# Segmented and Nonsegmented Polyurethanes: Polyaddition Products of 4,4'-Bis(2-Hydroxyethoxy)Diphenyl Ether and 1,6-Hexanediisocyanate

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ABSTRACT: New linear polyurethanes (PUs) derived from 4,4'-bis(2-hydroxyethoxy)diphenyl ether (4-HEDE) and 1,6-hexanediisocyanate (HDI) were synthesized by either melt or solution polymerization. We found that the properties of PUs obtained are dependent mainly on the kind of organic solvent, contribution of the catalyst, and concentration of the monomers used. Good results are obtained using aprotic solvent-N,N-dimethylformamide,  $\sim 30$  wt % concentration of monomers, dibutyltin dilaurate as a catalyst, and conducting the process at 90–100°C for 4 h. This article presents basic properties of the series of PUs obtained. Thermal properties of the polymers were investigated by means of thermal gravimetric analysis and differential scanning calorimetry. Molecular weight distribution was determined by gel permeation chromatography. Shore hardness and tensile test results are also presented. The structure of the resulting products was confirmed by elemental analysis, Fourier transform infrared spectroscopy and X-ray diffractometry. We also present the properties of copolyurethanes type 4-HEDE/HDI/1,6-hexanediol or 4-HEDE/HDI/polytetramethylene oxide containing variable amounts of 1,6-hexanediol or polytetramethylene oxide ( $\overline{M}_n \sim 650$ ) synthesized in the optimal conditions established earlier for PU 4-HEDE/HDI. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 83–91, 1999

**Key words:** linear polyurethanes; polyaddition optimal conditions; segmented polyurethanes; characterization

# INTRODUCTION

Polyurethanes (PUs), a well-known class of polymers can be mainly prepared by polyaddition of diols with diisocyanates. As known from the reviewed literature,<sup>1-3</sup> their properties are dependent on the amount of hard and soft segments in the polymer structure. Hard segments derived from the reaction of diisocyanates with low molecular weight diols affect the modulus, hardness, and tear strength of polymers. Then, the soft segments derived from the reaction of diisocyanates with high molecular weight diols primarily influence the elastic characteristics of PUs.

As was experimentally established, the introduction of long flexible spacers as polyetherdiol or polyesterdiol into the polymer main chains changed the properties of PUs.

Thus, Lorenz and colleagues<sup>4</sup> and Penczek and colleagues<sup>5–7</sup> described the properties of segmented PUs with the use of polytetramethylene oxide (PTMO), with various molecular weights as soft segments. The authors discovered that the molecular weight of PUs and the chain length of polyetherdiol soft segments greatly influenced the value of glass transition and phase transition temperatures of the PUs.

For many years, the derivatives of diphenyl ether have attracted attention in our laboratory

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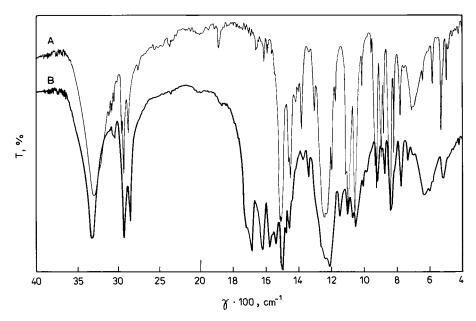


Figure 1 FTIR spectra of (A) HEDE and (B) PU-OH.

for preparation of linear polythioesters,<sup>8,9</sup> polyesters,<sup>10</sup> thioetherglycidyl resins,<sup>11,12</sup> and recently PUs<sup>13,14</sup> that exhibit good thermal stability and chemical resistance.

In previous studies, 4,4'-bis(2-hydroxyethylenethio)diphenylether (4-HETDE) was successfully applied to prepare PUs from methylene bis(4-phenylisocyanate) or aliphatic diisocyanate [1,6-hexanediisocyanate (HDI)].

The purpose of this study was to synthesize a new series of PUs on the base of 4,4'-bis(2-hydroxyethoxy)diphenylether (4-HEDE) and HDI by melt or solution polymerization with or without catalyst. At the next stage, we studied the effect of variable amounts of 1,6-hexanediol (1,6-HD) and PTMO  $\sim 650$  on the thermal and mechanical properties of obtained PUs.

#### **EXPERIMENTAL**

#### **Materials**

4-HEDE (m.p.  $124-126^{\circ}$ C) was obtained in a hydroxylation reaction of bis(4-hydroxyphenyl)ether (4-HPE) with ethylene carbonate in the presence of K<sub>2</sub>CO<sub>3</sub>. 4-HPE (m.p.  $160-161^{\circ}$ C) was synthesized according to the reported method<sup>15</sup> by hydrolysis of 4,4'-diiododiphenyl ether in the presence of CuI and NaOH at 150°C.

HDI [b.p.  $127^{\circ}$ C/13.34 Pa (Merck)] was used as received. Dibutyltin dilaurate (DBTDL) and tributyltin acetate (from Merck) were used as

purchased. Triethylamine (Fluka, Ronkonkoma, NY) was freshly distilled over anhydrous KOH. 1,6-HD (Merck) was distilled before use. PTMO ( $\bar{M}_n \sim 650$ , BASF, Schwarzheide) was heated before using at 120°C *in vacuo* for 1 h. *N*,*N*-Dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (all supplied by Merck) were subsequently distilled and dried over 3 Å molecular sieves.

#### **Monomer Synthesis**

The initial 4-HEDE was obtained from 4-HPE and ethylene carbonate using the following procedure. Into a 250-mL round-bottomed flask equipped with stirrer and reflux condenser, 10.1 g (0.05 mol) of 4,4'-dihydroxydiphenyl ether, 50 g (0.5 mol) of ethylene carbonate, and 19.52 g (0.16 mol) of anhydride  $K_2CO_3$  were placed. The reaction mixture was then heated in an oil bath for 4 h at 100–120°C. After cooling, the resulting precipitate was filtered off, washed with distilled hot water until neutral, and dried *in vacuo* at 80°C to a constant weight (yield: 100%).

By recrystallization from benzene (1 g from 10 mL), the diol with a m.p. of  $124-126^{\circ}$ C was obtained. Purity of the compound obtained in this manner was checked by elemental analysis, Fourier transform infrared (FTIR) (Fig. 1) and <sup>1</sup>H-NMR spectroscopies, as determined in the following: IR (KBr, cm<sup>-1</sup>) 1060, 1240, 1500, and 3200. <sup>1</sup>H-NMR [dimethylsulfoxide (DMSO)- $d_6$ , ppm] 4.86 (7, -OH, 2H, J = 5, 1H<sub>2</sub>); 3.73 (2-CH<sub>2</sub>-,

4H,  $J = 4.7H_2$ ); 3.91–4.00 (m, –-CH<sub>2</sub>–, 4H); 6.61 (s, Ar-H, 8H). Anal. Calcd for C<sub>16</sub>H<sub>18</sub>O<sub>5</sub>: C, 66.23%; H, 6.20%. Found: C, 66.48%, H, 6.38%.

# **Polymer Synthesis**

PUs were obtained with the strictly equimolar ratio of the dixydroxyl compound to diisocyanate by both melt and solution polymerization with or without a catalyst.

# **Melt Polymerization**

A typical procedure for the synthesis of PUs by this method is as follows. In a four-necked, roundbottomed flask fitted with a condenser, mechanical stirrer, thermometer, and nitrogen inlet tube, 2.9014 g (0.01 mol) of 4-HEDE and 1.681 g (0.01 mol) of HDI were placed and gradually heated in an oil bath in a dry nitrogen atmosphere until a clear solution was formed ( $\sim 100^{\circ}$ C). Then, two drops of DBTDL were added. When vigorously stirred, polymerization began rapidly after 120°C was reached. The resulting light-yellow waxy product was additionally heated at this temperature for 0.5 h. Without a catalyst, the reaction at this temperature was far slower, and a time of 2 h was needed.

# **Solution Polymerization**

# Procedure 1

Using the same apparatus as previously described, 2.9014 g (0.01 mol) of 4-HEDE and 10 mL of freshly distilled DMF (with 3 drops of DBTDL) were placed. Nitrogen was kept flowing continuously through the system. Then, as the temperature was raised to 90°C, 1.681 g (0.01 mol) of HDI in 5 mL of DMF was added dropwise to this solution over a period of 10 min with vigorous stirring. The content was kept at the same temperature and stirred for 4 h until the reaction was completed (disappearance of the NCO band). More solvent ( $\sim 5 \text{ mL}$ ) was added to allow stirring if the viscosity of the solution increased considerably. 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 solid. The product was filtered off, washed with fresh methanol, and subsequently dried under vacuum at 100°C for 15 h. The yield was 4.35 g (84.9%). ANAL. Calcd for PU: C, 83.84%; H, 6.55%; N, 6.11%. Found: C, 84.12%; H, 7.28%; N, 5.62%.

# **Procedure 2**

*One-step method.*—The apparatus was the same as described in procedure 1. To 1.681 g (0.01 mol)

of HDI, 0.01 mol PTMO ~ 650°C and 4-HETDE together in a mole ratio given in Table III (e.g., 1.41 g PTMO, 2.32 g 4-HEDE, and 12 mL DMF were added (~ 30 wt % of solution). Reagents were heated in an oil bath with vigorous stirring to 90°C, and then three drops of DBTDL were added. After 0.5 h, 8 mL DMF were added to avoid gelation; heating was continued for 4 h. (Another procedure was as described in procedure 1.) A clear, flexible product was obtained with a 90% yield. Colorless thin films may be cast from the tetrachloroethane solution.

Two-step method.—In the same apparatus as described in procedure 1, 1.681 g (0.01 mol) of HDI and 3.25 g (0.005 mol) of PTMO  $\sim$  650 were dissolved in 20 mL DMF. These components were heated in an oil bath at 90°C for 1 h. Then, 0.8705 g (0.005 mol) of 4-HEDE dissolved in 5 mL DMF were gradually added for 1 h, and the reaction mixture was heated additionally for 3 h. The procedure was as described previously.

Copolyurethanes (CPUs), with the use of 1,6-HD, were obtained according to procedure 2 (onestep method), taking the amounts of monomers (4-HEDE and HDI) as given in Table I.

# **Measurement of Properties**

# Spectral Analysis

FTIR spectra were obtained with a Perkin-Elmer 1725  $\times$  FTIR spectrophotometer using KBr discs or thin films, as appropriate. The <sup>1</sup>H-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<sup>-1</sup>) of 0.5% solutions of polymers in a phenol-tetrachloroethane mixture (1/3, w/w) was measured by a Ubbelohde viscometer at  $25^{\circ}$ C.

# Molecular Weight

Molecular weights were obtained using a Knauer gel permeation chromatograph equipped with  $10^6$ ,  $10^5$ ,  $10^4$ ,  $10^3$ ,  $10^2$  Å and 50  $\mu$ m of PL-gel columns with a refractrometric detector. Tetrahydrofuran (THF) was used as the eluent (flow rate was 1.0 mL min<sup>-1</sup>), and numerical values for molecular weight 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.

	1,6-HD or PTMO	4-HEDE	HDI	$\eta_{ m red}$			$T_{g}$
PU Code	(g)	(g)	(g)	$(dL g^{-1})$	$\bar{M}_n$	${ar M}_w$	(°Č)
PU-OH		1.4507	0.8405	0.42	_	_	33.1
PU-2OH	1.4127	2.3214	3.3618	0.46	_	_	28.27
PU-40H	1.6534	1.7408	3.3618	0.48	_	_	23.96
PU-6OH	1.8896	1.1604	3.3618	0.54	_	_	22.92
PU-80H	2.1258	0.5802	3.3618	0.58	_	_	17.70
PU-2OP	7.8	2.3212	3.3618	0.72	18,600	35,900	-56.3
PU-40P	9.1	1.7409	3.3618	0.77	21,400	51,700	-56.61
PU-40P <sup>a</sup>	4.5	0.8705	1.6909	0.38	2,650	18,300	-60.16
PU-60P	10.4	1.1606	3.3618	1.06	48,300	120,000	-57.34
PU-80P	11.7	0.5803	3.3618	1.08	15,300	34,100	-62.8

Table IInfluence of the Amount of 1,6-HD or PTMO on the Properties of PUs Derived from 4-HEDEand HDI

<sup>a</sup> Two-step polymerization.

Erdey) derivatograph at a heating rate of 10°C  $\min^{-1}$  in air.

### Hardness

The hardness of PUs was measured by using Shore A and D durometers at 25°C. Values were taken after 15 s.

## **Tensile Tests**

Tensile testing was performed with an Instron Model 6022 Universal Testing Machine at 50 mm min<sup>-1</sup> speed at 23°C. Tensile test pieces, 1 mm thick and 7 mm wide (for the section measured), were cut from pressed sheets. Results reported are the median values for three replicates.

## 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 (Tg)

Differential scanning calorimetry (DSC) thermograms over the range of  $-100-200^{\circ}$ C were recorded on a Du Pont 2000 TA. A thermal analysis processor at a heating rate of  $10^{\circ}$ C min<sup>-1</sup> and  $T_g$  were determined as the temperature of inflection point on the curves describing the rate of heat capacity changes.

# **RESULTS AND DISCUSSION**

#### **Monomer Synthesis**

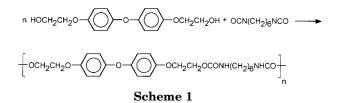
4-HEDE, the initial material, was successfully prepared by hydroxylation of 4-HPE by means of ethylene carbonate in the presence of anhydride  $K_2CO_3$ . The required diol can also be obtained with the reaction of 4-HPE with bromoethanol in the ethanolic solution of NaOH, but with a much lower yield and requiring a longer time of reaction (~ 10 h).

A chemical structure of the synthesized 4-HEDE was confirmed using elemental analysis, FTIR, and <sup>1</sup>H-NMR spectroscopic techniques.

#### **Polymer Synthesis and Characterization**

New linear nonsegmented PUs, consisting of only 4-HEDE/HDI units, were prepared according to Scheme 1 using melt or solution polymerization:

The reaction was conducted with or without a catalyst using equimolar amount of monomers. PUs obtained by melt polymerization were light-yellow, hard waxy products, or rubber-like when solution polymerization was used. Because these hard segment-type PUs were practically insoluble in common organic solvents like benzene, DMF, DMSO,



Catalyst	M.p. (°C)	$\begin{array}{c} \eta_{red} \\ (dL \; g^{-1}) \end{array}$	Yield (%)
_	250-260	0.42	70.28
DBTDL	255 - 262	$0.68^{\mathrm{a}}$	94.92
	240 - 248	$0.60^{ m b}$	78.34
	225 - 232	$0.58^{ m c}$	76.39
TBTA	234 - 240	0.48	62.27
TEA	230-236	0.45	50.28

Table IIInfluence of Catalyst and Solventon Properties of PUs Derivedfrom 4-HEDE and HDI

<sup>a</sup> Solvent used: DMF.

<sup>b</sup> Solvent used: DMAc.

<sup>c</sup> Solvent used: DMSO.

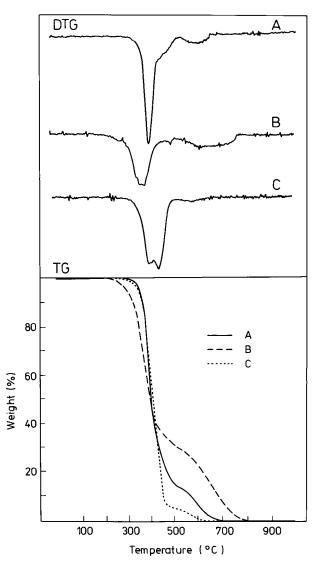
and THF at room temperature, determination of their molecular weight was not possible. They were soluble only in a phenol-tetrachloroethane mixture, m-cresol, N-methyl-2-pyrrolidone, and 1,1,1,3,3,3hexafluor-2-propanol. They were all resistant to dilute acids and alkali; only concentrated nitric and sulfonic acids could dissolve them with decomposition after a longer time of exposure.

In the previous work,<sup>14</sup> concerning the synthesis, structure, and characterization of hard segmenttype PUs obtained from 4-HETDE and HDI, we found that their properties were dependent on many factors. Among them, kind of organic solvent, contribution of catalyst, molar ratio and concentration of reagents, and time and temperature of polyaddition reaction. The previously described factors, as was experimentally established, influenced the value of reduced viscosity as well as the reaction yield of PUs obtained now from 4-HEDE and HDI. Because of this, the most advantageous results were obtained using DBTDL as catalyst, DMF as solvent,  $\sim 30$  wt % concentration of monomers, and reaction temperature in the range of 90–100°C.

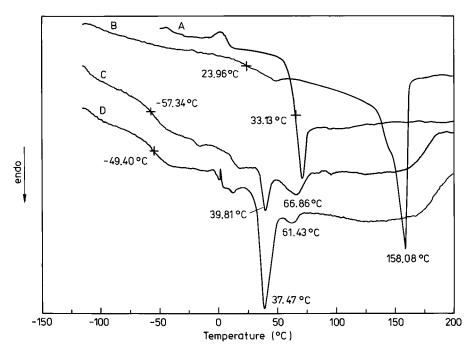
The basic properties of these PUs are summarized in Table II. As seen from the presented data, the presence of a catalyst significantly influenced the value of reduced viscosity and reaction yield. Thus, the highest value ( $\eta_{\rm red}$ : 0.68 dL g<sup>-1</sup>) and the best yield ~ 94% were obtained using DMF as a solvent and DBTDL as a catalyst. Slightly lower values of reduced viscosity were obtained using DMAc or DMSO as a reaction medium, but the yields were much lower.

Thermal stability of the PUs was evaluated using TGA and DSC. Typical curves for chosen polymers are given in Figures 2 and 3, and the results obtained for all polymers are quoted in Table III. The examined nonsegmented 4-HEDE/ HDI PU was stable up to 370°C in an air atmosphere. A 5% weight loss was taken as the criteria for thermal stability. The initial decomposition of this polymer was recorded at 310°C (1% weight loss), the maximum rate of decomposition occurred at ~ 400°C, and its weight loss at 380 and 400°C were 10 and 20%, respectively.

Nonsegmented PUs obtained independently of the method used were insoluble, brittle solids; thus, their mechanical properties could not be measured. The structure of polymers 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 1).



**Figure 2** Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of PUs: (A) PU-OH; (B) PU-4OH; and (C) PU-60P.



**Figure 3** DSC thermogram of PUs: (A) PU-OH; (B) PU-6OH; (C) PU-2OP; and (D) PU-40P.

As shown in Figure 1, the FTIR spectrum of the polymer showed characteristic absorption of the bonded carbonyl stretching vibration (the amide I band) at 1700–1690  $\text{cm}^{-1}$ , characteristic of the N—H bending vibration of the amide group (the amide II band), and at 3330–3310  $\text{cm}^{-1}$  charac-

	<i>T</i> <sub>1</sub> <sup>a</sup> (°C)	$U^{\mathrm{b}}$ (%)	$T_2^{\ c}$ (°C)	Weight Loss (°C)		
PU Code				5%	10%	20%
Nonsegmented						
PU-OH	310	1.0	400	370	380	400
PU-2OH	300	0.5	390	380	390	400
$PU-2OH^{d}$	290	1.0	380	370	400	400
PU-40H	280	1.0	400	300	320	350
PU-6OH	290	1.0	410	260	390	400
PU-80H	280	1.0	400	380	390	400
Segmented						
PU-20P	260	0.5	400	350	370	390
			460			
PU-40P	280	1.0	400	350	370	380
			440			
PU-60P	280	1.0	400	360	380	400
			440			
PU-80P	260	1.0	400	310	350	380
	_00		430		200	000

 Table III
 Thermal Properties of Polyurethanes Obtained from 4-HEDE, HDI with Variable Amounts of 1,6-HD or PTMO

Codes of PUs: e.g., PU-OH was obtained from 4-HEDE and HDI. PU-2OH CPU was obtained from 4-HEDE, HDI, and 20 mol % of 1,6-HD. PU-2OP was the CPU obtained from 4-HEDE, HDI, and 20 mol % of PTMO.

 $^{\rm b}$  Mass loss in temperature  $T_1.$ 

<sup>c</sup> Temperature of maximum rate of decomposition from the DTG curve.

<sup>a</sup> Temperature of initial decomposition from the TG curve.

<sup>d</sup> Polymerization in melt.

teristic of the banded N—H stretching vibration. The band at  $1280-1200 \text{ cm}^{-1}$  was attributed to the asymetric vibration of the aromatic ether bond. The band of the isocyanate group at 2270 cm<sup>-1</sup> was not observed.

The influence of 1,6-HD or PTMO  $\sim$  650 on the properties of polymers has been studied; taking the same concentration of HDI equals, for example, 0.01 mol under optimal conditions established earlier for 4-HEDE/HDI PU, but changing the molar ratio of the remaining components: 4-HEDE, 1,6-HD, or PTMO. These two last modifiers were taken in the amount of 20–80 mol % in relation to used diol-4-HEDE.

The influence of variable amounts of the first modifier on the properties of CPUs is presented in Table I.

As seen from the presented data, the value of reduced viscosity increases from 0.42 to 0.58 (dL  $g^{-1}$ ) with an increasing amount of 1,6-HD. Thermal properties of nonsegmented CPUs 4-HED/HDI/1,6-HD are indicated in Table III and in Figure 2. Temperatures of initial decomposition of these CPUs are in the range of 280–300°C, and their 5% weight losses are in the range of 260–380°C, depending on the amounts of 1,6-HD.

The  $T_g$  behavior of these CPUs shows differences, depending on the amount of 1,6-HD. Thus, this value is ~ 33°C when 4-HEDE/HDI PU was obtained, and it drops to 17°C when 80 mol % of 1,6-HD was incorporated into the polymer structure. The DSC thermograms presented in Figure 3 show the sharp endothermic peak corresponding to the melting point of hard segments at ~ 158°C for CPUs with 40 mol % of 1,6-HD chain extender. For PU consisting of only 4-HEDE/HDI units (100% hard segments), characteristic peak in the presented range of temperatures is not observed because they melt over 200°C (Table II).

Nonsegmented polymers with 1,6-HD content were strong, waxy products soluble only in m-cresol and N-methyl-2-pyrrolidone and 1,1,1,3,3,3-hexafluor-2-propanol. Therefore, determination of their molecular weight was not possible.

However, segmented CPUs with a variable amount of thermal-sensitive aliphatic segments derived from PTMO ~ 650 exhibited nearly the same thermal stability; for these with 40–60 mol % content of this polyetherdiol, 5% weight losses occurred ~ 350–360°C. In the case of CPUs into which 80 mol % of PTMO was incorporated, this characteristic value is the smallest and equals 310°C. All CPUs based on PTMO were thermoplastic elastomers with low softening temperatures in the range of 36-45°C. CPU 4-HEDE/HDI/PTMO with code PU-40P containing 40 mol % of PTMO (Table I), obtained in one-step polymerization, showed two times higher value of reduced viscosity and a little higher  $T_g$  value in comparison with the two-step method.

The DSC thermograms for segmented CPUs (4-HEDE/HDI/PTMO series) are presented in Figure 3 (curves C and D). For the polymer containing 20 mol % of soft segments derived from PTMO, the peak at  $\sim 39^{\circ}$ C is detected as typical for the soft segments of polyetherdiol used with a small amount of hard segment domains dispersed in a continuous phase. Another peak at  $\sim 66^{\circ}$ C is connected with a melting point of hard segments plasticized by soft segments from PTMO. However, for CPUs with 40 mol % of PTMO, the melting temperatures of soft and hard segments are shifted to lower values.

It is suggested that the molecular weight of soft segments derived from PTMO was not enough to ensure adequate phase separation and poor tensile strengths of tested CPUs were obtained. We plan further research to concentrate on synthesis and properties of PUs with longer flexible spacers.

On the other hand, an increasing amount of soft segments in polymer structure caused only a little decrease of  $T_g$ . This fact might be explained by weak interaction between hard and soft segments caused by miscibility or compatability of these two segments.

Segmented PUs derived from polyether-PTMO, in contrast with nonsegmented PUs, were easily soluble in chloroform, tetrachloroethane, methylene chloride, and THF; thus, determination of their molecular weight was possible.

Among CPUs presented in Table I, special attention was paid to the one with the highest value of reduced viscosity ( $\eta_{\rm red}$ : 1.06 dL g<sup>-1</sup>) and, at the same time, the highest molecular weight  $M_w \sim 120,000$ .

These results corresponded with the literature quoted earlier stating that these polymers containing  $50-70 \mod \%$  of soft segments had the highest molecular weight. When the two-step method was used, CPUs with a lower value of molecular weight and larger dispersion were obtained in comparison with the one-step method.

# **Mechanical Properties**

Some mechanical properties of the 4-HEDE/HDI/ PTMO CPUs were studied after pressing at  $100-120^{\circ}$ C under the pressure of  $\sim 10$  MPa. Results of mechanical tests for these polymers obtained in melt or solution polymerization are listed in Table IV.

PU Code	Hardness (Shore A/D)	Tensile Strength (MPa)	Elongation of Break (%)	Modulus of Elasticity (MPa)
$PU-20P^{s}$	73/18	3.75	153.24	29.80
$PU-20P^{m}$	72/23	3.58	162.13	35.51
$PU-40P^{s}$	72/15	3.62	364.44	32.27
$PU-40P^{m}$	78/17	3.72	314.11	38.56
$PU-60P^{s}$	78/16	3.69	393.70	22.40
$PU-60P^{m}$	72/23	4.25	371.78	24.36
$PU-80P^{s}$	74/18	4.32	372.38	23.14
PU-80P <sup>m</sup>	84/28	4.52	138.28	25.26

Table IV Mechanical Properties of CPUs Derived from 4-HEDE, HDI, and PTMO

<sup>m, s</sup> Polymerization in melt or in solution.

As seen, there is no significant change in mechanical properties of these polymers while increasing the amount of PTMO. The values of shore A hardness in the range of 72–84 predispose them to be used as thermoplastic elastomers with high elasticity. Elongation at break of CPUs obtained by both methods significantly increased with the amount of soft segment content in polymer structure. The highest value,  $\sim 430\%$ , was obtained for CPU 4-HEDE/HDI/ PTMO, the product of melt polymerization with the use of 80 mol % PTMO  $\sim 650$ . From the data presented, no clear regularity between modulus of elasticity and percent content of PTMO spacers follows.

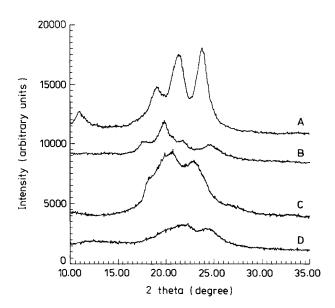
X-ray diffraction analysis of the PUs conducted at room temperature presented in Figure 4 indicates the decrease of crystallization degree with an increase of soft segments. CPU 4-HEDE/HDI/ PTMO with 60 mol % PTMO is amorphous in character. Crystalline phase observed for 4-HEDE/HDI PU is formed from its hard segments.

For CPUs 4-HEDE/HDI/1,6-HD, mechanical property measurements were not possible because they turned out strong and hard products.

## CONCLUSIONS

The new aromatic-aliphatic linear PUs composed of 4-HEDE and HDI obtained by a polyaddition reaction was brittle and hard when obtained by melt polymerization, or rubber-like products obtained by solution polymerization. Nonsegmented PUs possessing high melting points are insoluble in common organic soluents at room temperature. They exhibit good thermal stability up to 370°C, and chemical resistance to dilute acids and alkali.

CPUs type 4-HEDE/HDI/1,6-HD with various amounts of 1,6-HD are strong wax-like products slightly more soluble in organic solvents in comparison with polymer 4-HEDE/HDI; they have a slightly higher thermal stability when 20 or 80 mol % of 1,6-HD are used, and all reveal chemical resistance. Then, CPUs type 4-HEDE/HDI/PTMO have softening temperature points in the range of 36–45°C and are easily soluble in common organic solvents. They behave as thermoplastic elastomers, but CPU with a high molecular weight ( $\bar{M}_w \sim 120,000$ ) and with good thermal stability proved to be most interesting.



**Figure 4** X-ray patterns of PUs: (A) PU-OH; (B) PU-2OP; (C) PU-4OP; and (D) PU-6OP.

CPU elastomers with varying amounts of soft segments derived from PTMO are considered to find use as new promising elastic polymeric materials.

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