with glycidol

IA reacts with GL upon heating the reaction mixture to 145–150°C. The exothermic reaction occurs fast without catalyst. When the molar ratio of reagents IA : GL = 1 : 1 to 1 : 3, the postreaction mixture consists of precipitate of unreacted IA and resin

TABLE I
Analysis of Reactions Products of IA with GL

Molar ratio IA : GL	Composition of initial mixture (wt %)		Postreaction mixture (wt %)		Acidic number (mg KOH/g)	
	IA	GL	Solid Residue	Resinous product	Solid residue	Resinous Product
1 : 1	63.2	36.8	45.8	54.2	415	57.4
1 : 2	46.2	53.8	15.2	84.8	386	34.9
1 : 3	36.4	63.6	6.4	94.6	188	29.7
1 : 4	30.0	70.0	0.0	100	–	6.15
1 : 6	22.5	77.5	0.0	100	–	3.45

Comment: The epoxide number of every resin was equal zero.

products. When amount of GL increases, the yield of solid product drops down; when molar ratio IA : GL = 1 : 4, the sole product is the resin (Table I).

The progress of reaction between IA and GL was followed by ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectrum of IA consists of one averaged resonance of all imide groups proton at 11.4 ppm. The ^{1}H-NMR spectra of resin products obtained at IA : GL 1 : 1–1 : 4 systems are similar to each other. The absence or very low intensity of imide proton resonance of IA substrate clearly demonstrates that the IA is reacted almost completely (Fig. 1). The resonances attributed to methylene group protons at N—CH_2 and CH_2—OH 3.7 ppm and 3.35 ppm as well as methine proton resonance $CH(OH)$ at 3.8 ppm are present. The hydroxyl proton resonances appear at 4.55 ppm (from primary hydroxyl group) and 4.75 ppm (from secondary hydroxyl group). Their integral intensity ratio is 1 : 1, which corroborates well with structure of product III, where $x = y = z = 1$. The low intensity resonance at 4.95 ppm was attributed to proton of associated hydroxyl groups. The integral intensity ratio of resonances of —OH : N—CH_2 : —CH_2OH : CH is 2 : 2 : 2 : 1, which is consistent with formula III, where $x = y = z = 1$. The elemental analytical data correspond to
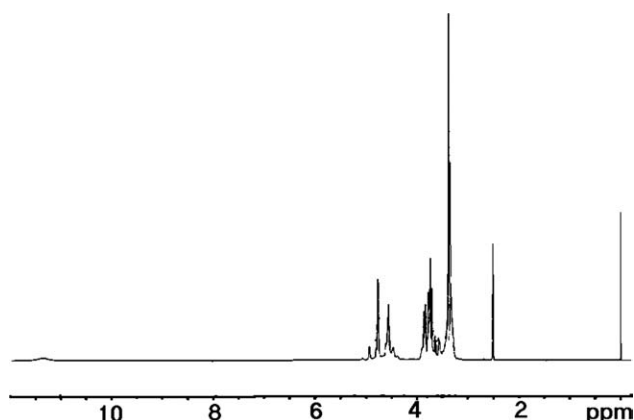
III. Thus, the resin product is formed independent on molar ratio of GL/mol IA, and the ratio of IA : GL is 1 : 3 in this product (Table II). The formation of tris(2,3-dihydroxyalkyl) derivative of IA, obtained in the reaction between IA and slight excess of GL, is additionally confirmed by the comparison of calculated and experimentally found mass of precipitated IA. Thus, if assumed that 1 mol of IA (129 g) reacts with 3 mol of GL (222 g), at initial molar ratio IA : GL = 1 : 1, 43 g of IA should be consumed to form this derivative. The resulting mass of the resin is as follows: 43 g + 74 g = 117 g, and the amount of unreacted IA in this system is: 129 g − 43 g = 86 g. The mass of postreaction mixture is 86 g + 117 g = 203 g. The percentage of unconsumed IA in postreaction mixture should be: (86/203) 100% = 42.4%. This corresponds to mass of precipitate isolated (40.9%). Similar mass balance for IA : GL = 1 : 2 system gives 15.5% of unreacted IA (exp.14.8%). The analysis of precipitates formed at 1 : 1 to 1 : 4 IA: GL systems indicated that they are mostly composed of unreacted IA by the presence of imide proton resonance at 11.4 ppm in ^{1}H-NMR spectrum. The signal disappeared upon addition of deuterium oxide. The presence of minor resonances at 3.7 and 3.35 ppm as well as at 4.5–4.9 ppm assigned to hydroxyalkyl derivatives of IA are also present. Therefore, the precipitates have slightly lower value of acid number than IA (434.8 mg KOH/g), and the acid number decreases upon increase of amount of GL in starting reaction mixture (Table I). The precipitate-free product was obtained at IA : GL = 1 : 4

Figure 1 ^{1}H-NMR spectrum of the resinous product obtained in molar ratio IA : GL = 1 : 1.

TABLE II
Elemental Analysis of Resinous Products Obtained After Reaction IA with GL

Molar ratio IA : GL	1 : 3	1 : 1	1 : 2	1 : 3
Composition\Element content (wt %)	Calculated (wt %)	Found (wt %)	Found (wt %)	Found (wt %)
N	11.96	11.04	11.02	11.13
C	41.03	41.45	41.29	41.59
H	5.98	5.63	6.11	6.24

TABLE III
Some Physical Properties of Oligoetherols Obtained from IA, GL, Alkylene Carbonates, or PO in the Temperature Range 20–80°C

Initial molar ratio IA : GL : EC : PC (or PO)	Temperature (°C)	Refractive index n_{20}^D	Density d (g/cm³)	Viscosity η (N·s/m²) × 10³	Surface Tension τ (N/m) × 10³
1 : 6 : 0 : 0	20	1.5148	1.3465	631,100	–
	30	1.5120	1.3407	146,220	–
	40	1.5090	1.3334	39,420	33.34
	50	1.5069	1.3264	13,417	50.82
	60	1.5038	1.3194	4734	47.74
	70	1.5016	1.3124	2077	45.92
	80	1.4988	1.3067	945	45.22
1 : 9 : 0 : 0	20	1.5106	1.3406	521,100	–
	30	1.5098	1.3346	135,320	–
	40	1.5068	1.3273	39,720	56.98
	50	1.5041	1.3203	13,693	54.74
	60	1.5021	1.3134	5003	53.34
	70	1.4995	1.3066	2209	51.66
	80	1.4970	1.3001	1009	48.30
1 : 6 : 6 : 0	20	1.4981	1.2803	17,220	52.64
	30	1.4957	1.2746	6399	49.70
	40	1.4937	1.2688	2549	48.30
	50	1.4908	1.2607	1075	47.18
	60	1.4880	1.2540	538	45.78
	70	1.4850	1.2469	298	44.94
	80	1.4823	1.2391	168	44.24
1 : 6 : 0 : 6	20	1.4869	1.2030	16,968	46.90
	30	1.4850	1.1969	6146	45.64
	40	1.4815	1.1898	2448	44.24
	50	1.4877	1.1824	1019	42.70
	60	1.4759	1.1749	523	41.44
	70	1.4723	1.1681	274	40.04
	80	1.4691	1.1592	154	39.34
1 : 6 : 0 : (6)	20	1.4888	1.2194	32,350	46.76
	30	1.4869	1.2133	23,548	45.36
	40	1.4834	1.2062	7193	43.96
	50	1.4808	1.1992	2775	42.56
	60	1.4776	1.1924	1133	41.30
	70	1.4748	1.1862	667	41.02
	80	1.4709	1.1787	266	40.04

system. The resin products have very low value of acid number, which suggests the presence of minor amount of unreacted IA, as confirmed by ^{1}H-NMR spectra. The products are clear, semisolid light-brown resins with epoxide number equal zero indicating the absence of unreacted GL. This also indicates that in studied systems no reaction between imide groups and hydroxyl groups of GL occurs.

When larger amount of GL was used in synthesis (IA : GL 1 : 9), the viscosity of obtained oligoetherols was too large (Table III) to use them further for mixing with isocyanates and conversion to polyurethane foams. They were however convenient for further reaction with oxiranes such as EO and PO, because they were readily miscible with oxiranes at 60°C in pressure reactor. In presence of catalysts such as triethylamine, they reacted to form multifunctional oligoetherols of lower viscosity, which could be used further for synthesis of polyurethane foams. The

reaction involving EO or PO required pressure reactor because of low boiling point of EO or PO (14°C and 34°C, respectively). According to method of conversion of IA with EO or PO without solvent, the solvent-free method was earlier optimized (cf. Experimental—Syntheses—Reactions of obtained semiproduct with oxiranes). The straightforward reaction between IA and GL and further with oxiranes allows to obtain oligoetherols of higher degree of functionality than that based on reaction of IA with oxiranes. The obtained oligoetherols react readily with multifunctional isocyanates to form polyurethane foams with perhydro-1,3,5-triazine ring.

Our studies on synthesis of oligoetherols was performed using alkylene carbonates instead of oxiranes,[16–18] which are convenient hydroxyalkylating agents leading to the analogous products as those formed in the reaction with oxiranes according to the scheme:

TABLE IV
Elemental Analysis of Products Obtained in Reaction of IA with GL and Alkylene Carbonates or Oxiranes

Molar ratio IA : GL : EC : PC (or PO)	Element content (wt %)					
	Calculated			Found		
	N	C	H	N	C	H
1 : 4 : 0 : 0	9.88	42.35	6.35	9.47	42.35	5.98
1 : 6 : 0 : 0	7.33	43.98	6.81	7.56	43.89	6.54
1 : 9 : 0 : 0	5.28	45.28	7.17	5.16	45.52	6.80
1 : 6 : 6 : 0	5.02	47.31	7.53	5.04	47.51	7.24
1 : 6 : 0 : 6	4.56	50.81	8.14	4.84	50.69	8.44
1 : 6 : 0 : (6)	4.56	50.81	8.14	4.71	50.70	8.32
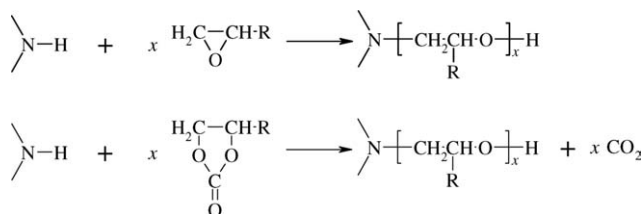
The alkylene carbonates are advantageous reagents in comparison with oxiranes, because they are nontoxic and nonflammable and do not require pressure reactors.
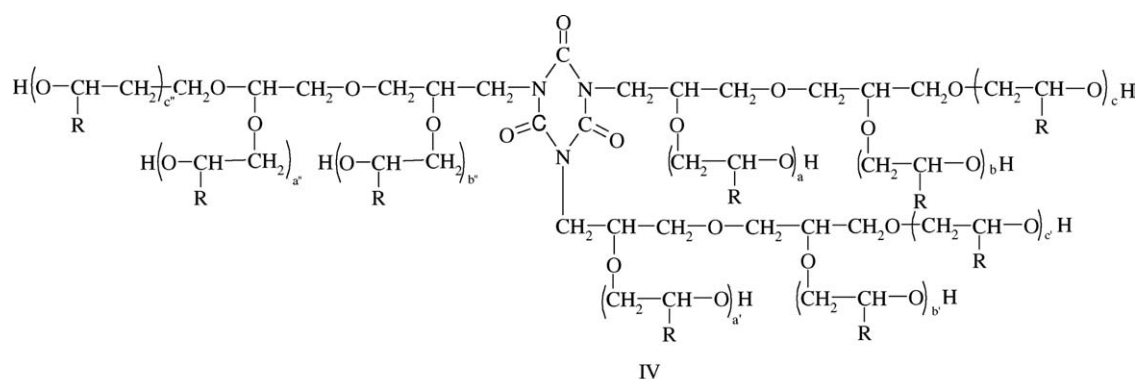
where: R = -H, CH$_3$

a, a$'$, a$''$, b, b$'$, b$''$, c, c$'$, c$''$ – number of oxyalkylene units formed from EC or PC

Reactions of semiproduct with alkylene carbonates

The semiproduct obtained from the IA : GL 1 : 6 was used for the reaction with alkylene carbonates. The semiproduct is nonfunctional because of the presence of hydroxyl groups (cf. formula III with $x + y + z = 6$). The reaction according to the stoichiometry of at least six equivalents of alkylene carbonate per one equivalent of the obtained semiproduct leads to the oligotherols miscible with isocyanates. The composition and structure of products exemplified by formula IV is confirmed by elemental analysis (Table IV), ^{1}H-NMR, and IR spectra. In the ^{1}H-NMR spectrum of product of reaction IA : GL = 1 : 6, the increase of integral intensity of the resonances at 3.35 and 3.7 is observed in comparison with that of the resin obtained from the IA : GL = 1 : 3 system according to the increase of amount of methylene
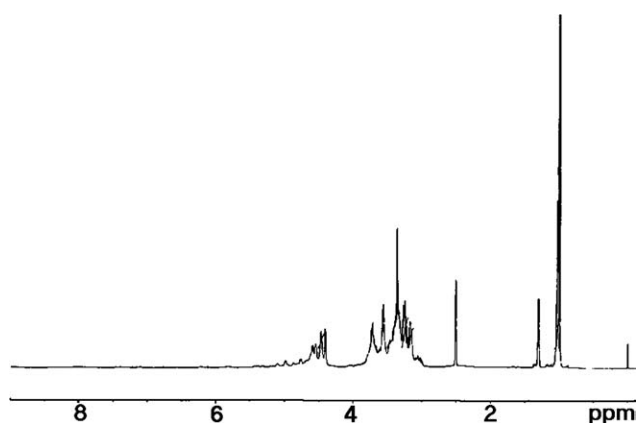

Figure 2 ^{1}H-NMR spectrum of the product obtained in molar ratio IA : GL : PC = 1 : 6 : 6.
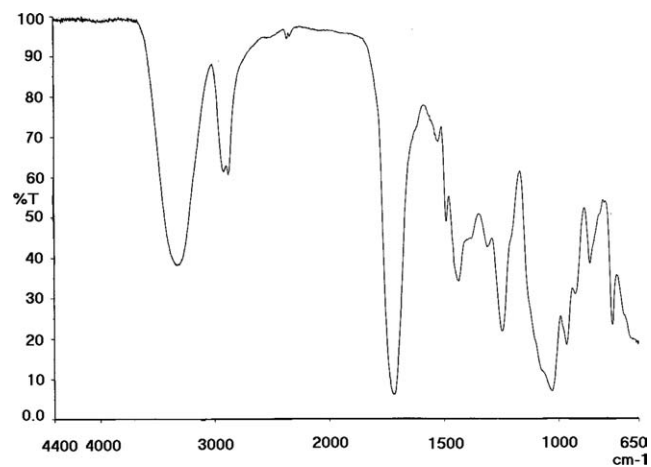
Figure 3 IR spectrum of the product obtained in molar ratio IA : GL = 1 : 6.

Figure 4 IR spectrum of the product obtained in molar ratio IA : GL : EC = 1 : 6 : 6.

groups attached to hydroxyl groups as well as number of methine groups CH(OH) in the product. Within the 4.5–4.9 ppm region, the number and intensity of resonances attributed to primary and secondary hydroxyl groups increases (the hydroxyl groups are located statistically within oxyalkylene chains). These resonances disappear upon deutera-
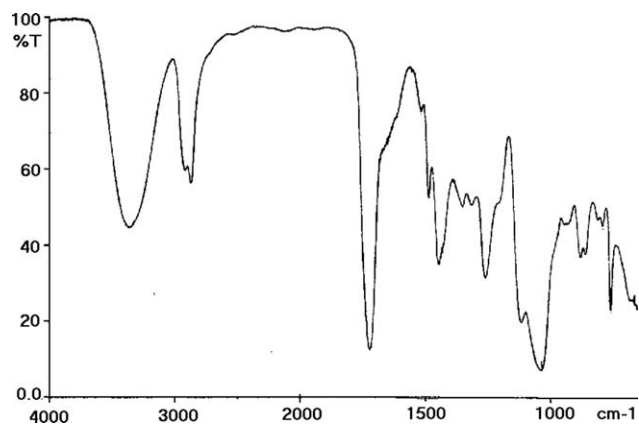
tion with D_2O. In the ^{1}H-NMR spectra of products obtained from IA : GL = 1 : 6 and EC or PC, the methylene group resonances of oxyalkylene chains at ca 3.45 ppm appear illustrating the reaction of semiproduct with alkylene carbonates. Additionally, in the product of reaction with PC (Fig. 2), the resonances at 0.95 ppm the additional methyl proton resonance can be observed (formula IV, where R =

TABLE V
Interpretation of MALDI ToF Spectrum of Reaction Product Obtained from 1 mol of IA and 4 mol of GL

Signal position m/z	Relative intensity of signal (%)	The molecular ion structure	Calc. molecular weight (g/mol)
184.9	100	IA + GL − H_2O	185
209.0	39	(IA + GL − H_2O) + Na^+	208
240.1	40	(IA + GL − H_2O) + CH_3OH + Na^+	240
316.2	28	(IA + 3GL − $2H_2O$) + H^+	316
334.1	46	(IA + 3GL − $2H_2O$) + H^+	334
352.1	16	(IA + 3GL) + H^+	352
376.1	12	(IA + 3GL) + Na^+	374
408.1	19	(IA + 4GL − H_2O) + H^+	408
425.1	15	IA + 4GL	425
450.1	10	(IA + 4GL) + Na^+	448
499.1	17	IA + 5GL	499
500.1	9	(IA + 5GL) + H^+	500
506.2	5	(IA + 5GL − H_2O) + Na^+	504
524.1	10	(IA + 5GL) + Na^+	522
573.1	13	IA + 6GL	573
574.1	7	(IA + 6GL) + H^+	574
596.2	6	(IA + 6GL) + Na^+	596
610.1	8	(IA + 6GL − H_2O) + CH_3OH + Na^+	610
647.1	9	IA + 7GL	647
670.1	6	(IA + 7GL) + Na^+	670
744.2	5	IA + 8GL + Na^+	744
832.2	3	(IA + 9GL − H_2O) + CH_3OH + Na^+	832
875.2	3	(IA + 10GL − H_2O) + Na^+	874
892.1	5	(IA + 10GL) + Na^+	892
943.2	3	IA + 11GL	943
980.4	4	(IA + 11GL − H_2O) + CH_3OH + Na^+	980
1017.4	3	IA + 12GL	1017

GL—oxyalkylene unit from GL.

TABLE VI
Interpretation of MALDI ToF Spectrum of Reaction Product Obtained from 1 mol of
Semiproduct IA : GL = 1 : 6 and 6 mol of EC

Signal position m/z	Relative intensity of signal (%)	The molecular ion structure	Calc. molecular weight (g/mol)
206.0	21	(IA + GL) + H$^+$	204
207.0	100	(IA + GL $-$ H$_2$O) + Na$^+$	208
274.0	65	(IA + GL) + CH$_3$OH + K$^+$	274
280.1	37	(IA + GL + OE) + CH$_3$OH + H$^+$	280
310.1	15	(IA + 2GL) + CH$_3$OH + H$^+$	310
316.3	3	(IA + GL + 2OE) + Na$^+$	314
341.3	28	(IA + 2GL + OE $-$ H$_2$O) + K$^+$	342
341.3	28	(IA + 2GL + OE) + Na$^+$	344
360.1	27	(IA + 2GL + OE $-$ H$_2$O) + CH$_3$OH + Na$^+$	358
379.2	17	(IA + 3GL + OE $-$ H$_2$O) + H$^+$	378
400.2	12	(IA + 3GL + 2OE $-$ H$_2$O) + Na$^+$	400
404.2	22	(IA + 2GL + 2OE) + K$^+$	404
409.2	14	IA + 2GL + 3OE	409
411.2	14	(IA + 2GL + 3OE) + H$^+$	410
434.2	12	(IA + 2GL + 2OE) + CH$_3$OH + K$^+$	436
448.2	9	(IA + 3GL + OE $-$ H$_2$O) + CH$_3$OH + K$^+$	448
453.1	7	IA + 2GL + 4OE	453
478.1	6	(IA + 3GL + 2OE $-$ H$_2$O) + CH$_3$OH + Na$^+$	476
508.1	5	(IA + 4GL + OE $-$ H$_2$O) + CH$_3$OH + Na$^+$	506
508.1	5	IA + 3GL + 4OE $-$ H$_2$O	509
552.1	4	(IA + 3GL + 3OE) + CH$_3$OH + K$^+$	554
601.1	3	IA + 4GL + 4OE	601
626.1	3	(IA + 4GL + 4OE) + Na$^+$	624
626.1	3	(IA + 4GL + 3OE) + CH$_3$OH + K$^+$	628
638.1	8	(IA + 6GL + OE) + Na$^+$	640
666.1	6	(IA + 6GL + 2OE $-$ H$_2$O) + Na$^+$	666

GL—oxyalkylene unit from GL.
OE—oxyethylene unit (from EC).
ion K$^+$ comes from molecules of catalyst K$_2$CO$_3$.

CH$_3$). The minor resonance at 1.3 ppm indicates the presence of product of abnormal PC ring opening[17]:

$$\overset{|}{\underset{\underset{CH_3}{|}}{C}}H - CH_2 - OH$$
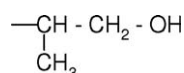
The integration of this resonance indicated that the percentage of this structure is around 13%.

The ^{1}H-NMR spectrum of oligoetherol obtained from semiproduct synthesized in IA : GL = 1 : 6 system with 6 mol of PO is similar in the 3.0–3.8 ppm region. Within the 0.95 to 1.3 ppm, additional signals from methylene protons in the oxyalkylene chains (at 1.2 and 1.3 ppm) are present. All hydroxyl protons resonate as 4.5 ppm suggesting the intermolecular hydrogen bonds. This leads to high viscosity of obtained product in comparison with that obtained from PC (Table III).

In the IR spectra of products obtained from IA and GL (Fig. 3), the carbonyl bond stretching vibration of IA is observed at 1720 cm^{-1}, while the triazine ring skeleton bands are found at 763 cm^{-1}. The presence of these bands indicates the presence of the ring in the structure of synthesized oligoetherols. Moreover, strong band centered at 1030 cm^{-1} is attributed to ether C—O—C fragment formed at lower than 1 : 3 molar ratio of IA : GL. The valence and deformation O—H bands are present at 3325 and 1100 cm^{-1}, respectively. Such bands are also present in the IR spectra of products obtained from EC and PC (Fig. 4). Similar tendencies are observed in the H-NMR and IR spectra of products of reaction between oxiranes with semiproduct obtained from the IA : GL = 1 : 6 system.

The MALDI-TOF spectra are consistent with the structure of products of hydroxy-alkylation of IA with GL. In these spectra, the molecular peaks differing by $m/z = 74$ are observed, which indicates consecutive incorporation of oxyalkylene units from GL into oligomers. In the product of reaction in the IA : GL 1 : 4 (Table V) system various derivatives of variable degree of substitution of IA with GL are present. In the spectra of products obtained from EC or PC, additional peaks differing of $m/z = 44$ (Table VI) and 58 are observed, indicating the presence of oxyethylene and oxypropylene units. Also, the products of water elimination from products and semiproducts, i.e., from products of reaction between IA with both GL and alkylene carbonates, are present as it has been deduced on the basis of detailed analysis of the spectra.
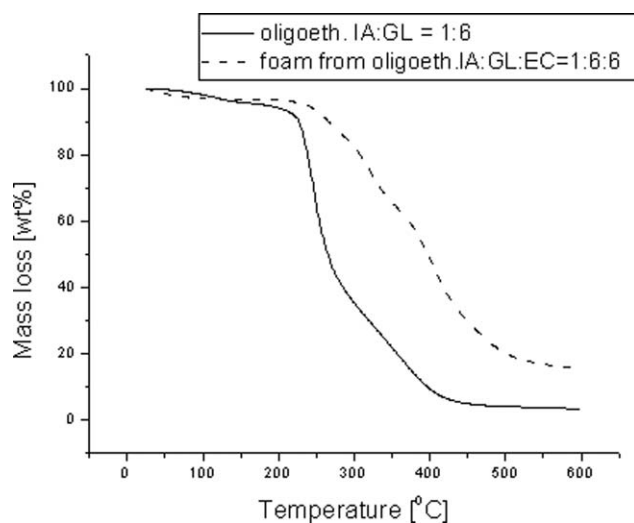
Figure 5 Thermal analysis of semiproduct IA : GL = 1 : 6 and polyurethane foam obtained from oligoetherol IA : GL : EC = 1 : 6 : 6.

The elimination process is minor pathway as can be concluded from the H-NMR spectra, in which the resonances of unsaturated fragments at 4.8–4.2 and 5.6–6 ppm have low intensity or are absent. The products of elimination are not observed in the mass spectra of semiproduct converted with oxiranes because of lower temperature of synthesis.

Thermal analysis of obtained oligoetherols shows the 5% mass loss from the semiproduct obtained from IA : GL = 1 : 6 system occurs at ca 180°C, while 50% mass loss is observed at 265°C (Fig. 5). Maximal decomposition occurs at 250°C, and decomposition is completed at ca 420°C. In thermograms of products obtained from alkylene carbonates, two peaks are observed at 250 and 340°C because of endothermic decomposition of perhydro-1,3,5-triazine ring[3] and exothermic oxidation of products of decomposition, respectively.

Some physical properties of the oligoetherols in function of temperature were studied (Table III). It has been observed that viscosity, density, and surface tension decreased upon increase of length of oxyalkylene chain; the typical relationship were observed. Generally, the obtained results demonstrate that oligoetherols obtained from IA and GL of alkylene carbonates or oxiranes are useful candidates for formation of polyurethane foams, especially considering the surface tension and viscosity as well as its temperature dependence.

Synthesis of polyurethane foams

Preliminary studies on preparation of polyurethane foam from obtained oligoetherol were performed on laboratory scale. The oligoetherol obtained from IA,

TABLE VII
Comparison of Some Properties of Foam Obtained from Oligoetherols Synthesized in Reaction IA with GL and EC with Foams Obtained from THMI and EO[4]

Oligoetherol	Amount of cosubstrate[a] (g/100 g oligoetherol)			Apparent density (kg/m³)	Water uptake (wt %)	Linear shrinkage (%)	Thermal stability measured as the weight loss (wt %) after									
							1 day in temp.		14 days in temp.			30 days in temp.			
	Isocyanate	Water	Catalyst				150°C	175°C	150°C	175°C	200°C	150°C	175°C	200°C		
IA : GL : EC = 1 : 6 : 6	184	2	3.4	49.5	4.8	0.0	3.7	6.3	7.8	18.1	15.2	9.00	27.36	40.10		
THMI : EO = 1 : 9	124	3	2.8	41.5	5.7	0.3	2.6	6.5	6.0	15.5	14.0	–[b]	–[b]	–[b]		
THMI : EO = 1 : 12	111	3	3.0	49.7	7.9	0.3	2.0	7.1	5.3	18.2	15.2	–[b]	–[b]	–[b]		

[a] The surfactant "SILICON 5340" was introduced into the reaction mixture at the level of 1 g/100 g oligoetherol at the beginning of synthesis.
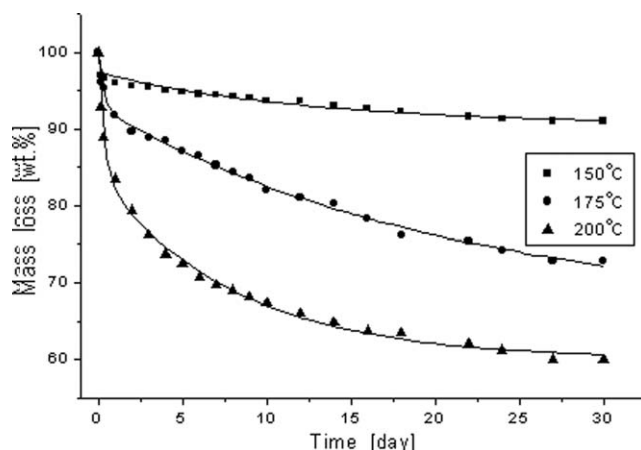[b] no data in Ref. 4.

Figure 6 Thermal stability of the polyurethane foam obtained from oligoetherol IA : GL : EC = 1 : 6 : 6 as the mass loss after heating at high temperature.

GL, and EC were tested. The synthesized polyurethane was stiff foam. The optimized composition and properties of the foam are collected in Table VII. The apparent density of the foam was $\sim$ 50 kg/m^3, the water uptake was 4.8 wt %. The foam did not show the shrinkage upon heating at 150°C. The studies of thermal stability were performed using static method at 150, 175, and 200°C within one month period. The stepwise decrease of foam mass was observed (Fig. 6) with the largest mass loss within first day. The dynamic studies with TG, DTG, and DTA allowed to conclude that the 5% mass loss occurred at 236°C, while 50% mass loss was found at 396°C (Fig. 5). Summarizing, the studied foam is similar to classic stiff foams except for higher thermal stability. The thermal stability of the studied foam was compared with those synthesized from oligoetherols obtained from THMI and oxiranes,[4] containing also perhydro-1,3,5-triazine ring and oxyalkylene chains of comparable length (Table VII). It has been found that it had comparable apparent density and thermal stability but lower shrinkage upon heating at 150°C and slight lower water uptake because of higher degree of crosslinking.

The presented preliminary results on formation of polyurethane foams using oligoetherols obtained from IA and GL will be the matter of separate report, including oligoetherols synthesized from IA, GL, and alkylene carbonates.

CONCLUSIONS

(1) Hydroxyalkyl derivatives containing perhydro-1,3,5-triazine ring were obtained from IA and GL, which are valuable precursors for synthesis of oligoetherols by their conversion with oxiranes or alkylene carbonates without solvent.
(2) The polyurethane foams are not formed by straightforward reaction of polyetherol obtained from IA and GL with isocyanates because of high viscosity of the oligoetherols.
(3) Instead the polyurethane foams can be obtained in the reaction between isocyanates and oligoetherols formed in the reaction between the semiproduct obtained from IA : GL = 1 : 6 system and ethylene carbonate.

References

1. Frisch, K.; Tummers, D.; Nijenhuis, A. U. S. Pat. 4,198,505, 1980.
2. Śnieżek, T.; Andrysiak, E.; Montewski, W.; Gniadowski, H.; Wojciechowski, J. PL. Pat. 69,168, 1973.
3. Wirpsza, Z. Polyurethane; WNT: Warsaw, 1991 (in Polish).
4. Kucharski, M.; Lubczak, J. Polimery (Warsaw) 1985, 30, 354.
5. Kucharski, M.; Lubczak, J.; Rokaszewski, E. Chemia Stos 1983, 65, 2791.
6. Kucharski, M.; Lubczak, J.; Rokaszewski, E. PL. Pat. 130,709, 1986.
7. Nagano, K.; Fujita, T. Jap. Pat. 53,024,080, 1978.
8. Shimasaki, Ch.; Nakayama, T.; Iino, Y. Nippon Kagaku Kaishi 1979, 3, 375.
9. Brojer, Z.; Hertz, Z.; Penczek, P. Epoxy Resins; WNT: Warsaw, 1972 (in Polish).
10. Poplewska, I.; Węglowska, E.; Lubczak, J. J Appl Polym Sci 2004, 91, 2750.
11. Dryński, T. Laboratory Practice from Physics; PWN: Warsaw, 1967 (in polish).
12. Cellular Plastics and Rubbers. Determination of Apparent (Bulk) Density, Polish (European) Standards PN-EN ISO 845–2000, Ed. Polish Committee for Standardization.
13. Cellular Plastics, Rigid. Determination of Water Absorption, Polish (European) Standards PN-EN ISO 2896–1986, Ed. Polish Committee for Standardization.
14. Cellular Plastics, Rigid. Test of Dimensional Stability, Polish (European) Standards PN-EN ISO 2796–1986, Ed. Polish Committee for Standardization.
15. Cellular Plastics, Compression Test for Rigid Materials, Polish (European) Standards PN- EN ISO 844–1978, Ed. Polish Committee for Standardization.
16. Kucharski, M.; Kijowska, D. J Appl Polym Sci 2001, 80, 1776.
17. Węglowska, E.; Lubczak, J. J Appl Polym Sci 2005, 98, 2130.
18. Kosterna, J.; Lubczak, J. Heterocycl Comm 2008, 14, 199.