Research Article

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Improved thermally stable oligoetherols from 6-aminouracil, ethylene carbonate and boric acid

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Abstract: Syntheses of oligoetherols with a 1,3-pyrimidine ring and boron atoms using 6-aminouracil, ethylene carbonate and boric acid has been proposed. The structure of the obtained products were determined by instrumental methods (IR, $^1\text{H-NMR}$ and MALDI-ToF spectra). The physicochemical and thermal properties of oligoetherols were examined. The products were characterized by high thermal stability. Based on the tests performed, it was found that oligoetherols obtained from 6-aminouracil, boric acid and ethylene carbonate are suitable for the manufacturing of polyurethane foams with improved thermal stability and reduced flammability.

Keywords: 1,3-pyrimidine ring; improved thermal stability; polyurethane foams; reduced flammability.

1 Introduction

Thermal resistance and the flammability of polyurethane foams were considered as the most important problems concerning the applications of these foams as insulating materials. The thermal stability of foams can be improved by using a polyol component containing heat-resistant heterocyclic rings, e.g. 1,3-pyrimidine ring, in their structure [1-4].

Oligoetherols with 1,3-pyrimidine ring (I) were obtained in a reaction of 6-aminouracil (AU) with oxiranes or alkylene carbonates [5-7].

where: $4 \leq x + y + w + z \leq 12$

In our previous work [5], the synthesis of oligoetherols with AU and oxiranes, such as ethylene oxide (EO) or propylene oxide (PO) were described. The reactions were carried out for 78-194 hrs, under higher pressure, in a temperature range of 50-70°C, with triethylamine (TEA) as a catalyst and dimethyl sulfoxide (DMSO) as solvent [5]. We have shown [6, 7], that reactions of AU with alkylene carbonates were conducted without solvent, since AU dissolves in ethylene carbonate (EC) or propylene carbonate (PC) and reacts with them. Synthesis was carried out for 5.5-15.5 hrs, in a temperature range 160-180°C, with potassium carbonate or potassium carbonate and 1,4-diazabicyclo[2.2.2]octane [6, 7].

Oligoetherols with a 1,3-pyrimidine ring were previously obtained [3] also in a reaction of AU with EC, and next with PO. The first stage was carried out for 18.5-22 hrs at a temperature of 140°C and with potassium carbonate as a catalyst, while the second stage - in the pressure reactor at a temperature of 70°C, with TEA for 12.5-38 hrs [3].

Oligoetherols obtained by the aforementioned methods can be applied for synthesis of polyurethane foams. Thermal resistance of the foams was very good [1-3], but unfortunately, they were flammable.

The flammability of foams can be reduced by introducing atoms, such as: chlorine, bromine, phosphorus, silicon or boron, into their structure [8-10]. One of the boron compounds that can be incorporated into the structure of oligoetherols, e.g. in esterification reactions is boric acid. Such studies, initiated by Czupryński et al., have shown that organic boron compounds can be beneficial as reactive flame retardants [11-14]. The purpose of this work was to reduce the flammability of polyurethane foams by using oligoetherols with 1,3-pyrimidine ring and boron atoms for their synthesis. With this aim, oligoetherols with boron atoms and 1,3-pyrimidine rings using AU, EC and boric acid (BA) - one of the cheapest flame retardants - have been obtained. The structure and thermal properties of the obtained products were determined. The oligoetherols

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as polyol agents for synthesis of the foams have also been used. Thermal stability and flammability of the foams were tested.

2 Experimental

2.1 Oligoetherol synthesis

To a three-neck round bottom flask equipped with a reflux condenser, thermometer, and mechanical stirrer 6.36 g (0.05 mol) of AU (pure, Sigma-Aldrich, Steinheim, Germany), 17.61 (0.2 mol) of EC (pure, Fluka, Buchs, Switzerland) and 0.2 g of potassium carbonate (pure, POCH, Gliwice, Poland) as a catalyst were added. After the substrates were melted (50°C), a mechanical stirrer was turned on and the mixture was heated for 4 hours at 160°C [5]. Next the reaction mixture was cooled, an appropriate amount of BA (pure, POCH, Gliwice, Poland) and EC was added (9.28 g (0.15 mol) BA and 52.84 g (0.6 mol) EC or 12.37 g (0.2 mol) BA and 61.64 g (0.7 mol) EC), and the mixture was heated with continuous stirring for 4 hours at 120°C. After this time, 0.8 g potassium carbonate (catalyst) was added and the temperature was increased to 160°C. The end of the reaction was determined by analyzing the IR spectrum (the disappearance of the band at 1800 cm⁻¹ of valence vibrations of carbonyl group C=O of unreacted EC was used as the indicator). The time of this synthesis step was 17.5 or 32.5 hours.

2.2 Foams synthesis

A 10 g quantity of oligoetherol was introduced into a 500 cm³ polypropylene cup, then 3% distillate water, 3.89-5.84% silicon L-6900 (pure, Houdry Hüls, USA) as a surfactant, and 3.36-3.77% TEA (pure, POCH, Poland) as a catalyst were added. The mixture was vigorously stirred and then polymeric 4,4'-diphenylmethane diisocyanate (pMDI, mixture of di- and triisocyanates (30%) for synthesis; Merck-Schuchardt, Hohenbrunn, Germany) was added. The mixture was vigorously stirred until creaming started.

2.3 Analytical methods

The infrared spectra were registered on ALPHA FT-IR spectrometer (Bruker, Germany) or FT-IR Nicolet 8700 spectrometer (Thermo Electron Corp., USA) in ATR

technique. The ¹H-NMR spectra of products were recorded with a 500 MHz Bruker UltraShield spectrometer. The solvent was d₆-DMSO with HMDSO internal standard. Elemental analysis for C, H, N, were done with EA 1108, Carlo-Erba Analyzer. MALDI-ToF spectra were obtained on a Bruker Autoflex Speed reflectron time-of-flight mass spectrometer (Bruker, Germany), equipped with a SmartBeam II laser (352 nm) in 80-2000 m/z range. The laser impulse energy was approximately 60-120 μJ, the laser repetition rate was 1000 Hz, and the deflection value was set on m/z < 80 Da. The first accelerating voltage was held at 19 kV, and the second ion-source voltage was held at 16.7 kV. The reflector voltages used were 21 kV (first) and 9.55 kV (second). The data were recorded and analyzed using the software provided with the Autoflex instrument (FlexAnalysis version 3.3). Mass calibration (typically cubic calibration based on five to seven points) was performed using internal standards (gold ions and clusters from Au⁺ to Au₁₀⁺ depending on m/z range). The sample solution (ca. 5 mg/ml in H₂O) was placed on AuNPET [15] (0.5 μL) with a 0.5 μL standard α-cyano-4-hydroxycinnamic acid solution (1:1 water:acetonitrile with 0.2% TFA). The sum of ca. 7000 scans was collected for each sample. The thermal analysis of oligoetherols and foams was conducted with a thermogravimetric analyzer TGA/DSC 1 (Mettler Toledo, Spain); the recording conditions were as follows: sample weight 1-2 mg, temperature range 20-600°C, recording time 60 min, and nitrogen atmosphere. Some other properties of the oligoetherols were evaluated, such as density (pycnometrically), viscosity (Höpler viscometer, type BHZ, VEB Prüfgerate - Werk Medingen Sitz Freital, Germany) [16], and surface tension, by the detaching ring method [17].

The following properties of the foams were determined: apparent density [18], water absorption [19], stability of dimensions [20], thermal stability as the mass loss after heating at 150, 175, and 200°C for month, thermal conductivity coefficient [21], oxygen index [22] and horizontal burning tests [23].

Ethical approval: The conducted research is not related to either human or animal use.

3 Results

Dark brown resin-like products were obtained in one-pot reactions of AU with EC and BA (scheme 1, 2).

The structure of the products was determined by instrumental methods, using IR spectra (Figure 1), ¹H-NMR spectra (Supplementary material), elemental analysis (Table 1) and MALDI-ToF spectra (Supplementary

where: $x + y + w + z = 4$

Scheme 1: First stage of oligoetherols synthesis – reaction of 6-aminouracil (AU) with ethylene carbonate (EC).

where: $a + b = n$

where: $n + c + d = 12 \text{ or } 14$

Scheme 2: Second stage of oligoetherols synthesis - reactions of hydroxyethyl derivative of 6-aminouracil (AU) with boric acid (BA) and ethylene carbonate (EC) presented on structural fragments.

material). Spectrum analysis confirmed the assumed structure of oligoetherols. MALDI-ToF spectra show that the product is a mixture of oligols with various degrees of substitution with oxyethylene groups (Supplementary material).

The physicochemical and thermal properties of oligoetherols were examined (Table 2). Thermal analysis of obtained oligoetherols confirms that they are characterized by good thermal resistance.

Foaming tests were carried out using the obtained oligoetherols as polyol components (Supplementary material).

The physical properties of selected polyurethane foams, like apparent density, water uptake, dimension stability and thermal conductivity coefficient were studied (Table 3).

Thermal resistance and flammability of selected polyurethane foams were also studied (Table 4). The tests confirmed the obtaining of foams with good thermal resistance and reduced flammability.

4 Discussion

In the first stage, the reaction of AU with EC (Scheme 1) was carried out for four hours at 160°C in the presence of potassium carbonate as a catalyst [5]. EC was employed as both reagent and solvent. 4 moles of EC per mole of AU was used - it was the minimum amount of carbonate needed to block the reactive groups of AU (nitrogen atoms in the ring, an amino group) and to produce hydroxyethyl

Figure 1: IR spectrum of the oligoetherol obtained from 1 mol of 6-aminouracil (AU), 16 (4+12) moles of ethylene carbonate (EC) and 3 moles of boric acid (BA).

Table 1: Elemental analysis of oligoetherols.

Product of reaction	Elemental analysis [wt%]					
	calculated			found		
	C	H	N	C	H	N
(AU:EC):BA:EC (1:4) : 3 : 12	42.5	7.73	4.13	41.25	8.21	4.18
(AU:EC):BA:EC (1:4) : 4 : 14	41.16	7.68	3.60	40.62	7.95	3.82

groups that can react with BA. Next the reaction mixture was cooled, the BA (3 or 4 moles) and EC (12 or 14 moles) were added to the obtained hydroxyethyl derivative of AU and the reaction mixture was heated at 120°C for four hours (Scheme 2). This temperature allows the start of the esterification of the hydroxyethyl derivative of AU with BA and the reaction of BA with EC [24]. The yield of the side reaction of BA dehydration to metaboric acid is very small in this conditions. After this time, the catalyst (potassium carbonate) was added and the temperature was increased to 160°C, to allow for the reaction of EC with hydroxyethyl and hydroborate groups (Scheme 2). It was observed, that the foams with a larger number of 1,3-pyrimidine rings (obtained from oligoetherols of shorter length of etherol chains) show better thermal resistance [1-3], while foams with a larger amount of boron exhibit reduced flammability [8, 10]. Additionally, oligoetherols have to be in a liquid state at room temperature to be easily miscible with isocyanate. This condition was met by oligoetherols synthesized from 1 mol of AU, 3 moles of BA and 16 (4+12) moles of EC, as well as 4 moles of BA and 18 (4+14) moles of EC. If a smaller amount of EC was added, oligoetherols of large density at room temperature were obtained. In turn, the addition of a larger amount of BA needs a larger amount of EC and results in longer etherol chains.

Based on the spectrums analysis it was observed that the substrate reacted to oligoetherols. The signals of protons connected to nitrogen atoms in the AU-ring (10.1 ppm) and amine group (6.1 ppm) are not observed in the ¹H-NMR spectra (Supplementary material). It can be inferred from the spectra that hydrogen atoms were substituted by hydroxyethyl groups. Instead, there are observed signals of methylene protons, connected with nitrogen atoms (in the ring and amine group -N-CH₂-) and oxygen atoms (in oxyethylene groups -O-CH₂-CH₂-O- and borate groups -CH₂-O-B-) at a chemical

Table 2: The physicochemical and thermal properties of oligoetherols.

Product of reaction	Density [g/cm ³]	Viscosity [N·s/m ²] · 10 ³	Surface tension [N/m] · 10 ³	Thermal analysis			
				T _{5%} [°C]	T _{10%} [°C]	T _{25%} [°C]	T _{50%} [°C]
(AU:EC):BA:EC (1:4) : 3 : 12	1.2803	12629	49.98	102	135	185	270
(AU:EC):BA:EC (1:4) : 4 : 14	1.2578	18891	61.04	108	135	180	258
AU:EC* 1 : 12	1.2132	1600	46.20	100	130	210	280

* Data from work [5]

Table 3: Some properties of selected polyurethane foams.

Compo- sition number	Density [kg/m³]	Absorption of water [wt%]			Linear dimensions stability at temperature 150°C						Thermal conductivity coefficient λ [W/m•K]
					Length increase [%]		Width increase [%]		Depth increase [%]		
		after 5 min	after 3 h	after 24 h	after 20 h	after 40 h	after 20 h	after 40 h	after 20 h	after 40 h	
2	98.51	9.44	22.45	30.86	0.67	1.31	1.38	1.87	1.01	1.97	0.0396
5	92.17	11.68	21.06	26.78	0.76	0.97	0.67	0.97	0.01	1.13	0.0410

Table 4: Thermal resistance, horizontal burning tests and oxygen index of selected polyurethane foams.

Composition number	The mass loss after 30 days heating at temperature [wt %]			Thermal analysis				Horizontal burning tests			Oxygen index [vol%]
	150°C	175°C	200°C	T _{5%} [°C]	T _{10%} [°C]	T _{25%} [°C]	T _{50%} [°C]	Linear burning rate [mm/s]	Distance burnt [mm]	Mass loss during burning [% mas.]	
2	15.06	35.03	37.45	170	214	260	318	0.44	20.3	7.94	21.8
5	15.03	34.27	42.39	120	206	245	310	0	0	0	22.4

shift of 3.0-4.0 ppm (Supplementary material). Signals of hydroxyl protons appear in the range of 3.6-4.9 ppm and overlap with the signals of protons of carbon C(5) in the ring (4.2-4.3 ppm), which is confirmed by the spectra with D₂O (Supplementary material). The splitting of the signal of proton of carbon C(5) in the ring is associated with various atomic surrounding of the proton. Since, after D₂O addition the signals in the range of 4.5-4.8 ppm (Supplementary material) do not disappear completely, it can be concluded that unsaturated bonds are present in the products. Unsaturated bonds are formed at the ends of chains as a result of water elimination in the high-temperature process (160°C). Their amount is not significant. In the ¹H-NMR spectra small signals of boric acid at 8.15 ppm and hydroborate groups at 7.12 ppm are observed (these signals disappear after D₂O addition, Supplementary material). The analysis of the IR spectra of the products also confirms formation of oligoetherols. The spectra (Figure 1) include the stretching vibration bands of hydroxyl groups (3340 cm⁻¹), the asymmetric and symmetric stretching vibration bands and the deformation vibration bands of methylene groups at 2936, 2872 and 1460 cm⁻¹, respectively, stretching vibration bands of B–O bonds at 1407 and 1326 cm⁻¹, stretching vibration bands of C–O–C groups at 1123 cm⁻¹ and C–O groups in primary alcohols at 1050 cm⁻¹. Stretching vibration bands of carbonyl groups and of a double bond in the ring are present at 1690 and 1640 cm⁻¹, respectively, while vibration bands of 1,3-pyrimidine ring can be observed at 924, 883 and 776 cm⁻¹. Elemental analysis of

oligoetherols does not show any significant differences between calculated and found values (Table 1). In MALDI-ToF spectra for products of reactions of AU with EC and BA (Supplementary material) the peaks of molecular ions differing by M/z=44.05 (oxyethylene sub-units) can be observed. It indicates that oligoetherols different by length of oxyethylene chain are formed. The peaks of molecular ions confirm the occurrence of the reactions presented in scheme 2. Moreover, molecular ion masses increased by the mass of potassium cation (from catalyst) are recorded. The MALDI-ToF spectra show that unsaturated structures are formed (Supplementary material). Many of the unsaturated structures are generated in the conditions of registration of the spectrum (high temperature favors the elimination of water from the hydroxyethyl groups). The ¹H-NMR spectra with D₂O show that the small number of unsaturated structures in oligoetherols is present.

Measured density, viscosity and surface tension values of the obtained oligoetherols (Table 2) show that these compounds are suitable substrates for obtaining polyurethane foams.

Thermal analysis of oligoetherols (Table 2) confirms that they are characterized by good thermal resistance. However, it is slightly worse than the resistance of oligoetherols without boron atoms in the structure. A 50% mass loss of oligoetherols synthesized from AU, EC and BA occurs at lower temperature (258 and 270°C) than 50% mass loss of oligoetherols based on AU and EC (280-290°C) [5].

Foaming tests were carried out using the obtained oligoetherols as polyol components. Foaming was carried out in a laboratory scale. The composition of foaming samples was selected experimentally, taking into account one of the formerly obtained foams with a 1,3-pyrimidine ring [13]. Polymeric MDI was used as an isocyanate agent, and water was a foaming agent. TEA was used as a catalyst and silicone was applied as a surfactant (Supplementary material).

A significant exothermic effect (up to temperature 80°C) was observed during the foaming of polyurethane foams. The best foams of regular pores correspond to compositions 2 and 5 (Supplementary material) and they were accepted for further investigations.

The apparent density of the foams was in the range of 92.17–98.51 kg/m³ (Table 3), so they are classified as rigid materials. The foams have a larger density than those obtained from the products of AU reaction with EC as the sole coreactant (30.5–59.9 kg/m³) [2].

Investigations of water uptake indicate that the absorbability of the obtained foams is significantly larger than the one of the foams without boron incorporated (Table 3). Water absorption after 24 h of exposition was between 26.78–30.86 wt%, while absorption of the foams obtained from the products of AU reaction with EC as the sole reactant was no more than 15.2 wt% [2].

Dimensional stability tests show that shrinkage of the foams is very small (Table 3). A change of dimensions of the foams after 40 hours of exposition at temperature 150°C was less than 2% (Table 3). A slightly larger change of dimensions was observed for the foams obtained from oligoetherol with a lower amount of boron incorporated.

The thermal conductivity of the obtained materials (Table 3) is comparable with the thermal conductivity of Styrofoam (0.04 W/m•K).

The thermal resistance tests of the foams by static method were carried out. The samples were exposed to thermal treatment for 30 days at 150°C, 175°C and 200°C and mass loss was measured (Table 4). The results indicate that the foams made from oligoetherols obtained from AU, EC and BA show a larger mass loss than the foams obtained from oligoetherols which do not contain boron atoms. The foams obtained from oligoetherol with initial molar ratio of AU:EC equal to 1:6 showed the mass loss 6.9 wt.% at 150°C, 23.1 wt.% at 175°C and 33.1 wt.% at 200°C [2]. Dynamic thermal analysis (Table 4) indicates, that the foams have a 50% mass loss at a significantly lower temperature than those obtained from the products of AU reaction with the EC as the sole coreactant (430–550°C) [2].

Flammability of the foams were studied as follows: horizontal burning tests were made and oxygen index was

measured (Table 4). The foam obtained from oligoetherol synthesized at molar ratio (AU:EC):BA:EC = (1 : 4) : 4 : 14 (composition 5) in the test did not flame, for this reason its low oxygen index (22.4%) is rather surprising. The foam produced from oligoetherol synthesized at molar ratio (AU:EC):BA:EC = (1 : 4) : 3 : 12 (composition 2) is a self-extinguishing one; the flame did not reach the 150 mm line from the point of inflammation [25]. The flammability tests indicate that the obtained materials are self-extinguishing and flame-retardant [22, 23, 25] ones, in contrast to the foams synthesized from the products of the AU reaction with EC as the sole coreactant.

The research carried out confirmed the assumptions presented in the opening of the article. The introduction of boron atoms into the structure of oligoetherols causes a reduction in the flammability of the obtained polyurethane foams, without significant detrimental effects on their thermal resistance.

5 Conclusions

Oligoetherols obtained in the reaction of AU with EC and BA are characterized by high thermal resistance and can be used as a polyol component for the production of rigid polyurethane foams with improved thermal stability and reduced flammability. Polyurethane foams obtained from these oligoetherols show better thermal resistance than the resistance of classical polyurethane foams and can be applied up to 200°C. The obtained materials are flame-retardant and self-extinguishing under normal atmospheric conditions, in contrast to the foams obtained from oligoetherols synthesized from AU and EC.

Conflict of interest: Authors declare no conflict of interest.

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