Oligoetherols and polyurethane foams with carbazole ring

Renata Lubczak*

*Rzeszów University of Technology, Department of Organic Chemistry, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland; e-mail: rlubczak@prz.edu.pl

(Received: 14 November, 2011; published: 15 August, 2012)

Abstract: The method of synthesis of oligoetherols with carbazole ring from 9-(2,3-epoxypropyl)carbazole and glycerol and oxiranes like ethylene and propylene oxide is presented. Structure and some physicochemical properties of the products is described. The oligoetherols were demonstrated as good substrates for synthesis of polyurethane foams of enhanced thermal resistance.

Introduction

The polymers with carbazole ring included have some unique physical properties. They are photo- and electroluminescent materials, liquid crystals, electroconductors, and non-linear optical materials [1-7]. Carbazole decomposes at temperatures higher than 260 °C. High thermal resistance of carbazole [8] allow to anticipate that introducing such a ring into oligoetherols increases thermal resistance of them as well as polymers obtained from oligoetherols. The multifunctional oligo- and polyetherols with carbazole ring were not known until now except some preliminary results from this lab [9-11]. Carbazole is mono-functional compound and this is the reason for limited application of synthesis of oligoetherols by its reaction with oxiranes. Therefore, previous studies were devoted to increase its functionality and solubility of carbazole derivatives in oxiranes [12]. Synthesis of linear oligoetherols by reaction of carbazole with epichlorohydrin resulted in formation of 9-(2,3-epoxypropyl)carbazole according to the scheme [9-11]:

where the epoxide ring was later opened by reaction with water or glycerol.

Obtained products (I) and (II) were then converted into bi-functional oligoetherols by reaction with oxiranes:

where: $\text{R} = -\text{H}, -\text{CH}_3$; $x + y = n$;
 n – number of molecules of attached oxirane

Oligoetherols with carbazole ring were also obtained by reaction of carbazole with ethylene chloride and further reaction diethanolamine into diol and its conversion in reaction with excess oxiranes: ethylene and propylene oxides (EO and PO, respectively) [11]:

The oligoetherols obtained in that way have similar properties like regular polyols used for obtaining polyurethanes. The reaction of those oligoetherols with bifunctional isocyanates led to linear polyurethanes of promising high thermal resistance [9-11]. Here the further results on multifunctional oligoetherols with carbazole ring, the convenient substrates to obtain polyurethane foams of enhanced thermal resistance are presented.

Results and discussion

Synthesis of oligoetherols

The reaction of carbazole with epichlorohydrin led to the formation of 9-(2,3-epoxypropyl) carbazole (EPC) according to the scheme (1), which underwent ring opening upon reaction with glycerol in presence of TEA to give three-functional 7-(9-carbazolyl)-4-oxaheptane-1,2,6-triol (COHT,III) [12] according to the following reaction scheme:

The process was performed without any solvent, using two equivalents of glycerol. The obtained COHT was semisolid resin, which was identified by elemental analytical, IR and ^1H NMR spectra (see Experimental; Analytical data of product). In the ^1H NMR spectrum the multiplet at 7.0 – 8.3 ppm from carbazole ring protons was observed. The resonances of $-\text{OH}$ were present with 4.8 – 5.1 ppm region, the signals of methylene protons of $-\text{CH}_2\text{O}-$ were found at 3.2– 3.7 ppm, while methine proton resonances were observed at 3.9 – 4.1 ppm. The aromatic C–H bands were observed at 747 and 720 cm^{-1} in the IR spectra, the stretching $-\text{OH}$ bands were found at 3350 cm^{-1} and 1152 cm^{-1} , while valence bands of C–O–C were found at 1021 cm^{-1} and 1056 cm^{-1} . The obtained product is readily soluble in oxiranes: EO and PO at room temperature. Addition of TEA to such a solution and heating the mixture to 60 $^\circ\text{C}$ triggered the reaction of formation of three-functional oligoetherols according to the scheme:

where: $\text{R} = -\text{H}, -\text{CH}_3$

$$x + y + z = n$$

n – number of molecules of attached oxirane

IR spectra of oligoetherols IV are remarkably different from that of COHT (III). The intensity of the band at 1050 cm^{-1} increased indicating formation of ether bonds (Fig.1) Also the band at 2900 cm^{-1} grew, indicating the incorporation of oxyalkylene units into oligoetherol. The intensity of the resonance at 3.5 ppm in the ^1H -NMR of oligoetherols IV (Fig.2) increased according to the increase of number of oxyalkylene

units in a product. Simultaneously the resonances at 4.5 – 5.1 ppm diminished illustrating the disappearance of hydroxyl protons due to progressing reaction of OH with oxirane. The structure of products of hydroxyalkylation of COHT was further confirmed by MALDI-TOF spectra (Table 1). The series of molecular peaks differing by $m/z = 44$ or 58, depending on used oxirane were characteristic for series of products, containing various amount of oxirane units.

The oligoetherols were obtained from the COHT: oxirane 1:6 molar ratio system. Some physical parameters like refraction index, density, viscosity and surface tension in function of temperature were studied (Fig. 3). Typical changes of those parameters in function of temperature were observed. The products obtained from EO had higher refraction index and density than those synthesized from PO. Generally the physical properties of oligoetherols synthesized here are similar to those of typical polyols used for obtaining polyurethane foams [13]. The synthesized oligoetherols have good thermal resistance (Table 2), especially these obtained from EO. Their thermal decomposition starts at 270-280 °C (mass loss 5%), while their temperature of 50% decomposition falls into 490-540 °C region. High thermal resistance of these products suggested their usefulness as substrates for thermally resistant polyurethane foams.

Fig. 1. IR spectrum of product of reaction of COHT with EO.

Fig. 2. ^1H -NMR spectrum of product of reaction of COHT with EO.

Tab. 1. Interpretation of MALDI ToF spectrum of reaction product obtained from 1 mole of COHT and 6 moles of PO.

Signal position m/z	Relative intensity of signal [%]	The molecular ion structure	Calc. molecular weight [g/mol]
276.3	84.7	EPC + CH ₃ OH + Na ⁺	278
334.4	100	COHT + Na ⁺	336
392.4	46.9	COHT + PO + Na ⁺	394
450.4	10.2	COHT + 2 PO + Na ⁺	452
473.3	9.2	COHT + 3 PO + Na ⁺	475
531.3	3.1	COHT + 4 PO + Na ⁺	533
606.4	2.0	COHT + 5 PO + H ⁺	606
664.4	3.1	COHT + 6 PO + H ⁺	664
722.5	2.4	COHT + 7 PO + H ⁺	722

PO -oxyalkylene unit from propylene oxide

Tab. 2. Thermal stability of oligoetherols and polyurethane foams.

Product	T _{5%} [°C]	T _{10%} [°C]	T _{25%} [°C]	T _{50%} [°C]
Oligoetherol COHT + EO	280	300	380	540
Foam obtained from oligoetherol COHT + EO	220	290	340	380
Oligoetherol COHT + PO	270	280	330	490
Foam obtained from oligoetherol COHT + PO	190	240	310	360

Studies of foams

The polyurethane foams were performed on laboratory scale (Table 3). The optimization of amount of isocyanate, foaming agent (amount of water), catalyst and kind of oligoetherol was performed for foaming. The water amount was optimized for the oligoetherol obtained from EO as 2% water related to mass of oligoetherol; the use of higher water percentage led to the formation of irregular pores. The amount of catalyst was also crucial; the rigid foams were obtained when 1.25% catalyst was applied in case of oligoetherol obtained from EO was used and 3.34% in case of oligoetherol obtained from PO.

The best foams were obtained when the molar ratio of 4,4'-diphenylmethane diisocyanate to number of hydroxyl groups was maintained at the level of 1.6 for the oligoetherol obtained from EO and 1.4 in case of the oligoetherol synthesized from PO. Lower or higher ratio led to underhardened foams with large pores.

Foaming compositions showed short creaming times (8 sec.) and grow times (to 30 sec.). Drying times in case of compositions from EO was 3 s, while in case of PO it was as long as 90 seconds.

Fig. 3. Physical properties of oligoetherols obtained in reaction of COHT with oxiranes versus temperature.

The best foams, the rigid ones and with unisized pores were subjected to density, size stability at 150 °C, water uptake, thermal resistance and change of mechanical properties upon thermal exposure (Table 4). It has been found that the obtained foams are rigid at room temperature and their apparent density was 40 – 44 kg/m³. The water uptake was low, maximum to 6.5 mass%. The dimensional stability at 150 °C measurements revealed that the dimension change was no larger than 5% of initial dimension.

Dynamic thermal analysis showed that 5% mass loss starts at ca. 200 °C, while temperature of 50% mass loss was 360-380 °C (Table 2). Long-lasting, static measurements of thermal resistance were conducted at 150 °C for one month (Fig. 4). Continuous decrease of foam mass was observed throughout the test, however the largest mass loss was noticed at the first day of heating. The mass loss of foam obtained from oligoetherol synthesized from COHT and EO was 11,5 mass % within one month. Concomitantly the increase of compression strength was observed, for instance the foams obtained from oligoetherol synthesized with EO showed twice increase of compression strength after one month heating at 150 °C, presumably due to extended crosslinking upon thermal exposition. Thermal stability of obtained foams was compared with thermal stability of a typical, industrial, rigid polyurethane foam (Table 4). It is said that mass loss in 150 degree after 14 days is significant and reaches almost 50%. At the same time, these conditions cause deformation of foams and they are no more suitable for tests of strength.

Tab. 3. The influence of composition of foaming process.

Oligoetherol obtained with the use of	Compo- sition number	Composition* g/100g of oligoetherol			Molar ration OH:NCO (isocy- anate coeffi- cient	Foaming process			Characteristics of foams just prepared
		izocya- nate	TEA	wa- ter		Time of creaming [s]	Time of expan- ding [s]	Time of drying [s]	
EO	1	116	1.25	2	1.57	15 ±1	28±2	2±0.5	underhardened
	2	144	2.08	2	2.00	12±1	14±1	5±1	large pores
	3	132	2.92	3	1.82	-	-	-	irregular pore sizes
	4	240	3.75	4	3.48	6±1	10±1	2±0.5	large pores
	5	116	1.67	2	1.57	10	14±2	2±0.5	large pores
	6	116	1.25	2	1.57	8±1	17±2	3±0.5	rigid
	7	116	1.25	2	1.57	8±1	23±2	3±0.5	rigid
PO	8	104	2.50	2	1.39	8±1	42±3	90±5	fragile
	9	104	3.34	2	1.39	8±1	28±2	97±5	rigid
	10	104	3.75	2	1.39	5±1	30±2	90±5	underhardened
	11	104	4.17	2	1.39	8±1	30±2	90±5	underhardened
	12	104	3.34	2	1.39	6±1	32±2	90±5	rigid

* Amount of surfactant 2g per 100 g of oligoetherols

Fig. 4. Thermal stability of polyurethane foams as the weight loss after heating at 150 °C for a month.

Tab. 4. Some properties of polyurethane foams.

Polyurethane foams	Density [kg/m ³]	Water uptake [%] after			Linear dimension stability [%] at temperature 150° C after 40 h			Mass loss in temp. 150°C after 14 day [%]	Compression Strength [MPa]	
		5 min.	3 h	24 h	Length change	width change	depth change		before exposition	after exposition by month in temperature 150°C
obtained from oligoetherol on EO	44.0±3.1	2.25±0.10	4.33±0.12	6.52±0.25	5.14±0.05	4.58±0.10	0.51±0.01	7.77	0.172±0.005	0.324±0.006
obtained from oligoetherol on PO	40.0±5.0	1.79±0.08	3.75±0.10	6.54±0.34	2.16±0.06	0.14±0.01	1.54±0.12	11.36	0.324±0.008	0.394±0.004
classical industrial	26.0±3.2	2.13±0.07	4.05±0.13	5.52±0.28	*	*	*	49.14	*	*

* Foam undergoes deformation

Conclusions

Three-functional oligoetherols with carbazole ring can be obtained starting from carbazole, by consecutive conversions with epichlorohydrin to 9-(2,3-epoxypropyl)carbazole, ring opening with glycerol, and finally by reaction with oxiranes EO or PO. The oligoetherols have similar properties as those used regularly for obtaining polyurethane foams except higher thermal resistance of the former. Obtained oligoetherols are useful substrates for synthesis of polyurethane foams which have enhanced thermal resistance and remain unchanged upon long exposure at 150 °C.

Experimental

Synthesis

The synthesis of 9-(2,3-epoxypropyl)carbazole (EPC) was performed as previously reported [12].

Opening of epoxide ring with glycerol

To a 100 cm³ three-necked round bottom flask equipped with reflux condenser, mechanical stirrer and thermometer 25.0 g (0.11 mole) of EPC and 11.8 cm³ (0.16 mole) of glycerol (pure, POCH, Gliwice, Poland) were introduced. The mixture was stirred and heated until dissolving of substrated (at temperature ca. 60 °C), then 0.1 cm³ triethylamine (TEA, pure, Fluka, Buchs, Switzerland) catalyst was added. The mixture was heated to 120 °C. The progress of reaction was monitored by determination of epoxide number (EN). Then 50 cm³ distilled water was added, the mixture was vigorously stirred and heated at 90 °C for about one hour to rinse the glycerin off. The mixture was cooled down to room temperature and water layer was removed, washed couple of times with water and final product: (COHT, III) as dense brown resin was vacuum dried at 80 °C to remove water.

Analytical data of COHT (III): Yield – 65 %; elemental analysis - % Calcd.: C 68.55%; N 4.44%; H 6.71%; % Found: C 68.22%; N 4.52%; H 6.73%; IR (HATR) [cm⁻¹], 3350 (O-H), 3048 (Ar-H), 2858 – 2926 (CH₂, CH), 1626, 1595 (C=C), 1451 (CH₂), 1324 (C-N), 1212, 1152 (C-O), 1021, 1056 (C-O-C), 747, 720 (C-H in ring); ¹H-NMR (d₆-

DMSO), [ppm] a 3.2 – 3.7(m); b 3.8 – 4.1(m); c 4.2 – 4.6 (m); d 4.8 – 5.1 (m), e 7.0 – 8.3 (m).

Reaction of COHT with oxiranes

In a pressure reactor of 250 cm³ volume equipped with magnetic stirrer and thermometer 25.0 g (0.08 mole) of COHT, 1 cm³ (0.007 mole) catalyst (TEA) and 21.0 g (0.48 mole) EO or 27.6 g (0.48 mole) PO were placed. The mixture was stirred and heated to 60 – 90 °C. The progress of reaction was monitored by determination of EN. The products were brown resins, from which the catalyst was removed by distillation under reduced pressure (p = 2132 Pa, temp. 80 °C).

Analytical data of oligoetherols (IV):

R= –H: IR (HATR) [cm⁻¹]: 3424 (OH), 3050 (Ar-H), 2986 – 2912 (CH₂, CH), 1626, 1624, 1597 (C=C), 1484, 1452 (CH₂), 1325 (C-N), 1215 (C-O in alcohols), 1064–1113 (C-O-C), 747, 720 (Ar-H), (Fig.1); ¹H-NMR (DMSO-d₆) [ppm]: 7.0–8.1 (Ar- H); 4.5 (–OH); 4.3(>N–CH₂–); 3.9 (C–H); 3.2 – 3.7 (CH₂–O–) (Fig.2).

R= –CH₃: IR (HATR) [cm⁻¹]: 3428 (OH), 3054 (Ar-H), 2969 – 2870 (CH₂, CH), 1626, 1597 (C=C), 1484, 1453 (CH₃), 1373 (C-N), 1215, 1152 (C-O in alcohols), 1084–1113 (C-O-C), 758, 730 (Ar-H); ¹H-NMR (DMSO-d₆) [ppm]: 7.0 – 8.1 (Ar- H); 4.5 – 4.3 (–OH and >N–CH₂–); 3.7– 3.9 (–CH); 3.2– 3.7 (CH₂–O–, CH–O–); 0.7 – 1.2 (CH₃).

Analytical determinations

The course of reaction between carbazole and epichlorohydrin, EPC and glycerol and between COHT and oxiranes was followed by measuring the content of unreacted epoxide groups by hydrochloric acid method in dioxane [13]. Elemental analysis for C, H, N, were done with EA 1108, Carlo-Erba analyzer. The ¹H-NMR spectra of products were recorded at 500 MHz Bruker UltraShield in DMSO-d₆ 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 Ionization Time of Flight) of oligoetherols were obtained on Voyager-Elite Perseptive Biosystems (USA) mass spectrometer working at linear mode with delayed ion extraction, equipped with nitrogen laser working at 337 nm. The method of laser desorption from matrix was used with 2,5-hydroxybenzoic acid in THF at mg/cm³ concentration. The samples were diluted with methanol to 1 mg/cm³, followed by addition of 10 mg/cm³ NaI in acetone. Therefore in some cases the molecular ion masses were increased by the mass of Na⁺ and CH₃OH. 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.

Foam Preparation

Foaming tests were conducted on laboratory scale in 250 cm³ paper cups at room temperature. In details oligoetherol (10 g) was mixed with 0.2 g of Silicone 5340

(pure, Houdry Hüls, USA) as surfactant, TEA as catalyst (1-3 wt %) and water (2% wt %) with respect to oligoetherols. A calculated portion of diphenylmethane 4,4'-diisocyanate (commercial isocyanate containing three-functional isocyanates at the level of 30%; MDI, pure, Merck, Darmstadt, Germany, was used) 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 foams

The following properties of foams were studied: apparent density [15], water uptake [16], linear shrinkage estimated on the basis of the change of linear dimension of the sample heated for 4 hours at 100 °C [17], thermal stability as the weight loss at 150 °C within one month and compression strength [18].

References

- [1] Jpn Pat. **1989**, 01311161; *Chem. Abst.* **1990**, 81, 144251c.
- [2] Ke, X. J.; Yan, X. Z.; Srisanit, N.; Wang, M.; Yang, J.W.; Huang, X., F.; Shong, S. Z. *Appl. Phys.*, **2003**, 217, 69.
- [3] Gratt, J. A.; Cohen, R.E. *J. Appl. Polym. Sci.*, **2003**, 88, 177.
- [4] Zhu, W. H.; Hu, M.; Rao, R.; Tian, H. *J. Photochem. Photobiol. A-Chem.*, **2003**, 154,169.
- [5] Lee, J., H.; Woo, H., S.; Kim, T.W.; Park, J. W. *Optical Mat.*, **2003**, 21, 225.
- [6] Zhang, X.J.; Thian, Y.P.; Jiang, S.L.M. *Polyhedron*, **2003**, 22, 397.
- [7] Tirapattur, S.; Belletete, M.; Drolet, N.; Leclerc, N.; Durocher, G. *Chem. Phys. Lett.*, **2003**, 370, 799.
- [8] Joule, J. A. *Adv. Heterocyclic Chem.*, **1984**, 35, 83.
- [9] Lubczak, R. *Polimery*, **2008**, 53, 587.
- [10] Lubczak, R. *J. Appl. Pol. Sci.*; **2008**, 110, 3501.
- [11] Lubczak, R. *J. Appl. Pol. Sci.*; **2010**, 117, 16.
- [12] Lubczak, R. *Heterocycl. Comm.*; **2006**, 12, 201.
- [13] Wirpsza Z. *Polyurethane*, WNT, Warsaw 1991 (in polish).
- [14] Kastierina, T.; Kalinina, L. *Chemical analysis of plastics* Ed. WNT, Warsaw 1965 (in Polish).
- [15] Cellular Plastics and Rubbers. Determination of apparent (bulk) Density, *Polish (European) Standards PN-EN ISO 845-2000*, Ed. Polish Committee for Standardization.
- [16] Cellular Plastics, rigid. Determination of Water Absorption, *Polish (European) Standards PN-EN ISO 2896-1986*, Ed. Polish Committee for Standardization.
- [17] Cellular Plastics, rigid. Test of dimensional Stability, *Polish (European) Standards PN-EN ISO 2796-1986*, Ed. Polish Committee for Standardization.
- [18] Cellular Plastics, Compression Test for rigid Materials, *Polish (European) Standards PN- EN ISO 844-1978*, Ed. Polish Committee for Standardization.