

Synthesis and Selected Properties of Polyurethanes with Monodisperse Hard Segments Based on Hexane Diisocyanate and Three Types of Chain Extenders

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ABSTRACT: Poly(tetramethylene oxide)-based segmented polyurethanes were synthesized by the chain extension of a poly(tetramethylene oxide) with a length of 1270 g/mol that was end-capped with 1,6-hexane diisocyanate. Three types of uniform chain extenders were used: a diamine diamide, a diol diamide, and a diol diester. The concentration of the monodisperse hard segments was approximately 32 wt %, and the materials were clear and tough. The polyurethanes with monodisperse hard segments were subsequently characterized with differential scanning calorimetry, dynamic mechanical thermal analysis, and compression set measurements and were found to display low glass-transition temperatures, an almost temperature-independent rubbery plateau, and sharp melting temperatures. The rate of

crystallization (melting temperature – crystallization temperature) was moderately fast (36–54°C). Moreover, the melting temperature of the polyurethanes increased with the number of hydrogen-bonding groups in the hard segment, whereas the modulus at room temperature was more dependent on the structural regularity of the extender. The best elastic properties were found for the materials extended with the diamine diamide. Finally, an interesting combination of properties was revealed for the polyurethane with a diol diamide extender based on aminopropanol. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1302–1315, 2012

Key words: block copolymers; polyurethanes; structure-property relations

INTRODUCTION

Thermoplastic polyurethanes (TPUs) are linear copolymers that can be synthesized from a long-chain diol (polyether or polyester), a diisocyanate, and a chain extender.^{1,2} The often used diisocyanates are 4,4'-diphenylmethane diisocyanate (MDI), toluene diisocyanate (TDI), and 1,6-hexane diisocyanate (HDI). The hard segments consist of alternating isocyanate residues and extender units, thus providing the material with dimensional stability. The hard segments in TPUs are usually partly crystalline, and their maximum utilization temperature is related to the crystalline melting temperature. The processing of these polyurethanes occurs a few tens of degrees above the melting temperature. As polyurethanes are not very thermally stable, the melting temperature should be below 220°C. The hard-segment concentration in polyurethanes influences their me-

chanical properties, and with an increase in the hard-segment content, the modulus and tensile strength increase. Chain extenders are low-molecular-weight reactants (60–400 g/mol), and the structural regularity of the hard segments has a strong effect on their crystallization and on the properties of TPUs, such as the melting temperature, modulus, fracture strength, and elasticity. Because of incomplete crystallization of the hard segment, some of it dissolves in the soft-segment phase; this increases the glass-transition temperature of this phase and thereby reduces the low-temperature flexibility.^{1–4} Possible chain extenders are diols and diamines.

The most important chain extenders for TPUs are linear diols such as ethylene glycol and 1,4-butanediol.¹ The length of the diol chain extender influences the polymer properties.^{5–9} In MDI-diol polyurethane hard segments, increasing the diol length led to a decrease in the glass-transition temperature of the polymers of about 5°C. Moreover, the modulus was found to be highest with an even number of methylene groups^{6,7} because this gave rise to better packing.^{7,10}

Diamine chain extenders can also be used in polyurethanes, and the reaction of diamines with isocyanate leads to urea groups in the polymer chain. Poly(urethane urea)s have high melting

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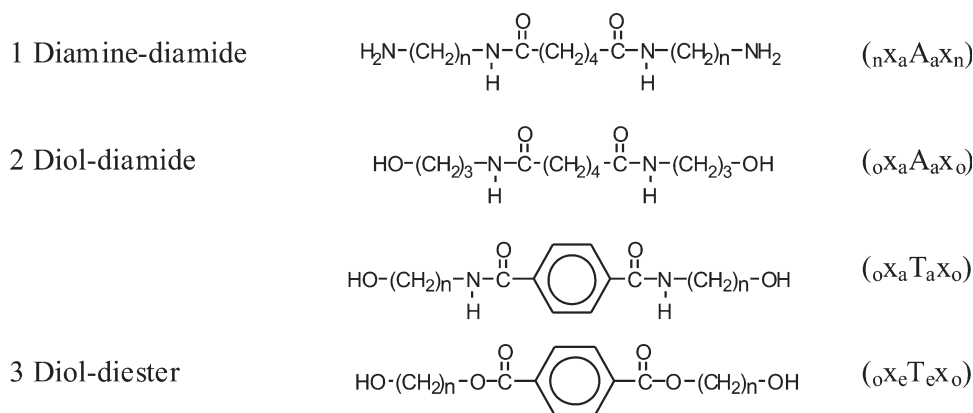


Figure 1 Three chain extenders: (1) diamine diamide, (2) diol diamide, and (3) diol diester [a = amide, A = adipic acid, e = ester, n = amine, o = hydroxyl group, T = terephthalic acid, x = $(\text{CH}_2)_n$].

temperatures; however, sometimes they are too high for melt synthesis and melt processing without degradation. With aliphatic diamine extenders ($\text{C}_1\text{--}\text{C}_8$), the tensile strength and elongation at break have been found to oscillate with the number of methylene groups in the diamine.^{11–15} Poly(urethane urea)s with diamines with even numbers of methylene groups have displayed higher moduli, higher melting temperatures, lower glass-transition temperatures, and higher stresses. This effect has been attributed to better phase separation of the hard segments with even-numbered diamine chain extenders.

The hard segments in TPUs normally consist of multiple diisocyanate and extender units and have random length distributions; this results in partially crystalline hard segments. However, the crystallinity of the hard segment is usually higher when the polyurethanes have a monodisperse distribution.^{4,16–26} Copolymers with monodisperse hard segments display a low glass-transition temperature of the soft-segment phase, a relatively high room-temperature modulus, an almost temperature-independent rubber modulus, and a narrow melting transition.

In certain studies, the poly(urethane urea) extender unit contained amide groups.^{25–28} Such poly(urethane urea) amides were capable of forming additional hydrogen bonds. When the extender was changed from a diamine to either a diamine diamide or a diamine tetraamide, the modulus and the melting temperature increased, and the compression set values were lowered.²⁵ Moreover, poly(urethane urea)s with a diamine diamide extender in combination with a TDI unit displayed hard-segment melting temperatures that were not too high.^{25,26}

For TPUs, the most commonly employed diisocyanate is MDI. However, because of its irregular structure, the hard-segment crystallinity is not very high, and the aromatic diisocyanate easily discolors the polymer. Polyurethanes with HDI are more regular

and, because it is an aliphatic polyurethane, less colored. HDI copolymers with diamine diamide extenders have been found to display high moduli and good properties, but unfortunately, the melting temperatures have been high ($>200^\circ\text{C}$).²⁶

It was deemed of interest to study the effect of the type of monodisperse extender on the properties of HDI-based polyurethanes. Three chain extenders were selected, namely, diamine diamide, diol diamide, and diol diester (Fig. 1).

The diamine diamide was based on adipic acid and aliphatic diamines, the diol diamide was based on either adipic or terephthalic acid and amino alcohols, and the diol diester was based on terephthalic ester and aliphatic diols. The subscript a corresponds to amide, the subscript n corresponds to amine, the subscript e corresponds to ester, and the subscript o corresponds to a hydroxyl group. The uniformity of the extenders was an important parameter as only uniform chain extenders could give rise to polyurethanes with monodisperse hard segments. The influence of the structure of the uniform chain extender on the polymer properties was investigated; the thermal properties of the polyurethanes were explored with differential scanning calorimetry (DSC), the dynamic mechanical characteristics were explored with dynamic mechanical thermal analysis (DMTA), and the elastic behavior was explored with compression set measurements.

EXPERIMENTAL

Materials

1,3-Diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,12-diaminododecane dimethyl adipate, anhydrous *N,N*-dimethylacetamide (DMAc), 2-amino-ethanol, 3-amino-1-propanol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, and a 0.5M sodium methoxide solution in methanol were purchased

from Aldrich (Mijdrecht, Netherlands) and used as received. Dimethyl terephthalate (DMT) and 1,4-dioxane were purchased from Across, butyl acetate was purchased from Fluka (Mijdrecht, Netherlands), and sodium methylate was purchased from Merck (Haarlem, Netherlands). Also, these chemicals were used as received. Poly(tetramethylene oxide) (PTMO; weight-average molecular weight = 1270 g/mol), end-capped with HDI (LFH520), was generously donated by Crompton Corp. This prepolymer had a low free isocyanate content (<0.1 wt % diisocyanate) and was dried *in vacuo* at 80°C overnight before use.

Synthesis of the diamine diamide ($n_x A_a x_n$, where A indicates an adipic acid group)

The synthesis of the 4A4- and 6A6-diamine diamides was performed as described elsewhere,²⁹ and the synthesis of the 12A12-diamine diamide was similar to that of the 6A6-diamine diamide. Moreover, the synthesis of the 3A3-diamine diamide resembled that of the 4A4-diamine diamide.

Synthesis of the diol diamide ($o_x A_a x_o$ and $o_x T_a x_o$, where T indicates a terephthalic acid group)

The diol diamide extenders were all synthesized in the same way, and the synthesis of the 2T2-diol diamide is given here as an example. 1-Amino-2-ethanol (200 g, 3.3 mol) and DMT (105 g, 0.5 mol) were charged to a round-bottom flask equipped with a reflux condenser, a calcium chloride tube, a magnetically coupled stirrer, and a nitrogen inlet. The reaction was carried out for 16 h at 120°C, and during the reaction, the product partially precipitated. Ethanol was added to the cooled reaction mixture, and the precipitate was collected by filtration with a glass filter (no. 4). The product was washed three times with diethyl ether.

¹H-NMR [deuterated dimethyl sulfoxide (DMSO-*d*): 7.9 (s, 4H, terephthalate H), 4.67 (t, 2H, hydroxyl group), 3.50 (q, 4H, CH₂ amide x), 3.33 (q, 4H, CH₂ hydroxyl x), 3.26 (s, 2H, amide).

Synthesis of the diol diester^{30–32}

3T3-diol diester ($o_3 T_e 3_o$)

1,3-Propanediol (72.3 mL, 1.0 mol) and DMT (19.4 g, 0.1 mol) were charged to a round-bottom flask equipped with a reflux condenser, a calcium chloride tube, a magnetically coupled stirrer, and a nitrogen inlet. Zinc acetate (0.05 g) was added as a catalyst. The reaction was carried out for 5 h at 160°C, during which time methanol was distilled off with a Dean–Stark trap. The temperature was increased to 210°C for 30 min to distill off the excess

1,3-propanediol. The product was cooled to 100°C and added to 1 L of 50°C water. The precipitate (the longer blocks) was filtered over a no. 3 glass filter. Upon further cooling to 7°C, the $o_3 T_e 3_o$ -diol diester crystallized and was collected by filtration over a glass filter (no. 4). The precipitate was then recrystallized in water (100°C, 20 g/L).

¹H-NMR [deuterated chloroform (CDCl₃), δ]: 8.10 (s, 4H, terephthalate H), 4.52 (m, 4H, CH₂ hydroxyl x), 3.81 (m, 4H, second CH₂), 2.05 (m, 4H, CH₂ ester x), 1.84 (t, 2H, hydroxyl group).

4T4-diol diester ($o_4 T_e 4_o$)

1,4-Butanediol (355 mL, 3.95 mol) and DMT (39 g, 0.2 mol) were charged to a round-bottom flask equipped with a reflux condenser, a calcium chloride tube, a magnetically coupled stirrer, and a nitrogen inlet. Titanium butoxide (0.08 g) was added as a catalyst. The reaction was carried out for 5 h at 160°C, and methanol was distilled off with a Dean–Stark trap. The temperature was increased to 210°C to distill off the excess 1,4-butanediol. Once the reaction mixture was cooled, diethyl ether (3 L) was added, and the formed precipitate was collected by filtration over a glass filter (no. 4). The product was heated in water (100°C, 20 g/L) and filtered over a hot glass filter (100°C), after which the filtrate was cooled. The white, needle-shaped crystals that were formed were collected by filtration over a glass filter (no. 4).

¹H-NMR (DMSO-*d*): 8.09 (s, 4H, terephthalate H), 4.45 (t, 2H, hydroxyl group), 4.32 (t, 4H, CH₂ ester x), 3.45 (t, 4H, CH₂ hydroxyl x), 1.75 (m, 4H, second CH₂ ester x), 1.55 (m, 4H, second CH₂ hydroxyl x).

6T6-diol diester ($o_6 T_e 6_o$)

1,6-Hexanediol (236 g, 2.0 mol) and DMT (39 g, 0.2 mol) were charged to a round-bottom flask equipped with a reflux condenser, a calcium chloride tube, a magnetically coupled stirrer, and a nitrogen inlet. Titanium butoxide was used as a catalyst (0.08 g). The reaction was carried out for 5 h at 175°C. After cooling, the precipitate was filtered over a glass filter (no.3) and washed twice with diethyl ether. The product was recrystallized in water (20 g/L).

¹H-NMR (DMSO-*d*): 8.09 (s, 4H, terephthalate H), 4.36 (t, 2H, hydroxyl group), 4.30 (t, 4H, CH₂ ester x), 3.41 (t, 4H, CH₂ hydroxyl x), 1.70 (m, 4H, second CH₂ ester x), 1.55 (m, 12H, second to fourth CH₂ hydroxyl x).

Copolymerization

The polymerization of –PTMO₁₂₇₀–HDI–_n6_aA₆_n–HDI– is given here as an example. A dried 250-mL stainless steel reactor equipped with a nitrogen inlet

and a magnetically coupled stirrer was charged with HDI-PTMO₁₂₇₀-HDI (30 g, 0.019 mol) and a solution of 6A6-diamine diamide (6.39 g, 0.019 mol) in 100 mL of anhydrous DMAc. The stirred reaction mixture was heated to 140°C and reacted for 5 h under a flow of nitrogen. Subsequently, the pressure was carefully reduced (<20 mbar) to distill off the DMAc and then further reduced (<0.3 mbar) for 60 min. After that, the reactor was slowly cooled, the low pressure being maintained. The synthesized copolymer was transparent, slightly yellowish, and tough.

¹H-NMR

NMR spectra were recorded on a Bruker AC 300 spectrometer (Delft, Netherlands) at 300 MHz. Deuterated trifluoro acid, DMSO-*d*, and CDCl₃ were used as solvents.

Viscometry

The inherent viscosity was measured at a concentration of 0.1 dL/g with a mixture of phenol and 1,1,2,2-tetrachloroethane (1 : 1 molar ratio) at 25°C and with an Ubbelohde-type 1B capillary.

Compression molding

Test samples for DMTA and compression set measurements were fabricated by compression molding with the use of a Lauffer 40-ton press (Horb am Neckar, Germany). The TPU (2.1 g), cut into small pieces and dried overnight, was spread into a bar-shaped mold (8 × 1.8 × 0.2 cm³) and pressed between press plates. The temperature of the press was set to 20° above the melting temperature of the TPU with a maximum of 230°C. First, air was removed from the polymer in the mold by quick pressurization and depressurization of the sample. This procedure was repeated three times before the actual pressing of the samples at 10 MP (≈ 8.5 MPa) for 2 min. Subsequently, the press was cooled, and the test bars were removed from the mold.

DSC

DSC spectra were recorded on a PerkinElmer DSC apparatus (Monza, Italy) equipped with a PE7700 computer and TAS-7 software. Dried samples (5–10 mg) were heated to approximately 30°C above their melting temperature and subsequently cooled at a heating/cooling rate of 20°C/min. The maximum of the peak in the heating scan was taken as the melting temperature, and a second heating scan was used to determine the melting peak and enthalpy (ΔH_m) of the sample. The crystallization temperature

was taken as the temperature of the onset of crystallization in the first cooling scan.

DMTA

The compression-molded test samples (70 × 9 × 2 mm³) were dried *in vacuo* at 50°C for 24 h before use. DMTA spectra were recorded with a Myrenne ATM3 torsion pendulum (Aachen, Germany) at a frequency of 1 Hz and 0.1% strain. The storage modulus (G') and loss modulus (G'') were measured as functions of temperature. The samples were cooled to –100°C and subsequently heated at a rate of 1°C/min. The temperature at the maximum of the G'' peak was taken as the glass-transition temperature. The flow temperature was defined as the temperature at which G' reached 1 MPa. The start of the rubbery plateau, more specifically the intercept of the tangents, was called the flex temperature. The decrease in G' of the rubbery plateau with increasing temperature was quantified with $\Delta G'$, which was calculated as follows:

$$\Delta G' = \frac{\Delta G'_{(T_{\text{flex}})} - G'_{(T_{\text{flow}} - 50^\circ\text{C})}}{\Delta G'_{25^\circ\text{C}}} * \frac{1}{\Delta T} (^\circ\text{C}^{-1}) \quad (1)$$

where T_{flex} is the flex temperature, T_{flow} is the flow temperature, and ΔT represents the temperature range [($T_{\text{flow}} - 50^\circ\text{C}$) – T_{flex}].

Compression set measurements

Samples for compression set measurements were cut from compression-molded bars. The compression set was measured at room temperature according to the ASTM 395 B standard. After 24 h, the compression was released at room temperature. After relaxation for half an hour, the thickness of the samples was measured. The compression set was taken as the average of three measurements. The compression set is defined as follows:

$$\text{Compression set} = \frac{d_0 - d_2}{d_0 - d_1} \times 100\% \quad (2)$$

where d_0 is the thickness before compression (mm), d_1 is the thickness during compression (mm), and d_2 is the thickness after 0.5 h of relaxation (mm).

RESULTS AND DISCUSSION

Polyurethanes with monodisperse hard segments were synthesized from prepolymers based on PTMO end-capped with HDI and a chain extender of uniform length. The molecular weight of the PTMO was 1270 g/mol (PTMO₁₂₇₀). As extenders, diamine diamides, diol diamides, and diol diesters were used (Fig. 1). The polyurethanes all had approximately

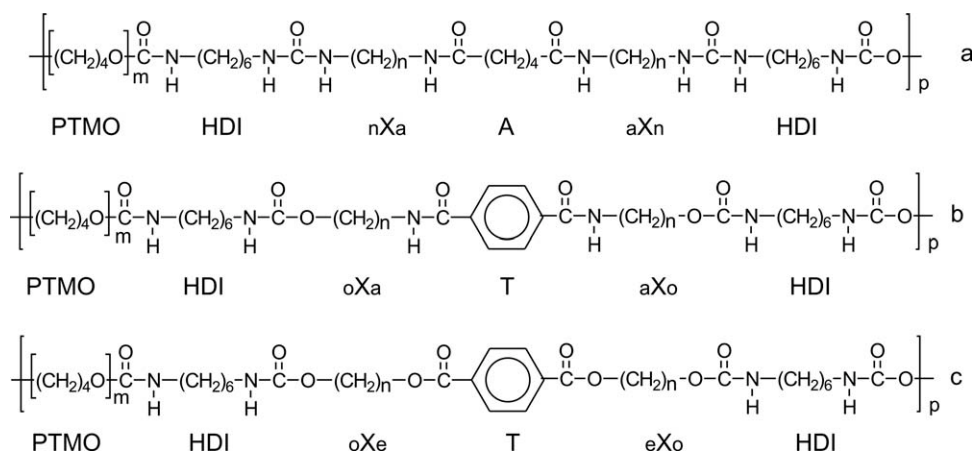


Figure 2 Polyurethanes based on PTMO end-capped with HDI and various chain extenders: (a) diamine diamide, (b) diol diamide, and (c) diol diester [a = amide, A = adipic acid, e = ester, n = urea, o = urethane group, T = terephthalic acid, x = (CH₂)_n].

the same hard-segment length but differed in the number of hydrogen-bonding groups and structural regularity. The effect of the chain extenders on the polymer properties was studied. Amine groups in the chain extender led to urea groups [Fig. 2(a)], and hydroxyl groups led to urethane groups [Fig. 2(b,c)].

The polyurethanes with diamine diamide chain extenders (_nX_aA_aX_n) had two amide groups, two urea groups, and two urethane groups in the hard segment. The length of the diamine (x_n) was varied from 3 to 12 methylene units (3A3 to 12A12, respectively). The copolymers with the diol diamide chain extenders (_oX_aA_aX_o and _oX_aT_aX_o) had two amide groups and four urethane groups in the hard segment, and the length of the amino alcohol (x) was varied from two to three methylene units. The copolymers with the diol diester chain extender (_oX_eT_eX_o) had four urethane groups in the hard segment,

and the diol length (x) was varied from three to six methylene units.

Synthesis of the chain extenders

Three types of chain-extender units were synthesized: diamine diamide, diol diamide, and diol diester (Fig. 1). The diamine diamide extenders were prepared from adipic esters and aliphatic diamines (Table I). With increasing diamine length (x), the molecular weight of the extender increased. After recrystallization, the purity of the compound was high.

The diol diamide chain extenders were prepared from amino alcohols with adipic acid or terephthalic acid and displayed two amide groups and two hydroxyl end groups. The recrystallization of the diol diamide compounds was unnecessary because

TABLE I
Properties of the Chain Extenders

Extender ^a	M_w (g/mol)	Purity (%)	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_m (J/g)
Diamine diamide						
- _n 3 _a A _a 3 _n -	258	99	181	—	—	220 ^b /—
- _n 4 _a A _a 4 _n -	286	98	180	153	27	330 ^b /42
- _n 6 _a A _a 6 _n -	342	98	183	162	21	290 ^b /33
- _n 12 _a A _a 12 _n -	510	100	164	149	15	210 ^b /36
Diol diamide						
- _o 2 _a T _a 2 _o -	254	98	234	172	62	115
- _o 3 _a T _a 3 _o -	280	98	207	100	107	114
- _o 3 _a A _a 3 _o -	284	97	186	136	50	115
Diol diester						
- _o 3 _e T _e 3 _o -	282	99	91	42	49	130
- _o 4 _e T _e 4 _o -	310	99	81	25	56	129
- _o 6 _e T _e 6 _o -	366	97	82	40	42	132

a = amide; e = ester group; M_w = weight-average molecular weight; n = diamine; o = hydroxyl; T_c = crystallization temperature; T_m = melting temperature.

^a The number in the denotation of the compounds represents the number of methylene units.

^b The melting enthalpy in the first heating run.

the compounds were already pure after synthesis, as the amine groups versus the hydroxyl groups were more reactive to the ester groups. Ethanol amine and 3-aminopropanol were used as the amino alcohols.

The diol diester chain extenders had two terephthalate ester groups and two hydroxyl groups. Here, terephthalate was used instead of the adipate to increase the melting temperatures. The length of the diol (x) was varied from three to six methylene units. The uniformity of the extenders was an important issue as only uniform chain extenders could give rise to polyurethanes with monodisperse hard segments. The purity of the chain extenders was estimated with $^1\text{H-NMR}$. To ensure their uniformity, the diamine diamide and diol diester chain extenders were recrystallized. All employed chain extenders were of high purity.

DSC

The melting temperature of the chain-extender unit depended on the number of amide groups and the flexibility of the extender. This flexibility was varied in one of two ways: the center group was either a terephthalic or adipic acid group, and the number of methylene groups (x) was changed from 3 to 12. Chain extenders with a terephthalic group, in comparison with those with an adipic acid group, demonstrated 20°C higher melting temperatures (${}_{\circ}3_a\text{T}_a3_{\circ}$ vs ${}_{\circ}3_a\text{A}_a3_{\circ}$). Increasing the number of methylene groups (x) only slightly decreased the melting temperature of the chain extender. The amount of amide groups (a) had the biggest influence on the melting temperature of the chain extenders. Those with two amide groups (i.e., diamine diamide and diol diamide) displayed 100°C higher melting temperatures versus that with two ester groups (e ; i.e., diol diester). The diamine diamide extender units showed a second transition upon heating and cooling, and this was probably caused by a crystalline transition, as reported previously.^{33–35}

Upon cooling, the chain-extender units crystallized. The undercooling (melting temperature – crystallization temperature) of the diamine diamide extenders with even x values was remarkably low, indicating a rapid crystallization of these units. For the diol diamide and diol diester extenders, the undercooling was approximately 50°C . The melting enthalpy for the diol diamide and diol diester extenders was high, but the melting enthalpy of the diamine diamide extenders was low. For the 3A3-diamine diamide, no crystallization peak was observed.

The diamine diamide extender units demonstrated a very high melting enthalpy during the first heating run, but the crystallization enthalpy and melting en-

thalpy of the second heating run were lower. This difference was probably due to the occurrence of a degradation of the amine end groups during the first heating run. The diamine diamide extenders did not appear to be stable in their melts. The diol diamide and diol diester displayed melting enthalpies in their second heating run that were comparable to those from the first heating run, and the crystallization enthalpies were also similar. This suggests that both the diol diamide and diol diester were stable at temperatures well above their melting temperatures.

Polyurethane copolymers

Synthesis

All the segmented polyurethanes were synthesized from a prepolymer of PTMO₁₂₇₀ end-capped with HDI (HDI-PTMO₁₂₇₀-HDI), and the chain-extender unit was varied. The hard segments of the polyurethanes were formed during the reaction and consisted of the HDI residues from the prepolymer and the chain extender (HDI-chain extender-HDI; Fig. 2).

The prepolymer and the extender unit, as well as the polymerization setup, were dried overnight at 80°C *in vacuo* before use. The prepolymer was weighed into the reactor, after which a solution of the chain extender in 100 mL of DMAc was added. The polymerization of these systems was fast and took place at relatively low temperatures because of the highly reactive isocyanate functional groups. The reaction was carried out for 5 h at 140°C in DMAc to ensure that the polymerization ran to completion. The polyurethanes based on chain extenders with hydroxyl groups (i.e., diol diamide and diol diester) were all transparent and colorless (Table II). The inherent viscosity of the polyurethanes after polymerization varied from 1.0 to 1.8 dL/g, and this suggested that they were high-molecular-weight copolymers. The type of extender had no effect on the inherent viscosities.

The weight percentage of hard segments in the copolymers was based on the chain extender and the isocyanate residues and varied from 32 to 40 wt %. This small difference in concentration was mainly due to the varying length of x in the chain extenders. Depending on the type of extender, the hard segments had different groups (i.e., amide, urea, and urethane) capable of forming hydrogen bonds, and these hydrogen bonds had a strong influence on the melting temperature of the copolymers (Fig. 2 and Table II).

Processing

The polyurethanes with diamine diamide extenders needed to be processed at high temperatures. Because polyurethanes are known to be unstable at

TABLE II
Thermal Properties of Polyurethanes (PTMO₁₂₇₀-HDI-Extender-HDI)

Extender	η_{inh} (dL/g)	HS (%) ^a	Hydrogen groups ^b			T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_m (J/g)	Color
			Amide	Urea	Urethane					
Diamine diamide										
- _n 3 _a A _a 3 _n -	1.6	31.9	2	2	2	222	143	79	5 ^c	Yellow
- _n 4 _a A _a 4 _n -	1.2	32.9	2	2	2	251	209	42	8 ^c	Yellow
- _n 6 _a A _a 6 _n -	1.4	34.8	2	2	2	231	176	55	8 ^c	Yellow
- _n 12 _a A _a 12 _n -	1.3	40	2	2	2	186	142	44	7 ^c	Yellow
Diol diamide										
- _o 2 _a T _a 2 _o -	1.2	31.8	2	0	4	156	105	51	19	Colorless
- _o 3 _a T _a 3 _o -	1.1	32.8	2	0	4	155	121	34	17	Colorless
- _o 3 _a A _a 3 _o -	1.0	32.7	2	0	4	142	98	44	19	Colorless
Diol diester										
- _o 3 _e T _e 3 _o -	1.8	32.7	0	0	4	106	39	67	13	Colorless
- _o 4 _e T _e 4 _o -	1.2	33.7	0	0	4	99	33	66	24	Colorless
- _o 6 _e T _e 6 _o -	1.1	35.6	0	0	4	87	23	64	23	Colorless

η_{inh} = inherent viscosity; a = amide; e = ester group; n = diamine; o = hydroxyl; T_c = crystallization temperature; T_m = melting temperature.

^a HS indicates the hard-segment content based on HDI-_n6_aA_a6_n-HDI, including the HDI residues.

^b Possible hydrogen-bonded groups per hard segment: amide, urea, and urethane.

^c Low because of the degradation or trans-reactions that possibly occurred during the first heating run of the polymer.

high temperatures, the inherent viscosity of the polyurethanes was measured before and after compression molding of the materials to explore possible degradation during the processing. The polyurethanes with diol diamide and diol diesters, processed at temperatures below 200°C, displayed unchanged inherent viscosities, which indicated that no degradation took place in this case. The polyurethanes with diamine diamide had melting temperatures in the range of 186–251°C and were compression-molded at 230°C for 1 min. For polyurethanes, compression molding into homogeneous samples below their melting temperature is quite possible. The inherent viscosity of the compression-molded samples of PTMO₁₂₇₀-HDI-_n3_aA_a3_n-HDI and PTMO₁₂₇₀-HDI-_n4_aA_a4_n-HDI increased to high values of 3.7 and 4.0 dL/g, respectively. These samples were difficult to dissolve. The very high inherent viscosities after pressing at 230°C were probably due to some network formation. At processing temperatures higher than 230°C, a strong decrease in the inherent viscosity was observed. For example, PTMO₁₂₇₀-HDI-_n3_aA_a3_n-HDI- compression-molded at 240°C (1 min) displayed a white color, and the inherent viscosity decreased from 1.6 to 0.7 dL/g. The degradation of the polyurethanes was due to the instability of the urea and urethane groups at higher temperatures.^{1,2,20} A similar decrease in the inherent viscosity was observed for MDI-based polyurethanes with diamine diamide extenders.²⁶

DSC

The thermal properties of the polymers were studied with DSC. During the heating cycle, a peak corre-

sponding to the melting of the hard segments was observed. The melting temperature of the hard segments depended on the type and number of hydrogen-bonding groups as well as the flexibility and structural regularity of the hard segments. As the concentration of hard segments in the copolymers was approximately the same for the entire series, the melting temperature was influenced only by the structure of the hard segment. The polyurethanes with hard segments based on diamine diamide chain extenders had two amide groups, two urea groups, and two urethane groups and displayed melting temperatures of 190–250°C. For the polymers with diamine diamide as an extender, a second endotherm transition was observed, and upon cooling, a second exotherm could be seen. This was probably a crystalline transition, which is often observed in (poly)amides.^{33–35} Polymers with diamine diamide extenders with an even number of methylene units in the diamine had a higher copolymer melting temperature.

The hydrogen bonding in an extended urethane-urea-amide segment is dependent on whether x in the diamine is an even or uneven number (corresponding to the number of methylene groups in the chains). When x is uneven (e.g., HDI-_n3_aA_a3_n-HDI), the segment has six possible hydrogen bonds, whereas for an even value of x (e.g., HDI-_n4_aA_a4_n-HDI, HDI-_n6_aA_a6_n-HDI and HDI-_n12_aA_a12_n-HDI), only four hydrogen bonds seem possible (Fig. 3). A two-dimensional scheme of the urethane-urea-amide segment with an uneven value of x had optimal hydrogen bonding. However, the planar extended structure of the hard segment with an even value of x shows that either the urethane or amide groups are hindered from forming hydrogen bonds.

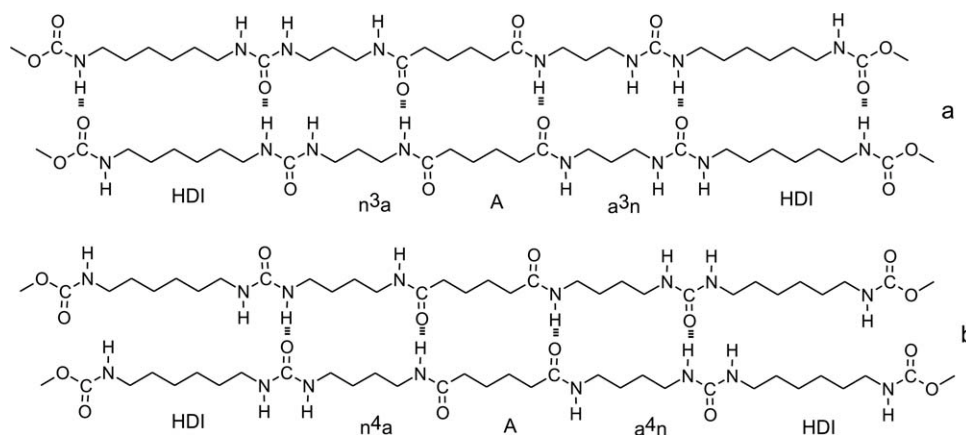


Figure 3 Packing of hard segments with (a) uneven and (b) even numbers of diamine diamide chain extenders.

Nevertheless, even though the hard segments with an even number of diamines had lower hydrogen-bonding possibilities in their extended form, they displayed higher melting temperatures. This suggests that with an even value of x , full hydrogen bonding took place in a nonextended form of the methylene units. Increasing x (even-numbered) in the extenders from 4 to 12 ($n_4A_4n_4$ vs $n_{12}A_{12}n_{12}$) led to a decrease in the melting temperature of the polymer by 65°C.

The polyurethanes with diol diamide extenders had two amides and four urethane groups in the hard segments and displayed a melting temperature of approximately 155°C (Table II). When a terephthalic acid was employed instead of an adipic acid in the hard segment ($o_3T_a3_o$ vs $o_3A_a3_o$), the melting temperature of the polyurethane was raised by only

13°C. The melting temperature for the material with ethylene units (ethanol amine) was slightly lower than for the material with propylene units (3-amino-propanol). It is known that ethylene units in poly(ethylene terephthalate) limit high crystallinity.

A scheme of a planar extended hard-segment packing of diol diamide with an even-numbered value of x (e.g., amino-ethanol) shows that hydrogen bonds were possible for the four urethane groups; however, the two amide groups were not hydrogen-bonded [Fig. 4(a)]. The packing of the hard segment with an uneven value of x (e.g., aminopropanol) in the chain extender demonstrates the possibility of hydrogen bonding in the four urethane groups and in the two amide groups [Fig. 4(b)]. In comparison with the hard segment based on 1,3-diamine [Fig. 3(b)], a hard segment with 1,3-aminopropanol [Fig.

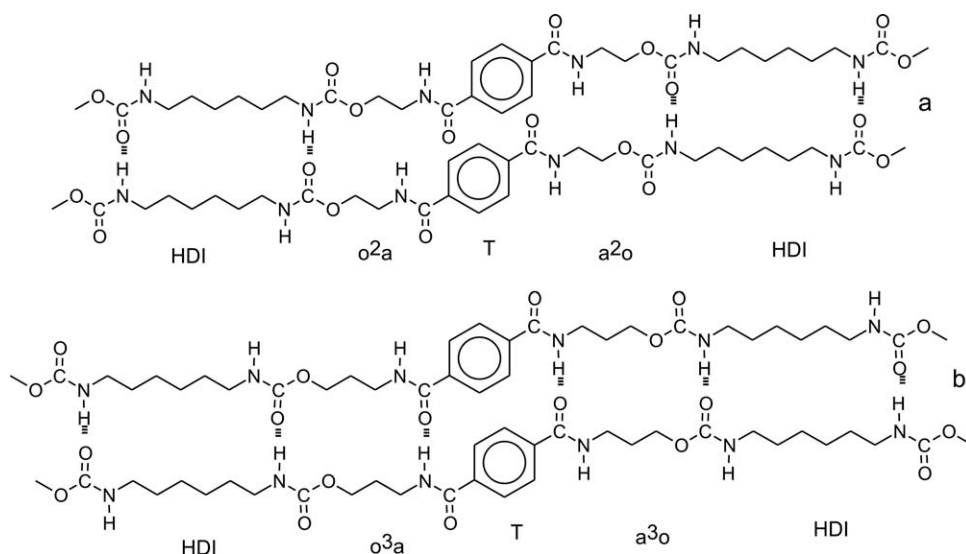


Figure 4 Packing of hard segments with (a) uneven and (b) even numbers of diol diamide chain extenders.

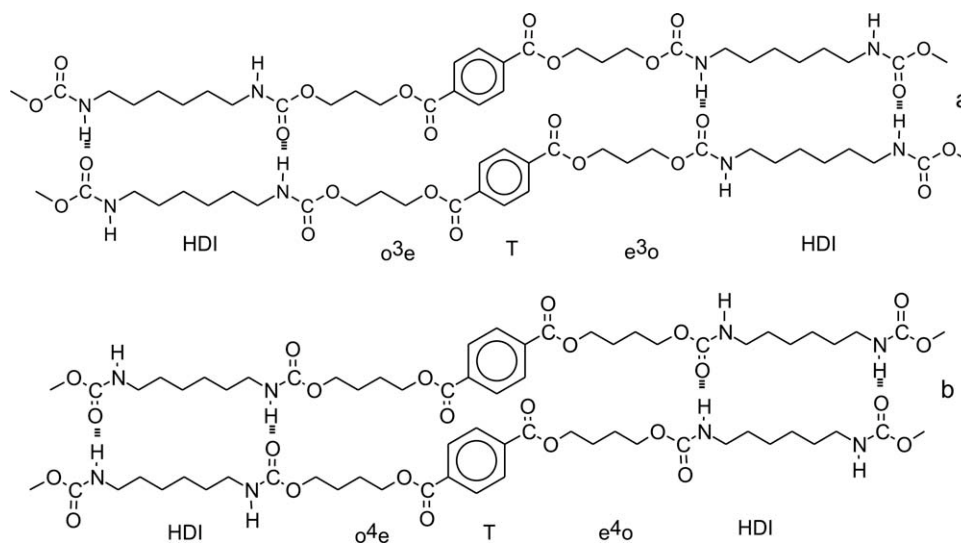


Figure 5 Packing of hard segments with uneven and even numbers of diol diester chain extenders.

5(b)] contains four urethane groups instead of two urethane groups and two urea groups, and as a result, the melting temperature was lowered by 80°C.

The polyurethanes with diol diester extenders with only four urethane groups displayed melting temperatures of about 100°C, and changing x from an even number to an uneven number of diols had little effect on the melting temperature of the polymers. The hard segments with an uneven value of x seemed to experience better packing than their even-numbered counterparts (Fig. 5). With respect to the packing of the hard segments with an even number of diol diester extenders (i.e., $x = 4$ or 6), the number of hydrogen bonds was still four, but the terephthalate ring seemed to be sterically hindered.

Leaving out the two amide groups in the hard segments (${}_{o3a}T_a3_o$ vs ${}_{o3e}T_e3_o$) lowered the melting temperature of the polymer by about 50°C. Moreover, changing x , that is, the number of methylene units, from an even number to an uneven number had a strong effect on the melting temperature in the case of the diamine diamide extended material, whereas only a small influence was seen on the copolymers with diol diamide and diol diester extenders.

The melting enthalpy of the hard segments in the polymers was determined in the second heating run and was found to vary from 5 to 24 J/g. It was particularly low for the diamine diamide extended material. This might have been due to the high temperatures employed during the first heating run, which increased the molecular weight and possibly caused some degradation to take place. A high-molecular-weight resulted in a high melt viscosity that lowered the rate of crystallization. Upon cooling, the monodisperse hard segments in the polymer crystal-

lized at a temperature 34–79°C below the melting temperature of the polymer. The hard segments based on diol diester displayed more significant undercooling values than their diol diamide and diamine diamide extended counterparts. A larger amount of hydrogen-bonding groups in the hard segments seemed to increase the crystallization rate; however, it is not yet clear whether the value of x had any effect on the crystallization rate of the polymer.

DMTA

The dynamic mechanical properties of the copolymers were determined by means of DMTA of compression-molded samples processed at 20°C above their melting temperature but never above 230°C. At temperatures higher than 230°C, serious degradation was expected during the melt processing. It is as of yet unclear how compression molding at or below the melting temperatures affects the properties of polyurethanes (e.g., polymers with ${}_n4_aA_a4_n$ and ${}_n6_aA_a6_n$). The results of DMTA are summarized in Table III.

TPUs with diamine diamide chain extenders. It should be stressed that the polyurethanes were thermally unstable above 200°C and that the DMTA results may be influenced by degradation of the polymer during processing. Polyurethanes with diamine diamide extenders displayed low values of the soft-segment-phase glass-transition temperature, G' values that were almost temperature-independent, and relatively sharp flow temperatures (melting; Fig. 6).

The soft-segment-phase glass-transition temperature for this polymer series was low (–68°C), indicating good phase separation. The glass transition of

TABLE III
DMTA Properties of Polyurethanes with Different Chain Extenders (PTMO₁₂₇₀-HDI-Extender-HDI)

Extender	HS (wt % ^a)	η_{inh} (dL/g)	NH groups ^b			T_g (°C)	$G'_{25^\circ C}$ (MPa)	Tan $\delta_{25^\circ C}$ (—)	T_{flow} (°C)	$\Delta G' \times 10^{-3}$ (°C ⁻¹)	CS (%)
			Amide	Urea	Urethane						
Diamine diamide											
- _n 3 _a A _a 3 _n -	31.9	1.6	2	2	2	-68	22	0.05	175	8	18
- _n 4 _a A _a 4 _n -	32.9	1.2	2	2	2	-67	49	0.05	245	4	21
- _n 6 _a A _a 6 _n -	34.8	1.4	2	2	2	-67	49	0.04	225	5	25
- _n 12 _a A _a 12 _n -	40.0	1.3	2	2	2	-65	47	0.05	195	10	14
Diol diamide											
- _o 2 _a T _a 2 _o -	31.7	1.2	2	0	4	-67	44	0.04	155	7	42
- _o 3 _a T _a 3 _o -	32.8	1.1	2	0	4	-65	56	0.03	160	7	37
- _o 3 _a A _a 3 _o -	32.7	1.0	2	0	4	-66	34	0.03	140	8	26
Diol diester											
- _o 3 _e T _e 3 _o -	32.7	1.8	0	0	4	-65	39	0.05	100	2	26
- _o 4 _e T _e 4 _o -	33.7	1.2	0	0	4	-66	31	0.05	95	3	26
- _o 6 _e T _e 6 _o -	35.6	1.1	0	0	4	-67	23	0.05	80	3	30

η_{inh} = inherent viscosity; a = amide; e = ester group; n = diamine; o = hydroxyl; T_{flow} = flow temperature; T_g = glass-transition temperature.

^a HS indicates the hard-segment content based on HDI-extender-HDI, including the HDI residues.

^b Possible hydrogen-bonded groups per hard segment: amide, urea, and urethane.

PTMO₁₂₇₀-HDI-_n12_aA_a12_n-HDI was somewhat broader than that of the other materials. G' at 25°C for the polymers with an even value of x was approximately 50 MPa, whereas the corresponding value for the materials with an uneven number of methylene units in the case of diamine ($x = 3$) was 22 MPa. The high G' value obtained for the polymers with an even number of diamine diamide extenders was probably a result of a high degree of crystallinity of the hard segment. The tan δ (G'/G'') value was low (0.05) for all the polyurethanes, suggesting low mechanical damping behavior. These copolymers had an almost temperature-independent G' value in the temperature range between room temperature and the flow temperature (a low $\Delta G'$

value), and this is typical behavior for segmented block copolymers with monodisperse hard segments.¹⁶⁻²⁶ However, the polymer with $x = 12$ displayed a modulus that was more temperature-dependent, and this suggested that the crystallites were not constant in thickness. This effect can be explained by a possible partial folding of the long $-(CH_2)_{12}-$ units. In polyamides, folding of the chain at the crystallite surface readily takes place for methylene lengths longer than six units.³⁶ If folding in the long $-(CH_2)_{12}-$ units of the diamine had taken place, then the crystallites would have had variations in their thicknesses.

The flow (melting) temperature of the polyurethanes was found to decrease with increasing even

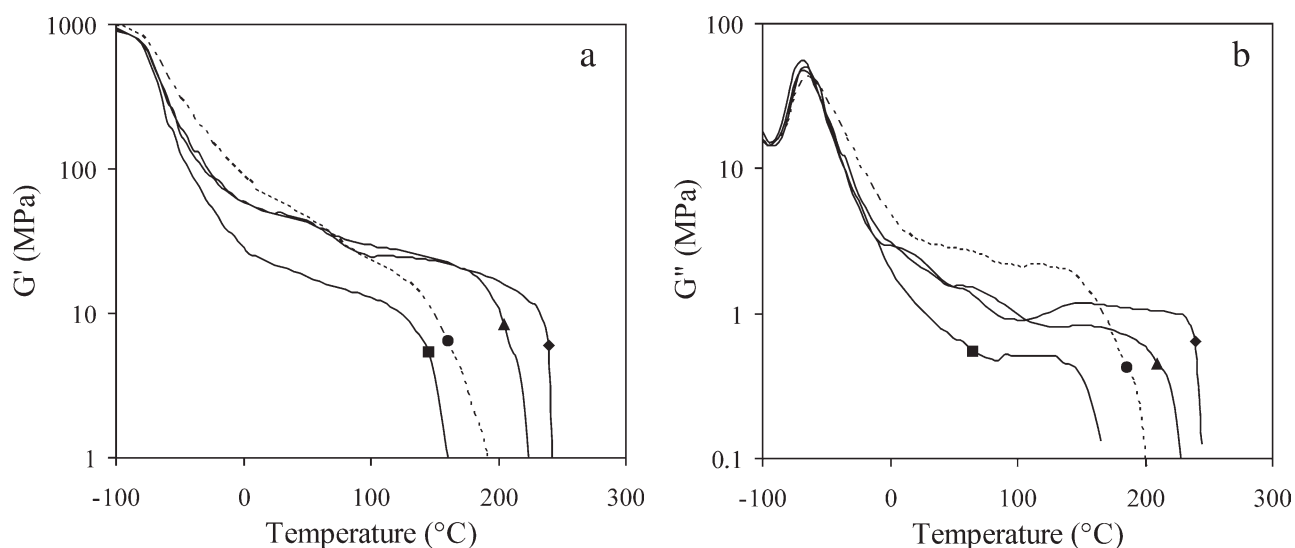


Figure 6 (a) Storage and (b) loss moduli of segmented polyurethanes with diamine-diamide chain extenders: (■) -_n3_aA_a3_n-, (◆) -_n4_aA_a4_n-, (▲) -_n6_aA_a6_n-, and (●) -_n12_aA_a12_n-.

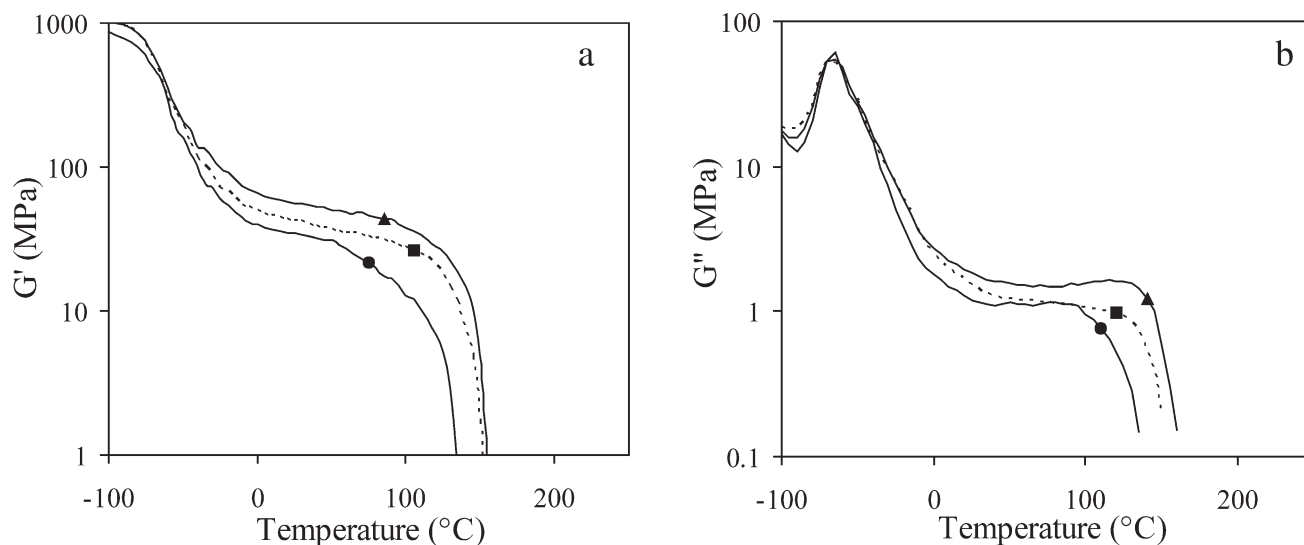


Figure 7 (a) Storage and (b) loss moduli of the segmented polyurethanes with diol-diamide extenders: (■) $-o_2aTa_2o-$, (▲) $-o_3aTa_3o-$, and (●) $-o_3aAa_3o-$.

x values and corresponded reasonably well to the melting temperatures measured by DSC (Table II). This decrease was a result of the more aliphatic structure for longer chain extenders. The flow temperature of $-n_3aAa_3n-$ (175°C) did not coincide with the melting temperature measured with DSC in the second heating run (222°C; Table II). However, in the first heating run of the polymer, an extra melting/crystallization peak was observed at about 175°C. During the second DSC heating run, only a small melting peak at 222°C was present. This indicates that upon fast cooling of very viscous materials, the crystallization of the hard segments was incomplete, and this possibly resulted in a low flow temperature and a low modulus at room temperature.

On the basis of the packing of the hard segments (cf. Fig. 3), the hard segments in the polyurethanes with uneven x chains in the chain extender were expected to display a higher degree of crystallinity than hard segments with an even number of methylene groups. Surprisingly, the polymer with uneven value of x (i.e., 3) exhibited both a low modulus and a low flow temperature, which led to the conclusion that the two-dimensional scheme of the extended hard segments did not give the full picture of the actual situation.

TPUs with diol diamide extenders. The DMTA properties of the polyurethanes with three diol diamide extenders, namely, o_2aTa_2o- , o_3aTa_3o- , and o_3aAa_3o- , are displayed in Figure 7. These polymers were transparent and tough and could be easily melt processed. The inherent viscosity of the polymers did not decrease during molding, and thus degradation did not occur.

The TPUs with diol diamide extenders had hard segments made up of two amide groups and four urethane groups. The melting temperatures of these polyurethanes were appreciably lower than that of the corresponding diamine diamide. Thus, changing the two urea groups into two urethane groups lowered the melting temperature (Table III).

The glass-transition temperature of the polyurethanes with diol diamide extenders was low (−68°C), indicating good phase separation. The G' values at 25°C for the polymers with 2T2-, 3T3-, and 3A3-diol diamides were 44, 56, and 34 MPa, respectively. The moduli of the polymers with 2T2- and 3T3-diol diamides were high, and thus the degree of crystallinity must have been high for these polymers. The modulus of PTMO₁₂₇₀-HDI- o_3aAa_3o -HDI was somewhat lower. The presence of a terephthalic group instead of an adipic group in the extender (o_3aTa_3o vs o_3aAa_3o) increased the modulus of the polymer. These polyurethanes displayed an almost temperature-independent rubber modulus from room temperature to near the melting temperature, and this was due to the presence of monodisperse hard segments. The flow temperatures of the polymers were 140–160°C, which corresponded well to the melting temperatures as measured by DSC. A terephthalic group in the hard segments, as opposed to an adipic group (o_3aTa_3o vs o_3aAa_3o), increased the flow temperature of the polymer by 20°C. The polymer with an x value of 2 had a somewhat lower modulus as well as lower melting and flow temperatures in comparison with its counterpart with an x value of 3. This might be due to the even/uneven effect of x and/or the fact that the crystallization is often slow and incomplete for ethylene groups

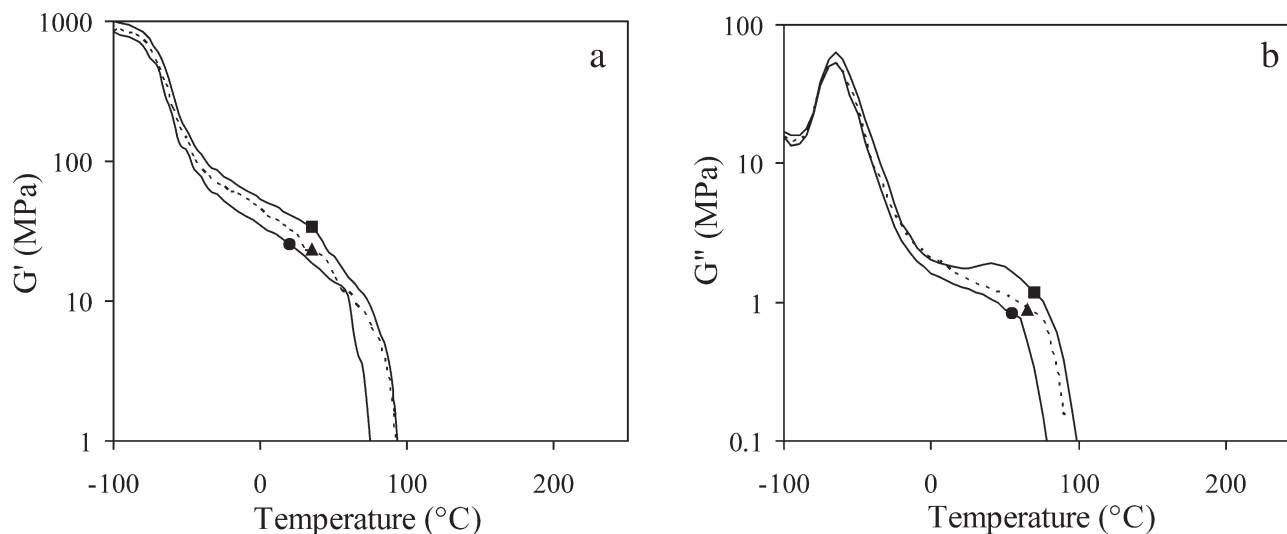


Figure 8 (a) Storage and (b) loss moduli of the segmented polyurethanes with diol-diester extenders: (■) $-o_3eTe_3o-$, (▲) $-o_4eTe_4o-$, and (●) $-o_6eTe_6o-$.

[poly(ethylene terephthalate) vs poly(butylene terephthalate)]. The planar extended hard-segment packing of diol diamide materials with even values of x showed that hydrogen bonding was a possibility for the four urethane groups but not for the two amide groups (Fig. 4). The packing of the hard segments with an uneven value of x demonstrated the possibility of hydrogen bonding in the four urethane groups and in the two amide groups. The moduli at room temperature were lower than those for the even-numbered diamine diamide extenders but higher than those for the uneven-numbered diamine diamide extenders. The two urea groups had a stronger effect on the melting temperature than the urethane groups as well as a slight effect on the modulus at room temperature.

TPUs with diol diester chain extenders. The hard-segment diol diester extenders contained four urethane groups. For this series of polymers, the glass-transition temperature values were approximately -66°C (Fig. 8). The low glass-transition temperature indicated good phase separation for the copolymers with diol diester extenders. The rubber modulus in the plateau region was not independent of temperature, although the diol diester units were uniform. This was probably a result of the low melting temperature creating only a small temperature window for the rubbery plateau. The flow temperature of these polyurethanes decreased with increasing x in the diol, as was also observed from the DSC measurements (Table II). This effect of the number of methylene units was also seen for the diamine diamide series and was due to a more flexible structure. The rubber modulus at 25°C for the polyurethane with the uneven value of x (i.e., 3) in the diol diester extender was relatively high (39 MPa) but decreased

with the diol length. The hard segments with an uneven value of x seemed to experience better packing than their counterparts with an even value of x , and consequently, the crystallinity of the hard segments was higher (Fig. 5).

DMTA conclusions. The overall picture of the DMTA results was that the glass-transition temperature of the polyether phase was low for all systems. The flow (melting) temperature of the polymers increased in the following order: four urethane groups < four urethane groups + two amide groups < two urethane groups + two urea groups + two amide groups in the hard segments. A terephthalic group in the hard segment provided a 20°C higher melting temperature in the polymer versus an adipic group. The moduli at room temperature were all comparatively high and were found to be particularly high with even numbers of diamines and terephthalamides in the amino alcohols. The length of the diamine, however, did not seem to have a strong effect on the modulus, and the influence that the number of hydrogen-bonding units in the hard segments had on the modulus was unclear. The modulus of the copolymers was higher with the diamine than with the diol.

Compression set

Compression set tests are standard measurements used to explore the elastic behavior of a polymer. A lower compression set value means more elastic behavior of the polymer. The compression set values of the studied polyurethanes ranged from 18 to 42% (Table III). The polyurethanes based on diamine diamide chain extenders displayed somewhat lower compression set values than their counterparts based

on diol diamide or diol diester chain extenders. The hard segments with diamine diamide extenders were thus more resistant to deformations. The length of x in the diamine diamide extenders did not seem to have a particular effect on the compression set values.

CONCLUSIONS

Polyurethanes with monodisperse hard segments were synthesized from prepolymers based on PTMO (with a length of 1270 g/mol and end-capped with HDI) and one of three uniform chain extenders: diamine diamide ($-_a x_n A_n x_a-$), diol diamide ($-_o x_n A_n x_o-$ and $-_o x_n T_n x_o-$), or diol diester ($-_o x_e T_e x_o-$). The chain extension of the prepolymer resulted in polyurethanes with monodisperse hard segments. The concentration of hard segments (HDI-chain extender-HDI) in the polymers was approximately 32 wt %, and the obtained polyurethanes were elastic, being colorless and transparent to slightly yellowish and transparent.

The polyurethanes with monodisperse hard segments all had low glass-transition temperatures ($\sim -67^\circ\text{C}$), and this indicated that very little hard segment was dissolved in the PTMO phase. The moduli of the polymers were almost temperature-independent from room temperature to near the melting temperature. Moreover, the melting transitions were sharp. This is typical behavior of segmented block copolymers with monodisperse hard segments and indicates that the monodispersity of the hard segments was maintained during the polymerization and processing.

The use of diamine diamide as the chain extender led to polyurethanes with hard segments consisting of 2 urea groups, 2 urethane groups, and 2 amide groups. The resulting polyurethanes had high melting temperatures ($186\text{--}251^\circ\text{C}$), high moduli at room temperature, and low compression set values. Increasing the length of the chain extender (x) resulted in polymers with lower melting temperatures, and employing a chain extender with an uneven value of x was expected to give rise to better packing of the hard segment. Nonetheless, both the melting temperature and the modulus at room temperature were lower.

The hard segments of the polyurethanes with diol diamide chain extenders contained four urethane groups and two amide groups, and the polymers displayed melting temperatures in the range of $140\text{--}160^\circ\text{C}$. The polyurethane with three methylene units in the amino alcohol $-_o 3_a A_a 3_o-$ had a lower melting temperature, a higher modulus, and a higher compression set value in comparison with the similar diamine diamide $-_a 3_a T_a 3_a-$ material. Incorporating a terephthalic acid group instead of an adipic acid

group increased the modulus and melting temperature of the polymer; however, the compression set value was also raised. The polyurethane with monodisperse HDI- $-_o 3_a T_a 3_o-$ HDI hard segments demonstrated an interesting combination of properties: it was a transparent, colorless material with a melting temperature of 165°C , a G' value at room temperature of 56 MPa, and a readily melt-processable nature.

The hard segments of the polyurethanes with diol diester chain extenders contained four urethane groups, and the resulting polymers exhibited low melting temperatures ($80\text{--}100^\circ\text{C}$) because of the small number of hydrogen-bonding possibilities. The type of diol used had an almost insignificant influence, and it was expected that the properties could be improved by the incorporation of longer ester segments.

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