Synthesis and Applications of Oligoetherols with Perhydro-1,3,5-triazine Ring and Boron

Jacek Lubczak, Beata Łukasiewicz, Bogdan Myśliwiec

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

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

ABSTRACT: A new method of preparation of oligoetherols containing perhydro-1,3,5-triazine rings and boron atoms is presented. The oligoetherols were obtained in the reaction of 1,3,5-tris(2-hydroxyethyl) isocyanurate with boric acid followed by reaction with alkylene carbonates. The structure and physical properties of the products render them good candidate for preparing the polyurethane foams. The foams were obtained and their properties were compared with those synthesized from isocyanuric acid and alkylene carbonates. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The most frequently used oxiranes like ethylene and propylene oxides react facile with isocyanuric acid (IA) {see reaction (1)} resulting in formation of 1,3,5-tris(hydroxyalkyl) isocyanurates (II, $x = y = z = 1$) in consecutive-parallel reactions.[1–3] These compounds can also be obtained from IA and excess alkylene carbonates, for instance ethylene carbonate (EC)[4]:

(1)
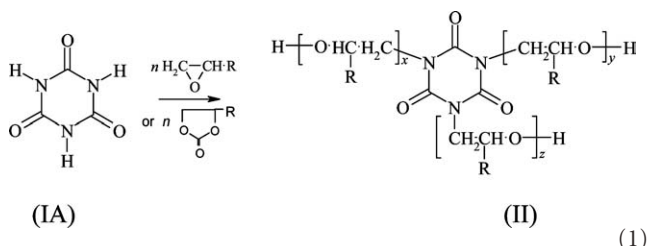
where R= —H, —CH$_3$, —

Hydroxyalkylation with oxiranes or alkylene carbonates proceeds with excess of hydroxyalkylating agent. In the first instance, the hydroxyalkyl derivatives of IA are formed, whereas further hydroxyalkylation results in formation of oligoetherols[5] with perhydro-1,3,5-tria-zine ring—the convenient substrates for polyurethane foams of enhanced thermal stability.[6] However, the foams are flammable. This disadvantage can be avoided by introduction of phosphorus, chlorine, bromine, or silicon.[7–9] There are patented some self-extinguishing polyurethane foams containing boric acid (ortho- or meta) or boron oxide.[10]

Most frequently, the decrease of flammability of classic foams was reached by the reaction between the mixtures of polyols with boron derivatives and isocyanates and water.[11–19] Czupryński et al. used some boroorganic compounds for such protocol, like hydroxyalkyl ester obtained from boric acid and diols in presence of sulfuric acid as catalyst. These derivatives were then introduced (up to 45 wt %) to compositions used for rigid polyurethane foams. The authors claimed that introduction of boron into polyurethane improved some of their properties like compression strength, diminishes fragility and flammability of foam, and in some cases also thermal stability.[11,12]

We have attempted to obtain the foams from oligoetherols containing boron to study the enhancement of thermal stability of the products. The boron-modified oligoetherols were obtained by esterification of hydroxyalkyl derivatives of IA with readily accessible boric acid. Here the studies on structure of products, their properties and synthesis of polyurethane foams are presented.

EXPERIMENTAL

Syntheses

The 1,3,5-tris(2-hydroxyethyl) isocyanurate (THEI) was obtained as described previously.[4]

Reaction of THEI with Boric Acid. In the open, round bottom 100 cm^3 flask equipped with mechanical stirrer and thermometer 6.52 g (0.025 mol) THEI and 4.65 g (0.075 mol) boric acid (pure, POCH, Gliwice, Poland; molar ratio THEI : H$_3$BO$_3$ = 1 : 3) were placed. The mixture was heated to melt (ca 70°C), then

heated at 120°C with stirring. The reaction was followed by determination of acidic number (AN) and mass loss and examining the ^{1}H-NMR spectra. The reaction ceased after *ca* 2 h (AN = 12 mg KOH/g). After cooling the mixture to room temperature, the white glassy solid products were obtained and identified as hydroesters of boric acid with perhydro-1,3,5-triazine ring.

Reactions of Hydroesters with Alkylene Carbonates. In a 250 cm[3] three-neck round bottom flask loaded with 29.4 g (0.075 mol) of products of reaction between 1 mol of THEI with 3 mol of H_3BO_3, equipped with mechanical stirrer, thermometer, and reflux condenser, 79.2 g (0.9 mol; molar ratio of reagents 1 : 12) or 99 g (1.125 mol; molar ratio of reagents 1 : 15) of EC (pure, Fluka, Switzerland) and 0.4 g of potassium carbonate (pure, POCH, Gliwice, Poland) as catalyst were introduced. The mixture was heated to melt EC (*ca* 50°C) and kept at 170–180°C with stirring up to the end of reaction. The reactions were completed after 18 and 21 h, respectively, as found by determination of amount of unreacted EC and mass balance. The obtained product was dark brown resin well soluble in water. In another synthesis, 29.4 g (0.075 mol) of products of reaction between 1 mol of THEI with 3 mol of H_3BO_3, 39.6 g of EC (0.45 mol, molar ratio 1 : 6) and 0.4 g of potassium carbonate as catalyst were introduced. The mixture was heated at 175°C to the end of reaction (*ca* 8 h). Then to the products 45.9 g (0.45 mol) of propylene carbonate (PC; pure, Fluka, Switzerland) and 0.3 g K_2CO_3 were added and the mixture was heated at 175°C up to the end of reaction (50 h).

Additional remark: The synthesis with boric acid was also performed, in which oligoetherol from 6.45 g (0.05 mol) of IA and 52.8 g (0.6 mol) of EC according to described protocol[20] (molar ratio IA : EC = 1 : 12), followed by esterification with 9.27 g (0.15 mol) of boric acid (the reagents ratio IA : EC : H_3BO_3 = 1 : 12 : 3).

Analytical

The course of reaction between semiproduct of reaction THEI and boric acid with EC or PC was followed by measuring the content of unreacted alkylene carbonate.[21] The sample was then treated with 2.5 cm[3] of 0.15 M barium hydroxide, vigorously shaken and the excess of barium hydroxide titrated off with 0.1 M HCl solution. In obtained products, the acid numbers were determined by titration with a standard potassium hydroxide solution.[22] Elemental analysis for C, H, N, were done with EA 1108, Carlo-Erba analyzer (Milan, Italy). The boron was emission atomic spectrometry (ICP-OES VISTA-MPX spectrometer, Varian, with 10% accuracy, Palo Alto, California).

The ^{1}H-NMR spectra of products were recorded at 500 MHz Bruker UltraShield (Rheinstetten, Germany) in DMSO-d[6] with hexamethyldisiloxane as internal standard. IR spectra were registered on PARAGON 1000 FT IR Perkin Elmer spectrometer (Waltham, Massachusetts) in KBr pellets or ATR technique. MALDI ToF (Matrix-Assisted Laser Desorption Ionization Time of Flight, München, Germany) of oligoetherols were obtained on Voyager-Elite Perseptive Biosystems 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 with 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_3OH. Thermal analyses of oligoetherols and foams were performed in ceramic crucible at 20–600°C temperature range, about 200 mg sample, under air atmosphere with Thermobalance TGA/DSC 1 derivatograph, Mettler.

Physical Properties of Oligoetherols

Refractive 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.[23]

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 silicone 5340 (pure, Houdry Hülls) as surfactant, the triethylamine (TEA, pure, Fluka, Buchs, Switzerland) catalyst (2.7–13.5 wt %) and water (2÷8% wt %) with respect to oligoetherols. The polyols used here were obtained from semiproduct synthesized in THEI : H_3BO_3 = 1 : 3 system with 12 and 15 mol of EC or 6 mol of EC and 6 mol of PC. A calculated portion of diphenylmethane 4,4'-diisocyanate (the commercial isocyanate was used contaning tri-functional isocyanates at 30% level; 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.

Studies of Foam

The following properties of foams were studied: apparent density,[24] water uptake,[25] dimension stability estimated on the basis of the change linear dimensions of the sample heated for 20 and 40 h at 150°C[26] and thermal stability as the weight loss at 150 and 175°C within 1 month as well as a compression strength.[27] The flammability was determined by test in horizontal position) according to official procedure.[28] The foam samples (150 × 50 × 13 mm) was weighed, located on horizontal support (wire net of 200 × 80 mm dimensions) and the line was marked at the distance of 25 mm from edge. The sample was set on fire from the opposite edge using Bunsen burner with the blue flame of 38 mm height for 60 s. Then the burner was removed and time of free burning of foam reaching marked line or cease of flame was measured by stopwatch. After that the samples were weighed again.

The rate of burning was calculated according to the expression:

$$v = \frac{125}{t_b}$$

if the sample was burned totally, or using equation:

$$v = \frac{L_e}{t_e}$$

if the sample ceased burining, where:

L_e, the length of burned fragment, measured as the difference 150 minus the length of unburned fragment (in mm). According to norms, if the burned fragment has the 125 mm length, the foam is considered as flammable.

t_b, t_e, the time of propagation of flame measured at the distance between starting mark up to the end mark or as the time of flame cease.
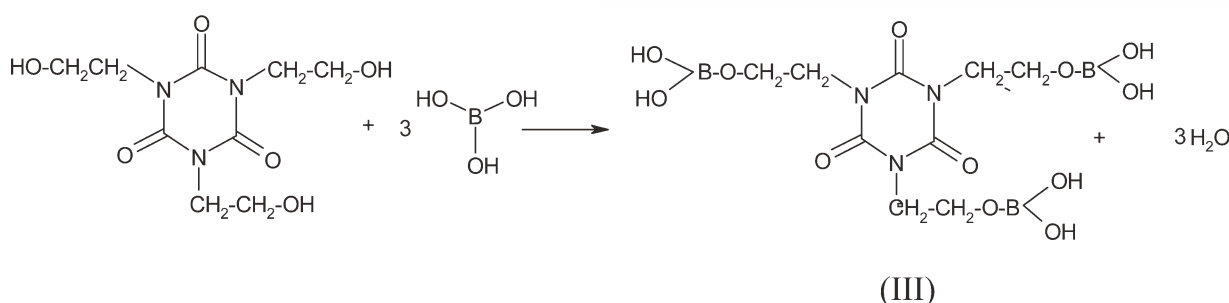
The mass loss Δm after burning was calculated from the formula:

$$\Delta m = \frac{m_o - m}{m_o} \cdot 100\%$$

where m_o and m mean the sample mass before and after burning, respectively.

RESULTS AND DISCUSSION

It seemed, that the most straightforward method of synthesis of polyurethane foams with perhydro-1,3,5-triazine ring, which might have decreased flammability would be the introduction of boric acid into oligoetherols containing the ring, followed by reaction of product with isocyanates and water, as it was described[10] for traditional polyurethane foams. Unfortunately, the foams obtained by this method were undercrosslinked, underfoamed, and irregularly pored.

The foams of similar properties were obtained when the foaming process is performed with oligoetherol synthesized from IA and EC, followed by esterification with boric acid (see Experimental, remark in p.1.2.), i.e., using oligoetherol ended with hydroxyl groups derived from hydroborates. Therefore, the boron was further introduced into oligoetherol; the THEI was obtained easily from 1 mol of IA and 3 mol of EC and then the product was esterified with 3 mol of boric acid according to the scheme of reaction:

(III)

The mixture became homogeneous on heating to 120°C. The elemental analysis of initial mixture (THEI + 3 H_3BO_3) showed the %N = 9.40; %C = 24.16; %H = 5.37 and agreed well with the composition of melted starting mixture (%N = 9,14; %C = 25,10; %H = 5,24; Table I entry1). In the course of reaction, the decrease of AN was observed. The good agreement of analytical data of reaction mixture (% N = 10.75; % C = 27.07; % H = 4.56; Table I, entry 5) with the results expected for the product described by formula III (calculated %: N = 10.68; C = 27.48; H = 4.58) is achieved when AN equals ca 12 mg KOH/g. Further heating of mixture (within 2 h) resulted in decrease of AN to 0 accompanied by the change of composition of product as a result of following esterification and condensation of obtained hydroborate (Table I, entries 7 and 8). The mixture became dense, presumably due to crosslinking and the product was not suitable for obtaining the oligoetherols. In the ^{1}H-NMR spectrum of initial reaction mixture [Figure 1(a)], the resonance of methylene protons of THEI was observed at 4.3 ppm, whereas broadened signal from hydroxyl protons of THEI was found at 6.5 ppm, indicating the involvement of these groups in hydrogen bonding. The resonance of boric acid protons was observed at 7.4 ppm, which disappeared on addition of D_2O. In the spectra of reaction mixtures, the continuous decrease of resonance at 6.5 ppm was observed, indicating the involvement of hydroxyl groups of THEI in esterification [Figure 1 (a,b)]. At the same time, the resonances of hydroxyl protons from boric acid esterof THEI appeared at 7.7–8.2 ppm. Also the IR spectrum confirms the esterification by appearance of B—O stretching vibration at 1340 cm^{-1}. The analysis of the ^{1}H-NMR spectrum showed that functionalization of hydroxyl groups of THEI was not completed when three equivalent of water were released. However, the esterification could not be continued due to mentioned crosslinking. The mixture obtained in this way, containing mostly hydroborate is insoluble in dioxane, toluene, or benzene, whereas it is soluble in warm DMSO, DMF, and acetone, as well as in hot EC. The latter was quite important feature because it provided the possibility of obtaining multifunctional oligoetherols of general formula:
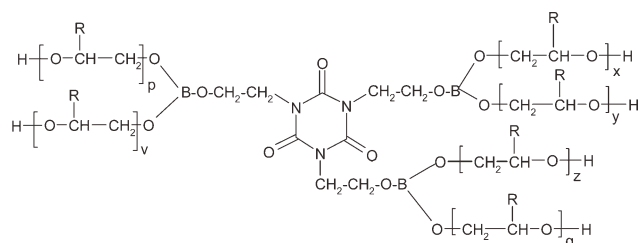
where: R = —H, CH$_3$—
$x + y + z + q + p + v = n$
n, number of oxyalkylene units from alkylene carbonates

with boron atoms in chain and with nitrogen atoms in heterocyclic ring, suitable product for obtaining the foams. The PC was

Table I. The Analysis of Reaction Course of 1 Equivalent of THEI with Three Equivalents of H_3BO_3 at 120°C

Entry	Time of heating (min)	Mass loss (%)	Acidic number (mg KOH/g)	Elemental analysis	Number of water equivalent released[a]
1	0	0.0	57.2	%N = 9.14	–
				%C = 25.10	
				%H = 5.24	
2	20	7.6	56.4	%N = 10.30	1.9
				%C = 26.23	
				%H = 3.82	
3	40	9.5	37.5	–	2.3
4	80	10.9	26.5	–	2.7
5	120	12.3	12.2	%N = 10.75	3.0
				%C = 27.07	
				%H = 4.56	
6	140	14.9	10.6	–	3.7
7	170	16.1	6.9	–	4.0[b]
8	230	17.3	0.0	%N = 10.06	4.3
				%C = 24.98	
				%H = 4.19	

[a]Amount of water released was measured by mass loss., [b]The viscosity of reaction mixture increases.

not good solvent for the semiproduct. Even prolonged heating of the mixture in 180–200°C did not initiate hydroxyalkylation.

To obtain the oligoetherols with secondary hydroxyl groups (formed on decomposition of PC), which might be able to react

with isocyanates toward the formation of polyurethane foams, first, the boric acid ester of THEI had to be reacted with EC, and then the obtained semiproduct was converted by reaction with PC (see Experimental, section 1.2.). The structure of obtained oligoetherols was confirmed by IR and H-NMR spectra. In the IR spectra (Figure 2), the bands of hydroxyl groups were observed (3338 cm^{-1} valence vibrations and 1120 cm^{-1} deformation vibrations) as well as those of ether bridges (at 1029 cm^{-1}, C—O—C), indicating the incorporation of oxyalkylene mers into oligoetherols. The presence of IA ring in products was confirmed by the presence of the band centered at 1738 cm^{-1} (C=O) and 763 cm^{-1} (vibration of perhydro-1,3,5-triazine ring). The band at 1329 cm^{-1} indicates the presence of B—O bonds. In the H-NMR spectrum (Figure 3), the resonances of methylene protons shift from 4.3 ppm in the spectrum of THEI to the 3.4–3.55 ppm region where 2 multiplets of integral
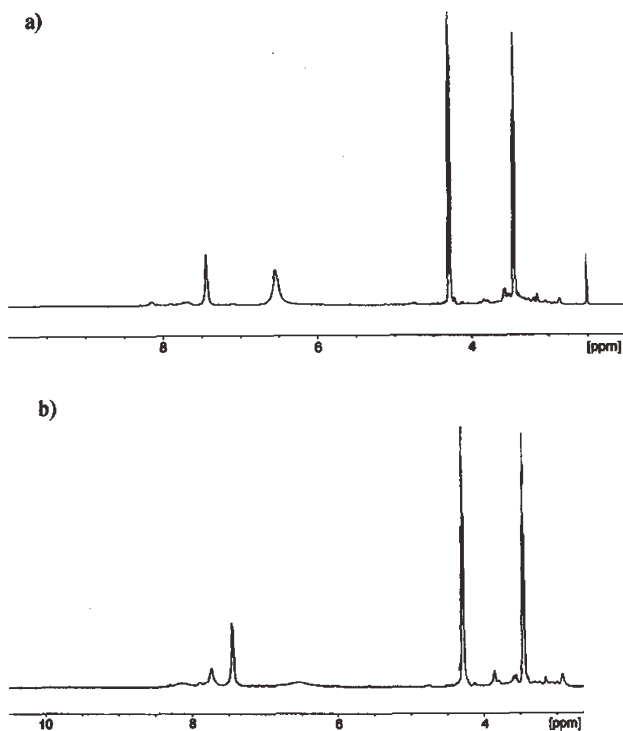
Figure 1. The ^{1}H-NMR spectrum of reaction mixture THEI–boric acid after heating to 120°C and homogenization of constituents (a) after 40 min of heating (b).
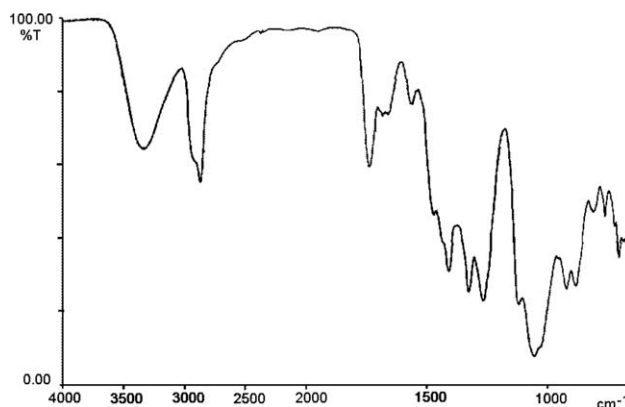
Figure 2. The IR spectrum of product obtained in molar ratio IA : H_3BO_3 : EC = 1 : 3 : 15.
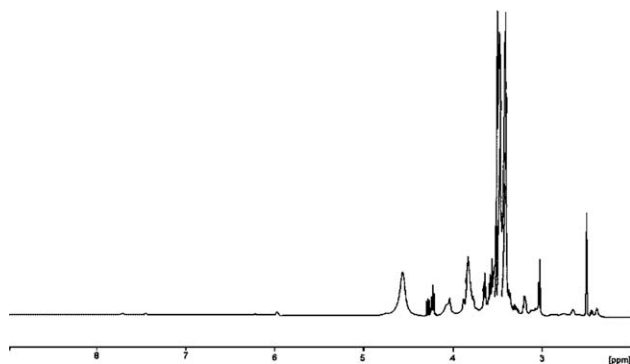
Figure 3. The ^{1}H-NMR spectrum of product obtained in molar ratio IA : H_3BO_3 : EC = 1 : 3 : 15.

intensity ration 1 : 1 at 3.4 and 3.5 ppm are present as a result of N—CH_2—CH_2—O—B—O—CH_2—CH_2—O structural fragment. The resonances of hydroxyl protons were observed at 3.8–4.3 ppm. They were collapsed on addition of deuterated water. The absence of signals within 7.6–8.2 ppm region was diagnostic for the hydroxyalkylation of all B—OH in hydroester by EC.

The structure of products of esterification of THEI with boric acid and hydroxyalkylation of obtained semiproducts with alkylene carbonates were eventually confirmed by Maldi-ToF spectra (Table II). The molecular peaks of semiproducts formed between THEI and boric acid showed that THEI underwent also lower derivatives of IA, namely mono- and bis-hydroxyalkyl derivatives (Table II, entries 2, 4 and 6), which were also esterified with boric acid (Table II, entries 4 and 10). In the Maldi-ToF spectra of oligoetherols obtained with EC, the series of sig-

nals differing of $m/z = 44$ were observed, indicating that oxyethylene groups from EC were incorporated in the hydroborates. In the spectra of products formed from PC additional signals differing of $m/z = 58$ were observed as a result of incorporation of oxypropylene fragments into oligoetherol. In the product obtained at appropriate molar ratio of reagents, the derivatives of variable degree of substitution were observed. The analysis of the spectra showed that elimination of water from semiproducts of hydroxyalkylation was the side process. In these spectra, the peaks corresponding to molecular ions (product-H_2O) both in case of semiproducts obtained from EC as from PC. The percentage of the products of water elimination is small; in the H-NMR spectra of products of reaction with EC (Figure 3), no additional resonances were observed, whereas in those of products obtained from PC, the low intensity resonances attributed to unsaturated regions were observed within 4.7–4.8 and 5.6–6.0 ppm region.

The thermal decomposition of obtained oligoetherols was achieved by thermal analysis. The 5% mass loss of the oligoetherols was observed at 90°C, 10% mass loss occurred at 105°C, whereas the temperature of maximum decomposition was noticed at *ca* 190°C (Figure 4, curve 1).

The decrease of refraction index, viscosity, density, and surface tension due to elongation of oxyalkylene chain and typical changes of those properties in function of temperature were found (Figures 5–8). It has been noticed that the least viscosity, density, and refraction index indicated the oligoetherols obtained from semiproduct synthesized from the IA : H_3BO_3 =1 : 3 system and EC and PC (Figures 5–7), which was probably due to the least packed structure of oligoetherol related to branched oxyalkylene chain caused by the presence of methyl

Table II. Interpretation of MALDI ToF Spectrum of Reaction Product Obtained from 1 mol of THEI and 3 mol of Boric Acid

Entry	Signal position (m/z)	Relative intensity of signal (%)	The molecular ion structure	Calc. molecular weight (g/mol)
1	150.1	53	IA + Na$^+$	152
2	195.3	40	IA + OE + Na$^+$	196
3	201.2	37	(IA + 2OE – H_2O) + H$^+$	200
4	219.7	15	((IA + OE) + H_3BO_3 − 2H_2O) + H$^+$	218
			IA + 2OE + H$^+$	218
5	239.7	25	IA + 2OE + Na$^+$	240
6	246.0	19	IA + 2OE + CH_3OH	249
7	262.0	17	THEI +H$^+$	262
8	282.2	49	THEI + Na$^+$	284
9	290.2	100	THEI + CH_3OH	293
10	304.0	27	(IA + 2 OE) + 2H_3BO_3 − 2H_2O	305
			(THEI + H_3BO_3 − H_2O)	305
11	326.3	36	(THEI + H_3BO_3 − H_2O) + Na$^+$	328
12	351.3	16	(THEI + 2H_3BO_3 − 2H_2O) + H$^+$	350
13	370.3	15	(THEI + 2H_3BO_3 − 2H_2O) + Na$^+$	272
14	395.3	8	(THEI + 3H_3BO_3 − 3H_2O)	393

n OE, means the number of oxyethylene units in the product; $n = 1$ or 2; −H_2O, means that product undergoes water elimination in the course of reaction; (THEI + nH_3BO_3 − nH_2O), means the hydroborate obtained in the reaction of n mol of H_3BO_3 with 1 mol of THEI; n = 1, 2 or 3.
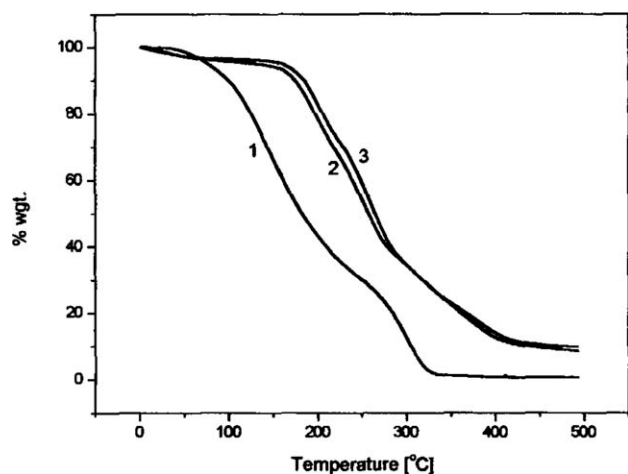
Figure 4. Mass changes during the heating of oligoetherol obtained from IA : H_3BO_3 : EC = 1 : 3 : 12 system (1) and obtained polyurethane foam (2) and polyurethane foam obtained from oligoetherol synthesized from IA : H_3BO_3 : EC : PC = 1 : 3 : 6 : 6 system (3).

group. Presented results suggest that oligoetherols obtained from THEI and boric acid and alkylene carbonates can be useful candidates for formation of polyurethane foams. The criterions for such application were surface tension, the viscosity, and its temperature dependence.

The attempts of obtaining the polyurethane foams using obtained oligoetherols were performed on laboratory scale. The optimization of amount of catalyst, isocyanate, water, and influence of polyether chain on foaming process were the subject of these studies. The thermal resistance of the foams by mass loss, changes in compression strength before and after thermal exposure and flammability of foams were estimated. It has been found that the best foams were formed when the molar ratio of isocyanate groups to hydroxyl groups in starting mixture reached (isocyanate coefficient) 1.8–2.4 (Table III, no of composition 5, 11,12, 21, 22, and 27) depending on kind of
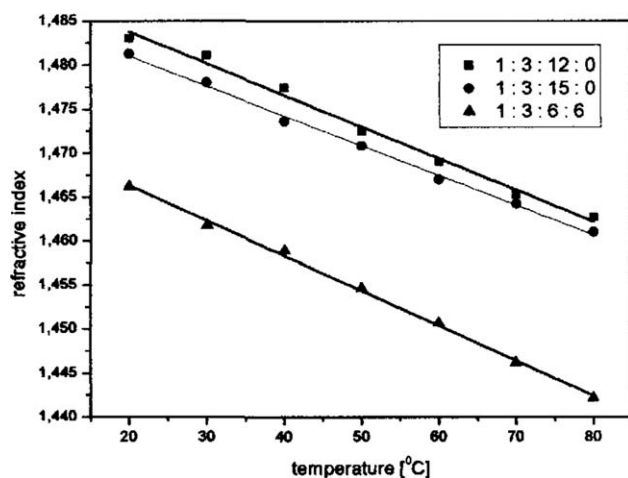

Figure 6. Dependence of density as a function of temperature for the oligoetherols obtained in molar ratio IA : H_3BO_3 : EC : PC as shown in insert.

Figure 7. Dependence of viscosity as a function of temperature for the oligoetherols obtained in molar ratio IA : H_3BO_3 : EC : PC as shown in insert.

Figure 5. Dependence of refractive index as a function of temperature for the oligoetherols obtained in molar ratio IA : H_3BO_3 : EC : PC as shown in insert.
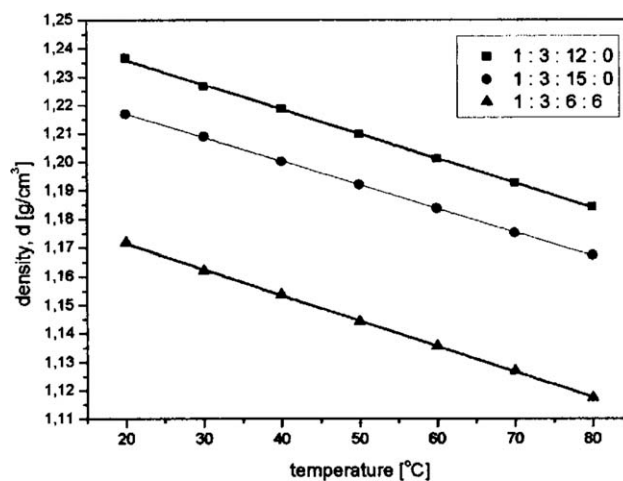

Figure 8. Dependence of surface tension as a function of temperature for the oligoetherols obtained in molar ratio IA : H_3BO_3 : EC : PC as shown in insert.
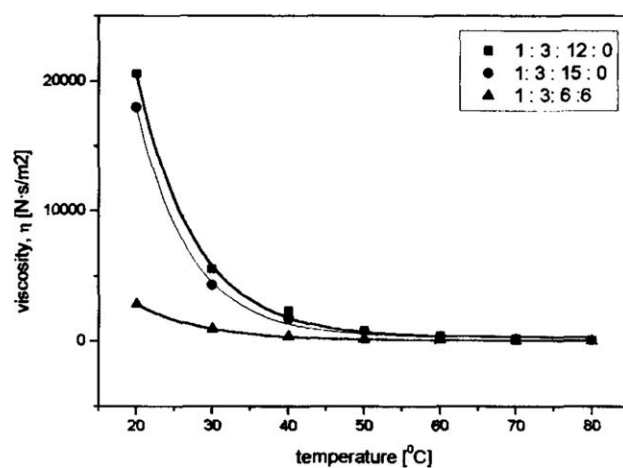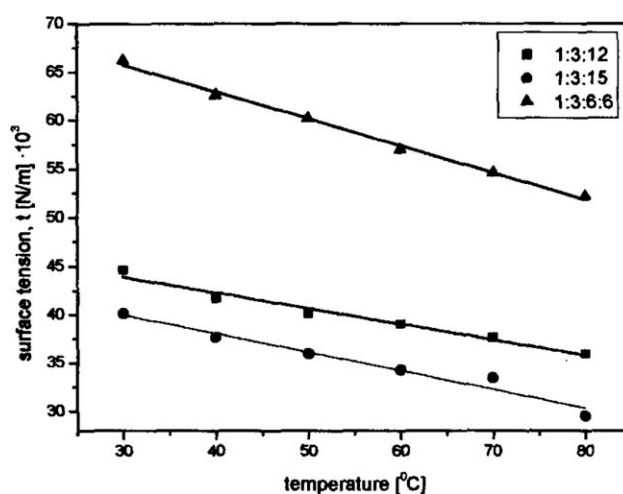
Table III. The Influence of Composition on Foaming Process

Molar Ratio THEI : H$_3$BO$_3$: EC : PC	Com. No	Composition (g/100 g of polyetherols)					Foaming process[a]			Remarks
		Isocyanate	Water	Catalyst	Silicon	Molar ratio NCO/OH	Time of creaming (s)	Time of expanding (s)	Time of drying (s)	
1	2	3	4	5	6	7	8	9	10	11
1 : 3 : 12 : 0	1	144	2	2,7	0,8	1,6	–	–	–	NGC
	2	144	3	5,4	0,8	1,5	48	–	–	NGC
	3	160	4	8,1	0,8	1,6	38	95	–	U, LDF
	4	180	6	10,8	1,6	1,7	41	48	5	U, LDF
	5	240	6	10,8	1,6	2,4	31	22	5	R, RP
	6	300	6	10,8	1,6	3,2	51	74	300	U
	7	260	6	13,5	1,6	2,7	32	24	5	R, RP
	8	240	4	13,5	1,6	2,6	32	12	–	LDF
	9	260	8	13,5	1,6	2,5	32	10	–	LDF, LP
	10	240	6	12,1	1,6	2,4	22	19	–	LP
	11	240	6	9,4	1,6	2,4	34	10	5	R, RP
	12	240	6	8,1	1,2	2,4	50	27	15	R, RP
1 : 3 : 15 : 0	13	168	3	8,1	1,6	1,8	44	52	5	R, LDF
	14	200	6	5,4	1,6	1,8	28	11	5	R
	15	200	6	8,1	1,6	1,8	20	8	5	LP
	16	180	4	5,4	1,6	2,0	35	27	5	R
	17	200	6	5,4	1,6	1,8	47	30	–	LP, SP
	18	180	4	6,5	1,6	2,0	25	10	5	LDF
	19	180	4	5,4	1,2	1,8	41	22	15	R, RP
	20	160	4	5,4	1,2	1,6	38	25	15	R, RP
	21	180	4	5,4	1,2	1,8	35	12	15	R, RP
	22	200	4	5,4	1,2	2,0	45	33	15	R, RP
1 : 3 : 6 : 6	23	176	2	5,4	1,6	2	19	23	5	LP
	24	204	4	4,3	1,6	2	22	60	5	–
	25	312	6	6,5	1,6	2,7	20	45	–	–
	26	312	6	5,4	1,6	2,7	30	105	300	LPD
	27	206	4	7	3,1	2	22	12	5	R, RP
	28	312	6	6,7	3,1	2,7	30	33	10	LP
	29	312	6	5,4	1,6	2,7	22	30	5	LP
	30	206	4	7	3,1	2	24	30	7	LP

[a]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.R, rigid foam; U, undercrosslinked foam; RP, regular pores; LP, large pores; NGC, no grow of composition; LDF, long drying time.

oligoetherol. The influence of water on foaming was studied using mainly oligoetherol obtained from THEI : H_3BO_3 : EC = 1 : 3 : 12. It has been found that addition of 2–4% water to composition, the low degree of foaming was obtained (Table III, compositions 1–3 and 13). The rigid foams were obtained at 6 wt % water for the oligoetherol obtained from THEI : H_3BO_3 : EC = 1 : 3 : 12 and 4 wt % water for other oligoetherols. The important parameter was the amount of the catalyst (TEA) in the protocol. In case of products obtained from 12 equivalents of EC, the optimal amount of catalyst was 8–11 g (Table III, compositions 5, 11, and 12), in case of product obtained from 15 mol of EC, the best results gave the 5.4 g of TEA (compositions 19–22), whereas in case of the product obtained from the EC and PC mixture, the optimum was 3.1 g catalyst per 100 g of oligoetherols (composition 27).

It has been noticed that to obtain the foams with regular pores and symmetric grow of foam, the more surfactant was required (1.6–3.1%) in comparison with the polyurethane foams with perhydro-1,3,5-triazine ring (*ca.* 1%). Creaming time depended on amount of catalyst. It was shortened with increasing amount of catalyst (Table III, compositions 10–12). For the compositions giving the best foams, the creaming time was within 22–50 s, whereas expanding time was short and usually was within 10–30 s. Change of defined parameters led to formation of undercrosslinked foams (too much or not enough isocyanate; Table III, compositions 4 and 6), or low foaming degree (too little water; Table III, compositions 1–3, and 13) or irregular pores (too much isocyanate or water; Table III, compositions 9, 15, 17). It should be emphasized that all foams were rigid. Their apparent density fall within 50–82 kg/m³ region (Table IV column 3) and is higher from thermally resistant foams obtained from IA and alkylene carbonates.[29] The lowest apparent density, close to that for the foams obtained from oligoetherols obtained from IA and EC have the foams based on oligoetherol synthesized from EC and PC. Water uptake was 1.5–2 times higher than that of foams obtained from oligoetherols based on IA and alkylene carbonates (Table IV, column 6). This seems to be the result of introducing the boron into structure of the foam, which is the suitable Lewis acid for water Lewis base. The water uptake was within 7.7–19%, whereas that for the foams obtained from IA and EC indicated averaged water uptake equal to 7–10 wt %. The least water uptake had the foams obtained from oligoetherols with oxypropylene units from PC. The foams obtained here from EC have characteristically very stable linear dimensions. When they are exposed to 150°C temperature for 40 h not linear changes are observed, the shape remains unchanged, whereas those obtained from IA and EC indicated (-0.5)–(-0.8)% linear changes.

The presence of boron (Table IV, column 16) renders the obtained foams less flammable in comparison with obtained from oligoetherols synthesized from IA and EC. This causes both decrease of flaming time and mass loss after combustion (Table IV, columns 13–15). The higher the percentage of boron (1.5), the less flammable was the foam (Table IV, compositions 12). The foam obtained from oligoetherol synthesized from IA : H_3BO_3 : EC = 1 : 3 : 12 system was self-extinguishing; the flame reached only 30 mm distance. In other cases, the

Table IV. Some Properties of Obtained Foams

Molar ratio THEI : H_3BO_3 : EC : PC	Comp. No as in Table III	Density (kg/m³)	Absorb. of water (wt %)			Dimensional stability (%)						Length of burned section L (mm)	Rate of burning (mm/s)	Mass loss during flaming (% mas)	Conten of boron (wt %)
			After 5 min	After 3 h	After 24 h	Length change		Broadness change		Thickness change					
						After 20 h	After 40 h	After 20 h	After 40 h	After 20 h	After 40 h				
1 : 3 : 12 : 0	12	77.6	7.1	11.1	27.0	0.0	-0.2	0.0	0.0	0.0	-0.2	30	0.4	19.6	1.50
1 : 3 : 15 : 0	22	81.7	7.4	10.9	19.0	0.0	0.0	0.0	-0.4	0.0	-0.1	150	1.8	49.5	1.32
1 : 3 : 6 : 6	27	50.3	2.7	5.0	7.7	0.3	0.5	0.3	0.9	0.0	0.6	150	1.4	40.7	1.38
IA : EC = 1 : 12	a	35.8–53.0			7–10		-0.5-(-0.8)					150	5.5	70.7	0.00

[a] From Ref. 29.

Table V. Thermostability and Compressive Strength of Foams

Molar ratio THEI : H_3BO_3 : E : C : PC	Comp. No as in Table III	Mass loss in % wt. after exposition in month in temperature		Compressive strength (MPa)			The % of change of compression strength after thermal exposure	
				Before exposition	After exposition in temperature			
		150°C	175°C		150°C	175°C	150°C	175°C
1 : 3 : 12 : 0	12	12.9	30.7	0.1176	0.1306	0.2998	+11.1	+155
1 : 3 : 15 : 0	22	14.2	33.2	0.3205	0.4799	0.5571	+49.7	+73.8
1 : 3 : 6 : 6	27	9.8	27.8	0.2485	0.3793	0.4246	+52.6	+71.0
IA : EC = 1 : 12	[a]	8.8-12.6	23.7-26.3	0.384-0.597	0.348-0.911	0.259 0.399	0-(+53)	−33

[a]From Ref. 29.
All foams changed color after thermal exposition to light yellow (150°C) or brown (175°C). Neither shape nor fragility nor pore disruption was observed in the course of the exposition. The only change noticed was the increase of compression strength.

flammable foams were obtained. However, the flaming time was lower (1.4–1.8 mm/s) than that for the foams obtained from oligoetherol based on IA and EC, where the flaming time was 3–4 times higher (5.5 mm/s). Moreover, their mass loss was lower (40–50%) than that for the foams obtained from polyetherols synthesized from IA and EC (70%).

The studies of thermal stability were performed for those polyurethane foams, which had regular pores, were rigid and well crosslinked. Static tests were done at 150 and 175°C by measuring mass loss with simultaneous estimation of mechanical properties before and after thermal exposures (Table V). The foams thermally exposed for 1 month. The continuous mass loss was observed. The largest mass losses were found at first day of the exposure. The compression strength increased on exposure giving in some cases even 150% increase of this parameter. The lowest mass loss indicated the foams obtained from oligoetherols synthesized from EC and PC (Table V, composition 27): 9.8 and 27.8% after exposures at 150 and 175°C, respectively, with accompanied increase of compression strength. Comparing these foams with those obtained from IA and EC[29] one can conclude that the boron-modified foams have similar or slightly lower thermal resistance as measured by mass loss. Their mechanical properties are usually worse in comparison with those based on oligoetherols obtained from IA and EC. The fragility of such modified foams was known to increase on increasing boron percentage. The compression strength increases with increasing number of oxyalkylene units, which is related to the decreasing of boron percentage in formed composition (Table V, compositions 12 and 22). Higher compression strength of obtained foams in comparison with those obtained from IA and EC showed only the foams obtained from oligoetherol obtained from IA : H_3BO_3 : EC = 1 : 3 : 15 system after exposure at 175°C. Dynamic studies (Figure 4) confirmed that the highest thermal resistances have the foams obtained from oligoetherol synthesized from EC and PC; 5% mass loss occurred at180°C and 50% at 275°C.

CONCLUSIONS

1. The hydroborates containing perhydro-1,3,5-triazine ring were obtained on esterification of THEI with threefold molar excess of boric acid.

2. Obtained hydroborates react with excess EC to give oligoetherols with boron incorporated into the structure of product.

3. Oligoetherols with perhydro-1,3,5-triazine ring and boron are useful for synthesis of polyurethane foams, which are resistant against long time exposure at 175°C. The compression strength of the foams increases after thermal exposure. The apparent density and water uptake of the obtained foams are higher than those for the polyurethane foams obtained from IA and EC.

4. The boron-modified foams show lower flammability or are self-extinguishing in contrary with those containing only perhydro-1,3,5-triazine ring, which are flammable.

REFERENCES

1. Morio, M.; Ryochi, T. Jpn Pat. 56,081,571 (**1979**).

2. Scheirer, D.; Nelson, E. U.S. Pat. 3,385,853 (**1968**).

3. Frisch, K.; Tummers, D.; Nijenhuis, A. Eur. Pat. 3,620 (**1979**).

4. Mikio, T. Jpn. Pat. 21,912,653 (**1990**).

5. Poplewska, I.; Węglowska, E.; Lubczak, J. *J. Appl. Polym. Sci.* **2004**, *91*, 2750.

6. Śnieżek, T.; Andrysiak, E.; Montewski, W.; Gniadowska, H.; Wojciechowski, J. Polish Pat. 69,168 (**1973**).

7. Lu, S.; Hamerton, I. *Prog. Polym. Sci.* **2002,** *27*, 1661.

8. Uhlig, K. Discovering Polyurethanes; Hanser Publishers: Monachium, **1999.**

9. Hilado, C. J. Flammability Handbook for Plastics; Technomic Publishing Co. Inc.: Lancaster, PA, **1998.**

10. Blount, D. U.S. Pat. 50,075,343 (**1992**).

11. Czupryński, B.; Paciorek-Sadowska, J.; Liszkowska, J. *Polimery* **2002,** *47*, 727.

12. Czupryński, B.; Liszkowska, J.; Paciorek-Sadowska, J. *J. Appl. Polym. Sci.* **2004,** *95*, 400.

13. Czupryński, B.; Liszkowska, J.; Paciorek-Sadowska, J. *Polimery* **2004,** *49*, 187.

14. Czupryński, B.; Paciorek-Sadowska, J.; Liszkowska, J. *J. Appl. Polym. Sci.* **2006,** *100*, 2020.

15. Czupryński, B.; Paciorek-Sadowska, J.; Liszkowska, J. *Chin. J. Chem.* **2006,** *24,* 1796.

16. Paciorek-Sadowska, J.; Czupryński, B. *J. Appl. Polym. Sci.* **2006,** *102,* 5918.

17. Czupryński, B.; Liszkowska, J.; Paciorek-Sadowska, J. *J. Appl. Polym. Sci.* **2006,** *102,* 768.

18. Czupryński, B.; Paciorek-Sadowska, J.; Liszkowska, J. *J. Appl. Polym. Sci.* **2010,** *115,* 2460.

19. Paciorek-Sadowska, J.; Czupryński, B.; Liszkowska, J. *J. Appl. Polym. Sci.* **2010,** *118,* 2250.

20. Węglowska, E.; Lubczak, J. *J. Appl. Polym. Sci.* **2005,** *98,* 2130.

21. Kijowska, D.; Wołowiec, S.; Lubczak J. *J. Appl. Polym. Sci.* **2004,** *93,* 294.

22. Kastierina, T.; Kalinina, L. Chemical Analysis of Plastics; WNT: Warszawa, **1965** (in Polish).

23. Dryński, T. Laboratory Practice from Physics; PWN: Warsaw, **1967** (in Polish).

24. Cellular Plastics and Rubbers. Determination of Apparent (bulk) Density, Polish (European) Standards PN-EN ISO 845–2000. Polish Committee for Standardization, Warsaw, Poland.

25. Cellular Plastics, Rigid. Determination of Water Absorption, Polish (European) Standards PN-EN ISO 2896–1986. Polish Committee for Standardization, Warsaw, Poland.

26. Cellular Plastics, Rigid. Test of Dimensional Stability, Polish (European) Standards PN-EN ISO 2796–1986. Polish Committee for Standardization, Warsaw, Poland.

27. Cellular Plastics, Compression Test for Rigid Materials, Polish (European) Standards PN-EN ISO 844–1978. Polish Committee for Standardization, Warsaw, Poland.

28. Flexible Cellular Polymeric Materials—Laboratory Characteristics of Small Specimens Subject to a Small Flame, Polish (European) Standards PN-EN ISO 3582–2002. Polish Committee for Standardization, Warsaw, Poland.

29. Węglowska, E.; Lubczak, J. In Proc. of Conf. on Polymer Modification; Wrocław Techn. Univ.: Wrocław, **2005**; p 643 (in Polish).