Chapter 2
SYNTHESIS AND CHARACTERIZATION OF
FUNCTIONALIZED POLYSTYRENE USING ATRP WITH
STRONG BASE TECHNIQUE

Abstract

The combination of Atom Transfer Radical Polymerization (ATRP) and strong base chemistry is employed for the efficient preparation of well-defined low molecular weight prepolymers based on styrene. α,Ω, Dibromo terminated polystyrene (Br-PSt-Br) is prepared by an ATRP technique using difunctional initiator. This technique preserves the terminal halogens till the reaction completed and the terminal halogens are substituted by various nucleophiles. α,Ω, Dihydroxy terminated polystyrene (OH-PSt-OH) is prepared by reacting Br-PSt-Br with potassium hydroxide. The synthesized polymers are characterized by different techniques. The FT-IR spectrum confirms the formation of -OH as end group. The weight average molecular weight (Mw) of the synthesized polymer is determined by $^1$H-NMR end group analysis, Gel Permeation Chromatographic (GPC) and mass spectrometric technique (GC-mass) are found to be around 2000 g/mol. Thermal stability of the polymer is studied by thermo gravimetric analysis (TGA) and it shows single stage decomposition centered at 400°C. The Tg value of the polymers are determined using Differential Scanning Colorimetry (DSC) method and its value varies from 58 to 60°C depending upon the type of end groups present in the polymer chain.

2.1. INTRODUCTION

In the past decade, the development of controlled/living radical polymerizations (CRP)\textsuperscript{1-3} allows the synthesis of co-polymers not only with a predetermined degree of polymerization with narrow molecular weight distribution, but also with high degree of functionality with desired microstructure. In the literature, several methods like Reversible addition fragmentation transfer polymerization (RAFT),\textsuperscript{4,5} Nitrooxide – mediated polymerization (NMP),\textsuperscript{6-7} Bulk atom transfer radical polymerization\textsuperscript{8} and Atom transfer radical polymerization (ATRP) techniques were available for the synthesis of low molecular weight polymer. Among these techniques, ATRP is considered as a convenient method for the synthesis of low molecular weight polymer with controlled degree of polymerization (DPs),\textsuperscript{9} preserved functionality, microstructure / architectures etc., ATRP is considered by many researchers as one of the most effective free radical living polymerization method due to the fact that, it can polymerize wide variety of prepolymer / monomer\textsuperscript{10-14}.

The polymer produced by ATRP preserve the terminal halogen atom(s) and can be successfully converted into various end groups through appropriate transformation, especially nucleophilic substitutions.\textsuperscript{15} The synthesized compound which contains bromine as a terminal group is used for a variety of chemical transformations to produce numerous types of end functional moieties, such as amino, hydroxy, carboxy groups, etc,\textsuperscript{16-21} Bifunctional polystyrene plays an important role in synthesize of variety of high performance polymers which is of commercially important. Often these synthetic methods encounter difficulties in functionalizing the polystyrene with narrow and desired molecular weights which leads to poor mechanical and elastic properties to the
system. Moreover, commercially available bifunctionalized polystyrenes are found to be very expensive and practically not feasible to use for the commercial applications. Several reports available worldwide for the synthesis of functionalized polystyrene with narrow molecular weight distribution but, none of them are found to be neither inexpensive nor simple synthetic route.

Herein, we are reporting the synthesis of $\alpha, \Omega$, Dihydroxy terminated polystyrene (PSt) by the ATRP technique followed by nucleophilic (-OH) substitutions using strong bases like potassium hydroxide. The polymer is characterized by NMR, GPC, TGA, DSC and FT-IR techniques.

2.2. EXPERIMENTAL

2.2.1. Materials

Styrene (St, 99%) is purchased from Aldrich Chemical Co. After it is passed through a basic alumina column to remove the inhibitor, the styrene is stored under nitrogen atmosphere at 0°C. Potassium hydroxide, Copper bromide, and Dimethyl-2,6-Dibromoheptadioate (DM-2,6-DBHD) are purchased from Aldrich Chemical Co. N,N,N,N,N-Pentamethyl diethyltriamine (PMDETA) is purchased from Aldrich Chemical Co. Basic alumina, Neutral alumina, Tetrahydrofuran, Toluene, Methanol, Dimethyl formamide and all other solvents are purchased from S.D Fine Chemicals and used as such without further purification.

2.2.2. Synthesis of $\alpha, \Omega$, Dibromo terminated polystyrene (Br-PSt-Br)

A Mixture of styrene (90 mL, 0.78 mol) and toluene (60 mL) is degassed in a Schlenk flask by 5 freeze-pump-thaw cycles. The ATRP catalyst, CuBr (0.75 g, 5.1 mmol) and PMDETA (1.2 mL, 4.2 mmol) is added to the above mixture. 2.25 mL
(4.5 mmol) of the difunctional initiator, dimethyl-2,6-dibromoheptanedioate (DM 2,6-DBHD) is added last, and the reaction is stirred at 80°C for 140 minutes. When the monomer conversion reached 30%, the reaction mixture is diluted with THF and the solution is passed through a column containing neutral alumina to remove the catalyst. The absorbent in the column washed with THF (30-40 mL) and the resulting solution polymer is concentrated by rotary evaporation. It is shown in Scheme 2.1.

\[ \text{Scheme 2.1: Synthesis of } \alpha, \Omega \text{-Dibromo terminated polystyrene.} \]

\[ \text{Figure 2.1: NMR spectrum of dibromo terminated polystyrene} \]
The polymer is precipitated in cold methanol and dried under vacuum, the yield is 28 g (30%).\textsuperscript{1}H-NMR (\(\delta\), ppm): 7.1-7.3 (m, 5H, aromatic proton), 4.7 (t, 1H, >CH-Br), 2.7 (m, 1H, -CH\textsubscript{-}), 2.2 (t, 2H, -CH\textsubscript{2}-). FT-IR (cm\textsuperscript{-1}): 3024 (aromatic C-H), 2848 (aliphatic C-H), 1594 (aromatic C=C), 1493 and 1450 (CH\textsubscript{2} bending frequency), 1335 and 965 (Ar-CH\textsubscript{2}-Br). \textsuperscript{1}H NMR of the Br-PSt-Br is given in the Figure 2.1.

2.2.3. Synthesis of \(\alpha, \Omega\), Dihydroxy terminated polystyrene (OH-PSt-OH)

10g (0.0052 mol) of Br-PSt-Br is dissolved in 250 mL of DMF in Schlenk flask and is degassed by freeze–pump-thaw cycles. To this solution 6g (0.28 mol) of potassium hydroxide dissolved in 15 mL methanol is added drop by drop with constant stirring at 80°C under nitrogen atmospheric condition. It is shown in Scheme 2.2. The content of the flask is stirred for 8 hrs at 80°C. Finally the OH-PSt-OH is precipitated by adding the reaction mixture to an excess of methanol with rapid stirring. The product is filtered and dried in air. Yield: 8.9g (89 %). \textsuperscript{1}H-NMR (\(\delta\), ppm): 7.1-7.3 (m, 5H, aromatic proton), 4.4 (t, 1H, >CH-OH), 2.8 (m, 1H, -CH\textsubscript{-}), 2.1 (t, 2H, -CH\textsubscript{2}-). FT-IR (cm\textsuperscript{-1}): 3343(-OH), 3024 (aromatic C-H), 2920, 2848 (aliphatic C-H), 1594 (aromatic C=C), 1491, 1440 (-CH\textsubscript{2} bending), 1161(>C-O) and 1054 (>CH-OH). \textsuperscript{1}H NMR of the OH-PSt-OH is given in the Figure 2.2.

![Scheme 2.2: Synthesis of \(\alpha, \Omega\), Dihydroxy terminated polystyrene.](image-url)
2.2.4. Characterization

2.2.4.1. Spectral measurements

Alpha Bruker FT-IR spectrometer is used for recording FT-IR spectrum and the spectra are recorded using the KBr pellet method. $^1$H-NMR spectra of the polymers are recorded on a Bruker spectrophotometer operating at 320 MHz at room temperature using deuterated chloroform (CDCl$_3$) as a solvent and tetramethylsilane (TMS) as an internal reference.

2.2.4.2. Thermal analysis

Thermal gravimetric analysis (TGA) of the polymers is carried out with a Dupont 951 thermo gravimetric analyzer. About 8-10 mg of the sample is heated from 30 to 600°C at the heating rate of 10°C /min in a nitrogen atmosphere with a gas flow rate of 100 mL/min. DSC thermo gram are recorded on a Perkin Elmer DSC 7 apparatus
equipped with a PE 7770 computer and TAS-7 software. 10-15 mg of dried polystyrene sample is heated at a rate of 20°C/min for recording DSC thermo gram.

2.2.4.3. Molecular weight determinations

The number average and weight average molecular weight of the polymer is obtained with a Shimadzu instrument using THF as an eluent at a flow rate of 0.3 mL/min. A styrage column of pore size 103-106 Å is used. GC-MS spectrum of the polystyrene sample is analyzed using Shimadzu instrument.

2.2.4.3. Solvent Resistivity

Injection moulded sample of dimension 10x10x2 mm are used for solvent resistance measurements. Previously weighed samples are dipped in 50 mL organic solvents and shaken for 60 minutes. After that, the solvent is decanted and the flask is dried for 24 hrs at 70°C. The dried flask is weighed again and from the weight loss, the amount of polymer sample dissolved in that solvent is calculated using Eqn.(2.1).

\[ \text{Solvent Resistivity} = \frac{m-m_0}{m_0} \times 100\% \quad \text{Eqn.-----(2.1)} \]

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

2.3. RESULTS AND DISCUSSION

Functionalized and narrow molecular weight polystyrene is prepared using combined technique of ATRP and strong base. The dibromo derivative of low molecular weight polystyrene is synthesized using the ATRP technique presented in Scheme 2.1. The dibromo polystyrene is effectively converted in to the hydroxyl using strong bases
like potassium hydroxide presented in Scheme 2.2. The synthesized polymer is characterized by FT-IR, NMR, GPC, GC-MS and TGA/DTA techniques. The synthesized polymer is called as soft segment which is used for the preparation of polyurethane-urea/amide.

2.3.1. Study of Molecular Weight

The molecular weight of the compound is determined by using NMR, GC-MS and GPC techniques. All these techniques confirm the weight average molecular weight (Mw) of the synthesized polymer is around 2000g/mol and there is no much difference between the polymers Br-PSt-Br and OH-PSt-OH which confirms that the basic polymer structure is preserved during the functionalization process.

2.3.1.1. $^1$H-NMR

$^1$H-NMR is the convenient technique to calculate the molecular weight of the low molecular weight polymer by end group analysis method$^{23}$. $^1$H-NMR spectra of Br-PSt-Br and OH-PSt-OH is shown in Figure 2.1 and 2.2. For the polymer OH-PSt-OH, the peaks at 7.1-7.3 ppm (Aromatic, 5 protons) and 4.4 ppm (1 proton, CH attached to OH group) represented the number of styrene molecule and the end group present in the polymer chain respectively. Since the two peaks are well distinct from each other, the integral values of these two peaks could be conveniently taken for determining the composition of the copolymer. The following equation is used for the calculation of molecular weight for the copolymer OH-PSt-OH.

$$C = \frac{\text{integral value of aromatic proton} (Ia)\ (7.1-7.3 ppm)}{\text{Integral value of } -CH-OH \text{ proton} (Im)\ (4.4 \ ppm)} - \text{(2.2)}$$

Number of styrene units present in the polymer chain will be,
\[ m_i = \frac{C}{5} \quad \text{and} \quad M_w = \left[ m_i \times 104 \right] + 34 \quad \text{(2.3)} \]

(Since each styrene molecules contains 5 aromatic protons)

Similarly, the molecular weight of the Br-PSt-Br is calculated and found to be around 2000g/mol. The integral values of the aromatic (I_a) and methine (I_m) protons of the polymers are presented in the Table 2.1.

Table 2.1: NMR Integral values of the aromatic and methine protons of the synthesized polymers.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Polymer Code</th>
<th>I_a</th>
<th>I_m</th>
<th>C=I_a/I_m</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br-PSt-Br</td>
<td>15</td>
<td>0.17</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>OH-PSt-OH</td>
<td>14</td>
<td>0.17</td>
<td>82</td>
</tr>
</tbody>
</table>

The molecular weight of the synthesized polymer calculated through \(^1\text{H}-\text{NMR}\) is presented in Table 2.2. It confirms that the molecular weight of the synthesized polymers is found to be in the range of 2000 g/mol which is the expected molecular weight. Also it is conclude that, during the functionalization process the polymer chain retain its stability thereby we found unaltered molecular weight.

### 2.3.1.2. GPC

Similar to the NMR, the molecular weight of the polymer is determined by the GPC and presented in the Table 2.2. The GPC curve of the dihydroxy terminated polystyrene is presented in the Figure 2.3. The number and weight average molecular weight of the dihydroxy polystyrene are 1380 and 1551 g/mol respectively with the polydispersity value of 1.12.
The molecular weight of the synthesized polymer is determined by the GPC and found to be comparable to each other. Also, it shows that the GPC values are concurrent with the NMR result and the low polydispersity (around 1.1) value is due to the ATRP method which employed in the polymerization process.

2.3.1.3. GC-MS

GC-MS is the convenient technique to determine molecular weight of the low molecular weight polymer by fragmentation analysis method. The molecular ion peak value of the polymer is shown in the Table 2.2. GC-MS graph of the OH-PSt-OH is given in the Figure 2.4 as a representative of the polymer series. Similar to NMR and GPC, the GC-MS value of the synthesized polymer shows a comparable molecular ion peak at 1999 and 1987 for Br-PSt-Br and OH-PSt-OH respectively.
Figure 2.4: GC-MS spectrum of α, Ω, Dihydroxy terminated polystyrene

Table 2.2: Molecular weight of the polymers determined by different techniques

<table>
<thead>
<tr>
<th>S.No</th>
<th>Polymer Code</th>
<th>NMR $M_w$ (g/mol)</th>
<th>GC-MS $[M_1]$ (g/mol)</th>
<th>GPC $M_w$ (g/mol)</th>
<th>GPC $M_n$ (g/mol)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br-PSt-Br</td>
<td>1942</td>
<td>1999</td>
<td>1800</td>
<td>1690</td>
<td>1.15</td>
</tr>
<tr>
<td>2</td>
<td>OH-PSt-OH</td>
<td>1802</td>
<td>1987</td>
<td>1551</td>
<td>1380</td>
<td>1.12</td>
</tr>
</tbody>
</table>

2.3.2. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectrum of the functionalized polymers is shown in the Figure 2.5. Important FT-IR peaks of the polymer are depicted in the Table 2.3.
FT-IR result of the synthesized Br-PSt-Br confirms the appearance of Ar-CH₂-Br at 965 cm⁻¹ and 1335 cm⁻¹. In OH-PSt-OH spectrum, the appearance of peak at 3345 cm⁻¹ confirms the presence of hydroxyl group and at the same time the disappearance peak at 1335 cm⁻¹ confirms the absence of bromide group at the terminal position of the polystyrene.

![FT-IR spectrum](image)

**Figure 2.5: Comparative of the FT-IR spectrum of Br-PSt-Br (●)OH-PSt-OH(●)**

**Table 2.3: Important FT-IR data of the synthesized polymers**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Polymer code</th>
<th>FT-IR Wavenumber ( cm⁻¹)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br-PSt-Br</td>
<td>965 and 1335</td>
<td>&gt;C-Br</td>
</tr>
<tr>
<td>2</td>
<td>OH-PSt-OH</td>
<td>3422 and 1161</td>
<td>-OH, C-O</td>
</tr>
</tbody>
</table>
2.3.3. Thermal analysis

2.3.3.1. Thermo Gravimetric Analysis (TGA)

Thermo gravimetric analysis is used to estimate the percentage weight loss of the copolymer against temperature. The TGA and DTA curve of dihydroxy polystyrene is presented in the Figure 2.6 as a representative of the functionalized polystyrene series. Table 2.4 shows the initial and final decomposition temperature of the functionalized polystyrene. These results confirms that the functionalized polystyrene shows a sharp single stage decomposition temperature centered at 400°C and which is consistent with the similar type polystyrene systems\(^{23}\). The initial and final decomposition temperature of the synthesized polystyrene is not varying much with one another. It confirms that the stability of the polymer is high during the functionalization process.

*Figure 2.6: TGA (○) and DTA (△) curve of α, Ω, Dihydroxy terminated polystyrene*
2.3.3.2. Differential Scanning Calorimetry (DSC)

The DSC data of the functionalized polystyrene are presented in the Table 2.4 and the DSC curve of dihydroxy polystyrene is presented in the Figure 2.7 as a representation of the polymer series. The Tg value of the functionalized polystyrene are centered around 58°C and not vary very much with one another as consistent with the data reported for the similar molecular weight polystyrene\textsuperscript{24}. But on a closer look, the Tg value of the polystyrene is in the order of dibromo < dihydroxy. This slight change in the Tg value may be due to the bulky end group present in the small polystyrene chain. The effect of end group on the chain flexibility in functionalized polystyrene is clearly presented in the Tg value.

![DSC curve of a, Ω, Dihydroxy terminated polystyrene](image)

*Figure 2.7: DSC curve of a, Ω, Dihydroxy terminated polystyrene*
Table 2.4: TGA and DSC data of the synthesized polymer

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Polymer Code</th>
<th>DSC (°C)</th>
<th>TGA (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T_{ig}$</td>
<td>$T_{mg}$</td>
</tr>
<tr>
<td>1</td>
<td>Br-PSt-Br</td>
<td>55.8</td>
<td>56.8</td>
</tr>
<tr>
<td>2</td>
<td>OH-PSt-OH</td>
<td>56.7</td>
<td>58.3</td>
</tr>
</tbody>
</table>

Where,

$T_{ig}$ = initial point, $T_{mg}$ = midpoint, $T_{eg}$ = end point and $D$ = Decomposition temperature.

2.3.4. Solvent Resistivity

Amorphous polymer like α, Ω, dibromo and α, Ω, dihydroxy polystyrene are easily attacked by the solvent on their physical network points thereby provides dimensional instability to the system. The solvent resistivity is studied by suspending injection moulded bars in organic solvents at room temperature for 1 hr. After drying the sample, the weight loss is determined. The solubility pattern of the amorphous polymer are presented in the Table 2.5 and found that the amorphous polymer is completely soluble in all tested solvent and shows poor solvent resistivity.

Table 2.5: Solubility data for the polymer at the room temperature

<table>
<thead>
<tr>
<th>Name of the Polymer</th>
<th>$M_w$ (NMR) (g/mol)</th>
<th>Solvents*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMF</td>
<td>Toluene</td>
</tr>
<tr>
<td>Br-PSt-Br</td>
<td>1942</td>
<td>+</td>
</tr>
<tr>
<td>OH-PSt-OH</td>
<td>1802</td>
<td>+</td>
</tr>
</tbody>
</table>

Where, * = + ; Soluble, - ; Insoluble
2.4. CONCLUSION

α, Ω, Dihydroxy terminated polystyrene are prepared using α, Ω, Dibromo prepolymer which is prepared by ATRP technique. The synthesized polymer is characterized by FT-IR, $^1$H-NMR, GPC, GC-MS and TGA techniques. The FT-IR result confirms that the formation of the functional group. The molecular weight of the polymer is calculated using $^1$H-NMR, GPC and GC-MS techniques and found to be around 2000 g/mol with narrow polydispersity value of 1.12. The synthesized prepolymer is stable up to 400°C and shows single stage decomposition on 400°C. The Tg of the polymer is found to be around 58°C and increasing with increasing the bulkiness of the end group. Synthesized prepolymer is poor solvent resistance in organic solvent. Therefore this polymer can be used for further processing and application in different polymeric fields. Overall an effective and simple method for synthesize the functionalized polystyrene is reported here and characterized with all available techniques. This synthesized prepolymer is used as soft segment for the preparation of poly(urethane-urea/amide)
REFERENCES


