Tri-block Copolymer Based on Crystallizable Amide Segments with Functionalized Polystyrene

Abstract

This article discusses on the synthesis and characterization of segmented tri-block copolymer using monofunctional hard segments (mHS) and difunctional polystyrene as a soft segment. Three hard segments used are T6T6B, T6A6B and T6m. The soft segment concentration is varying from 2500 to 10500 g/mol using the dimethyl terephthalate (DMT) as a chain extender. The viscosity of the copolymer is linearly increased with respect to molecular weight of the SS. The crystallization behaviour of the copolymer is studied by DSC and FT-IR method. The TGA results reveal that all copolymer have single stage decomposition centered around 427°C and solvent resistance of these materials are very high even at a low concentration (10%) of amide content. All the copolymer shows low water absorption properties.
7.1 INTRODUCTION

Tri-block copolymer are interesting two phase materials\textsuperscript{1,2} and polymer such as styrene–butadiene–styrene (SBS) usually displays liquid–liquid demixing phase structures with a dispersed amorphous polystyrene phase. In order to obtain good mechanical properties, the molecular weight of the SBS copolymer should be high and the hard segments should also have high molecular weights. The polystyrene segment length is often on the order of 25,000 g/mol. Due to the high molecular weight, the blocks are often immiscible and this is even in the melt. These SBS tri-block copolymer usually demonstrate low moduli and low maximum use temperatures. Tri-block copolymers with crystallizable end segments have been made from short, soft mid-segments (600–3000 g/mol) and long nylon-6 or nylon-11 hard segments\textsuperscript{3}. The long nylon blocks are phase separated from the soft segments and the nylon blocks are partly crystalline.

Thermoplastic elastomers based on short, hard segments shows excellent mechanical and thermal properties.\textsuperscript{1} The multi-block copolymer having hard segments (1000–3000 g/mol) has homogenous melts. The hard segment phase separate by crystallization upon cooling and the crystallites provide high modulus at room temperature and high maximum use temperature. If the hard segments (HS) are mono-disperse in length, then the copolymer has a sharper hard segment melting transition\textsuperscript{4,5}. The mono-disperse segments crystallize fast and almost completely, and as a result, the soft phase contains very little dissolved hard segments. The mono-disperse HS have crystallize with nano-ribbonlike structures with high aspect ratios (i.e., 300–1000)\textsuperscript{6-10}. When the HS is truly monodisperse, then the modulus at the room temperature will be the same to near the HS melting temperature, i.e., almost independent of temperature. If the mono-disperse HS contain amide segments, H-bonding is with the two neighbouring chains in the crystal and, ribbon-like H-bonded structures are formed. In the H-bonding direction, the crystallites can be as long as
1000 nm leads to high aspect ratio. These nano-ribbon crystallites are the physical crosslinks for the soft phase and in turn reinforce the soft phase.

Tri-block copolymer of telechelic mid-segments and short mono-disperse H-bonding end segments are a novel concept. The H-bonding end segments, e.g., ureidopyrimidinone (UP) units, are able to form dimer interactions\textsuperscript{11-14} and due to this dimer H bonding, the low molecular weight copolymer become non-covalently bonded to supramolecular polymers with properties of a high molecular weight polymer.\textsuperscript{15,16} However, the melting temperature of copolymer comprising these dimer interactions is low, as is the moduli of the copolymers.

It would be interesting to study tri-block copolymers with mono-disperse amide end segments in a high Tg soft segment like polystyrene. As a result of the amide end segments, H-bonding should be possible with the two neighbouring chains in the crystal, and in that way long H-bonded ribbon-like crystalline structures are expected to be formed. As the crystalline of the mono-disperse amide segments is normally very high, a network formation is expected to take place with these tri-block copolymers. A crystallization of all the end blocks leads to all the mid-blocks becoming part of a network (Figure 7.1.). Since the crystallizable segments in a tri-block copolymer are represented by the chain ends, the flexibility of the material is expected to be lower (i.e., high modulus) than if the crystallizable units position in the chain.

![Figure 7.1: Schematic representation of staging of hard segment.](image-url)
In this article, the synthesis and characterization of segmented tri-block copolymer based on functionalized polystyrene as an amorphous segment and three mHS as a crystallizable segment are presented. The main goal of this work is to modify the amorphous polystyrene to a semi-crystalline copolymer using crystallizable segments.

Figure 7.2: Chemical structures of (a) T6T6B-monomethyl (b) T6A6B-monomethyl. (c) T6m-monomethyl.

The hard blocks used in this study are namely, T6T6B, T6A6B and T6m (Figure 7.2). The hard segment can form hydrogen bonds, therefore the amide units
will show better crystallization rate and the morphology of the crystallites are studied by temperature dependent FT-IR, DSC and TGA techniques. Also, water absorption and solvent resistivity are studied in this chapter.

7.2. EXPERIMENTAL

7.2.1. Materials

Styrene (St, 99%) is purchased from Aldrich Chemical. After it is passed through a basic alumina column to remove the inhibitor, the styrene is stored under a nitrogen atmosphere at 14°C. Trifluoroacetic acid (TFA), Phenol, and 1,1,2,2 Tetrachloroethane are purchased from Aldrich Chemical. N-Hexylamine is purchased from Aldrich Chemical and purified through vacuum distillation. Dimethyl terephthalate (DMT) and N-methyl-2-pyrrolidone (NMP) are purchased from Merck. Tetraisopropyl orthotitanate (Ti(i-OC\textsubscript{3}H\textsubscript{7})\textsubscript{4}) and m-xylene are obtained from Merck. Tetrahydrofuran, Toluene, Methanol, Dimethyl formamide and Aluminium oxide are purchased from S.D Fine chemical and used as such without further purification. The dihydroxy terminated polystyrene unit is synthesized using the known route\textsuperscript{17,18}. Three types of monodisperse hard segments are synthesized using the known route\textsuperscript{5,6}.

7.2.2. General Procedure for the synthesis of the segmented block copolymer

Tri-block copolymer is synthesized with various mole ratios of soft to hard segments Table 7.1. All the polyamide is synthesized by condensation reactions, which is using a solution/melt polymerization method. The reaction is borne out in a 250 mL stainless steel vessel with a nitrogen inlet and a mechanical stirrer. As an example, the synthetic procedure of the polymer 3A is given here. The metal reactor is charged with T6m (1.32 g, 0.005 mol), PSt\textsubscript{250} (5 g, 0.0025 mol), the catalyst solution (0.2 mL of 0.05 M Ti (i-OC\textsubscript{3}H\textsubscript{7})\textsubscript{4} in m-xylene), and 75 mL of NMP under nitrogen flow. The stirred reaction mixture is heated to 180°C for 30 min, after which the temperature is raised in increments to 250°C with in a time period of 1 hr.
Dihydroxy terminated polystyrene (PSt$_{2500}$) + mHS (X) + Dimethyl terephthalate (T) → X-PSt-T-PSt-X

Where,

$X = T6T6B$ or $T6A6B$ or $T6m$

Here

1A, PSt=2500, Y=0 and T6T6B
1B, PSt=2500, Y=2500 and T6T6B
1C, PSt=2500, Y=5000 and T6T6B
1D, PSt=2500, Y=7500 and T6T6B

2A, PSt=2500, Y=0 and T6A6B
2B, PSt=2500, Y=2500 and T6A6B
2C, PSt=2500, Y=5000 and T6A6B
2D, PSt=2500, Y=7500 and T6A6B

3A, PSt=2500, Y=0 and T6m
3B, PSt=2500, Y=2500 and T6m
3C, PSt=2500, Y=5000 and T6m
3D, PSt=2500, Y=7500 and T6m

**Scheme 7.1: The synthetic route of the tri-block copolymers**

The reaction mixture is then stirred at 250°C for 2hr. Subsequently, the pressure is carefully reduced (P< 20 mbar) to distill off the NMP to <0.3 mbar and the polymerization is finished with a 1h reaction at 250°C at a high vacuum. The reaction mass is then cooled while maintaining the low pressure. The copolymer is transparent with a brown hue. This routine is adopted for the synthesis of polymer series 1A to 1D, 2A to 2D and 3A to 3D.

**7.2.3. Fourier Transform - Infrared Spectroscopy (FT-IR)**

Infrared spectra are recorded using Alpha Bruker FT-IR, with a resolution of 4 cm$^{-1}$, samples are prepared by adding a bead of a polymer solution (1 g/L in TFA) on a pressed KBr pellet and the measurements are carried out at room temperature. The temperature dependent FT-IR are recorded on an Alpha Bruker instrument connected with alpha-T accessory and recorded between 30 to 120°C under a nitrogen flow.
samples investigated for the use of this work, is prepared from the 5 Wt.% solution of polyamide in trifluoroacetic acid. The films are prepared by pouring the solution onto a potassium bromide pellet and by evaporating the solvent. This condition allows the polymer films to have a stable morphology with desirable properties.

The degree of crystallinity of the rigid segments in the polymers could be estimated with the following equations: (7.1 and 7.2)

\[
X_c = \frac{\text{crystalline amide peak}}{\text{amorphous+crystalline amide peak}} \quad \text{Eqn}\text{-}\text{--------}(7.1)
\]

\[
X_c = \frac{h(1733)}{[C_4h(1747)] + h(1733)} \times 100\% \quad \text{Eqn}\text{-}\text{--------}(7.2)
\]

The heights (l) of the amorphous and crystalline amide peaks are related by the factor “C” with a value of 2.432,33.

7.2.4. Inherent viscosity measurements

The inherent viscosity of the copolymers at a concentration of 0.1 dL/g in a 1:1 (molar ratio) mix of phenol/1,1,2,2-tetrachloroethane is determined at 25°C by using a capillary Ubbelohde and calculated by using Eqn. (7.3).

\[
\eta_{inh} = \ln \left( \frac{t}{t_0} \right) / c \quad \text{Eqn}\text{-}\text{--------}(7.3)
\]

\[t = \text{Elution time of the polymer solution}\]
\[t_0 = \text{Elution time of the solvent}\]
\[c = \text{Concentration of the polymer solution (dL/g)}\]

7.2.5. Differential Scanning Calorimetry (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 $20^\circ$C/min for recording DSC spectra. The second heating and first cooling curve are used to evaluate the Tm and Tc of hard segments respectively.

7.2.6. **Wide Angle X-ray Diffraction (WAXD)**

Wide angle 2D-X-ray Scattering is measured using the Xeuss WAXS instrument. Cu-K-alpha is the X-ray source. Sample to theta distance is 221.75 mm silver behenate is used for as distances calibration standard. 2D-X-ray scattering data is integrated using Fit-2D software.

7.2.7. **Thermo Gravimetric Analysis (TGA)**

Thermal stability of the polymers is studied using Dupont 951 Thermo gravimetric analyzers. Thermogram is recorded by heating approximately 8-10 mg of the sample from 30 to 600°C at the heating rate of 10°C min$^{-1}$ in a nitrogen atmosphere with a gas flow rate of 100 mL/min.

7.2.8. **Water Absorption**

The equilibrium water absorption is measured on pieces of injection-moulded polymer bars. The samples are placed in desiccators with a layer of demineralised water for four weeks at room temperature. The water absorption is defined as the weight gain of the polymer according to Eqn. (7.4)

\[ \text{Water absorption} = \frac{m_o-m}{m} \times 100 \text{ [wt.%]} \quad \text{Eqn}-----------(7.4) \]

Where $m$ is the weight of the dry sample and $m_o$ is the weight of the sample after conditioning to equilibrium.
7.2.9. Solvent Resistivity

Injection moulded sample of dimension 10x10x2 mm is used for solvent resistance measurements. Previously weighed sample is dipped in 50 mL of organic solvents taken in a flask and shaken for 60 min. After that, the solvent is poured and the flask is dried for 24 hr at 70°C. It is weighed again and from the weight loss, the measure of a polymer sample dissolved in that solvent is calculated by using Eqn. (7.5).

\[
\text{Solvent Resistivity} = \frac{m - m_0}{m_0} \times 100\%
\]

Eqn. -------- (7.5)

Where, \(m\) is weight of the substance (mg) before solvent treatment, \(m_0\)- weight of the substance (mg) after solvent treatment.

7.3. RESULTS AND DISCUSSION

7.3.1. Synthesis of Tri-block copolymer

The tri-block copolymer based on OH-PSt-OH\(_{2500}\) (SS) with monomethyl monoamide (mHS) (T6m) or tetra-amide (T6T6B or T6ATB) are prepared via a polycondensation reaction and a titanium-based catalyst is used. As mHS has a high melting temperature \(^{19, 20}\), NMP is used in the first reaction step. The maximum reaction temperature is limited to 250°C as SS degrades at high temperatures. In nitrogen surroundings SS starts to break down around 464°C and when air (oxygen) is present the decomposition starts at 220°C. In the first reaction step the T6m units are coupled to the SS, thereby lowering the melting temperature of the T6m. Therefore, the polycondensation reaction could subsequently be carried out in the melt at 250°C. During the condensation reaction, methanol is formed and removed.
Table 7.1: Mole fraction in feed, repeating length soft segment and the inherent viscosities of the polymers.

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>Mole fraction</th>
<th>mHS (Wt.%)</th>
<th>Repeating length of S.S (g/mol)</th>
<th>η&lt;sub&gt;inh&lt;/sub&gt; (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PST&lt;sub&gt;2500&lt;/sub&gt;</td>
<td>-- -- -- --</td>
<td>2500</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>1A</td>
<td>2 1</td>
<td>37</td>
<td>2500</td>
<td>0.15</td>
</tr>
<tr>
<td>1B</td>
<td>2 2 1</td>
<td>22</td>
<td>5194</td>
<td>0.29</td>
</tr>
<tr>
<td>1C</td>
<td>2 3 2</td>
<td>15</td>
<td>7888</td>
<td>0.34</td>
</tr>
<tr>
<td>1D</td>
<td>2 4 3</td>
<td>12</td>
<td>10582</td>
<td>0.41</td>
</tr>
<tr>
<td>2A</td>
<td>2 1</td>
<td>38</td>
<td>2500</td>
<td>0.15</td>
</tr>
<tr>
<td>2B</td>
<td>2 2 1</td>
<td>23</td>
<td>5194</td>
<td>0.30</td>
</tr>
<tr>
<td>2C</td>
<td>2 3 2</td>
<td>16</td>
<td>7888</td>
<td>0.36</td>
</tr>
<tr>
<td>2D</td>
<td>2 4 3</td>
<td>13</td>
<td>10582</td>
<td>0.39</td>
</tr>
<tr>
<td>3A</td>
<td>2 1</td>
<td>20</td>
<td>2500</td>
<td>0.10</td>
</tr>
<tr>
<td>3B</td>
<td>2 2 1</td>
<td>15</td>
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<tr>
<td>3D</td>
<td>2 4 3</td>
<td>10</td>
<td>10582</td>
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</tr>
</tbody>
</table>

The molecular weight of the PST (soft segment) is varying from 2500 to 10500 g/mol using DMT as an extender (T-PSt<sub>2500</sub>). The mole ratios of the starting materials, expected molecular weight and inherent viscosities of the tri-block copolymer are presented in the Table 7.1. Throughout the polymerization process the reaction mixture is transparent, which indicates that the melt phasing did not take place. Even in the solid state the polymer is transparent suggesting that the mHS crystals are small to scatter light. The materials have a slightly yellow in colour. The colour may be due to NMP in the presence of a titanium catalyst at high temperature.  

10, 19
7.3.2. Inherent Viscosity Measurements

![Graph showing the effect of soft segment length on the molecular weight of the polymer.](image)

**Figure 7.3: Effect of soft segment length on the molecular weight of the polymer:**
- ● T6T6B; ● T6A6B; ● T6m.

The synthesized compounds are capable of forming hydrogen bonding itself and also with other substrates. Synthesized segmented tri-block copolymers are difficult to dissolve in organic solvents and thus a GPC analysis could not be taken. Inherent viscosity of the copolymer is determined in Phenol/1,1,2,2-tetrachloroethane (1:1 molar mixture) to get an idea about the molecular weight. The pure PSt shows the inherent viscosity of 0.1 dL/g. The amide containing copolymer shows slightly higher inherent viscosities (0.1-0.45 dL/g), suggesting that the polymer indeed tri-block copolymer with both the ends are blocked by mHS. The mono amide based T6m (3A-3D) has inherent viscosities ranged between 0.1-0.45 dL/g, whereas the inherent viscosity of the series 1A-1D are 0.15-0.41 dL/g, 2A-2D are 0.15-3.9 dL/g. The 1D, 2D and 3D tri-block copolymers have higher inherent viscosities than the 1A, 2A and 3A segments. It is expected that with an increase in inherent viscosities an increase in
molecular weight is obtained. The data are shown in Table 7.1. In all the three series, the inherent viscosity is linearly increasing with increasing the repeating length of the SS as shown in the Figure 7.3. It indicates that as the length of the soft segment increases, the inherent viscosity increases accordingly.

7.3.3. FT-IR

FT-IR is a powerful tool for studying the crystallinity of the amide groups in the polymer. It is thus used to study the crystallinity of the amide carbonyl band that is sensitive to crystalline order. The room temperature FT-IR spectrum of the samples 1A, 2A and 3A are shown in the Figure 7.4. The absorbance band of the crystalline amide carbonyl groups is located at 1630cm$^{-1}$, the amorphous amide carbonyl at 1660–1670cm$^{-1}$ and the ester carbonyl at 1720–1730cm$^{-1}$ as shown in Figure 7.4 and Table 7.2. The studied amide carbonyl bands are sensitive to the hydrogen-bonding and the distance between the two hard segments. The crystallinity of the mHS can be obtained by comparing the intensity of crystalline amide carbonyl with amorphous amide carbonyl. In the melt, the amide segments are in the amorphous state and the amount of the amide carbonyl in the crystalline state is expected to be low. Similar calculations are performed on several amide containing TPEs. For calculating crystallinity in copolymer, the peak height at 1630cm$^{-1}$ ($h_{(1630cm^{-1})}$) and the peak height of 1660-1670cm$^{-1}$ ($h_{(1670cm^{-1})}$) are taken to represent crystalline and the amorphous respectively$^{20}$. 
### Table 7.2: FT-IR data of the tri-block copolymer at room temperature.

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>mHS (Wt.%)</th>
<th>$\eta$ inh (dL/g)</th>
<th>Amide I (C=O)</th>
<th>Ester (C=O)</th>
<th>Crystallinity (Xc %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSt$_{2500}$</td>
<td>--</td>
<td>0.1</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1A</td>
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<td>0.15</td>
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<td>1664</td>
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<tr>
<td>1B</td>
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<tr>
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<td>1D</td>
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<td>0.41</td>
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<td>1676</td>
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<tr>
<td>3D</td>
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<td>0.45</td>
<td>1633</td>
<td>1669</td>
<td>1723</td>
</tr>
</tbody>
</table>

The crystallinity data and the effect of hard segment on the crystallinity are presented in the Table 7.2 and Figure 7.5 respectively. The synthesized tri-block copolymer has a strong crystalline amide peak at 1630cm$^{-1}$, and a weak peak corresponding to the amorphous carbonyl amide at 1670cm$^{-1}$. This indicated that most of the hard segments are in the crystalline state.
Figure 7.4: FT-IR spectrum of copolymers at room temperature, ■, 1A; ▼, 2A; ●, 3A.

Figure 7.5: FT-IR spectra of 3A, sample recorded at different temperature from 30°C to 80°C.
Figure 7.6: Crystallinity of 3A as a function of temperature measured by FT-IR: heating (●) and cooling (★) cycle.

But as the amide contents decrease in the copolymer, the crystallinity decreases suggesting a less close packing of hard segment in the length soft segment. The crystallinity of the tetra amide containing hard segments (100%) are higher than the monoamide containing hard segments (97%) indicating that the tetra amide segments facilitate the better close packing of crystals than the monoamide counterpart (Table 7.2). All the tri-block segmented copolymer has almost 100% crystalline is due the low and high amide concentration as due to four types of hydrogen bond forming in the terminal position. Thereby low molecular weight of segmented block copolymer shows a very small window for crystallization at low concentrations.
Figure 7.7: The effect of the HS content on the crystallinity of the HS: ●, T6T6B; ○, T6A6B; ▲, T6m. The absorbance peak of the crystalline amide carbonyl decreases and the absorbance peak of amorphous amide carbonyl increases with increasing the temperature from 30 to 85°C. This modification is particularly strong when the temperature approaches the melting temperature of the 3A copolymer. In the melt, the peak at 1630cm⁻¹ has almost completely disappeared, while the peak at 1673cm⁻¹ is maximized. On heating the temperature higher than the melting temperature of the copolymer, there is no change in the intensity of 1630cm⁻¹ crystalline amide peak in the FT-IR spectra is observed. The wave number of the amorphous amide carbonyl band increase from 1660 to 1680cm⁻¹ with an increase in temperature. The absorbance peak of the ester
carbonyl shifted from 1725 to 1730 cm\(^{-1}\) with increasing temperature but the intensity is hardly affected. The crystallinity of the rigid segments is calculated by using 1640 and 1685 cm\(^{-1}\) peak intensities. (Eqn. 7.1 and 7.2) \(^{19, 21}\).

Figure 7.8: Representation of the tri-block copolymer stacking in (a) a parallel and (b) an anti parallel with reference to T6T6B.

In Figure 7.7 the crystalline 3A is given as a function of the temperature by heating and a cooling cycle. The crystallinity of the T6m segment in the copolymer is high (97\%) at room temperature. At 85°C, just before the melting temperature, a sharp decrease in crystalline is observed. Also, above the melting temperature a small portion of mHS is still present in a crystalline form and this is probably due to a small fraction of longer amide segments in the copolymer, which have a higher melting temperature. The cooling cycle takes a similar path as the heating curve and the crystallinity is recovered completely at room temperature.

The asymmetric structure of mHS may have an influence on the packing, melting temperature and the heat fusion. In the Figure 7.8, the stacking pattern in the
crystalline state of T6T6B-monomethyl is given as an example. It shows that T6T6B can adopt either parallel or anti-parallel structure.

7.3.4. DSC

The thermal properties of the tri-block copolymer are studied by DSC. A typical DSC thermogram of the second heating scans and first cooling scan of the polymer 1A, 2A and 3A are given in Figure 7.9 and the results are summarized in Table 7.3. The Tg of SS for the polymer 1A to 1D is started at 69°C and ends at 79°C and Tg of SS for the polymer 2A to 2D is started at 72°C and ends at 88°C.

![DSC thermogram](image)

**Figure 7.9:** DSC heating curve (closed symbol) and cooling curve (open symbol) of the tri-block copolymers: O, 1A ; ◊, 2A ; □, 3A.

Similarly, Tg of 3A to 3D series starts at 64°C and ends at 72°C. Three series Tg is higher than the pure PSt which is 63°C. However, the observed Tg value is very close to the pure PSt suggesting that the mHS are completely phase separated from the soft matrix.
### Table 7.3: DSC, TGA and water absorption data for tri-block copolymers.

<table>
<thead>
<tr>
<th>Polymers code</th>
<th>mHS (Wt.%)</th>
<th>SS Wt.%</th>
<th>$n_{inh}$ (d/Lg)</th>
<th>TGA °C</th>
<th>Water abs.</th>
<th>DSC (°C)</th>
</tr>
</thead>
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<td></td>
<td></td>
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<td>Tg Tm Tc</td>
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<tr>
<td>PST$_{2500}$</td>
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<td>100</td>
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<td>412</td>
<td>--</td>
<td>63</td>
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</tr>
<tr>
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<td>70</td>
</tr>
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<tr>
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<td>88</td>
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<tr>
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<tr>
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<td>0.33</td>
<td>420</td>
<td>0.4</td>
<td>69</td>
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<td>90</td>
<td>0.45</td>
<td>415</td>
<td>0.2</td>
<td>72</td>
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</table>

This explanation is further supported by the crystalline value obtained from the FT-IR measurement presented in the Table 7.2. The effect of hard segment content in the Tg of the soft phase is presented in the Figure 7.10. This small increase in Tg of SS upon decreasing HS content is believed to have been due to the presence of some portion of hard segments dissolved in the soft phase which, disturbing the Tg of the SS or due to increase in the soft segment length.

The DSC graph of the samples 1A, 2A and 3A shows both melting and crystallization transitions. These two transitions are (both melting and crystallinity) often observed for semi-crystalline polymers$^{20, 21}$. For the copolymer 3B, 3C and 3D
showed only melting peaks for HS and not crystalline exotherm. Apparently the concentration of the HS in these samples is too little to measure the crystalline exotherm in DSC measurement. As the length of the SS increased from 2500 to the 10500g/mol, the melting point of HS is decreasing, this is due to solvent effects of SS provided over HS.

Besides, this linear decrease in the melting point of HS upon varying the SS length clearly indicates that the HS is effectively incorporated in the polymer chain as a uniform HS length. Moreover the DSC graph shows a single peak for the melting of HS clearly indicates the transesterification method employed for the preparation of polymer is successful in these polymer samples. Similar to the Tm (melting of hard segments) peak, the Tc peak for the HS is sharp and the Tm-Tc data are presented in

**Figure 7.10: Effect of hard segment concentration on the Tg of the soft phase:**  
●, T6T6B; ♦, T6A6B; ▲, T6m.
the table 7.3 suggesting that this copolymer have low under-cooling values and this intern suggested that the monodisperse crystallizable rigid segments crystallized very fast.

7.3.5. WAXD

The WAXS graph of the 1A sample is presented in the Figure 7.11 and the graph shows six prominent peaks observed in 8.4, 18.67, 19.60, 20.76, 23.86 and 25.66 two thetas corresponding to six different planes and the length of the crystalline planes are 24.96,

22.23, 19.99, 15.32, 8.99 and 15.28 \( \text{Å} \) respectively. Six peaks at 2 theta values of 8.4, 18.67, 19.60, 20.76, 23.86 and 25.66 deg corresponding to (001), (100) and (111) planes of 1A are observed. Also, the WAXS pattern of the polymer shows sharp peaks which clearly suggesting that the hard segments are in crystalline form.

Figure 7.11: WAXD data of 1A samples at room temperature.
7.3.6. TGA

The TGA curve of the sample 1A, 2A and 3A and the data’s are shown in the Figure 8.12 and Table 8.3 respectively. All the amide containing tri-block copolymer structurally similar but chain lengths are variable, so that they did not show a drastic difference in their thermal behaviour. The initial decomposition of the pure PSt is 412°C. The polyamide based copolymer shows higher decomposition temperature around 425°C. This is somewhat higher than pure polystyrene.

![TGA thermograms](image)

**Figure 7.12:** TGA thermograms: a, T6T6B; b, T6A6B; c, T6m; d, PSt.

This may be due to the presence of HS in the main chain. The entire polymer shows the single stage decomposition temperature around 420°C. In general, all the synthesized 1A to 1D and 2A to 2D copolymer show slightly higher stability than the 3A to 3D polymer.
This may be due to the presence of a higher degree of hydrogen bonding and higher amount of HS content which gives higher stability to the copolymer. It is concluded that, the thermal stability depends on the length of the HS. The correlation between the hard segment content to that of the thermal stability is presented in the Figure 7.13. From the figure one can observe that, as the HS content increase, the thermal stability increase, which is preferable to the increasing rigidity of the system.

7.3.7. Water Absorption

Water absorption is measured using pieces of injection-moulded polymer bars (70x9x2 mm³). The water absorption data of the polymer show in the Table 7.4. The effect of amide concentration of the water absorption is presented in the Figure 7.14. These data reveals that the water absorption decreases with increase in the amide content on the copolymer. The crystallinity of the polymer plays an important role
in deciding water absorption. As the crystallinity increases the physical cross linking increases, thereby water absorption decreases. Also the water absorption of tetra amide (T6T6B and T6A6B) based copolymer is lower than the monoamide (T6m) based copolymer.

![Figure 7.14: The water absorption varying amide concentration for •, T6T6B; ▲, T6A6B; ●, T6m.](image)

7.3.8. Solvent Resistivity

Amorphous polymer like PSs very easily attacked by solvents, but the solvent resistance of semi-crystalline polymer is better. The crystalline regions are not easily dissolved and are physical network points that give the dimensional stability. The PSs modified with mHS (T6T6B or T6ATB or T6m) are semi-crystalline materials.
Solvent resistance behaviour of tri-block copolymer is studied by suspending injection moulded bars in chloroform and in other organic solvents at room temperature for 1hr. After drying the samples, the weight loss is determined. The solvent resistivity of the copolymer is presented in the Table 7.4. The amorphous PST dissolves completely in chloroform within 1hr. The tri-block copolymer has dramatic lower weight losses in chloroform and other organic solvents. The relationship between the solvent resistivity to that of mHS content is presented in the Figure 7.15. The weight losses after 1hr in chloroform and in other organic solvents decreased strongly with increasing HSs concentration. Even in very small amounts of HS content, the solvent resistivity of the copolymer improved strongly. This is due to the complete crystallization of mHS present in the copolymer which leads to excellent solvent resistivity.22, 23

Figure 7.15: Solvent resistivity of the copolymers with respect to HS concentration: ♦, T6T6B; ●, T6A6B; ▲, T6m.
Table 7.4: Solvent resistivity properties of monomer and copolymer at room temperature

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>n_{inh} viscosity (g/mol)</th>
<th>DMF</th>
<th>Toluene</th>
<th>Benzene</th>
<th>CHCl_3</th>
<th>THF</th>
<th>DCM</th>
<th>Ethyl acetate</th>
<th>Acetone</th>
<th>N,N-DMA</th>
<th>Hexene</th>
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<td>100</td>
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</tr>
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<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
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</tr>
<tr>
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<td>0.8</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
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*TCE/phenol =1:1 (molar ratio) mixture of phenol/1,1,2,2-tetrachloroethane

♦ Solubility in %
7.4. CONCLUSION

Tri-block copolymer based on dihydroxy polystyrene and mono functionalised crystallizable segments (T6m or T6T6B or T6A6B) have been synthesized via a high temperature condensation reaction. A copolymer series is prepared where the molecular weight of PSt segments is varied from 2500 to 10500g/mol, thereby changing the HSs concentration from 38 to 10 Wt.%. The FT-IR results confirm that the mHS are completely crystallized in the copolymer (i.e., 100%). The temperature dependent FT-IR measurement confirms that these materials are highly thermo reversible provided by the uniform monofunctional hard segment. DSC data show that these materials show a high Tg, a broad melting (Tm) and low Tm-Tc value. WAXD data’s confirms that these materials indeed semi-crystalline in nature. TGA data reveal that all the polymers show single stage decomposition which is centered around 427°C. The solvent resistivity of these materials is extremely very high even at a low concentration of (4%) amide content. Finally, we conclude that the synthesized copolymers are used in many industries in future. Because it shows a wide variety of applications like good solvent resistivity, excellent thermal stability, admirable water absorption properties, transparent materials as well as easily recyclable materials.
7.5. REFERENCES


5. Chapter 3 of this thesis.


18. Chapter 2 of this thesis.


