

## Synthesis of Poly(benzothiazole)s by Direct Polycondensation of Dicarboxylic Acids with 2,5-Diamino-1,4-benzenedithiol Dihydrochloride Using Phosphorus Pentoxide/Methanesulfonic Acid as Condensing Agent and Solvent

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**ABSTRACT:** A convenient method for the synthesis of poly(benzothiazole)s of high molecular weights has been developed. These polymers were prepared readily by direct polycondensation of aliphatic, alicyclic, and aromatic dicarboxylic acids containing phenyl ether structures with 2,5-diamino-1,4-benzenedithiol dihydrochloride using phosphorus pentoxide/methanesulfonic acid (PPMA) as both a condensing agent and solvent. Polycondensations proceeded smoothly and were completed within several hours at 140°C to produce poly(benzothiazole)s with inherent viscosities up to 2.9 dl g<sup>-1</sup>. The thermogravimetry of the aromatic poly(benzothiazole)s showed 10% weight loss in air and nitrogen at 405—490°C and 450—595°C, respectively.

**KEY WORDS** Poly(benzothiazole)/ Direct Polycondensation / Phosphorus Pentoxide—Methanesulfonic Acid / Condensing Agent / Thermal Behavior /

Since the utilization of liquid crystalline solutions of poly(*p*-benzamide) has produced highly ordered fibers of extremely high tensile modulus and strength, the synthesis of aromatic heterocyclic polymers has become of interest again in recent years. The poly(*p*-phenylenebenzobisthiazole) fibers, as spun and heat treated, exhibit both a high specific modulus and a high strength.<sup>1,2</sup>

A number of synthetic routes for producing poly(benzothiazole) (PBT) has been developed and reviewed.<sup>3</sup> These include the condensation of bis(*o*-aminobenzenethiol) with dicarboxylic acids and their derivatives, and the nucleophilic substitution of bis(2-substituted benzothiazole) with diphenolates or diamines. In the former reaction, polyphosphoric acid (PPA) has been widely employed as both a condensing agent and solvent.

A number of routes to the PBT stated above are available, but alternative procedures are

always of interest. A series of our studies on the synthesis of condensation polymers by direct procedure in phosphorus pentoxide/methanesulfonic acid (PPMA) in a weight ratio of 1:10 have revealed that PPMA is a suitable condensing agent and solvent for the preparation of poly(ketone)s,<sup>4</sup> poly(ether-sulfone),<sup>5</sup> and poly(benzimidazole)s.<sup>6</sup>

In order to demonstrate the versatility of this method, it was applied to the synthesis of poly(benzothiazole)s. We now report a successful synthesis of poly(benzothiazole)s by direct polycondensation of various dicarboxylic acids with 2,5-diamino-1,4-benzenedithiol in PPMA.

### EXPERIMENTAL

#### *Materials*

The reagent PPMA was prepared according to the reported procedure.<sup>7</sup> Reagent grade

substituted benzoic acids (**2**), sebacic acid (**5a**), *trans*-1,4-cyclohexanedicarboxylic acid (**5b**), and *o*-aminobenzenethiol (**1**) were used as received.

2,5-Diamino-1,4-benzenedithiol dihydrochloride (**4**) was prepared from *p*-phenylenediamine in the three steps by the reported procedure.<sup>1</sup>

4,4'-Oxybisbenzoic acid (**5c**), 3,3'-(*p*-phenylenedioxy)dibenzoic acid (**5d**), and 4,4'-(*p*-phenylenedioxy)dibenzoic acid (**5e**) were prepared through oxidation of the corresponding dimethyl compounds with potassium permanganate in pyridine-water. These dicarboxylic acids were purified by recrystallization. (**5c**): mp 337°C (by DTA) (lit.<sup>8</sup> 331–333°C from acetic acid), (**5d**): mp 312°C (by DTA) (lit.<sup>9</sup> 305–313°C, from acetic acid), and (**5e**): mp 333°C (by DTA) (lit.<sup>9</sup> 331–333°C, from dioxane).

#### Model Reaction

Typical examples are as follows:

**2-Substituted Benzothiazole (3): General Procedure.** A mixture of *o*-aminobenzenethiol **1** (2.5 mmol) and the carboxylic acid **2** (2.5 mmol) in the reagent PPMA (6 ml) was stirred at 100°C for 1 h. The solution was poured into water (300 ml), and neutralized with sodium carbonate. The product was filtered, washed with water, and dried. The products were vitually pure (IR, <sup>1</sup>H NMR spectra and TLC with ethyl acetate, or *n*-hexane-ethyl acetate, 1:1).

**2,2'-(trans-1,4-Cyclohexylene)dibenzothiazole (7b)** was prepared from **5b** was prepared from **5b** and **1** in a mole ratio of 1:2 as described above. The yield was 99%. It was recrystallized from dioxane to give pale yellow crystals, mp 181–182°C. *Anal.* Calcd for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>S<sub>2</sub>: C, 68.54%; H, 5.18%; N, 7.99%. Found: C, 68.4%; H, 5.5%; N, 7.9%.

**2,6-Dicyclohexylbenzo[1,2-d:4,5-d']-bisthiazole (6b).** 2,5-Diamino-1,4-benzenedithiol dihydrochloride **4** (0.245 g, 1.0 mmol) was stirred with PPMA (5 ml) at room tem-

perature under nitrogen until the dehydrochlorination was complete (30 min). Then cyclohexanecarboxylic acid (0.256 g, 2 mmol) was added to this solution. The mixture was stirred for 2 h at 100°C and worked up as described above. The yield was 91%. Recrystallization from dioxane gave pale yellow crystals, mp 247–248°C. *Anal.* Calcd for C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>S<sub>2</sub>: C, 67.37%; H, 6.78%; N, 7.85%. Found: C, 67.4%; H, 6.8%; N, 7.9%.

#### Polymer Synthesis

Two typical examples of the polymerization are as follows.

**Polymer (8b) from 5b and 4.** **4** (0.245 g, 1.0 mmol) was stirred in PPMA (5 ml) for 1 h at room temperature under nitrogen to effect dehydrochlorination. Then, **5b** (0.172 g, 1.0 mmol) was added to this solution. The mixture was stirred for 3 h at 140°C. An extremely viscous solution resulted and was diluted with methanesulfonic acid. This hot polymer solution was poured into an aqueous sodium hydroxide solution. The fibrous polymer was collected, washed with hot water, and refluxed in water for 2 h. The polymer was dried *in vacuo* at 100°C for 2 d. The yield was essentially quantitative. The inherent viscosity of the polymer in concentrated sulfuric acid was 1.4 dl g<sup>-1</sup>, measured at a concentration of 0.2 g dl<sup>-1</sup> at 30°C. *Anal.* Calcd for (C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>S<sub>2</sub>·H<sub>2</sub>O)<sub>n</sub>: C, 57.9%; H, 4.85%, N, 9.64%. Found: C, 57.8%; H, 5.1%; N, 9.7%.

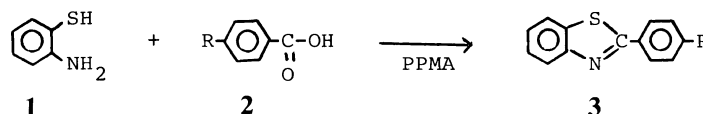
**Polymer (8c) from 5c and 4.** Polymer **8c** was prepared from **5c** and **4** at 140°C for 8 h as described above. The polymer was obtained in nearly quantitative yield and had an inherent viscosity of 1.1 dl g<sup>-1</sup> in concentrated sulfuric acid (0.2 g dl<sup>-1</sup> at 30°C). *Anal.* Calcd for (C<sub>20</sub>H<sub>10</sub>N<sub>2</sub>OS<sub>2</sub>·H<sub>2</sub>O)<sub>n</sub>: C, 69.70%; H, 3.51%; N, 8.13%. Found: C, 69.8%; H, 4.6%; N, 8.2%.

## RESULTS AND DISCUSSION

## Model Reaction

2-Substituted benzothiazoles (**3**) have been prepared directly from *o*-aminobenzenethiol (**1**) and carboxylic acids by treatment with PPMA at room temperature for 1 h and warming about 70–90°C for 10 h.<sup>10</sup> In the present study, the reactions of **1** and aromatic car-

boxylic acids (**2**) in PPMA were studied to determine if the method gave the desired model compounds in quantitative yields to constitute a polymer-forming reaction. The reaction was carried out by dissolving equimolar amounts of **1** and **2** in PPMA at 100°C. After the reaction was complete, the solution was poured into water, and the crude product was filtered.



The results are summarized in Table I. The condensation proceeded rapidly and gave **3** quantitatively in 1 h. In the synthesis of benzimidazoles from *o*-phenylenediamine and carboxylic acids, the reactivity of substituted benzoic acid increased with electron-donating groups and decreased with electron-withdrawing ones. But, such differences in the reactivity between substituted benzoic acids were not observed in the formation of benzothiazoles.

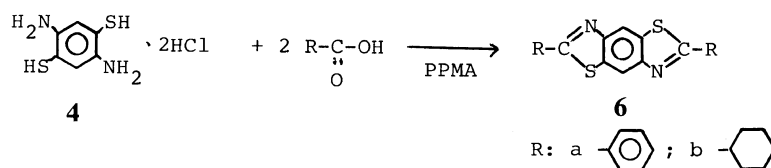
Next, a bifunctional model compound was studied by reactions of 2,5-diamino-1,4-benzenedithiol (**4**) with benzoic acid or cyclohexanecarboxylic acid. The reactions gave the model compounds, 2,6-disubstituted benzo-

Table I. Preparation of 2-substituted benzothiazoles<sup>a</sup>

No	Acid (RCOOH)	Reaction time/h	Product	
			No	Yield/%
<b>2a</b>	C <sub>6</sub> H <sub>5</sub> -	0.5	<b>3a</b>	93
<b>2a</b>	C <sub>6</sub> H <sub>5</sub> -	1	<b>3a</b>	95
<b>2b</b>	4-Cl-C <sub>6</sub> H <sub>4</sub> -	1	<b>3b</b>	94
<b>2c</b>	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -	1	<b>3c</b>	97
<b>2d</b>	4-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -	1	<b>3d</b>	95

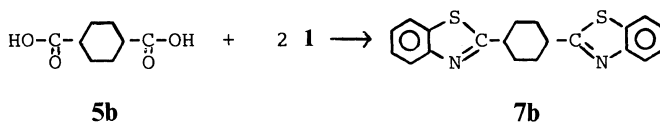
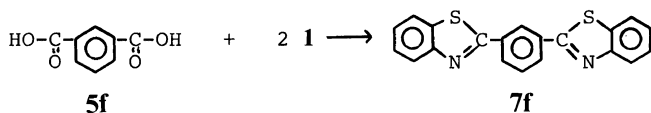
<sup>a</sup> The reaction was carried out with 2.5 mmol of each reactant in 6 ml of PPMA at 100°C.

[1,2-*d*: 4,5-*d'*]bisthiazole (**6a**), (**6b**) in excellent yields.



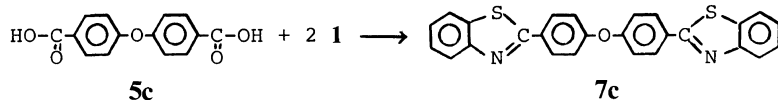
The reaction of **1** with isophthalic acid (**5f**) or *trans*-1,4-cyclohexanedicarboxylic acid (**5b**) was also carried out at 100°C in PPMA. The latter reaction afforded the model compound, 2,2'-(1,4-cyclohexylene)dibenzothiazole (**7b**), in quantitative yield in 2 h. However, the reaction of **5f** took place fairly slowly compared

with that of **5b** and required prolonged reaction time for completion.

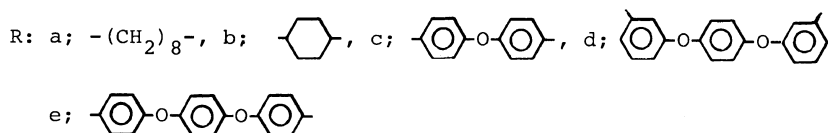
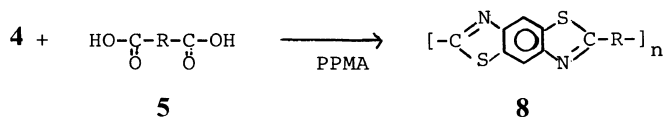


In contrast to the low reactivity of **5f**, the reaction of *p*-nitrobenzoic acid (**2d**) with **1** proceeded rapidly as described before. Although the difference in the reactivity of **2d** and **5f** both of which have groups electron-withdrawing from the carboxyl group is not understood clearly, the reaction intermediates are presumed to be acylium ions. Therefore, in

the same way as in the formation of polybenzimidazoles, 4,4'-oxybisbenzoic acid (**5c**) was chosen as an aromatic dicarboxylic acid. The condensation of **5c** with **1** proceeded rapidly, to give the desired product, bis[4-(2-benzothiazolyl)phenyl] ether (**7c**), in quantitative yield. These results are summarized in Table II.



### Polymer Synthesis



To determine the optimum conditions for the polycondensations, the initial polymer synthesis was conducted by the polycondensation of **4** with **5c** using 1 mmol of each monomer under nitrogen. Table III lists the effects of amount of PPMA on the polycondensation. Five ml of PPMA was found to be appropriate for the reaction on a 1.0 mmol scale. These data agree with the general observation in solution polycondensation. A higher concentration makes the solution difficult to stir and a lower concentration reduces the rate of polycondensation. The effects of the reaction temperature on the inherent viscosity of

the resulting polymer were examined over a temperature range 100–140°C. Since cyclization was incomplete at a temperature lower than 100°C and methanesulfonic acid began to decompose at over 150°C. The inherent viscosity increased with increasing temperature and the polycondensation resulted in an inherent viscosity up to 0.92 dl g<sup>-1</sup> in 5 h (Table IV).

On the basis of these studies, the direct polycondensation of various dicarboxylic acids **5** with **4** was carried out in PPMA for several hours at 140°C. The results are summarized in Table V. The polycondensations

## Synthesis of Poly(benzothiazole)s

**Table II.** Preparation of bis(benzothiazole)s<sup>a</sup>

Bis(benzothiazole)	Reaction time/h	Yield/%
<b>6a</b>	0.5	94
<b>6b</b>	2	91
<b>7f</b>	24	98
<b>7b</b>	2	99
<b>7c</b>	2	99

<sup>a</sup> The reaction was carried out with 1 mmol of monomer in 5 ml of PPMA at 100°C.

**Table III.** Effects of the amount of PPMA on polycondensation<sup>a</sup>

Amount of PPMA/ml	Polymer
	$\eta_{inh}/dl\ g^{-1\ b}$
3	0.82
5	0.92
7	0.82
9	0.40

<sup>a</sup> Polycondensation was carried out with 1 mmol of each monomer at 140°C for 5 h.

<sup>b</sup> Measured at a concentration of 0.2 g dl<sup>-1</sup> in concentrated sulfuric acid at 30°C.

**Table IV.** Effects of reaction temperature on polycondensation

Reaction temperature/°C	Polymer
	$\eta_{inh}/dl\ g^{-1}$
100	0.57
120	0.67
140	0.92

<sup>a</sup> Polycondensation was carried out with 1 mmol of each monomer in 5 ml of PPMA for 5 h.

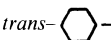
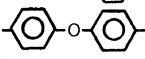
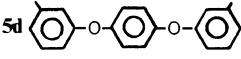
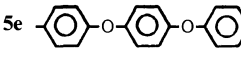
<sup>b</sup> Measured at a concentration of 0.2 g dl<sup>-1</sup> in concentrated sulfuric acid at 30°C.

proceeded in homogeneous solutions and gave quantitative yields of poly(benzothiazole)s (**8**) with high molecular weights.

#### Polymer Characterization

The polymers were defined as poly(benzothiazole)s by comparing their IR spectra with those of model compounds. The IR spectra

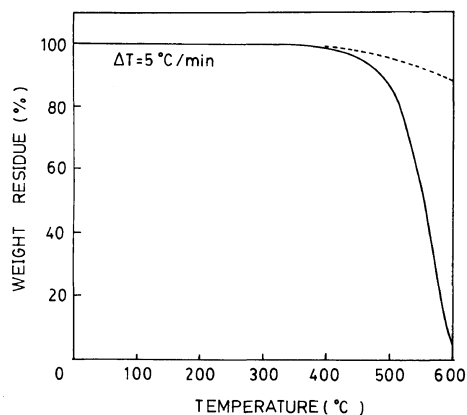
**Table V.** Preparation of poly(benzothiazole)s **8**<sup>a</sup>

No.	Dicarboxylic acid HOOC-R-COOH	Time/h	Polymer	
			No.	$\eta_{inh}/dl\ g^{-1\ b}$
<b>5a</b>	-(CH <sub>2</sub> ) <sub>8</sub> -	5	<b>8a</b>	1.5
<b>5b</b>	<i>trans</i> - 	3	<b>8b</b>	1.4
<b>5c</b>		8	<b>8c</b>	1.1
<b>5d</b>		1.3	<b>8d</b>	2.0 <sup>c</sup>
<b>5e</b>		0.5	<b>8e</b>	2.9 <sup>c</sup>

<sup>a</sup> Polycondensation was carried out with 1 mmol of each monomer in 5 ml of PPMA at 140°C.

<sup>b</sup> Measured at a concentration of 0.2 g dl<sup>-1</sup> in concentrated sulfuric acid.

<sup>c</sup> Measured at a concentration of 0.2 g dl<sup>-1</sup> in methanesulfonic acid.



**Figure 1.** TG curves of poly(benzothiazole) **8c**. (---), in nitrogen; (—), in air.

showed characteristic absorptions at around 1600 and 810 cm<sup>-1</sup> due to C=N stretching and benzothiazole rings. Elemental analyses also supported the formation of the expected polymers.

The polymers were brown solids and soluble only in strong acids, such as sulfuric acid and methanesulfonic acid, swelled in *m*-cresol.

The thermal stability of polymer **8** was examined by thermogravimetry (TG). The sample was cured for 0.5 h at 250°C in nitrogen and subsequently subjected to TG. A typical

**Table VI.** Thermal stability of poly(benzothiazole)s **8**

Polymer	Decomposition temperature/°C <sup>a</sup>	
	In air	In nitrogen
<b>8a</b>	355	395
<b>8b</b>	430	510
<b>8c</b>	490	595
<b>8d</b>	405	455
<b>8e</b>	410	450

<sup>a</sup> Temperature at which a 10% weight loss was recorded by TG at a heating rate of 5°C min<sup>-1</sup>.

trace for **8c** is shown in Figure 1. The polymer showed a 10% weight loss at 490°C in air and at 595°C in nitrogen. The TG data are listed in Table VI. These data reveal that the introduction of ether units into the main chain results in a decrease in thermooxidative stability of aromatic poly(benzothiazole)s such as the polymer derived from **4** and terephthalic acid.

In summary, we showed that poly(benzothiazole)s with high molecular weights are readily prepared by the direct polycondensation of **4** with **5** in PPMA as both a condensing agent and solvent. This method is advantageous for the formation of **8** on account of its rapidity and simplicity and milder reaction conditions compared to conventional

methods. The main disadvantage of this method is that typical dicarboxylic acids, such as isophthalic acid and terephthalic acid, cannot be used.

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