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## Oligoetherols and polyurethanes with carbazole ring in side chain

### RAPID COMMUNICATION

**Summary** — The epoxide ring of 9-(2,3-epoxypropyl)carbazole (EPC) opening occurred to give the semiproduct well soluble in ethylene oxide (EO) and propylene oxide (PO) and reactive towards these oxides at temperature above 60 °C to form oligoetherols. Application of these oligoetherols for syntheses of linear polyurethanes was studied in details.

**Key words:** carbazole, epichlorohydrine, reaction of semi-products with oxiranes, physical properties, polyurethanes.

#### OLIGOETEROLE I POLIURETANY Z PIERŚCIENIEM KARBAZOLU W ŁAŃCUCZU BOCZNYM

**Streszczenie** — Opracowano nową metodę otrzymywania dwufunkcyjnych oligoeteroli z pierścieniem karbazolu. W tym celu karbazol poddawano reakcji z epichlorohydryną otrzymując 9-(2,3-epoksypropylo)karbazol (EPC). Następnie na otrzymany związek działano wodą otwierając pierścień epoksydowy, w wyniku czego tworzył się 3-(9-karbazolilo)propano-1,2-diol (CPD) — półprodukt rozpuszczalny w oksiranach takich jak tlenek etylenu (EO) i tlenek propylenu (PO) i reagujący z nimi w kierunku dwufunkcyjnych oligoeteroli. Zbadano strukturę (tabela 1) i właściwości fizyczne (tabela 2 i 3) zsyntetyzowanych oligoeteroli stwierdzając ich dużą odporność termiczną. Oligoeterole te zastosowano więc do podwyższenia odporności termicznej poliuretanów. W tym celu poddano je reakcjom z izocyjanianami o różnej budowie (TDI, MDI i HDI). Wykazano, że charakteryzują się wysoką odpornością na rozkład termiczny. Ich temperatura zeszklenia mieści się w zakresie 53—77 °C. Stwierdzono, że badane poliuretany nie zawierają w swojej strukturze obszarów krystalicznych.

**Słowa kluczowe:** karbazol, epichlorohydryna, reakcja półproduktu z oksiranami, oligoeterole, właściwości fizyczne, poliuretany.

Carbazole rings introduced to polymer chains have important effects on the properties of such materials (for example on: phase transition temperatures, solubility in organic solvents, electric conductivity, or ability to form the charge-transfer complexes) [1—9]. High temperature of decomposition of carbazole prompted us to introduce carbazole into polyetherols in order to obtain polyetherols themselves and polymeric products made of them *i.e.* polyurethanes and polyesters, which all should be characterized by high thermal stability.

In this work the methods of syntheses of bi-functional polyetherols with carbazole rings in side chains and, in the next step, syntheses of polyurethanes were reported.

### EXPERIMENTAL

#### Materials

Carbazole, ethylene oxide (EO), propylene oxide (PO) and hexamethylene 1,5-diisocyanate (HDI) were

purchased from Fluka (Schwitzerland). Epichlorohydrin, toluilene 2,4-diisocyanate (TDI) and diphenylmethane 4,4'-diisocyanate (MDI) were delivered by Aldrich (Germany).

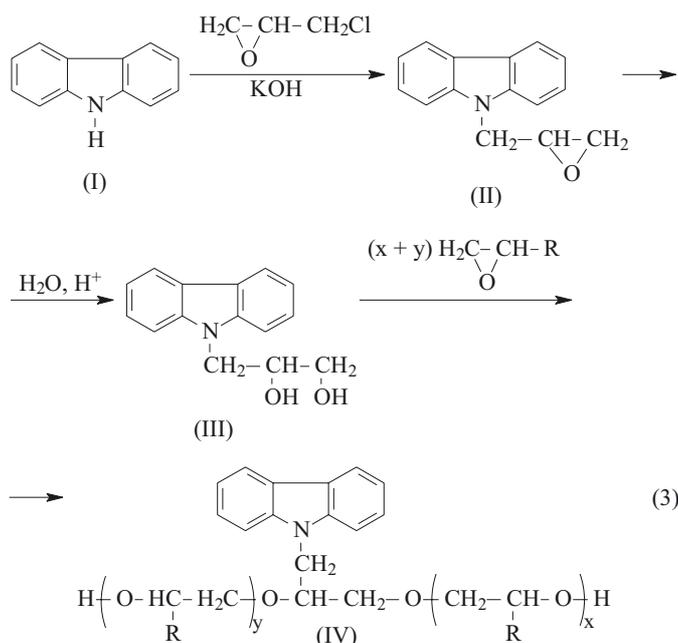
All substances were pure grade and were used as received.

#### Syntheses of semiproducts

Scheme A shows the reactions of syntheses of 9-(2,3-epoxypropyl)carbazole [EPC, formula (II) in Scheme A], 3-(9-carbazolyl)propano-1,2-diol [CPD, formula (III) in Scheme A] and CPD with oxiranes [formula (IV) in Scheme A] [10].

#### Synthesis of EPC

To the three-necked, round-bottomed flask of 250 cm<sup>3</sup> capacity, equipped with reflux condenser, mechanical stirrer, and thermometer, 0.111 mole (18.5 g) of carbazole and 130 cm<sup>3</sup> of acetone were introduced. The mixture was stirred and heated to 50—56 °C up to dissolution of



R: — H or — CH<sub>3</sub>, x + y = 6 — number of oxyalkylene units

Scheme A. Series of reactions leading to oligoetherol with carbazole ring

carbazole. Then 0.225 mole (12.6 g) of KOH was added in three portions in 30 min. After 3 h initially homogenic solution started to separate into two phases (aqueous and oil ones). The process was continued for the next 6 h. Afterwards the mixture was poured onto 5 dm<sup>3</sup> of water and stirred vigorously. The yellow precipitate formed, which was filtered off on Büchner funnel and vacuum dried at 80 °C.

#### Synthesis of CPD

In the three-necked flask, the same as in previous synthesis, 0.02 mole (5 g) of EPC obtained and 50 cm<sup>3</sup> of acetone were placed. The mixture was heated until it became homogeneous at 50–68 °C. Then 70 cm<sup>3</sup> of water was added and pH was adjusted to 1 with 50 % sulfuric acid. The reaction was monitored by determination of epoxide number. After reaction completed the mixture was poured into 3 dm<sup>3</sup> of water which immediately gave pale-pink precipitate. The product was filtered off and vacuum dried at 90–100 °C.

#### Synthesis of oligoetherols

To the pressure-resistant glass reactor equipped with thermometer and placed on magnetic stirrer 0.17 mole (41 g) of CPD, 0.018 mole (2.5 cm<sup>3</sup>) of triethylamine (TEA) as catalyst and 1.02 mole of EO or PO (45 g or 59.2 g, respectively) were introduced. The mixture was stirred magnetically and heated up to 60–90 °C. The process was finished when epoxide number reached an appropriate value. The product — brown resin was vacuum dried (p = 2132 Pa, temp. 80 °C) in order to remove TEA.

#### Syntheses of polyurethanes

In a three-necked 100 cm<sup>3</sup> flask equipped with mechanical stirrer, reflux condenser, and thermometer 0.01 mole (2.41 g) of CPD or 0.01 mole of appropriate oligoetherol (5.05 g of product obtained from CPD and EO or 5.89 g product obtained from CPD and PO), and 40 cm<sup>3</sup> of dioxane were placed. After dissolution of substrate the 0.01 mole of isocyanate (1.68 g of HDI or 1.74 g of TDI or 2.50 g of MDI and one drop of TEA) catalyst were added. The reaction was continued until the isocyanate groups were absent (9–11 h). The products were isolated by evaporation of solvent and dried under reduced pressure (t = 90 °C, p = 2 · 10<sup>-3</sup> MPa). The structure of obtained polyurethanes is illustrated by general formula (V).

#### Methods of testing

The progress of the reaction is isocyanates was followed by determination of isocyanate groups using ammonia method [11].

Elemental analyses of C, H, N were done using EA 1108, Carlo-Erba analyzer.

Polyetherols were investigated by MALDI-TOF method using Voyager-Elite Perseptive Biosystems (USA) mass spectrometer. As a matrix in this method 2,5-hydroxybenzoic acid in THF was used.

Molecular masses of polyurethanes were determined using Viscotec T60A gel chromatograph. THF was applied as an eluent and calibration was based on common polystyrene references.

The <sup>1</sup>H NMR spectra of products were recorded using BS 587A 80 MHz, Tesla instrument with hexamethyldisiloxane (HMDS) as internal standard in deuterated dimethyl sulfoxide (d<sub>6</sub>-DMSO).

IR spectra were registered using Paragon 1000 FT-IR Perkin Elmer spectrometer, in KBr pellets or ATR technique.

Thermal stability of oligoetherols and polyurethanes was studied by differential thermal analysis (DTA), differential thermogravimetric (DTG) and thermogravimetric (TG) methods in the range of temperatures 20–1000 °C.

Glass transition temperatures (T<sub>g</sub>) were determined according to PN-EN ISO 11357-1:2002; using differential scanning calorimeter Mettler Toledo 822<sup>e</sup> type Stare<sup>e</sup> System software.

Physical properties like refraction index (n<sup>D</sup>), density (d), viscosity (η) and surface tension (τ) of oligoetherols were determined using Abbe refractometer, pycnometer, Höppler viscometer and by the detaching ring method, respectively.

#### RESULTS AND DISCUSSION

The reaction of carbazole with epichlorohydrine was performed to get EPC [formula (II)]. Epoxide ring of EPC

**Table 1.** MALDI-TOF peaks of oligoetherol obtained from CPD and EO at 1:6 molar ratio

<i>M/z</i>	Relative intensity of peak, %	The structure of molecular ion <sup>*)</sup>	Calculated mass g/mol
222.3	5	EPC	223.3
241.2	15	CPD	241.4
250.3	75	CPD + EO + 2 H <sub>2</sub> O	249.3
278.3	92	CPD + K <sup>+</sup>	280.5
294.4	26	CPD + 2 EO - 2 H <sub>2</sub> O	293.3
322.4	100	CPD + EO + K <sup>+</sup>	324.5
338.9	23	CPD + 4 EO - 2 H <sub>2</sub> O	337.4
366.4	95	CPD + 2 EO + K <sup>+</sup>	368.5
373.3	34	CPD + 3 EO	373.5
410.5	73	CPD + 3 EO + K <sup>+</sup>	412.5
417.4	44	CPD + 4 EO	417.6
440.4	15	CPD + 4 EO + Na <sup>+</sup>	44.6
461.4	48	CPD + 5 EO	461.6
484.4	15	CPD + 5 EO + Na <sup>+</sup>	484.7
498.5	24	CPD + 5 EO + K <sup>+</sup>	500.7
505.4	38	CPD + 6 EO	505.4
528.5	15	CPD + 6 EO + Na <sup>+</sup>	528.7
549.5	29	CPD + 7 EO	549.5
572.5	18	CPD + 8 EO + Na <sup>+</sup>	616.8
660.6	10	CPD + 9 EO + Na <sup>+</sup>	660.8

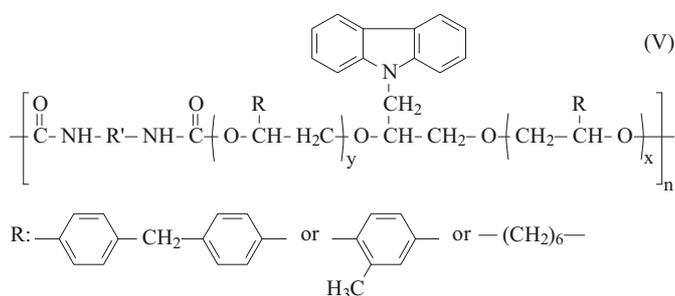
<sup>\*)</sup> EO — corresponds to -CH<sub>2</sub>CH<sub>2</sub>O-, CPD + *n* EO — consecutive products of reaction between CPD and EO, CPD + *n* EO - 2 H<sub>2</sub>O — product of condensation of oligoetherols obtained.

240 °C with temperature of maximum decomposition at *ca.* 330 °C. The total decomposition is completed at *ca.* 400 °C. The products obtained from PO start decomposition at lower temperature, namely 180 °C.

**Table 3.** Thermal decomposition data of oligoetherols; *T<sub>x</sub>*% denotes the temperature of *x* % weight loss of the sample

Oligoetherol from	<i>T</i> <sub>5%</sub> , °C	<i>T</i> <sub>10%</sub> , °C	<i>T</i> <sub>20%</sub> , °C	<i>T</i> <sub>50%</sub> , °C
EO	240	260	300	330
PO	180	215	285	310

The polyurethanes obtained can be approximately described by the formula (V). In Table 4 the chemical

**Table 2.** Some physical properties of oligoetherols and regression equations describing their dependence on temperature in the range 20—80 °C

Oxirane used in synthesis	$\tau$ , N/m			$n^D$			$\eta$ , MPa · s			$d$ , g/cm <sup>3</sup>		
	$\tau = at + b$		$R^2$	$n^D = at + b$		$R^2$	$\eta = Ae^{-t/a}$		$R^2$	$d = at + b$		$R$
	$a \cdot 10^4$	$b$		$a \cdot 10^4$	$b$		$A$	$a$		$a \cdot 10^4$	$b$	
EO	-1.4929	0.0450	0.9904	-3.443	1.5656	0.9982	66930.7	9.77	0.9981	-7.489	1.1847	0.9997
PO	-3.314	0.0524	0.9831	-3.900	1.5404	0.9982	10072.4	10.44	0.9980	-9.330	1.1052	0.9928

was opened by reaction with water. Product of ring opening — CPD [formula (III)] react further with oxiranes (EO or PO) in the presence of TEA. Syntheses were conducted to get molar ratio of product of epoxide ring opening to oxirane 1:6. The distribution of molar mass of polyetherols was determined by MALDI-TOF method (Table 1). The series of signals separated by *M/z* = 44 or 58 were seen, corresponding to the mass of attached EO or PO units (Table 1). The physical properties of oligoetherols, *i.e.*: density, viscosity, refraction index, and surface tension were determined (Table 2). It has been found that the products obtained from EO had higher values of those parameters in comparison with the corresponding ones obtained from PO. The derivatographic studies of oligoetherols were also performed. The results listed in Table 3 indicate that products possess high thermal stability, the slightly higher in case of products obtained from EO in comparison with that obtained from PO. The product obtained from EO decomposes starting from *ca.*

characteristics of all synthesized polymers is given. The IR spectra of the products evidenced the products were polyurethanes by diagnostic bands at 1730 and 1530 cm<sup>-1</sup> (I and II amide bands) and C-O bond stretching vibrations of ester at *ca.* 1220 cm<sup>-1</sup>. At <sup>1</sup>H NMR spectra the resonance signals from -NH-, methylene group attached to CO-O and aromatic ring protons at 8.0—9.5 ppm, 4.1—4.5 ppm and 6.9—8.3 ppm, respectively, were observed.

Number-average molecular weight ( $\overline{M}_n$ ), weight-average molecular weight ( $\overline{M}_w$ ), *z*-average molecular weight ( $\overline{M}_z$ ) and molecular weight distribution ( $\overline{M}_w/\overline{M}_n$ ) of polyurethanes obtained from CPD and different isocyanates are listed in Table 5.

The polyurethane obtained from CPD and MDI has much higher molecular weight and lower polydispersion than polyurethanes obtained from CPD and TDI. Polyurethanes precipitated from CPD and HDI reaction system have the lowest polydispersion.

Table 4. Syntheses yields and elemental analyses data of polyurethanes obtained

Substrates	Symbol of polyurethane	R	R'	x + y	Yield %	% of elements					
						calculated			found		
						C	H	N	C	H	N
CPD + MDI	PU-M	—		0	74.1	73.32	5.09	8.55	73.43	5.19	8.31
CPD + EO + MDI	PU-EO-M	H		6	66.2	66.75	6.49	5.56	66.92	6.24	5.33
CPD + PO + MDI	PU-PO-M	CH <sub>3</sub>		6	73.5	68.65	7.27	5.01	68.45	7.11	4.89
CPD + TDI	PU-T	—		0	78.9	69.40	5.06	10.12	69.10	5.04	9.99
CPD + EO + TDI	PU-EO-T	H		6	85.9	63.62	6.63	6.18	63.64	6.49	5.90
CPD + PO + TDI	PU-PO-T	CH <sub>3</sub>		6	91.8	66.05	7.47	5.50	66.18	7.23	5.71
CPD + HDI	PU-H	—	—(CH <sub>2</sub> ) <sub>8</sub> —	0	80.4	67.48	6.60	10.26	67.84	6.94	10.05
CPD + EO + HDI	PU-EO-H	H		6	68.9	62.41	7.58	6.24	62.25	7.45	6.11
CPD + PO + HDI	PU-PO-H	CH <sub>3</sub>		6	68.0	64.99	8.32	5.55	65.15	8.41	5.24

Table 5. Molecular weights, glass transition temperatures and thermal decomposition data of polyurethanes

Symbol of polyurethane	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	Molecular weight distribution $\bar{M}_w/\bar{M}_n$	$T_{g'}$ , °C	$T_{5\%}$ , °C	$T_{10\%}$ , °C	$T_{20\%}$ , °C	$T_{50\%}$ , °C
PU-M	1480	1935	2981	1.31	70—77	100	190	290	350
PU-T	1073	1734	2776	1.62	60—72	105	210	285	350
PU-H	1240	1338	1418	1.08	53—59	240	290	300	350

In Table 5 the results of thermal analyses of polyurethanes are also given. The increase in glass transition temperature ( $T_g$ ) was observed upon changing the aliphatic isocyanate (HDI) to aromatic ones (TDI, MDI). No presence of crystalline regions was found in polyurethanes obtained. The analysis of thermal weight loss of polyurethanes indicated clearly that carbazole ring introduced into molecule enhanced thermal stability of products. The 50 % weight loss was observed in all cases at temp. 350 °C. Generally the slight weight loss (ca. 5 %) was observed at temperature around 100 °C due to the presence of solvent in the product, except the polyurethane obtained from CPI and HDI, which remained untouched until 240 °C (cf. Table 4).

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Received 1 II 2008.