

Polyurethanes (III): Polyaddition Products of 4,4'-Bis(2-hydroxyethylenethio)diphenyl Ether and 2,4-Tolylene Diisocyanate

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ABSTRACT

New linear polyurethanes derived from 4,4'-bis(2-hydroxyethylenethio)diphenyl ether (4-HETE) and 2,4-tolylene diisocyanate (TDI) were synthesized by both melt or solution polymerization. Good results were obtained using aprotic solvent: *N,N*-dimethylformamide, dibutyltin dilaurate (DLDBT) as a catalyst ~1 wt % concentration and ~30 wt % concentration of monomers and conducting the process at 90–100 °C for 2 h. Basic physico-chemical properties of the series of PUs obtained are presented. Thermal properties of the polymers were investigated by means of thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Molecular weight distribution was determined by gel permeation chromatography. The structure of the resulting products was confirmed by elemental analysis, Fourier transform infra-red spectroscopy and X-ray diffractometry. The properties of copolyurethanes containing variable amounts of poly(oxytetramethylene)diol (PTMO-650 or 1000) synthesized in the conditions established earlier for non-segmented PUs are also presented.

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

INTRODUCTION

Segmented polyurethane block copolymers are composed of soft segments joined by a hard segment urethane linkage. The soft segments are typically polyethers, polyesters or polybutadiene-type macrodiols with molecular weight of a few thousand, while

the hard segments can be either aliphatic or aromatic diisocyanates with a low molecular weight diol or diamine as chain extender. The hard segments in PUs affect particularly the modulus, hardness and tear strength, whereas, soft segments primarily influence the elastic properties of PUs.

As a soft segment PTMO or polycaprolactone

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diol with various molecular weights are often used in preparation of segmented PUs [1–7].

The introduction of long flexible spacers derived from polyetherdiol or polyesterdiol was effective in increasing solubility reducing hydrogen bonding and showing elastic properties.

For a few years our investigations have been concerned with the synthesis, structure and properties of PUs containing sulphur, which reveal good thermal stability and chemical resistance, and are derivatives of 4,4'-bis(2-hydroxyethylenethio)diphenyl ether (4-HETE) and methylene bis(4-phenyl isocyanate) [8] or 1,6-hexane diisocyanate [9].

The purpose of this study was to synthesize a new series of PUs on the base of 4-HETE and TDI by melt or solution polymerization. As the next stage, we studied the effect of partial replacement of 4-HETE by 20–80 mol% PTMO ($M_n \sim 650$ or 1000) on the properties of PUs.

EXPERIMENTAL

Materials

4-HETE mp 93–4 °C, was synthesized from bis(4-mercaptodiphenyl)ether and bromoethanol in an ethanolic solution of NaOH following the reported procedure [8].

TDI (Fluka) and poly(oxytetramethylene)diol (PTMO ~ 650 or 1000, BASF) were used. Before using, PTMOs were heated at 120 °C in vacuo for 1 h.

N,N'-Dimethylformamide (DMF, Merck), with water content 0.02%, was used. Dibutyltin dilaurate (DLDBT, Merck) was used as received.

Polymer Synthesis

PUs were obtained with the 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, 0.01 M (3.22 g) 4-HETE and

0.01 M (1.7405 g) TDI were placed and the mixture was gradually heated under vigorous stirring on the oil bath under dry N_2 atmosphere until clear melt was obtained (ca. 125 °C).

The polymerization began at 130 °C after 10 min heating. Then the resulting product was additionally heated at this temperature for 0.5 h. In the presence of catalyst-DLDBT the polymerization process proceeded immediately.

Solution Polymerization

Procedure 1

Using the same apparatus as described above, 0.01 M (3.22 g) 4-HETE, 0.01 M (1.7405 g) TDI were dissolved in 10 mL DMF. Nitrogen was kept flowing continuously through the system. Then, as temperature was raised to 90 °C, 3 drops of DLDBT were added. The reaction mixture was kept at 90–100 °C for 2 h until the reaction was completed and, in the meantime, further 5 mL DMF was added to reduce the viscosity of the reaction mixture. The warm viscous solution was then poured into 200 mL of cold water to precipitate the polymer in the form of brittle solid.

The product was washed with methanol and subsequently dried under vacuum at 100 °C for 12 h. The yield was 1.56 g (80%). The result of elemental analysis is as follows:

PU	C (%)	H (%)	N (%)
Calculated (anal.)	60.48	4.84	5.64
Found	59.45	5.19	5.32

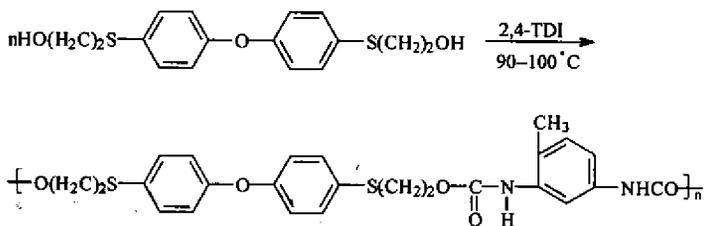
Procedure 2

The apparatus was the same as described in procedure 1. Using e.g., 20 mol% PTMO ~ 650 in relation to 4-HETE the amounts of monomers were as follows: 8 mM (2.5777 g) 4-HETE, 2 mM (1.3 g) PTMO ~ 650 and 0.01 M (1.7405 g) TDI in 10 mL DMF were used. Another procedure was as described in procedure 1. Clear and flexible copolyurethane was obtained with 70% yield.

Measurement of Properties

Spectral Analysis

FTIR spectra were obtained with a Perkin-Elmer



Scheme 1

1725×ETIR spectrophotometer using KBr discs.

Viscosity

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

Molecular Weight

Molecular weights were obtained using a Knauer gel permeation chromatograph equipped with 10^3 , 10^4 , 10^5 , 6.10^5 Å of PL-gel columns with a refractometric detector. Tetrahydrofuran (THF) was used as the eluent with flow rate of 1.0 mL/min, and the numerical values for molecular weights were obtained in comparison to polystyrene standards.

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 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. Measurements were taken every 0.02°.

Glass Transition Temperature (T_g)

Differential scanning calorimetry (DSC) thermograms over the range of 150–200 °C were recorded on a duPont TA. A thermal analysis processor at a heating

rate of 10 °C/min was used and T_g was determined as the temperature of inflection point on the curves describing the rate of heat capacity changes.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

New linear non-segmented PUs, consisting of only 4-HETE/TDI units, were prepared according to Scheme 1 using melt or solution polymerization.

The reaction was conducted with or without a catalyst using equimolar amounts of monomers.

Between the two isomers of tolylene diisocyanate, isomer 2,4- was chosen as being more active. PUs obtained by melt were strong and hard products or brittle ones were obtained when solution polymerization was used. These polymers have higher melting points in the range of 244–250 °C in comparison with analogous polymers obtained with aliphatic diisocyanate-HDI, 210–218 °C.

However, as was presented in the previous paper, MDI-based PUs containing mainly phenylene groups in their structure have the highest melting points above 300 °C [8]. The non-segmented TDI-based PUs were practically insoluble in common solvents, therefore, determination of their molecular weight was not possible. They reveal resistance to dilute acids and alkali. Thermal stability of the PUs was evaluated using TGA and DSC.

Typical curves for chosen polymers are given in Figures 1 and 2, and the results obtained are quoted in Table 1. The examined non-segmented PUs have the same thermal stability as those earlier described

Table 1. Thermal properties of PUs obtained from 4-HETE, TDI and PTMO.

PU	T _g (°C)	T ₁ ^a	T ₂ ^b	T ₅ ^c	T ₁₀	T ₂₀	T ₅₀
PU-1	42.54	280	350	320	350	400	440
	-1.95		440				
PU-20P	24.37	260	320	300	300	320	400
	-2.99		400				
PU-40P	-11.45	250	360	300	330	360	420
			440				
PU-80P	-22.34	250	380	300	330	360	420
			440				
PU-20P ₁	20.78	280	340	300	340	350	400
	-2.32		400				
PU-40P ₁	-15.62	240	360	300	330	360	430
			430				
PU-80P ₁	-45.9	280	340	300	340	380	430
			430				

(a) Temperature of initial decomposition from the curve T_g; (b) Temperature of max. rate of weight loss from curve DTG; (c) T₅, T₁₀, T₂₀.

T₅₀-Temperatures of 5, 10, 20 and 50% of weight loss, respectively, from curve TG.

Codes of PUs: The examples: PU-1 polyurethane was obtained from 4-HETE and TDI; PU-20P copolyurethane was obtained from 4-HETE, TDI, and 20 mol % PTMO – 850; PU-20P₁ copolyurethane was obtained from 4-HETE, TDI, and 20 mol % PTMO – 1000.

from MDI and HDI. A 5% weight loss took place at 320 °C in air atmosphere. The maximum rate of decomposition occurred in two stages at 350 and 440 °C, and its weight losses at these temperatures were 10 and 50%, respectively. T_g values of analogous PUs, obtained from MDI, HDI and recently TDI, were different and were dependent on the kind of diisocyanate used.

The highest values 51.87 and 45.17 °C were obtained for MDI and HDI-based PUs [8, 9], and in the case of PUs obtained from TDI two T_g values, -1.95 and 42.54, were observed.

The structure of polymers obtained was confirmed by elemental analysis and FTIR spectroscopy, and as expected, the obtained values were in good agreement with those calculated for the proposed structure (Scheme I). As shown in Figure 3, the FTIR spectrum of the polymer showed characteristic absorption of the strong bonded carbonyl stretching of urethane group (the amide I band) at 1700–1650 cm⁻¹, at 1620–1510 cm⁻¹ characteristic of the N–H bonding vibration of the amide group (the amide II band), and at 3350–3180 cm⁻¹ characteristic of the bonded N–H

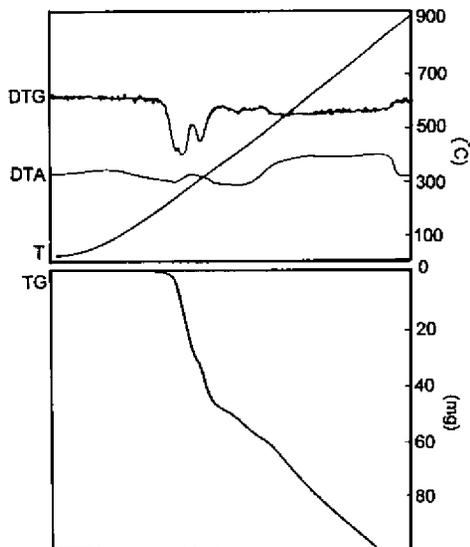


Figure 1. DTA and TGA of PU-1; heating time in air, 100 min; measurement relative to Al₂O₃; heating rate 10 °C/min; amount of PU, 100 mg.

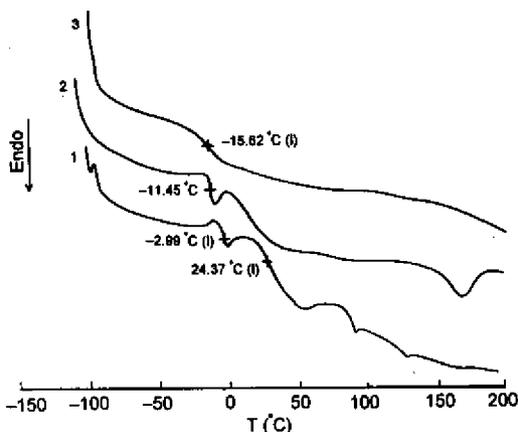


Figure 2. DSC thermogram of PUs; (1) PU-20P, (2) PU-40P and (3) PU-40P₁.

stretching vibration. The band at 1280–1200 cm^{-1} was attributed to the asymmetric vibration of the aromatic ether bond. The band of the isocyanate group at 2270 cm^{-1} was not observed.

Segmented PUs type 4-HETE/TDI/PTMO were obtained in melt or in solution (one-step) polymerization in the presence of the catalyst. The influence of PTMO – 650 or 1000 on the properties of polymers was studied taking the amounts of 20–80 mol % of polyetherdiol in relation to 4-HETE at the conditions established earlier for non-segmented PUs.

The influence of variable amounts of PTMOs on the properties of CPUs is presented in Table 2.

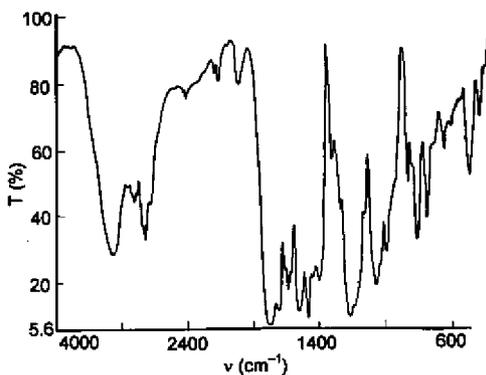


Figure 3. FTIR spectrum of PU-1.

The thermoplastic CPUs contained 80 mol % of PTMO–650 or 60–80 mol % of PTMO–1000 obtained in melt were rubber-like products soluble in phenol/tetrachloroethane mixture, and their high values of η_{red} (1.42–2.30) presented in Table 2 indicate high molecular weights of these polymers.

All CPUs obtained in solution were soluble in common organic solvents at room temperature, so it was possible to determine their molecular weight by gel permeation chromatography. In the case of CPUs obtained with 20 mol % PTMO – 650 or 40 mol % of PTMO ~ 1000 the narrow distribution of molecular weight was observed (Figure 4). In the case of CPUs obtained with 60 or 80 mol % PTMO ~ 1000, after dissolving them in THF gelation took place and therefore determination of their molecular weights

Table 2. Reduced viscosity and molecular weights of PUs.

PU	η_{red} (dL/g)	$\bar{M}_n \times 10^3$	$\bar{M}_w \times 10^4$	$\bar{M}_z \times 10^4$	\bar{M}_w / \bar{M}_n	
PU-1	–	0.20	3.5	6.91	42.8	19.7
PU-20P	–	0.25	2.29	0.437	0.727	1.9
PU-40P	–	0.36	6.00	1.28	3.63	2.14
PU-60P	–	0.42	7.17	12.7	185.0	17.8
PU-80P	2.3	0.48	7.33	4.44	20.2	6.06
PU-20P ₁	–	0.32	6.64	2.14	7.08	3.21
PU-40P ₁	–	0.38	6.61	1.30	2.19	1.97
PU-60P ₁	1.46	0.42	–	–	–	–
PU-80P ₁	1.52	0.44	–	–	–	–

was not possible. From the numerical data presented in Table 2 follows that relatively low values of reduced viscosities were reflected in low M_n of these copolymers obtained in one-step method. However, Szczepeniak B. and co-workers using two-step method obtained higher molecular weights about 37000 for PUs derived from 4,4'-bis(2-hydroxyethoxy)biphenyl (BHBP) and PTMO-650 or 1000 [4].

The T_g behaviour of our CPUs obtained from 4-HETE shows considerable differences depending on the amount of flexible spacers coming from PTMO. As can be seen from the presented data in Table 1, T_g values of these polymers decreased with increasing amount of soft segments derived from polyetherdiol.

The DSC thermograms of chosen PUs are presented in Figure 2. Two-phase behaviours cannot be seen, because, as it seems, molecular weight of soft segments derived from polyetherdiol is not enough to ensure adequate phase separation. This fact results from weak interactions between hard and soft segments probably owing to miscibility or

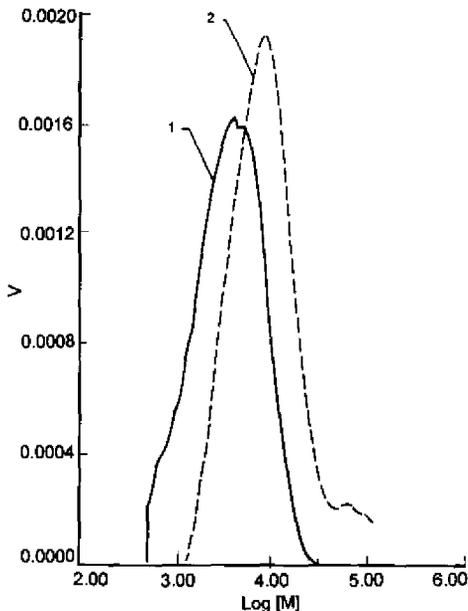


Figure 4. Molecular weight distributions of PUs; (1) PU-20P and (2) PU-40P₁.

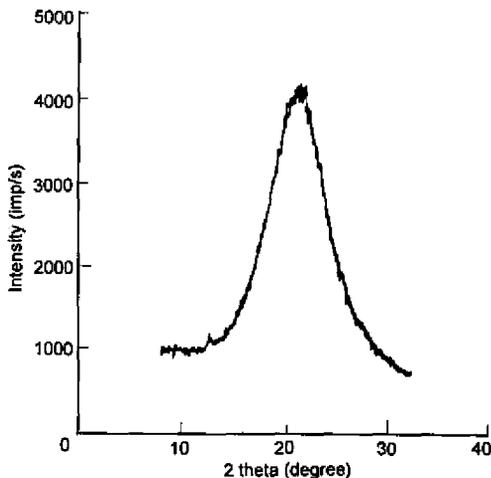


Figure 5. X-ray diffraction pattern of PU-40P₁.

compactness of these segments. Thermal stability of the examined CPUs is the same independent of their chemical composition. Numerical data are presented in Table 1.

T_g values of liquid crystalline PUs obtained by Penczek and co-workers from BHBP, TDI and PTMO were higher because those polymers contained more rigid molecule of diphenyl in their structure. X-ray diffraction pattern given in Figure 5 for the chosen PU-40P₁, indicates near-amorphous character for this polymer; as this was confirmed by DSC spectrum where endothermic peaks were not observed.

Mechanical properties of polymers could not be measured because of difficulties that occurred in preparation of samples by moulding.

CONCLUSION

The new non-segmented linear PUs composed of 4-HETE and TDI obtained by melt are strong, hard solids or brittle ones when solution polymerization was used. These hard-segment-type PUs possessing high melting points above 200 °C are insoluble in common organic solvents. They exhibit good thermal

stability up to 320 °C, and reveal chemical resistance to dilute acids and alkali, whereas, segmented PUs type 4-HETE/TDI/PTMO, with 20–60 mol % PTMO~650 obtained in melt are strong waxy like products and slightly better soluble in organic solvent in comparison with non-segmented PUs.

CPUs obtained with various amounts of PTMO~1000 in melt are rubber-like products, easily soluble in organic solvents. All CPUs obtained in solution are viscous plastic masses having high adhesion to many substrates.

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