

Bifunctional Oligoetherols with Carbazole Ring

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ABSTRACT: A new synthetic method for bifunctional oligoetherols with carbazole ring was presented. 9-(2,3-Epoxypropyl)carbazole was obtained from carbazole and epichlorohydrine. The epoxide ring opening occurred upon the consecutive reaction with ethylene glycol to give the semiproduct well soluble in ethylene oxide and propylene oxide and reactive toward these epoxides at temperatures above 60–90°C to form oligoetherols. Structure

of these oligoetherols and their physical properties and application for synthesis of linear polyurethanes were studied in details. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3501–3507, 2008

Key words: oligomers; ring-opening polymerization; polyurethanes; thermal properties

INTRODUCTION

Introducing heterocyclic ring into polymer structure such as polyurethanes or polyesters enhances their thermal stability. The examples are 1,3,5-triazine, perhydrotriazine or purine rings.^{1–3} The polyurethane foams with these rings included into polymer structure are thermally resistant up to 200°C and can be used for long time at 140–150°C and temporarily (up to 30 min) even at 800°C,⁴ whereas typical polyurethane foams remain unchanged within the 90–110°C.⁵ The substrates used for the synthesis of those thermally stable polyurethanes are polyetherols containing the azaaromatic rings. The substrates can be obtained from isocyanuric acid, melamine, uric acid or their derivatives, and oxiranes such as ethylene and/or propylene oxides.^{6–9}

Another candidate for such modification is carbazole, which itself is also thermally resistant. Carbazole decomposes at temperatures higher than 260°C. Moreover, the polymers with carbazole ring included have some unique physical properties. They are photo- and electroluminescent materials, liquid crystals, electroconductors, and nonlinear optical materials.^{10–16} There are no reports on synthesis of bifunctional oligoetherols obtained from carbazoles. Here, we present the results on synthesis of polyetherols based on carbazole ring, which are intended to be applied for formation of new thermal stability polymers.

EXPERIMENTAL

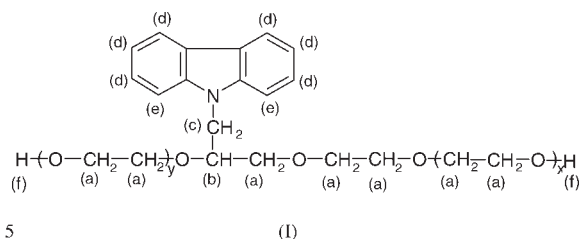
Syntheses of semiproducts

Syntheses of 9-(2,3-epoxypropyl)carbazole (EPC), 6-(9-carbazolyl)-3-oxahexane-1,5-diol (COHD) were described in.¹⁷

Reaction of COHD with oxiranes

To the high pressure reactor equipped with magnetic stirrer and thermometer, 48.5 g (0.17 mol) COHD and 2.5 cm³ (0.018 mol) triethylamine (TEA, pure, Fluka, Buchs, Switzerland) and 37.4 g ethylene oxide (EO) or 49.3 g propylene oxide (PO) (0.85 mol, pure, Fluka, Buchs, Switzerland) were introduced. The mixture was stirred and heated to 60–90°C. Progress of reaction was monitored via determination of epoxide number (EN). The brown-resin products were obtained, which were subjected to vacuum heating ($p = 2132$ Pa, temp. 80°C) to remove the catalyst.

Product of reaction of COHD with EO:

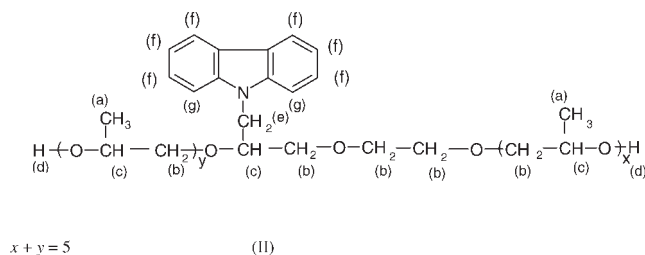


Analytical data on oligoetherols obtained from COHD and EO: Yield: 100%; IR (capillary film) [cm^{-1}], 3443 (O–H), 3050, 3021 (=CH in carbazole ring), 2927, 2866 (CH_2), 1626, 1484 (C=C), 1459,

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1451, 1373, 1348 (CH₂), 1325 (C—N), 1120 (C—O), 1095, 1063 (O—H), 750, 723 (C—H in carbazole ring); ¹H NMR (d₆-DMSO), [ppm], 3.1–3.7 (*a* + *f*, 28H, m), 3.9 (*b*, 1H, m), 4.5 (*c*, 2H, m), 7.1–7.8 (*d*, 6H, m), 8.0–8.3 (*e*, 2H, d).

Product of reaction of COHD with PO:

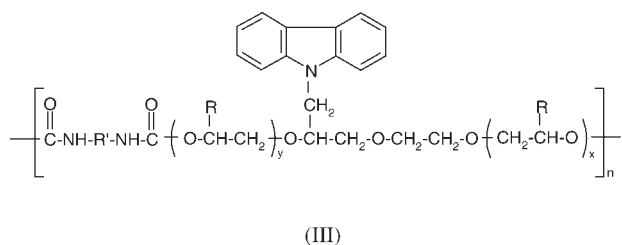


Analytical data on oligoetherols obtained from COHD and PO: Yield: 100%; IR (capillary film) [cm⁻¹], 3442 (O—H), 3049 (=CH in carbazole ring), 2968, 2927, 2881, 2868 (CH₂, CH₃), 1627, 1459 (C=C), 1453, 1348 (CH₂), 1373 (CH₃), 1325 (C—N), 1120 (C—O), 1086, 1063 (O—H), 750, 723 (C—H in carbazole ring); ¹H NMR (d₆-DMSO), [ppm], 1.0 (*a*, 15H, d), 3.0–4.0 (*b* + *c* + *d*, 24H, m), 4.5 (*e*, 2H, d), 7.1–7.8 (*f*, 6H, m), 8.0–8.3 (*g*, 2H, d).

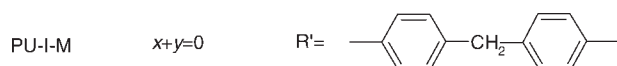
Synthesis of polyurethanes

In a three-necked 100 cm³ flask equipped with mechanical stirrer, reflux condenser, and thermometer 2.85 g (0.01 mol) COHD or 0.01 mol of appropriate oligoetherol (5.5 g of product obtained from COHD and EO or 5.76 g of product obtained from COHD and PO), and 40 cm³ dioxane were placed. After dissolution of substrate, the 0.01 mol of isocyanate: 1.68 g of hexamethylene 1,6-diisocyanate (HDI) or 1.74 g of toluilene 2,4-diisocyanate (TDI) or 2.50 g diphenylmethane 4,4'-diisocyanate (MDI), and one drop of TEA catalyst were added. The reaction was continued until the isocyanate groups were absent (4–7 h). The products were isolated as solid or resins after evaporation of solvent and dried under reduced pressure ($t = 90^\circ\text{C}$, $p = 2 \times 10^{-3}$ Mpa).

The general formula of polyurethanes was:



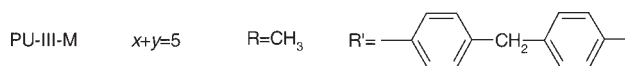
$x + y$, number of oxyalkylene units



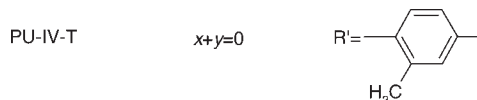
Analytical of product: Yield: 92.4%; elemental analysis % Calcd: C 71.77; H 5.42; N 7.85; % Found: C 71.42; H-5.46; N-7.55; IR (KBr) [cm⁻¹], 3302 (NH), 3048 (=CH in carbazole ring), 2962–2859 (CH₂), 1724, 1712 (I amide bond), 1627, 1596 (C=C), 1534, 1511 (II amide bond), 1484, 1452, 1412 (CH₂), 1261, 1216 (CO—O), 1120, 1020 (C—O—C), 750, 723 (C—H in carbazole ring); ¹H NMR (DMSO-d₆) [ppm], 3.20–3.80 (m, 6H, Ar—CH₂—Ar, —O—CH₂), 3.80–4.20 (m, 3H, —CO—O—CH<, —CO—O—CH₂), 4.20–4.45 (m, 2H, N—CH₂), 6.90–8.25 (m, 16H in Ar), 9.60 (s, 2H, Ar—NH—CO).



Yield: 83.7%, elemental analysis - %Calcd. C 66.75; H 6.49; N 5.56; % Found.: C-66.56; H 6.53; N 5.89; IR (capillary film) [cm⁻¹], 3307 (NH), 3049 (Ar—H), 2868 (CH₂), 1726 (I amide bond), 1626, 1458 (C=C in carbazole rings), 1596, 1538 (II amide bond), 1484, 1459, 1452, 1349 (CH₂), 1325 (C—N), 1222 (CO—O), 1095, 1066, 1021 (C—O—C), 818, 751, 723 (Ar—H); ¹H NMR (DMSO-d₆) [ppm]: 2.90–3.90 (m, 26H, Ar—CH₂—Ar, —O—CH₂), 4.00–4.25 (m, 3H, —CO—O—CH<, —CO—O—CH₂), 4.25–4.60 (m, 2H, N—CH₂), 6.90–8.20 (m, 16H in Ar), 9.60 (s, 2H, Ar—NH—CO).

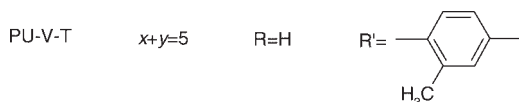


Yield: 88.7%; elemental analysis - %Calcd. C 68.36; H 7.15; N 5.09; % Found.: C 68.44; H 7.41; N 5.11; IR (capillary film) [cm⁻¹], 3420 (NH), 3050 (Ar—H), 2970, 2890 (CH₂), 1708 (I amide bond), 1643, 1597 (C=C in carbazole rings), 1545, 1511 (II amide bond), 1485, 1453 (CH₂), 1375 (CH₃), 1326 (C—N), 1262, 1235 (CO—O), 1094 (C—O—C), 815, 752, 724 (Ar—H); ¹H NMR (DMSO-d₆) [ppm]: 0.90 (m, 15H, CH₃), 3.00–3.65 (m, 16H, O—CH₂), 3.75 (s, 2H, Ar—CH₂—Ar), 3.80–4.30 (m, 8H, CH—O—C, N—CH₂, —CO—O—CH<), 6.80–8.20 (m, 16H in Ar.), 8.50 (s, 2H, Ar—NH—CO).

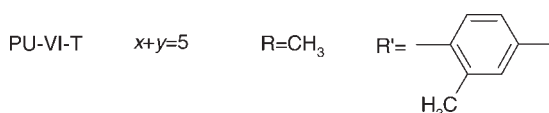


Yield: 91%; elemental analysis - % Calcd. C 67.97; H 5.45; N 9.15; % Found.: C 67.87; H 5.39; N 9.33; IR (KBr) [cm⁻¹], 3342 (NH), 3048, 3023 (Ar—H), 2962, 2864 (CH₂), 1714 (I amide bond), 1626, 1597 (C=C in carbazole rings), 1533 (II amide bond), 1484, 1459, 1452 (CH₂, CH₃), 1370 (CH₃), 1325 (C—N), 1218 (CO—O), 1091 (C—O—C), 751, 723 (Ar—H); ¹H NMR (DMSO-d₆) [ppm], 2.10 (s, 3H, CH₃—Ar), 3.20–3.80

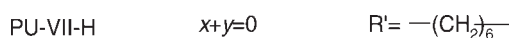
(m, 4H, O—CH₂), 3.80–4.90 (m, 5H, N—CH₂, —CO—O—CH<, —CO—O—CH₂), 5.10 (s, 2H, Ar—NH—CO), 6.90–8.30 (m, 11H, in Ar).



Yield: 79.2%; elemental analysis - %Calcd. C 63.62; H 6.63; N 6.18; % Found. C 63.34; H 6.33; N 6.41; IR (capillary film) [cm⁻¹], 3288 (NH), 3050 (Ar—H), 2867 (CH₂), 1725 (I amide bond), 1637, 1597 (C=C in carbazole rings), 1533 (II amide bond), 1484, 1459, 1452, (CH₂), 1370 (CH₃), 1325 (C—N), 1220 (CO—O), 1100 (C—O—C), 801, 751,724 (Ar—H); ¹H NMR (DMSO-d₆) [ppm] 2.10 (m, 3H, CH₃—Ar), 2.90–3.70 (m, 24H, O—CH₂), 3.70–4.20 (m, 5H, N—CH₂, —CO—O—CH<, —CO—O—CH₂), 4.50 (m, 2H, Ar—NH—CO), 6.90–8.30 (m, 11H in Ar).



Yield: 69.5%; elemental analysis C 65.69; H 7.34; N 5.61; % Found. C 65.34; H 7.33; N 5.41; IR (capillary film) [cm⁻¹], 3440 (NH), 3050, 3021 (Ar—H), 2967, 2869 (CH₂, CH₃), 1716 (I amide bond), 1627, 1460 (C=C in carbazole rings), 1597,1537 (II amide bond), 1484, 1459, 1452 (CH₂), 1325 (C—N), 1373 (CH₃), 1217, 1118 (CO—O), 1100 (C—O—C), 795, 750,723 (Ar—H); ¹H NMR (DMSO-d₆) [ppm] 0.90 (m, 15H, CH₃—), 2.10 (s, 3H, CH₃—Ar), 2.90–4.00 (m, 24H, N—CH₂, —CH₂—O—, >CH—O—C, —CO—O—CH), 4.15–4.65 (m, 2H, Ar—NH—CO), 6.90–8.20 (m, 11H in Ar).



Yield: 68.9%; elemental analysis C 66.23; H 6.84; N 9.27; % Found. C 66.04; H 6.53; N 9.41; IR (KBr) [cm⁻¹] 3335 (NH), 3050 (Ar—H), 2933, 2855 (CH₂), 1706 (I amide bond), 1627, 1460 (C=C in carbazole rings), 1576 (II amide bond), 1483, 1460, 1349, 1335 (CH₂), 1254, 1215 (CO—O), 1122–1022 (C—O—C), 752, 724 (Ar—H); ¹H NMR (DMSO-d₆) [ppm] 1.10 (s, 8H, (CH₂)₄), 2.70–3.70 (m, 11H, O—CH₂, —CO—O—CH<, —CO—O—CH₂, —CH₂—NH—CO—O—), 4.2 (d, 2H, N—CH₂), 5.50–5.85 (t, 2H, CH₂—NH—CO—O—), 7.00–8.25 (m, 8H, in Ar).



Yield: 96%; elemental analysis C 64.19; H 6.69; N 6.24; % Found. C 64.15; H 6.53; N 6.41; IR (capillary film) [cm⁻¹], 3411 (NH), 3050 (Ar—H), 2967 (CH₂),

1716 (I amide bond), 1626, 1460 (C=C in carbazole rings), 1596, 1541 (II amide bond), 1484, 1460, 1452, 1349 (CH₂), 1325 (C—N), 1251 (CO—O), 1110 (C—O—C), 751, 724 (Ar—H); ¹H NMR (DMSO-d₆) [ppm] 1.10–1.40 (m, 8H, (CH₂)₄), 2.70–3.60 (m, 30H, O—CH₂, CH₂—NH—CO), 3.80–4.3 (m, 5H, N—CH₂, —CO—O—CH<, —CO—O—CH₂), 4.40 (m, 2H, CH₂—NH—CO), 7.00–8.20 (m, 8H, in Ar).



Yield: 92.8%; elemental analysis C 64.60; H 8.21; N 5.65; % Found.: C 64.80; H 8.32; N 5.95; IR (capillary film) [cm⁻¹], 3435 (NH), 3051, 3023 (Ar—H), 2969, 2869 (CH₂, CH₃), 1713 (I amide bond), 1627, 1459 (C=C in carbazole rings), 1597 (II amide bond), 1484, 1452 (CH₂), 1325 (C—N), 1373 (CH₃), 1254 (CO—O), 1110 (C—O—C), 750, 723 (Ar—H); ¹H NMR (DMSO-d₆) [ppm], 0.90–1.20 (m, 23H, CH₃—, (CH₂)₄), 2.90–4.20 (m, 20H, O—CH₂, —CO—O—CH<, N—CH₂), 4.20–4.60 (m, 6H, —CH₂—NH—CO), 7.00–8.20 (m, 8H in Ar).

Analytical methods

The progress of reaction of EPC with ethylene glycol and COHD with oxiranes was monitored by EN, which was determined by hydrochloric acid method in dioxane,¹⁸ whereas the reaction of isocyanates was followed by determination of isocyanate groups with ammonia method.¹⁹

Elemental analyses for C, H, N, were done with EA 1108, Carlo-Erba analyzer. 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 10 mg/cm³ concentration. The samples were diluted with methanol to 1 mg/cm³, followed by addition of 10 mg/cm³ NaI in acetone.

Molecular mass of polyurethanes [number-average (\bar{M}_n), weights-average (\bar{M}_w), z-average (\bar{M}_z)] and molecular weight dispersion were determined on Viscotec T60A gel permeation chromatograph equipped with three detector system: RI (refractive index). LS (light scattering detector) and DV (viscosimeter detector). Separation has been performed using two independent columns: PSS SDV (of 7.8 mm × 300 mm size with TSK bed—100 and 1000 Å pore diameter gel, using the following recording parameters: temperature 25 ± 0.1°C, volume flow of eluent 1 cm³/min, the injection loop volume of 20 μdm³, concentration of polymer solution 4/5 mg/cm³, analysis time 30 min, eluent, THF (distilled

from over sodium prior to use), calibration was based on common polystyrene references.

The ^1H NMR spectra of products were recorded with BS 587A 80 MHz, TESLA instrument with HMDS internal standard in DMSO-d_6 . IR spectra were registered on PARAGON 1000 FTIR Perkin-Elmer spectrometer in KBr pellets or capillary film technique.

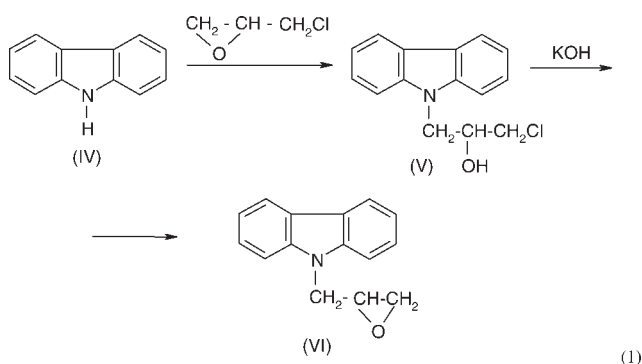
Thermal stability of oligoetherols and polyurathanes was studied with dynamic method to obtain DTA, DTG, and TG curves at 20–1000°C temperature range, under air atmosphere within 100 min and 200 mg samples. Physical and phase transitions determined according to PN-EN ISO 11357-1:2002; using differential calorimeter Mettler Toledo 822^e type with Stare^e System software. The results were registered as heat flow (in [W/g]) versus temperature (in [deg]).

Properties of oligoetherols

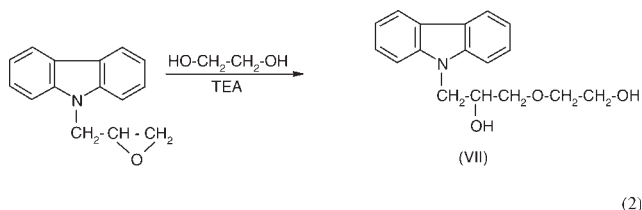
Refractive index, density, viscosity, and surface tension of polyetherols were determined with Abbe refractometer, Höppler viscometer and by the detaching ring method respectively.

RESULTS AND DISCUSSION

To obtain bifunctional diol with carbazole ring in side chain the carbazole (IV) was reacted with epichlorohydrin (ECH) to get EPC (VI) in Reaction (1):



Then VI was the subject of epoxide ring opening by the reaction with ethylene glycol in presence of TEA as catalyst:



Epoxidation of carbazole was performed in acetone at 50–56°C temperature with sixfold molar

excess of ECH and over twofold excess of KOH in relation to carbazole. Epoxide ring of EPC was opened by reaction with ethylene glycol (EG) in dioxane, in presence of TEA catalyst at 110–118°C temperature. After dioxane removal the product was obtained as brown, hard resin. Both product of ring opening are well soluble in EO and PO at 60°C; they react further with oxiranes in presence of TEA.

Thus, oligoetherols with hydroxy groups in main chain and carbazole ring in side chain could be obtained at 60–90°C within 56 h. Obtained products are represented by Formulas I and II. Syntheses were conducted to molar ratio of product of epoxide ring opening to oxirane was 1 : 5. The ^1H NMR spectra of oligoetherols obtained here differ slightly from those of semiproduct, i.e., COHD. By comparing the ^1H NMR spectrum of oligoetherol obtained from EO with that of COHD one can see:

1. Considerable increase of the resonance at 3.5 ppm according to incorporation of oxyethylene groups into semiproduct,
2. The decrease of the signal attributed to secondary hydroxyl group proton at 5.1 with simultaneous growth of the resonance at 4.5 ppm from primary hydroxyl proton of COHD, overlapping with the resonance from oxyethylene protons.

The presence of low-intensity residual resonance from TEA (0.9 ppm) catalyst is due to formation of hydrogen-bonded adducts of the $-\text{OH}\cdots\text{N}(\text{C}_2\text{H}_5)_3$ type, which was noticed previously.²¹ In the ^1H NMR spectra of products obtained from COHD with PO additional methyl resonance at 1.0 ppm was observed, which was attributed to product of PO ring opening. Signals from methylene and methine protons occur at 3.1–3.9 ppm region and overlaps with the OH resonance.

IR spectra of products in addition of EO or PO were also similar to this of semiproduct; the remarkable change was the increase of intensity of absorption at 1020 cm^{-1} indicating the formation of ether bridges in products.

To determine the distribution of molar mass of oligoetherols the MALDI-ToF spectrometry was applied (Tables I and II). The mass spectrum showed the signals from expected molecular ions of oligomers increased of the masses of Na^+ , K^+ , H^+ cations, or methanol, according to the excitation method and kind of solvent applied. The series of signals separated by $M/z = 44$ or 58 were seen, corresponding to the mass of attached EO ($\text{CH}_2\text{CH}_2\text{O}$) (Table I) or PO ($\text{CH}_2(\text{CH}_3)\text{CHO}$) (Table II) units. Moreover the trace resonances from polyglycols formed from ethylene glycol and oxirane become visible. In the spectra, the peaks corresponding to

TABLE I
The MALDI-ToF Peaks of Oligoetherol Obtained from COHD and EO at 1 : 5 Molar Ratio

M/z	Relative intensity (%)		The structure of molecular ion ^a	Calculated mass (g/mol)
	1	2		
86.1	60		EG + Na ⁺	85.1
102.2	12		EG + K ⁺	101.2
137.1	28		EG + EO + CH ₃ OH	138.2
146.2	70		EG + EO + K ⁺	145.2
190.3	14		EG + 2EO + K ⁺	189.2
206.3	40		EG + 2EO + K ⁺ + H ₂ O	207.2
234.3	26		EG + 3EO + K ⁺	233.3
278.4	55		EG + 4EO + K ⁺	277.3
294.4	90		EG + 4EO + Na ⁺ + CH ₃ OH	293.3
322.4	75		COHD + K ⁺	324.4
349.3	15		COHD +EO +H ₂ O	347.4
366.4	84		EG + 6EO + K ⁺ or COHD + EO + K ⁺	365.4 368.4
382.4	100		COHD + EO + Na ⁺ + CH ₃ OH	382.4
410.5	66		EG + 7EO + K ⁺	409.5
426.5	86		COHD + 2EO + Na ⁺ + CH ₃ OH	428.5
470.5	70		EG + 8EO + K ⁺	453.5
498.6	24		EG + 9EO + K ⁺ lub COHD + 4EO + K ⁺	497.6 500.6
514.6	34		COHD + 4EO+ Na ⁺ + CH ₃ OH	514.6
606.8	24		COHD + 6EO+H ₂ O	606.8
652.7	16		COHD + 7EO + H ₂ O + K ⁺	650.9
696.7	14		COHD + 8EO + H ₂ O + K ⁺	694.9

EO corresponds to $-\text{CH}_2\text{CH}_2\text{O}-$; COHD + n EO, consecutive products of reaction between COHD and EO; EG, ethylene glycol; EG + n EO, consecutive products of reaction between EG and EO.

the products of condensation of two molecules of products of reaction between COHD and PO with release of water were also observed (Table II). Because the ¹H NMR spectrum of such oligoetherol did not show olefinic proton resonances at 5–7 ppm region, it can be concluded that the percentage of the selfcondensation product was very low.

Some physical parameters in obtained oligoetherols were determined, which were: density, viscosity, refractive index, and surface tension (Table III). It has been noticed that temperature dependencies of mentioned parameters were quite typical. It has been found that products obtained from EO had higher density, refractive index, surface tension, and viscosity

TABLE II
The MALDI-ToF Peaks of Oligoetherol obtained from COHD and PO at 1 : 5 Molar Ratio

M/z	Relative intensity (%)		The structure of molecular ion ^a	Calculated mass (g/mol)
	1	2		
86.2	60		EG + Na ⁺	85.1
103.2	22		EG + K ⁺	101.2
190.3	35		EG+2EO+ K ⁺ + CH ₃ OH	191.3
278.4	55		EG+4EO+ K ⁺	277.3
248.4	50		EG+ 2PO+ K ⁺ + CH ₃ OH	249.4
288.5	14		COHD + H ⁺	285.4
306.4	83		EG+ 3PO+ K ⁺ + CH ₃ OH lub COHD + Na ⁺	307.5 308.4
364.5	98		COHD + 4PO+ Na ⁺	365.5
380.5	18		COHD +2PO +K ⁺	382.5
422.6	100		GE +5PO +K ⁺ + CH ₃ OH	423.6
433.5	15		COHD + 2PO+ CH ₃ OH	433.6
480.7	83		EG+ 6PO+ K ⁺ + CH ₃ OH or COHD + 3PO+Na ⁺	481.7 482.6
491.6	10		COHD + 3PO+K ⁺	491.7
517.6	32		COHD + 4PO	417.7
538.8	63		EG+ 7PO+ K ⁺ + CH ₃ OH	539.8
575.7	22		2COHD–H ₂ O +Na ⁺	575.7
578.7	30		COHD + 5PO	575.8
598.7	42		COHD + 5PO+Na ⁺	598.8
636.8	25		2COHD–H ₂ O + PO+Na ⁺	633.8
656.8	20		COHD + 6PO+Na ⁺	656.9
694.8	25		2COHD–H ₂ O + 2PO+Na ⁺	691.8
705.8	10		2COHD–H ₂ O + 2PO+K ⁺	708.0
752.9	18		2COHD–H ₂ O + 3PO+Na ⁺	750.0
821.9	15		2COHD–H ₂ O + 3PO+K ⁺	824.1
976.0	18		2(COHP+3PO)-H ₂ O + PO	977.3
1034.2	13		2(COHP+3PO)-H ₂ O + 2PO	1035.4
1092.3	12		2(COHP+3PO)-H ₂ O + 3PO	1093.4

^a PO corresponds to $-\text{CH}_2\text{CH}(\text{CH}_3)\text{O}-$; EG + n PO, consecutive products of reaction between COHD and EO; 2COHD–H₂O, the product of condensation of two molecules of COHD with elimination of water molecule.

than those synthesized from PO. Moreover, physical parameters of polyetherols are close to those of typical polyetherols suitable to polyurethanes.

Thermal analysis of products indicated their high-thermal stability; it is higher in products with oxyethylene groups. These products decompose starting from 250°C (mass loss weight 5%); they decompose totally at 410°C (Fig. 1). Products from PO

TABLE III
Some Physical Properties of Oligoetherols and Regression Equations Describing Their Dependence on Temperature, in the Range 20–80°C

Oxirane	Surface tension τ (N/m)			Refractive index n_{20}^D			Viscosity η (MPa s)				Density d (g/cm ³)		
	$\tau = at + b$			$n_{20}^D = at + b$			$\eta = b + e^{-t/a}$				$d = at + b$		
	$a \times 10^4$	b	r	$a \times 10^4$	b	r	b	A	a	r^2	$a \times 10^4$	b	r
EO	–1.986	0.0493	0.9960	–3.686	1.5600	0.9997	0.00	53788.5	11.63	0.9994	–7.568	1.1182	0.9989
PO	–8.771	0.0500	0.9936	–3.646	1.5309	0.9912	17,50	1725.2	12.19	0.9999	–7.739	1.099	0.9999

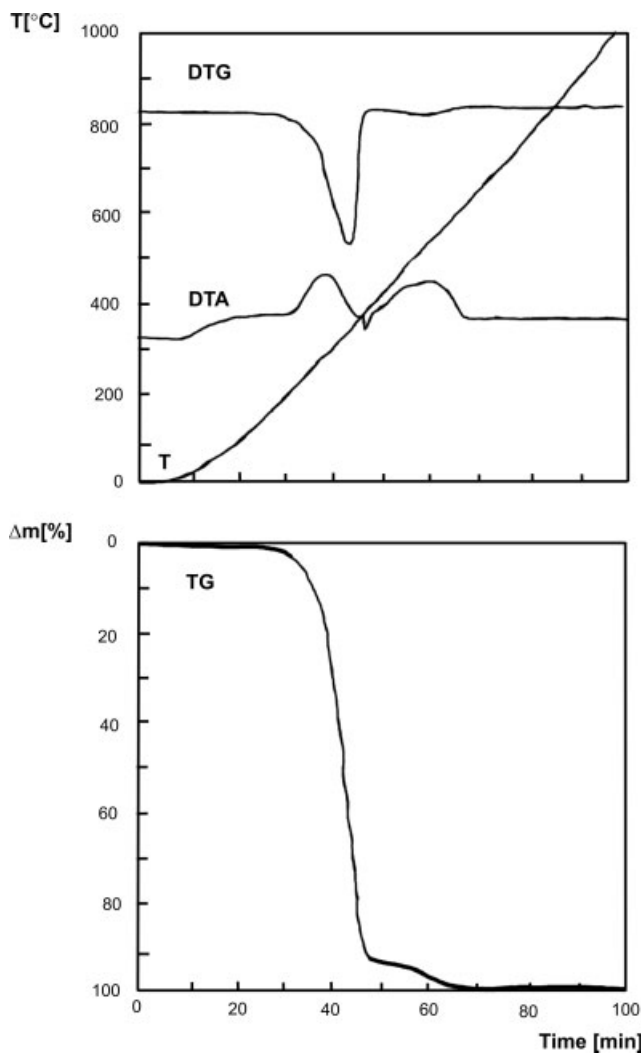


Figure 1 Thermal analysis of oligoetherols obtained in reaction of COHD with EO.

decompose at lower temperature; starting from 90°C, with total decomposition at 360°C. Very high-thermal resistance of products obtained from oxiranes suggests that oligoetherols obtained here can be successfully used to synthesis of polymers of high-thermal stability such as polyurethanes.

Therefore, the obtained diols (oligoetherols and COHD) were subjected for the reaction of isocyanates of variable structure. The polyurethanes obtained from these substrates can be approximately described by the Formula (III). The formula is some simplification of structure of real polyurethane, considering that isocyanates can react with various hydroxyalkyl groups of diol.

The elemental analyses confirmed the structure III (cf. Analytical product in Synthesis of polyurethanes). The polyurethane obtained from COHD and TDI has much higher molecular weights and similar molecular weight polydispersity to polyurethanes obtained from COHD and MDI (Table IV).

TABLE IV
Molecular Masses, Phase Transitions, and Thermal Decomposition of Polyurethanes

Polyurethane abbreviation	Substrates	M_n (kg/mole)	M_w (kg/mole)	M_z (kg/mole)	Molecular weight polydispersity M_w/M_n	T_g (°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	Notes
PU-I-M	COHD+MDI	1.61	2.12	3.26	1.32	45–51	140	250	320	380	resin product
PU-II-M	(COHD : EO 1 : 5) + MDI	2.19	3.40	5.23	1.55	(–22)–(–16)	135	240	320	380	resin product
PU-III-M	(COHD : PO 1 : 5) + MDI	1.07	1.59	2.44	1.48	–	140	250	320	380	
PU-IV-T	COHD+TDI	1.10	1.67	2.51	1.52	59–68	210	290	320	390	resin product
PU-V-T	(COHD : EO 1 : 5) + TDI	1.96	3.03	4.72	1.54	(–38)–(–37)	210	250	310	380	resin product
PU-VI-T	(COHD : PO 1 : 5) + TDI	1.63	2.14	2.69	1.31	–	220	240	300	360	m.p. 255°C;
PU-VII-H	COHD+HDI	^a	^a	^a	^a	–	210	295	330	360	crysts.temp. 252°C; $\Delta H_{\text{cryst.}} = 26.3$ kJ/mol; $\Delta H_{\text{m.}} = -35.0$ kJ/mol.
PU-VIII-H	(COHD : EO 1 : 5) + HDI	1.74	2.35	2.94	1.35	(–32)–(–29)	200	280	320	360	resin product
PU-IX-H	(COHD : PO 1 : 5) + HDI	1.92	2.33	2.64	1.21	–	220	270	330	350	resin product

T_g , glass transition.

$T_{x\%}$ is the temperature at which x wt % of the sample evaporated.

^a The molecular mass not determined due to solubility problems.

The analysis of IR spectra of the products (cf. Analytical product in Synthesis of polyurethanes) evidenced the products were polyurethanes by diagnostic bands at 1710–1730 and 1510–1590 cm^{-1} (I and II amide bands), the band at 3440 cm^{-1} attributed to the valence —NH— band and C—O bond stretching vibrations of ester at $\sim 1220 \text{ cm}^{-1}$. At the ^1H NMR spectra, the resonances from —NH— protons at 8.5–9.6 or 4.1–5.1 ppm and protons of methylene or methine groups attached to CO—O at 4.1–4.5 ppm were observed. All polyurethanes contained carbazole ring, which was visualized by the presence of resonances within the 6.9–8.3 ppm region.

The physical and phase transitions of polyurethanes were studied. The temperature of glass transition of the polyurethane obtained from COHD and TDI is higher than that for the polyurethane synthesized from COHD and MDI (compare Table IV PU-I-M and PU-IV-T). The presence of hexamethylene chain in polyurethane obtained from COHD and HDI causes its structure ordering resulting in formation of crystalline phase (Table IV, PU-VII-H). Melting temperature of crystalline polyurethanes obtained from COHD and HDI is about 255°C, whereas the values of enthalpy of crystallization and melting indicate that the total recovery of crystalline phase is not attained upon cooling. The presence of flexible segments introduced as oxyalkylene units causes decrease of glass transition temperature, which goes down below 0°C (cf. Table IV, PU-II-M, PU-V-T, and PU-VIII-H).

The analysis of thermal mass loss of polyurethanes indicated clearly their enhanced thermal stability, and 50% mass loss was observed at 360°C. Generally the slight mass loss ($\sim 5\%$) was observed at temperature around 140–220°C due to the presence of solvent in the product. The kind of isocyanate used influences the thermal resistance of polyurethanes, which increases in the following order: HDI < MDI < TDI (the temperature of maximal thermal decomposition equals 340, 380, and 400°C, respectively). It has been found that introducing the oxyalkylene groups into polymeric chain did not cause the increase of thermal resistance of polyurethane. Thus, this modification can result in formation of more flexible polyurethanes with unaltered thermal resistance.

CONCLUSIONS

1. Bifunctional oligoetherols with carbazole ring in side chain can be prepared by the reaction of carbazole with glycerine epichlorohydrine to get 9-(2,3-epoxypropyl)carbazole, which has the epoxide ring susceptible to opening with ethylene glycol. The products of ring opening can be effectively further transformed by reaction with oxiranes like ethylene or propylene oxides.
2. Obtained oligoetherols have similar properties like typical polyols used to obtain polyurethanes; they have, however, advantageous thermal stability.
3. These successful results prompted us to incorporate polyetherols into linear polyesters and polyurethanes to make an effort of synthesis of high-thermal stability new polymeric materials.

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