

## Synthesis and Characterization of Novel Aromatic Polyimides from 3,4-Bis(4-aminophenyl)-2,5-diphenylthiophene and Aromatic Tetracarboxylic Dianhydrides

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**ABSTRACT:** New aromatic polyimides containing tetraphenylthiophene unit were synthesized from 3,4-bis(4-aminophenyl)-2,5-diphenylthiophene and various aromatic tetracarboxylic dianhydrides by the conventional two-step procedure that included ring-opening polyaddition in a polar amide-type solvent and subsequent thermal cyclodehydration. These polyimides had inherent viscosities of 0.18—0.35 dl g<sup>-1</sup> and were readily soluble in a wide range of organic solvents such as *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidone, *m*-cresol, and pyridine. The glass transition temperatures of the polyimides were in the range of 269—327°C, and the 10% weight loss temperatures were 550—660°C in nitrogen.

**KEY WORDS** High Temperature Polyimides / Soluble Polyimides /  
3,4-Bis(4-aminophenyl)-2,5-diphenylthiophene / Thermal Behavior /

Aromatic polyimides are well known since the 1960s for their high performance properties and have been used in a variety of fields including aerospace and microelectronics industries.<sup>1,2</sup> These polyimides are characterized by high glass transition temperatures ( $T_g$ ) along with high decomposition temperatures and good mechanical properties, however, one major drawback was that they were typically insoluble in organic solvents and unprocessable after conversion from the polyamic acid to the polyimide form. Several attempts have been made to improve the solubility of polyimides while maintaining the excellent thermal and mechanical properties.<sup>3–12</sup> One of the attractive methods for the enhanced solubility was incorporation of bulky pendant phenyl groups into the polyimide backbone.<sup>13</sup> Recently we have utilized the methodology to attain this goal; a number of organic-soluble polyimides

having high  $T_g$ s were successfully prepared by using aromatic diamines containing tetraphenylthiophene,<sup>14</sup> tetraphenylfuran,<sup>15</sup> tetraphenylpyrrole,<sup>16</sup> and triphenylamine<sup>17</sup> moieties. Very recently we have found that aromatic polyamides from 3,4-bis(4-aminophenyl)-2,5-diphenylthiophene and various aromatic dicarboxylic acid chlorides had good solubility and high thermal stability.<sup>18</sup> Therefore, this diaminotetraphenylthiophene would be expected to be another potential monomer for the preparation of soluble and thermally stable polyimides. In the present communication, we describe the synthesis and characterization of novel polyimides involving the diamine by the polymerization with various aromatic tetracarboxylic dianhydrides, and the properties are compared with those of the structurally related polyimides derived from the isomeric diamine, 2,5-bis(4-aminophenyl)-3,4-diphenylthio-

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phene.<sup>14</sup>

## EXPERIMENTAL

### Materials

3,4-Bis(4-aminophenyl)-2,5-diphenylthiophene (**I**) was synthesized according to the method reported previously.<sup>18</sup> Pyromellitic dianhydride (**IIa**), 3,3',4,4'-biphenyltetracarboxylic dianhydride (**IIb**), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (**IIc**), and 4,4'-oxydiphthalic anhydride (**IId**) were obtained commercially and purified by sublimation under reduced pressure. 4,4'-Sulfonyldiphthalic anhydride (**IIe**) was supplied by New Japan Chemical Co., Japan, and used without further purification. Solvents such as *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) were purified by vacuum distillation with calcium hydride.

### Polymerization

**Polyimide IVb from I and IIb.** In a three neck flask, 0.588 g (2.0 mmol) of solid **IIb** was added to a solution of 0.837 g (2.0 mmol) of **I** in 2.8 ml of NMP in one portion. The mixture was stirred at room temperature for 5 h under nitrogen. A part of the viscous solution formed was poured into 200 ml of methanol. The precipitated polymer was filtered, washed with hot methanol, and dried under vacuum. The inherent viscosity of the polyamic acid (**IIIb**) in NMP was 0.26 dl g<sup>-1</sup>, measured at a concentration of 0.5 g dl<sup>-1</sup> at 30°C. The rest of the reaction solution was cast onto a glass plate and the solvent was removed at 80°C. The thermal cyclodehydration of the polyamic acid was performed by heating at 150°C for 1 h and then at 280°C for 2 h under nitrogen. The inherent viscosity of the polyimide (**IVb**) was 0.29 dl g<sup>-1</sup> in concentrated sulfuric acid. The IR spectrum (film) exhibited absorption bands at 1776 and 1716 cm<sup>-1</sup> (C=O) and 1360 cm<sup>-1</sup> (C-N).

*Anal.* Calcd. for (C<sub>44</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>S)<sub>n</sub>: C, 78.09%; H, 3.57%; N, 4.14%; S, 4.74%.

Found: C, 77.83%; H, 3.45%; N, 4.03%; S, 4.28%.

Other polymers were synthesized by similar procedure.

### Measurements

IR spectra were recorded on a JASCO FTIR-5000 spectrophotometer. Differential thermal analysis (DTA), thermogravimetry (TG), and differential scanning calorimetry (DSC) were performed with Shimadzu thermal analyzers DTA-40M, TGA-40M, and DSC-41M, respectively, and the measurements were made at a heating rate of 10°C.min<sup>-1</sup> in air or nitrogen. The wide angle X-ray diffraction patterns were obtained for film specimens on a Rigaku Denki XG X-ray diffraction apparatus with nickel-filtered Cu-K<sub>α</sub> radiation (35 kV, 50 mA).

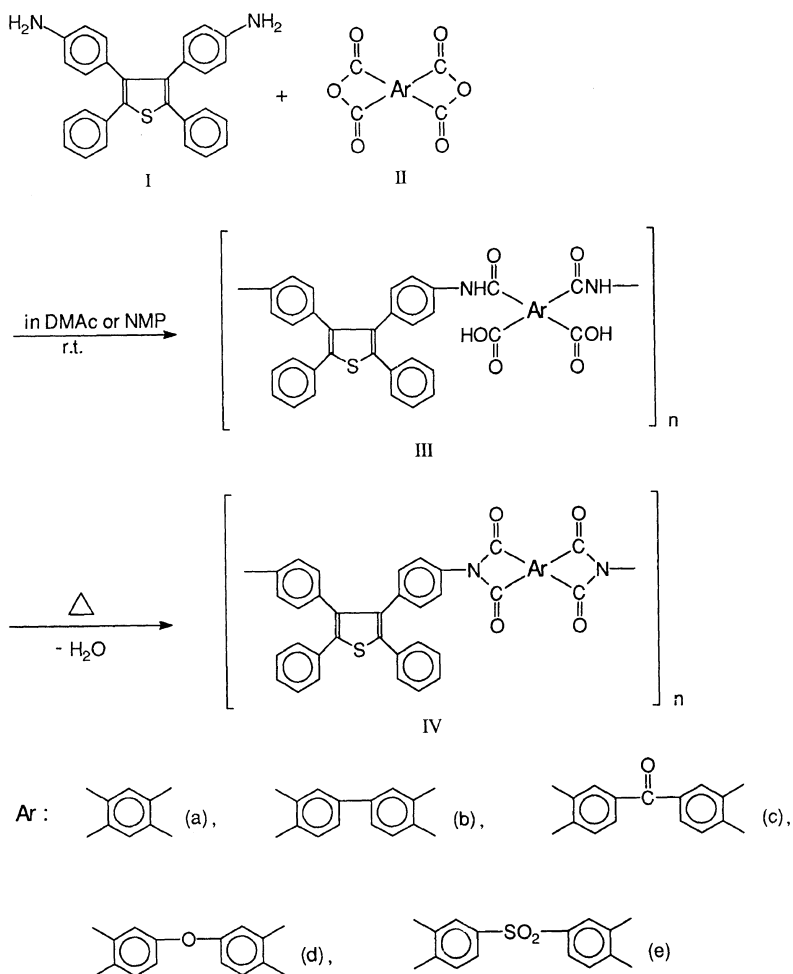
## RESULTS AND DISCUSSION

### Polymer Synthesis

Aromatic polyimides **IVa—IVe** were synthesized by the usual two-step procedure which involved the ring-opening polyaddition of diamine **I** to aromatic tetracarboxylic dianhydrides **IIa—IIe** giving polyamic acids **IIIa—IIIe** and the subsequent thermal cyclodehydration as shown in Scheme 1.

In the first step, the ring-opening polyadditions were carried out in DMAc or NMP at room temperature, leading to the formation of polyamic acids having inherent viscosities of 0.18—0.28 dl g<sup>-1</sup> in NMP, mostly regardless of the kind of aromatic tetracarboxylic dianhydrides used (Table I). The reaction media (DMAc and NMP) had almost no effect on the viscosity values of the polyamic acids formed. Although the polymerizations proceeded in homogeneous solution in these reaction media, the viscosity values of the polyamic acids were rather low. This might be partly due to the steric hindrance of the diamine monomer based on the narrow angle between two aminophenyl groups.

### Synthesis of Novel Aromatic Polyimides



**Scheme 1.**

In the second step, the thermal conversion of the polyamic acids to polyimides was performed by heating the precursor polymers in the form of film successively at 150°C and 280°C for 1 and 2 h, respectively, under nitrogen. The inherent viscosities of the polyimides formed were in the range of 0.17–0.35 dl g<sup>-1</sup> in concentrated sulfuric acid (Table I), and hence these polyimides gave brittle films with yellow to dark red in color.

The formation of polyimides was confirmed by the appearance of absorption bands at around 1770 and 1720 cm<sup>-1</sup> (C=O) and at about 1360 cm<sup>-1</sup> (C–N) characteristic of imide

group in the IR spectra. The elemental analysis values were in close agreement with the calculated values, and this also supported the polyimide formation.

#### Polymer Properties

All the polyimides were readily soluble in a wide range of organic solvents such as DMAc, NMP, *o*-chlorophenol, *m*-cresol, and pyridine. The solubility of these new polyimides was better than that of the previously reported polyimides containing tetraphenylfuran<sup>15</sup> and tetraphenylpyrrole<sup>16</sup> units. In addition, the new polyimides exhibited very similar solubility

**Table I.** Synthesis of polyamic acids and polyimides

Dianhydride	Reaction medium	Polyamic acid <sup>a</sup>		Polyimide <sup>b</sup>	
		Code	$\eta_{inh}^c$ dl g <sup>-1</sup>	Code	$\eta_{inh}^b$ dl g <sup>-1</sup>
<b>IIa</b>	DMAc	<b>IIIa</b>	0.19	<b>IVa</b>	0.18
<b>IIa</b>	NMP	<b>IIIa</b>	0.18	<b>IVa</b>	0.17
<b>IIb</b>	DMAc	<b>IIIb</b>	0.23	<b>IVb</b>	0.25
<b>IIb</b>	NMP	<b>IIIb</b>	0.26	<b>IVb</b>	0.29
<b>IIc</b>	DMAc	<b>IIIc</b>	0.24	<b>IVc</b>	0.22
<b>IIc</b>	NMP	<b>IIIc</b>	0.26	<b>IVc</b>	0.32
<b>II d</b>	DMAc	<b>III d</b>	0.22	<b>IV d</b>	0.25
<b>II d</b>	NMP	<b>III d</b>	0.21	<b>IV d</b>	0.35
<b>II e</b>	DMAc	<b>III e</b>	0.28	<b>IV e</b>	0.19
<b>II e</b>	NMP	<b>III e</b>	0.25	<b>IV e</b>	0.18

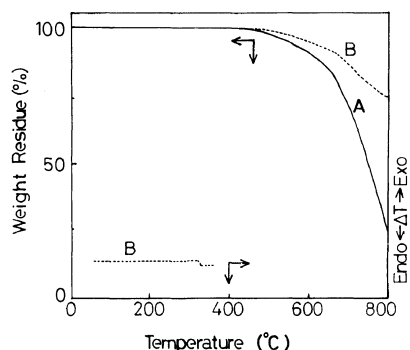
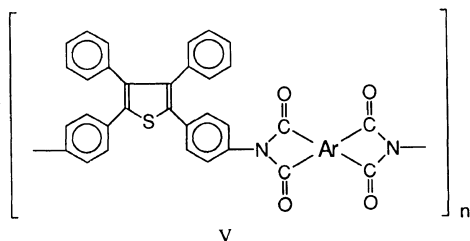
<sup>a</sup> Polymerization was carried out with 2.0 mmol of diamine **I** and 2.0 mmol of the dianhydride in 2.8 ml of the solvent at room temperature for 5 h under nitrogen.

<sup>b</sup> Thermal conversion was performed by heating at 150°C for 1 h and at 280°C for 2 h under nitrogen.

<sup>c</sup> Measured at a concentration of 0.5 g dl<sup>-1</sup> in NMP at 30°C.

<sup>d</sup> Measured at a concentration of 0.5 g dl<sup>-1</sup> in concentrated sulfuric acid at 30°C.

behavior to polyimides **V** having isomeric structure derived from 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene, where the arylene moiety (Ar) for polymer **V** corresponds individually to that for polymer **IV**. These results are well compatible with the fact that the solubility of these two tetraphenylthiophene-based polyamides was better than that of the tetraphenylfuran- and tetraphenylpyrrole-containing polyamides.<sup>18–20</sup> The X-ray diffraction study of the present polyimides showed that they were amorphous.

**Figure 1.** DTA and TG curves for polyimide **IVa** at a heating rate of 10°C min<sup>-1</sup> in (A) air and (B) nitrogen.**Table II.** Thermal behavior of aromatic polyimides

Polymer	$T_g^a$ °C	$T_{10}^b$		Char yield <sup>c</sup> %
		In air °C	In nitrogen °C	
<b>IVa</b>	327	605	660	74
<b>IVb</b>	302	625	640	76
<b>IVc</b>	279	560	585	72
<b>IVd</b>	269	600	625	73
<b>IVe</b>	303	540	550	66
<b>Va</b>	335	520	580	68
<b>Vb</b>	351	535	600	70
<b>Vc</b>	322	545	590	63
<b>Vd</b>	320	560	600	70
<b>Ve</b>	343	550	550	63

<sup>a</sup> Determined by DSC in nitrogen at a heating rate of 10°C min<sup>-1</sup>.

<sup>b</sup> Temperature at which 10% weight loss was recorded by TG at a heating rate of 10°C min<sup>-1</sup>.

<sup>c</sup> Char yield in nitrogen at 800°C by TG.

The thermal behavior of these polyimides **IV** and **V** was evaluated by means of DTA, TG, and DSC. Figure 1 shows typical DTA and TG curves of polyimide **IVa**, and the glass transition temperatures ( $T_g$ ) and 10% weight loss temperatures ( $T_{10}$ ) of these polymers are summarized in Table II. The present polyimides **IV** had relatively high  $T_g$  values in the range of 269–327°C, and the  $T_g$  values of isomeric polyimides **V** (320–343°C) were much higher than those of polyimides **IV**. In general, polyimides **IVa**, **IVb**,

and **IVe** having rigid or polar connecting group had higher  $T_g$  values than polymers **IVc** and **IVd** with flexible connecting groups. On the whole, the  $T_g$  values of the structurally related polyimides decreased in the following order: the tetraphenylpyrrole-containing polyimides (302—359°C) > the tetraphenylfuran-based polyimides (281—344°C) > the tetraphenylthiophene-bearing polyimides **IV**.

All the present polyimides **IV** did not lose weight below 400°C in air or nitrogen, and the  $T_{10}$  values in air and nitrogen were higher than 540°C and 550°C, respectively, indicating high thermal stability. In addition, the polyimides retained more than 66% in weight in nitrogen even at 800°C. Again, polyimides **IV** had somewhat higher values of  $T_{10}$  and char yield at 800°C in nitrogen than the isomeric polyimides **V**. This is probably due to dense molecular packing of polymers **IV** compared with polymer **V**. The thermal stability with respect to  $T_{10}$  of the structurally related polyimides were in the following order: the tetraphenylthiophene-containing polyimides **IV** > the tetraphenylpyrrole-based polyimides > the tetraphenylfuran-bearing polyimides. This order of thermal stability was consistent with that for the corresponding polyamides containing tetraphenylated heterocycles.<sup>18–20</sup> This is attributable to difference in inherent thermal stability between these five-membered heterocycles as discussed previously.<sup>20</sup>

### CONCLUSION

New aromatic polyimides containing tetraphenylthiophene unit were synthesized from 3,4-bis(4-aminophenyl)-2,5-diphenylthiophene and various aromatic tetracarboxylic dianhydrides by the conventional two-step procedure that included ring-opening polyaddition and subsequent cyclodehydration. Although the polyimides formed had low inherent viscosities,

they were characterized as organic-soluble polyimides with both high  $T_g$ s of 269—327°C and high thermal stability.

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