

## Catalyst-Transfer Polycondensation for the Synthesis of Poly(*p*-phenylene) with Controlled Molecular Weight and Low Polydispersity

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Conductive polymers are an attractive class of materials owing to their potential applications to organic electronic materials and devices such as organic thin-film transistors (TFTs).<sup>1</sup> These polymers have generally been synthesized by polycondensation with metal catalysts<sup>2</sup> and therefore possess uncontrolled molecular weight and a broad molecular weight distribution.<sup>3</sup>

We and McCullough, however, have recently independently reported that the polycondensation of a Grignard thiophene monomer (2-bromo-5-chloromagnesio-3-hexylthiophene) with Ni-(dppp)Cl<sub>2</sub> (dppp = 1,3-bis(diphenylphosphino)propane) as a catalyst<sup>4</sup> proceeds via a chain-growth polymerization mechanism to yield head-to-tail poly(3-hexylthiophene)s with narrow polydispersity and that the molecular weight is controlled by the feed ratio of the monomer to the Ni catalyst.<sup>5</sup> This chain-growth polymerization is based on a specific reactivity of the Ni catalyst, which is transferred to the elongated polymer propagating end without diffusion after the coupling reaction.<sup>6</sup> Therefore, we call this type of polymerization *catalyst-transfer polycondensation*.<sup>7</sup> It is important to clarify whether this polymerization is specific to polythiophene or whether it is generally applicable for the synthesis of well-defined conjugated polymers. If other conjugated polymers could also be synthesized in a chain-growth polymerization manner, block copolymers consisting of different kinds of conjugated polymers should be easily obtainable. In particular, block copolymers of electron-donor conjugated polymers and electron-acceptor ones would be intriguing as a potential new class of light-emitting diodes.<sup>8</sup> Therefore, we decided to investigate the synthesis of poly(*p*-phenylene) (PPP),<sup>9</sup> to see whether a monomer containing no heteroatom in the aromatic ring undergoes catalyst-transfer polycondensation. Well-defined PPP with low polydispersity has not previously been obtained, and only model reactions, indicating the possibility of chain-growth polymerization based on Suzuki coupling reaction, have been reported.<sup>10</sup> In this Communication, we demonstrate that the Ni-catalyzed polycondensation of 1-bromo-4-chloromagnesio-2,5-dihexyloxybenzene (**1**) proceeds by a chain-growth mechanism to afford PPP with a narrow polydispersity and that the molecular weight of PPP is controlled by the feed ratio of the monomer to the Ni catalyst. Furthermore, LiCl is shown to play a crucial role in the chain-growth polymerization of **1**.

Treatment of 1,4-dibromo-2,5-dihexyloxybenzene (**2**) with 1 equiv of <sup>i</sup>PrMgCl in THF at room temperature for 24 h gave **1** via a magnesium–bromine exchange reaction (89% yield based on analytical GC).<sup>11,12</sup> Polymerization was carried out by the addition of 1.8 mol % of Ni catalyst to the reaction mixture (Scheme 1). First, Ni(dppp)Cl<sub>2</sub> was used as a catalyst because it is a suitable Ni catalyst for the synthesis of well-defined poly(3-hexylthiophene).<sup>5</sup> The polymerization proceeded smoothly at room temperature, and the conversion of **1** was 87% in 12 h. The polydispersity, however, was broad (Table 1, entry 1). When Ni catalysts with different ligands, Ni(dppe)Cl<sub>2</sub> (dppe = 1,2-bis-

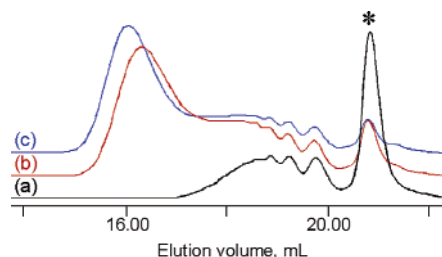
### Scheme 1



**Table 1.** Polycondensation of **1** with Various Ni Catalysts<sup>a</sup>

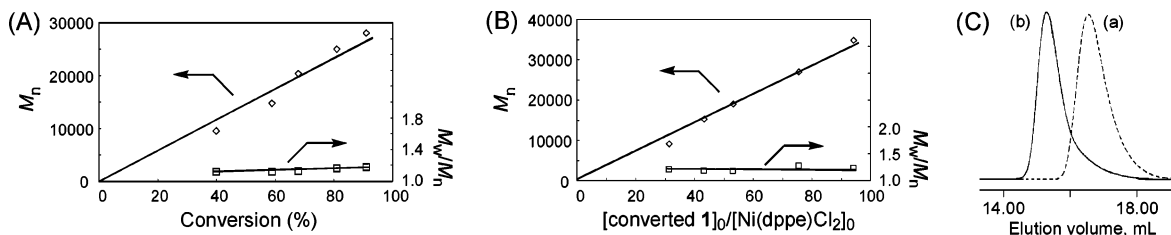
entry	catalyst	equiv of LiCl	time (h)	conversion of <b>1</b> (%) <sup>b</sup>	$M_n^c$	$M_w/M_n^c$
1	Ni(dppp)Cl <sub>2</sub>	0	12	87	3200	1.74
2	Ni(dppe)Cl <sub>2</sub>	0	6	80	3600	2.66
3	Ni(dppf)Cl <sub>2</sub>	0	46	93	4700	2.40
4	Ni(dppp)Cl <sub>2</sub>	1.0	6	94	14600	1.33
5	Ni(dppe)Cl <sub>2</sub>	1.0	1	92	12900	1.18
6	Ni(dppf)Cl <sub>2</sub>	1.0	24	86	3100	2.78

<sup>a</sup> Polymerization was carried out by treatment of **2** with 1.0 equiv of <sup>i</sup>PrMgCl in THF ([**2**]<sub>0</sub> = 0.20 M) at 25 °C for 24 h to form **1**, followed by addition of the Ni catalyst (1.8 mol % to **2**). <sup>b</sup> Determined by GC. <sup>c</sup> Estimated by GPC based on polystyrene standards (eluent: THF).



**Figure 1.** GPC profiles of PPP, synthesized by the polymerization of **1** with 1.0 equiv of <sup>i</sup>PrMgCl and 1.8 mol % Ni(dppe)Cl<sub>2</sub> in THF ([**1**]<sub>0</sub> = 0.088 M) at room temperature. Polymerization time and conversion of **1** were (a) 5 min (34%), (b) 30 min (64%), and (c) 6 h (80%). The peak indicated by the asterisk is due to 1-bromo-2,5-dihexyloxybenzene formed by hydrolysis of **1**.

(diphenylphosphino)ethane) and Ni(dppf)Cl<sub>2</sub> (dppf = 1,1'-bis(diphenylphosphino)ferrocene), were used, the products also showed broad polydispersity (entries 2, 3). Nevertheless, the polymerization behavior with Ni(dppe)Cl<sub>2</sub> was unique: the GPC profile of the products obtained in the early stage showed several peaks in the low-molecular-weight region (Figure 1a), whereas a relatively narrow peak appeared in the higher-molecular-weight region from the middle stage (Figure 1b). The narrow peak shifted toward the higher-molecular-weight region with an increase of conversion (Figure 1c), whereas the peaks in the low-molecular-weight region did not shift. This observation implied that side reactions occurred mainly in the initial stage to give polymer with low molecular weight and broad polydispersity, and that chain-growth polymerization proceeded from the middle stage. We thought that the accumulation of MgBrCl with progress of the reaction might have promoted the chain-growth polymerization. This salt may break the aggregation of Grignard type monomer **1** in a similar manner



**Figure 2.** (A)  $M_n$  and  $M_w/M_n$  values of PPP as a function of monomer conversion in the polymerization of **1** with 0.88 mol % of Ni(dppe)Cl<sub>2</sub> in THF at room temperature ( $[\mathbf{1}]_0 = 0.080$  M). (B)  $M_n$  and  $M_w/M_n$  values of PPP, obtained with **1** and Ni(dppe)Cl<sub>2</sub> in THF at room temperature, as a function of the feed ratio of **1** to Ni(dppe)Cl<sub>2</sub> ( $[\mathbf{2}]_0 = 0.10$  M).  $[\text{Ni}(\text{dppe})\text{Cl}_2]_0 = 0.7\text{--}3.0$  mM; conversion of **1** = 85–95%. (C) GPC profiles of the monomer addition experiment: (a) prepolymer ( $[\mathbf{1}]_0/[\text{Ni}(\text{dppe})\text{Cl}_2]_0 = 34$ ), conversion of **1** = 76%,  $M_n = 8000$  and  $M_w/M_n = 1.22$ ; (b) postpolymer ([remaining and added  $\mathbf{1}]_0/[\text{Ni}(\text{dppe})\text{Cl}_2]_0 = 49$ ), conversion of **1** = 80%,  $M_n = 20400$  and  $M_w/M_n = 1.25$ .

to LiCl, which is effective in the halogen–magnesium exchange reaction between *i*PrMgCl and electron-rich aromatic halides.<sup>13</sup> Accordingly, the polymerization of **1** with the above three Ni catalysts was carried out in the presence of 1 equiv of LiCl. When Ni(dppp)Cl<sub>2</sub> and Ni(dppe)Cl<sub>2</sub> were used, the polymerization proceeded faster than that without LiCl, the multimodal peaks in the low-molecular-weight region of the GPC chromatogram disappeared, and only a narrow monomodal peak was observed in the high-molecular-weight region (Table 1, entries 4, 5), as we had expected. When Ni(dppf)Cl<sub>2</sub> was used, LiCl was not effective (entry 6).

Since the polymerization of **1** with Ni(dppe)Cl<sub>2</sub> in the presence of LiCl gave PPP with the narrowest molecular weight distribution, the  $M_n$  and  $M_w/M_n$  values of the crude PPP (without purification by precipitation or fractionation) at each conversion in this polymerization were analyzed by GPC to evaluate the polymerization in detail. The  $M_n$  values increased in proportion to the conversion, and the  $M_w/M_n$  ratios were less than 1.18 over the whole conversion range (Figure 2A), indicating that **1** polymerized in a chain-growth polymerization manner.<sup>14</sup> Furthermore, when the polymerization of **1** was carried out with various feed ratios of **1** to Ni(dppe)Cl<sub>2</sub>, the  $M_n$  values of the polymer increased linearly in proportion to the feed ratio (Figure 2B). This polymerization behavior indicates that PPP with any desired  $M_n$  up to at least 30000 can be obtained by appropriately controlling the feed ratio of **1** to the Ni catalyst, as was the case in catalyst-transfer polycondensation for polythiophene.<sup>5</sup> The crude products contained small amounts of unreacted **2** and 1-bromo-2,5-dihexyloxybenzene formed by quenching of **1**, and those low-molecular-weight compounds were easily washed out with MeOH. For example, the crude product ( $M_n = 19000$ ,  $M_w/M_n = 1.17$ ), obtained by the polymerization with  $[\text{converted } \mathbf{1}]_0/[\text{Ni}(\text{dppe})\text{Cl}_2]_0$  of 53, was washed with MeOH to give pure PPP in 79% yield ( $M_n = 19600$ ,  $M_w/M_n = 1.14$ ).

The chain-growth nature of this polymerization was also examined by means of a monomer addition experiment, in which a fresh feed of **1** was added to the prepolymer ( $M_n = 8000$ ,  $M_w/M_n = 1.22$ ) in the reaction mixture. As shown in Figure 2C, the GPC profile of the product clearly shifted toward the higher-molecular-weight region ( $M_n = 20400$ ,  $M_w/M_n = 1.25$ ), and the prepolymer did not remain. This result indicates that the added **1** was polymerized from the propagating end of the prepolymer owing to the chain-growth nature of this polymerization, and that block copolymers composed of different conjugated polymers could be synthesized by successive addition of a different monomer.

In conclusion, we have demonstrated that catalyst-transfer chain-growth polymerization with a metal catalyst is applicable not only

to the synthesis of well-defined polythiophenes, but also to that of PPP. We have also found that LiCl is necessary for optimizing the chain-growth polymerization leading to well-defined PPP. Synthesis of block copolymers of different conjugated polymers by this polymerization method is now under way.

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**Supporting Information Available:** Synthesis and polymerization of monomer **1** and <sup>1</sup>H NMR spectrum of PPP. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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