

# Trifunctional Oligoetherols and Polyurethane Foams with Carbazole Ring

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## ABSTRACT

The method of synthesis of trifunctional oligoetherols with carbazole ring from 9-(2,3-epoxypropyl)carbazole and diethanolamine and oxiranes like ethylene and propylene oxide was presented. Structure and some physicochemical properties of the products were described. The oligoetherols were demonstrated as good substrates for synthesis of polyurethane foams of enhanced thermal resistance. It has been found that the obtained foams are rigid at room temperature and their apparent density was  $34 \text{ kg/m}^3$  -  $44 \text{ kg/m}^3$ . The water uptake was low, maximum to 10.5 mass%. Dynamic thermal analysis of this foams showed that 5% mass loss starts at  $200^\circ\text{C}$  -  $220^\circ\text{C}$ , while temperature of 50% mass loss was  $340^\circ\text{C}$  -  $370^\circ\text{C}$ . Concomitantly the increase of compression strength was observed.

**Keywords:** Oligomers; Ring-Opening Polymerization; Polyurethanes; Thermal Properties

## 1. Introduction

Polymers containing carbazole ring have the critical importance for physical parameters of polymers, like: phase transition temperatures, solubility in polymer in organic solvents, electric conductivity, and ability to form charge-transfer complexes [1-7]. Carbazole decomposes at temperatures higher than  $260^\circ\text{C}$ . High thermal stability of carbazole prompted us to introduce carbazole into polyetherols in order to obtain products of high thermal stability, *i.e.* polyetherols themselves and polymeric products obtainable from them; polyurethanes and polyesters. Carbazole is mono-functional compound and this is the reason of limited application for synthesis of oligoetherols by its reaction with oxiranes. Therefore, previous studies were devoted to increase its functionality and solubility of carbazole derivatives in oxiranes [8]. The di-functional oligo and polyetherols with carbazole ring were not known till now except for some preliminary results from this lab [9-11]. Here we have presented the method of synthesis of tri-functional oligoetherols with carbazole ring inside chain and apply them to obtain polyurethane foams with enhanced thermal resistance.

## 2. Experimental

### 2.1. Syntheses

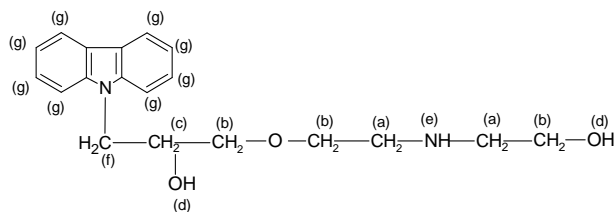
The synthesis of 9-(2,3-epoxypropyl)carbazole (EPC) was performed as previously [8].

### 2.2. Opening of Epoxide Ring with Diethanolamine

To a  $100 \text{ cm}^3$  three-necked round bottom flask equipped with reflux condenser, mechanical stirrer and thermometer  $18.0 \text{ g}$  ( $0.11 \text{ mole}$ ) of EPC and  $15.6 \text{ cm}^3$  ( $0.16 \text{ mole}$ ) of diethanolamine (DEA, pure, Fluka, Buchs, Switzerland) were introduced. The mixture was stirred and heated until dissolving of substrates (at temperature ca.  $60^\circ\text{C}$ ), then  $0.1 \text{ cm}^3$  triethylamine (TEA, pure, Fluka, Buchs, Switzerland) catalyst was added. The mixture was heated to  $120^\circ\text{C}$ . The progress of reaction was monitored by determination of epoxide number (EN). Then,  $50 \text{ cm}^3$  distilled water was added, the mixture was vigorously stirred and heated at  $90^\circ\text{C}$  for about one hour to rinse the diethanolamine off. The mixture was cooled down to room temperature and water layer was removed, washed couple of times with water and final product:

9-(9-carbazolyl)-3-aza-6-oxanonane-1,6-diol (CAOD, I) as dense brown resin was vacuum dried at  $80^\circ\text{C}$  to remove water.

Analytical of CAOD



(I)

Analytical of products: Yield: 61.5%; elemental analysis-% Calcd. C 69.49, N 8.53, H 7.37, % Found C 69.63, N 8.31, H 7.54; IR (ATR) [ $\text{cm}^{-1}$ ]: 3300 (NH, OH), 3049 (Ar-H), 2818 - 2927 ( $\text{CH}_2$ , CH), 1652 (NH), 1626 (C=C in carbazole ring), 1451 ( $\text{CH}_2$ ), 1324 (C-N), 1210, 1152 (C-O), 1034 - 1066 (C-O-C), 747, 720 (Ar-H);  $^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ ) [ppm]: a 2.5 - 2.7, b 3.2 - 3.5, c 4.65, d + e 3.9 - 4.1, f 4.4 - 4.6, g 7.0 - 8.1.

### 2.3. Reaction of CAOD with Oxiranes

In a pressure reactor of 250  $\text{cm}^3$  volume equipped with magnetic stirrer and thermometer 25.0 g (0.076 mol) of CAOD, 1  $\text{cm}^3$  (0.007 mole) catalyst (TEA) and 20.1 g (0.46 mola) of ethylene oxide (EO, pure, Fluka, Buchs, Switzerland) or 26.5 g (0.46 mol) of propylene oxide (PO, pure, Fluka, Buchs, Switzerland) were placed. The mixture was stirred and heated to 75°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 of oligoetherols (III, formula in Results and Discussion) obtained from CAOD and oxiranes:

R = -H; IR (ATR) [ $\text{cm}^{-1}$ ]: 3409 (OH), 3046 (Ar-H), 2866 - 2919 ( $\text{CH}_2$ , CH), 1626, 1596 (C=C), 1484, 1452 ( $\text{CH}_2$ ), 1326 (C-N), 1214 (C-O in alcohols), 1061 - 1098 (C-O-C), 751, 721 (Ar-H) (**Figure 1**);  $^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ ) [ppm]: 7.0 - 8.1 (Ar-H), 4.4 - 4.6 (>N- $\text{CH}_2$ -), 3.95 (-CH-OH), 3.4 - 3.5 (- $\text{CH}_2$ -O-), 2.6 - 2.8 (- $\text{CH}_2$ -N- $\text{CH}_2$ - $\text{CH}_2$ -O-) (**Figure 2**).

R = - $\text{CH}_3$ ; IR (ATR) [ $\text{cm}^{-1}$ ]: 3414 (OH), 3051 (Ar-H), 2868 - 2968 ( $\text{CH}_3$ ,  $\text{CH}_2$ , CH), 1627, 1597 (C=C), 1484, 1453 ( $\text{CH}_2$ ), 1372 ( $\text{CH}_3$ ), 1325 (C-N), 1215, 1152 (C-O in alcohols), 1087 (C-O-C), 759, 724 (Ar-H);  $^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ ) [ppm]: 7.0 - 8.1 (Ar-H), 4.4 - 4.6 (>N- $\text{CH}_2$ -; -OH), 3.7 - 3.9 (CH), 3.2 - 3.7 ( $\text{CH}_2$ -O-, >CHO-), 2.7 (- $\text{CH}_2$ -N- $\text{CH}_2$ - $\text{CH}_2$ -O-), 0.7 - 1.1 (- $\text{CH}_3$ ).

### 2.4. Analytical Methods

The progress of reaction of carbazole with epichlorohydrin and oxiranes was monitored by EN, which was determined by hydrochloric acid method in dioxane [12]. Elemental analysis for C, H, N, were done with EA 1108, Carlo-Erba analyzer. The  $^1\text{H-NMR}$  spectra of products were recorded at 500 MHz Bruker UltraShield in  $\text{DMSO-d}_6$  with hexamethyldisiloxane as internal standard. IR spectra were registered on PARAGON 1000 FT IR Perkin Elmer spectrometer in KBr pellets or ATR technique. The number-average molecular mass  $M_n$  of obtained oligoetherols was determined cryoscopically in DMSO solvent. Thermal analyses of oligoetherols and foams (DTA, DTG and TG) were performed in ceramic crucible at 20°C - 600°C temperature range, about 200 mg sample, under air atmo-

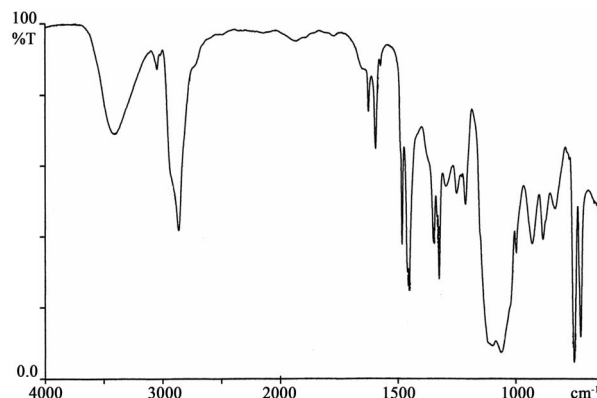
sphere with Termowaga TGA/DSC 1 derivatograph, Mettler.

### 2.5. Physical Properties of Oligoetherols

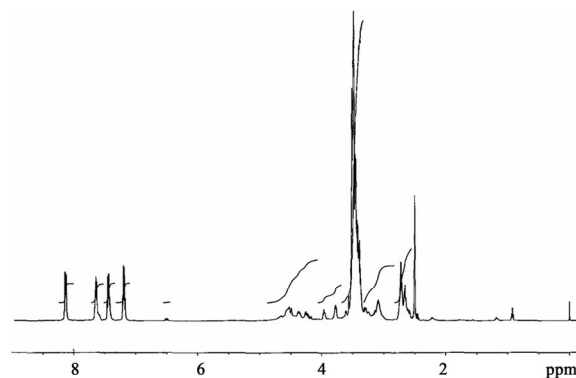
Refraction index, density, viscosity, and surface tension of oligoetherols were determined with Abbe refractometer, picnometer, Höppler viscometer (typ BHZ, prod. Prüfgeratewerk, Germany) and by the detaching ring method, respectively.

### 2.6. Foam Preparation

Foaming tests were conducted on laboratory scale in 250  $\text{cm}^3$  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 (1.25 - 3.76 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.



**Figure 1.** IR spectrum of oligoetherols obtained in reaction of CAOD with EO.



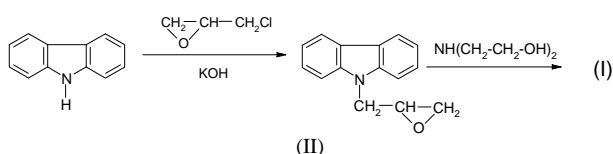
**Figure 2.**  $^1\text{H-NMR}$  spectrum of oligoetherols obtained in reaction of CAOD with EO.

## 2.7. Studies of Foams

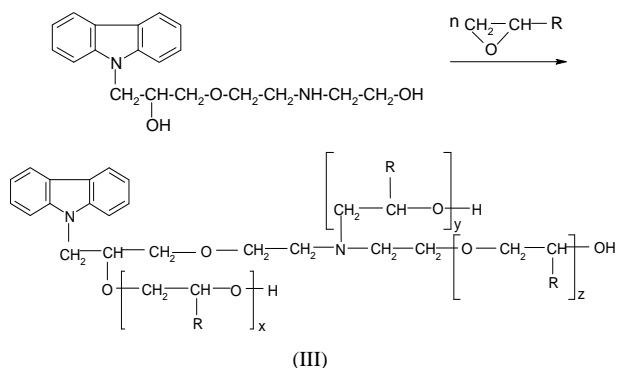
The following properties of foams were studied: apparent density [13], water uptake [14], linear shrinkage estimated on the basis of the change of linear dimension of the sample heated for 4 hours at 100°C [15], thermal stability as the weight loss at 150°C within one month and compression strength [16].

## 3. Results and Discussion

The reaction of carbazole with epichlorohydrin led to the formation of EPC (II), which underwent ring opening upon reaction with diethanolamine in presence of TEA to give three-functional semiproduct (I) according to the following reaction scheme:



The process was performed without any solvent, using two equivalents of diethanolamine. The obtained product was semisolid resin, which was identified by elemental analytical, IR and  $^1\text{H}$  NMR spectra (see Experimental; Analytical of CAOD). In the  $^1\text{H}$  NMR spectrum the multiplet at 7.0 - 8.1 ppm from carbazole ring protons was observed. The resonances of -OH and NH were present together with 3.9 - 4.1 ppm region, the signals of methylene protons of  $-\text{CH}_2\text{O}-$  were found at 3.2 - 3.5 ppm, while methine proton resonances were observed at 4.65 ppm. The aromatic C-H bands were observed at 747 and 720  $\text{cm}^{-1}$  in the IR spectra, the stretching OH and NH bands were found at and 1152  $\text{cm}^{-1}$  and 1652  $\text{cm}^{-1}$  respectively, while valence bands of C-O-C were found at 1034 - 1066  $\text{cm}^{-1}$ . 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°C triggered the reaction of formation of three-functional oligoetherols III according to the scheme:



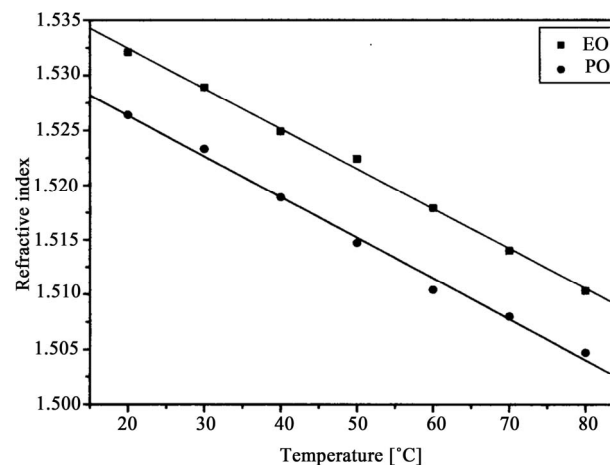
Elemental analysis and  $M_n$  confirm the structure of the oligoetherols (III,  $x + y + z = 6$ , Table 1). IR spectra of

oligoetherols (Figure 1) are remarkably different from that of semiproduct. The intensity of the band at 1098  $\text{cm}^{-1}$  increased indicating formation of ether bonds. Also the band at 2900  $\text{cm}^{-1}$  grew, indicating the incorporation of oxyalkylene units into oligoetherol. The intensity of the resonance at 3.5 ppm in the  $^1\text{H}$ -NMR of oligoetherols (Figure 2) increased according to the increase of number of oxyalkylene units in a product. Simultaneously the resonances at 4.2 - 4.6 ppm diminished illustrating the disappearance of hydroxyl protons due to progressing reaction of OH with oxirane.

The oligoetherols were obtained from the CAOD: oxirane 1:6 molar ratio system. Some physical parameters like refraction index, density, viscosity and surface tension in function of temperature were studied (Figures 3-6). 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 [17], with

**Table 1. Table type styles (Table caption is indispensable).**

Oxirane	Element content [% wt]						$M_n$ [g/mol]	
	Calc.			Found			Calc.	Found
	%C	%H	%N	%C	%H	%N	Calc.	Found
EO	62.83	8.11	4.73	62.54	7.99	4.75	592	575
PO	65.68	8.88	4.14	65.45	8.57	4.02	676	653



**Figure 3. Refractive index of oligoetherols obtained in reaction of CAOD with oxiranes versus temperature.**

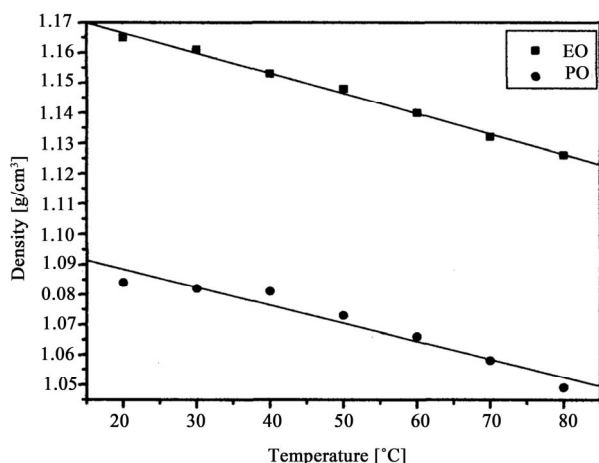


Figure 4. Density of oligoetherols obtained in reaction of CAOD with oxiranes versus temperature.

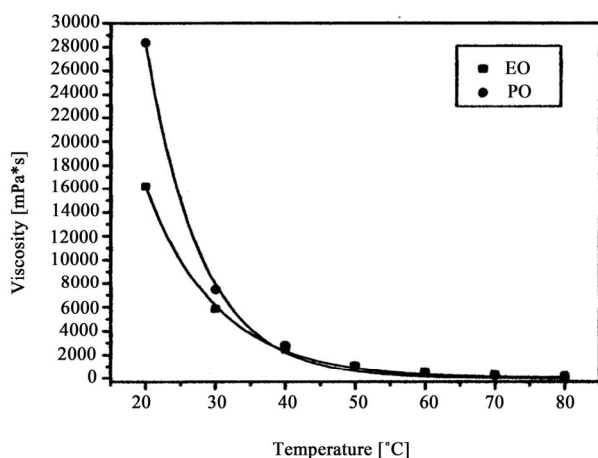


Figure 5. Viscosity of oligoetherols obtained in reaction of CAOD with oxiranes versus temperature.

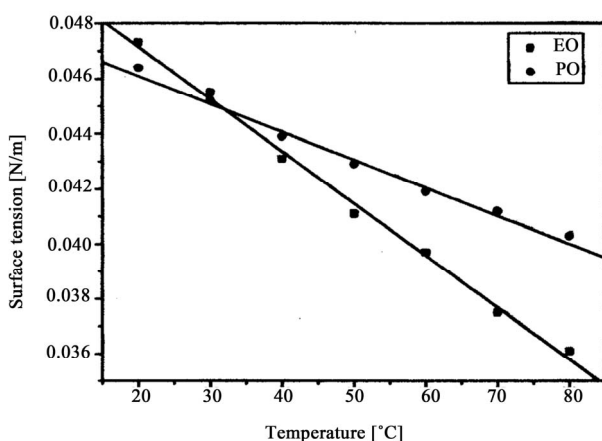


Figure 6. Surface tension of oligoetherols obtained in reaction of CAOD with oxiranes versus temperature.

the exception of viscosity, whichever is higher. The synthesized oligoetherols have good thermal resistance (Table 2). Their thermal decomposition starts at 230°C -

240°C (mass loss 5%), while their temperature of 50% decomposition falls into 460°C - 480°C region. High thermal resistance of these products suggested their usefulness as substrates for thermally resistant polyurethane 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 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 3.76% 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 1.80 for the oligoetherol obtained from EO and 1.44 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 (to 15 sec) and expanding times (to 44 sec). Drying times in case of compositions from EO was 1 seconds, while in case of PO it was as long as 60 seconds.

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 34 kg/m<sup>3</sup> - 44 kg/m<sup>3</sup>. The water uptake was low, maximum to 10.5 mass%. The dimensional stability at 150°C measurements revealed that the dimension change it was no larger than 8.0% of initial dimension.

Dynamic thermal analysis showed that 5% mass loss starts at 200°C - 220°C, while temperature of 50% mass loss was 340°C - 370°C (Table 2). Long-lasting, static measurements of thermal resistance were conducted at 150°C for one month (Figure 7). Continuous decrease of foam

Table 2. Thermal stability of oligoetherols and polyurethane foams.

Product	T <sub>5%</sub> [°C]	T <sub>10%</sub> [°C]	T <sub>25%</sub> [°C]	T <sub>50%</sub> [°C]
Oligoetherol CAOD + EO	230	260	320	480
Foam obtained from oligoetherol CAOD + EO	220	260	320	370
Oligoetherol CAOD + PO	240	260	300	460
Foam obtained from oligoetherol CAOD + PO	200	220	290	340

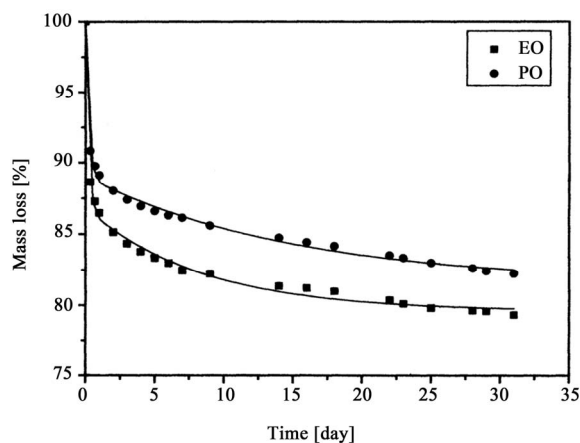
**Table 3. The influence of composition of foaming process.**

Oligoetherol obtained with the use of	Composition number	Composition* g/100 g of oligoetherol		Molar ratio OH:NCO (isocyanate coefficient)	Foaming process			Characteristics of foams just prepared
		Izocyanate	TEA		Time of creaming [s]	Time of expanding [s]	Time of drying [s]	
EO	1	116	1.25	1.80	10	13	2	rigid
	2	118	1.25	1.64	8	12	2	large pores, underhardened
	3	116	1.25	1.80	10	21	1	rigid, regular pores
	5	124	1.25	1.74	10	22	1	rigid, regular pores
PO	6	95	3.76	1.28	15	44	120	underhardened
	7	104	3.76	1.44	7	35	60	rigid, regular pores
	8	114	3.76	1.58	12	42	90	underhardened

\*Amount of surfactant and water 2 g per 100 g of oligoetherols.

**Table 4. Some properties of polyurethane foams.**

Oligoetherol obtained with the use of	Density [kg/m <sup>3</sup> ]	Water uptake [%] after			Linear dimension stability [%] at temperature 150°C after 40 h			Compression Strength [MPa]	
		5 min.	3 h	24 h	Length change	Width change	Depth change	Before exposition	After exposition
EO	33.7	6.29	7.65	10.54	4.05	8.04	2.55	0.151	0.336
PO	43.6	4.35	5.08	8.77	0.75	3.17	0.00	0.217	0.367

**Figure 7. Thermal stability of polyurethane foams as the weight loss after heating at 150°C for a month.**

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 CAOD and PO or EO it was 15 - 20 mass% within

one month. Concomitantly the increase of compression strength was observed (Table 4), 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.

#### 4. Summary and Conclusions

1) 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 diethanolamine, and finally by reaction with oxiranes EO or PO.

2) The oligoetherols have similar properties as those used regularly for obtaining polyurethane foams except higher thermal resistance of the former.

3) Obtained oligoetherols are useful substrates for synthesis of polyurethane foams which have enhanced thermal resistance and remain unchanged upon long exposure at 150°C.

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