Research Article

Reactions of N,N'-bis(2-hydroxyethyl)oxalamide with Ethylene Carbonate and Use of the Obtained Products as Components of Polyurethanes Foams

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N,N'-bis(2-hydroxyethyl)oxalamide (BHEOA) was subject to hydroxyalkylation with ethylene carbonate (EC). By means of instrumental methods (IR, $^1\text{H-NMR}$, MALDI ToF, GC, and GC-MS), an influence of the reaction conditions on structure and compositions of the obtained products was investigated. The hydroxyalkyl and hydroxyalkoxy derivatives of oxalamide (OA) were obtained by reaction of BHEOA with 2–10-molar excess of ethylene carbonate (EC, 1,3-dioxolane-2-one). The products have a good thermal stability and possess suitable physical properties as substrates for foamed polyurethanes. The obtained products were used in manufacturing the rigid polyurethane foams which possess enhanced thermal stability and good mechanical properties.

1. Introduction

N,N'-bis(2-hydroxyethyl)oxalamide (BHEOA, I) can be obtained in the reaction of dialkyl oxalate or oxalic acid with 2-aminoethanol [1–3], where $R = \text{H-}$, $\text{CH}_3\text{-}$ lub $\text{C}_2\text{H}_5\text{-}$; see Scheme 1.

Apart from oxalamide (OA) itself which is very important in many branches of industry [4–9], BHEOA has found application in industry, the synthesis of polymers including. N,N'-bis(2-hydroxyethyl) derivatives of OA are used for manufacturing the flame-retardant polyurethanes [10], amide urethanes [11, 12], and also tension-resistant flexible fibers [13, 14]. The presence of oxalamide group in the structure of polymers obtained during reactions of dialkyl oxalates with polymethylenediamines is responsible for higher strength of fibers and their better light resistance as compared to traditional polyamides [15, 16]. BHEOA was also used as a component in the flame-retardant polyurethane foams. Its presence not only decreased flammability but at the same time did not deteriorate any mechanical properties of the foamed polyurethane plastics [17].

In these studies BHEOA was subject to hydroxyalkylation with EC, and the obtained hydroxyethoxy derivatives were used for obtaining polyurethane foams of the enhanced thermal stability.

2. Experimental

2.1. Synthesis

2.1.1. Synthesis of BHEOA. BHEOA was synthesized according to procedure [3].

2.1.2. Reactions of BHEOA with EC. In a 100 cm³ three-necked round bottom flask 6.6 g (0.037 mole) BHEOA and the appropriate amount of EC (pure, Fluka, Switzerland) were placed to reach the molar ratio of reagents of 1:2–1:10 and 0.31–0.47 g potassium carbonate (4.14–12.42 g/mole BHEOA, 0.03–0.09 mole/mole BHEOA), or 0.28 g diazabicyclo[2.2.2]octane (DABCO) (7.6 g/mole BHEOA, 0.06 mole/mole BHEOA) was added. The reaction mixture was protected from moisture (by tube filled with

SCHEME 1

SCHEME 2

magnesium sulfate) and stirred mechanically at 120, 140, or 160°C with monitoring of progress of reaction by determination of unreacted EC [18].

2.1.3. Foam Preparation. Attempts of foaming the reactions products of BHEOA with EC were carried out in small 250 cm³ test cups at room temperature. To 5 g of hydroxyethoxy derivatives of OA, 0.1 g of surfactant (Silicon 5340, Houdry Hüls), 0.0–0.22 wt.-% of triethylamine (TEA) catalyst (pure, Avocado, Germany), and 2 wt.-% of water were added. After careful mixing of the components, a preweighed amount of 4,4'-diphenylmethane diisocyanate (pure, Merck, Germany) was added, calculated as described in [19]. The amounts of diisocyanate and water were adjusted to give OH:NCO molar ratio varying from 1:1.7 to 1:2.0. Each composition was vigorously mixed until it started to cream (see Table 4). The samples for testing were cut out from the foams thus obtained after ca. 48 hrs.

2.2. Analytical Methods. ¹H-NMR spectra of BHEOA and products of its reactions with EC were recorded with 500 MHz spectrometer (Bruker, Germany) in deuterated dimethyl sulfoxide (d₆-DMSO) and hexamethyldisiloxane (HMDS).

IR spectra of BHEOA and products of its reactions with EC were recorded from a capillary film or KBr pellets on a PARAGON 1000 FT spectrometer (Perkin-Elmer).

GC-MS experiments were conducted with Hewlett Packard 6890N chromatograph equipped with 5973 Network mass detector and HP-5MS 30 m × 0.25 mm column packed with film of 0.25 μm thickness. The samples were dissolved in acetonitrile.

Chromatographic analysis of by-products, that is, ethylene glycol (EG) and products of its consecutive reactions with EC and N-(2-hydroxyethyl)oxazolidinone (OXON), was performed with gas chromatograph HP 4890A (Hewlett Packard, Ringoes, NJ, US) with FID detector and HP1 30 m × 0.53 mm column packed with crosslinked methylsiloxane film of 1.5 μm thickness. Initial temperature was 50°C, heating rate 20°C/min, end temperature 220°C, time of heating at 220°C 6 min, loader temperature 250°C, detector temperature 300°C. The samples were dissolved in methanol

(0.01 M). Internal reference was cyclohexanone. Percentage of diols and polyols was calculated according to calibration curves as described in [20].

MALDI ToF spectra of reaction products of BHEOA with EC were obtained on Voyager-Elite Perseptive Biosystems (US) mass spectrometer working at linear mode with delayed ion extraction, equipped with nitrogen laser working at 337 nm. The matrix was 2,5-hydroxybenzoic acid. The samples were diluted with methanol to 1 mg/cm³, followed by addition of 10 mg/cm³ NaI in acetone. Therefore, in some cases the molecular ion weights were increased by the mass of Na⁺, K⁺, H⁺, and CH₃OH.

Thermal analyses (DTG and TG) of hydroxyethoxy derivatives of OA were performed in ceramic crucible, at 20–600°C temperature range, about 2 mg sample, under nitrogen atmosphere with Termowaga TGA/DSC 1 derivatograph, Mettler.

The following properties of hydroxyethoxy derivatives of OA have been determined: pycnometer density [21], refractive index, Höppler viscosity [22], and surface tension by ring detach method [23]. All measurements were made in temperature range of 20–80°C.

The following properties of foams were determined: apparent density [24], water uptake [25], stability of dimension [26], glass transition temperature (by DSC), thermal stability as the weight loss after heating at 150, 175, and 200°C for a month, and the compressive strength [27].

The differential scanning calorimetry (DSC) measurements were made using a DSC822^e Mettler Toledo instrument, in 20–200°C temperature range and 10 deg/min heating rate under nitrogen atmosphere. The results were recorded as heat flow in (W/g) versus temperature

3. Results and Discussion

In order to obtain higher hydroxyethyl derivatives with OA unit, reactions of BHEOA with a 2–10-molar excess of EC in the presence of potassium carbonate or DABCO as a catalyst at temperature 120–160°C (Table 1) were carried out. While maintaining reactions of BHEOA with a 2-molar excess of EC (Table 1, syntheses 1–4), generation of N,N,N',N'-tetrakis(2-hydroxyethyl)oxalamide (II) was expected; see Scheme 2.

TABLE 1: Reaction conditions of BHEOA with EC.

Run	Initial Molar Ratio	Amount of K ₂ CO ₃ (mole K ₂ CO ₃ /mole OA)	Temp. (°C)	Time of Reaction (h)	Molar Ratio BHEOA : x in PostReaction Mixture (from Mass Balance)
1.	1 : 2	0.03	120	25*	—
2.	1 : 2	0.06	140	5	1 : 1.87
3.	1 : 2	0.06**	140	11	1 : 1.74
4.	1 : 2	0.06	160	2	1 : 1.82
5.	1 : 4	0.06	140	10	1 : 3.76
6.	1 : 6	0.06	140	14	1 : 5.61
7.	1 : 6	0.06	160	5	1 : 5.45
8.	1 : 10	0.09	140	24.5	1 : 9.07
9.	1 : 10	0.09	160	8	1 : 9.14

x: oxyethylene unit, *same EC was unreacted, **DABCO was used as catalyst.

TABLE 2: Percentage of by-products in reaction products of BHEOA with excess of EC.

Entry*	Initial molar ratio	Percentage of OXON in post-reaction Mixtures (wt.-%)	Percentage of glycols in postreaction mixtures (wt.-%)		
			DEG ^a	TRIEG ^b	TETRAEG ^c
1.	1 : 2	0	0	0	0
2.	1 : 2	5.49	0	0	0
3.	1 : 2**	18.48	0	0	0
4.	1 : 2	4.74	0	0	2.26
5.	1 : 4	0	2.15	0	0
6.	1 : 6	0	1.41	3.41	0
7.	1 : 6	0	2.75	3.49	2.35
8.	1 : 10	1.75	0	0	1.47
9.	1 : 10	2.65	0	0	2.45

*Entry according to Table 1, **DABCO was used as catalyst, ^adiethylene glycol, ^btriethylene glycol, ^ctetraethylene glycol.

TABLE 3: Thermal stability of reaction products of BHEOA with EC.

Entry	Initial molar ratio OA : EC	T _{5%} (°C)	T _{10%} (°C)	T _{20%} (°C)	T _{50%} (°C)	Temperature of max. decomposition (°C)
1.	BHEOA	230	250	265	270	270
2.	1 : 6	160	180	220	260	250 and 360
3.	1 : 10	90	160	190	240	220 and 350
4.	1 : 10*	90	160	210	290	250 and 350
5.	comp. 1	200	220	240	330	260

*after heating of the product at 200°C for 4 hours, T_{x%}—temperature at which the weight loss is x%.

TABLE 4: Parameters of foaming process.

Initial molar ratio BHEOA : EC in polyol	Composition No.	Composition (g/100 g of tetraol)				Foaming process			Properties of foams just prepared
		isocyanate ^a	water	catalyst ^b	molar ratio OH : NCO	time (s)			
						creaming ^c	expanding ^d	drying ^e	
1 : 6	1.	200	2	0.50	1 : 1.57	36.5	18	0	rigid
1 : 10	2.	212	2	0.50	1 : 2.31	17	7	0	rigid

a: 4,4'-diphenylmethane diisocyanate, b: triethyloamine,

c: Time of Creaming: the time elapsed from the moment of mixing to the start of volume expansion.

d: Time of Expanding: the time from the start of expansion to the moment of reaching the sample final volume.

e: Time of Drying: the time from reaching by the sample its final volume to the moment of losing its surface adhesion to powdered substances.

TABLE 5: Properties of foams.

Kind of polyol	Comp. No. ^a	Density (kg/m ³)	Water uptake (wt.-%)			Linear dimension change after heating at 150°C (%)					
			after 5 min	after 3 hrs	after 24 hrs	length		width		thickness	
						after 20 hrs	after 40 hrs	after 20 hrs	after 40 hrs	after 20 hrs	after 40 hrs
EC6	1.	37.79	3.80	9.39	9.63	0.00	1.17	0.00	0.00	0.39	0.19
EC10	2.	30.86	4.92	9.66	11.71	2.15	3.01	1.39	1.74	0.00	0.00

TABLE 6: Compressive strength of polyurethane foams (MPa).

Kind of polyol	Comp. no.	Compressive strength σ_M (MPa)	Increase of Compressive Strength in (%) after exposition in temperature (°C)	
			150	175
EC6	1.	0.14	112	5
EC10	2.	0.16	115	2

FIGURE 1: ¹H-NMR spectrum of the reaction product of BHEOA:EC 1:2 in the presence of 0.06 mole K₂CO₃/mole OA at 140°C. FIGURE 2: IR spectrum of the reaction product of BHEOA:EC 1:2 in the presence of 0.06 mole K₂CO₃/mole OA at 140°C.

At the temperature of 120°C and higher, reactions with alkylene carbonates are proceeded while releasing carbon oxide (IV), without building up carbonate groups into the product's structure [28]. A mass balance (Table 1) made for the reaction of BHEOA with EC on the a.m. assumption demonstrated that EC was partially decomposed into ethylene oxide and carbon dioxide [28].

Basing on the analysis of ¹H-NMR spectra in the obtained products, it was found that with a 2-molar excess of EC there are secondary amide groups in a derivative's structure. There is a signal at 8.5 ppm in the derivative's spectrum (Figure 1), similarly as in ¹H-NMR BHEOA spectrum. Next, in IR spectrum of the product (Figure 2), the first and the second amide bands of secondary amide at 1651 and 1520 cm⁻¹ are observed.

Further, in ¹H-NMR spectrum of the product (Figure 1) a signal at 8.0 ppm is present from protons of the secondary amide groups of oxalamidoester; a similar one was observed in spectra of the reaction products of oxamic acid with alkylene carbonates [29, 30]. Presence of this signal demonstrates possibility of BHEOA dimerization while creating oxalamidoester unit in the product (III), similarly as it occurred during reaction of the OA alone with EC [31]; see Scheme 3.

Confirmation of such course of the reaction provides the presence (in spectrum of the post-reaction mixture BHEOA with a 2-mole excess of EC/Figure 1/) of signals at app. 2.6 and 2.7 ppm originated from protons of NH₂ group and methylene group at nitrogen atom in 2-aminoethanol, which is created during condensation.

An increase of the reaction temperature up to 160°C (Table 1, synthesis 4) causes a decrease of intensity of the signal at 8.0 ppm in ¹H-NMR spectrum, which can mean reduction of condensation contribution of hydroxyethyl derivatives of OA. On the other hand, a change of the catalyst from potassium carbonate to DABCO (Table 1, synthesis 3) results in an increase of the said signal.

In ¹H-NMR spectra of the reaction products of BHEOA with a 2-molar excess of EC (Figure 1), there are also signals at 4.20 and 4.25 ppm sourced from protons of the methylene groups at ester unit-oxalamidoester and/or carbonate one. During the reaction, there is a possibility of building up of the carbonate groups into the product's structure, but at the same time the carbonate group can join amide group forming product (IV) or hydroxyl group giving product (V); see Scheme 4.

The presence of ester groups is confirmed by analysis of IR spectrum (Figure 2) of the BHEOA reaction product

SCHEME 3

SCHEME 4

SCHEME 5

SCHEME 6

with a 2-molar excess of EC; bands in the spectrum were observed at 1727 and 1268 cm^{-1} from C=O and -O-(CO) valence vibrations of ester, respectively.

Furthermore, a band at 1122 cm^{-1} has appeared in the spectrum which is specific for C-O-C valence vibrations and demonstrates a distinctly easier course of the consecutive

reactions in the hydroxyethyl groups with EC as compared to reactions of the secondary amide groups see Scheme 5.

Signals at 8.0 and 8.5 ppm disappear only at a 6-molar or higher excess of EC (Table 1, syntheses 6–10, Figure 3).

In IR spectra of products obtained at 6-molar or high or excess of EC bands at 1724 and 1268 cm^{-1} are still present,

FIGURE 3: ^1H -NMR spectra of the reaction product of BHEOA:EC: (a) 1:4 at 140°C , (b) 1:6 in the presence of 0.06 mole K_2CO_3 /mole OA at 160°C .

which indicates the presence of OA dimers and/or carbonate groups in the product's structure. The actual structure of the product can be presented with a general formula (VII), where $m \geq 1$, $x, y, r \geq 0$, n, s, t, w and $z = 4\text{--}10$ —number of moles of EC, which reacted with BHEOA see (Scheme 6).

MALDI ToF spectrography enabled an assessment of the composition of the obtained OA hydroxyethyl derivatives. The products obtained with a 6- and 10-molar excess of EC (Figures 4) consist of oligomers containing up to 10 and 14 oxyethylene units per mole of OA, respectively. No OA dimers in the post-reaction mixtures were found. MALDI ToF method cannot be used for confirmation of a presence of carbonate groups in the products because the molar mass of oxyethylene and carbonate units is 44 g/mol.

However, GC-MS analysis of the reaction products of BHEOA with EC exhibits dimerization of hydroxyethyl derivatives of OA, as it has evidenced the presence of N-(2-hydroxyethyl)oxazolidinone (OXON, VIII) in their composition, formed in the reaction of 2-aminoethanol with EC, similarly as in the reaction products of OA with EC (see Scheme 7).

Quantity analysis of OXON by GC method enabled the assessment of dimerization contribution. The largest amount of OXON was formed in the post-reaction mixture obtained with a 2-molar excess of EC (Table 2, entries 1–4), especially in the presence of DABCO as a catalyst (app. 18.48 wt.-%).

FIGURE 4: MALDI ToF spectrum of reaction product of BHEOA:EC 1:6 in the presence of 0.06 mole K_2CO_3 /mole at 160°C .

OXON at a 4- and 6-molar excess of EC is not formed and with a 10-molar excess of EC, the content of OXON does not exceed 3 wt.-% (Table 2). The increase of the reaction temperature does not influence significantly the contribution of OXON (Table 2, entries 2 and 4, 8, and 9). It has been found that contribution of OXON is distinctly lower than in the reaction products of OA with EC; the presence of the secondary amide groups distinctly limits contribution of condensation of hydroxyethyl derivatives of OA. MALDI ToF analysis was performed for the reaction products of BHEOA with a 6- and 10-molar excess of EC, composition of which does not show presence of OXON or its insignificant content via GC method; that is why the MALDI ToF method has not confirmed the presence of OXON in these products.

Due to the fact that in the products obtained with a 4- and 6-molar excess of EC, no presence of OXON was found; on the basis of spectral analysis, an explicit confirmation of contribution of carbonate groups in the structure of hydroxyalkylation products of BHEOA with EC can be provided. A signal at 4.2 ppm noted at ^1H -NMR spectra originates from protons of the methylene groups at the carbonate group.

Furthermore, GC analysis of the post-reaction mixtures evidenced the presence of by-products poly (ethylene glycols) in their composition (Table 2). It should be noted that in the reaction products of BHEOA with EC no presence of GE itself was found. Content of poly (ethylene glycols) does not exceed 9 wt.-% and is not correlated simply to the EC excess used for the reaction. The largest contribution of glycols occurs in case of the product obtained with a 6-molar excess of EC (Table 2, entries 6 and 7).

Thermogravimetric studies demonstrated enhanced thermal stability of the obtained hydroxyethoxy derivatives of OA. There is only one peak with the maximum at

SCHEME 7

FIGURE 5: Thermal analysis of the reaction product of BHEOA:EC 1:10 in the presence of 0.06 mole K_2CO_3 /mole OA at 160°C: (a) before heating at 200°C, (b) after heating at 160°C for 4 hours.

270°C on the DTG BHEOA curve what means the complete decomposition of the compound—a simultaneous decomposition of 2-hydroxyethyl groups and oxalamide unit (Table 3, entry 1). On the other hand, in case of BHEOA reaction products with the EC excess, two peaks on the DTG curve are noticeable (Table 3, entry 2 and 3, Figure 5). The first of them having its maximum at 250°C results from decomposition of carbonate units while the second one at 350°C originates from decomposition of oxalamide and oxalamidoester units. Thermal analysis of the BHEOA reaction product with a 10-molar excess of EC before and upon holding at 200°C (in decomposition conditions of carbonate groups [32, 33]) demonstrated a decrease of the first peak from the maximum at 220°C, which confirms decomposition of carbonate groups present in the product (Table 3, entry 4, Figure 5). Since decomposition of oxalamide groups occurs at the temperature of 350°C, their presence in the product's structure guarantees its thermal stability. Upon comparison of thermal analysis curves for the reaction products of OA with EC and BHEOA with EC, it can be observed that the maximum of the first peak on the DTG curve is distinctly transferred to a higher temperature than in case of the reaction products of BHEOA with EC, which means a lower contribution of carbonate groups in the structure of products.

Some selected physical properties of the obtained products in the reaction of BHEOA with the excess of EC were

investigated and it was found that while increasing the temperature refractive index, density and surface tension decrease linearly and the viscosity in exponential mode (Figure 6). Therefore, they are subject to change in the way typical for polyols used traditionally for obtaining polyurethane foams [33].

The obtained products of hydroxyalkylation of BHEOA with 6- and 10-molar excess of EC were foamed using MDI, water as foaming agent and TEA as a catalyst, carrying out the foaming in small laboratory scale.

Foams of the highest thermal stability were achieved from polyol obtained from BHEOA and the 6-molar excess of EC (EC6) with 0.5 wt.-% contribution of TEA (Table 4).

Apparent density of foams obtained with contribution of EC6 and EC10 is within 31–38 kg/m³ (Table 5), and glass transition temperature 104 and 96°C, which justifies an explicit classification of the obtained foams as rigid foams [34].

The lowest water uptake (9.6 wt.-%) after a 24-hour exposure in water at room temperature is displayed by foams obtained from polyol EC6 (Table 5). The obtained foams upon holding at 150°C are subject to shrinkage, while the maximum change of dimensions is 3% linear and it concerns the foams obtained wt.-% with EC10 contribution (Table 5).

Thermogravimetric studies of the obtained polyurethane foams confirm their enhanced thermal stability; a 5% weight loss occurs not before temperatures 200°C, and the

FIGURE 6: Physical properties of reactions products of BHEOA with EC in function of temperature.

maximum decomposition temperature is 260°C for foams with EC6 (Table 3). Static studies of thermal stability of foams have demonstrated that weight loss in the foams while heating for 30 days was increased together with the increase of exposure to temperature. The lowest weight loss is demonstrated by foams obtained from polyol EC6 and is 14.5 wt.-% at 150°C, 24 wt.-% at 175°C, and 43 wt.-% at 200°C. Weight losses of the foams obtained from EC10 are slightly higher.

The foams hold for 30 days at the temperature of 150 and 175°C were tested for compression strength (Table 6). The foams after the temperature exposure are featured principally by an increased compression strength, whereby the biggest increase, even by 115%, has been observed upon heating the foams with EC12 at 150°C. A higher holding temperature of the foams (175°C) affects a decrease of the compression strength.

4. Conclusions

- (1) In the reactions of N,N'-bis(2-hydroxyethyl)oxalamide with an excess of ethylene carbonate, the hydroxyethoxy derivatives of oxalamide were obtained, which in their structure contain, apart from oxalamide groups, also carbonate and oxalamidoester groups.
- (2) The obtained oligomers are accompanied by insignificant amount of by-products: poly(ethylene glycols) and N-(2-hydroxyethyl)oxazolidinone.
- (3) The obtained hydroxyethoxy derivatives of oxalamide are characterized by the enhanced thermal stability and show physical properties of typical polyols used for manufacturing polyurethane foams.

- (4) The polyurethane foams obtained with the contribution of hydroxyethoxy derivatives of oxalamide are characterized by good stability of dimensions, enhanced thermal stability.

References

- [1] W. H. Rauscher and W. H. Clark, "Identification of esters of dibasic acids by the use of ethanolamine," *Journal of the American Chemical Society*, vol. 70, no. 1, p. 438, 1948.
- [2] E. S. Lane, *J. Chem. Soc.* 1956, 2006-10; CA: 51, 263d, 1957.
- [3] F. Strain, *pat. USA* 2 379 261, 1945.
- [4] L. Lorenzoni, G. Messina, and V. Bruzzi, *pat. eur.* 271 161, 1988; CA: 109, 189854q, 1988.
- [5] R. H. Hansen, C. A. Russell, T. De Benedictis, W. M. Martin, and J. V. Pascale, "Inhibition of the copper-catalyzed oxidation of polypropylene," *J. Polymer Sci.* 2, 587, 1964.
- [6] T. Tateyama, *pat. jap.* 7 385 636, 1973; CA: 80, 96792k, 1974.
- [7] H. Hermann and E. Fischer, *pat. niem.* 1 104 695, 1961.
- [8] Y. Kawashima and A. Yamanouchi, *pat. jap.* 74 066 783, 1974; CA: 81, 170783x, 1974.
- [9] H. Beck, *pat. USA* 3 896 100, 1975; CA: 83, 180250b, 1975.
- [10] T. Reetz and J. Britain, *pat. USA* 3 719 639, 1973; CA: 79, 6515z, 1973.
- [11] H. Bassilios, A. Farag, and H. Asfour, *Kolor. Ert.* 16(1-2), 19, 1974; CA: 81, 122521p.
- [12] G. Yangol and K. Kornev, *Vysokomol. Soedin.* 3, 55, 1966; CA: 68, 30526x, 1968.
- [13] C. Grandclement and A. Rio, *pat. fr.* 1 380 681, 1964; CA: 62, 7927f, 1965.
- [14] K. Sakata, T. Tanabe, S. Yamashiro, H. Okada, and T. Tose, *pat. jap.*, 20 299, 1963; CA: 68, 22685h, 1968.
- [15] G. Braz, J. Kardash, V. Yakubovich, G. Myasnikova, and A. Yakubovich, "Poly benzoxazoles their synthesis and thermal desolation," *Vysokomolekul. Soedin.*, vol. 8, no. 2, p. 272, 1966.
- [16] G. Starnatoff and N. Symons, *pat. USA* 3 247 168, 1966.
- [17] P. Haas, H. Hettel, and A. Ruckes, *pat. niem.* 3 829 958, 1990; CA: 113, 41996z, 1990.
- [18] D. Kijowska, S. Wołowicz, and J. Lubczak, "Kinetics and mechanism of initial steps of synthesis of polyetherols from melamine and ethylene carbonate," *Journal of Applied Polymer Science*, vol. 93, no. 1, pp. 294–300, 2004.
- [19] D. Kijowska and M. Kucharski, "Polyetherols from melamine and alkylene carbonates: properties and application of foamed polyurethanes," *Journal of Applied Polymer Science*, vol. 94, no. 6, pp. 2302–2308, 2004.
- [20] J. Lubczak, I. Zarzyka-Niemiec, and D. Naróg, "Hydroxyalkylation of parabanic acid. III. Polymers from parabanic acid and ethylene carbonate," *Journal of Applied Polymer Science*, vol. 100, no. 2, pp. 1443–1449, 2006.
- [21] P. Kowalski, *Laboratorium z Chemii Organicznej*, WNT, Warszawa, Poland, 2004.
- [22] D. Kocot-Bończak, *Ćwiczenia Laboratoryjne z Chemii Fizycznej*, PZWL, Warszawa, Poland, 1977.
- [23] T. Dryński, *Ćwiczenia Laboratoryjne z Fizycznej*, PWN, Warszawa, Poland, 1967.
- [24] Polish (European) Standards: PN-EN ISO 845.
- [25] Polish (European) Standards: PN-EN ISO 2896.
- [26] Polish (European) Standards: PN-EN ISO 2796.
- [27] Polish (European) Standards: PN-93C/89071, ISO 884:1978.
- [28] J. H. Clements, "Reactive applications of cyclic alkylene carbonates," <http://www.huntsman.com/>.
- [29] I. Zarzyka-Niemiec, "Synthesis and application of oligomers obtained from oxamic acid and ethylene carbonate," *Polimery/Polymers*, vol. 54, no. 2, pp. 99–105, 2009.
- [30] I. Zarzyka-Niemiec, "Hydroxyalkylation of oxamic acid with propylene carbonate: synthesis, composition, and properties of products," *Journal of Applied Polymer Science*, vol. 110, no. 1, pp. 66–75, 2008.
- [31] I. Zarzyka-Niemiec, "Reactions of oxalamide with ethylene carbonate," *Journal of Applied Polymer Science*. In reviews.
- [32] H. Nariyuki and T. Miyuki, *pat. jap.* 3 052 838, 1991, CA: 115, 71109w, 1991.
- [33] W. Olczyk, *Poliuretany*, WNT, Warszawa, Poland, 1968.
- [34] Z. Wirpsza, *Poliuretany*, WNT, Warszawa, Poland, 1991.