Chapter 3
SYNTHESIS AND CHARACTERIZATION OF DIAMINE-DIAMIDE SEGMENTS

Abstract

Uniform diamine-diamide hard segments are synthesized and characterized. The structure, purity and melting behaviour of these segments are analyzed using $^1$H-NMR and DSC. All the amide segments are studied by FT-IR spectra. The purity of the hard segment is enhanced by recrystallizable method. The FT-IR spectrum confirms the presence of amine and amide groups. The synthesized hard segments crystallizing fast and complete. The synthesized hard segments 6A6 and 6T6 are used for the preparation of segmented Poly(urethane-urea-amide).
3.1. INTRODUCTION

Segmented or multi-block copolymers often consist of alternating crystallizable and amorphous segments. The high melting crystalline phase gives the material dimensional stability, heat stability and solvent resistance. If the crystallizable segment has a regular structure and a uniform length then the crystallization of the segment is faster and more complete and the properties of the copolymer are better\textsuperscript{1-4}. So far the only uniform amide segments which have been described are di-amides\textsuperscript{5-13}. The extended di-amide segments have a higher melting temperature because the lamellar thickness is higher\textsuperscript{14}. However, the melting temperature is broad due to a distribution in the segment lengths.

Currently, there is interest in crystallizable amide segments in segmented block copolymers\textsuperscript{15-19}. The melting temperature of the crystalline segments in these block copolymer depends on the type, size of the crystallizable segment and the concentration of the amorphous segment\textsuperscript{17,20}. The properties of the copolymers also depend on the size distribution of the crystallizable segments. If the crystallizable segments have a regular structure and are uniform, then crystallization is fast and the degree of crystallization is high\textsuperscript{1,4}. The structure and regularity of the rigid segments are of importance for the crystallization behaviour. For example, Van der Schuur\textsuperscript{21} compared amide containing segments based on para and meta substituted phenylene rings in copolymers. Segments containing para substituted segments crystallize rapidly while meta substituted segments are almost unable to crystallize.

An effective way to improve the phase separation in segmented copolymers is using crystallizable hard segments of uniform length. Harrell\textsuperscript{1} and Ng et al.\textsuperscript{2} studied non-
hydrogen bonding segmented polyurethanes with both uniform and non-uniform hard segments, while Eisenbach et al.\textsuperscript{3} and Miller et al.\textsuperscript{4} did similar studies on hydrogen bonding polyurethanes. Gaymans et al.\textsuperscript{22} investigated segmented copolyetherester amides with uniform crystallizable bisester diamides based on 1,4-butanediamine and dimethyl terephthalate. All studies showed that the hard segments of uniform length offer the following advantages:

- they crystallize over their full length and as a result:
  
  very short segments are able to crystallize

- they crystallize nearly completely and as a result:
  
  the glass transition temperature of the copolymer approaches that of the soft segments and the mechanical property will be enhanced.

- the crystalline lamellae are stable and melt in a narrow temperature range\textsuperscript{23} and as a result:
  
  the rubbery plateau is temperature independent.

The aim of this chapter is to synthesize and characterize the two types of hard segments 6A6 and 6T6 that can be used for the preparation of segmented poly(urethane-urea-amide). The structure of the hard segment is confirmed by using IR and NMR studies. The melting temperature is measured by DSC.

3.2. EXPERIMENTAL

3.2.1. Materials

Dimethyl terephthalate (DMT), 1,6-hexamethylenediamine (HMDA), 1,4 diamino benzene, n-hexyl amine, phenyl benzoate, adipic acid, sodium methoxide, dimethyl adipate, n-butyl acetate, diethyl ether, methanol, toluene and N-methyl-2-pyrrolidone (NMP) are purchased from Merck. All chemicals are used as received.
3.2.2. \(^1\)H-NMR

\(^1\)H-NMR spectra of the polystyrene are run on a Bruker FT-NMR spectrophotometer operating at 320 MHz at room temperature using CDCl\(_3\) as a solvent and tetramethylsilane (TMS) as an internal reference.

3.2.3. FT-IR Spectra

Infrared spectra are recorded using Alpha Bruker FT-IR with a resolution of 2 cm\(^{-1}\). Samples are prepared by adding a droplet of a polymer solution (HFIP (1 g/L)) on a pressed KBr pellet and the measurements are carried out at room temperature. The temperature dependent FT-IR are recorded on a Alpha Bruker instrument connected with alpha-T accessory and recorded between 30°C to 120°C under a nitrogen flow.

3.2.4. DSC

DSC spectra are recorded on a Perkin Elmer DSC 7 apparatus equipped with a PE 7770 computer and TAS-7 software. 10-15 mg of dried copolymer sample is heated at a rate of 20°C/min for recording DSC spectra. The second heating and first cooling curve is used to evaluate the Tm and Tc of hard segments respectively.

3.2.5. General procedure for the synthesis of 6T6-diamine- diamide

DMT (45 g, 0.23 mol) is added to an excess amount of 1,6-hexamethylene diamine (250 g, 2.15 mol) in a round bottomed flask with a nitrogen inlet, mechanical stirrer and a reflux condenser. The reaction mixture is heated to 80°C and 6T6-diamine started to precipitate. After 2 hrs at 80°C, the reaction mass is nearly solid and 500 mL toluene is added to allow stirring. After 16 h reaction at 80 °C, the reactor is cooled and the product is collected by filtration. The crude 6T6 is washed twice with hot toluene...
(80°C) and twice with diethyl ether to remove the excess of 1,6-hexamethylene diamine. The purity as determined by $^1$H-NMR is 71% (Eqn. 3.1). The 6T6 is recrystallized using hot butyl acetate (25 g/L) and the purity as determined by NMR is found to be 98% with a yield of 40%. $^1$H-NMR (TFA-d6): 7.98 (s, 4H, terephthalic H), 6.6-7.0 (s, 4H, NH$_2$ end groups), 3.69 (t, 4H, CH HMDA amide side), 3.31 (s, 4H, CH$_2$ and HMDA amine side), 1.85 (t, 8H, CH$_2$ HMDA), 1.58 (s, 8H, CH$_2$ HMDA).

![Scheme 3.1: Synthesis of 6T6-diamine-diamide](image)

### Scheme 3.1: Synthesis of 6T6-diamine-diamide

#### 3.2.6. General procedure for the synthesis of 6A6-diamine- diamide

1,6-hexamethylene diamine (500 g, 4.3 mol) is melted in a round bottomed flask and dimethyladipate (53 g, 0.3 mol) is added. Sodium methoxide (6 mL of a 0.5 M solution in methanol) is added as a catalyst. The reaction is performed at 75°C for 16 h. After cooling, the product is collected over a no. 4 filter and washed twice with diethyl ether. The purity as determined by $^1$H-NMR is 85% (Eqn. 3.1). 6A6 is recrystallized from hot 1,4-dioxane (16 g/L) at 100°C. After recrystallization with a yield of 63% and
the purity is 98%. $^1$H-NMR: (TFA-d, $\delta$) 6.80 (s, 4H, NH$_2$ end groups), 3.56 (d, 4H, CH$_2$ HMDA amide side), 3.28 (s, 4H, CH and 4 CH HMDA amine side), 2.77 (s, 4H, 12 adipate), 1.90 (t, 8H, CH$_2$ HMDA), 1.74 (d, CH and 4 CH adipate), 1.54 (s, 8H, ).

![Scheme 3.2: Synthesis of 6A6-diamine-diamide](image)

3.3. RESULTS AND DISCUSSION

Two types of hard segments (6T6 and 6A6) are prepared and characterized. The synthetic route of diamine-diamide ($T=$Dimethylterephthalate or $A=$Adipic acid) is presented in Scheme 3.1 and Scheme 3.2. In the synthesis, a molar excess of 8 times diamine is used to limit the formation of longer blocks. The reaction between dimethyl terephthalate and the diamine is fast and catalyst is not needed. The toluene is added to the reaction mixture after some times. The reaction product is filtered and washed with diethylether to remove the free diamine.

3.3.1 $^1$H-NMR

The molecular structure of 6X6-diamide is analyzed by $^1$H-NMR. The peak assignments, integral values and purity calculations of diamine-diamide are presented in
the Table 3.1. The integral values of the peaks are close to the calculated values and correspond with data from literature\textsuperscript{21,24}. The \textsuperscript{1}H-NMR spectrum of the product contains no peaks for side products. Therefore it can be concluded that diamine-diamine is prepared with a very high purity after recrystallization. The \textsuperscript{1}H-NMR spectra of 6T6 before and after recrystallization are given in the Figure 3.1.

The 6T6 unit is recrystallized from hot n-butyl acetate to further improve the purity (>98%). The purity is calculated from the \textsuperscript{1}H-NMR integral ratio (Eqn. 3.1) of CH amide side (c) to CH amine side (d) (Figure 3.2).

\[ \text{purity of 6T6 or 6A6} = \left(2 - \frac{\text{integral CH}_2 \text{amide side}}{\text{integral CH}_2 \text{amide side}}\right) \times 100\% \quad \text{Eqn. (3.1)} \]

![Figure 3.1: 6T6-diamine before (lower curve) and after recrystallization (upper curve).](image)
Figure 3.2: Peak assignment of protons of 6T6 and 6A6

Table 3.1: Properties of 6T6-diamine and 6A6-diamine

<table>
<thead>
<tr>
<th>Diamine-diamide</th>
<th>After synthesis</th>
<th>After recrystallization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield (%)</td>
<td>Purity (%)</td>
</tr>
<tr>
<td>6T6-diamine</td>
<td>88</td>
<td>71</td>
</tr>
<tr>
<td>6A6-diamine</td>
<td>85</td>
<td>85</td>
</tr>
</tbody>
</table>

After synthesis the 6T6 and 6A6-diamine yield is 88% and 85% with the purity 71% and 85% but after recrystallization the 6T6 and 6A6-diamine yield is only 40% and 63% with the purity of 98%. The melting temperature of 6T6-diamine and 6A6-diamine is 201°C and 180°C respectively. The melting temperature is decreased by increasing the aliphatic amine or by replacing the central terephthalic group by an adipic group. The melting temperature and the heat of melting decrease with decreasing purity of the product.

3.3.2. FT-IR spectra

With IR spectroscopy the formation of amide groups can be observed. In Figure 3.3, the IR spectrum of 6T6-diamine and 6A6-diamine are compared. Both 6T6-diamine and 6A6-diamine shows the amide carbonyl band at 1629 and 1623 cm⁻¹ respectively.
The absorption peaks of amine group (NH$_2$) are presented at wave number of 3295-3311 cm$^{-1}$. Also, the absorption peak at 3012 cm$^{-1}$ shows the presence of aromatic group in 6T6 hard segment but this peak is absent in the case of 6A6 hard segment.

![FT-IR Spectrum](image)

**Figure 3.3: Comparative of the FT-IR spectrum of 6A6 and 6T6**

### 3.3.3 DSC

With DSC it is shown that the 6X6-diamine segments after synthesis show multiple melting transitions. After recrystallization all 6X6-diamines have a high purity and show a sharp melting peak. With DSC, the melting endotherms of 6A6-diamine before and after recrystallization are measured. In Figure 3.4, the first heating scans of 6A6-diamine before and after recrystallization are compared. The DSC heating curve of recrystallized 6A6-diamine shows a sharp melting peak with a peak temperature of 180°C. At 80-100°C there is a broad peak that is possibly due to a transition in the crystalline structure of the 6A6-diamine. This phenomenon is well known polyamides, for example nylon-6,6$^{25,26}$. 
3.4 CONCLUSION

Diamine-diamide segment is synthesized by single step reaction, followed by recrystallization to obtain a highly pure diamine-diamide (6T6 or 6A6). The product of diamine-diamide does not contain any side products like 6A6A6, 6T6T6 etc. All the hard segments are crystallizing fastly. The structure is confirmed by using FT-IR, $^1$H-NMR studies. Melting temperature is measured by DSC. It clearly shows that the purity of the sample increases upon recrystallization and it leads to increase in the melting temperature. 6T6 and 6A6 are used as hard segments for the preparation of segmented poly(urethane-urea-amide).
REFERENCES


