ANNA ŚLĄCZKA, JACEK LUBCZAK[*)]

Rzeszów University of Technology
Department of Organic Chemistry
Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

Urethane oligomers with pyrimidine rings

RAPID COMMUNICATION

Summary — New urethane oligomers containing pyrimidine rings were obtained from *N,N'*-bis(hydroxymethyl)barbiturate and bifunctional isocyanates. The products were isolated and identified on the basis of elemental analysis, IR and ^{1}H NMR spectroscopy. The oligomers obtained have higher thermal stability in comparison with their analogues obtained from aliphatic diols.

Key words: *N,N'*-bis(hydroxymethyl)barbiturate, isocyanates, polyaddition, urethane oligomers, thermal stability.

OLIGOMERY URETANOWE Z PIERŚCIENIAMI PIRIMIDYNOWYMI

Streszczenie — Wykorzystując reakcje kwasu barbiturowego (BA) z odpowiednim nadmiarem formaldehydu w temperaturze 96 °C otrzymano barbituran *N,N*-bis(hydroksymetylu) (BHMB), który zastosowano jako diol do otrzymywania oligomerów uretanowych. Opracowano warunki syntezy oligomerów z pierścieniem pirimidynowym z zastosowaniem BHMB i jednego z izocyjanianów: 4,4'-diizocyjanianu difenylometanu (MDI), 2,4-diizocyjanianu toluilenu (TDI) lub 1,6-diizocyjanianu heksametylenu (HMDI). Reakcje prowadzono w środowisku dimetyloformamidu (DMF), w temperaturze 60 °C w czasie 1—2 godzin. Otrzymane produkty analizowano na zawartość węgla, wodoru i azotu oraz wykonano ich widma ^{1}H NMR i IR. Stwierdzono niewielkie odstępstwa zawartości oznaczonych pierwiastków w otrzymanych oligomerach w stosunku do wartości obliczonej, co wynika z eliminacji, podczas reakcji z izocyjanianami w podwyższonej temperaturze, części formaldehydu związanego nietrwale w grupach *N*-hydroksymetylowych. Zbadano przemiany fizyczne oraz odporność termiczną otrzymanych oligomerów uretanowych. Obecność w strukturze pierścieni pirymidynowych zwiększa ich odporność termiczną w porównaniu z oligomerami nie zawierającymi takich grup.

Słowa kluczowe: barbituran *N,N*-bis(hydroksymetylu), izocyjaniany, poliaddycja, oligomery uretanowe, odporność termiczna.

The isocyanuric acid and uric acid react with oxiranes to give polyetherols with azacyclic ring [1]. Similar reactions of barbituric acid (BA) was not explored till now. Such polyetherols are promising candidates for syntheses of polyurethane foams showing good thermal stability [1]. BA is another useful substrate for this purpose, however it undergoes conversion into insoluble enol form in the presence of oxiranes [2]. Therefore we have explored another route to hydroxyalkyl derivatives of BA, based on the reaction of BA with formaldehyde [3]. According to those studies various hydroxymethyl derivatives of BA can be obtained depending on the initial molar ratio of BA/CH_2O. The reactive hydrogens are placed on nitrogen and C_5. At BA/CH_2O 1/≥4 all the hydrogen atoms can be replaced with hydroxymethyl groups. For the system with BA/CH_2O ratio equal 1/2 the structure of the product depends on the temperature of reaction.

At ambient temperature the major reactive center is methylene group of BA, while at temperature above 90 °C the imide groups react predominantly. Within the range 40—60 °C formaldehyde reacts with both groups. The reactivity of BA is then typical for kinetic versus thermodynamic control. This has been further confirmed by observation that 5,5-bis(hydroxymethyl)barbituric acid rearranges into 1,3-bis(hydroxymethyl)barbiturate (BHMB) upon prolonged heating [3].

Multihydroxymethyl derivatives of BA can be applied for the syntheses of polymers with pyrimidine rings, because they dissolve well in oxiranes and react with them to give polyetherols [4]. The latter are convertible into polyurethane foams upon reaction with isocyanates and water. The foams are of remarkably thermal stability due to the presence of pyrimidine rings [4]. The

---

[*)] Author for correspondence; e-mail: jml@prz.rzeszow.pl

ease of BHMB preparation renders it useful as bifunctional diol substrate for syntheses of urethane oligomers with pyrimidine rings. The results of these studies are reported here. It should also be mentioned that literature data on improvement of thermal resistance of linear polyurethanes are scarce [5]. Recently the syntheses of cationomeric polyurethanes [6, 7] and luminescence of polyurethanes have drawn much attention [8]. The subject was widely covered in the review by Król [9].

EXPERIMENTAL

Materials

Barbituric acid (BA, pure) was purchased from BDH Laboratory Supplies (UK).

36 % formalin (pure) was supplied by POCh (Gliwice, Poland).

Dimethylformamide (DMF, pure) purchased from Merck was purified before use by azeotropic distillation with water/benzene system and stored over molecular sieves 4A.

Hexamethylene-1,6-diisocyanate (HMDI, pure) was delivered by Fluka (Switzerland).

4,4′-Diphenylmethane diisocyanate (MDI, pure), toluilene-2,4- -diisocyanate (TDI, pure) and butane-1,4- -diol (BD, pure) were supplied by Aldrich (Germany).

1,3-Bis(hydroxymethyl)barbiturate (BHMB) was obtained in our laboratory according to the procedure described in [3].

Reactions of BHMB with isocyanates

In 100 cm^3 three-necked round bottom flask equipped with mechanical stirrer, reflux condenser and thermometer the 0.94 g of BHMB (0.005 mole) in 20 cm^3 of DMF was dissolved with slight heating. Then 0.005 mole of isocyanate: (HMDI or MDI or TDI) in 5 cm^3 of DMF were added and heated at 60 °C. The process was continued until no free isocyanate groups were present. The mixture was poured onto water, the precipitated product was filtered off, washed with water and dried at 100 °C. The residual DMF was removed by washing with hot water and dried again at 100 °C. For comparison of the products the similar reaction of 0.45 g (0.005 mole) of BD and 0.87 g (0.005 mole) of TDI in 20 cm^3 of DMF was performed.

Analytical methods

Unstably bounded formaldehyde (as hydroxymethyl groups) in BHMB was determined iodometrically [10].

The reaction with isocyanates was monitored by determination of isocyanate groups by ammonia method [10].

Elemental analyses for C, H and N contents were performed using EA 1108, Carlo-Erba (Italy) elemental analyzer.

The number-average molecular weights ($\overline{M}_n$) of obtained oligomers were determined cryoscopically in dimethyl sulfoxide (DMSO) solvent.

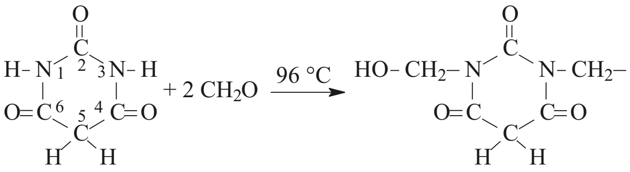
The ^1H NMR spectra were recorded using TESLA instrument (type BS586A, 80 MHz) in d_6-DMSO and IR spectra were registered in KBr pellets using PARAGON 1000 FT-IR Perkin Elmer spectrophotometer.

Thermal analyses (DTA, DTG and TG) of urethane oligomers were performed in ceramic crucible at 20—1000 °C temperature range, with 100 min registration time, 200 mg sample, under air atmosphere, using Paulik — Paulik—Erdey derivatograph (MOM, Hungary).

Differential scanning calorimetry (DSC) studies were done under nitrogen atmosphere using DSC822^e Mettler Toledo calorimeter at 20—300 °C temperature range with 10 deg/min heating rate and 10—20 mg samples.

RESULTS AND DISCUSSION

The percentage of hydroxymethyl groups (determined by iodometric method) in the product of hydroxymethylation of BA (at initial molar ratio BA/CH_2O equal 1/2.6 at temp. 96 °C) followed by vacuum removal of water under reduced pressure (p = 13.33 hPa) at temp. 60 °C equals 32.0 wt. %. This result correspond to the presence of two hydroxymethyl groups in the product:



(1)

The ^1H NMR clearly confirms that the product of reaction is BHMB [3]. Vacuum removal of water results to partial splitting of formaldehyde from the product, therefore the initial overstoichiometric excess of CH_2O was used. As it was mentioned earlier [3] thermal stability of hydroxymethyl groups attached to BA depends on the place of attachment; predominantly the hydroxymethyl groups attached to C_5 (65—75 °C) and further the *N*-hydroxymethyl groups (145—160 °C) undergo the removal. If BA/CH_2O molar ratio is lower then 1/2 part of formaldehyde is attached to C_5 and the product must be exposed to thermal treatment at 90 °C up to the moment of removal of appropriate amount of formaldehyde. This thermal conversion leads to splitting of hydroxymethyl groups from C_5 leaving *N*-hydroxymethyl groups untouched.

Urethane oligomers were obtained with one of three different isocyanates: HMDI, or MDI, or TDI. Products were investigated by elemental analysis, ^1H NMR and IR spectroscopy. The elemental analytical data listed in Table 1 show slight deviation from calculated values due to partial removal of formaldehyde unstably bounded in *N*-hydroxymethyl groups. This behavior was noted pre-

Table 1. Results of elemental analyses, number-average molecular weight $\overline{M}_n$ and thermal stability of urethane oligomers obtained

Number of sample	Urethane oligomers made of	Content of nitrogen, wt. %		Content of carbon wt. %		Content of hydrogen, wt. %		$\overline{M}_n$ g/mole	$T_{5\%}$ °C	$T_{10\%}$ °C	$T_{20\%}$ °C	$T_{50\%}$ °C
		calc.	found	calc.	found	calc.	found					
1	BHMB + HMD	15.73	16.28	48.13	49.17	5.62	6.12	980	180	250	310	560
2	BHMB + MDI	12.79	12.86	58.68	59.89	4.11	5.12	1234	160	210	260	370
3	BHMB + TDI	15.47	16.67	50.72	51.18	3.87	4.10	1094	100	200	280	420
4	BD + TDI	10.61	10.38	59.09	58.89	6.06	5.94	3250	110	190	250	300

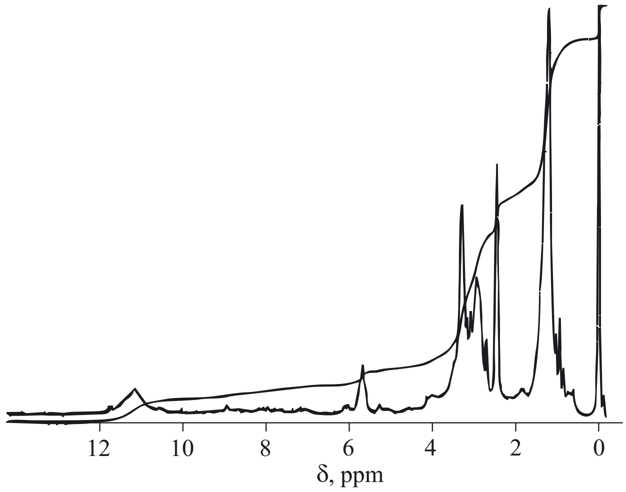
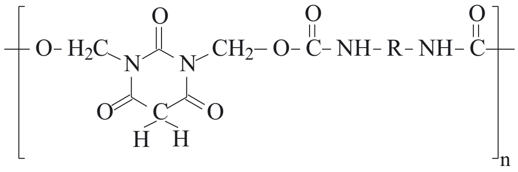


Fig. 1. ^{1}H NMR spectrum of urethane oligomer obtained from BHMB and HMDI

viously [3]. Due to limited solubility of oligomers the number-average molecular weight was determined cryoscopicaly in DMSO as 980—1234 (Table 1).

The ^{1}H NMR spectrum of urethane oligomers obtained in the reaction between BHMB and HMDI in shown in Figure 1. The resonance signal attributed to four internal methylene groups of isocyanate chain —$(CH_2)_4$— are present at 1.25 ppm, while two external groups give signal at 3.30 ppm. Methylene group proton attached to pyrimidine nitrogen are chemical shift around 3.0 ppm. The integral intensity ratio of methylene protons attached to ring nitrogen signal and that of methylene protons attached to nitrogen in the chain is 1:1, which indicates the following structure of oligomers:



(I)

R = —CH_2—$(CH_2)_4$—CH_2—

Furthermore the shift at 5.7 and 11.2 ppm assigned to -NH group protons (collapsing upon addition of D_2O) correspond to two protons. In the spectra of the product obtained from BHMB and MDI the methylene groups signal at 3.1 ppm are attributed to methylene group protons attached to the pyrimidine ring nitrogen, while the signal at 3.7 ppm belongs to methylene group protons located between aromatic rings. The signals of aromatic protons are observed at 6.4—7.6 ppm region and amide proton signals are at 8.4 and 11.2 ppm. The integral intensity ratio is 4:2:8:1:1 indicating the structure of oligomer, where R = *p*-Ph-CH_2-Ph-*p*. Similarly, the spectrum of urethane oligomers with R = 2-methyl-*p*-phenylen corroborate well the structure of product. The broad signals at 10.9—11.7 ppm and 7.8—8.4 ppm were

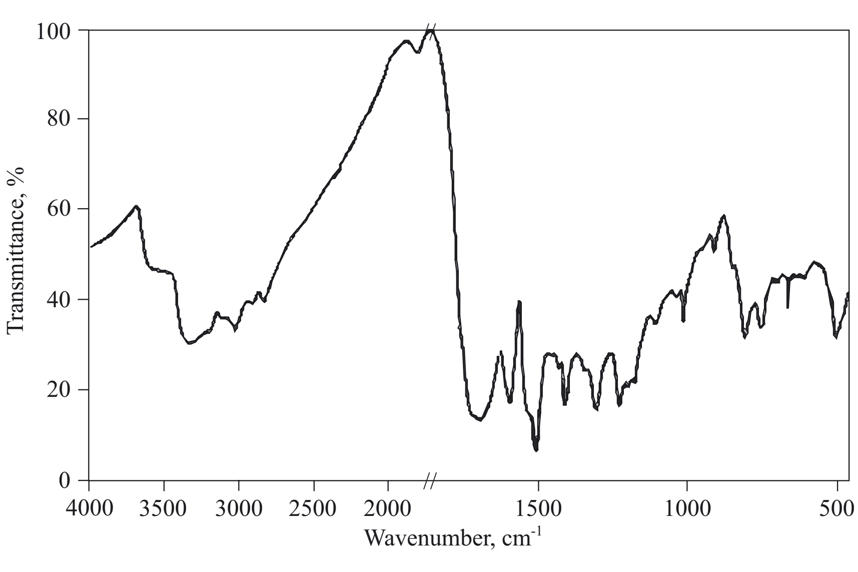


Fig. 2. IR spectrum of urethane oligomer obtained from BHMB and MDI

attributed to amide group protons in oligomers, aromatic proton signals are present in 6.4—7.6 region, while proton signals from methyl groups attached to aromatic ring are present at about 2 ppm.

IR spectra are typical for urethane oligomers. In Figure 2 IR spectrum of oligomer obtained from BHMB and MDI is presented. The valence vibrations of *N*-bond are present at 3100 to 3500 cm^{-1}. Amide I and II bonds are observed at 1710 and 1530 cm^{-1}. In the IR spectra of esters the C-O bond vibration is located at 1220—1230 cm^{-1}.

The physical and phase transitions as well as thermal stability of obtained urethane oligomers were studied. On the DSC curves in the temperature range 40—170 ^{o}C no inflections characteristic for physical phenomena in polymers were observed except the urethane oligomers obtained from BHMB and TDI, which indicated glass transition at *ca.* 128 ^{o}C, *i.e.* at temperature slightly higher than for typical linear polyurethanes. This oligomers reveals crystalline state with melting temperature at *ca.* 186 ^{o}C. The melting enthalpy is as low as 123 J/mol. Cooling the sample does not recover the crystalline phase. Thermal analyses of urethane oligomers indicated the higher thermal stability of oligomers obtained in comparison with those of commonly used ones. The 10 % weight loss was observed at *ca.* 200 ^{o}C, while the temperature of 50 % decomposition was found at 370—540 ^{o}C (Table 1). The 3 % weight loss at 100 ^{o}C was due to occluded water evaporation. The endothermic peak at 270—280 ^{o}C at thermograms of oligomers obtained from aromatic isocyanates was attributed to thermal decomposition of pyrimidine ring, which was observed previously [3]. The oligomers obtained have higher thermal stability (especially at temperatures over 250 ^{o}C) in comparison with their analogues obtained from aliphatic diols (sample 4).

CONCLUSIONS

Urethane oligomers with pyrimidine rings can be obtained from 1,3-bis(hydroxymethyl)barbiturate with bifunctional isocyanates. These polymers have enhanced thermal stability in comparison with classic polyurethanes due to the presence of pyrimidine rings.

Obtained products can be used as chain extenders; they form rigid segments in linear polyurethanes.

REFERENCES

1. Lubczak J.: *Curr. Trends Polym. Sci.* 2003, **8**, 73.
2. Lubczak J., Mendyk E.: *Heterocycl. Commun.* 2008, **14**, 149.
3. Ślączka A., Lubczak J.: *J. Appl. Polym. Sci.* 2006, **101**, 3468.
4. Ślączka A., Lubczak J.: *J. Appl. Polym. Sci.* 2007, **106**, 4067.
5. Datta J., Podlawski D.: *Elastomery* 2005, **9**, 20.
6. Król P., Król B.: *Polimery* 2004, **49**, 531.
7. Król P., Król B.: *Polimery* 2004, **49**, 615.
8. Ryszkowska J., Zawadzak E., Hreniak D., Stręk W., Kurzydłowski J.: *Polimery* 2007, **52**, 340.
9. Król P.: *Prog. Mater. Sci.* 2007, **52**, 915.
10. Kastierina T., Kalinina L.: "Chemiczna analiza tworzyw sztucznych", WNT, Warszawa 1965.

Received 25 III 2008.