A series of polyurethane tri-block copolymers were synthesized by reacting a 4,4′-methylenebis(phenyl isocyanate) (MDI)-endcapped poly(tetramethylene oxide) (PTMO, \(M_n = 2,000\) g/mol) with a monoamine-diamide \((6T6m)\) hard segment (HS). The concentration of the HS in the copolymer was varied between 9 and 33 wt % by changing the length of the soft mid-block segment. The structure of the copolymers was analyzed by nuclear magnetic resonance, the amide crystallinity was investigated by Fourier transform infra-red and the thermal properties were studied by differential scanning calorimetry. The mechanical and elastic properties of the tri-block copolymer were subsequently explored by dynamic mechanical analysis, compression set and tensile experiments, and the melt rheological behavior was studied by a parallel plate method. The amide end groups displayed a high crystallinity and the modulus of the tri-block copolymers was relatively high. The fracture strain increased strongly with the molecular weight and the copolymers demonstrated a ductile fracture behavior for molecular weights above 6000 g/mol. Good compression set values were obtained for the tri-block copolymers despite their low molecular weight. In the molten state, the tri-block polymers displayed a gelling effect at low frequencies, which was believed to be a result of a clustering of the end-segments.

INTRODUCTION

Polyurethanes (TPU) make up an important class of thermoplastic elastomers with a wide variety of applications in industry [1–3]. Generally, thermoplastic polyurethanes consist of PTMO soft segments and 4,4′-methylenebis(phenyl isocyanate) (MDI)-butanediol hard segments (HS) [3–9]. Phase separation usually occurs by a combination of liquid-liquid demixing and crystallization. The HS crystallinity in the copolymers is often low, but higher crystallinity can be obtained by using monodisperse HS [8–15]. Copolymers with monodisperse HS display higher moduli, higher fracture strains and sharper melting transitions [4, 8–15]. However, monodisperse polyurethane and/or urea segments can undergo transesterification reactions when subjected to high temperatures [8], and such transreactions lead to a loss of the monodisperse distribution of the HS. Nevertheless, polyurethanes that contain diurethane/diurea segments are less susceptible to such randomization by transreactions as transesterification on the symmetrical diurethane/diurea segments does not change the polydispersity. Diurethane/diurea segments are usually prepared with diamines [2], but diamine-diamides can also be used [13–16]. A typical diame-diamide extender is 6T6, based on hexamethylenediamine (HMDA) and terephthalic acid. Polyurethaneureas with diamine-diamide extenders display high HS crystallinities, high moduli at room temperature, sharp melting transitions, good elastic behaviors and are melt processable without losing these specific properties [13–16].

A special case of polyurethane copolymers are tri-block copolymers [17–20]. Aneja and Wilkes et al. [17] have studied TPU tri-block copolymers BAB type with a urethane HS (A) as the mid-block and the soft segments (B) as end-block. These tri-block copolymers were transparent solid materials. A single urethane mid-segment in the copolymer was thus sufficient for giving the material dimensional stability. TPU tri-block copolymers with urethane end-segments, the so-called ABA type, are new [20]. In these ABA tri-block copolymers the end-segments (A) were HS which were monodisperse in length. In that study the concentration of the end-block (A) was varied by changing its length of these A end-blocks. With an increasing end-block length A (concentration), the modulus was found to increase as did the HS melting temperature. The tri-block copolymers with diamide extender displayed a melting temperature that were not too high...
The diamide used was a mono-aminediamide 6T6m, where 6 stands for hexamethylene diamine, 6m for a hexyl amine group and T for a terephthalic group (Fig. 1). Since monodisperse HS crystallize well, the majority of the monodisperse A end-blocks were expected to reside in a crystalline phase (network points) with the mid-blocks B connecting these network points. The structure of the crystallites of the mono disperse segments is that of nano ribbons with a high aspect ratio [10, 13, 21]. The studied tri-block copolymers were of low molecular weights and thus had a brittle nature [20]. It would be interesting to explore the ABA tri-block copolymer in more detail and varying the molecular weight of the mid block as it is hoped that by increasing the molecular weight of the mid block B the copolymers become ductile. Also worth while studying is the melt rheological behavior as in ABA tri-block copolymers with amide A segments the materials had a thixotropic behavior [21].

The work presented here concerns polyurethane ABA tri-block copolymers with from MDI end-capped PTMO and monoamine-diamide (6T6m) as the extender segment (Fig. 1). The length of the mid-segment B was varied from 2300 to 12,600 g/mol and with that the HS content A decreased from 33 to 9 wt %. The effect of tri-block copolymers’ molecular weight and HS content (soft segment length) on the properties of the copolymers was investigated. It was of particular interest to study the phase structure, the thermal mechanical behavior, the tensile properties, the elastic properties and the rheological behavior. The results of the tri-block copolymer were compared with the properties of similar multiblock copolymers [15].

**EXPERIMENTAL SECTION**

**Materials**

Hexamethylenediamine, hexylamine, N-methyl-2-pyrrolidinone (NMP), N,N-dimethylacetamide (DMAc) and deuterated trifluoroacetic acid (TFA-d) were purchased from Aldrich. Methyl(4-chlorocarbonyl)benzoate (MCCB) was obtained from Dalian (No. 2 Organic Chemical Works, China). Poly(tetramethylene oxide) endcapped with MDI (2847 g/mol) was generously donated from the Crompton Corporation. This prepolymer was analyzed and the PTMO was found to be little extended with MDI units and had the composition of MDI-PTMO\textsubscript{2000}\textsuperscript{−}(MDI-PTMO\textsubscript{2000})\textsubscript{0.2} - MDI [20]. PTMO\textsubscript{2000} was generously donated by Bayer. All chemicals were used as received. The synthesis of 6T6m (N-(aminohexyl)-N-hexyl terephthalamide) has been described in detail elsewhere [20].

**General Synthetic Procedure for the polyether (urethane-area-amide)-based tri-block Copolymer (Fig. 1)**

As an example, the synthetic procedure of the polymer with $y = 3.4$ is given. All polymerizations were carried out using a 250 mL stainless steel reactor, fitted with a glass lid, magnetic coupled stirrer and a nitrogen inlet. The experimental set-up was dried before the reaction to prevent foaming and unwanted reactions with water. The MDI endcapped prepolymer (20 g, 0.007 mol) and the extender (PTMO\textsubscript{2000} (8.2 g, 0.004 mol)) were weighed into the reactor, heated and kept at 80°C for 1 h while being stirred. The 6T6m (2.0 g, 0.006 mol) was dissolved in 80 mL DMAc at 120°C and added to the reactor which had been heated to 130°C before the addition of the 6T6m solution. The reaction was continued for 4 h at 130°C in a nitrogen atmosphere under stirring. Finally the solvent was stripped in vacuo (pressure $\sim 2$ mbar), after which the reactor was slowly cooled, while maintaining the low pressure. The obtained copolymer was transparent with a slight yellow color.

**1H NMR**

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

**Inherent Viscosity**

The inherent viscosity of the tri-block copolymers at concentrations of 0.1 g/dL in DMAc at 25°C was determined by using a capillary Ubbelohde viscometer.

**Differential Scanning Calorimetry (DSC)**

DSC spectra were recorded on a Perkin–Elmer DSC7 apparatus, equipped with a PE7700 computer and TASS-7 software. The dried samples (10 mg) were heated and cooled at a rate of 20°C/min. The melting temperature ($T_m$) was taken as the temperature of the maximum of the endotherm of the second heating scan. The first cooling curve was used to determine the crystallization temperature.
**Fourier-Transform Infrared (FTIR) Spectroscopy**

Infrared transmission spectra were recorded using a Nicolet 20 SXB FTIR spectrometer with a resolution of 4 cm\(^{-1}\). Polymer samples were dissolved in DMAc and cast on pressed KBr tablets. After evaporation of the solvent, a thin polymer film remained on the KBr tablet, which was used in the measurements of the spectra. The samples were measured at room temperature.

**Compression Molding**

The produced polymers were processed by compression molding in a Lauffer 40 press at \(\sim 8.5\) MPa and at various temperatures (for polymer \(y = 0.2\) at 240\(^\circ\)C and remaining polymers at 200\(^\circ\)C) for a time period of \(\sim 2\) to 3 min. In advance, \(\sim 2\) g of the polymer was cut into a small pieces and dried overnight. After preheating the press plates, the polymer pieces were spread out evenly in a bar-shaped mold \((8 \times 1.8 \times 0.2\) cm\(^3\)). Just before pressing, the air was removed from the polymer by pressurizing and quickly depressurizing the sample. After cooling, the resulting test bars were removed from the mold and used for DMA, tensile and compression set experiments.

**Dynamic Mechanical Analysis (DMA)**

The storage \((G')\) and loss \((G'')\) moduli as functions of temperature were measured on injection molded test bars \((70 \times 9 \times 2\) mm\(^3\)) using a Myrenne ATM3 torsion pendulum at a frequency of 1 Hz. The samples were first cooled to \(-100\)\(^\circ\)C and subsequently heated at a rate of 1\(^\circ\)C/min and 0.1% strain. The glass transition temperature was determined as the maximum of the loss modulus. The flow or softening temperature \((T_{flow})\) was defined as the temperature where the storage modulus reached 0.5 MPa. The flex temperature \((T_{flex})\) was defined as the temperature at the start of the rubber plateau region, more specifically, the intersection of the tangents. The decrease in storage modulus of the rubbery plateau with increasing temperature was quantified by the intersection of the tangents. The decrease in storage modulus was varied by extending the MDI-PTMO\(_{2000}\)-(MDI-PTMO\(_{2000}\))\(_{0.2}\)-MDI with PTMO\(_{2000}\) segments to MDI-PTMO-(MDI-PTMO\(_{2000}\))\(_{y}\)-MDI. By changing the ratio of MDI-PTMO\(_{2000}\)-(MDI-PTMO\(_{2000}\))\(_{0.2}\)-MDI to PTMO\(_{2000}\) the soft segment length \(-\text{PTMO}_{2000}\)-(MDI -\text{PTMO}_{2000})\(_{y}\)-MDI the average \(y\) value could be increased 0.2 to 4.47 and with that the SS \(M_n\) from 2,300 to 12,000 g/mol. With this increase in the SS length of the tri-block copolymer, the HS content was reduced from 33 to 9 wt % (Table 1). All the copolymers were transparent and could be molded.

**RESULTS AND DISCUSSION**

The ABA tri-block copolymers were prepared by reacting a MDI-end-capped PTMO prepolymers with the mono functional amine-diamide segment 6T6m (Fig. 1). The hard end-segments (HS) of these tri-block copolymers were -MDI-6T6m units. The length of the prepolymers was varied by extending the MDI-PTMO\(_{2000}\)-(MDI-PTMO\(_{2000}\))\(_{0.2}\)-MDI with PTMO\(_{2000}\) segments to MDI-PTMO-(MDI-PTMO\(_{2000}\))\(_{y}\)-MDI. By changing the ratio of MDI-PTMO\(_{2000}\)-(MDI-PTMO\(_{2000}\))\(_{0.2}\)-MDI to PTMO\(_{2000}\) the soft segment length \(-\text{PTMO}_{2000}\)-(MDI -\text{PTMO}_{2000})\(_{y}\)-the average \(y\) value could be increased 0.2 to 4.47 and with that the SS \(M_n\) from 2,300 to 12,000 g/mol. With this increase in the SS length of the tri-block copolymer, the HS content was reduced from 33 to 9 wt % (Table 1). All the copolymers were transparent and could be molded.

**Molecular Weights**

The composition of the copolymers was studied by \(^1\)H NMR analysis using the integral values at 8.0 ppm (terephthalamide protons in 6T6m) and 1.8 ppm \((-\text{CH}_2-\) ) respectively. The polymer composition was found to be equivalent to the feed composition. From the feed composition the molecular weights of the copolymers

\[
\text{Compression set} = \frac{d_0 - d_2}{d_0 - d_1} \times 100\% \tag{2}
\]

Here, \(d_0\) is the thickness (mm) before compression; \(d_1\) the thickness (mm) during compression (mm) (here \(d_1 = 1.65\) mm); and \(d_2\) the thickness (mm) 30 min after the release of the pressure.

**Tensile Measurements**

Stress–strain curves were obtained on the compression molded bars with a thickness of 2 mm, cut to dumbbells (ISO 37 type 2), using a Zwick Z020 universal tensile machine equipped with a 500 N load cell. The strain was measured with extensometers. Standard tensile tests were performed at a strain rate of 0.4 s\(^{-1}\) (corresponding to a test speed of 60 mm/min).

**Melt Rheology**

Rheology measurement was carried out on a Paar Physica UDS200 rheometer with a Paar Physica TC 20 temperature control unit. A parallel plate set-up was used with a fixed EHH-TEK 350 plate and a MP 306 rotating plate. The diameter of the upper plate was 25 mm and the gap between the two parallel plates was 0.5 mm. Paar Physica software was used for all the rheology calculations. Low amplitude oscillatory shear experiments were performed on the polymer samples over the frequency range of 0.1–100 (s\(^{-1}\)). Dynamic frequency sweeps were carried out on the tri-block copolymers at a strain of 5%.
were calculated. The inherent viscosities increased with increasing soft segment length (SS) as well as with the molecular weight as determined by NMR (Fig. 2).

**DSC**

The melting and crystallization behavior of the tri-block copolymers was measured by DSC and the results are presented in Table 2. As an example, the heating and the cooling curve of the polymer with \( y = 0.2 \) is given in Fig. 3. The heating curve showed two endothermic peaks, one at 25°C due to the melting of the crystalline soft phase (PTMO) and one at 232°C due to the melting of the HS. Similar to the heating curve, the cooling curve showed two exothermic peaks, one at 201°C corresponding to the crystallization of the HS and one at −12°C where the soft phase crystallized. The melting temperature of the soft segments \( (T_{m,s}) \) was found to be between 16 and 25°C for all copolymers. The heat of fusion of the copolymers with extended soft segments \( (\Delta H_{m,s}) \) was lower than that of the nonextended polymer \( (y = 0.2) \), and this was believed to be due to the higher content of MDI groups in the extended soft segments restricting their crystallization. The melting temperature of the HS \( (T_{m,h}) \) was also found to decrease with increasing SS length. This has been explained as being due to the solvent effect of the SS on the HS melting temperature [22]. The melting endotherms of the HS were shallow and the heat of enthalpy was difficult to measure accurately. The heat of fusion \( (\Delta H_{m,h}) \) seemed to increase with decreasing HS concentration. The value for \( T_m - T_c \) for the HS was found to be in the range of 20–40°C thus suggesting a fast crystallization of HS. Such a fast crystallization was due to the mono-disperse HS length [12–15, 20].

**FTIR**

In the FTIR spectra, five peaks were present in the carbonyl (C=O) region between 1600 cm\(^{-1}\) and 1750 cm\(^{-1}\) (Fig. 4). The IR peak around 1735 cm\(^{-1}\) was assigned to the amorphous urethane carbonyl group, the one at 1715 cm\(^{-1}\) to the crystalline urethane carbonyl groups, the peak at 1680 cm\(^{-1}\) corresponded to the amorphous amide I, the one around 1640 cm\(^{-1}\) to the bidendate crystalline urea groups and the peak at 1625 cm\(^{-1}\) to the crystalline amide I carbonyl groups. Apart from these peaks, a peak at 1597 cm\(^{-1}\) was attributed to the benzene rings in the MDI and the terephthalamide group. The peak observed at 3300 cm\(^{-1}\) was assigned to the crystalline N–H groups, and the broad peak at 1540 cm\(^{-1}\) to \( \delta (N-H) + \nu (C=O) \) (Amide II). It was very difficult to determine the crystallinity of the urethane with IR-spectroscopy due to the overlap of the peaks of crystalline urethane and amorphous urea. However, in the case of the amide group, both the crystalline and amorphous peaks could be measured without problem. The crystallinity of the amide was calculated by comparing the intensity of the peaks around 1680 cm\(^{-1}\) (amorphous amide) and 1625 cm\(^{-1}\) (crystalline amide), using the equation

\[
X_c = \frac{\text{amide}_{\text{crystalline}}}{\text{amide}_{\text{amorphous}} + \text{amide}_{\text{crystalline}}} = \frac{\lambda (1625 \text{ cm}^{-1})}{\alpha \times \lambda (1680 \text{ cm}^{-1}) + \lambda (1625 \text{ cm}^{-1})} \times 100
\]
where “a” is 2.4 [14]. The crystallinity of the amide group in the polymers calculated by this method was found to be around 75–80% (Table 1). This was in agreement with what has been observed earlier on similar copolymers [20, 21, 23]. The amide crystallinities were found to be high even at low HS contents. The HS crystallinity is thus little influenced by the soft segment length (concentration). The crystallinities from FTIR seemed to be higher than expected from the DSC results. A possible explanation might be that the MDI units in the MDI-6T6m HS were not that crystalline. It thus seemed that not all MDI units had taken part in the crystallization of the HS.

**DMA**

The thermo-mechanical properties of melt pressed samples of the copolymers were studied by DMA. The storage modulus as a function of temperature for the five polymers can be seen in Fig. 5 and Table 3 displays a vast range of results from the measurements. For all compositions, the $T_g$ was around $-60^\circ$C, which is close to the $T_g$ of the pure PTMO$_{2000}$ thus confirming the good phase separation of mono-dispersed 6T6m from the soft matrix. Slightly higher values of $T_g$ were found for the copolymers with longer SS ($y > 0.2$). This was probably due to the MDI units in the -PTMO$_{2000}$- (MDI -PTMO$_{2000}$)$_y$ mixing with the PTMO segments. The PTMO$_{2000}$ melting peak was observed as a shoulder on the $T_g$ peak in the $G'$-temperature graph, and the end of the PMTO melting peak (shoulder) was taken as the $T_{flex}$. Values for $T_{flex}$ were found between 15 and 25°C, which corresponded well with the PTMO melting temperatures as determined by DSC. The rubbery storage modulus ($G'_ {35 ^ \circ C}$) of the tri-block copolymers increased with increasing HS content. This increase in storage modulus was due to a higher crosslinking density and to a stronger reinforcing effect of the HS crystallites [21, 23, 24]. The low temperature dependence of the storage modulus in the region between 35°C and $T_{flow}$ was due to the presence of 6T6m segments of uniform length. Mono-disperse HS generally give rise to a single melting temperature and there is no

**TABLE 2. Thermal and crystallization properties of the tri-block polyurethanes with varying soft segment length.**

<table>
<thead>
<tr>
<th>Polymer ($y$)</th>
<th>HS$^*$ (%)</th>
<th>HS$^b$ (%)</th>
<th>$T_{m,s}$ (°C)</th>
<th>$\Delta H_{m,s}$ (J/gSS)</th>
<th>$T_{m,h}$ (°C)</th>
<th>$\Delta H_{m,h}$ (J/gHS)</th>
<th>$T_{c,s}$ (°C)</th>
<th>$T_{c,h}$ (°C)</th>
<th>$T_{m,h} - T_{c,h}$ (°C)</th>
<th>$X_{c,d}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>33.8</td>
<td>19.6</td>
<td>25</td>
<td>53</td>
<td>11</td>
<td>-12</td>
<td>202</td>
<td>20</td>
<td>30</td>
<td>79</td>
</tr>
<tr>
<td>1.27</td>
<td>20.1</td>
<td>11.7</td>
<td>18</td>
<td>29</td>
<td>15</td>
<td>-28</td>
<td>136</td>
<td>41</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>2.34</td>
<td>14.3</td>
<td>8.3</td>
<td>25</td>
<td>38</td>
<td>36</td>
<td>-12</td>
<td>133</td>
<td>31</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>3.40</td>
<td>11.1</td>
<td>6.7</td>
<td>16</td>
<td>33</td>
<td>46</td>
<td>-22</td>
<td>129</td>
<td>38</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>4.47</td>
<td>9.0</td>
<td>5.3</td>
<td>24</td>
<td>36</td>
<td>33</td>
<td>-15</td>
<td>103</td>
<td>36</td>
<td>76</td>
<td></td>
</tr>
</tbody>
</table>

$^*$ Hard segment including MDI.

$^b$ Hard segment excluding MDI.

$^c$ Heat of enthalpy for HS excluding MDI.

$^d$ Determined by IR.

**FIG. 3.** DSC heating and cooling traces of the tri-block polyurethane with $y = 0.2$: ●, heating curve; ○, cooling curve.

**FIG. 4.** FTIR spectra of tri-block polyurethanes with varying soft segment length $y$: ●, 0.2; ■, 1.27; ●, 2.34; ▲, 3.4; □, 4.47.
early drop in the modulus due to an earlier melting of low melting segments. The $T_{\text{flow}}$ of the tri-block copolymer was sharp and increased with increasing HS content. This has been explained as a solvent effect of the soft segments [22]. For the copolymer with $y = 0.2$ at high temperatures ($220^\circ$C) surprisingly the modulus increased. On other polyurethanes similar peaks have been observed in their DMA thermograms and these peaks have been explained as being due to a secondary crystallization [20]. The values of $T_{\text{flow}}$ were very similar to those of $T_m$ as measured by DSC (Table 2). Apart from the polymer with $y = 0.2$, the $T_{\text{flow}}$ of all other the samples were below 200°C. The melting temperature of polyurethanes should not be too high as degradation often takes place above 220°C.

A comparative graph of the temperature evolution of the storage modulus of a tri-block and a PTMO-MDI-6T6-MDI multiblock copolymer [15] is presented in the Fig. 5b. The rubbery modulus of the tri-block copolymer with MDI-6T6m HS was higher than that of the multiblock copolymer with MDI-6T6-MDI HS at an equivalent HS concentration. The higher storage modulus may be due to the higher crystallinity and/or higher aspect ratio of the HS crystallites in the tri-block material [21]. However, the $T_{\text{flow}}$ of the tri-block copolymer was much lower than that of its multiblock counterpart [15], as a result of the presence of shorter HS. Although the diamides 6T6 and 6T6m were almost of similar size, the thickness of

![Fig. 5a](image-url)  
**FIG. 5.** (a) The temperature evolution of the storage modulus curve for the tri-block copolymers ($\bullet$, 32.8%; ■, 19.7%; ◆, 14.1%; ▲, 11.0%; □, 9.0% HS) and (b) a comparative graph of tri-block and multiblock [15] copolymers with 11.0% of hard segment: ▼, tri-block; ▽, multiblock.

![Fig. 5b](image-url)  
**FIG. 6.** The effect of the percentage of hard segments on the rubbery modulus: ❄, with MDI units; and ◆, without MDI units in the HS.

### Table 3. DMA results for the tri-block copolymers.

<table>
<thead>
<tr>
<th>Polymer ($y^a$)</th>
<th>$M_n$ (g/mol)</th>
<th>$M_n^b$ (g/mol)</th>
<th>$\eta_{inh}$ (dL/g)</th>
<th>HS$^c$ (%)</th>
<th>HS$^d$ (%)</th>
<th>$T_s$ (°C)</th>
<th>$T_{flow}$ (°C)</th>
<th>$T_{flex}$ (°C)</th>
<th>$G^\prime$35 (MPa)</th>
<th>$G^\prime$035 (MPa)</th>
<th>$\tan \delta$ (%)</th>
<th>$\Delta G^\prime$ (%/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>3500</td>
<td>3800</td>
<td>0.13</td>
<td>33.8</td>
<td>19.6</td>
<td>−66</td>
<td>255</td>
<td>15</td>
<td>48</td>
<td>1.7</td>
<td>0.04</td>
<td>0.5</td>
</tr>
<tr>
<td>1.27</td>
<td>6000</td>
<td>6400</td>
<td>0.32</td>
<td>20.1</td>
<td>11.7</td>
<td>−60</td>
<td>180</td>
<td>20</td>
<td>15</td>
<td>1.0</td>
<td>0.07</td>
<td>0.5</td>
</tr>
<tr>
<td>2.34</td>
<td>8400</td>
<td>8700</td>
<td>0.39</td>
<td>14.3</td>
<td>8.3</td>
<td>−56</td>
<td>170</td>
<td>25</td>
<td>13</td>
<td>1.3</td>
<td>0.10</td>
<td>−0.1</td>
</tr>
<tr>
<td>3.40</td>
<td>10,800</td>
<td>9900</td>
<td>0.47</td>
<td>11.1</td>
<td>6.7</td>
<td>−56</td>
<td>160</td>
<td>25</td>
<td>6</td>
<td>0.9</td>
<td>0.15</td>
<td>0.3</td>
</tr>
<tr>
<td>4.47</td>
<td>13,200</td>
<td>12,600</td>
<td>0.60</td>
<td>9.0</td>
<td>5.3</td>
<td>−61</td>
<td>140</td>
<td>25</td>
<td>5</td>
<td>0.6</td>
<td>0.12</td>
<td>0.7</td>
</tr>
</tbody>
</table>

$^a$ Soft segment repeat length.  
$^b$ From $^1$H NMR analysis.  
$^c$ Hard segment including MDI.  
$^d$ Hard segment excluding MDI.
the MDI-6T6-MDI-based lamellar structure with two MDI units was expected to be higher than that of the MDI-6T6m. Thus, from the DMA results, it was clear that the 6T6m-based tri-block copolymer presented a higher G\(_{35}\)C modulus as compared to 6T6 multiblock copolymers without having a too high melting temperature.

The storage moduli at 35°C for the tri-block copolymer showed a strong increase with HS content (Fig. 6). Such a strong increase was expected to be mainly due to the reinforcing effects of the HS crystallites [21, 23]. Since the MDI units of the HS might or might not take part in the crystallization, the results were plotted for both cases. If compared to results from the literature [13], the best match was found for the data corresponding to the sample in which the MDI units in the HS did not take part in the crystallization. This thus suggested that the MDI units were not included in the HS crystallites.

**Tensile Properties**

The tensile properties of the tri-block copolymers were studied on compression molded bars cut into dumbbells (ISO 37 type 2). With increasing molecular weight of the tri-block copolymer, the HS content decreased. The tensile curves of the polymers with \(y = 0.2\) and \(y = 4.47\) are presented in Fig. 7 and the results combined in Table 4. The low molecular weight tri-block copolymer with a high HS content displayed a high modulus and a low fracture strain. This copolymer fractured in a brittle manner. The tri-block copolymer with a \(M_n\) of 12,000 (\(y = 4.47\)) had a low modulus, a low yield strength and a high fracture strain and fracture stress.

The E-modulus increased with increasing HS content and followed the same trend as the \(G'\)-modulus measured by the DMA. Also the yield stress increased when increasing the HS content (Fig. 8). This was expected since the yield strength of segmented block copolymers generally displays a linear increase with the concentration of crystallites [23]. As can be seen in Fig. 8, the yield stress was plotted as a function of the HS concentration both for the case where the MDI units took part in the crystallization and where they did not. The results for the latter case were found to follow the earlier observed trend best [20].

The fracture stress and fracture strain of the tri-block polyurethanes increased with increasing molecular weight. At high strains (>250%), the fracture stress increased significantly due to the strain-hardening of the PTMO soft segments (Fig. 7). The transition from brittle to ductile

![FIG. 7. Stress–strain curves for the tri-block copolymers with varying \(y\): ●, 0.2; □, 4.47.](image)

![FIG. 8. The yield stress as a function of the hard segment content: □, with MDI units; ●, without MDI units in the HS.](image)

<table>
<thead>
<tr>
<th>Polymer (y)(^a)</th>
<th>HS(^b) (%)</th>
<th>(\eta_{inh}) (dL/g)</th>
<th>(M_n) (g/mol)</th>
<th>G-Mod (MPa)</th>
<th>E-Mod (MPa)</th>
<th>(\varepsilon_{yield}) (%)</th>
<th>(\sigma_{yield}) (MPa)</th>
<th>(\varepsilon_{fra.}) (%)</th>
<th>(\sigma_{fra.}) (MPa)</th>
<th>CS(_{40\degree C}) (%)</th>
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<td>brittle</td>
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</table>

\(^a\) \(y\) = SS repeat length.

\(^b\) Hard segment excluding MDI.

\(^c\) From \(^1\)H NMR analysis.

TABLE 4. The tensile properties of the tri-block copolymers.
for these tri-block copolymers seemed to occur at a $M_n$ of $\sim 6,000$ g/mol.

**Compression Set Tests**

The elastic properties of the tri-block copolymer were determined by CS experiments performed at 40°C, well above the melting temperature of PTMO (Table 3). The compression set values were found to be low, irrespective of the HS content.

**Melt Rheology**

Low molecular weight polymers are generally Newtonian. The rheological behavior of the tri-block polyurethanes was studied on the copolymer with $y = 3.4$ using a dynamic test (Fig. 9). The complex modulus can be described by $G^* = G' + iG''$, where, $G'$ and $G''$ are the storage and the loss moduli, respectively. The $G'$ of the polymer was found to decrease with a decreasing oscillation frequency, however at low frequencies it displayed a low slope. The $G''$ also decreased with frequency and at about 1 Hz the curves of $G'$ and $G''$ crossed each other. Both the low slope of $G'$ and the tan $\delta (G''/G')$ of $<1$ suggested a gelling effect at low frequencies [16, 25]. This gelling of the melt must have been due to a clustering of the end-HS of the tri-block copolymer. The end-HS have more freedom to cluster and the hydrogen bonding might have reinforced such a clustering effect. The effect of frequency on the complex viscosity is presented in Fig. 9b. The complex viscosity varied strongly with frequency and at low frequencies the viscosities demonstrated very high values. For a copolymer with an $M_n$ of $\sim 10,000$ g/mol, a more Newtonian behavior, with a low melt viscosity, was expected. The strong change in complex viscosity with decreasing frequency supported the suggestions of a gelling effect. The ABA end-HS tri-block copolymers seemed to display a strong thixotropic effect, as observed on ABA tri-block copolymers with mono disperse amide end segments, but not seen on similar multiblock copolymers [21].

**CONCLUSION**

A series of ABA tri-block copolymers with MDI-6T6m end-segments were synthesized by increasing the length of the mid-SS. The crystallinity of the amide units in the 6T6m diamide was high whereas that of the MDI units was probably low. The storage modulus increased significantly with the HS content and was even higher than for a comparable multiblock copolymer. The fracture strains of the tri-block copolymers decreased with decreasing copolymer $M_n$ but were, for a molecular

![Diagram](https://via.placeholder.com/150)
weight of 6000 g/mol, still above 100%. The tri-block copolymers demonstrated a brittle-ductile transition at a molecular weight of \( \sim 6000 \) g/mol. The CS values were low, suggesting a good low strain elastic behavior even for low molecular weight copolymers. At low frequencies, the melt viscosities of the tri-block copolymers were unusually high and a crossover point in the \( G''/G' \) could be observed. This suggested a gelling effect at low frequencies due to the clustering of the MDI-6T6m end-segments. In the solid state the amide end segments are arranged in ribbon like crystallites [21] and in the melt as non crystalline clusters (Fig. 10). The tri-block copolymers seemed to display a thixotropic behavior. In short, these tri-block copolymers with monodisperse end-blocks demonstrated low melt viscosities combined with interesting tensile and elastic properties.

REFERENCES