

## Synthesis and Characterization of Novel Polyarylates from 2,5-Bis(4-hydroxyphenyl)-3,4-diphenylthiophene and Various Aromatic Dicarboxylic Acids

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(Received October 19, 1993)

**ABSTRACT:** A new tetraphenylated heterocyclic diol, 2,5-bis(4-hydroxyphenyl)-3,4-diphenylthiophene, was synthesized in three steps starting from 4-methoxydeoxybenzoin. The tetraphenylthiophene-containing polyarylates having inherent viscosities of 0.29—0.84 dl g<sup>-1</sup> were prepared by the high temperature solution polycondensation of the diol with various aromatic dicarboxylic acid chlorides. All the polyarylates were crystalline or semicrystalline, and the crystalline polyarylates were quite insoluble in organic solvents, while the others dissolved readily in a variety of solvents including *N*-methyl-2-pyrrolidone and *sym*-tetrachloroethane. These polymers had glass transition temperatures in the range of 209—260°C, with no weight loss below 400°C in both air and nitrogen atmospheres.

**KEY WORDS** High Temperature Polyarylates / Tetraphenylthiophenediol / Solubility / Crystallinity / Thermal Behavior /

Polyarylates have been known for their usefulness in meeting the high performance requirements for various applications.<sup>1,2</sup> We already reported that the introduction of pendant phenyl groups through tetraphenylthiophene,<sup>3</sup> tetraphenylfuran,<sup>4</sup> and tetraphenylpyrrole units<sup>5</sup> into polyarylate backbones afforded organic-soluble polymers with high glass transition temperatures. The incorporation of these tetraphenylated heterocyclic moieties were also found to be highly effective to produce aromatic polyamides and polyimides with the above desirable properties.<sup>6-12</sup>

As part of an effort to develop organic-soluble high performance polyarylates with high glass transition temperatures, we have aimed at the synthesis of a new tetraphenylthiophene-containing diol monomer,

2,5-bis(4-hydroxyphenyl)-3,4-diphenylthiophene, as an alternative monomer to the polyarylate-forming diacid, 2,5-bis(4-carboxyphenyl)-3,4-diphenylthiophene.<sup>3</sup> This article deals with the synthesis of the tetraphenylthiophenediol as well as of new tetraphenylthiophene-containing polyarylates derived from various aromatic dicarboxylic acid chlorides. Their properties are also described, which are compared with those of the tetraphenylated heterocycle-containing polyarylates reported previously.<sup>3-5</sup>

### EXPERIMENTAL

#### *Materials*

Isophthaloyl chloride (**IVa**) and terephthaloyl chloride (**IVb**) were obtained commercially and distilled before use. 4,4'-Bibenzoyl chlo-

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ride (**IVc**), 2,6-naphthalenedicarbonyl chloride (**IVd**), 4,4'-oxybibenzoyl chloride (**IVe**), and 4,4'-sulfonyldibenzoyl chloride (**IVf**) were prepared by the reaction of the corresponding dicarboxylic acids with thionyl chloride and purified by distillation. All the solvents employed were purified by distillation before use.

#### Monomer Synthesis

*2,5-Bis(4-methoxyphenyl)-3,4-Diphenylthiophene (II)*. 1,2-Bis(4-methoxybenzoyl)-1,2-diphenylethane (**I**), composed of two isomers with high melting point (272–273°C) and low melting point (148–149°C), was prepared in 76% total yield by the oxidative coupling of 4-methoxydeoxybenzoin using sodium ethoxide and iodine according to the procedure reported previously.<sup>5</sup>

A mixture of 46.0 g (0.102 mol) of compound **I** with low melting point and 63.8 g (0.122 mol) of the Lawesson reagent, 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide, in 500 ml of dry toluene was heated with stirring at 110°C for 5 h. The reaction solution was evaporated to dryness under reduced pressure, and the solid residue was washed with acetic acid, followed by drying at 100°C under vacuum. Recrystallization from a mixture of methanol and acetone (1:1 by volume) gave white needles (**II**); mp 208–209°C. The yield was 29.3 g (64%). The IR spectrum (KBr) exhibited absorption bands at 2940–2820 cm<sup>-1</sup> (methoxy C–H). *Anal.* Calcd. for C<sub>30</sub>H<sub>24</sub>O<sub>2</sub>S: C, 80.33%; H, 5.39%; S, 7.15%. Found: C, 80.18%; H, 5.15%; S, 7.23%.

The reaction between compound **I** with high melting point and the Lawesson reagent under the similar conditions, followed by recrystallizations twice from a mixture of methanol and acetone, afforded the same product **II** in 32% yield.

*2,5-Bis(4-hydroxyphenyl)-3,4-Diphenylthiophene (III)*. A mixture of 30.0 g (0.067 mol) of compound **II** and 45 ml of 47% hydrobromic

acid in 500 ml of glacial acetic acid was heated with stirring at 120°C for 7 h under nitrogen. The reaction solution was poured into 2 l of water and the precipitate was collected. The product was washed thoroughly with water and dried at 100°C under vacuum. Recrystallizations twice from toluene afforded white needles (**III**); mp 236–237°C. The yield was 16.3 g (58%). The IR spectrum (KBr) showed an absorption band at 3300 cm<sup>-1</sup> (O–H). *Anal.* Calcd. for C<sub>28</sub>H<sub>20</sub>O<sub>2</sub>S: C, 79.97%; H, 4.79%; S, 7.63%. Found: C, 79.65%; H, 4.60%; S, 7.65%.

#### Polymerization

A typical example of the polycondensation is given below.

*Polymer Ve from III and IVe by High-Temperature Solution Method.* In a flask equipped with a stirrer, and gas inlet and outlet were placed 0.841 g (2.0 mmol) of **III**, 0.590 g (2.0 mmol) of **IVe**, and 10 ml of 1-chloronaphthalene. The mixture was heated with stirring at 150°C for 1 h, and the temperature was raised to 220°C. The solution was further stirred for 15 h at that temperature. The hydrogen chloride evolved by the polycondensation was swept away by passing a slow stream of nitrogen. The resulting polymer was isolated by pouring the reaction solution into 300 ml of methanol. The precipitated polymer was collected and dried at 100°C under vacuum, which weighed 1.23 g (96%). The inherent viscosity of the polymer was 0.67 dl g<sup>-1</sup> in *sym*-tetrachloroethane, measured at a concentration of 0.5 g dl<sup>-1</sup> at 30°C. The IR spectrum (film) showed an absorption band at 1750 cm<sup>-1</sup> (C=O). *Anal.* Calcd. for (C<sub>42</sub>H<sub>26</sub>O<sub>5</sub>S)<sub>n</sub>: C, 78.49%; H, 4.08%; S, 4.99%. Found: C, 78.71%; H, 3.79%; S, 4.89%.

#### Measurements

IR spectra were recorded on a Hitachi EP-G3 spectrophotometer. Differential thermal analysis (DTA), thermogravimetry (TG), and differential scanning calorimetry (DSC) were

performed with Shimadzu thermal analyzers DTA-40, TGA-40M, and DSC-41M, respectively, and the measurements were made in air or nitrogen at a flow rate of  $50 \text{ ml min}^{-1}$ . The wide angle X-ray diffraction patterns were recorded with a Rigaku Denki XG X-ray diffraction apparatus using nickel-filtered  $\text{Cu-K}_\alpha$  radiation (35 kV, 50 mA).

## RESULTS AND DISCUSSION

### Monomer Synthesis

A new heterocycle-containing bisphenol, 2,5-bis(4-hydroxyphenyl)-3,4-diphenylthiophene (**III**) was synthesized in three steps starting from 4-methoxydeoxybenzoin according to Scheme 1.

Recently the Lawesson reagent, 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide, was used as a highly efficient substitute for classical sulfurizing agent of phosphorus pentasulfide for the synthesis of thiophenes from 1,4-dicarbonyl compounds.<sup>13</sup> This reagent was successfully applied to the synthesis of 2,5-bis(4-methoxyphenyl)-3,4-diphenylthiophene (**II**) from 1,2-bis(4-methoxybenzoyl)-1,2-diphenylethane (**I**), prepared by the oxidative coupling of 4-methoxydeoxybenzoin. Although compound **I** has two isomers, high melting point and low melting point components, both isomers afforded the same thiophene compound **II** in moderate

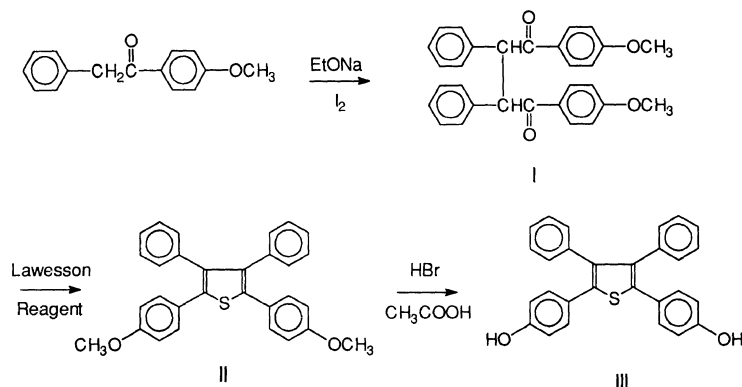
yields. The complete ring closure of compound **I** giving **II** was confirmed by the disappearance of the characteristic carbonyl band at  $1669\text{--}1667 \text{ cm}^{-1}$  in the IR spectrum, with retention of absorption bands due to methoxy group at  $2940\text{--}2820 \text{ cm}^{-1}$ .

In the second step, the demethylation of compound **II** was effectively achieved by using strong protic acid such as hydrobromic acid, giving compound **III** in reasonable yields. Compound **III** exhibited an absorption band based on O-H function at  $3300 \text{ cm}^{-1}$  in the IR spectrum, with the disappearance of the characteristic methoxy absorptions. The overall yield of the new bisphenol starting from compound **I** was approximately 35%.

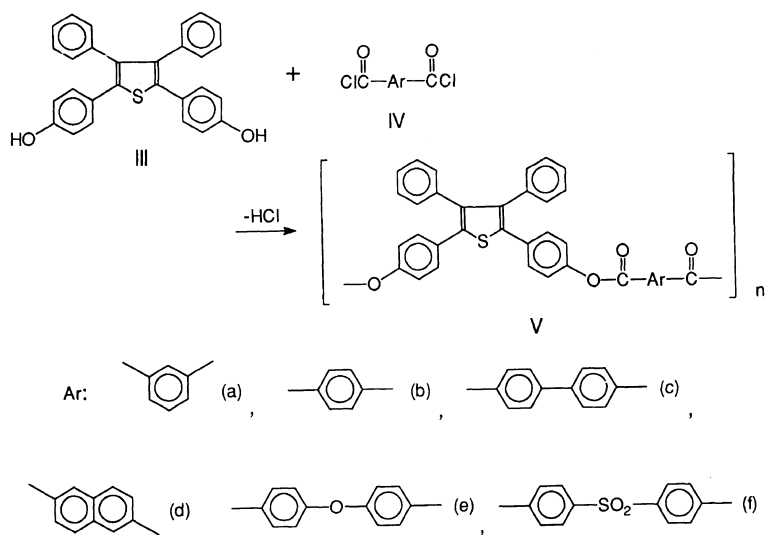
### Polymer Synthesis

Tetraphenylthiophene-containing polyarylates **V** were synthesized by the polycondensation of bisphenol **III** with various aromatic dicarboxylic acid chlorides **IVa**—**IVf**, as shown in Scheme 2, by high temperature solution method.<sup>4,5</sup>

To find suitable polymerization conditions for the preparation of high molecular weight polyarylate **Ve** from **III** and **IVe**, the reaction variables such as reaction medium and temperature were investigated. Table I summarizes the results of the polycondensation, where the reaction time was fixed to 15 h. The high temperature solution polycondensation



Scheme 1.



Scheme 2.

**Table I.** Synthesis of polyarylate **Ve** by high temperature solution method<sup>a</sup>

Reaction medium <sup>b</sup> ml	Reaction temperature °C	Polymer	
		Yield %	$\eta_{inh}^c$ dl g <sup>-1</sup>
CN (10)	220	96	0.67
TCB (10)	220	94	0.60
ODCB (10)	180	86	0.72
PDCB (10)	180	92	0.53
Tol (10)	110	88	0.44
CN (5)+Py (1.5)	220	92	0.42
TCB (5)+Py (1.5)	220	93	0.49
ODCB (5)+Py (1.5)	180	88	0.84
PDCB (5)+Py (1.5)	180	90	0.47

<sup>a</sup> Polymerization was carried out with 2.0 mmol of **III** and 2.0 mmol of **IVe** in the reaction medium for 12 h under nitrogen.

<sup>b</sup> CN, 1-chloronaphthalene; TCB, 1,2,4-trichlorobenzene; ODCB, *o*-dichlorobenzene; PDCB, *p*-dichlorobenzene, Tol, toluene; and Py, pyridine.

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

was carried out either in a high-boiling-point solvent alone, where the hydrogen chloride evolved during the reaction was swept away with a slow stream of nitrogen, or in the solvent

in the presence of pyridine which acts as a hydrogen chloride acceptor. In the case of the polycondensation in the solvent alone, higher reaction temperature around 200°C tended to afford the polyarylate having higher inherent viscosity, mostly regardless of the kind of solvent. Although a mixture of the solvent and pyridine also effected the polymerization giving the polyarylate with reasonable inherent viscosity, the *o*-dichlorobenzene and pyridine system at 180°C was the most effective one to produce the polymer with the highest inherent viscosity of 0.84 dl g<sup>-1</sup>, which was used in the further polymerizations.

A series of polyarylates were synthesized by the high temperature solution polycondensation of **III** with **IVa**–**IVf**, and the results are listed in Table II. In the case of the polycondensations with **IVa**–**IVd**, the precipitation of the polymers occurred during the reaction, and hence the inherent viscosities of the polyarylates **Va**–**Vd** could not be determined due to their insolubility in any organic solvents. Of course, the diacid chloride **IVf** yielded the polyarylate with inherent viscosity of 0.29 dl g<sup>-1</sup> by this method, in addition to polyarylate **Ve**.

**Table II.** Synthesis of various polyarylates by high temperature solution method<sup>a</sup>

Diacid chloride	Polymer			Remarks <sup>c</sup>
	Code	Yield	$\eta_{inh}^b$	
		%	dlg <sup>-1</sup>	
<b>IVa</b>	<b>Va</b>	89	—	P
<b>IVb</b>	<b>Vb</b>	93	—	P
<b>IVc</b>	<b>Vc</b>	93	—	P
<b>IVd</b>	<b>Vd</b>	90	—	P
<b>IVe</b>	<b>Ve</b>	88	0.84	S
<b>IVf</b>	<b>Vf</b>	86	0.29	S

<sup>a</sup> Polymerization was carried out with 2.0mmol of **III** and 2.0mmol of the diacid chloride in 5ml of *o*-dichlorobenzene and 1.5ml of pyridine at 180°C for 15h under nitrogen.

<sup>b</sup> Measured at a concentration of 0.5gdl<sup>-1</sup> in *sym*-tetrachloroethane at 30°C.

<sup>c</sup> Appearance of the polymerization mixture: P, precipitation of the polymer occurred during the reaction; S, homogeneous solution throughout the reaction.

These polymers were characterized by means of IR spectroscopy. The IR spectra of all the polymers exhibited a characteristic ester absorption band at 1750–1740 cm<sup>-1</sup>. The elemental analysis values of the polymers agreed quite well with the calculated values for the proposed polyarylates.

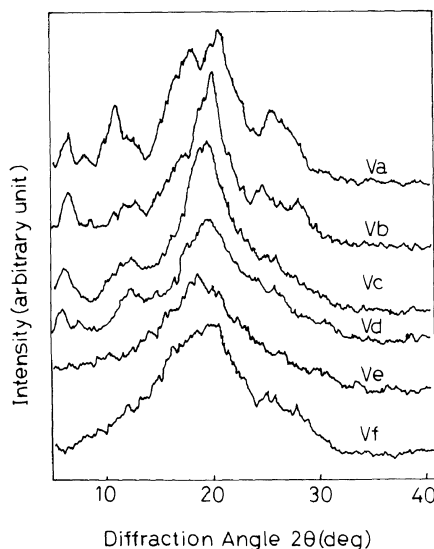
#### Polymer Properties

The solubility behavior of the tetraphenylthiophene-containing polyarylates were tested qualitatively, and the results are summarized in Table III. The polyarylates **Va**–**Vd** composed of rigid aromatic moieties were quite insoluble in any organic solvents, whereas the polymers **Ve** and **Vf** having flexible ether and sulfone connecting groups in the polymer backbones dissolved readily in a variety of organic solvents such as *N*-methyl-2-pyrrolidone (NMP), *o*-chlorophenol, *m*-cresol, *sym*-tetrachloroethane, pyridine, and 1,4-dioxane. Polyarylate **Ve** only gave a transparent and flexible film by casting from the NMP solution. The solubility behavior of

**Table III.** Solubility of polyarylates<sup>a</sup>

Solvent	Polymer			
	<b>Va, Vb, Vc, Vd</b>	<b>Ve</b>	<b>Vf</b>	
<i>N</i> -Methyl-2-pyrrolidone	—	++	++	
<i>o</i> -Chlorophenol	—	++	++	
<i>m</i> -Cresol	—	+	+	
<i>sym</i> -Tetrachloroethane	—	++	++	
Pyridine	—	+	++	
1,4-Dioxane	—	+	+	
Dimethyl sulfoxide	—	—	—	
Acetone	—	—	—	
Methano	—	—	—	

<sup>a</sup> Solubility: ++, soluble at room temperature; +, soluble on heating; —, insoluble.

**Figure 1.** X-Ray diffraction diagrams of various polyarylates.

the tetraphenylthiophene-containing polyarylates markedly differed from that of the structurally related tetraphenylfuran- and tetraphenylpyrrole-based polyarylates,<sup>4,5</sup> most of which were soluble easily in the above solvents.

Figure 1 shows the wide angle X-ray diffraction diagrams of the polyarylates. Polyarylates **Va**–**Vd** had several diffraction peaks, indicative of crystallinity, whereas polymers

**Table IV.** Thermal properties of polyarylates

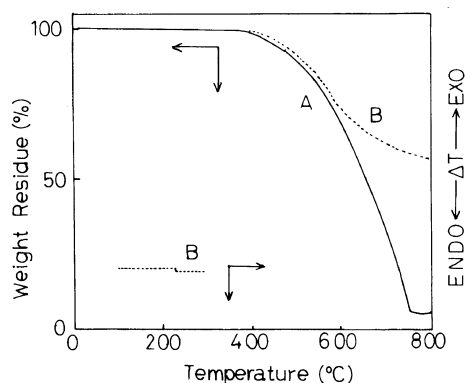
Polymer	$T_g^a$ °C	Decomposition temperature <sup>b</sup>		Char yield <sup>c</sup>	
		°C		%	
		In air	In nitrogen	In air	In nitrogen
<b>Va</b>	229	505	515	5	58
<b>Vb</b>	239	475	510	11	53
<b>Vc</b>	— <sup>d</sup>	480	515	6	56
<b>Vd</b>	— <sup>d</sup>	475	515	7	53
<b>Ve</b>	209	500	515	15	56
<b>Vf</b>	260	510	520	20	58

<sup>a</sup> By DSC at a heating rate of 20°C min<sup>-1</sup> in nitrogen.

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

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

<sup>d</sup>  $T_g$  could not be detected.



**Figure 2.** DTA and TG curves for polyarylate **Va** in air (A) and in nitrogen (B).

**Ve** and **Vf** had similar diffraction patterns with a broad peak at around 20° in  $2\theta$ , suggesting that they were semicrystalline. The crystalline nature of polymers **Va**—**Vd** was probably reflected in the insolubility of these polymers. In addition, the crystalline nature of the tetraphenylthiophene-containing polyarylates was quite different from the semicrystalline behavior of the tetraphenylfuran- and tetraphenylpyrrole-based polyarylates.<sup>4,5</sup>

The thermal behavior of the polyarylates was evaluated by means of DTA, TG, and DSC. Figure 2 exhibits the DTA and TG curves for typical polyarylate **Va**, and the thermal

properties of all the polyarylates are summarized in Table III. The glass transition temperatures ( $T_g$ ) of the polyarylates except for **Vc** and **Vd** were in the range of 209—260°C. All the polymers did not lose weight below 400°C in both air and nitrogen atmospheres, and their 10% weight losses were recorded at 475—510°C and 510—520°C in air and nitrogen, respectively, with 53—58% char yields at 800°C in nitrogen. In the present polyarylates, polymer **Vf** having polar sulfone connecting group had high  $T_g$  value than the other polyarylates. No appreciable difference in the thermal stability with respect to decomposition temperature and char yield was observed for the polyarylates with different compositions.

The present tetraphenylthiophene-containing polyarylates had a little higher  $T_g$  values and decomposition temperatures than the structurally related tetraphenylfuran-based polyarylates,<sup>4</sup> and were almost comparable to the tetraphenylpyrrole-derived polyarylates with respect to these thermal behavior.<sup>5</sup> The difference in thermal stability is probably due to inherent stability between these three five-membered heterocyclic rings as discussed elsewhere.<sup>14</sup>

## CONCLUSIONS

A new heterocyclic diol, 2,5-bis(4-hydroxyphenyl)-3,4-diphenylthiophene, was synthesized readily by the oxidative coupling of 4-methoxydeoxybenzoin giving 1,2-bis(4-methoxybenzoyl)-1,2-diphenylethane, followed by thiophene ring formation and demethylation. The tetraphenylthiophenediol was subjected to the polycondensation with various aromatic diacid chlorides, producing the polyarylates having relatively high  $T_g$  values and good thermal stability.

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