Linear Oligoetherols and Polyurethanes with Carbazole Ring

Renata Lubczak

Faculty of Chemistry, Rzeszów University of Technology, Avenue Powstańców Warszawy, Rzeszów 35-959, Poland

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ABSTRACT: Reaction of 9-(2-chloroethyl)carbazole with excess of diethanolamine led to 5-[2-(carbazol-9-yl)ethyl]-3-azapentane-1,5-diol. The product is well soluble in ethylene and propylene oxides and reacted with them at temperature 60–90°C to give bifunctional oligoetherols with carbazole ring. Structure of these oligoetherols, their physical properties, and application for synthesis of linear polyurethanes were studied in detail. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 16–23, 2010

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

INTRODUCTION

Carbazole and its derivatives are used in polymer chemistry and technology, dye, pesticide, pharmaceutical, surfactant, and polymer stabilizers chemistries.[1–7] Some of carbazole derivatives have unique physical properties; they are photo-electroluminescent, liquid crystals, electroconductors, and nonlinear optical materials.[8–14] Their polymers are usually thermoplasts and therefore are cheaper to fabricate than inorganic materials. Their properties promise advantageous use in electronic industry, xerographic materials, holographic memory, modulation systems, low-voltage displays, and artificial photosynthetic systems.[15–19] Carbazole is thermally resistant; it decomposes starting at 260°C. High thermal stability of carbazole prompted me to introduce carbazole into polyetherols to obtain products of high thermal stability, i.e., polyetherols themselves and polymeric products obtainable from them, e.g., polyurethanes. The method on synthesis of bifunctional polyetherols containing carbazole was reported previously.[20,21] Here, the method of synthesis of bifunctional polyetherols with carbazole in side chain is described together with their physical properties as well as their application synthesis of linear polyurethanes.

EXPERIMENTAL

Syntheses

Synthesis of 9-(2-chloroethyl)carbazole

A total of 2.5 g of carbazole (pure, Fluka, Switzerland) (0.015 mol), 150 g (120 cm^3) of 1,2-dichloroethane (pure, POCH, Poland), 8.42 g (0.15 mol) of KOH (pure, POCH, Poland), 20.73 g (0.15 mol) of K_2CO_3 or 17 g (0.16 mol) of Na_2CO_3 (pure, POCH, Poland), and 0.55 g (0.0015 mol) of tetrabutylammonium iodide (pure, Windsor Laboratories Limited, UK) were placed in a three-necked 250 cm^3 round-bottom flask equipped with mechanical stirrer, reflux condenser, and thermometer. The reaction mixture was stirred and heated for 6 h at 50°C. Then solid residue was filtered off, organic filtrate was washed with water, dried over $MgSO_4$, and removed organic remaining 1,2-dichloroethane on rotary evaporator.

Analytical data of product Yield—75%; mp.—Found: 125–128°C, from literature[22] 130–131°C; elemental analysis—% Calcd.: C, 73.14; H, 5.22; N, 6.09; % Found: C, 73.31; H, 5.32; N, 6.31; IR (KBr) [cm^{-1}], 2959, 2921 (CH_2), 1626, 1486 (C=C), 1461, 1452, 1437 (CH_2), 1357 (CH_3), 1327 (C—N), 1017, 927 (ring band), 660 (C—Cl); ^{1}H-NMR (d_6-DMSO), [ppm] 4.0 (2H, t, N-CH_2), 4.8 (2H, t, $CH_2{-}Cl$), 7.0–8.2 (8H, m, C—H in ring).

Reaction of 9-(2-chloroethyl)carbazole with diethanolamine

The mixture 23 g (0.076 mol) of 9-(2-chloroethyl)carbazole (CEC) and 76 g (0.76 mol) of diethanolamine (DEA-pure, POCH, Poland) in the reaction vessel as described in Synthesis of 9-(2-chloroethyl)carbazole section was heated to 105–110°C, added 8.4 g (0.076 mol) of Na_2CO_3 and continued heating at 115–120°C for 10 h. Then the mixture was poured onto 1500 cm^3 water. The solid product 3-[2-(carbazol-9-yl)ethyl]-3-azapentane-1,5-diol (CEAD) was filtered off and dried at 35°C.

Analytical data of product: Yield—74%; mp. Found: 53–56°C; elemental analysis—% Calcd.: C, 72.43; H, 7.38; N, 9.39; % Found: C, 72.23; H, 7.05; N, 9.07; IR (KBr) [cm^{-1}], 3277 (O—H), 2944, 2923, 2877, 2841 (CH_2), 1626, 1458 (C=C), 1458, 1451 (CH_2), 1335,

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Correspondence to: R. Lubczak (rlubczak@prz.edu.pl).

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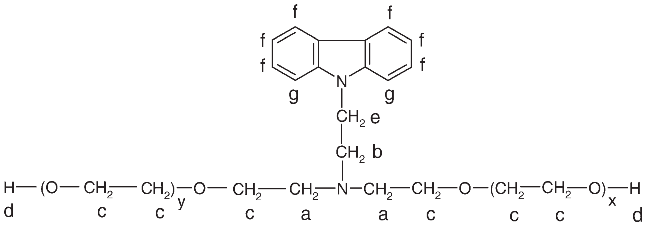
1327 (C—N), 1151 (O—H), 1072, 1048, (ring band), 748, 725 (C—H in ring); ^{1}H-NMR (d_6-DMSO), [ppm] 2.7 (4H, t, N—CH_2—CH_2—O), 2.9 (2H, t′ N_{ring}—CH_2—CH_2—N), 3.4 (4H, t, N—CH_2—CH_2—O), 4.5 (2H, t, N_{ring} —CH_2—CH_2—N), 5.9 (2H, s, OH), 7.0–7.7 (6H, m, C2—7—H in ring), 8.0–8.3 (2H,d,C_1—H, C_8—H).

Syntheses of oligoetherols

Twenty-three gram (0.077 mol) of CEAD, ethylene oxide (EO) or propylene oxide (PO), (pure, Fluka, Switzerland) and 2.5 cm^3 or 3.5 cm^3 of triethylamine (TEA, pure, Fluka, Switzerland), respectively were loaded into high pressure reactor and heated at 60–90°C. Reactions with 1 : 4 molar ratio [corresponding to 13.6 g EO (0.31 mol)] or 18.0 g PO (0.31 mol) were performed according to this protocol. The reactions were monitored by epoxide number (EN) determination. The crude, brownish products were heated under reduced pressure ($p = 2666$ Pa, 20 mm Hg, temp. = 100°C) to remove the catalyst.

Analytical data of oligoetherols obtained from CEAD and EO by molar ratio 1 : 4

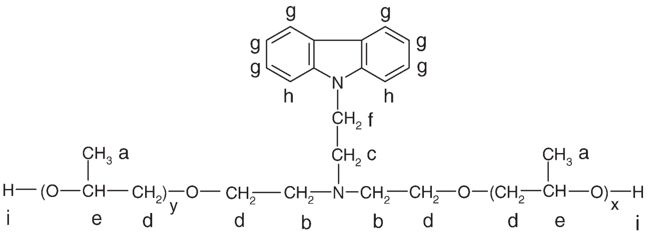


(I)

where: $x + y = 4$.

Yield: 100%; $n_D{}^{20} = 1{,}5872$; density 1,1459 g/cm^3; viscosity 3603 MPa s; surface tension 0,0371 N/m in temperature 20°C; elemental analysis—% Calcd.: C, 65.82; H, 8.02; N, 5.91; % Found: C, 65.73; H, 7.92; N, 5.62; IR (ATR) [cm^{-1}]: 3500 (OH), 3049 (Ar—H), 2914 (CH_2), 1626, 1460 (C=C in carbazole rings), 1460, 1452, 1369 (CH_2), 1349 (OH), 1325 (C-N), 1063, 1025 (C—O in primary alcohols), 1101 (C—O—C), 749, 723 (Ar—H);^{1}H-NMR (DMSO-d_6) [ppm]: 2.8 (*a*, 4H, t), 3.0 (*b*, 2H, t), 3.5 (*c*, 20H, m), 4.5 (*e*, 2H, m), 7.1–7.8 (*f*, 6H, m), 8.0–8.3 (*d*, 2H, d).

Analytical data of oligoetherols obtained from CEAD and PO by molar ratio 1 : 4



(II)

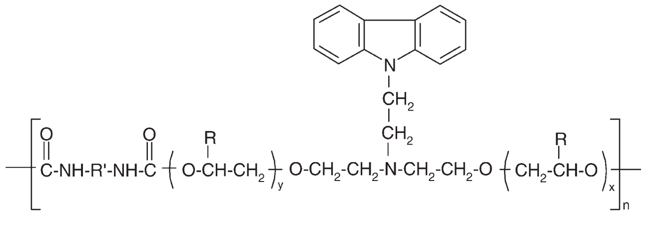
where: $x + y = 4$.

Yield: 100%; $n_D{}^{20}$ =1,5599; density 1,0886 g/cm^3, viscosity 4830 MPa s, surface tension 0,0349 N/m in temperature 20°C; elemental analysis—% Calcd.: C, 67.92; H, 8.68; N, 5.28; % Found: C, 67.73; H, 8.92; N, 5.62; IR (ATR) [cm^{-1}]: 3427 (OH), 3050, 3021 (Ar—H), 2928 (CH_2) 1627, 1458 (C=C in carbazole rings), 1452 (CH_2), 1373 (CH_3) 1325 (C—N) 1100 (OH, C—O—C), 1088, 1063 (OH), 749, 722 (Ar—H);^{1}H-NMR (DMSO-d_6) [ppm]: 0.95 (*a*, 12H, m), 2.7 (*b*, 4H, t), 3.0 (*c*, 2H, t), 3.1–3.6 (*d*, 12H, m), 3.6–4.0 (*e*, 4H, m), 4.2–4.5 (*f*+*i*, 4H, m), 7.1–7.8 (*g*, 6H, m), 8.0–8.3 (*h*, 2H, d).

Syntheses of polyurethanes

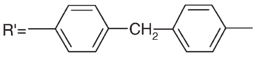
In a three-necked 100 cm^3 flask equipped with mechanical stirrer, reflux condenser, and thermometer 2.98 g (0.01 mol) CEAD or 0.01 mol of appropriate oligoetherol (4.74 g of product obtained from CEAD and EO or 5.30 g of product obtained from CEAD and PO), and 40 cm^3 dioxane were placed. After dissolution of substrate, 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 (9–11 h). The products were isolated as solid or resins after evaporation of solvent, which were dried under reduced pressure ($t = 90$°C, $p = 2 \times 10^{-3}$ Mpa = 15 mm Hg).

Analytical data



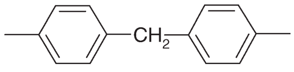
(III)

PU-I-M x+y=0



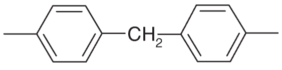
Yield: 88%, elemental analysis—% Calcd.: C, 72.26; H, 5.84; N, 10.22; % Found: C, 72.53; H, 5.92; N, 9.98; IR (KBr) [cm^{-1}]: 3418, 3295 (NH), 3049 (Ar—H), 2930, 2851 (CH_2), 1723 (I amide band), 1640, 1460 (C=C in carbazole rings and in aromatic isocyanate), 1525 (II amide band), 1484, 1451 (CH_2), 1327 (C—N), 1220 (CO—O), 1052, 1017 (C—O—C), 813, 749, 725 (Ar—H); ^{1}H-NMR (DMSO-d_6) [ppm]: 2.80 (t, 6H, N—CH_2), 3.40 (m, 4H, CH_2—O), 3.75 (s, 2H, Ar—CH_2—Ar), 4.00 (t, 4H, CH_2—O—CO), 4.50 (t, 2H, N_{ring}—CH_2), 6.80–8.30 (m, 16H in Ar), 8.50, 9.50 (2s, 2H, NH—CO).

PU-II-M x+y=4 R=H R'=



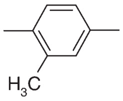
Yield: 70.7%, elemental analysis—% Calcd.: C, 67.96; H, 6.78; N, 7.73; % Found: C, 67.87; H, 6.77; N, 7.93; IR (ATR) [cm^{-1}]: 3297 (NH), 3048 (Ar—H), 2858 (CH_2), 1725 (I amide band), 1641, 1458 (C=C in carbazole rings and in aromatic isocyanate), 1597, 1533 (II amide band), 1484, 1460, 1452 (CH_2), 1325 (C—N), 1219 (CO—O), 1118, 1050 (C—O—C), 871, 815, 750, 723 (Ar—H); ^{1}H-NMR (DMSO -d_6) [ppm]: 2.60–2.90 (t, 6H, N—CH_2), 3.10–3.60 (m, 20H, CH_2—O), 3.75 (s, 2H, Ar—CH_2—Ar), 4.00 (m, 4H, CH_2—O—CO), 4.40 (m, N_{ring}—CH_2), 7.00–8.20 (m, 16H in Ar), 9.50 (s, 2H, NH—CO—).

PU-III-M x+y=4 R=CH_3 R'=



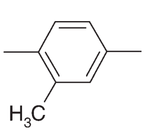
Yield: 85%, elemental analysis—% Calcd.: C, 69.23; H, 7.18; N, 7.18; % Found: C, 69.42; H, 7.46; N, 7.29; IR (ATR) [cm^{-1}]: 3419, 3315 (NH) 3049 (Ar—H), 2969, 2868 (CH_2, CH_3) 1725, (I amide band), 1641, 1458 (C=C in carbazole rings and in aromatic isocyanate), 1537 (II amide band), 1484, 1460, 1452 (CH_2, CH_3), 1375 (CH_3), 1325 (C—N), 1220 (CO—O), 1118 (C—O—C), 817, 749, 722 (Ar—H); ^{1}H-NMR (DMSO-d_6) [ppm]: 0.90 (m, 12H, CH_3—), 2.80 (t, 6H, N—CH_2), 3.0–4.0 (m, 20H, CH_2—O, Ar—CH_2—Ar—, CH—O—), 4.40 (d, 2H, N_{ring}—CH_2), 7.00–8.20 (m, 16H in Ar), 8.5, 9.5 (s, 2H, NH—CO).

PU-IV-T x+y=0 R'=



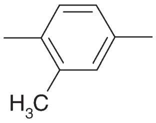
Yield: 82.6%, elemental analysis—% Calcd.: C, 68.64; H, 5.93; N, 11.86; % Found: C, 68.85; H, 6.08; N, 11.81; IR (ATR) [cm^{-1}]: 3299 (NH), 3050 (Ar—H), 2959, 2858 (CH_2, CH_3), 1710 (I amide band), 1620, 1458 (C=C in carbazole rings and in aromatic isocyanate), 1540 (II amide band), 1484, 1457, 1451 (CH_2, CH_3), 1375 (CH_3), 1327 (C—N), 1220 (CO—O), 1054 (C—O—C), 809, 749, 725 (Ar—H); ^{1}H-NMR (DMSO-d_6) [ppm]: 2.00 (m, 3H, CH_3—Ar), 2.70 (m, 6H, N—CH_2), 3.20–3.70 (m, 4H, CH_2—O), 4.00 (m, 4H, CH_2— CO—O), 4.20–4.60 (m, 2H, N_{ring}—CH_2), 6.90–8.20 (m, 11H in Ar) 9.4, 11.2 (2s, 2H, NH—CO).

PU-V-T x+y=4 R=H R'=



Yield: 85%, elemental analysis—% Calcd.: C, 64.81; H, 6.79; N, 8.64; % Found: C, 64.58; H, 6.51; N, 8.78; IR (ATR) [cm^{-1}]: 3298 (NH), 3049 (Ar—H), 2957, 2858 (CH_2, CH_3), 1725 (I amide band), 1612, 1458 (C=C in carbazole rings and in aromatic isocyanate), 1533 (II amide band), 1484, 1460, 1452 (CH_2, CH_3), 1375 (CH_3) 1325 (C—N), 1216 (CO—O), 1100, 1024 (C—O—C), 871, 749, 723 (Ar—H); ^{1}H-NMR (DMSO-d_6) [ppm]: 2.20 (m, 3H, CH_3—Ar), 2.70 (m, 6H, N—CH_2), 3.10–3.60 (m, 20H, CH_2—O), 4.00 (m, 4H, CH_2—CO—O—), 4.40 (m, 2H, N_{ring}—CH_2), 6.80–8.20 (m, 11H in Ar), 8.7, 9.5 (2s, 2H, NHCO).

PU-VI-T x+y=4 R=CH_3 R'=



Yield; 91.6%, elemental analysis—% Calcd.: C, 66.48; H, 7.39; N, 7.95; % Found: C, 66.75; H, 7.31; N, 7.70; IR (ATR) [cm^{-1}]: 3315 (NH), 3052, 3022 (Ar—H), 2970, 2868 (CH_2, CH_3), 1710 (I amide band), 1618, 1658 (C=C in carbazole rings and in aromatic isocyanate), 1540 (II amide band), 1484, 1452 (CH_2, CH_3), 1375 (CH_3), 1325 (C—N) 1220 (CO—O), 1120 (C—O—C), 749, 723 (Ar—H); ^{1}H-NMR (DMSO-d_6) [ppm]: 1.00 (m, 12H, CH_3—), 2.00 (m, 3H, CH_3—Ar), 2.70 (m, 6H, N—CH_2) 3.00–3.90 (m, 12H, CH_2—O), 4.40 (m, 2H, N_{ring}—CH_2), 4.90 (m, 2H, CH—O—CO), 6.70–8.20 (m, 11H in Ar), 8.7, 9.5 (2s, 2H, NH—CO).

PU-VII-H x+y=0 R'= $-(CH_2)_6-$

Yield: 77.6%; elemental analysis—% Calcd.: C, 66.67; H, 6.84; N, 11.97; % Found: C, 66.75; H, 6.81; N, 11.70; (IR (KBr) [cm^{-1}]: 3321 (NH), 3050 (Ar—H), 2963, 2856 (CH_2), 1701 (I amide band), 1626, 1450 (C=C in carbazole rings), 1540 (II amide band), 1484 (CH_2), 1327 (C—N), 1262, 1238 (CO—O), 1097, 1021, (C—O—C), 802, 748, 725 (Ar—H); ^{1}H-NMR (DMSO-d_6) [ppm]: 1.20 (m, 8H, CH_2—$(CH_2)_4$—CH_2), 2.60–3.10 (m, 10H, N—CH_2, CH_2—NH), 3.20 (m, 4H, CH_2—O), 3.90 (m, 4H, CH_2—O—CO), 4.20 (t, 2H, N_{ring}—CH_2), 5.60 (m, 2H, NH—CO), 6.90–8.20 (m, 8H in Ar).

PU-VIII-H x+y=4 R=H R'= $-(CH_2)_6-$

Yield: 86%, elemental analysis—% Calcd.: C, 63.55; H, 7.78; N, 8.72; % Found: C, 63.85; H, 7.53; N, 8.49;

IR (ATR) [cm^{-1}]: 3337 (NH), 3049 (Ar—H), 2931, 2861 (CH_2), 1702 (I amide band), 1626, 1460 (C=C in carbazole rings), 1538 (II amide band), 1484,1452, 1349 (CH_2), 1325 (C—N), 1249 (CO—O), 1119, 1062 (C—O—C), 749, 723 (Ar—H); ^{1}H-NMR (DMSO-d_6) [ppm]: 1.05–1.40 (m, 8H, CH_2—$(\underline{CH_2})_4$—CH_2), 2.50–3.00 (m, 10H, N—CH_2, CH_2—$\underline{NH}$), 3.40 (m, 20H, CH_2—O), 3.90 (m, 4H, CH_2—O—CO), 4.30–4.60 (m, 2H, N_{ring}—CH_2), 5.60 (t, 2H, NH—CO), 6.80–8.20 (m, 8H in Ar).

PU-IX-H $x+y=4$ $R=CH_3$ $R' = —(CH_2)_6—$

Yield: 90%, elemental analysis—% Calcd.: C, 65.33; H, 8.31; N, 8.02; % Found: C, 65.49; H, 8.36; N, 7.95; IR (ATR) [cm^{-1}] 3414 (NH), 3051 (Ar—H), 2968, 2929, 2887 (CH_2, CH_3), 1716 (I amide band), 1626, 1460 (C=C in carbazole rings), 1570 (II amide band), 1484, 1460, 1453 (CH_2, CH_3), 1373 (CH_3), 1325 (C—N), 1255 (CO—O), 1086 (C—O—C), 749, 723 (Ar—H); ^{1}H-NMR (DMSO-d_6) [ppm]: 0.70–1.30 (m, 20H, CH_3—CH, CH_2—$(\underline{CH_2})_4$—CH_2), 2.70 (t, 6H, N—CH_2), 3.00–4.00 (m, 21H, CH_2—O, CH—O, CH_2—O—CO) 4.40 (m, 4H, N_{ring}—CH_2, NH—CO), 6.90–8.20 (m, 8H in Ar).

Analytical methods

The progress of reaction of CEAD with oxiranes was monitored by epoxide number (EN), which was determined by hydrochloric acid method in dioxane,[23] while the reaction of isocyanates was followed by determination of isocyanate groups with ammonia method.[24]

Elemental analyses for C, H, N, were done with EA 1108, Carlo-Erba analyzer. Matrix-assisted laser desorption ionization time of flight (MALDI TOF) 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 (DHB) in THF at mg/cm^3 concentration. The samples were diluted with methanol to 1 mg/cm^3, followed by addition of 10 mg/cm^3 NaI in acetone.

Molecular mass of polyurethanes (number-average ($\overline{M}_n$), weights-average ($\overline{M}_w$), z-average ($\overline{M}_z$) and molecular weight dispersion were determined on Viscotec T60A gel chromatograph equipped with three detector system: RI (refractive index), LS (light scattering detector), and VD (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 cm^3/min, the injection loop volume of 20 μdm^3, concentration of polymer solution 4–5 mg/cm^3, analysis time 30 min, eluent – THF (distilled from over sodium prior to use), calibration was based on common polystyrene references.

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

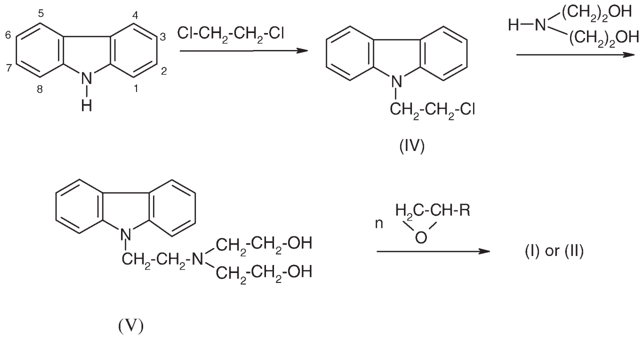
Thermal stability of oligoetherols and polyurethanes was studied with dynamic method to obtain DTA, DTG, and TG curves at 20–1000°C temperature range, under air atmosphere within 100 min and 200 mg samples. Physical and phase transitions determined according to PN–EN ISO 11357–1 : 2002; using differential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

Properties of oligoetherols

Refraction 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

Oligoetherols with carbazole ring were obtained according to the reaction scheme shown below:



Carbazole was converted into CEC (IV), which was then treated with diethanolamine to give oxirane soluble CEAD (V). Synthesis of IV was conducted in presence of ethylene chloride, which was used as reactant and solvent in this procedure, in presence of potassium carbonate and potassium hydroxide and tetrabutylammonium iodide as phase transfer catalyst. Crude product was purified by recrystallization from ethanol. In the next, Step I underwent the reaction with 10-fold excess of

TABLE I
The MALDI-TOF Peaks of Oligoetherol Obtained from CEAD and EO at 1 : 4 Molar Ratio

M/z	Relative intensity (%)	The structure of molecular ion[1]	Calculated mass (g/mol)
137	100	DEA + CH_3OH	137
180.1	81.4	DHB + CH_3OH	177.2
194.1	37.2	DHB + K^+	193.1
299.2	31.9	CEAD + H^+	299.4
342.2	21.3	CEAD + EO + H^+	343.1
382.2	10.6	CEAD + 2 EO	386.2
387.2	16.3	CEAD + 2 EO + H^+	387.2
475.3	11.6	CEAD + 4 EO + H^+	475.2
519.3	90	CEAD + 5 EO + H^+	518.0
563.3	9.3	CEAD + 6 EO + H^+	563.3
607.2	6.4	CEAD + 7 EO + H^+	607.2

[1] CEAD+ n EO, products of reaction between CEAD and n moles EO. DEA, diethanolamine; DHB, dihydroxybenzoic acid used as matrix; EO, corresponds to $-CH_2CH_2O-$.

diethanolamine. The reaction mixture was heated in presence of sodium carbonate to remove HCl side product. Product V was isolated by pouring postreaction mixture onto water. Product V was well soluble in EO and PO at ambient temperature. Product V reacted with EO or PO in presence of TEA at temperature 60–90°C to give desired oligoetherols with carbazole ring. In the ^{1}H-NMR spectra of oligoetherols obtained from EO, the pattern of resonances was analogous to that of V, except grown intensity of resonances from oxyethylene protons $-CH_2-CH_2-O-$ centered at 3.5 ppm. The resonance assigned to hydroxylic proton at 5.0 ppm in the spectrum of CEAD shifts into 4.3 ppm in the spectrum of the oligoetherol. The presence of small intensity resonance at 1.1 ppm from TEA was observed in the spectra of oligoetherols, which was still present despite extensive efforts to remove TEA by vacuum evaporation. This resonance was assigned tentatively TEA, which was hydrogen bonded to $-OH$ groups of polyetherols, as observed previously.[25] In the ^{1}H-NMR spectra of products obtained from CEAD and PO, the resonance at ca 0.9 ppm from methyl group protons was found. The resonances of methylene and methine protons were present at 3.1–3.9 ppm region.

IR spectra of oligoetherols are only slightly different from that of semiproducts. The only spectral effect was the increase of intensity of the band centered above 1050 cm^{-1} attributed to ether groups present in oxyalkylene fragments.

To determine the distribution of molar mass of polyetherols, 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 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 (CH_2CH_2O) (Table I) or PO ($CH_2(CH_3)CHO$) (Table II) units. The products formed upon reaction are the statistical mixtures containing more and less oxyalkylene groups then the initial molar ratio of substrates used for synthesis. Moreover, in the spectra of products of reaction between CEAD with PO the additional products are observed, i.e., those which result from elimination of water from terminal hydroxyalkyl groups.

In the products obtained from oxiranes, some physical properties were determined, i.e., density, viscosity, refractive index, and surface tension. It has been found that temperature relationship of those properties is quite typical. It has been noted that products of reaction with EO had higher density, refraction index, and surface tension than those obtained from PO with comparable numbers of oxyalkylene units. From the values of physical parameters of oligoetherols obtained here, one can conclude that obtained products are useful candidates for synthesis of polyurethanes.

Thermal analysis indicated that products have good thermal stability. Thermal decompositions for products with oxyethylene or oxypropylene units start at 200°C (Fig. 1) or 130°C (mass loss 5%), respectively and ends at 340°C. On this basis, it can

TABLE II
The MALDI-TOF Peaks of Oligoetherol Obtained from CEAD and PO at 1 : 4 Molar Ratio

M/z	Relative intensity (%)	The structure of molecular ion[1]	Calculated mass (g/mol)
147.1	100	DEA + K^+	144
180.7	55.7	DHB + CH_3OH	177.2
234.6	27.7	CEC + H^+	230.5
283.8	37.1	CEAD − H_2O	280.0
341.7	92.9	CEAD + TP − H_2O	338.0
350.4	94.3	CEAD + Na^+ + CH_3OH	386.2
387.2	16.3	CEAD + 2 TE + H^+	387.2
408.4	82.9	CEAD + TE + THF − H_2O	410.0
415.6	31.4	CEAD + 2 TP + H^+	51.0
531.8	54.3	CEAD + 4 TP + H^+	531.0
589.9	68.6	CEAD + 5 TP + H^+	589.0
648.0	65.7	CEAD + 6 TP + H^+	647.9
706.0	40.0	CEAD + 7 TP + H^+	705
738.2	34.3	CEAD + 7 TP + CH_3OH	738
796.2	35.7	CEAD + 8 TP	796.2
854.6	17.1	CEAD + 9 TP	854.2
944.7	12.1	CEAD + 10 TP + CH_3OH	944.6

[1] CEAD + n PO, products of reaction between CEAD and n moles PO. DEA, diethanolamine; DHB, dihydroxybenzoic acid used as matrix; PO, corresponds to $-CH_2CH(CH_3)-$; $-H_2O$, corresponds to product of condensation of two molecules of compound with elimination of water molecule.

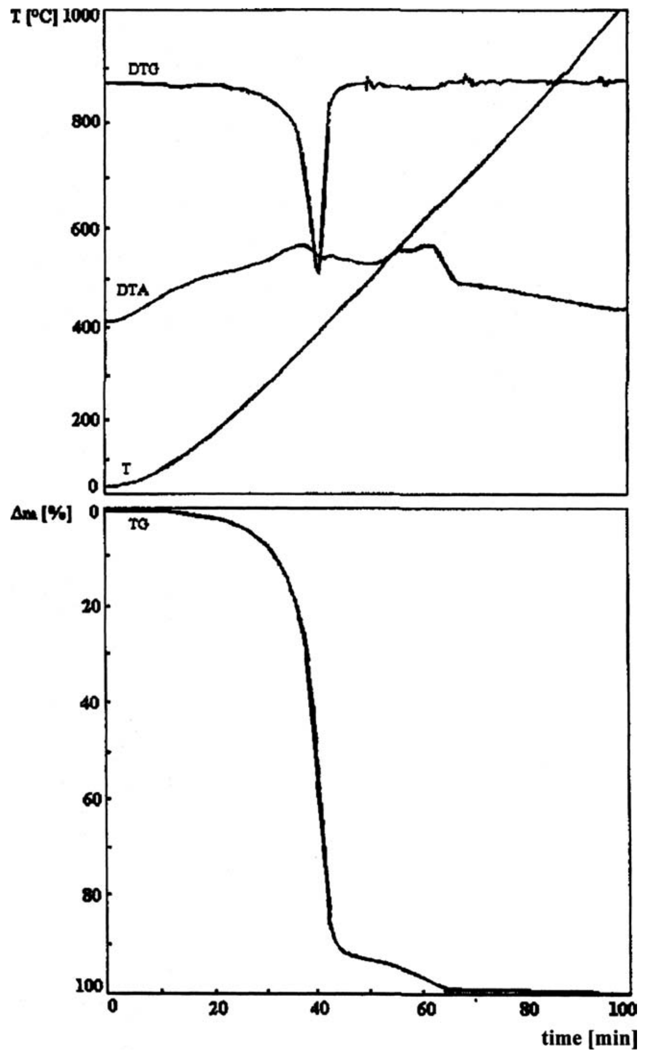


Figure 1 Thermal analysis of oligoetherol obtained in reaction of CEAD with EO.

be concluded that oligoetherols obtained in this procedure are suitable substrates for polyurethanes of higher thermal stability.

Therefore, the obtained diols (oligoetherols and CEAD) were subjected for the reaction of isocyanates of variable structure. The urethane oligomers obtained from these substrates can be approximated by the formula (III). Actually, the polymeric products are formed in the reaction of isocyanates with hydroxyalkyl groups on both ends.

The elemental analyses confirmed the structure III (conf. Analytical data in Syntheses of polyurethanes). The urethane oligomers resulted in the synthesis have M_n within 1050–1920 g/mol and M_w in 1720–5450 g/mol region (Table III). They are rather largely polydispersed (2.4–2.8) with exception of the oligomer obtained from HDI and oligomer prepared from CEAD and PO (1.50).

The analysis of IR spectra of the products (conf. Analytical data in Syntheses of polyurethanes and

TABLE III

Molecular Masses, Phase Transitions, and Thermal Decomposition of Polyurethanes

Polyurethane abbreviation	Substrates	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	Molecular weight dispersion M_w/M_n	T_g [°C]	$T_{5\%}$ [°C]	$T_{10\%}$ [°C]	$T_{20\%}$ [°C]	Remarks
PU-I-M[a]	CEAD + MDI					51–60	180	220	280	m.p 117°C, $\Delta H_{cryst.} = 4.2$ kJ/mol
PU-II-M	(CEAD : EO 1 : 4) + MDI	1540	4200	9320	2.73	–	200	260	340	Resin product in room temperature
PU-III-M	(CEAD : PO 1 : 4) + MDI	1710	4190	9350	2,45	–	200	240	300	Resin product in room temperature
PU-IV-T[a]	CEAD + TDI					54–64	200	225	280	
PU- V-T	(CEAD : EO 1 : 4) + TDI	1920	5450	11100	2.84	(−5) – (+4)	210	230	280	Resin product in room temperature
PU-VI-T	(CEAD : PO 1 : 4) + TDI	1280	3220	9430	2,51	–	210	230	290	Resin product in room temperature
PU-VII-H[a]	CEAD + HDI					24–28	200	220	280	
PU-VIII- H	(CEAD : EO 1 : 4) + HDI	1050	2550	4850	2.43	(−23) – (−19)	200	220	280	Resin product in room temperature
PU-IX-H	(CEAD : PO 1 : 4) + HDI	1150	1720	2100	1.50	–	200	210	270	Resin product in room temperature

[a] The molecular mass not determined due to solubility problems.

T_g, glass transition; $T_{x\%}$, temperature at which x wt % of the sample evaporated.

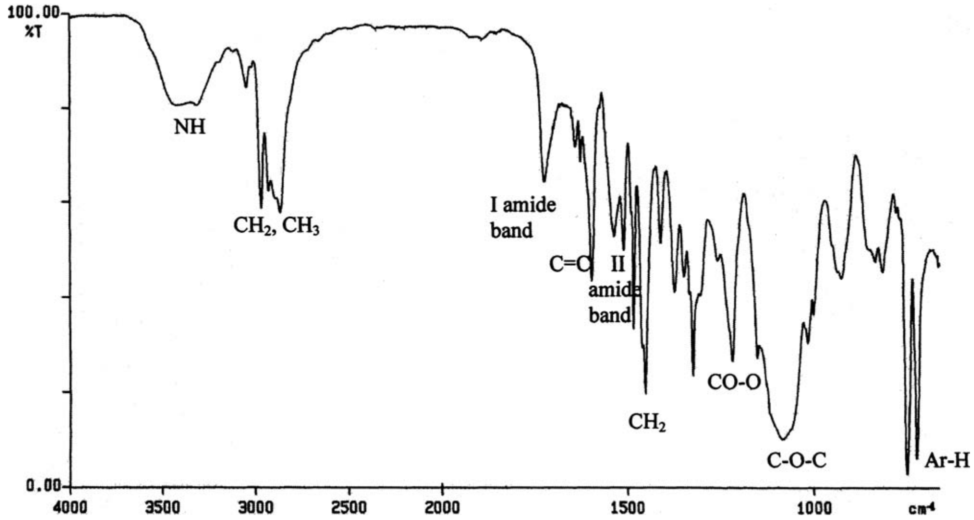


Figure 2 IR spectrum of the polyurethane obtained from (CEAD : PO 1 : 4) and MDI.

Fig. 2) evidenced the products were urethane oligomers by diagnostic bands at 1700–1725 cm^{-1} and 1525–1597 cm^{-1} (I and II amide bands), the band at 3290–3400 cm^{-1} attributed to the valence NH band and C—O bond stretching vibrations of ester at ca. 1220–1250 cm^{-1}. At the ^{1}H-NMR spectra (Fig. 3) the resonances from —NH— protons at 8.5–9.5 ppm or 5.6 ppm and protons of methylene or methine groups attached to CO—O above 4.0 ppm were observed. All oligomers contained carbazole ring, which was visualized by the presence of resonances within the 6.8–8.2 ppm region.

The physical and phase transitions of nonresin urethane oligomers were studied (Table III). The decrease of glass transition temperature of oligomer obtained from CEAD and HDI in comparison with that prepared from MDI and TDI was observed. Tentatively, when elastic segments introduced by synthesis with EO are present in polyurethanes, the temperature of glass transition should be lower and even negative. The presence of crystalline segments was observed only in the urethane oligomer obtained from CEAD and MDI.

It presents an analysis of thermal mass loss of polyurethanes as shown in Table III. The slight mass loss (ca. 5%) was observed at temperature around 200°C. Generally, the kind of oligoetherols used did small influence to the thermal resistance of polyurethanes except the one synthesized from (CEAD : EO 1 : 4) or (CEAD : PO 1 : 4) and TDI. These products started to decompose at 210°C (at a temperature 30°C higher in comparison with polyurethane

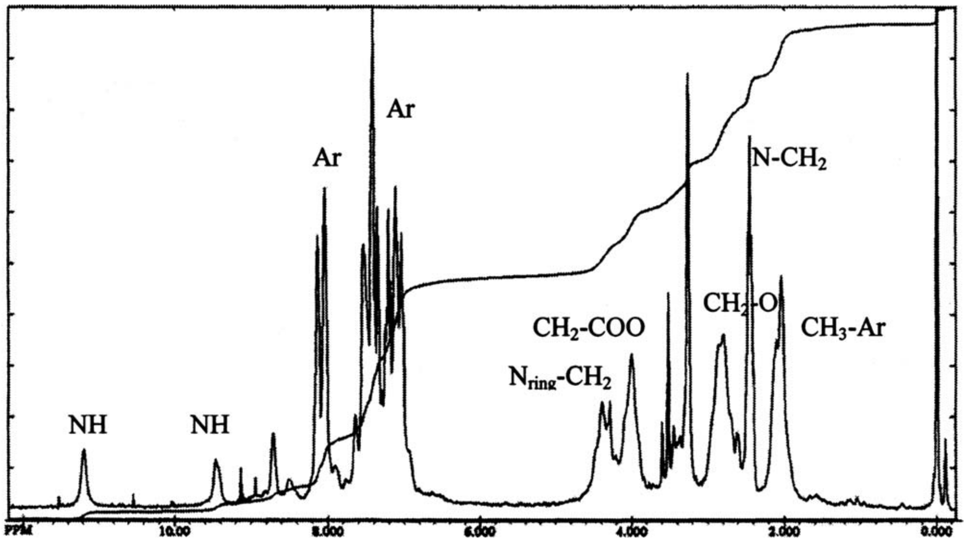


Figure 3 ^{1}H-NMR spectrum of the polyurethane obtained from CEAD and TDI.

prepared from CEAD and MDI). It has been found that introducing oxyalkylene units into polymer chain did not cause the diminishing of thermal resistance of products. This gave the opportunity to enhance the elasticity of products with unaltered thermal resistance.

CONCLUSIONS

Oligoetherols with carbazole ring can be obtained at straightforward reaction of carbazole with oxiranes according to its monofunctionality. Bifunctional oligoetherols with carbazole ring can be obtained in reaction pathway based on reaction of carbazole with ethylene chloride, followed by reaction with diethanolamine, and finally by the reaction of obtained diol with excess oxirane.

Obtained oligoetherols have similar properties like other typical polyols used to synthesize polyurethanes; however, they posses higher thermal stability. These successful results allowed to incorporate oligoetherols into linear and urethane oligomers to enhance their thermal resistance.

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