Polyurethane Triblock Copolymers With Mono-Disperse Hard Segments. Influence of the Hard Segment Length on Thermal and Thermomechanical Properties

Araichimani Arun,^{1,2} Kasper K.J. Baack,¹ Reinoud J. Gaymans¹

¹ Department of Polymer and Biomaterials, University of Twente, 7500 AE Enschede, The Netherlands

² Dutch Polymer Institute (DPI), 5600 AX Eindhoven, The Netherlands

Polyurethane triblock copolymers were synthesized by reacting 4,4'-methylenebis(phenyl isocyanate) (MDI)endcapped poly(tetramethylene oxide) (PTMO) with mono-amine-amide (MMA) units. Four different MMA units were used, i.e. no-amide (6m), mono-amide (6B), di-amide (6T6m) and tri-amide (6T6B), based on hexylamine (6m), 1,6-hexamethylenediamine (6), terephthalic acid (T), and benzoic acid (B). The PTMO had a molecular weight of 2000 g/mol. Thermal and thermo-mechanical properties were studied by means of differential scanning calorimetry and dynamic mechanical analysis, respectively. The structure of the carbonyl bond was explored by infra-red analysis and the elastic behavior of the materials by compression set experiments. The triblock polyurethanes with mono-disperse, hard end-segments displayed low molecular weights (3200-3800 g/mol). The crystallinity of the MDI urethane-urea group was found to depend on the structure of the amide. Increasing the number of amide bonds in the mono-disperse hard segment increased the modulus and the hard segment melting temperature, and decreased the compression set values. The low temperature properties were hardly affected by the amide length. POLYM. ENG. SCI., 48:1222-1230, 2008. © 2008 Society of Plastics Engineers

INTRODUCTION

Thermoplastic polyurethanes (TPUs) are linear segmented block copolymers inherent of thermoplastic elastomer properties [1, 2]. The hard segments in the polyurethanes act as physical crosslinks as well as reinforcing fillers. TPUs are generally comprised of poly(tetramethylene oxide) (PTMO) as the soft segment (SS) and 4,4'methylenebis(phenyl isocyanate) (MDI) and butanediol (BDO) as the hard segment (HS). The PTMO SS has a low T_g and a melting temperature just below room tem-

Published online in Wiley InterScience (www.interscience.wiley.com). © 2008 Society of Plastics Engineers perature, and due to a strain-induced crystallization of PTMO, polyurethanes often display high fracture stresses. The MDI-BDO HS is able to crystallize, but both the crystallinity and the crystallization rate are low leading to moderate melting temperatures. A faster crystallization and a higher crystallinity of the HSs can be obtained when the HS are mono-dispersed in length [3–14]. Unfortunately, such mono-disperse polyurethane segments are not thermally stable due to the fast randomization of the urethane segments in the melt [7]. Upon such randomization, the mono-dispersity is lost and with that the specific properties. Polyurethanes with mono-disperse HSs with an enhanced thermal stability have been obtained with amide extenders [12, 13]. These TPUs were prepared from diisocyante-endcapped polyether with diamine-diamide extenders. HSs based on diamine-amide extenders can crystallize into nano-ribbons with high aspect ratios and thereby give rise to a nanofiber-reinforced system. Because of the high crystallinity of the mono-disperse HSs, nearly all of the HS are in the crystalline state. As a result of this high crystallinity, the network formation is efficient and also even at low HS contents. Other investigated copolymers include those based on crystallizable amide endgroups [15]. The presence of crystallizable amide groups at the chain ends have led to increased moduli and, surprisingly, also to the formation of network structures (gelling) in the melt. Studies have also been carried out on triblock copolymers with noncrystallizing hydrogen bonding groups at the chain-ends [16, 17]. Such triblock copolymers displayed the behavior of high-molecularweight polymers. It would thus be interesting to explore preferably thermally stable, triblock polyurethanes with mono-disperse HSs at the chain-ends.

Triblock polyurethanes with mono-functional amineamide extenders were therefore prepared and investigated with respect to the influence of the endblock length on their thermal, thermo-mechanical, and tensile properties. The copolymers were based on MDI-endcapped PTMO₂₀₀₀ reacted with mono-amine-amide (MMA) units. Four different

Correspondence to: Reinoud J. Gaymans; e-mail: r.j.gaymans@tnw. utwente.nl

DOI 10.1002/pen.21083

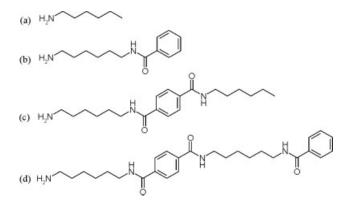


FIG. 1. The chemical structure of (a) 6m, (b) 6B, (c) 6T6m, and (d) 6T6B.

MMA units were used, i.e. no-amide, mono-amide, di-amide, and tri-amide (see Fig. 1), and these MMA units were derived from hexylamine (6m), 1,6-hexamethylenediamine (6), terephthalic acid (T), and benzoic acid (B). When combined with the amine group, the isocyanate formed a urea group, which led to urethane-urea groups being present in the copolymer. The number of amide bonds in the HSs was varied from 0 to 3 and the properties of the synthesized polyurethanes were studied. The properties were expected to depend strongly on the network structure formation of the end-groups. The present study thus reports on the effects of varying the length of the amide in the MAA and a subsequent investigation will be devoted to varying the mid segment length. These low-molecularweight materials showed good mechanical property and processability.

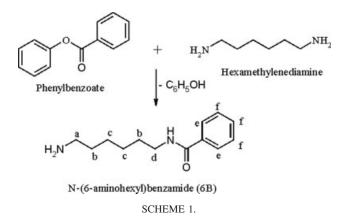
EXPERIMENTAL

Materials

Anhydrous *N*,*N*-dimethylacetamide (DMAc), 1,6-hexamethylenediamine (HMDA), phenylbenzoate, hexylamine, and *N*-methyl-2-pyrrolidinone (NMP) were purchased from Aldrich. Methyl(4-chlorocarbonyl)benzoyate (MCCB) was purchased from Dalian (No.2 Organic Chemical Works, China) and PTMO endcapped with MDI (2847 g/mol) was generously donated by Crompton Corporation. Butyl acetate was obtained from Fluka. *N*hexane, acetone, and toluene were purchased from Biosolve, and diethyl ether was obtained from Lamers and Plueger. All chemicals were used as received.

Synthesis of N-(6-Aminohexyl)Benzamide (6B) (Scheme 1)

The synthetic procedure of mono-amine-mono-amide is given below. The set-up consisted of a three-necked 100 mL round-bottomed flask equipped with a reflux condenser and fitted with a calcium chloride tube, a magnetic stirrer and a nitrogen inlet. HMDA (34.9 g, 0.30 mol) and



phenylbenzoate (5.95 g, 0.03 mol) were charged to the flask. A large excess of HMDA was used to prevent the formation of by-products. The reaction was carried out in the melt (without a solvent) at 120°C for 8 h. Excess HMDA was distilled off under reduced pressure at a temperature rising from 120 to 160°C. After the distillation, ~ 100 mL of a 5% HCl solution was added and the mixture was stirred for half an hour. The formed precipitate was filtered off, after which the filtrate was transferred into a separating funnel and 100 mL of a 10% sodium hydroxide (NaOH) solution was added batch-wise until precipitation no longer formed upon addition of the NaOH. After ~ 2 h, the lower aqueous layer was decanted and the oily layer was kept and dried overnight in air. The compound had a melting temperature of 24-26°C. Moreover, ¹H NMR (TFA-d, δ) spectra were taken and the observed peaks are presented in Table 1.

The purity of the 6B was calculated according to the following equation,

Purity =
$$\frac{\left(\frac{\text{peak}_{a}}{\text{peak}_{b} + \text{peak}_{c} + \text{peak}_{d}}\right)}{\text{TR}} \times 100\% = \frac{\left(\frac{2}{10.13}\right)}{0.2} = 99\%$$
 (1)

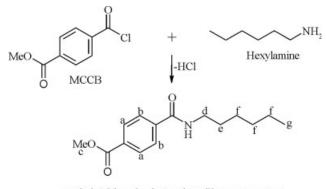
where, TR = Theoretical ratio.

Synthesis of N-(Aminohexyl)-N-Hexylterephthalamide $(6T6_m)$

The mono-amine-di-amide (6T6m) was synthesized in a two-step procedure, where the first step consisted in obtaining the intermediate T6m.

 TABLE 1.
 ¹H-NMR results of the mono-amine-mono-amide (6B) corresponding to the structure in Scheme 1.

Proton peak	δ (ppm)	Туре	H-atoms	Integral
а	3.3	singlet	2	2.07
b	1.8	singlet	4	4.09
с	1.5	singlet	4	4.04
d	3.8	singlet	2	2
e	7.6	doublet	2	1.98
f	7.8	doublet	3	3



methyl-4-[(hexylamino)carbonyl]benzoate (T6m)

SCHEME 2.

Step 1: Synthesis of Methyl-4-[(Hexylamino)Carbonyl]-Benzoate (T6_m) (Scheme 2). The set-up for the synthesis of methyl-4-[(hexylamino)carbonyl]benzoate $(T6_m)$ consisted of a three-necked round-bottomed flask equipped with a pressure equalizer and fitted with a calcium chloride tube, a magnetic stirrer and a nitrogen inlet. MCCB (5.16 g, 0.026 mol) was weighed into the flask, 50 mL of NMP was added and this was stirred until the solution became homogeneous. Hexylamine (2.53 g, 0.075 mol) was stirred in a separate beaker with 50 mL NMP and was then added drop-wise (during ~ 30 min) to the MCCB solution using the pressure equalizer. After 2 h of stirring, 30 mL of methanol was added and after stirring for another 2 h, the solution was precipitated in water and filtered. The precipitate was washed with *n*-hexane at 70°C for 15 min, after which this solution was cooled to \sim 35°C and filtered. The precipitate was dried in air. A yield of 60% was obtained and the $T_{\rm m}$ was 103–105°C. ¹H NMR (TFA-d, δ): 8.3 (2H, d, marked as 'a'), 7.9 (2H, d, marked as 'b'), 4.1 (3H, s, marked as 'c'), 3.7 (2H, t, marked as 'd') 1.8 (2H, m, marked as 'e'), 1.4 (6H, m, marked as 'f'), and 0.9 (3H, t, marked as 'g').

Step 2: Synthesis of N-(Aminohexyl)-N-Hexylterephthalamide ($6T6_m$) (Scheme 3). The set-up for the synthesis of N-(aminohexyl)-N-hexylterephthalamide ($6T6_m$) consisted of a three-necked 100 mL round bottomed flask equipped with a water cooler and fitted with a calcium

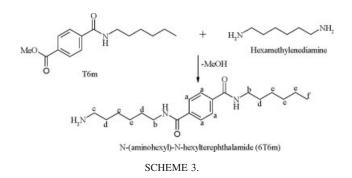


TABLE 2. ¹H-NMR results of mono-amine-di-amide (6T6m) corresponding to the structure in Scheme 3.

Proton peak	δ (ppm)	Туре	H-atoms	Integral
а	8	singlet	4	4
b	3.8	triplet	4	4
с	3.4	singlet	2	1.83
d	2.0	multiplet	6	5.82
e	1.6	multiplet	10	9.84
f	1.0	triplet	3	2.61

chloride tube, a magnetic stirrer and a nitrogen inlet. HMDA (11.64 g, 0.1 mol) and T6m (2.64 g, 0.01 mol) were weighed into the flask, and this mixture was stirred for 8 h at 80°C after which the product was precipitated in water. The reaction product was repeatedly washed with water and then filtered. The precipitate was washed with acetone, filtered, and dried in air. The yield was 50% and the $T_{\rm m}$ was 185–187°C. The results form ¹H NMR (TFA-d, δ) experiments are summarized in the Table 2.

The purity of the HS (6T6m) was calculated using the formula,

Purity
$$=\frac{\frac{\text{peak}_{f}}{\text{peak}_{c}} \times 100 = \frac{\left(\frac{2.61}{1.83}\right)}{1.5} \times 100 = 95\%$$
 (2)

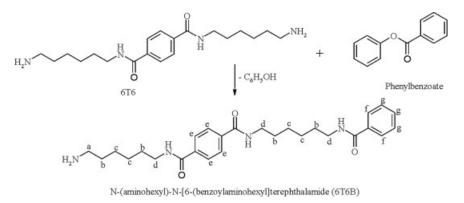
Synthesis of N-(Aminohexyl)-N-

[6-(Benzoylaminohexyl)Terephthalamide] (6T6B) (Scheme 4)

The mono-amine-tri-amide (6T6B) was synthesized in a two-step procedure. In the first step, 6T6 was obtained according to the procedure given by Krijgsman and coworkers. [14]. In Step 2, the set-up consisted of a threenecked round-bottomed 1-L flask equipped with a reflux condenser and fitted with a calcium chloride tube, a magnetic stirrer and a nitrogen inlet. 6T6-diamine (18.10 g, 0.05 mol) and phenylbenzoate (9.90 g, 0.05 mol) were charged to the flask, and 300 mL of NMP was added after which the solution was stirred for 8 h at 120°C. The solution became clear after ~ 30 min and remained clear during the rest of the reaction. The mixture was allowed to cool overnight and was then filtered. To the filtrate, 1.5 L of diethyl ether was added and the formed precipitate was filtered and washed with diethyl ether. The precipitate was then suspended in water (\sim 300 mL) at 70°C for 1 h and filtered under warm conditions. The precipitate was further washed with acetone (~300 mL) and dried in air. The yield was 35%, and the $T_{\rm m}$ was 195-197°C. The ¹H NMR (TFA-d, δ) results are summarized in the Table 3.

The purity of the 6T6B was calculated using the formula,

Purity =
$$\frac{\left(\frac{\text{peak}_{e}}{\text{peak}_{f} + \text{peak}_{g}}\right)}{\text{TR}} \times 100\% = \frac{\left(\frac{4}{5.17}\right)}{0.8} = 97\%$$
 (3)



SCHEME 4.

General Synthetic Procedure for the Polyether(urethaneurea-amide)-Based Triblock Copolymer (Scheme 5)

The polymerizations of the triblock copolymers were carried out using a 250 mL stainless steel reactor, fitted with a glass lid, a magnetic coupled stirrer, and a nitrogen inlet. The experimental set-up was dried prior to the reaction. The reaction of the MDI-endcapped $PTMO_{2000}$ (20 g, 0.007 mol) with 6B (2.70 g, 0.014 mol) in anhydrous DMAc is given here as an example. The prepolymer was weighed into the reactor and heated to 100°C. The reactor was further heated to 130°C after which 6B was dissolved in 100 mL of DMAc at 120°C and charged to the reactor. The reaction was continued while stirring for 4 h at 130°C under a nitrogen atmosphere. Subsequently, the solvent was stripped in vacuo at a pressure <0.4 mbar, and the reactor was slowly cooled while maintaining the low pressure. The copolymer obtained was brittle and displayed transparency with a yellowish hue. The general reaction of the mono-amine with the prepolymer is given in Scheme 5.

$^{1}H NMR$

¹H NMR spectra were recorded on a Bruker AC 300 spectrophotometer operating at 300.1 MHz. Deuterated trifluoroacetic acid (TFA-d) was used as the solvent.

Differential Scanning Calorimetry

DSC thermogram was recorded on a Perkin Elmer DSC-7 apparatus equipped with a PE-7700 (professional

TABLE 3. ¹H-NMR results for mono-amine-tri-amide (6T6B) corresponding to the structure in Scheme 4.

Proton peak	δ (ppm)	Туре	H-atoms	Integral	
a	3.4	singlet	2	1.73	
b	2.0	triplet	8	8.41	
с	1.6	singlet	8	8.8	
d	3.8	multiplet	6	6.43	
e	8.0	singlet	4	4	
f	7.7	doublet	2	2.11	
g	7.9	triplet	3	3.06	

computer) and a TAS-7 software. Dried samples of 10–15 mg were heated to $\sim 30^{\circ}$ C above their melting temperature and subsequently cooled. Both the heating and cooling were carried out at a rate of 20°C/min. The melting temperatures ($T_{\rm m}$), melting enthalpies ($\Delta H_{\rm m}$), and crystallization temperatures ($T_{\rm c}$) were determined from the thermogram. The $T_{\rm c}$ was taken at the maximum of the exotherm.

Infrared Spectroscopy

Infrared spectra were obtained using a Biorad FTS-60 spectrometer. The spectra for the HSs were recorded on tablets pressed from ground samples and KBr. The polymer samples, on the other hand, were dissolved in DMAc and cast on pressed KBr tablets. After evaporation of the solvent, a thin polymer film remained on the KBr tablet. All the measurements were performed at room temperature.

Inherent Viscosity

The inherent viscosity of the triblock copolymers at a concentration of 0.1 dL/g in DMAc was determined at 25° C by using a capillary Ubbelohde 0C.

Compression Molding

The triblock polyurethanes were processed by a compression moulding technique. A Lauffer 40 press was used with a pressure of ~8.5 MPa at either of two temperatures (150 or 240°C). Prior to the compression moulding, ~2 g of polymer was ground and dried overnight. After preheating the press plates, the ground polymer was

$$MDI - (CH_2)_4O - MDI + 2 MAA$$

$$[MDI-PTMO-(MDI-PTMO)_{0,20}-MDI] \downarrow [monoamine-amide segment]$$

$$MAA - MDI-PTMO-MDI - MAA$$
Where,

MAA = Hexylamine or 6B or 6T6m or 6T6B and X = 2400

SCHEME 5.

spread out evenly in a bar-shaped mould ($8 \times 1.8 \times 0.2$ cm³), and just before pressing, the air was removed by quickly pressurizing and depressurizing the sample. These materials were exposed to high temperature for ~ 2 min. After cooling, the resulting test bars were removed from the mold and used for DMA and compression set experiments. The inherent viscosity of the molded bar is same as the synthesized polymer.

Dynamic Mechanical Analysis

The storage (G') and loss modulus (G") as functions of temperature were measured on the compression moulded test bars (8 × 1.8 × 0.2 cm³) using a Myrenne ATM3 torsion pendulum operating at a frequency of 1 Hz. The samples were first cooled to -100° C and subsequently heated at a rate of 1°C/min at 0.1% strain. The glass transition temperature was defined as the maximum of the loss modulus. The flow or softening temperature (T_{flow}) was defined as the temperature at which the storage modulus reached 0.5 MPa and the temperature at the start of the rubber plateau region, i.e. the intersection of the tangents, was denoted the T_{flex} temperature. The decrease in storage modulus of the rubbery plateau upon increasing the temperature was quantified by the $\Delta G'$ value and was calculated from the equation,

$$\Delta G' = \frac{G'_{(\text{Tflex})} - G'_{(\text{Tflow}-50^{\circ}\text{C})}}{G'_{35^{\circ}\text{C}}} \times \frac{1}{\Delta T} \quad (\%/^{\circ}\text{C}) \qquad (4)$$

Here, ΔT describes the temperature range, i.e. $(T_{\rm flow} - 50^{\circ}{\rm C}) - T_{\rm flex}$.

Compression Set

The compression set was determined according to the ASTM 395 B standard. Samples for compression set experiments were cut from the compression moulded bar. The samples were compressed to 25% at room temperature for 24 h and then released. After half an hour, the thickness of the samples was measured and the compression set was determined by the equation,

Compression set
$$= \frac{d_0 - d_2}{d_0 - d_1} \times 100\%$$
(5)

Here, d_0 is the sample thickness (mm) before compression, d_1 is the sample thickness (mm) during compression (i.e. 1.5 mm) and d_2 is the sample thickness (mm) after compression. An average of three values was taken.

RESULTS AND DISCUSSION

Synthesis of the Extenders

Four types of mono-functional amine-amide units were synthesized and used in the subsequent synthesis of the triblock polyurethane (see Fig. 1). These mono-amines dif-

TABLE 4. Properties of the mono-functional amine-amides.

Name	No. amide groups	Mol. weight (g/mol)	Melting point (°C)	Purity by NMR (%)
6m	0	101	liquid	
6B	1	192	24-26	99
6T6m	2	348	185-187	95
6T6B	3	455	195–197	97

fered with respect to their number of amide bonds (i.e. between 0 and 3). The synthesized amine-amide units were based on hexylamine (6m), hexamethylene diamine (6), benzoic acid (B), and terephthalic acid (T). The 6m (mol. wt. = 101 g/mol), 6B (mol. wt. = 192 g/mol), 6T6m (mol. wt. = 348 g/mol), and 6T6B (mol. wt. = 455 g/mol) units were contained no amide, mono-amide, di-amide, and triamide, respectively. The molecular weight of the extender was increased with increasing the amide content. The 6T6m and 6T6B were novel units, and they were prepared with high purity (95%). The properties of these mono-functional amine-amides are given in Table 4. It can be seen from the table that the melting point of the amine-amides increased when increasing the number of amide groups.

Synthesis of Triblock Polyurethane

Polyurethane triblock copolymers were synthesized from the PTMO endcapped with MDI and mono-functional amine-amide units. The MDI-endcapped prepolymer had a molecular weight of 2800 g/mol with a low content of free MDI. The average SS length without the MDI ends was 2300 g/mol. NMR analysis of the prepolymer revealed that, along with the endcapped MDI unit, some MDI groups were also present in the chain. The composition of the SS appeared to be -PTMO₂₀₀₀-(MDI-PTMO₂₀₀₀)_{0.20}- and the overall composition of the prepolymers was thus MDI-PTMO₂₀₀₀-(MDI-PTMO₂₀₀₀)_{0.20}-MDI. The molecular weight of the polymers was determined by comparing the ¹H NMR integral values at 3.8 ppm ($-O-CH_2-$, representing the SS) with either 1.0 ppm (CH₃, for 6m) or 7.8 ppm ("e" in 6B) or 8.0 ppm ("a" in 6T6m and "e" in 6T6B). The molecular weights of the synthesized polyurethanes were found to be in agreement with what was expected (Table 5). Upon increasing the number of amide groups in the amine-amide units, the molecular weights of the tri-block copolymers was expected to increase slightly and was confirmed to do so by the inherent viscosities values. The MDI-amine-amide segments were considered to be the HSs in the copolymers and this HS content was found to increase from 23 to 38 wt% upon increasing the amine-amide length.

DSC

The melting and crystallization behavior of the copolymers was measured by DSC and the results are presented in Table 5. As a representative of this series, the DSC heating

TABLE 5. Properties of PTMO2300-MDI-amine-amide tri-block copolymers.

Amine	Amide units	Exp. mol. wt.(g/mol)	Calc. mol. wt. (g/mol) ^a	HS (wt%)	$\eta_{\rm inh}$ (dL/g)	$T_{m,s}$ (°C)	$\Delta H_{\rm m,s}$ (J/g SS)	$T_{c,s}$ (°C)	$T_{m,h}$ (°C)	$\Delta H_{\rm m,h}$ (J/g RS)	$T_{c,h}$ (°C)	$T_{\rm m} - T_{\rm c} (^{\circ}{\rm C})$
6m	0	3000	3200	23	0.14	24	27	-20	97	39	63	34
6B	1	3200	3400	27	0.17	27	23	-18	_		_	_
6T6m	2	3500	3800	34	0.13	25	53	-12	232	11	201	31
6T6B	3	3700	3800	38	0.24	27	77	-4	232	21	198	34

^a Determined using an ¹H NMR end group analysis method.

and cooling curve of the 6T6m-based polymer is shown in Fig. 2. The heating curve displayed two endothermic peaks, at $\sim 25^{\circ}$ and 97–232°C, corresponding to the melting of the crystalline soft phase (PTMO) and the HS, respectively. Similarly, the cooling curve showed two exothermic peaks representing the crystallization of the soft phase and the HS. For the 6B-based polymer, no melting or crystallization of the rigid segment was found. The observed melting temperature of 26°C for the PTMO segment was unusually high [18] suggesting that the presence of MDI units in the chain (PTMO-MDI-PTMO) must have increased the PTMO melting temperature. The PTMO melting temperature remained identical upon increasing the length of the HS, whereas, the crystallization temperature and the heat of melting of PTMO was found to increase with increasing HS length. Thus, although the SS length remained unchanged, the PTMO crystallization was faster and the crystallinity higher with longer end segments. This indicated that the HS crystalline phase influenced the SS crystallization and acted as a nucleation agent.

The HS melting temperature increased significantly when increasing the number of amide groups in the HS. Parameters that influence the HS melting temperature include: the number of amide groups in the segments, the thickness of the HS crystallites, the aromatic content and the HS content [19]. The value of $T_{\rm m} - T_{\rm c}$ represents a measure of the

rate of crystallization and these values were low for the copolymers, i.e. 31–34°C, suggesting a fast crystallization of the end groups. With increasing amide length this value remained unchanged, and it was not possible to increase the crystallization rate by increasing the HS length.

IR

Infrared spectroscopy is a common tool for studying the hydrogen bonding in segmented polyurethanes and the carbonyl bands are particularly sensitive to the structure [12]. In polyether(urethane-urea-amide)-based triblock copolymers, three groups have carbonyl bands that can form H-bonds: urethane, urea, and amide groups. In the solid state, these carbonyl bonds are present in amorphous and crystalline states. For urea groups, it is known that the H-bonding can occur in two different forms, i.e. bidendate and mono-dendate [12].

FTIR spectra (1500–1800 cm⁻¹) of the polymers are displayed in Fig. 3, and the important carbonyl peaks from these spectra are presented in Table 6. Because of the overlapping of the peaks, it was difficult to quantify the crystalline/amorphous contents in the polymers. All copolymers showed prominent peaks at 1733 and 1706 cm⁻¹ for the amorphous and crystalline urethane car-

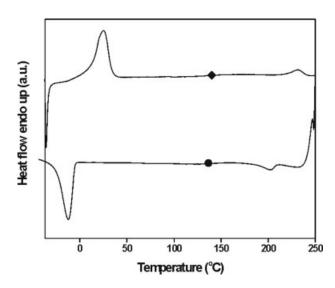


FIG. 2. DSC heating (\spadesuit) and cooling (\spadesuit) traces of triblock polyurethane 6T6m.

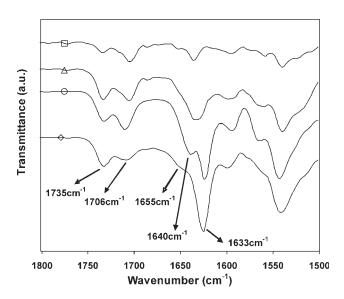


FIG. 3. Infrared spectra (1500–1800 cm⁻¹) of 6m (\Box), 6B (\triangle), 6T6m (\bigcirc) and 6T6B (\diamondsuit) polyurethanes.

TABLE 6. IR characteristics for the triblock polyurethanes.

No. of $C=O$ Urethane (cm ⁻¹)			C=O Urea (cm ⁻¹)			C=O Amide (cm ⁻¹)		
amides	Amorph.	Cryst.	Amorph.	Mono-dendate	Bi-dendate	Amorph.	Cryst.	
0	1735	1706	1690	1655	1640	_	_	
1	1733	1706	1690	1652 —		(1670)	1633	
2	1733	1709	1690	_	1640	(1670)	1625	
3	1733	1709	1690	1652	_	(1670)	1625	

bonyl, respectively, and the intensity of the crystalline urethane peak (1706 cm⁻¹) was high in the 6m- and 6T6m-based polyurethanes. When benzyl end-units were present, the crystallinity of the urethane seemed to decrease. The carbonyl peak of the urea group in the polyurethane had three forms: amorphous (1690 cm⁻¹), mono-dendate (1655 cm⁻¹), and bi-dendate (1640 cm⁻¹). In all cases, the amorphous urea peak was small. In 6m and possibly also 6T6m, the bi-dendate form was present. For the amide carbonyl, only the crystalline peak (1625 cm⁻¹), was observed with the, exception of the 6m polymer which did not contain any amide bond. With an increas-

ing number of amide bonds the crystalline amide peak increased in size. The crystallinity of the amide groups seemed to be higher than that of the urethane and/or urea groups. This was probably due to the higher structural regularity of the amide units. Possible structures of a parallel packing of the HS in the triblock polyurethane are presented in Fig. 4. In all the structures, the H-bonding between the amide groups appeared to be good. In the case of the 6m copolymer, even an antiparallel packing was possible with a good H-bonding between the urea and urethane groups. Although the 2-dimensional packing structure did not provide any evidence of a bi-dendate urea H-bonding, the IR spectrum nevertheless showed

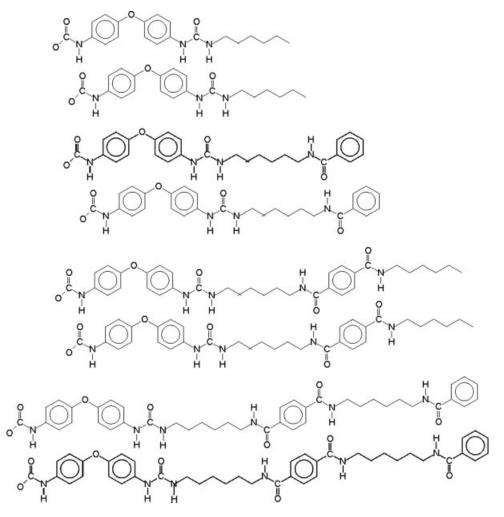


FIG. 4. Possible structures of the hard segment packing.

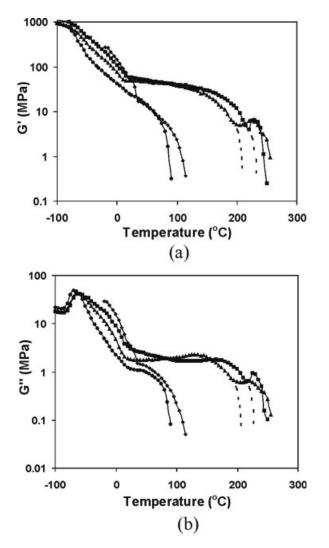


FIG. 5. The (a) storage and (b) loss moduli for MAA-MDI-PTMO-MDI-MAA: \bullet , noamide; \blacklozenge , mono-amide; \blacktriangle , di-amide; \blacksquare , tri-amide (possible flow is indicated by the dotted line).

bi-dendate urea peaks for the 6m- and 6T6m-based polymers. The exact reason behind this difference between the HSs with respect to the bi-dendate urea peak is not yet known, but the most probable explanation is a the better packing of the 6m-based HSs as opposed to the 6B ones.

DMA

The thermo-mechanical behavior of melt pressed samples of the triblock copolymers was studied by DMA (Fig. 5, Table 7). The melt pressing of the 6T6m and 6T6B triblock copolymers was performed at 240° C which is just above the $T_{\rm m}$ of the materials as measured by DSC. Higher temperatures gave rise to an excessive degradation.

The DMA graphs for the 6m (no amide) and the 6B (mono-amide) copolymers seemed to be very similar. Also the DMA graphs of the 6T6m (di-amide) and the 6T6B (tri-amide) looked alike. This suggests that the benzyl-amide groups in the mono- and tri-amide did not contribute much to the HS melting temperature ($T_{\rm flow}$) or the modulus. The DSC and IR results also indicate that the benzamide group did not increase the $T_{\rm m}$ or the crystallinity of the HS. The $T_{\rm g}$ of these triblock copolymers was -65° C (Table 7), which is very close to the $T_{\rm g}$ of the pure PTMO₂₀₀₀, thus confirming a pronounced phase separation of the mono-disperse HSs from the soft matrix.

Certain problems were encountered with regard to the DMA measurement of the 6B polymer. The starting temperature could not be set lower than -20° C, as at lower temperatures the sample broke before the measurement started. The T_{flex} , i.e. the starting point of the rubbery plateau, was $\sim 20^{\circ}$ C and corresponded to the PTMO melting temperature as measured by DSC. Because of the presence of the crystalline PTMO phase, a shoulder could be observed between $T_{\rm g}$ and $T_{\rm flex}$. At -10° C, the size of this shoulder increased in strength in the order of 6m<6T6m<6T6B, thus suggesting that the crystallinity of the SS increased with increasing HS length. This suggestion was further supported by the higher melting enthalpy of the SS with increasing amide length (Table 5). An almost temperature-independent rubbery plateau was observed for the 6T6m and 6T6B polymers. Such a low temperature dependence is typical for mono-disperse HS [3-14], and the fact that the 6T6m and 6T6B copolymers had a very low temperature dependence ($\Delta G'$ values) even after melt pressing at 230°C indicated good thermal stabilities.

The synthesized polymers displayed well-defined flow temperatures due to the mono-disperse HSs melting in a narrow temperature range. Moreover, the graphs show an enormous increase in $T_{\rm flow}$ when going from the 6m and 6B (~80°C) to the 6T6m and 6T6B (~220°C) triblock copolymers. The $T_{\rm flow}$ corresponded well with $T_{\rm m}$ as observed by DSC. The 6T6m and 6T6B copolymers both displayed recrystallization peaks at temperatures above 200°C. If no recrystallization had taken place, the $T_{\rm flow}$ would have been lower as indicated by the dotted line in

TABLE 7. Inherent viscosities, DMA, and CS properties for the various polyurethane triblock copolymers.

Polymer	Amide	HS (%)	$T_{\rm g}$ (°C)	$T_{\rm flow}$ (°C)	$T_{\rm flex}$ (°C)	$G'_{\rm 35^\circ C}$ (MPa)	$G_{35^\circ C}^{\prime\prime}$ (MPa)	tan δ	$\Delta G' (\%/^{\circ}C)$	CS at 35°C (%)
6m	0	23	-65	87	15	20	1.1	0.05	2.2	47
6B	1	27		114	35	17	1.5	0.09	1.6	53
6T6m	2	34	-66	210 ^a	15	48	1.7	0.04	0.5	28
6T6B	3	38	-60	230 ^a	15	54	2.7	0.05	0.5	25

^a Extrapolated DMA value.

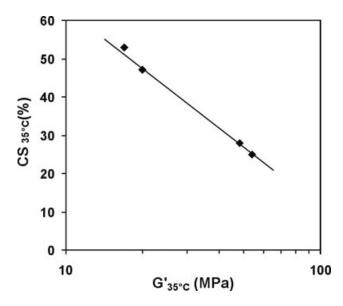


FIG. 6. The compression set as function of the storage modulus.

Fig. 5. Polyurethanes based on crystallizable amide segments are known to recrystallize when the T_{flow} lies above 200°C [13]. The first HS melting temperatures are given in Table 5.

Compression Set

The elastic behavior of the triblock copolymers was studied by compression set (CS) tests. The CS experiments were performed at 35°C, i.e. above the melting temperature of PTMO (Table 7). The CS values were found to decrease with an increasing amide content and thus also with an increasing modulus. The presence of a benzamide group did not have any effect on the CS values which were found to decrease steadily with increasing (log) modulus (see Fig. 6). This diminution in CS values can be explained by two effects: the number of amide groups in the HS and the crystallinity of the HS. Surprisingly, the CS values of the 6T6m and 6T6B materials were low despite their high modulus and their very low molecular weight.

CONCLUSION

Triblock polyurethanes based on MDI-endcapped PTMO₂₀₀₀ and mono-functional amine-amides were synthesized and characterized. The four types of MMAs used were no-amide (6m), mono-amide (6B), di-amide (6T6m), and tri-amide (6T6B). Out of the four amine-amides, 6T6m and 6T6B were novel compounds, synthesized to high purity (95%). The triblock copolymers displayed low molecular weights (3200–3800 g/mol). The characterizations demonstrated that, with an increasing amide length (HS content), the modulus increased, the HS melting temperature increased and the CS values were lowered. However, the benzamide units did not seem to contribute much to the melting temperature, crystallinity and modulus of the HS. The rigid segments crystallized fast and the

polyurethanes could be melt processed at high temperatures without losing their mono-disperse character. The low-molecular-weight triblock copolymers had relatively high moduli and remarkably low CS values. The crystallization temperature of the SS as well as the degree of crystallinity displayed a surprising increase with HS length, which was probably due to nucleation effects of the HS crystallites. It was expected that H-bonding would be possible in the molten state thereby providing a network structure in the melt.

ACKNOWLEDGMENTS

This work is part of the research program of the Dutch Polymer Institute (DPI), project no. 479.

REFERENCES

- 1. G. Holden, N.R. Legge, R.P. Quirk, and H.E. Schroeder, *Thermoplastic Elastomers*, 2nd ed., Hanser, Munich (1996).
- 2. C. Hepburn, Polyurethane Elastomers, London, Elsevier (1992).
- 3. L.J. Harrell, Macromolecules, 2(6), 607 (1969).
- H.N. Ng, A.E. Allegrezza, R.W. Seymour, and L.S. Cooper, *Polymer*, 14(6), 255 (1973).
- 5. A.E. Allegrezza, R.W. Seymour, H.N. Ng, and S.L. Cooper, *Polymer*, **15**(7), 433 (1974).
- C.D. Eisenbach, M. Baumgartner, and C. Guenter, in Advances in Elastomer and Rubber Elasticity, J. Lai and J.E. Mark, Eds., Plenum, New York, 51 (1986).
- C.D. Eisenbach and H. Nefzger, "Multiphase Macromolecular Systems," in *Contemporary Topics in Polymer Science, Vol. 6*, W.M. Cumbertson, Ed., Plenum, New York, 339 (1989).
- C.D. Eisenbach, E. Stadler, and V. Enkelmann, *Macromol. Chem. Phys.*, **196(3)**, 833 (1995).
- D.B. Klinedinst, E. Yilgor, I. Yilgor, F.L. Beyer, J.P. Sheth, and G.L. Wilkes, *Rubber Chem. Technol.*, 78(5), 737 (2005).
- R.M. Versteegen, R.P. Sijbesma, and E.W. Meijer, *Macro-molecules*, 38(8), 3176 (2005).
- 11. R.M. Versteegen, R. Kleppinger, R.P. Sijbesma, and E.W. Meijer, *Macromolecules*, **39**(2), 772 (2006).
- M. Van der Schuur, B. Noordover, and R.J. Gaymans, *Polymer*, 47(4), 1091 (2006).
- G.J.E. Biemond, K. Brasspenning, J. Feijen, and R.J. Gaymans, J. Appl. Polym. Sci., 107(4), 2180 (2008).
- D. Husken, J. Krijgsman, and R.J. Gaymans, *Polymer*, 45, 4837 (2004).
- A. Arun and R.J. Gaymans, *Macromol. Chem. Phys.*, DOI: 10.1002/macp.200700532.
- B.J.B. Folmer, R.P. Sijbesma, R.M. Versteegen, J.A.J. van der Rijt, and E.W. Meijer, *Adv. Mater.*, **12**, 874 (2000).
- 17. L. Brunsveld, B.J.B. Folmer, E.W. Meijer, and R.P. Sijbesma, *Chem. Rev.*, **101**, 4071 (2001).
- M.C.E.J. Niesten, J. Feijen, and R.J. Gaymans, *Polymer*, 41, 8487 (2000).
- M. Van der Schuur, J. de Boer, and R.J. Gaymans, *Polymer*, 46, 9243 (2005).