Poly(sulfone ether amide amide)s as a new generation of soluble, thermally stable polymers

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Abstract

A new sulfone ether amide diamine was synthesized via three steps, starting from reaction of 4-aminophenol with 4-nitrobenzoyl chloride in the presence of propylene oxide afforded N-(4-hydroxy phenyl)-4-nitrobenzamide (HPNB). In the next step, reduction of nitro group resulted in preparation of 4-amino-N-(4-hydroxy phenyl) benzamide (AHPB). Final step in the preparation of diamine was the reaction of AHPB with bis(4-chlorophenyl) sulfone in the presence of K2CO3. All the materials were characterized using conventional spectroscopic methods. Poly(sulfone ether amide amide)s were synthesized by polycondensation reactions of prepared diamine with different diacid chlorides (aromatic and aliphatic ones). The obtained polymers were fully characterized and their physical properties including thermal behavior, thermal stability, solubility, and inherent viscosity were studied.

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Keywords: Thermal property; Polyamide; Polycondensation; Synthesis

1. Introduction

Thermally stable polymers have received extensive interest due to the increasing demands for high temperature polymers as replacements for ceramics and metals in the automotive, aerospace, and microelectronics industries. Aromatic polyamides are one of the most important classes of high performance polymers, because they possess excellent mechanical properties, thermal stability, chemical resistance, and low flammability [1,2]. However, they encounter processing difficulties due to limited solubility in organic solvents and high glass transition or melting temperatures. It is a result of chain stiffness and intermolecular hydrogen bonding between amide groups [3].

Modification of high performance materials by increasing the solubility and lowering the transition temperatures while maintaining thermal stability are of particular interest. Copolycondensation is one of the possible ways for modification of polymer properties. Thus, for the processing of polyamides many copolyamides, such as poly(sulfone-amide)s, poly(ether-amide)s, and other copolymers have been prepared [4–7].

Aromatic polymers that contain aryl ether or aryl sulfone linkages generally have lower glass transition
temperatures, greater chain flexibility and tractability than their corresponding polymers without these groups in the chain [8–10]. Polymers containing both aryl ether and aryl sulfone linkages are amorphous, have low glass transition temperatures, and show excellent mechanical properties [11,12]. The lower glass transition temperatures and also improved solubility are attributed to the flexible linkages that provide a polymer chain with a lower energy of internal rotation [13].

According to our interests to prepare novel polyamides [14–17], here we wish to express the synthesis of a new sulfone ether amide diamine and resulting poly(sulfone ether amide amide)s. The diamine was synthesized by nucleophilic substitution reaction of 4-aminophenol with 4-nitrobenzoyl chloride, followed by reduction of nitro group and subsequent reaction of AHPB with bis(4-chlorophenyl) sulfone in the presence of K2CO3. Polycondensation reaction of the prepared diamine with terephthaloyl chloride (TPC), isophthaloyl chloride (IPC), sebacoyl chloride (SC), and adipoyl chloride (AC) resulted in preparation of two fully aromatic and two semi-aromatic poly(sulfone ether amide amide)s.

2. Experimental

2.1. Materials

All chemicals were purchased either from Merck or Aldrich chemical Co. 4-aminophenol and bis-(4-chlorophenyl)sulfone were recrystallized from ethanol. TPC, and IPC were purified by sublimation. N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF) and toluene were distilled over calcium hydride under reduced pressure.

2.2. Instruments

Infrared measurements were performed on a Bruker-IFS 48 FTIR spectrometer (Ettlingen, Germany). The H-NMR spectra were recorded in DMSO-δ6 solution using a Bruker Avance DPX 250MHz (GmbH, Germany). Elemental analyses were performed by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA), Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK). The dynamic mechanical measurements were recorded on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) in the bending mode at 1Hz and a heating rate of 5°C/min (Surrey, UK). Inherent viscosities were measured by using an Ubbelohde viscometer in a concentration of 0.5 g/dl in NMP at 30°C. Wide angle X-ray diffraction patterns were performed at room temperature on an X-ray diffractometer (Siemens model D 5000) using Ni-filtered CuKα radiation (40kV, 25mA) with scanning rate of 3°/min.

2.3. Monomer synthesis

2.3.1. Synthesis of N-(4-hydroxy phenyl)-4-nitrobenzamide (HPNB)

A 100-ml, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and calcium chloride drying tube was charged with 5.1mmol of the 4-aminophenol and 15ml of dry NMP. The mixture was stirred at 0°C for 0.5h. Then about 3ml of propylene oxide was added, and after a few minutes 5mmol of 4-nitrobenzoyl chloride was added and the mixture was stirred at 0°C for 0.5h. The temperature was raised to room temperature and the solution was stirred for 6h. HPNB was precipitated by pouring the flask content into water. Then it was filtered, redisolved in minimum amounts of NMP and precipitated in water. It was filtered, washed several times with hot water and dried overnight under vacuum at 70°C. Mass spectrum: m/z 258.

2.3.2. Synthesis of 4-amino-N-(4-hydroxy phenyl)benzamide (AHPB)

2.3g of the HPNB, 0.1g of 10%Pd-C, and 130ml of ethanol were introduced in to the three-neck flask to which 10ml of hydrazine monohydrate was added drop-wise over a period of 1h at 85°C. After the complete addition, the reaction was continued at reflux temperature for another 4h. To the suspension, 20ml of tetrahydrofuran was added to redissolve the precipitated product, and refluxing was continued for 1h. The mixture was filtered to remove the Pd-C and the filtrate was poured into water. The product was filtered off and purified by solvent–nonsolvent techniques using DMF and water. Then it was filtered, washed with hot water successively, and dried. Mass spectrum: m/z 228.

2.3.3. Synthesis of sulfone ether amide diamine (SEAD)

Into a 100-ml, three-necked, round-bottomed flask equipped with a Dean-Stark trap, a condenser, a nitrogen inlet tube, a thermometer, an oil bath, and a magnetic stirrer was placed 0.01 mol of bis-(4-chlorophenyl)sulfone, 25ml of dry NMP, and 15ml of dry toluene and 0.021mol of AHPB. Then 0.0315mol of K2CO3 was added to the mixture and the reaction mixture was heated to 140°C for 6h with continuous stirring. The generated water was removed from the reaction mixture by azeotropic distillation. The reaction temperature was raised to 165°C by removing more toluene, and kept at the same temperature for 18 h. During this time, progress of the reaction was monitored by thin-layer chromatography (TLC). The resulting reaction mixture was cooled and poured into water. Then 100ml of 3% NaOH was added to the mixture and the mixture was washed repeat-
edly with a 3% NaOH solution and water. It was washed with THF using a Soxhlet extractor for a few hours. The obtained diamine was dried in a vacuum oven at 60°C. Mass spectrum: m/z 670.

2.4. Polyamide synthesis

The synthesis of polyamide typically was carried out as follows: A 100-ml, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and calcium chloride drying tube was charged with 2mmol of the diamine and 15ml of dry NMP. The mixture was stirred at 0°C for 0.5h. Then about 1ml of propylene oxide was added, and after a few minutes 2mmol of diacid chloride was added and the mixture was stirred at 0°C for 0.5h. The temperature was raised to room temperature and the solution was stirred for 6h. Polyamide was precipitated by pouring the flask content into water. Then it was filtered, washed with hot water, Soxhleted with methanol for 5h, and dried overnight under vacuum at 120°C. (Yields over 92%).

3. Results and discussion

3.1. Synthesis of sulfone ether amide diamine (SEAD)

Aromatic diamines are valuable building blocks for the preparation of high performance polymers including polyamides, polyimides, and polyureas. To extend the utility of the thermally stable materials it has been a long desired goal to synthesize diamines, which afford soluble and processable polymers without too much sacrificing thermal stability. In this way, the synthetic route for the preparation of new diamine containing sulfone ether amide (SEAD) monomer is shown in Schemes 1–3. The diamine was synthesized by nucleophilic substitution reaction of 4-aminophenol with 4-nitrobenzoyl chloride in the presence of propylene oxide (PO) to afford N-(4-hydroxy phenyl)-4-nitrobenzamide (HPNB) (Scheme 1). The catalytic hydrogenation of nitro group in the HPNB to amino compound AHPB was accomplished by using hydrazine monohydrate and catalytic amount of Pd/C as reducing agent (Scheme 2). Common spectroscopic methods such as IR, NMR, and Mass spectroscopy as well as elemental analysis were used to characterize the structures of these compounds (Table 1). According to the IR spectra that are shown in Fig. 1 conversion of nitro group to amine group was confirmed by disappearance of absorption bands at 1551 and 1346cm⁻¹ and presence of bands at 3285–3320cm⁻¹ (–N–H stretching) and 1609cm⁻¹ (–N–H deformation), respectively.

Reaction of two moles of AHPB with bis(4-chlorophenyl) sulfone in the presence of K₂CO₃ resulted in preparation of SEAD (Scheme 3). The IR spectrum of the SEAD showed absorption bands at 3350–3430 (NH₂), 1649 (C=O), 1605 (NH), 1312 (SO₂ symmetric),
1229 (C–O), 1180 cm$^{-1}$ (SO$_2$ asymmetric) confirming the structure (Fig. 2). The H-NMR spectrum (Fig. 3) and elemental analysis of the diamine were confirmed the proposed structure (Table 1).
Fig. 2. IR spectrum of SEAD.

Fig. 3. (a) H-NMR spectrum of SEAD and (b) Expanded H-NMR spectrum of SEAD.
3.2. Synthesis of poly(sulfone ether amide amide)s

Polycondensation reaction of the SEAD with various diacid chlorides including TPC, IPC, AC, and SC in the presence of propylene oxide as an acid scavenger led to preparation of fully aromatic and semi-aromatic polyamides (Scheme 4). Structures of the polyamides were characterized by IR, NMR, and elemental analysis. The representative IR and NMR spectroscopy of the polymers are brought in Figs. 4 and 5, respectively. IR spectrum of the SEAD-SC showed bands at about 3300–3380 (NH), 3010 (Ar–CH), 2926 (alkylene CH), 1655–1660 (C=O), 1603 (NH), 1489–1508 (C=C), 1406 (C–N), 1313 (SO$_2$ symmetric), 1231 (C=O), and 1148 cm$^{-1}$ (SO$_2$ asymmetric) confirming the structure. H-NMR spectrum of SEAD-TPC showed peaks at about $\delta$ 10.66 (2H, NH), 10.28 (2H, NH), 8.13 (d, 4H, phenyl), 8.00 (d, 4H, phenyl), 7.96 (d, 4H, phenyl), 7.91 (d, 4H, phenyl), 7.86 (d, 4H, phenyl), 7.14 (d, 4H, phenyl), and 7.10 (d, 4H, phenyl). The yield, inherent viscosity, and elemental analysis of the polyamides are collected in Table 2. All the polymers were obtained in high yields (92–97%) and the inherent viscosity were in the range of 0.36–0.53 dLg$^{-1}$ in a concentration of 0.5 g dL$^{-1}$ in NMP at 30°C. According to the wide-angle X-ray spectroscopy in the region of $2\theta$ = 5°–70° at room temperature, the polymers showed low crystallinity (below 10%) and therefore, they were almost amorphous.

The solubility behaviors of the polymers were studied in different solvents and the results are summarized in Table 3. The polymers showed good solubility in dipolar aprotic solvents including DMF, DMAc, NMP, dimethyl sulfoxide (DMSO) and also in less efficient solvent m-cresol. This is as a result of introducing flexible sulfone and ether groups into the polymer backbone. Presence of alkyl groups in the semi-aromatic polyamides derived from aliphatic acid chlorides caused increasing of solubility in comparison to fully aromatic polyamides.

The thermal properties and behaviors of the polyamides were studied in air at a heating rate of 10°C/min using DSC, DMTA, and TGA techniques. The polymers showed the glass transition temperatures in the range of 165–229°C according to their DSC ($T_g$ was taken as the midpoint of the change in slope of the baseline) and DMTA ($T_g$ was taken as the tan $\delta$ went...
through a maximum) curves. The initial decomposition temperatures ($T_0$) of the polyamides were about 191–290°C. Although, the polymers were dried before thermal analysis the $T_0$ was low. It could be attributed to the nature of these polymers for high tendency to moisture uptake. Heating the polymers up to 250°C, cooling and heating again would be an effective method for minimizing the moisture uptake and obtaining real value of $T_0$. The temperatures for 10% gravimetric loss ($T_{10}$) that are important criterion for evaluation of thermal stability, were in the range of 375–418°C and also the char yields of polymers at 500°C were about 45–70%. The results are collected in Table 4. According to the obtained results, the polyamides demonstrated high thermal stability and fully aromatic ones were more stable than the semi-aromatic polyamides. High thermal stability could be contributed to the incorporation of preformed amide group and phenylation of the backbone.

Therefore, presence of sulfone, ether, and alkyl group caused improving of the solubility and accordingly SC-derived polyamides showed the highest solubility among the prepared polymers. On the other hand, introduction of preformed amide unit, phenylation of backbone, avoid of weak linkages, and symmetry of the structures were most important structural modification for increasing of the thermal stability. Accordingly, TPC-derived polyamides revealed the most thermal stability among the prepared polymers.

Comparison of the obtained structures and their properties with similarly prepared monomer and
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Elemental analysis</th>
<th>Yield (%)</th>
<th>$\eta_{\text{Inherent}}$ (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Found</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>(1) SEAD-TPC</td>
<td>69.00</td>
<td>4.00</td>
<td>7.00</td>
</tr>
<tr>
<td>(2) SEAD-IPC</td>
<td>69.00</td>
<td>4.00</td>
<td>7.00</td>
</tr>
<tr>
<td>(3) SEAD-AC</td>
<td>67.69</td>
<td>4.62</td>
<td>7.18</td>
</tr>
<tr>
<td>(4) SEAD-SC</td>
<td>68.90</td>
<td>5.26</td>
<td>6.70</td>
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</table>
polymers [5] showed that presence of additional amide units in the monomer and therefore in the polymer backbone led to higher \( T_g \) and thermal stability. This could be attributed to the intense chain stiffness and intermolecular hydrogen bonding between additional amide groups. Also, it was revealed that the obtained polymers in the present work showed lower \( T_g \) in comparison with the similar structures possessing alkyl groups on a ring unit at ortho positions to the ether linkage [18]. This was due to the hindrance effect of the chain rotation in the methyl-substituted polymers. It seems that this factor was more effective in increasing of \( T_g \) than the presence of additional amide units. Also, it should be noted that these comparisons would be more accurate when the viscosities (molecular weights) were comparable.

4. Conclusion

A new sulfone ether amide diamine was prepared via three step reactions. Reaction of 4-aminophenol with 4-nitrobenzoyl chloride resulted in preparation of HPNB. Reduction of nitro group afforded AHPB. The diamine was synthesized via reaction of AHPB with bis(4-chlorophenyl) sulfone in the presence of \( \text{K}_2\text{CO}_3 \). A series of new polyamides were prepared by polycondensation of the diamine with aromatic and aliphatic diacid chlorides. Polymers showed high thermal stability and improved solubility due to the presence preformed amide group, phenylation of backbone, and symmetry and also introduction of sulfone, ether, and alkyl groups, respectively.

References


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Table 3

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>NMP</th>
<th>DMAC</th>
<th>DMF</th>
<th>DMSO</th>
<th>m-Cresol</th>
<th>Pyridine</th>
<th>THF</th>
<th>Dioxane</th>
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<tbody>
<tr>
<td>SEAD-TPC</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SEAD-IPC</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SEAD-AC</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SEAD-SC</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</table>

* Solubility: ++: soluble at room temperature; +: soluble on heating; +–: partially soluble on heating; –: insoluble.

Table 4

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( T_g (^\circ \text{C}) )</th>
<th>( T_0 (^\circ \text{C}) )</th>
<th>( T_{10} (^\circ \text{C}) )</th>
<th>Char yield at 500(^\circ)C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEAD-TPC</td>
<td>229</td>
<td>290</td>
<td>418</td>
<td>70</td>
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<tr>
<td>SEAD-IPC</td>
<td>212</td>
<td>282</td>
<td>407</td>
<td>64</td>
</tr>
<tr>
<td>SEAD-AC</td>
<td>172</td>
<td>208</td>
<td>379</td>
<td>46</td>
</tr>
<tr>
<td>SEAD-SC</td>
<td>165</td>
<td>191</td>
<td>375</td>
<td>45</td>
</tr>
</tbody>
</table>

\( T_g \): glass transition temperature, \( T_0 \): initial decomposition temperature, \( T_{10} \): temperature for 10\% weight loss, Char yield: weight of polymer remained.