Synthesis and Study of Thermal Properties of New Heat Stable Poly(ether-ketone)s and Poly(ether-ketone-sulphone)s

Ahmad Banihashemi* and Batool Akhlaghinia**
Chemistry Department, Faculty of Science, Shiraz University, Shiraz 71454, I.R.Iran

Received: 10 November 1997; accepted 19 April 1998

ABSTRACT

Benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid reacts with a number of diaryl ethers in phosphorous pentoxide/methanesulphonic acid (PPMA) media. The resulting poly(ether-ketone)s and poly(ether-ketone-sulphone)s, obtained by direct polycondensation reaction, are characterized with FT-IR spectroscopy and elemental analysis. Thermal properties of polymers are investigated by TGA and DSC methods and their heat stabilities are compared. The thermal properties can be modified by introducing an equimolar amount of a diacid or diarylether by which thermal cross-linking sites are provided.

Key Words: benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid, direct polycondensation, poly(ether-ketone)s, poly(ether-ketone-sulphone)s, heat stable polymers

INTRODUCTION

The synthesis of certain thermally stable laminating resins having aromatic ether, aromatic ketone, and aromatic sulphone units in the polymer backbone was reported earlier [1, 2]. Poly(arylene ethers) such as poly(ether-sulphone), poly(ether-ketone), poly(ether-ether-ketone), and poly(ether-ketone-sulphone) [3] belong to the family of high performance engineering thermoplastics.

These poly(arylene ether)s are applied in electronics, aircraft automobile, medical, and aerospace industries as coatings, adhesives, composites, moulded components, toughening agents, and ultrafiltration membranes because they show high thermal stability, high hydrolytic stability, good mechanical properties, and inert behaviour against organic solvents [4].

There are two main synthetic routes for preparation of poly(ether-ketone-sulphone)s. First, the nucleophilic aromatic displacement of carbonyl or sulphonyl activated halides by phenoxide anions and second, the Friedel-Crafts electrophilic aromatic polyacylation condensation (Scheme I) [3c, 5].

In the latter route, diacid chlorides are most often used as the monomers in the synthesis of polymers. However, they have a number of significant limitation associated with their easy hydrolyzability, which creates difficulties in their synthesis and storage. Moreover, a high reactivity of these monomers causes several side reactions, which leads to the formation of low molecular weight polymers.

One of the ways to circumvent this situation is

(* To whom correspondence should be addressed; (**) The present address: Department of Chemistry, Damghan University, Damghan, I.R.Iran
to use the dicarboxylic acids themselves. The answer was found in direct polycondensation recently reported by M. Ueda [6] et al. They showed a new method for direct polycondensation of dicarboxylic acids with diphenoxy benzene, or self-polycondensation of various benzoic acids containing phenyl ether structure for the synthesis of aromatic poly(ether-ketone-sulphone)s of high molecular weight using phosphorous pentoxide/methanesulphonic acid (PPMA) as condensing agent and solvent (Scheme II).

In this report we describe the synthesis of a number of new poly(ether-ketone)s and poly(ether-ketone-sulphone)s by direct polycondensation reaction using benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid and several diaryl ethers (Scheme III). FT-IR Spectra, TGA, and DSC curves are recorded and thermal properties are compared with each other.

**EXPERIMENTAL**

**Materials and Instruments**

FT-IR Spectra were recorded on a Shimadzu DR-8001 spectrometer. Melting points were determined with a Buchi-535 melting point apparatus. Mass spectra were recorded on a Shimadzu GC-MS-QP 1000 PX.

The thermal gravimetric analysis and differential scanning calorimetry were performed on a Staton STA-625 under Ar or N₂ atmosphere and elemental analyses were performed by Alfred Bernhardt Microanalytical Laboratories, Germany.

All solvents and reagents were purchased from Fluka or Merck Chemical Companies.

**Preparation of Monomers**

**Diacid Synthesis**

Benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid (1) was prepared from 2,9-dimethyl[5a,10b]dihydro benzofuro[2,3-b]benzofuran as previously described [7].

**Diaryl Ethers Synthesis**

1,4-Bis(p-phenoxybenzoyl)benzene (2ₖ)

Terephthaloyl chloride (2 g, 9.9 mmol) was dissolved in 40 mL of diphenyl ether. Aluminium chloride (2 g)
was added, and the mixture was heated at 80 °C under dry nitrogen for 20 h. The mixture was washed with water to remove inorganic components. The product of reaction precipitated in organic layer and separated by filtration. The precipitate was washed with hot water and recrystallized from chloroform (yield 70% mp: 209–213 °C, Lit. [8] 215–215.5 °C).

**FT-IR:** 3067, 1652, 1601, 1584, 1502, 1456, 1322, 1302, 1234, 1195, 1164, 974, 921, 818, 753, 699, 645, 496.

**m/e:** 470 (molecular ion), 197, 141, 115.

**1,3-Bis(p-phenoxybenzoyl)benzene** [1] (2a), **3,9-bis(p-phenoxybenzoyl)[2,2]p-cyclophane** [9] (2c), **4,4′-diphenoxydiphenyl sulphone** [10] (2d), **4,4′-di(1-naphthoxy)benzophenone** (2e), and **4,4′-di(1-naphthoxy)diphenyl sulphone** [11] (2f) were prepared as described in literature.

**4,4′-Bis(4-phenoxybenzenesulphonyl)biphenyl** (2e) Biphenyl-4,4′-disulphonyl chloride (2.63 g, 7.5 mmol), diphenyl ether (25 mL) and anhydrous ferric chloride (0.2 g) were stirred under nitrogen atmosphere at 160 °C for 24 h. The reaction mixture was poured into water. The organic layer was separated. The precipitates were filtered and washed several times with water. The crude product was recrystallized from chloroform to give the product in yield 40%, (mp: 263–266 °C, Lit. [12] 263–267 °C).

**FT-IR:** 3063, 1586, 1490, 1456, 1409, 1321, 1286, 1195, 1152, 1073, 1003, 905, 872, 825, 762, 706, 636, 559, 490.

**Polymer Synthesis**

A solution of dicarboxylic acid 1 (0.148 g, 0.5 mmol) and diaryl ether (0.5 mmol) (2e–2f) in PPMA 1.5 mL was stirred at 100 °C for 24 h. The resulting viscous solution was diluted with methanesulphonic acid. This solution was poured into water and neutralized with sodium carbonate. The polymer was collected, washed with water. It was then suspended in a solution of sodium hydroxide (20 mL: 0.1 N) and refluxed for 2 h. The polymer was filtered, washed several times with water, ethanol and ether. It was dried under vacuum at 100 °C for 10 h.

**RESULTS AND DISCUSSION**

All monomers were synthesized as described in literature except 1,4-bis(p-phenoxybenzoyl)benzene (2a) which were synthesized by the reaction of an excess amount of diphenyl ether with terephthaloyl chloride and biphenyl-4,4′-disulphonyl chloride, respectively.

The development of efficient and mild method for the synthesis of condensation polymers continues to be a significant aspects of polymer chemistry. There has been a considerable research effort to develop new methods [13].

Diacid chlorides are most often used as the monomers in the synthesis of condensation polymers. However, they have a number of significant limitations associated with their easy hydrolyzability, which creates difficulties in their synthesis and storage. Moreover, a higher activity of these monomers cause several side reactions, which lead to the formation of low molecular weight polymers. One of the ways to circumvent this situation may be to use the dicarboxylic acids themselves and for the polymer formation process to take place at moderate temperature with a high rate. The answer was found in direct polycondensation.

The former synthesis was carried out in the presence of aluminium chloride as catalyst. Anhydrous ferric chloride was used as catalyst in the latter synthesis. The products were identified by melting point and FT-IR spectroscopy.

All the polymers which are illustrated in Scheme III were synthesized by direct method polycondensation in PPMA at 100 °C for 24 h.

Direct polycondensation using condensing agents had been used for the in situ activation of dicarboxylic acids, followed by condensation under mild conditions. Phosphorus pentoxide/methanesulphonic acid (PPMA) in the ratio of 1:10 is a very useful dehydrating agent for the preparation of aromatic poly(ether-ketone)s. This reagent was prepared according to the reported procedure [6, 14].

PPMA was used as reagent and solvent in these polycondensation reactions. The reactant's role in PPMA reagent, however, is not certain yet. Most probably it is a very active mixed anhydride.
Figure 1. FT-IR Spectrum of polymer 4.

Figure 2. TGA and DSC curves of polymer 1.
Although methanesulphonic anhydride is clearly present in the PPMA mixture, as observed with NMR by Eaton et al., appropriate methanesulphonic anhydride-methanesulphonic acid solutions are less effective in carrying out these transformations; the reaction rates are slower and product yields are generally poorer. Pure methanesulphonic acid will not promote the reactions considered under comparable conditions [14].

After 24 h, the reaction mixture became viscous. The reaction mixtures were diluted with methanesulphonic acid. Work-ups of PPMA reaction mixtures are easy and clean. The reagent can be destroyed conveniently with aqueous sodium carbonate solution thus, the reaction mixtures were poured into water and neutralized with sodium carbonate. The precipitates were filtered and washed several times with water.

IR Spectra of these products showed two bands at 1820, 1750 cm\(^{-1}\) due to the carbonyl of anhydride which was formed during polymerization reaction in the reaction media. To remove this side product, we tried to hydrolyze it. The product of reactions was refluxed in dilute solution of sodium hydroxide for 2 h. FT-IR Spectra exhibited only characteristic absorptions at 1640 cm\(^{-1}\) and 1240 cm\(^{-1}\) due to the carbonyls of ketones and C–O–C stretching, respectively. A representative FT-IR spectra is shown in Figure 1 and the results are summarized in Table 1.

It was impossible to assign their chemical structure by NMR spectroscopy and measure their inherent viscosities because of the lack of their solubility in polar aprotic solvents.

Elemental analysis was carried out on the polymer and was found to be in good agreement with the expected values. The results are summarized in Table 2.

### Thermal Properties

The most important and yet least reliable factor in the study of heat stable polymers is the measurement or evaluation of thermal stability. There are numerous methods used, and no two can be directly compared in all cases.

Thermal properties of polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

A representative TGA and DSC curve is shown in Figure 2 and the results are summarized in Table 3.

The initial decomposition temperature (IDT), the temperature at 10% weight loss (PDT), and the maximum polymer decomposition temperature (PDT\(_{\text{max}}\)) ranged from 308–400 °C, 340–416 °C, and 467–520 °C.

The residual weights (\(\gamma_c\)) of the polymers were reported at 600 °C. These polymers were stable in N\(_2\) up to 340–416 °C.

Differential scanning calorimetry (DSC) is a common laboratory method of which the polymer chemist avails himself to determine the \(T_g\) (glass transition temperature). This is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>FT-IR characterization bands (v) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3063, 55, 1587, 1497, 1414, 1381, 1308, 1238, 1161, 845</td>
</tr>
<tr>
<td>2</td>
<td>3063, 1655, 1589, 1497, 1308, 1242, 1165, 1105, 926, 843</td>
</tr>
<tr>
<td>3</td>
<td>3063, 2928, 2854, 1649, 1587, 1495, 1410, 1397, 1238, 1161, 1013, 970, 928, 872, 766, 690, 613, 496</td>
</tr>
<tr>
<td>4</td>
<td>3065, 1647, 1583, 1487, 1381, 1292, 1240, 1150, 1105, 1011, 964, 872, 835, 793, 649, 579</td>
</tr>
<tr>
<td>5</td>
<td>3069, 1840, 1585, 1489, 1439, 1321, 1244, 1153, 1107, 1072, 1003, 872, 839, 791, 733, 669, 581, 481</td>
</tr>
<tr>
<td>6</td>
<td>3063, 1649, 1574, 1501, 1458, 1423, 1279, 1234, 1159, 1113, 1045, 1015, 928, 839, 766, 602</td>
</tr>
<tr>
<td>7</td>
<td>3067, 1640, 1572, 1508, 1489, 1423, 1321, 1290, 1238, 1150, 1105, 1045, 833, 770, 690, 642, 567</td>
</tr>
</tbody>
</table>
Table 2. Polycondensation of benzofuro[2,3-b]benzofuran-2,9-dicarboxylic acid (A) with various diaryl ethers, the elemental analysis data and yields of reactions.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Diaryl ether</th>
<th>Elemental analysis (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Diagram" /></td>
<td>Calc. 72.51</td>
<td>3.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found. 71.02</td>
<td>3.20</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Diagram" /></td>
<td>Calc. 75.59</td>
<td>3.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found. 73.20</td>
<td>3.22</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Diagram" /></td>
<td>Calc. 80.99</td>
<td>3.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found. -</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Diagram" /></td>
<td>Calc. 71.07</td>
<td>3.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found. 69.81</td>
<td>3.09</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Diagram" /></td>
<td>Calc. 80.63</td>
<td>4.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found. 78.6</td>
<td>3.62</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6.png" alt="Diagram" /></td>
<td>Calc. 78.9</td>
<td>3.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found. 78.9</td>
<td>3.26</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7.png" alt="Diagram" /></td>
<td>Calc. 78.9</td>
<td>3.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found. 78.9</td>
<td>3.26</td>
</tr>
</tbody>
</table>

Table 3. Thermal analysis data.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg (°C)(a)</th>
<th>TDT (°C)(b)</th>
<th>PDT (°C)(c)</th>
<th>PDT (°C) max(d)</th>
<th>Yc (%) (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>295</td>
<td>400</td>
<td>416</td>
<td>520</td>
<td>44</td>
</tr>
<tr>
<td>2*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>263</td>
<td>332</td>
<td>395</td>
<td>508</td>
<td>46</td>
</tr>
<tr>
<td>4</td>
<td>232</td>
<td>308</td>
<td>340</td>
<td>548</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>283</td>
<td>375</td>
<td>400</td>
<td>543</td>
<td>56</td>
</tr>
<tr>
<td>6</td>
<td>291</td>
<td>371</td>
<td>379</td>
<td>467</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>279</td>
<td>371</td>
<td>400</td>
<td>540</td>
<td>44</td>
</tr>
</tbody>
</table>

(a) Glass transition temperature; (b) Initial decomposition temperature; (c) Polymer decomposition temperature; (d) Maximum polymer decomposition; (e) Char yield at 800 °C; (f) It was not determined.
Tg values ranged from 232–295 °C. The high glass transition temperature of these polymers can be rationalized on the basis of stiffness of polymer chain which is the result of rigid diacid moiety, high carbonyl to ether ratios in polymer [15] and incorporation of a biphenyl [16] moiety.

As it is evident in Table 3 these polymers were stable in N2 up to 340–410 °C and formed char yield of 24–60 % at 600 °C.

**CONCLUSION.**

In this research one group of heat stable polymers...
were synthesized by polycondensation of benzofuro-[2,3-b]-benzofuran-2,9-dicarboxylic acid with some diaryl ethers.

In accordance with obtained results from thermal analysis, we can modify thermal properties by introducing an equimolar amount of another diacid or diaryl ether which contains cyano group as a thermal cross-linking site. Because of the rigidity of polymer backbone, they are not soluble in polar solvents, so sulphonamide groups are introduced along the polymer chain as pendant groups.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to Prof. Tammami for his advises and the Research Council of Shiraz University, for financial support of this research.

REFERENCES