

Polyurethanes (II): Products of Polyaddition of Bis(4-hydroxyethylenethio)diphenyl Ether with 1,6-Hexane Diisocyanate

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ABSTRACT

We report new linear polyurethanes synthesized by polyaddition reaction of bis(4-hydroxyethylenethio)diphenyl ether with 1,6-hexane diisocyanate. Two synthetic variants are applied, in solution or in melt, with or without a catalyst. Good results are obtained using aprotic solvent, *N,N*-dimethylformamide, ca. 25% weight concentration of monomers, dibutyl tin dilaurate as a catalyst, and conducting the process at 90–100 °C for 3.5–4.0 h. Basic physico-chemical properties of polyurethanes obtained are presented. Thermal behaviour of the polymers is analyzed by means of thermogravimetry and DSC. The structure of resulting products is characterized by elemental analysis, FTIR spectrum and X-ray analysis. Effect of partial replacement of bis(4-hydroxyethylenethio)diphenyl ether by 20–70 mol% 1,6-hexanediol on the properties of polyurethanes obtained in the optimal conditions established earlier has been investigated.

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

INTRODUCTION

polyurethanes (PUs) are a well-known class of polymers with a variety of applications due to their unique properties which could be easily changed according to day's requirements. Thus, we observe significant growth of interest in their preparation because of their use mainly as adhesive coatings, elastomers, foams and fibres.

Among the many factors influencing their properties to be mentioned are: the kind and

quantitative ratios of monomers, the effect of catalyst and the type of short chain extender. Their excellent mechanical properties are depending on their structure, and the presence of strong hydrogen bonding between the urethane linkages which form the hard segment [1–4].

As was earlier experimentally established by Schneider and co-workers [5], Senich and MacKnight [6] PUs exhibit increasing glass transition temperatures with growing content of hard segment. Consequently, owing to the presence of

aromatic units in the polymer structure, they reveal good chemical resistance and thermal stability. In the last decade many papers have related the synthesis, structure and properties of PUs, obtained by means of three methods:

- interfacial polymerization of secondary amines with dichloromates.
- melt polycondensation of diols with alkylene di-phenyl dicarbamates.
- polyaddition of diols with diisocyanates leading to nonsegmented and segmented PUs [7–12].

Among the chosen diols those containing sulphur in their structure are still of our interest [13–14].

In part I [13] we reported the synthesis, structure and properties of nonsegmented PUs composed of bis(4-hydroxyethylenethio)diphenyl ether(4-HETDE) and methylene bis(4-phenyl isocyanate). We found that their properties are mainly dependent on the kind of organic solvent, presence of catalyst, molar ratio and concentration of reagents, time and temperature of polyaddition reaction.

The object of this research is to investigate the PUs forming from 4-HETDE and 1,6-hexane diisocyanate (HDI). As previously, in this case we also examined the influence of 1,6-hexanediol (1,6-HD) as short chain extender on the properties of PUs synthesized.

EXPERIMENTAL

Materials

4-HETDE, mp 93–4 °C, was synthesized from bis(4-mercaptodiphenyl)ether and bromoethanol in an ethanolic solution of NaOH following the reported procedure [13].

Dibutyltin dilaurate (DLDBT), tributyl tin acetate (TBTA) from Merck, were used as received.

Triethylamine (TEA, Fluka), bp 88–90 °C, was freshly distilled over anhydrous KOH.

1,6-HD, from Merck, mp 41–43 °C, was distilled before use. *N,N*-Dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc),

1-methyl-2-pyrrolidone (NMP) were supplied by Merck, then they were distilled and dried over the 3 Å molecular sieves.

HDI from Merck, bp 127 °C/1.33 kPa was used as purchased.

Polymer Synthesis

The PUs were obtained with the strictly molar ratio of the dihydroxyl compound to diisocyanate equals 1:1 for both melt and solution polymerizations with or without a catalyst.

Melt Polymerization

A typical procedure for synthesis of PUs by this method is as follows.

In a dry four-necked round bottom flask fitted with a condensor, mechanical stirrer, thermometer and nitrogen inlet tube, 0.01 M (3.22 g) 4-HETDE and 0.01 M (1.681 g) HDI were placed and gradually heated on the oil bath under dry N₂ atmosphere until a clear solution was found (ca. 90 °C), and then two drops of DLDBT were added and during vigorous stirring the polymerization rapidly began after the temperature 120 °C was reached. The light-yellow waxy product obtained was additionally heated at this temperature for 0.5 h. Without a catalyst the reaction was far slower and practically the time of 2 h was needed.

Solution Polymerization

Using the same apparatus as described above, 0.01 M (3.22 g) 4-HETDE in 10 mL of freshly distilled DMF with 3 drops of DLDBT were used. Nitrogen was kept flowing through the system continuously. Then, as temperature was raised to 90 °C, 0.01 M (1.68 g) HDI in 5 mL of DMF was added to this solution dropwise over a period of 10 min; or all at once with vigorous stirring. The content was kept at the same temperature and stirred for 4 h, until the reaction was completed. In the meantime, as the viscosity of the reaction mixture increased, further solvent (about 5 mL) was added as the reaction proceeded.

The warm viscous solution was then poured into 200 mL of cold methanol to precipitate the polymer in the form of a light-yellow rubber-like

Table 1. Thermal properties of polyurethanes.

Polymer	T ₁ ^a (°C)	U ^b (%)	T ₂ ^c (°C)	Weight loss (%)			
				5	10	20	50
PU-1	230	0.5	380	320	350	360	380
PU-2 ^d	220	1.0	370	300	320	340	400
PU-3	260	0.5	370	330	340	360	400
PU-4	280	1.0	400	300	315	350	400
PU-5	300	1.0	380	340	360	380	450

a: Temperature of initial decomposition from TG curve; b: Mass loss in temperature T₁; c: Temperature of max. velocity of decomposition from DTG curve; d: PU obtained in melt.

solid. The product was filtered off, washed with fresh methanol, and subsequently dried under vacuum at 100 °C for 23 h. The yield was 3.7 g (85.54%).

Results of elemental analysis obtained are as follows:

Polymer	%C	%H	%S	%N
Calculated	58.75	6.17	13.05	5.71
Found	59.01	6.67	13.45	5.98

Polymer Characterization

Spectroscopy

FTIR spectra were obtained with Elmer 1725x FTIR spectrophotometer using KBr discs or thin films, as appropriate.

Thermogravimetric Analysis

Measurement of weight loss was conducted in a

MOM Budapest-3427 derivatograph (F. Paulik, J. Paulik and L. Erdey) at a heating rate of 10 °C/min in air.

Glass Transition Temperature (T_g)

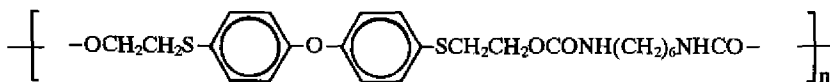
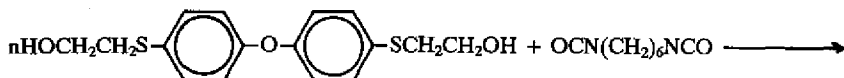
Differential scanning calorimeter (DSC) thermograms were obtained using DuPont 2000 TA calorimeter at a heating rate of 10 °C/min for the samples, and T_g was determined as the temperature of inflection point on the curves describing the rate of capacity changes (Table 1).

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 °C.

X-ray Analysis

Diffraction measurements were performed using the X-ray apparatus DRON-3 (Buriwiestnik,



Scheme 1

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

Polymer	1,6-HD (%mol)	Melting point (°C)	Yield (%)	η_{red} (dL/g)	T_g (°C)
PU-1	0	210–218	85.51	0.32	45.17
PU-2 ^d	0	203–206	95.60	0.41	38.42
PU-3	20	174–185	86.21	0.44	36.73
PU-4	50	150–165	88.52	0.56	35.99
PU-5	70	145–153	93.24	0.68	33.13

USSR) with a Cu tube and Ni filter. X-Ray patterns of the investigated samples were obtained by measuring the number of impulses within a given angle over 10°. The measurements were taken every 0.02°.

RESULTS AND DISCUSSION

Polymer synthesis and characterization of linear PUs were performed by polyaddition reaction of 4-HETDE and HDI (Scheme I) both in a melt and in a solution.

Among the aliphatic diisocyanates commercially available such as isophorone diisocyanate (IPDI), 1,4-cyclohexane diisocyanate (CHDI), and HDI, the last was chosen for the study of the effect of reaction conditions on the properties of PUs. Roughly equimolar quantities of diol and diisocyanate ($-OH:-NCO=1$) must be used to obtain high yield and linear polymers.

In conducting polyaddition reaction in a melt we obtained brittle, yellow waxy polymers insoluble in common organic solvents like methylene chloride, chloroform, benzene, DMF, CCE at room temperature, and for this reason it was not possible to determine their molecular weight by means of GPC. They are only soluble in polar aprotic solvents as DMF, DMAc, etc, at elevated temperatures (above 70 °C).

We found that polymers containing a larger amount of methylene units in their structure have melting points lower than those containing mainly phenylene groups.

As was presented in the previous paper the melting point of the latter, derived from 4-HETDE

and methylene bis(4-phenyl isocyanate), was higher than 300 °C, while the melting point of the polymers obtained from the same diol and HDI is 210–218 °C, as can be seen from Table 2.

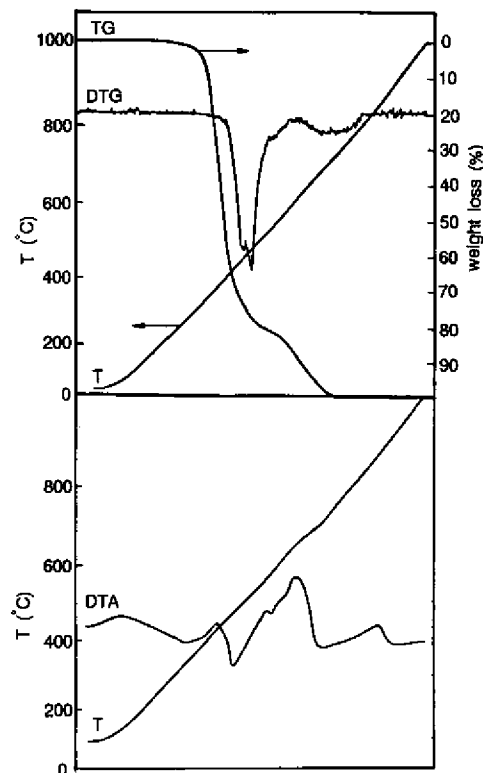


Figure 1. TGA and DTA of PU-1; heating time in air: 100 min, measurement relative to Al_2O_3 ; heating rate: 10 °C/min; amount of PU-1: 100 mg.

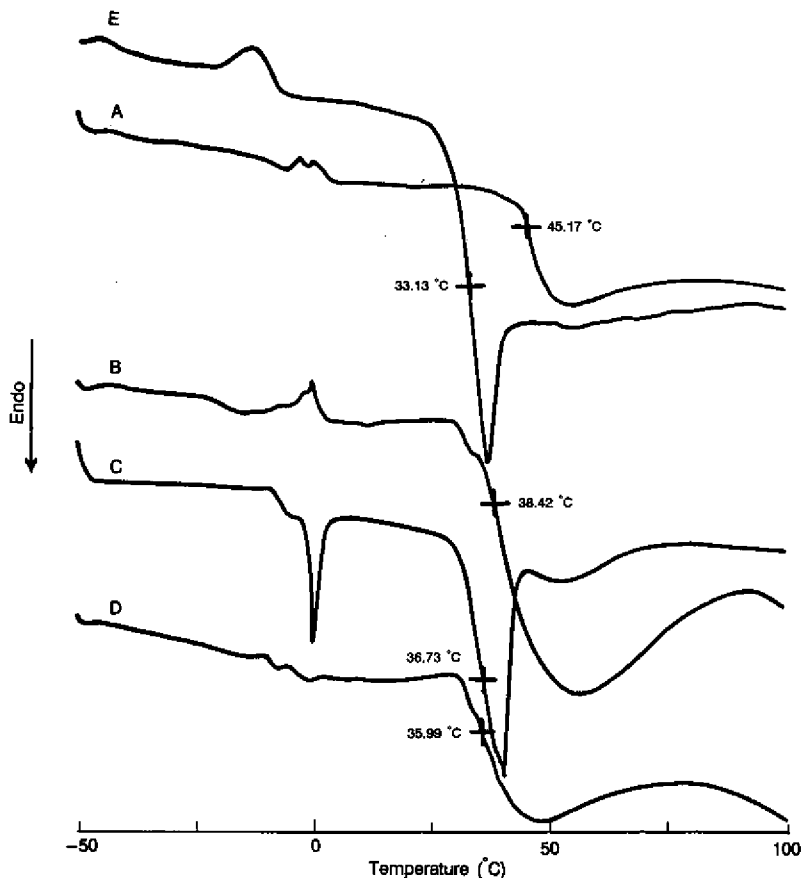


Figure 2. DSC - thermograms of polyurethanes; (A): PU-1, (B): PU-2, (C): PU-3, (D): PU-4, (E) PU-5.

The glass transition temperatures of the aliphatic series were observed to be lower than those of the aromatic ones as we compared with the data presented in the previous paper. These values are 45.17 and 51.81 °C, respectively. All the polymers obtained reveal chemical resistance to diluted acids and alkalis after longer time of exposure. Hot concentrated nitric and sulphuric acids dissolve them with decomposition.

The influence of catalyst (DLDBT, TBTA and TEA), kind of organic medium (DMF, DMSO,

DMAC), concentration of monomers, temperature and time of polyaddition reaction were investigated.

When using TBTA as catalyst both the yield of the polyurethane and the value of viscosity are lower, 79.8% and $\eta_{red}=0.28$. In contrast, using ammonium catalyst-TEA the yield of the polyurethane obtained is 29.8%, and its reduced viscosity value is 0.19.

It was experimentally established that the most advantageous results were obtained with the

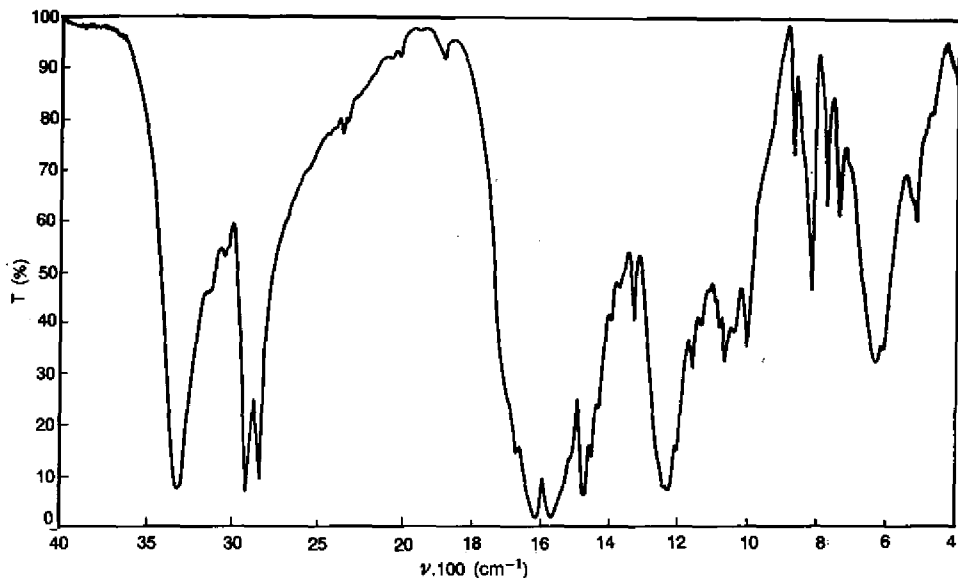


Figure 3. FTIR spectrum of polyurethane PU-1.

use of DLDBT as catalyst, DMF as an aprotic polar solvent, with about 25% weight concentration of monomers, at reaction temperature of the 80–90 °C, and 3–4 h time of reaction.

The thermal stability of the polymers was evaluated by TG and DSC. Typical curves for chosen polymer are given in Figures 1 and 2. The obtained data are quoted in Tables 1 and 2.

The PUs derived from 4-HETDE and HDI exhibit thermal stability up to 300–320 °C in air atmosphere.

The initial decomposition begins at 220 °C and 230 °C for polymers obtained in a melt and in a solution, respectively. A 5% weight loss, which was taken as the criteria for thermal stability begins for the examined polymers at 300 and 320 °C, respectively.

The influence of 1,6-HD on the properties of PUs has been studied taking the same concentration of HDI, equal 0.01 M, under the earlier established optimal conditions for polymers obtained from this diisocyanate and 4-HETDE, but

changing the concentration of diol and glycol. The latter was used in amount of, 20, 50 and 70 mol% in relation to diol.

The modified polymers were better soluble in organic solvents and completely soluble in 1-methyl-2-pyrrolidone and in *m*-cresol.

Addition of 1,6-HD causes in certain cases slightly higher thermal resistance, as can be seen from the data summarized in Table 1. Their 5% weight loss occurs at 300–340 °C.

Introducing of a large amount of modifiers does not influence considerably the thermal stability of HDI-based copolymers. In modified polymers we observe decrease of T_g 's value caused by the increase in the number of flexible groups, which cause the greater rotation of rigid segments.

The obtained data are collected in Table 2. The increase of the amount of glycol gives higher values of reduced viscosity up to $\eta_{red}=0.68$ dL/g.

As can be seen from Table 2 there is a direct interdependence between the melting points of the polyurethanes and their values η_{red} and T_g . A rise

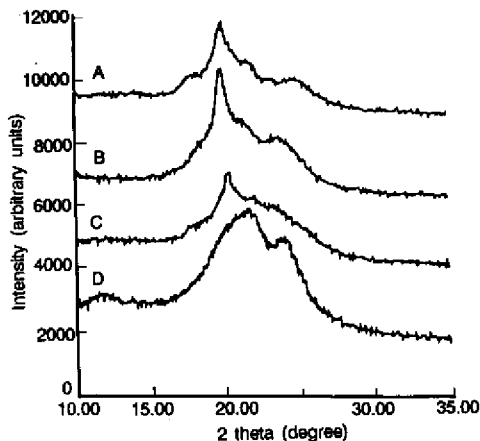


Figure 4. X-ray patterns of polyurethanes: (A): PU-1, (B): PU-3, (C): PU-4, (D): PU-5.

in the mol% of 1,6-HD causes a drop in melting points of polymers and also in the values of η_{red} and T_g .

The structures of the resulting PUs were confirmed by means of elemental analysis, FTIR spectra and X-ray diffraction.

Elemental analysis values of PUs is in good agreement with those calculated for the proposed structure (Scheme I) as was expected.

As shown in Figure 3, the FTIR spectra of polymer showed the characteristic absorption of $\nu(C=O)$ bond of urethane groups at 1780–1600 cm^{-1} , $\nu(-NH)$ stretching of urethane groups at 3500–3100 cm^{-1} , $\nu(-NH)$ bending vibration of the urethane group at 1600–1510 cm^{-1} and $\nu(-CH_2)$ stretching at 2960 cm^{-1} . The band of $\nu(-NCO)$ at 2270 cm^{-1} is not observed.

X-ray diffraction patterns depicted in Figure 4 obtained for PUs indicate a few more or less intensive diffraction peaks. The degree of crystallinity significantly decreases with the increase in the amount of modification agent.

The strong reflections for PU-3, PU-1 and PU-4 appear around $2\theta=20^\circ$ corresponding to d spacings of 4.46, 4.44 and 4.38 Å, respectively. It corresponds to the lateral distances of neigh-

boring chains. All polymers show diffraction peak with d spacing equals 1.834 Å which probably corresponds to the size of the repeated parts of polymer chain.

A broad reflection at $Q=12^\circ$ was observed for polyurethane PU-5, representing a lower order of lateral chain packing.

CONCLUSION

The new aromatic-aliphatic linear PUs composed of 4-HETDE and HDI formed by polyaddition reaction turned out to be brittle, hard or rubber-like solid depending on the method used.

They are insoluble in common organic solvents at room temperature but soluble in a few aprotic polar solvents at elevated temperatures.

They exhibit good thermal stability up to 300 °C, while these modified by means of 1,6-HD have slightly better thermal stability than others, and also reveal good chemical resistance.

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