Chapter-1

GENERAL INTRODUCTION ABOUT SEGMENTED
BLOCK COPOLYMERS

1.1. THERMOPLASTIC ELASTOMERS

Thermoplastic elastomers (TPE’s) are melt processable materials that show elastomeric properties at their service temperature. TPE’s possess many rubber-like properties like softness, flexibility and elasticity but in contrast to conventional rubbers have the advantage of being melt processable. These materials can be melt processed repeatedly as the physical crosslinks are thermally reversible\(^1,2\).

The TPE industry covers about 1% of the total polymer consumption and is a growing part of the polymer industry\(^3,4\). The global TPE consumption is expected to be 2.15 million metric ton in 2006 with a turnover of $10 billion\(^5,6\). The TPE market is forecast to grow with 7% yearly due to the replacement of conventional rubbers and to new applications\(^3,5,6\). The global TPE market is mainly concentrated in developed countries like US, Western Europe and Japan. However, many developing countries, particularly in Asia, are rapidly expanding their positions in TPE’s\(^5,6\).

The first work on thermoplastic elastomers was based on plasticized poly(vinylchloride) (PVC) discovered in 1926\(^7\), later marketed by Goodrich under the trade name Koroseal. In 1937 Prof. Dr.Otto Bayer and co-workers of German I.G.Farben Industrie applied the reaction between isocyanates and alcohols to
synthesize polyurethane fibres which could compete with nylon\textsuperscript{8}. The elastomeric properties of these polyurethane materials were recognised by Dupont and ICI and the materials were soon produced on an industrial scale (Lycra\textsuperscript{1959}). In the 1960’s, other block copolymers such as PC/Polyether were found to have elastomeric properties. Anionic polymerization introduced in the 1950’s, led to the development of styrenic tri-block copolymers (SBC) that were commercialized by Shell Chemical Company (now Kraton) in 1965\textsuperscript{1,9}.

In 1970, the polyether ester elastomers (TPE-E) were developed and became commercially available in 1972 as Hytrel (Dupont) and in 1975 as Arnitel (Akzo Plastics, now DSM) and later others followed\textsuperscript{1,6}. It was not until 1980 that thermoplastic elastomers based on polyamide (TPE-A) like Pebax (Atochem) and Vestamid-E (Creanova) were developed and produced\textsuperscript{1,6,10}.

TPE’s can be divided in three main groups of which the styrenic tri-block copolymers (SBC’s) is the largest group. The second largest group is elastomeric blends: thermoplastic olefins (TPO) and thermoplastic vulcanisates (TPV)\textsuperscript{1,3,6,10}. The last group consist of segmented block copolymers (TPU, TPE-E, TPE-A) that became more and more important over the last years\textsuperscript{3,5}. Global demand for TPE’s is forecast to increase 6.3 percent per year through 2011 to 3.7 million metric tons.
Figure 1.1: Application of TPE’s in Europe

Table 1.1: Expected European TPE consumption and growth for 2005

<table>
<thead>
<tr>
<th>Serial No</th>
<th>Elastomer</th>
<th>Approx Consumption ((10^3))</th>
<th>Average Growth %(%/2005)</th>
<th>World TPE Demand (%) 2011 (3.7 million metric tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>SBC</td>
<td>2</td>
<td>3</td>
<td>45</td>
</tr>
<tr>
<td>II</td>
<td>TPO</td>
<td>1</td>
<td>8</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>TPV</td>
<td>5</td>
<td>--</td>
<td>11</td>
</tr>
<tr>
<td>III</td>
<td>TPU</td>
<td>7</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>TPE-E</td>
<td>3</td>
<td>15</td>
<td>11(others)</td>
</tr>
<tr>
<td></td>
<td>TPE-A</td>
<td>1</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>5</td>
<td>7</td>
<td>99</td>
</tr>
</tbody>
</table>

TPE’s are used in a broad range of applications like for example cushions, mattresses, footwear, automotive and all kind of soft touch materials. In Europe, TPE’s are mostly used in the automotive industry followed by footwear and bitumen.
Chapter-1

modification (Figure 1.1). The important commercial TPE’s are listed in Table 1.2 with the commercial name and company that produces the polymer.

Table 1.2: Important commercial thermoplastic elastomeric segmented block copolymers.

<table>
<thead>
<tr>
<th>Commercial Name</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPE-E</td>
<td>Arnitel, Hytrel, Riteflex, Pibiflex, DSM, Dupont, Ticona, Enichem</td>
</tr>
<tr>
<td>TPE-A</td>
<td>Pebax, Vestamid-E, Grilon/Grilamid, Atochem, Creanova, EMS-Chemie</td>
</tr>
<tr>
<td>TPU</td>
<td>Desmopan, Elastollan, Estane, Pellethane, Bayer, Elastogran, Noveon, DOW</td>
</tr>
</tbody>
</table>

1.1.1. **TPE-E** \(^{1,6,10}\)

Most polyester based multi-block copolymers are prepared by polycondensation reactions of a poly(ether) diol with a mixture of a terephthalate ester and a low molecular weight diol. The rigid segments have a random length distribution. Most commercial TPE-E’s have poly(butylene terephthalate) (PBT) as the rigid segment and poly(ethylene oxide) (PEO) poly(tetra methylene oxide) (PTMO) or poly(propylene glycol) (PPG) as flexible segment. Properties of TPE-E can vary from soft to hard by changing the concentration of the rigid segment.

1.1.2. **TPE-A** \(^{1,6,10}\)

Thermoplastic polyamide elastomers consist of alternating flexible polyether segments and rigid polyamide segments. The polyamide can be partially aromatic or aliphatic but commercial TPE-A’s are derived from aliphatic polyamide. TPE-A’s are characterized by their excellent toughness, flexibility at low temperature, chemical resistance and elastic recovery. The properties of the segmented block copolymers can be varied by changing the block length of the flexible and rigid segments. Commercial TPE-A’s are Pebax, Vestamid and Grilon/Grilamid (Table 1.2). TPE-A’s are more chemically resistant than TPE-E’s \(^{1}\).
1.1.3. (TPU)

Thermoplastic polyurethanes (TPU’s) are linear copolymers that can be synthesized with a long chain diol, diisocyanate and a chain extender. The long chain diol can either be a polyester or a polyether. Several diisocyanates can be used but the commercially most important are diphenyl-4,4’-diisocyanate (MDI) and toluene diisocyanate (TDI). The chain extender is usually a low molecular weight component; diol or diamine. Important commercial segmented polyurethanes are Desmopan (Bayer), Elastollan (Elastogran) and Pelletehane (DOW). Polyurethanes form a versatile class of polymers which are used in all kind of applications like cushions, mattresses, footwear and foams. A disadvantage of polyurethanes is their low thermal stability at temperatures above 180°C.

1.2. SEGMENTED BLOCK COPOLYMERS

Segmented block copolymers are multi-block copolymers consist of alternating crystallizable rigid segments and flexible soft segments (Figure 1.2). The flexible segments form the continuous amorphous soft phase with a low Tg, which gives the material low temperature flexibility. The rigid segments can phase separate by crystallization and form lamellae in the low Tg phase, acting as physical crosslink’s, giving the material dimensional stability and solvent resistance. The rigid segments in segmented block copolymers are normally fast crystallizing segments, such as esters or amide groups. Also, urea and urethane groups are well known for their ability to self-associate via hydrogen bonding. Thermoplastic elastomers with ester, amide and urethane groups are discussed below in more detail.
The morphology of segmented block copolymers is determined by the phase separation between flexible and rigid segments. Phase separation can occur by liquid-liquid demixing or crystallization. TPE’s that phase separate by crystallization have a morphology that comprises a soft phase with dispersed crystalline lamellae (Figure 1.3)\textsuperscript{1,6}. The lamellae are built up of rigid segments that crystallize perpendicular to the length of the lamellae (phase B), as proposed by Cella\textsuperscript{14,15}. Some rigid segments that do not crystallize will mix with the amorphous segments (A). This incomplete phase separation leads to an increase in glass transition temperature of the soft phase and is typically seen in TPE-E’s.

Figure 1.2: Representation of a segmented block copolymer; A, flexible segment; B, rigid segment.

Figure 1.3: Schematic diagram of the two phase morphology of segmented copolymers with rigid segments as proposed by Cella A) amorphous phase; B) crystalline lamellae.
Phase separation by liquid-liquid demixing is due to thermodynamic incompatibility between the segments. Especially in polyurethanes the flexible and rigid urea/urethane segments are known to phase separate by liquid-liquid demixing, followed by partially crystallization of the rigid segments\textsuperscript{1,11,12}. The resulting morphology is complex and consists of liquid-liquid demixed hard phase (non crystallized and partially crystalline), non crystallized rigid segments dispersed in the soft phase and crystalline rigid segments in the polyether phase.

### 1.2.1. Uniform Rigid Segment

An important parameter which is affecting the properties of segmented block copolymers is the segment length distribution of the rigid segments. Commercially available segmented block copolymers normally have a random length distribution of the rigid segment. The properties of segmented block copolymers can be improved by using uniform rigid segments. For example, polyurethanes with uniform rigid segments have a better phase separation of the rigid and flexible segments resulting in a narrow glass transition and a high degree of crystallinity compared to polyurethanes with random rigid segments\textsuperscript{16-19}. Also, the properties of polyether(ester amide)s (PEEA) with uniform rigid amide segments were studied\textsuperscript{20-25} in detail. The uniform rigid amide segments crystallize nearly complete. PEEA’s with uniform rigid segments have a high degree of crystallinity, low T\textsubscript{g}, temperature independent rubbery plateau, a relatively high and sharp melting temperature and are transparent. Segmented block copolymers with uniform rigid segments have a two-phase morphology almost without any rigid segment dissolved in the soft phase.
1.3. POLYAMIDES (PA’S)

Polyamides (PAs) are high molecular weight materials containing amide units. The hydrocarbon segments between the amide groups can be aliphatic, partially aromatic, or wholly aromatic. The type of hydrocarbon segment used has an effect on the chain flexibility and structural regularity and this is important for the formation of the crystalline phase. Polyamides, in common with polypeptides, contain an amide group and are often called Nylons, the trade name given to them by DuPont\textsuperscript{26-36}. PAs can be divided into polymers synthesized from diamines and diacids, called AA – BB type polymers as in (Scheme 1.1) and polymers based on amino acids, called AB-type polymers as in (Scheme 1.2)

\begin{equation}
\text{Scheme (1.1)}
\end{equation}

\begin{equation}
\text{Scheme (1.2)}
\end{equation}

PAs are used as neat fibers, films, engineering plastics and may contain fillers in engineering plastics applications\textsuperscript{37}. Reinforced PA accounts for about 80\% of the engineering plastic market. Most of the reinforced PA is filled with glass fibers and to a lesser extent with particles like talc, kaolin, and mica. For engineering plastics applications, dimensional stability at high temperatures is often sought. Solvent resistance to hydrocarbons is also important for use in automotive applications such as PA-11 in fuel lines. The processing of engineering plastics is achieved by injection molding and to a lesser extent by extrusion. To ensure good processability, a low melt viscosity is required and rapid crystallization is
important. Semi-crystalline partial aromatic PAs have a very high melting temperature, often too high for melt synthesis and melt processing. Amorphous partial aromatic PAs do not have a melting temperature and can thus be synthesized and processed at lower temperatures. They are transparent and have good solvent resistance and relatively low water absorption. Wholly aromatic PAs can be processed from solution into film and fibers. These polymers have very good dimensional stability and excellent heat stability. Wholly aromatic PAs form liquid crystalline solutions and their fibers can be obtained which are highly oriented and have a para-crystalline structure. There all-aromatic PA fibers have a very high modulus and fracture strength.

1.3.1. Amide Concentration

Linear polymers have crystalline order, which is a function of the amide content and the regularity of the spacing of the amide units. The melting temperature \( (T_m) \) increases with amide concentration and is highest for the even–even PAs. The glass transition temperature \( (T_g) \) also increases with amide content, and this steady increase in \( T_g \) with amide content is due to the strong inter chain hydrogen bonding of amide groups. The melting temperature is a function of the melting enthalpy and entropy.

\[
T_m = \frac{\delta H_m}{\delta S_m}
\]

Although the amide groups allow the formation of strong inter chain hydrogen bonding, the increase in melting temperature is generally not due to an increase in \( \delta H_m \) but due to a decrease in \( \delta S_m \). The minimal effect of amide content on \( \delta H_m \) is due to the fact that, in melting, the hydrogen bonding is not broken.
1.4. SOFT SEGMENT

The long flexible soft segment largely controls the low temperature properties, weather resistance, solvent resistance and mechanical properties. The structure and the molecular weight of soft segments also influence the morphology of polyurethanes. Typically, soft segments with average molecular weights of 2000–2500 are used for synthesis of thermoplastic elastomers.

Table 1.3: The effect of molecular weight on the Tg of polystyrene.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mw</th>
<th>Tg(^{*1})</th>
<th>Tmg(^{*2})</th>
<th>Teg(^{*3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS 1</td>
<td>1940</td>
<td>56.8</td>
<td>60.4</td>
<td>64.2</td>
</tr>
<tr>
<td>PS 2</td>
<td>4380</td>
<td>76.2</td>
<td>79.9</td>
<td>83.7</td>
</tr>
<tr>
<td>PS 3</td>
<td>5480</td>
<td>77.0</td>
<td>82.4</td>
<td>87.8</td>
</tr>
<tr>
<td>PS 4</td>
<td>12600</td>
<td>89.6</td>
<td>93.4</td>
<td>96.7</td>
</tr>
<tr>
<td>PS 5</td>
<td>35100</td>
<td>100.2</td>
<td>103.1</td>
<td>105.9</td>
</tr>
<tr>
<td>PS 6</td>
<td>65000</td>
<td>1006</td>
<td>104.0</td>
<td>107.3</td>
</tr>
<tr>
<td>PS 7</td>
<td>275000</td>
<td>103.5</td>
<td>106.4</td>
<td>109.4</td>
</tr>
<tr>
<td>PS 8</td>
<td>950000</td>
<td>103.9</td>
<td>106.7</td>
<td>109.7</td>
</tr>
</tbody>
</table>

*1 Onset temperature of Tg, *2 Mid-Ponit Temperature of Tg, *3 End temperature of Tg

1.4.1. Polystyrene (PS)

The parent of the styrene plastics family, is a high molecular weight, linear polymer that is commercialized on a very high volume world wide and has a wide
range of applications, which is the reason why it has been classified as commodity plastic (along with polyethylene, polypropylene, polyvinyl chloride, polymethyl methacrylate, etc.). The most common form of commercial PS is atactic polystyrene (aPS), which is an important thermoplastic material due to its well-balanced physical properties, easiness of moulding, its good dimensional stability and its general transparency\textsuperscript{59,60}. The polymer chain stiffening effect of the pendant phenyl groups gives it a relatively high glass-transition temperature ($T_g$) of about 100 °C, which translates into a glassy polymer under ambient conditions and a viscous liquid above the $T_g$. It should be emphasized that, from a physical properties point of view, in order to have optimal strength the PS must have a weight-average molecular weight ($M_w$) of about ten times higher than its chain entanglement molecular weight ($M$). A PS having an $M_w < 150,000$ is generally too brittle to be useful and thus, for general-purpose moulding and extrusion grades, the PS grades sold commercially have $M_w > 180,000$ g/mol. This result in a high melt viscosity. An extensive compilation of physical properties of PS is given elsewhere\textsuperscript{1}.

The given tabulation (Table 1.3) is reveals that the increases in molecular weight leads to increases in $T_g$ values. It was concluded that the $T_g$ values depends upon the molecular weight.

The important characteristics of the polystyrenes are listed below:

- Polystyrene (PS) is being used as crystal clear, stiff, but brittle homopolymer ‘general purpose polystyrene’ (GPPS) or as impact modified, stiff but opaque ‘high impact polystyrene’ (HIPS).

- Expandable polystyrene (EPS): It is a foam based on GPPS beads containing pentane, which are expanded under heat. EPS is light weight, strong, and offers excellent thermal insulation, making it ideal for use in the packaging and construction industries.
Styrene-acrylonitrile copolymer (SAN): It is a transparent, stiff and thermoplastic polymer material with enhanced stress cracking resistance. SAN is based on the monomers styrene and acrylonitrile.

Styrene–methyl methacrylate copolymer (SMMA): It is a transparent and brittle polymer with enhanced scratch resistance compared to that of polystyrene (GPPS). It is often used in blends with styrene-butadiene copolymers (SBC) for clear and tough goods, which need enhanced scratch resistance.

Acrylonitrile-butadiene-styrene copolymer (ABS): is an opaque, ductile and stiff thermoplastic polymer with a broad processing window, which is strong and durable even at low temperatures, with good resistance to heat and chemicals.

Methyl methacrylate-acrylonitrile-butadiene-styrene copolymers (MABS): are transparent, ABS-like materials with improved resistance against fats and oils compared to acrylonitrile-free styrenic polymers.

Acrylonitrile-styrene-acrylate copolymer (ASA): is a product similar to ABS, but with excellent weather ability because of the use of butyl acrylate rubber containing no double bonds compared to butadiene rubber. It is widely used for automotive exterior parts (mirror housings, grilles, and so on) and for other outdoor applications in the area of sports / leisure and durable electrical and electronics (E&E) housings.

Blends: polystyrene blends homogeneously with polyphenylene (PPE) ether to yield high temperature resistant, stiff and tough materials (polyphenylene ether (PPE/HIPS). ABS and ASA blend well with polycarbonate (PC) and PA to yield PC/ABS, PC/ASA, PA/ABS and PA/ASA
blends combining the excellent thermal properties of the engineering thermoplastics PC and PA with those of ABS and ASA.

- Unsaturated polyester resins: are durable, resinous polymer derived from styrene and used mainly in the construction, boat building, automotive and electrical industries.

- Styrene-butadiene copolymers (SBC): are transparent, stiff and tough polystyrenes manufactured by a specific anionic process. SBC are widely used in food packaging (beakers, multi-layer co-extruded and thermoformed ‘modified atmosphere packaging’ or shrink sleeves). They are different from styrene-butadiene rubber (SB) made by similar technologies, which have rubber-like properties. They also need to be differentiated from (crosslinked) styrene-butadiene latexes, which are used, for example, as paper sizing dispersions.

- Syndiotactic polystyrene: a material being produced by a specific catalytic polymerisation process to yield a semi-crystalline, high temperature-resistant material.

- Other copolymers: styrene-maleic anhydride (SMA) copolymers, as well as styrene/N-phenyl maleimide copolymers display high heat resistance and are often used as blend components in high heat ABS and high heat ASA.

Styrenic polymers offer many industries a wide variety of benefits, including:

- Light weight, water resistant and excellent thermal insulation. Rigid, with a high strength-to-weight ratio that offers energy-savings benefits in transportation and an excellent cost performance.
- Can be shatter proof and transparent if required.
- Good electrical insulation.
- Easy to process and produce in a range of attractive colours.
- Easy to recycle.

An overview of the different major classes of styrene polymers is shown in Figure 1.4.

**Figure 1.4 Overview: major styrenic polymer classes and their structural relationships**

Manufacturers use styrene-based resins to produce a wide variety of everyday goods ranging from computer to yoghurt cups, extruded polystyrene (XPS) foam used as a boards for insulation, kitchen appliances, toys, consumer electronics, automobile parts, and durable lightweight packaging of all kinds. Styrene polymers are present in a variety of highly demanding applications. Their unique selling point is to combine cost efficiency, high performance and easy processing and thus make it the material of
choice for use in electronic equipment, high-end domestic appliances and state of the art packaging.

1.5. ABOUT TRI-BLOCK COPOLYMER

Tri-block copolymers are interesting two phase materials\textsuperscript{1}, and polymers such as styrene–butadiene–styrene (SBS) usually display liquid–liquid demixed phase structures with a dispersed amorphous polystyrene phases as shown in the Figure 1.5. In order to obtain good mechanical properties, the molecular weights of the SBS copolymers 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.

Figure 1.5: Phase structure of S-B-S and similar block copolymers

These SBS tri-block copolymers 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{54-58,59,84}. The long nylon blocks were phase separated from
the soft segments and the nylon blocks were partly crystalline. In Figure 1.6 shows the schematic representation of staging of hard segment.

The hard segments phase separate by crystallization upon cooling and the crystallites provide the copolymers with a low T, a relatively high modulus at room temperature and high maximum use temperature. If the hard segments (HS) are mono-disperse in length the copolymer has a lower soft segment Tg and a sharper hard segment melting transition. 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 crystallites with nano-ribbon-like structures with high aspect ratios (i.e., 300–1000)\(^ {74,83}\). When the HS are truly monodisperse the modulus is from room temperature to near the HS melting temperature 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 were formed. These nano-ribbon-like crystallites had high aspect ratios.

![Schematic representation of staging of hard segment](image)

**Figure 1.6: Schematic representation of staging of hard segment**

In the H-bonding direction, the crystallites can be as long as 1000 nm. These nano-ribbon crystallites are the physical cross-links for the soft phase and also reinforce the soft phase.
1.6. REVIEW OF LITERATURE

1.6.1. Review of Literature based on block copolymer

Segmented copolymers based on polyamide (TPE-A) hard segments are one of the newer developments in TPE’s. A wide variety of aliphatic and aromatic amides can be used and so a wide range of property variations are available. TPE-A’s are more chemically solvent resistant than TPE-E’s.

E.W. Meijer et al in his paper reported the synthesis and characterization of the multiple hydrogen bonding in reversible polymer network. The hydrogen bonding moiety forms supramolecular structure. Also, in his paper thermal and rheological properties were discussed. R.J.Gaymans group in his paper explained the synthesis of block copolymers based on various amide segments and soft segments as like poly (tetra methylene oxide) and polyethylene oxide (PEO). Niesten et al in his paper studied and synthesize, mechanical and elastic properties of the block copolymer.

Arun et al discussed about the segmented block copolymer with mono-dispersed amide TΦT as a end segments. The aramide and PTMO segment ratio was increased from 1:1 to 2:1 thereby changing the structure from a higher molecular weight multi-block copolymer to lower molecular end-block copolymer and they found out that the presence of hard segment in end position altered the mechanical property drastically. Also in his other paper Arun et al compared the position of hard segment (mono, di and tri) in the polymer chain and concluded that tri-block copolymer shows an excellent property.

Arun et al in his paper studied aromatic diamide (diaramide TΦT) as a end segment and polyether as mid-segment. In order to increase the soft segment (SS) length, PTMOs are extended with terephthalic groups. The length of the mid-soft
segment is varied from 1000 to 20,000 and there by the concentration of the hard end segment changed from 22 to 3 Wt.%. The crystallinity of the hard segment also studied in his paper.

![Figure 1.7: Schematic diagrams of the structure in the melt of (a) a multiblock((AB)\textsubscript{n}) and (b) a tri-block(ABA)copolymer](image)

The effect of hard segment in the mid or end position on the rheological property is clearly explained by Arun et al\textsuperscript{71,79,83}. Figure 1.7 show that the tri-block copolymer forms network structure in the melt whereas multiblock copolymer is not. Ranimol Stephen et al\textsuperscript{82,84} synthesized and analyzed the melt and solution polymerization of the segmented block copolymers based on polysulphone with mono dispersed amide segments. The high T\textsubscript{g} amorphous polysulphone was modified to a high T\textsubscript{g} semi-crystalline PSU-T6T6T copolymer. This copolymer has a high dimensional and solvent resistance.

1.6.2. Review of Literature based on hydrogen bond

Hirt and Herlinger et al\textsuperscript{67} studied an alternating poly(ether ester amide)s with uniform aromatic amide segments and alkane diols or poly(tetra methylene oxide) (PTMO) as a soft segments. Miller et al\textsuperscript{56} found at a higher strain, the segmented copolymers are broken with a narrow length distribution of the hard and soft
segments. At the same time tensile strength, inherent viscosity and elastic properties are raised.

Kirikihira et al\textsuperscript{53} synthesized the segmented copolymers with crystallizable uniform aramid segments and poly(tetra methylene oxide) soft segments. The rubbery plateau of these polymers is temperature independent. J. Feijen et al group\textsuperscript{63, 64,65,70} investigated the behaviour of uniform and non-uniform hard segments in non-hydrogen bonding systems while Edwin Biemond et al\textsuperscript{66, 70} did similar studies on hydrogen bonded system. All these studies shows that hard segments of uniform length crystallize faster and better than the hard segments of non-uniform length. If the crystallized hard segments are poorly miscible i.e (phase separated in the solid) with the amorphous soft segments, hardly any hard segments will be present in the amorphous phase, resulting in a low glass transition temperature (T_g) and high melting temperature (T_m).

Niesten et al\textsuperscript{23,61,72} observed a higher strain at break for polymers with uniform polyamide segments than for similar polymers with non-uniform polyamide segments. In accordance with this observation, R. J. Gaymans groups found a higher strain at break for segmented copolymers with a narrow length distribution of the hard and soft segments than for polymer with broad segment length distributions. The number of hydrogen bonding like mono, di, tri, tetra and etc., on the property of supramolecular polymer was studied by E.W.Meijer group\textsuperscript{56, 57,58,60}.

All literature survey reveals that, if the crystallizable segments have a regular uniform structure, then the crystallization is fast and the degree of crystallization is high. In polyether (ester amide) copolymers, uniform crystallizable amide segments result in fast crystallization, a sharp melting transition, low compression set and no decrease of the modulus in the plateau region\textsuperscript{74}. Short amide containing units have a
good thermal stability and side reaction like transmidation reactions and exchange between ester groups hardly takes place \textsuperscript{67,76}.

1.7. SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

The main goal of this work is to modify the high $T_g$ amorphous PSt to a high $T_g$ semi-crystalline copolymers and thereby improve poor solvent resistivity to high solvent resistivity for dihydroxy terminated polystyrene (OH-PSt-OH). This study starts with the synthesis, characterization of dihydroxy terminated polystyrene (OH-PSt-OH). Different uniform amide segments are used as a rigid segments. The effect of type and concentration of amide segment on thermal and crystallization properties are studied in detail. The crystallization properties are related to the morphology of the copolymers. Other parameters studied are the influence of hydrogen bonding in the crystallinity behaviour and the effect of the crystallinity on the solvent resistivity of the segmented block copolymers. On the basis of the above said aim, the following objectives are put forward.

- To synthesis and characterize difunctionalized polystyrene using ATRP with strong base techniques.

- To synthesis and characterize different type of monodispersed mono and difunctionalised hard segments containing amide linkage. The hard segments intended to synthesis are $T_\phi T$, $T_6T$, $T_6T_6T$, $T_6A_6T$, $T_6m$, $T_6T_6B$ and $T_6A_6B$.

- To synthesis and characterize the multiblock copolymer containing trtra-amide hard segments and dihydroxy terminated polystyrene. The tetra-amide hard segments are to be synthesized by \textit{in situ} method.

- To synthesis and characterize segmented copolymers based on uniform tetra-amide units and hydroxy terminated polystyrene: to study the
effect of hard segment content on thermal and solvent resistivity of the polymer.

- To synthesis and characterize semi-crystalline segmented block copolymer with dihydroxy terminated polystyrene (PSt) and uniform crystallizable TϕT or T6T di-amide units. To study the effect of di-amide segment concentration on the properties of the polymer.

- To study three series of tri-block copolymer based on di-functionalized polystyrene with mono functionalized amide segments like monoamide T6m and tetra-amide (T6A6B and T6T6B). To compare the crystallization and solvent resistivity of the tri-block copolymer with that of multiblock copolymer.
1.8. REFERENCES


Chapter 1


32. E. Trommsdorff and C. E. Shildknecht, In, *Polymer process*” P.175 inter science 1956


44. E. Trommsdroff and G. Abel, Germany. Patent. 749016


Chapter-1