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Urethane oligomers with a carbazole ring and azo group

RAPID COMMUNICATION

Summary — Oligoetherols with a carbazole ring and azo group were used in reaction with certain diisocyanate to obtain urethane oligomers. The compounds were isolated and characterized by elemental analysis, IR, UV-Vis and ^{1}H NMR spectroscopy. It has been found that the oligomers possess enhanced thermal stability in comparison with analogous oligomers with no azo groups.

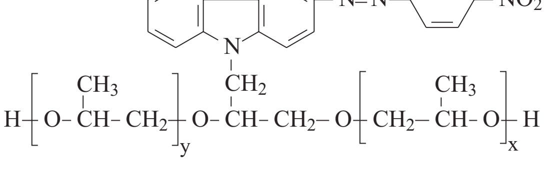
Keywords: carbazole, azo group, oligoetherols, urethane oligomers, thermal stability.

OLIGOMERY URETANOWE Z PIERŚCIENIEM KARBAZOLU I GRUPĄ AZOWĄ

Streszczenie — Dwufunkcyjne oligoeterole z pierścieniem karbazolu i grupą azową w łańcuchu bocznym poddano reakcjom z izocyjanianami o różnej budowie (TDI, MDI i HDI). Reakcje prowadzono w rozpuszczalniku (dioksan) w obecności katalitycznych ilości trietyloaminy (TEA). Za pomocą metod spektroskopowych (IR, UV-Vis i ^{1}H NMR) zbadano skład elementarny oraz strukturę otrzymanych oligomerów uretanowych (tabela 1), a metodą kriometryczną oznaczono ich liczbowo-średnią masę molową (M_n). Zbadano rozkład termiczny otrzymanych oligomerów uretanowych (tabela 2) stwierdzając, że wprowadzenie do struktury poliuretanów ugrupowania fenyloazowego zwiększa znacząco ich odporność termiczną.

Słowa kluczowe: karbazol, grupa azowa, oligoeterole, oligomery uretanowe, odporność termiczna.

Polyurethanes containing heterocyclic moieties in the main chain are a new class of polymers for electronic applications [1—3]. Epoxy resins with carbazole units are interesting materials as well [4—6]. Novel research perspectives are offered by oligomers with built-in carbazole structures that can be further copolymerized to produce tailor-made macromolecular materials. The epoxide ring opening of 9-(2,3-epoxypropyl)carbazole with water results in formation of 3-(carbazol-9-yl)propane-1,2-diol (CPD) [7], which upon reaction with excess oxiranes like ethylene oxide (EO) or propylene oxide (PO) lead to linear oligoetherols [8]. Diazotization of this product with 2-chloro-4-nitrobenzene-diazo chloride results in formation of oligoetherols containing azo and carbazole moieties:



(I)

The previous studies, described in [9], showed that obtained oligoetherols have high thermal stability. That prompted us to apply them as components for obtaining oligourethanes of expected enhanced thermal stability. This paper presents their synthesis, spectral characteristics and preliminary estimation of thermal stability.

EXPERIMENTAL

Materials

Carbazole, ethylene oxide (EO), propylene oxide (PO), triethylamine (TEA), and 2-chloro-4-nitroaniline were purchased from Fluka (Switzerland). Toluilene 2,4-diisocyanate (TDI), diphenylmethane 4,4'-diisocyanate (MDI) and hexamethylene 1,6-diisocyanate (HDI) were delivered by Aldrich (Germany). All substances were pure grade and were used as received.

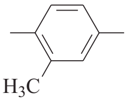
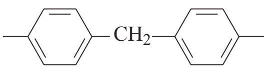
Syntheses of semiproducts

Synthesis of CPD and its reactions with oxiranes (EO and PO) were described previously [7, 9]. Diazotization of obtained oligoetherols was performed as in [9].

Synthesis of oligourethanes

In a three-necked 100 cm^3 capacity flask, equipped with a mechanical stirrer, reflux condenser, and thermometer, 0.01 mole of corresponding diol (*i.e.* CPD or 4.25 g of product of reaction between 3-[3-(2-chloro-4-nitrophenylazo)carbazol-9-yl]propane-1,2-diol with 5 equivalents of EO or PO) were placed and 40 cm^3 of dioxane was added. After dissolving the substrate 0.01 mole of an appropriate isocyanate (1.68 g of HDI or 1.74 g of TDI or 2.5 g of MDI) was introduced. Then one drop of triethylamine was added. The reaction was stopped when the amount of isocyanate groups was zero (after *ca.* 10 h). The product was isolated by addition of 500 cm^3 of water and small amount of salt, the precipitate was filtered off, washed with water and solvent was removed under reduced pressure. The products were powders or resins. The yield of isolated product was 62—98 %.

T a b l e 1. Thermal stability of urethane oligomers; symbols in oligourethane abbreviations inform about the type of diol used in oligourethane synthesis: 0 — CPD, I — 3-[3-(2-chloro-4-nitro-phenylazo)propane-1,2-diol, II — 3-[3-(2-chloro-4-nitrophenylazo)propane-1,2-diol with 5 equivalents of EO, III — 3-[3-(2-chloro-4-nitro-phenylazo)propane-1,2-diol with 5 equivalents of PO

Oligourethane (OUR)	Formula II				% of elements						M_n g/mol
					calc.			found			
	azo group	R	R′	x + y	C	H	N	C	H	N	
OUR-0-HDI	—	—	$(CH_2)_6$	0	67.48	6.60	10.26	67.84	6.94	10.05	1240[a]
OUR-I-HDI	+	—		0	58.73	4.89	14.18	59.19	5.13	13.89	2690
OUR-II-HDI	+	H		6	57.44	6.19	9.81	57.66	6.22	9.55	3005
OUR-III-HDI	+	CH_3		6	59.97	6.91	8.93	59.65	6.65	8.63	3475
OUR-0-TDI	—	—		0	69.40	5.06	10.12	69.10	5.04	9.99	1073[a]
OUR-I-TDI	+	—		0	60.15	3.84	14.04	60.25	3.55	14.10	1920
OUR-II-TDI	+	H		6	58.43	5.45	9.74	58.65	5.16	9.55	2674
OUR-III-TDI	+	CH_3		6	60.86	6.23	8.87	61.04	6.48	8.44	3216
OUR-0-MDI	-	—		0	73.32	5.09	8.55	73.43	5.19	8.31	1480[a]
OUR-I-MDI	+	—		0	64.04	4.03	8.30	64.38	4.86	8.41	2069
OUR-II-MDI	+	H		6	60.10	6.40	8.95	60.18	6.10	8.66	2583
OUR-III-MDI	+	CH_3		6	63.37	6.16	8.21	63.17	6.34	8.13	2970

[a] from ref. [9].

Methods of analysis

The disappearance of isocyanates was followed by determination of isocyanate groups with ammonia method [10].

Elemental analysis for C, H, N, was done with EA 1108, Carlo-Erba analyzer.

The number-average molecular mass (M_n) of obtained polymers was determined cryoscopically in dimethyl sulfoxide (DMSO) solvent.

The IR spectra of products were recorded with Specord 71 IR, Carl Zeiss spectrophotometer in capillary film or in KBr pellet.

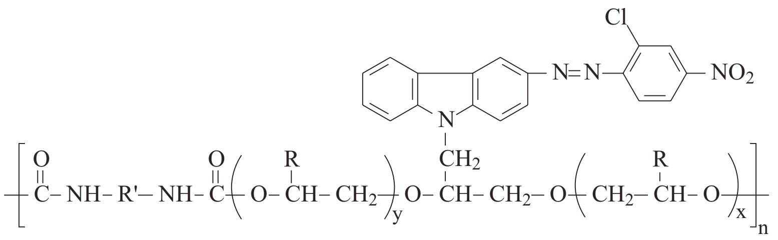
The ^{1}H NMR spectra were recorded at 500 MHz using BECKMAN DU-640 spectrometer in d$_6$-DMSO, with hexamethyldisiloxane (HMDS) internal reference.

The thermal analysis of urethane oligomers was conducted with F. Paulik, J. Paulik, L. Erdey (MOM, Hungary) derivatograph.

RESULTS AND DISCUSSION

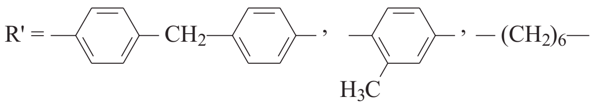
Reaction with diisocyanates was performed starting from equimolar amount of diol or oligoetherol containing an azo group in dioxane at 80 °C in presence of TEA catalyst. Elemental analysis results and experimentally determined $\overline{M}_n$ values of products obtained in reaction of diisocyanates with oligoetherols containing carbazole ring, which are presented in Table 1, indicate that they are urethane oligomers of the formula (II).

The IR spectra of polymers clearly demonstrate the urethane character of products. Amide I and II bands are present at around 1730 and 1530 cm^{-1}, N-H vibration band at 3300 cm^{-1} as well as ester C-O stretching vibration at 1220 cm^{-1}. The presence of an azo group is confirmed by the band within 1590—1600 cm^{-1}. The UV-Vis spectra of products have maximum in the visible region at 450—470 nm. All the expected resonances of oxyalkylene protons, which are present in oligoetherol, methyl protons and amide protons can be observed at the ^{1}H NMR spectra of products. Exemplary spectrum is presented in Figure 1. Oxyalkylene proton signals occur at 3.2—3.6 ppm. Moreover, the resonances at 0.9—1.4 ppm correspond to the resonance of a methyl group derived from oxyalkylene formed in result of reaction with PO. The carbazole ring protons resonate at 6.9—8.5 ppm region, where also the aromatic proton resonances, *i.e.* phenyl



(II)

where: R = − H, − CH_3



x + y = 0 or x = y = number of oxyalkylene units

ring from diazo substituent and those derived from diisocyanates are present. The protons of the methylene group — linker of carbazole resonate at 4.45 ppm. Also the amide proton resonances can be observed most often in the region 4.6—5.3 ppm, and in some cases above 9.4 ppm (in the spectra of oligourethanes obtained from aromatic diisocyanates), which disappear upon addition of deuterium oxide. In the spectra of urethane oligomers obtained from TDI the resonance of the methyl group attached to the aromatic ring of isocyanate is observed at 2.1 ppm. Furthermore, in the spectra of oligomers obtained from MDI the resonance at 3.8 ppm from methylene protons located between two aromatic rings, and in case of oligourethanes obtained from HDI the methylene resonances located in -$(CH_2)_4$- are observed at 0.9—1.3 ppm, while resonances of the methylene group attached to the amide group in -CH_2NHCO- group are present at 2.8 ppm.

The thermal stability of oligomers was studied in details and obtained results are listed in Table 2. The mass loss in function of temperature indicated their high thermal stability. In particular, maximum mass loss occurs at ca. 300 °C. Slight mass loss (*ca.* 10 %) is observed within 260—300 °C region. It has been found that higher thermal stability have urethane oligomers obtained from oligo-

Table 2. Characteristic temperatures of thermal degradation of urethane oligomers

Oligourethane (OUR)	$T_{5\,\%}$ °C	$T_{10\,\%}$ °C	$T_{25\,\%}$ °C	$T_{50\,\%}$ °C	$T_{max\ decomp.}$ °C
OUR-0-HDI	240	270	305	340	300
OUR-I-HDI	170	260	300	460	300
OUR-II-HDI	260	290	330	400	300
OUR-III-HDI	240	300	340	400	410
OUR-0-TDI	120	200	285	350	360
OUR-I-TDI	140	260	300	600	300
OUR-II-TDI	240	290	330	420	290
OUR-III-TDI	280	300	350	400	300
OUR-0-MDI	100	160	300	360	360
OUR-I-MDI	240	280	325	560	270
OUR-II-MDI	240	280	340	400	320
OUR-III-MDI	280	300	350	400	380

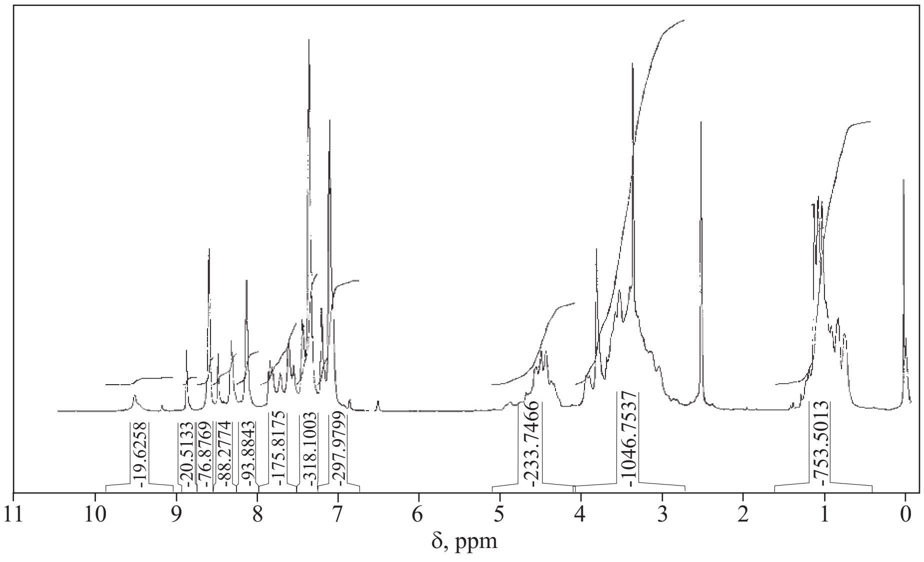


Fig. 1. ^{1}H NMR spectrum of OUR-III-MDI

etherols rather than those obtained from CPD. The highest thermal stability reveal mostly oligourethanes synthesized from oligoetherols obtained from PO. Comparing thermal stability of polyurethanes with and without azo groups one can see that considerable increase of thermal resistance is achieved upon introduction of azo group with phenyl ring.

CONCLUSIONS

The linear urethane oligomers of enhanced thermal stability can be obtained in reaction of diols or oligoetherols containing a carbazole ring and azo groups with izocyanates like: MDI, TDI, and HDI. The syntheses can be performed in dioxane at 80 °C in the presence of a catalytical amount of triethylamine. The introduction of a phenylazo group into the oligourethane structure considerably increases their thermal resistance. The influence of the oxyalkylene chain of oligoetherol on thermal stability was also noticed.

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