

Polyaddition Products of Bis[4-(6-Hydroxyhexoxy)phenyl]ether and Toluene Diisocyanate

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ABSTRACT

New linear polyurethanes (PUs) derived from bis[4-(6-hydroxyhexoxy)phenyl]ether (HHPE) and toluene diisocyanate were synthesized by melt step growth or solution polymerization. In conducting the process of polyaddition in solution at 80–90 °C for about 4 h, *N,N*-di-methylformamide as aprotic solvent, 1 wt % conc. of dibutyltin dilaurate as catalyst and ~25 wt % conc. of monomers were used. We found η_{red} , molecular weight (by GPC), and melting temperature for the reaction products. Thermal properties of the polymers were investigated by means of thermal gravimetric analysis and differential scanning calorimetry. The structure of the resulting products was confirmed by elemental analysis, Fourier transform infrared spectroscopy and X-ray diffractometry. Segmented PUs were synthesized from variable amount of polytetramethylene oxide, toluene diisocyanate and HHPE as chain extender in conditions established earlier for non-segmented PUs.

Key Words: linear polyurethanes, polyaddition, non-segmented and segmented polyurethanes, characterization

INTRODUCTION

It is well-known that properties of polyurethanes (PUs) depend largely upon the kind and content of soft and hard segments in polymer structure. Polyethers or polyesters used as soft segments, are mainly polytetramethylene oxide (PTMO) or polycaprolactone diol (PCD) with various molecular weights and influence the elastic properties of segmented PUs, whereas hard segments affect mechanical properties such as modulus, hardness and tear strength of polymers. Thermoplastic polyurethane elastomers are usually obtained from the above-mentioned polydiols, MDI or TDI and short

aliphatic diols as chain extenders such as ethanediol or 1,4-butanediol [1–7].

Recently many papers reported the use of various aliphatic-aromatic diols as chain extenders in the synthesis of PUs having good thermal stability and chemical resistance [8–13]. In our laboratory, derivatives of diphenyl ether were successfully used for the synthesis of various kinds of polymers: polyesters, polythioesters, thioether glycidyl resins and recently PUs with good thermal stability and chemical resistance [11]. In previous studies, bis[4-(2-hydroxyethoxy)phenyl]ether was successfully applied in preparation of HDI-polyurethanes with good thermal stability. The aim of

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the present paper is the synthesis, structure and properties of PUs on the basis of bis[4-(6-hydroxyhexoxy)phenyl]ether (HHPE) and tolylene diisocyanate, by melt or solution polymerization with or without a catalyst. Subsequently, we studied the effect of variable amounts of PTMO-650 on the properties of segmented PUs.

EXPERIMENTAL

Materials

The compound HHPE with mp 110–111 °C, was synthesized from bis(4-hydroxyphenyl)ether (HPE) and 6-chloro-1-hexanol in an ethanolic solution of NaOH. HPE (mp 160–161 °C) was synthesized according to the reported method [14] by condensation of the hydroquinone in an inert solvent at 180–195 °C in the presence of acid activated montmorillonite as catalyst. TDI (mixture of 80% -2,4- and 20% of -2,6-isomers, Fluka) and poly(oxytetramethylene)-diol (PTMO-650, BASF) were used. Before using, PTMO was heated at 120 °C in vacuum for 1 h. *N,N'*-Dimethylformamide (DMF, Merck) with water content 0.02% was used. Dibutyltin dilaurate (DLDBT, Merck) was used as received.

Measurement of Properties

Spectral Analysis

FTIR Spectra were obtained with a Perkin-Elmer 1725X FTIR spectrometer using KBr discs. ¹H NMR Spectrum was obtained with a Tesla BS-567-17 spectrometer at 100 MHz using trimethylsilane as an internal reference. A sample was run in DMSO-*d*₆.

Viscosity

Reduced viscosity (dL/g) of 1% solutions of polymers in a phenol-tetrachloroethane mixture (2/3, w/w) was measured by an Ubblohe viscometer at 25 °C.

Molecular Weight

Molecular weights were obtained using a Knauer gel permeation chromatograph equipped with 10², 10³, 10⁴, 6×10⁵ Å of PL-gel columns with a refractometric detector. THF was used as the eluent with flow rate

of 1.0 mL/min and numerical values for molecular weights were obtained in comparison to polystyrene standards. The error of GPC measurements was ~5%.

Thermal Gravimetric Analysis (TGA)

Measurement of weight loss was conducted in a MOM Budapest-3427 (P. Paulik, F. Paulik, and L. Erdey) derivatograph at a heating rate of 10 °C min⁻¹ in air.

X-Ray Analysis

Diffraction measurements were performed using a DRON-3 X-ray apparatus 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 s. Readings were recorded every 0.02°.

Glass Transition Temperature (*T*_g)

Differential scanning calorimetry (DSC) thermograms over the range of 200–200 °C were recorded on a Du Pont 2000 TA. A Thermal analysis processor at a heating rate of 100 °C min⁻¹ and *T*_g were determined at the temperature of inflection point on the curves describing the rate of heat capacity changes.

Monomer Synthesis

The initial HHPE was obtained from HPE and 6-chloro-1-hexanol using the following procedure. Into a 250 mL round-bottomed flask equipped with stirrer and reflux condenser, 10.10 g (0.05 M) of bis(4-hydroxyphenyl)ether in 100 mL of ethanol containing 8 g (0.2 M) of NaOH were placed. The reaction mixture was then heated on water bath to reflux, and 30.05 g (0.22 M) of 6-chloro-1-hexanol was added dropwise during a 20 min. The heating was continued for 20 h, and after cooling 100 mL of water was added to precipitate a monomer. The resulting product was filtered off, washed with distilled water until neutral, and dried in vacuum at 100 °C to constant weight to give a yield of 18.6 g (92.5 %). By recrystallization from benzene (1 g from 5 mL), the diol with a mp 110–111 °C was obtained. Purity of the compound obtained in this manner was checked by elemental analysis, FTIR (Figure 1) and ¹H NMR (Figure 2) spectroscopies, as determined in the following: IR (KBr, cm⁻¹) 1012, 1240, 1510 and 3300.

¹H NMR, dimethylsulphoxide, DMSO, -*d*₆,

PPM] 1.3–1.7 (m, $(-\text{CH}_2)_4$, 16H); 2.5 (m, $-\text{OH}$, 2H); 3.4 (m $-\text{CH}_2-\text{OH}$, 4H), 3.9 (t- OCH_2OH , 4H, $J=6.1$ Hz); 6.89 (s, Ar-H, 8 H). Elemental analysis calculated for $\text{C}_{24}\text{H}_{34}\text{O}_5$: C, 71.61 % and H, 8.50 %. Found: C, 71.05 % and H, 8.36 %.

Polymer Synthesis

PU were obtained with strictly molar ratio 1:1 of the dihydroxyl compound to diisocyanate for both melt or solution polymerization with or without a catalyst. A typical procedure for synthesis of PUs in melt is as follows: In a dry four-necked round bottom flask fitted with a condenser, mechanical stirrer, thermometer and nitrogen inlet tube, 0.01M (4.0227 g) HHPE and 0.01M (1.7405 g) TDI were placed and the mixture was gradually heated under vigorous stirring in the oil bath under dry N_2 atmosphere until clear melt was obtained (ca. 120 °C). The polymerization began at 130–140 °C after 15 min heating. Then, the resulting product was additionally heated at this temperature for 0.5 h. In the presence of one drop of catalyst-DLDBT the polymerization process proceeded immediately.

Solution Polymerization

Procedure 1

Using the same apparatus as described above, 5mM (2.0114 g) HHPE and 5 mM (0.8702 g) TDI were dissolved in 10 mL DMF. Nitrogen was kept flowing through the system continuously. The temperature

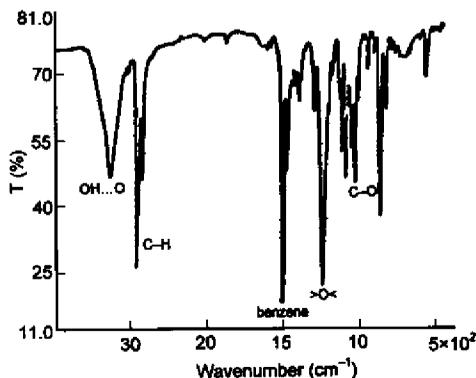


Figure 1. FTIR Spectrum of the monomer HHPE.

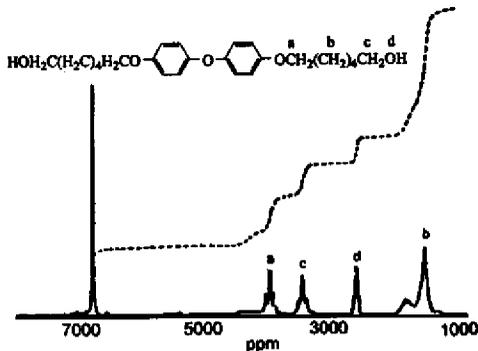


Figure 2. ^1H NMR Spectrum of HHPE.

was raised to 80 °C and 3 drops of DLDBT were added to the solution and heating was continued for 4 h as the reaction proceeded, and then DMF was added as needed to keep the solution viscosity low enough to allow stirring. The hot viscous solution was poured into cold methanol to precipitate the polymer as fibrous material. The polymer was filtered, boiled with fresh methanol, and subsequently dried under vacuum at 100 °C for 24 h. The yield was 2.15 g (75%). Elemental analysis calculated for PU: C, 69.05 %, H, 6.96 % and N, 4.88 %. Found: C, 68.65 %, H, 5.78 % and N, 4.25 %.

Procedure 2 (one-step)

The apparatus was the same as described in procedure 1. By using e.g., 20 mol% of PTMO-650 in relation to HHPE, the amounts of monomers applied were as follows: 8 mM (3.2174) HHPE, 2 mM (1.3 g) PTMO-650 and 0.10-M (1.7405 g) TDI in 20 mL DMF, 3 drops of DLDBT were used. Further procedure was as described in procedure 1. Clear and flexible copolyurethane was obtained with 90% yield.

RESULTS AND DISCUSSION

HHPE as the initial material was obtained from HPE and 6-chloro-1-hexanol in an ethanolic solution of NaOH.

Polymer Synthesis and Characterization

New linear aliphatic-aromatic non-segmented PUs type HHPE/TDI were prepared according to Scheme I using melt or solution polymerization. The reaction was conducted with or without a catalyst using equimolar amount of monomers.

PUs obtained by melt step-growth polymerization without a catalyst were tough masses, soluble only in phenol-tetrachloroethane mixture, *m*-cresol and 1,1,1,3,3,3-hexafluoro-2-propanol, but those obtained in the presence of DLDBT were insoluble in these solvents. They were both resistant to dilute acids and alkali. In the previous work [11], by the synthesis, structure and characterization of hard segment PUs obtained from bis[4-(2-hydroxyethoxy)phenyl]ether and 1,6-hexane diisocyanate, we found that properties of PUs were dependent on the kind of organic solvent, contribution of catalyst, molar ratio and concentration of reagents, and the time and temperature of the polyaddition reaction. Because of this, the most advantageous results were obtained by using DLDBT as catalyst, DMF as solvent, ~25 wt.% conc. of monomers, and the reaction temperature in the range of 80–90 °C. The previously described factors, as experimentally established, influenced both the yield and value of reduced viscosity of PUs now obtained from HHPE and TDI.

The basic properties of these PUs are summar-

Table 1. Reduced viscosity and molecular weights of the PUs obtained in solution.

Polymer	η_{red} (dL/g)	$\bar{M}_n \cdot 10^3$	$\bar{M}_w \cdot 10^3$	$\bar{M}_z \cdot 10^3$	\bar{M}_z / \bar{M}_w
PU-1 ^a	0.33	6.97	13.50	22.60	1.93
PU-2 ^b	0.42	11.40	24.90	50.20	2.19
PU-20P	0.37	4.11	8.29	13.40	2.02
PU-40P	0.48	5.12	10.60	17.20	2.08
PU-60P	0.66	14.21	28.60	50.30	1.81
PU-80P	0.51	11.70	24.30	46.70	2.08

PU codes: e.g., PU-1-polyurethane was obtained from HHPE and TDI; PU-20P-copolyurethane was obtained from HHPE, TDI and 20 mol% of PTMO-850

(a) Polyurethane obtained without a catalyst; (b) Polyurethane obtained in presence of a catalyst.

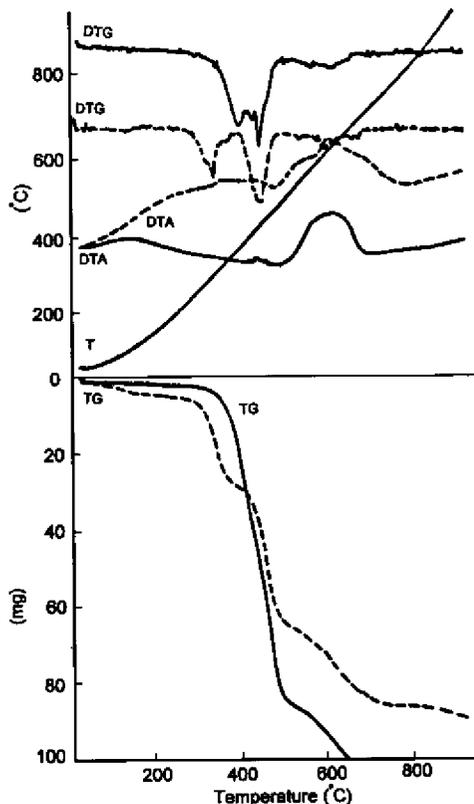


Figure 3. DTG and TG of PU-1; (—) in presence of DLDBT, (---) without a catalyst; heating time in air: 100 min, measurement relative to Al₂O₃; heating rate: 10 °C/min; amount of PU-1:100 mg.

ized in Table I. Non-segmented PUs obtained in solution were sticky, rubber-like products soluble in common organic solvents such as DMSO, DMF, THF; thus, determination of their molecular weight was possible. The best value of reduced viscosity equal (0.42 dL/g) and the corresponding molecular weight ($\bar{M}_w = 24,900$) were obtained for the PU synthesized in the presence of a catalyst. The thermal behaviour of the PUs was examined by means of differential thermal analysis (DTA) as well as differential scanning calorimetry (DSC).

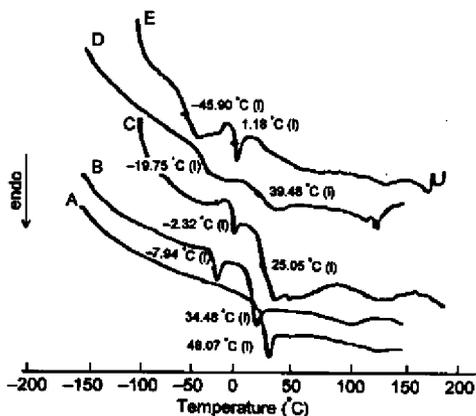


Figure 4. DSC Thermograms of polyurethanes; (A) PU-1, (B) PU-20P, (C) PU-40P, (D) PU-80P, (E) PU-80P.

Figure 3 shows typical TGA and DTA curves of PU-1 both without a catalyst and in its presence; while Figure 4 shows typical DSC curves and the thermal behaviour data of PUs are given in Table 1.

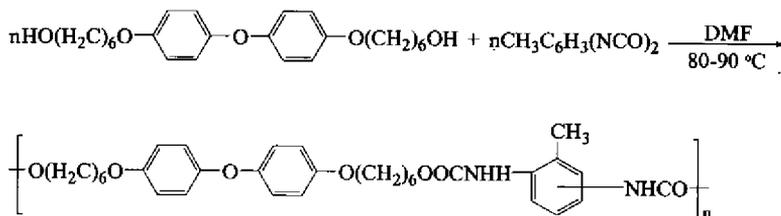
As can be seen, the temperature of initial decomposition exhibits at 280 °C in air atmosphere, and its T_5 (5 % decomposition temperature) taken as the criterion of thermal stability, is observed at 360 °C. The glass transition temperature (T_g), characteristic of the hard segment took place at 48 °C. The structure of the polymer obtained was confirmed by elemental analysis and FTIR spectroscopy; as expected, the obtained values were in good agreement with those calculated for the proposed structure (Scheme I). As shown in Figure 5, the FTIR spectrum of the polymer showed characteristic

absorption of carbonyl stretching vibration (the amide I band) at 1700–1680 cm^{-1} , characteristic absorption of the N–H bending vibration of the amide group (the amide II band) at 1560–1500 cm^{-1} and at 3380–3310 cm^{-1} characteristic of the banded N–H stretching vibration. The band at 1280–1200 cm^{-1} was attributed to the asymmetric vibration of the aromatic ether bond. X-Ray diffraction patterns depicted in Figure 6 for the PU examined indicated the partially crystalline structure of this polymer.

Stenhouse and co-workers [9] obtained novel liquid crystalline PUs by condensation of 2,4-TDI with a diol similar in its structure to ours, e.g. 4,4'-bis(6-hydroxyhexoxy)diphenyl using solution method (DMF). They were characterized by intrinsic viscosity in the range of 0.30–0.57 dL/g and molecular weights (M_w) in the range of 50,000–140,200, respectively. Because these polymers contained more rigid diphenyl units in their structure, their glass transition temperatures (T_g) were higher in comparison with our polymers, and were equal to 95 °C, and melted at 152 °C.

Segmented PUs of the type HHPE/TDI/PTMO were obtained by us from PTMO-650, MDI and HHPE as chain extender by melt or solution one-step polymerization in the presence of DLDBT. Polyether-diol PTMO was taken in the amount of 20, 40, 60 and 80 mol % in relation to HHPE. Copolymers obtained by melt were yellow thermoplastic elastomers soluble only in phenol-tetrachloroethane mixture (2:3) with the value of reduced viscosity, equal to about 0.98 dL/g. The poor solubility of these polymers was probably caused by the formation of more cross-linking products, therefore they possessed a higher reduced viscosity than those obtained in solution method.

However, segmented PUs obtained in solution



Scheme I

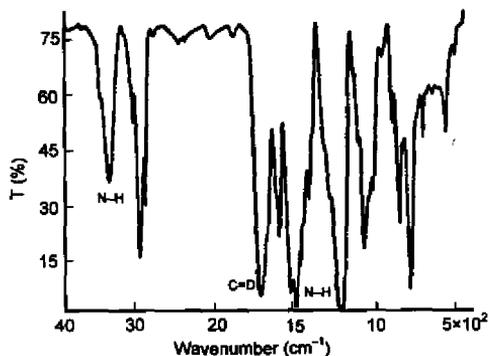


Figure 5. FTIR Spectrum of polyurethane PU-1.

occurred to be yellow thermoplastic elastomers soluble in common organic solvents such as DMSO, DMF, THF. Some of their properties are presented in Table 1. The highest value of reduced viscosity of 0.66 dL/g, and the same highest value of molecular weight $M_w=28,600$, was obtained for the polymer containing 60 mol% of soft segment derived from PTMO (phase inversion). In this method the lower values of η_{red} comparison with melt method resulted from the limited degree of polymerization caused by gelation which occurred in reaction medium. The

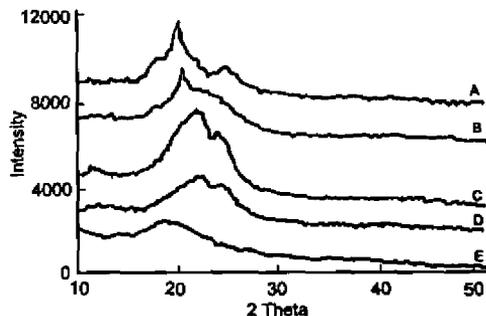


Figure 6. X-Ray patterns of polyurethanes: (A) PU-1, (B) PU-20P, (C) PU-40P, (D) PU-60P, (E) PU-80P.

thermal properties of these polymers are presented in Table 2. From the numerical data it follows that the values of T_g decreased as the amount of $-CH_2-$ group increased in polymer structure, and fell from 34 to 1 °C and from -8 to -45 °C, respectively. The DSC thermograms of polymers are depicted in Figure 4 where the broad, enthalpic peaks of melting points can be vaguely observed for some polymers. This fact is confirmed by X-ray analysis (Figure 6), which indicates nearly amorphous character of these copolymers. The small value of the enthalpy of

Table 2. Thermal properties of the PUs obtained in melt from HHPE, TDI and PTMO.

Polymer	DSC			TGA (°C)				
	T_g (°C)	T_m (°C)	ΔH (J/g)	T_1	T_5	T_{10}	T_{20}	T_{max}
PU-1	48.6	170.43	1.51	280	360	400	380	420
PU-20P	-7.94	144.24	4.41	250	300	340	360	460
	34.48							460
PU-40P	-2.32	143.83	2.95	260	300	330	360	340
	25.05							350
PU-60P	-19.75	171.42	9.14	270	310	330	360	360
	39.48							390
PU-80P	-45.90	146.19	1.41	260	290	300	320	330
	1.18							380

T_1 - Temperature of initial decomposition from the curve DTG.

T_5 , T_{10} , T_{20} - Temperatures of 5, 10, 20 % weight loss, respectively, from the curve.

TG - Thermal gravimetry

T_{max} - Temperature of maximum rate of weight loss from the curve DTG.

fusion (ΔH) of these polymers also confirmed their disordered structure. We suggest that the molecular weight of the soft segments derived from PTMO-650 was not enough to ensure adequate phase separation; therefore the T_g values of the soft segments of copolyurethanes containing 20–60% mol of PTMO considerably differ from the T_g determined for pure polyurethane from PTMO and TDI (-48°C).

We plan further research on the synthesis and properties of PUs with longer flexible spacers, which may result in further publications.

The thermal stability of copolyurethanes insignificantly depended on the amount of soft segments and their 5% weight loss ranged from 290–310 $^\circ\text{C}$. The mechanical properties of non-segmented and segmented PUs could not be measured because of the difficulty that occurred in the preparation of samples by moulding; the former were too tough, and the latter were viscous masses having high adhesion to many substances.

CONCLUSION

The new non-segmented PUs containing HHPE/TDI units in their structure obtained in melt turned out to be tough solids, and brittle ones when solution polymerization was used. These hard-segment type PUs with melting points about 170 $^\circ\text{C}$ were insoluble in common organic solvents. They exhibited good thermal stability up to 360 $^\circ\text{C}$, whereas segmented PUs containing variable amount of PTMO-650 in their structure obtained in melt were thermoplastic elastomers better soluble in organic solvents in comparison with non-segmented ones. The polymers obtained in DMF turned out to be viscous masses soluble in common organic solvents with the highest value of reduced viscosity of 0.66 dL/g and $\overline{M}_w=28,600$. They were stable up to 290–310 $^\circ\text{C}$, depending slightly on the amount of soft segments, and their values of T_g ranged from 34 to 1 $^\circ\text{C}$ and from -8 to -45°C , respectively. The non-segmented PUs possessed a partially crystalline structure, whereas segmented PUs exhibited a rather amorphous character.

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