Chapter 8

Summary and Conclusion

Polystyrenes are general purpose thermoplastics with a high Tg (100°C), high thermal stability, transparency and high impact strength materials. The polystyrene is extensively used in electrical, electronics, medical, home application, packaging industry, etc., Hydroxy terminated polystyrene based segmented block copolymers containing alternating amorphous flexible segments (PSt) and crystallizable rigid segments are thermoplastic elastomers (TPE’s). The flexible segments form the continuous amorphous phase with a high Tg and give the material high temperature flexibility and brittle nature in room temperature. The rigid segments can crystallize and form lamellae in the high Tg phase acting as thermo-reversible physical cross-links, giving the material dimensional stability and solvent resistance.

The aim of the work in thesis is to study the synthesis and characterization of the tri and multi block copolymer based on hydroxyl terminated polystyrene. Hydroxy terminated polystyrene is synthesized using ATRP techniques and it shows low molecular weight, expected polydispersity (1.12), amorphous nature and poor solvent resistivity. This amorphous polystyrene is modifying to high Tg semi-crystalline polystyrene by using the different type of hard segments. It is expected that this novel high Tg polymer crystallizes fast from the melt, has a good solvent resistance and is transparent. Such a material may serve as an alternative to known engineering systems, e.g. for use as in electrical insulation, thermal insulation, spray coating in military force and construction materials in high temperature applications.

In Chapter 1, of this thesis deals with the general introduction about the thermoplastic elastomer like TPE’E, TPE’A, TPE’U, segmented block copolymer,
uniform rigid segment, tri and multiblock copolymer, polystyrene, literature review based on hydrogen bond and block copolymer. The special attention is given towards tri and multiblock copolymerization methods. In this section the chemistry of tri and multi-block copolymerization is discussed in detail. In Chapter 2, synthesis and characterization of di-functionalised polystyrene using the ATRP with strong base techniques was discussed in detail. This polymer shows poor crystallization, poor solvent resistivity and expected polydispersity (1.12) as well as low molecular weights.

In chapter 3, the synthesis and characterization of different type of monomethyl monoamide, monomethyl tetra-amide, dimethyl di-amide and dimethyl tetra-amide units with varying length and composition that can be used in the copolymerization for segmented block copolymers are studied. Monomethyl monoamide and dimethyl diamide is synthesized in single step process, dimethyl tetra-amide is synthesized in two step process and monomethyl tetra-amide is synthesized via three step process. In the first step, the diamine diamide segment is synthesized diamine-diamide (6X6) high purity. By reacting the diamine – diamide with methyl phenyl terephthalate gives dimethyl tetra amide with high purity. Similarly, by reacting the diamine-diamide (6X6) with phenyl benzoate gives the 6X6B, subsequently, the 6X6B hard segment react with MCCB gives monofunctional T6X6B. The purity of the hard segments are confirmed IR and NMR technique. The melting temperature is measured by DSC. The dimethyl tetra-amide units have high melt temperatures (240 for T6A6T and 303 °C for T6T6T) and upon cooling, the uniform units crystallize rapidly. Similarly, dimethyl diamide units have high melting temperature (232 for T6T and 371°C for TΦT) compared to tetra-amide. All the hard segments are crystallising easily.

Synthesis and characterization of two types of monodisperse diamine-diamide (6T6 and 6A6 ) hard segments reacted with dihydroxy terminated polystyrene using
DMT as a chain extender is discussed in Chapter 4. This reaction is based on solution/melt polymerization (in situ) method. In this way tetraamide unit is prepared by in situ. These copolymers have a very high inherent viscosity and depending on the amide concentration, the melting temperature of the polymers is ranged between 129°C to 248°C. The crystallinity of the amide segments is up to 75%. The AFM analysis shows the presence of crystalline ribbons with a high aspect ratio. All the polymers showed single stage decomposition temperature centered around 420°C. The solvent resistivity of these materials is very high even at a low amide content. DSC heating curve of the synthesized segmented copolymers shows two transitions, Tg of SS and the melting of HS. The under cooling value of these materials is very low (<10°C) suggesting fast crystallization of HS. Thermal stability of these materials is very high (around 420°C). The segmented block copolymer shows excellent solvent resistivity than the PSt even at a very low HS content of 5 Wt.%.

In chapter 5, the segmented copolymers based on uniform tetra-amide units prepared separately and hydroxyl terminated polystyrene is synthesized and characterized. The inherent viscosity increases with increasing soft segment length. Depending on the amide concentration in the copolymers, the HS melting temperature ranged between 248 to 287°C. From the FT-IR, DSC and WAXD results, it is concluded that the hard segments in the copolymer is crystallized completely. This chapter reveals that the crystallinity of the hard segments is increased up to 100%, thereby, increases the admirable solvent resistivity as well as very little water absorption (0.1) compare to commercial Noryl-GTX®, PPO-803® and PPE-2T/Cl2/T6T6T. All the polymers shows single stage decomposition temperature centered around 430°C.

In Chapter 6, describes the synthesis of semi-crystalline -[-(-T-PSt)-]_x-PSt-TXT-]- segmented block copolymer based on flexible PSt segments and monodispersed crystallizable di-amide as a hard segments (T6T or TΦT). Two series
of copolymer is prepared where the molecular weight of soft segment varies from 2500 to 10500 g/mol, thereby changing the HS concentration from 15 to 4 Wt.%. These copolymers have high molecular weight, melt-processable, high solvent resistant and transparent materials. The FT-IR measurement confirms that the materials are highly thermo reversible provided by the uniform hard segment. The crystallinity of the hard segments is very high upto 90%. DSC spectrum shows that the materials are having high Tg, a broad melting (Tm) and low Tm-Tc value. As the T6T or TΦT content increased (4–15Wt.%), the Tm value increases as typical for semi-crystalline materials. TGA data reveal that the polymers shows single stage decomposition centered around 413°C. WAXS data confirm that the materials are semi-crystalline in nature. The solvent resistivity of these materials is extremely very high even at a low concentration of (4%) amide content.

In Chapter 7, the synthesis and characterization of tri-block copolymer based on dihydroxy terminated polystyrene with monofunctional hard segments like, T6T6B, T6A6B and T6m are discussed in detail. The soft segment concentrations are varying from low molecular weight (2500 to 10500 g/mol) to high molecular weight using the DMT as a chain extender. 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 these synthesized copolymers can be used in many industries in future. Because of its good solvent
resistivity, excellent thermal stability, admirable water absorption properties, transparent materials as well as easily recyclable materials.

Finally chapter 8 describe the summary and conclusion of the present investigation.
Patent Applied


List of Published Papers


List of Communicated Papers

1. Semi-Crystalline Segmented Block Copolymers based on Dihydroxy Terminated Polystyrene and Amide Segments. (Communicated)

2. Highly Solvent Resistivity Polystyrene based on using Uniform Tetra-amide Units.(Communicated)
3. Thermoplastic Elastomers based on Functionalized Polystyrene with Crystalizable Di-amide. (Communicated)

4. Tri-block Copolymer Based on Crystallizable Amide Segments with Functionalized Polystyrene. (Communicated)

5. Spacer Length Controlled Highly Thermo Reversible Polyurethane-Urea Based on Polystyrene: Synthesis and Crystallization Studies.(Communicated)

6. Poly(urethane-urea) based on functionalized Polystyrene with HMDI: Synthesis and Characterization.(Communicated)

7. Synthesis and Characterization of Poly(urethane-urea-amide) based on functionalized Polystyrene.(Communicated)

8. Synthesis and Characterization of Poly (urethane-urea-amide) by using functionalized Polystyrene and MDI.(Communicated)