

Polyurethanes I. Product of Polyaddition of Bis(4-hydroxyethylenethio)diphenyl Ether with Methylene Bis(4-phenyl isocyanate)

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ABSTRACT

New polyurethanes are synthesized by polyaddition reaction of bis(4-hydroxyethylenethio)diphenyl ether with methylene bis(4-phenyl isocyanate) in optimal established conditions. Good results are obtained using a non-reactive solvent such as benzene, dibutyltin dilaurate as a catalyst, ca. 15% wt concentration of monomers and conducting the process at 80-90 °C for 1.5-2 h. Basic physicochemical properties of the polyurethane obtained are defined. The thermal behaviour of the polymers is evaluated by means of thermogravimetry and differential scanning calorimetry. The structure of synthesized polyurethane is determined by elemental analysis, FT-infrared and ¹H NMR spectroscopies and X-ray analysis. Polyurethanes with 20 and 50% molar 1,6-hexamethylenediol in relation to bis(4-hydroxyethylenethio)diphenyl ether are obtained under the same conditions established earlier as optimal for synthesis of these polymers from the above mentioned compounds.

Key Words: linear polyurethanes, polyaddition, optimal conditions, thermal stability, modification

INTRODUCTION

Among the large number of works related to polyurethanes (PU) synthesis, we have concentrated on those concerning polyaddition reactions of diisocyanates with diols [1-11].

There are only some works that have been devoted to the methods of preparation and properties of polyurethanes containing sulphur in their structure.

In a very early paper Schonfeld [12] reported

the preparation of linear, hydroxy-terminated polyacetals containing sulphide linkages, and their subsequent conversion into cross-linked urethane elastomers.

In another work Zochniak [13] described the synthesis and properties of polyurethanes based on 1,5-pentanediol dithioglycolate.

The present paper deals with the preparation and properties of aromatic-aliphatic polyurethanes containing sulphur in their structure employing unknown bis(4-hydroxyethylenethio)diphenyl ether

(4-IIETDE).

Finally, attempts have been made to improve some properties of these polymers by hexanediol as a chain extender.

EXPERIMENTAL

Materials

4-HETDE, mp 93–4 °C, was obtained by reaction of bis(4-mercaptophenyl)ether (4-MPE) with bromoethanol in an ethanolic solution of NaOH.

Methylene bis(4-phenyl isocyanate) (MDI) from Farbenfabriken Bayer AG was purified by vacuum distillation. The distillation fraction at 148–150 °C/0.12 mm Hg was collected. Dibutyltin dilaurate (DBTDL) from Merck was used as purchased.

Triethylamine (TEA, Fluka) was freshly distilled over anhydrous KOH.

1,6-Hexamethylenediol (1,6-HMD) from Lobe-Chemie, Wicn-Fischamend was distilled, and the fraction was collected at 135 °C/0.1 mm Hg.

Dimethylformamide obtained from POCH-Gliwice, Poland, was purified by distillation.

Monomer Synthesis

4-HETDE was obtained from 4-MPE and bromoethanol as the following procedure:

Into a 250 mL round-bottom flask equipped with stirrer and reflux condenser was placed 0.05 M (11.6 g) 4-MPE in 100 mL aqueous sodium hydroxide solution (2N NaOH). After thorough mixing it was heated to reflux, and 0.1 M (12.5 g) bromoethanol in 30 mL ethanol was added dropwise during 15 min, and the mixture was heated at 80 °C for the following 2 h.

After cooling, the resulting precipitate was filtered, washed with distilled water until neutral and then dried in vacuum at 60 °C to constant weight (yield 80%). By recrystallization from benzene (1 g from 15 mL) the diol with mp 104–5 °C was obtained. The purity of the compound obtained in this manner was checked by elemental analysis, FT-infrared and ¹H NMR spectroscopies as detailed in the following:

Results of elemental analysis are as follows:

C ₁₆ H ₁₈ O ₃ S ₂	%C	%H	%S
Calculated	63.75	6.25	20.0
Found	63.20	5.94	19.61

IR (KBr): 820 cm⁻¹, 1043 cm⁻¹, 1093 cm⁻¹, 1285 cm⁻¹, 1490 cm⁻¹, 3290 cm⁻¹.

¹H NMR (DMSO-d₆): 4.99 ppm (t, -OH, 2H, J=5.7 Hz); 3.00 ppm (t, -CH₂, 4H, J=6.6 Hz), 3.48–3.66 ppm (m, CH₂, -4H); 6.98 ppm (d, Ar-H, 4H, J=8.75 Hz); 7.47 ppm (d, Ar-H, 4H).

Polymer Synthesis

PU from 4-HETDE and MDI was prepared in a heat-dried five-necked round bottom flask fitted with a condenser, mechanical stirrer, thermometer, dropper and a nitrogen inlet tube.

In a typical run, 0.01M(3.22 g) 4-HETDE in 50 mL anhydrous benzene and 3 drops of DBTDL were used. Then as temperature was raised to 80 °C, 0.01M(2.5 g) MDI in 10 mL anhydrous benzene was added dropwise to the solution.

After addition was completed, the heating and stirring of the reaction mixture was continued for 1.5 h as the reaction proceeded. The resulting precipitate was filtered, washed with fresh acetone and subsequently dried under vacuum at 90 °C for 70 h. The yield was 5.49 g (96%).

Results of elemental analysis obtained are as follows:

Polymer	%C	%H	%N
Calculated	65.01	4.93	4.89
Found	64.43	4.75	5.25

Polymer Characterization

Spectral Analysis

FT-Infrared spectra were obtained with Perkin-

Elmer 1725x FT-IR spectrophotometer using KBr discs or thin films, as appropriate. The ^1H NMR (DMSO-d_6) spectrum of diol (4-HETDE) was obtained with a Tesla BS-5767-17 spectrometer at 100 KHz using TMS as an internal reference.

Thermogravimetric Analysis

Measurement of weight loss was conducted in a MOM Budapest-3427 derivatograph (F. Paulik, J. Paulik and L. Erdcy) at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ in air.

Glass Transition Temperature (T_g)

Differential scanning calorimeter (DSC) thermograms were obtained using DuPont 2000 TA calorimeter at a heating rate of $10\text{ deg}/\text{min}$ for the samples, and T_g was determined as the temperature of inflection point on the curves describing the rate capacity changes.

Viscosity

Reduced viscosity (dL/g) of 0.5% solution of polymers in a phenol/tetrachloroethane mixture with the weight ratio 1:3 was measured by a Ubbelohde viscometer at $25\text{ }^\circ\text{C}$.

X-ray Analysis

Diffraction measurements were performed using DRON-3 X-ray apparatus (Buriwiestnik, USSR) with a Cu tube acid Ni-filter.

X-Ray patterns of the investigated samples were obtained by measuring the number of impulses within a five degree angle over 10 seconds. The measurements were taken every 0.04 sec.

RESULTS AND DISCUSSION

Monomer Synthesis

New polymer forming 4-HETDE was successfully obtained from 4-MPE with bromoethanol in an ethanolic solution of sodium hydroxide. The chemical structure of the synthesized diol was confirmed by means of elemental analysis, FTIR and ^1H NMR (Figure 1) spectroscopic techniques. The obtained data are in accordance with the proposed structure of monomer.

Polymer Synthesis and Characterization

The synthesis of PU was performed by polyaddition reaction, starting from 4-HETDE and

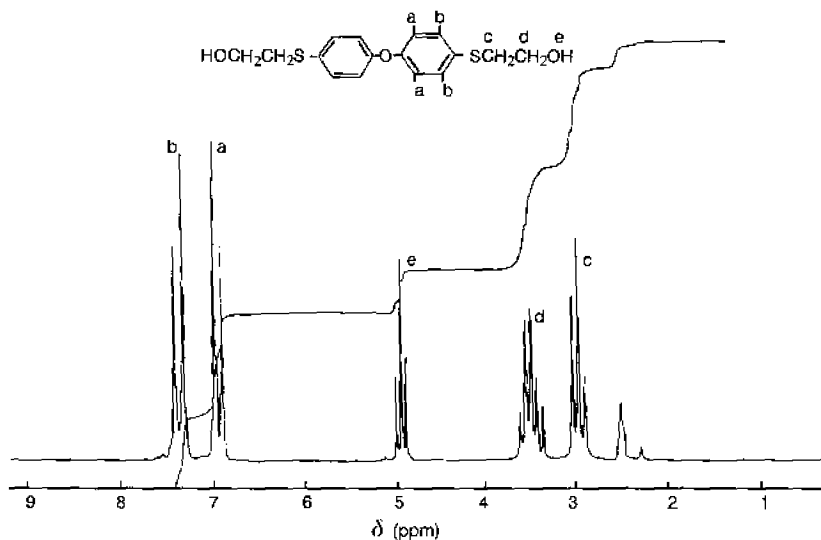
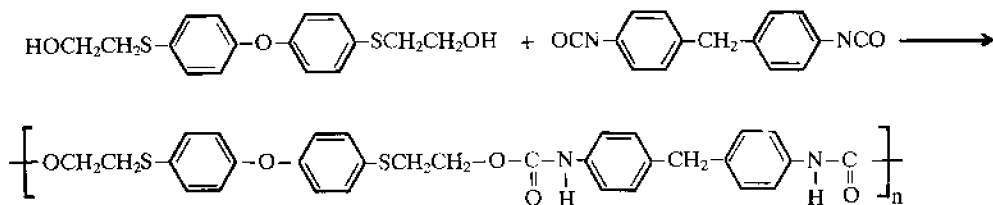


Figure 1. ^1H -NMR spectrum of 4-HETDE.



Scheme 1

MDI (Scheme 1) in a solution.

MDI was chosen because of its ready availability and also the two isocyanate groups have been shown to be nearly equal in their reactivity. Essentially equimolar quantities of diol and diisocyanate [$-\text{OH} : -\text{NCO} = 1$] must be used to obtain high molecular weight and linear PU.

Polyaddition products isolated from solution accrued to be hard, brittle dark brown solids, nonfusible below 300 °C and insoluble in common organic solvents like benzene, chloroform, methylene chloride, dimethyl sulphoxide, dimethylformamide, nitrobenzene, and also in a mixture of phenol-tetrachloroethane at room temperature.

They reveal chemical resistance to diluted acids and alkalis after 120 h of exposure. Only hot coned nitric and sulphuric acids dissolve them with decomposition. The influence of catalyst (DBTDL or TEA), temperature, kind of organic medium and concentration of monomers was investigated. It is to be noted that the polyaddition reaction without catalyst practically does not take place.

It was experimentally affirmed that the most advantageous results were obtained with the use of DBTDL as catalyst, benzene as an aromatic solvent, with about 15% wt concentration of monomers, with temperature of the reaction 80–90 °C, and 1.5–2 h time of reaction.

PU obtained from 4-HETDE and MDI was stable up to 320 °C in air atmosphere. 5% Weight loss was taken as the criteria for thermal stability.

The initial decomposition began at 270 °C and maximum velocity of decomposition at 380 °C, and weight losses in these temperatures were 1% and 20%, respectively.

The drastic decomposition (50% weight loss) occurred at 560 °C.

The results of thermogravimetric analysis are presented in Table 1 and in Figure 2.

The influence of 1,6-HMD on the properties of polymers has been studied taking the same concentration of MDI, equal 0.05 M, under the established optimal conditions for PU obtained from diisocyanate and 4-HETDE, but changing the concentration of diol and glycol. The latter was used in the amount of 20 and 50% molar in relation to diol. The modified polymers were partly soluble in common organic solvents and completely soluble in a mixture of phenol-tetrachloroethane and in *m*-cresol. Addition of 1,6-HMD causes slightly smaller thermal resistance of the obtained aromatic-aliphatic PU.

Their 5% weight loss occur around 280–300 °C. As can be seen from the data summarized in Table 2 and in Figure 3, PU obtained from 4-HETDE and MDI exhibits the highest value of

Table 1. Thermal properties of polyurethanes.

Polymer	T ₁ ^a (°C)	U ^b (%)	T ₂ ^c (°C)	Weight loss (%)			
				5	10	20	50
				Temperature (°C)			
PU-1	270	1	380 520	320	340	380	560
PU-2	240	2	340	300	320	340	340
PU-3	220	1	300	280	300	350	570

a: Temperature of initial decomposition from TG curve.

b: Mass loss in temperature T₁.

c: Temperature of max velocity of decomposition from DTG curve.

Table 2. The influence of the amount of 1,6-HMD in polyaddition of 4-HETDE with MDI.

Polymer	1,6-HMD % molar	mp °(C)	Reduced Viscosity (dL/g)	Yield (%)	T _g °(C)
PU-1	0	>300	—	93.15	51.87
PU-2	20	265–280	0.19	89.39	29.35
PU-3	50	240–265	0.43	95.12	29.35

T_g. The increasing tendency in T_g is caused by smaller rotation of rigid segments of polymer. In the modified polymers the observed decrease of this value is caused by increase in the number of flexible groups (greater rotation).

The structure of PU was confirmed by means of elemental analysis, FTIR spectra and X-ray

analysis.

Elemental analysis values of PU are in good agreement with values calculated for the proposed structure (Scheme I).

The FTIR spectra presented in Figure 4 showed strong absorption at 1800–1700 cm⁻¹ which is characteristic of the C=O bond stretching vibration (the amide I band); at 1600–1540 cm⁻¹ which is characteristic for N–H bending vibration of the urethane group (the amide II band), and 3520–3100 cm⁻¹ which is characteristic of the NH bond stretching vibration.

X-ray diffraction patterns depicted in Figure 5 obtained for PU indicate amorphous character of the examined polymers.

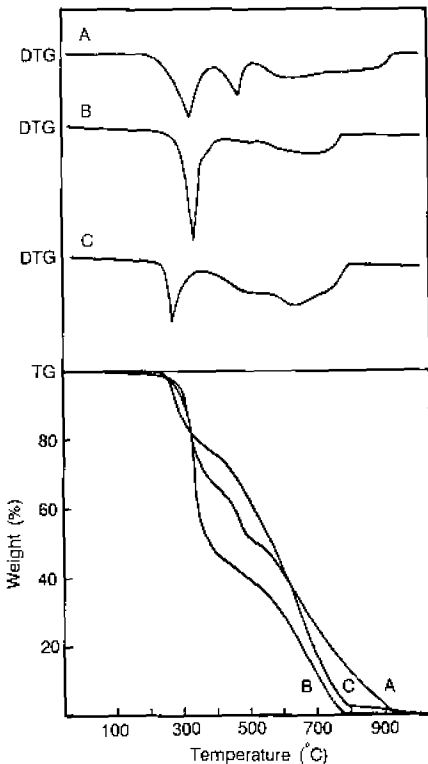


Figure 2. TGA and DTG curves of (A): PU-1, (B): PU-2 and (C): PU-3.

CONCLUSION

The new linear PU derived from 4-HETDE and MDI formed by polyaddition reaction proved to be

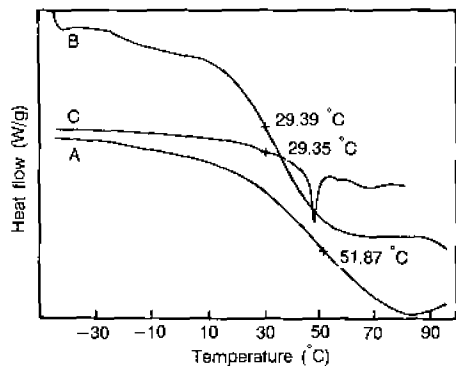


Figure 3. DSC-thermogram of (A): PU-1, (B): PU-2 and (C): PU-3.

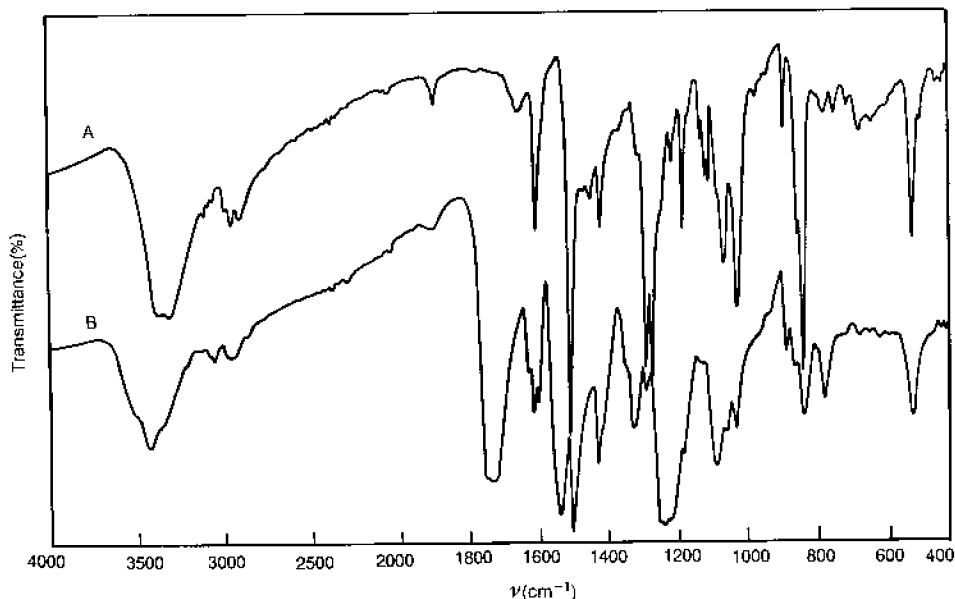


Figure 4. FTIR spectra of (A): HETDE and (B): PU-1.

strong, brittle solids and nonfusible up to 300 °C.

Owing to the high aromaticity of the polymer backbone they exhibit good thermal stability up to 320 °C, and are practically insoluble in common organic solvents, whereas those modified by means of 1,6-HMD are better soluble than others, and reveal also good thermal resistance.

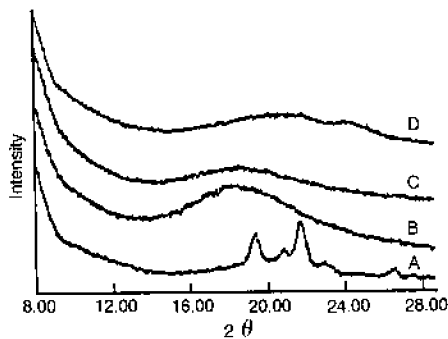


Figure 5. X-Ray patterns of (A): HETDE, (B): PU-1, (C): PU-2 and (D): PU-3.

REFERENCES

- Hill R. and Walker E. E., *J. Polym. Sci.*, **3**, 49, 1948.
- Lyman D. J., *J. Polym. Sci.*, **45**, 49–59, 1960.
- Lyman D. J., Heller J. and Barlow M., *Macromol. Chem.*, **84**, 64, 1965.
- Hollander J., Trischler F. D. and Gosnell R. B., *J. Polym. Sci. Polym. Chem. Ed.*, **5**, 2757–2767, 1967.
- Saotome K. and Komoto H., *J. Polym. Sci. Polym. Chem. Ed.*, **5**, 119–126, 1967.
- MacKnight W. J. and Yang M., *J. Polym. Sci. Polym. Symp.*, **42**, 817–832, 1973.
- Zdráhala R. J., Cerkin R. M., *J. Appl. Polym. Sci.*, **24**, 2041–2050, 1979.
- Imura K., et. al. *Macromol. Chem.*, **182**, 2569–2575, 1981.
- Penczek P., Frisch K. C., Szczepaniak B. and Rudnik E., *J. Polym. Sci. Polym. Chem. Ed.*, **31**, 1211–1220 1993.
- Stenhouse P. J., Valles E. M., Kantor S. W. and MacKnight W. J., *Macromolecules*, **22**, 1467–1473, 1989.
- Mix R., Goering H., Schultz G., Gründemann F. and Gähde J., *J. Polym. Sci. Polym. Chem. Ed.*, **33**, 1523–1536, 1995.

12. Schonfeld E., *J. Polym. Sci. Polym. Chem. Ed.*, **49**, 277–282, 1961.
13. Zochniak Z., Koźbial-Moldyk B., *J. Macromol. Sci., Chem.*, **A9**, **7**, 1265–1271, 1975.
14. Podkościelny W. and Wdowicka D., *J. Appl. Polym. Sci.*, **30**, 1579–1585, 1985.