

## Regioregular Poly(*p*-alkoxyphenylene)s Prepared from Facile Solid-state Oxidative Coupling Polymerization

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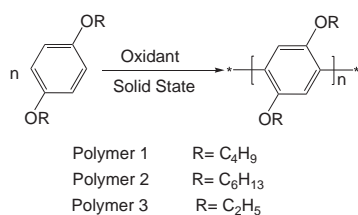
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By grinding 1,4-dialkoxybenzene with anhydrous FeCl<sub>3</sub> powder using a glass pestle in a mortar at ambient and solvent-free condition, poly(*p*-phenylene)s (PPP) was obtained in high yield up to 90% in 30 min. The products were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, WAXD, and UV-vis and the regioregular structure was suggested. The solid-state oxidative coupling polymerization is a facile, time saving, "green-chemistry" method.

Poly(*p*-phenylene) (PPP) is a conjugated polymer and has been regarded as a candidate for high performance materials used in sensor, battery technologies, organic transistors, and organic light emitting devices (OLED).<sup>1,2</sup> Many researchers have attempted various chemical reactions to obtain all-para linked PPP with high molecular weight, such as the Wurtz-Fittg reaction of dichlorobenzene,<sup>3</sup> dehydrogenation of polycyclohexylenes<sup>4</sup> cycloaddition reactions,<sup>5</sup> and oxidative coupling reaction.<sup>6</sup> Among all the synthesis methods, oxidative coupling polymerization is a facile method for preparing PPPs, unfortunately, only region-irregular polymers consisted of both 1,4-(para-) and 1,2-(ortho-) units were obtained, except oxovanadium-catalyzed one.<sup>10</sup> Oxidative coupling polymerization was developed from a classic organic reaction named Scholl reaction<sup>1,6</sup> and involves the coupling of aromatic nuclei by an oxidative process. Because the conjugated aromatic polymers are hardly soluble, it is necessary to introduce flexible side chain on the aromatic rings in order to increase the solubility of PPPs.<sup>7</sup> For example, Mukai et al.<sup>8</sup> prepared poly(2,5-dimethoxy-1,4-phenylene) in nitrobenzene; Ueda et al.<sup>9,10</sup> synthesized poly(2,5-di-*n*-butoxyphenylene) with equal fractions of 1,4- and 1,3-linkage in nitrobenzene, and this facile synthesis gave regiorandom products. To solve the region-selective problem, solid-state reaction may be a good method. Since molecules in a crystal are arranged tightly and regularly, the product may be regioregular.<sup>11</sup>

Here we report a novel solid-state oxidative coupling polymerization to prepare the poly(dialkoxyphenylene)s and we have found that the method is facile and region-selective. The reaction is shown in Scheme 1 and the synthesis procedure is illustrated by the polymerization of 2,5-di-*n*-butoxy-1,4-phenylene



**Scheme 1.** Solid-state oxidative coupling polymerization of dialkoxybenzenes.

as an example: 0.61 g (3 mmol) of 1,4-di-*n*-butoxybenzene and 1.50 g (9 mmol) of anhydrous FeCl<sub>3</sub> powder were added into a mortar. After grinding for 20 to 30 min with a glass pestle, the mixture was put into ethanol (100 mL) containing 5% hydrochloric acid and then stirred for 5 min. The precipitated polymer was collected by filtration, washed with ethanol until the solution looked colorless, and dried in oven at 50 °C. Then the polymer was extracted with alcohol by Soxhlet extractor for 24 h and dried overnight in oven at 50 °C. The final product was 0.51 g of light brown solid and the yield was 83%. This polymer can dissolve in a wide range of organic solvents, such as THF and CHCl<sub>3</sub>.

For comparison, the polymer was also prepared by oxidative coupling polymerization in solution according to the procedure of previous reports.<sup>9,12</sup>

We have found that grinding the monomer with anhydrous FeCl<sub>3</sub> powder using a glass pestle in a mortar produced poly(*p*-phenylene)s with high yield. The effects of the different kinds of oxidants on the polymerization of 1,4-di-*n*-butoxybenzene are showed in Table 1.

It can be seen that anhydrous FeCl<sub>3</sub> gave a yield of 72% at room temperature (Entries 3 and 4) while FeCl<sub>3</sub>·6H<sub>2</sub>O had a poor yield at room temperature (Entry 2), but a yield of 50% when the system was put in the oven (50 °C) for 5 h after grinding (Entry 1). The result indicates that polymerization was initiated by grinding, which generated cation-radicals mechanically, and was accelerated at 50 °C and FeCl<sub>3</sub> was a better oxidant than FeCl<sub>3</sub>·6H<sub>2</sub>O. CuCl<sub>2</sub> and mixed rare earth chlorides did not give good yields even at higher temperature (Entries 5 and 6). The results showed that the anhydrous FeCl<sub>3</sub> was the proper one among the all oxidants used and ambient was the best reaction condition among these reactions. In addition, the solid-state polymerization offered high yields with theoretical amount of oxidant and without gel formation. The yield of 72, 65, and 57% were obtained for DBB, DHB, and DEB, respectively (Table 2, Entries 2, 5, and 7). When the amount of FeCl<sub>3</sub> was increased, the yields increased too, especially a yield of 90% was obtained for DHB with 3 molecular equivalents FeCl<sub>3</sub> (Entry 6).

**Table 1.** Effects of different oxidants on polymerization of 1,4-dibutoxybenzene

Entry	Oxidant <sup>a</sup>	Time/h	Condition <sup>b</sup>	Yield/%
1	FeCl <sub>3</sub> ·6H <sub>2</sub> O	1	50 °C	50
2	FeCl <sub>3</sub> ·6H <sub>2</sub> O	1	rt	little
3	FeCl <sub>3</sub>	0.5	rt	72
4	FeCl <sub>3</sub>	1	IR.	72
5	CuCl <sub>2</sub>	0.5	50 °C	little
6	ReCl <sub>3</sub>	0.5	50 °C	trace

<sup>a</sup>The molecular ratio to the monomer was 2:1. <sup>b</sup>RT: room temperature; IR.: under infra red lamp.

**Table 2.** Effect of amount of FeCl<sub>3</sub> on polymerization

Entry <sup>a</sup>	FeCl <sub>3</sub> amount <sup>b</sup>	Monom. <sup>c</sup>	Yield/%
1	0.5	DBB	10
2	2	DBB	72
3	3	DBB	83
4	4	DBB	83
5	2	DHB	65
6	3	DHB	90
7	2	DEB	57
8	3	DEB	58

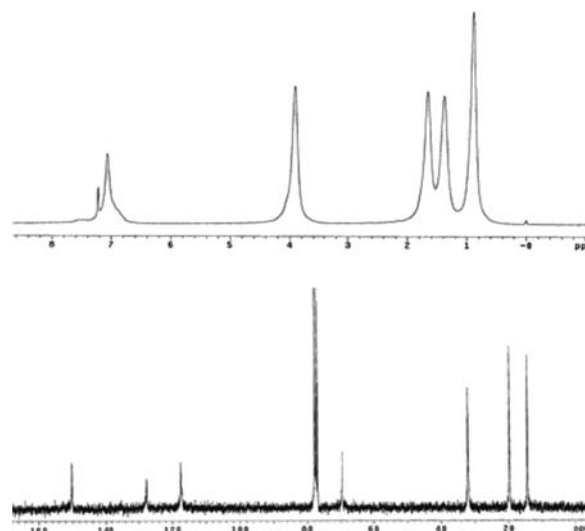
<sup>a</sup>Polymerized at ambient conditions for 30 min. <sup>b</sup>FeCl<sub>3</sub> amount refer to the molecular equivalent based on the monomer. <sup>c</sup>DBB: 1,4-dibutoxybenzene; DHB: 1,4-di(hexyloxy)-benzene; DEB: 1,4-diethoxybenzene.

There are several advantages using solid-state polymerization as compared with solution-state one. Firstly, the polymers with high molecular weight could be prepared by the solid-state polymerization. Polymer 1 had a molecular weight of *M<sub>n</sub>* 14000, *M<sub>w</sub>* 58000 and the inherent viscosity values of the polymers were ca. 0.5 dL·g<sup>-1</sup>. Secondly, the solid-state polymerization is easier to handle. The solution polymerization required strict anhydrous procedures and vacuum distilled anhydrous FeCl<sub>3</sub><sup>9,12</sup> but in the solid-state reactions the anhydrous FeCl<sub>3</sub> was used directly from purchased chemicals without further purification, the all procedures processed at ambient condition. Especially, the solid-state polymerization is region-selective, which was deduced by 300 MHz <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. The 300 MHz <sup>1</sup>H NMR spectrum of polymer 1 (Figure 1) exhibits five defined signals at 0.89, 1.38, 1.66, 3.92, and 7.07 ppm, ascribed to the methyl,  $\gamma$ -methylene,  $\beta$ -methylene, and  $\alpha$ -methylene protons of the butoxy group and aromatic protons. The absence of the signals at 4.1, 7.5, and 7.6 ppm, resulted from the 1,3-linkage, confirms the 1,4-linkage.<sup>9</sup> The para-structure of the poly(*p*-phenylene) was also suggested by the 300 MHz <sup>13</sup>C NMR spectroscopy (Figure 1): Polymer 1 shows absorptions at 117.5, 127.5, and 150.0 ppm. No signal at 153 ppm in the aromatic region is found, which is regarded as the evidence of the 1,3-linkage and observed by 125 MHz NMR.<sup>9,10</sup> These evidences suggested that the coupling took place selectively at the 1,4-position on the benzene moieties and gave region-controlled polymer.

The regioregularity was also observed in polymer 2 and polymer 3 prepared from the solid-state oxidative coupling polymerization.

The wide-angle X-ray scattering curve of the polymer 1 produced by the solid-state oxidative coupling reaction shows crystal structure. The curve of the polymer 1 shows several peaks at 6.6, 10.1, 13.2, 19.9, and 22.2 deg, which is close to the  $\beta$ -structure of crystalline hexaphenyl.<sup>13</sup> But the polymer obtained by solution-state reaction is entirely non-crystalline. It is reasonable that structurally regular macromolecules are easy to crystallize.

In conclusion, solid-state oxidative coupling polymerization



**Figure 1.** <sup>1</sup>H NMR (upper) and <sup>13</sup>C NMR spectrum (bottom) of Polymer 1 in CDCl<sub>3</sub>.

of 1,4-dialkoxybenzenes is facile, efficient, and anhydrous FeCl<sub>3</sub> is the best oxidant and ambient is the proper condition. The solid-state reaction resulted in all para-linked PPPs with high yield and high molecular weight.

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