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# 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).[1] These polymers have generally been synthesized by polycondensation with metal catalysts[2] and therefore possess uncontrolled molecular weight and a broad molecular weight distribution.[3]

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)$Cl_2$ (dppp = 1,3-bis(diphenylphosphino)propane) as a catalyst[4] 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.[5] 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.[6] Therefore, we call this type of polymerization *catalyst-transfer polycondensation*.[7] 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.[8] Therefore, we decided to investigate the synthesis of poly(*p*-phenylene) (PPP),[9] 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.[10] 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 $^{i}$PrMgCl in THF at room temperature for 24 h gave **1** via a magnesium−bromine exchange reaction (89% yield based on analytical GC).[11,12] Polymerization was carried out by the addition of 1.8 mol % of Ni catalyst to the reaction mixture (Scheme 1). First, Ni(dppp)$Cl_2$ was used as a catalyst because it is a suitable Ni catalyst for the synthesis of well-defined poly(3-hexylthiophene).[5] 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)$Cl_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) and Ni(dppf)$Cl_2$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene), were used, the products also showed broad polydispersity (entries 2, 3). Nevertheless, the polymerization behavior with Ni(dppe)$Cl_2$ 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

***Scheme 1***

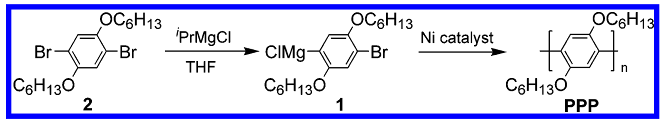


***Table 1.*** Polycondensation of **1** with Various Ni Catalysts[a]

| entry | catalyst | equiv of LiCl | time (h) | conversion of **1** (%)[b] | $M_n$[c] | $M_w/M_n$[c] |
|---|---|---|---|---|---|---|
| 1 | Ni(dppp)$Cl_2$ | 0 | 12 | 87 | 3200 | 1.74 |
| 2 | Ni(dppe)$Cl_2$ | 0 | 6 | 80 | 3600 | 2.66 |
| 3 | Ni(dppf)$Cl_2$ | 0 | 46 | 93 | 4700 | 2.40 |
| 4 | Ni(dppp)$Cl_2$ | 1.0 | 6 | 94 | 14600 | 1.33 |
| 5 | Ni(dppe)$Cl_2$ | 1.0 | 1 | 92 | 12900 | 1.18 |
| 6 | Ni(dppf)$Cl_2$ | 1.0 | 24 | 86 | 3100 | 2.78 |

[a] Polymerization was carried out by treatment of **2** with 1.0 equiv of $^{i}$PrMgCl in THF ($[\mathbf{2}]_0$ = 0.20 M) at 25 °C for 24 h to form **1**, followed by addition of the Ni catalyst (1.8 mol % to **2**). [b] Determined by GC. [c] Estimated by GPC based on polystyrene standards (eluent: THF).

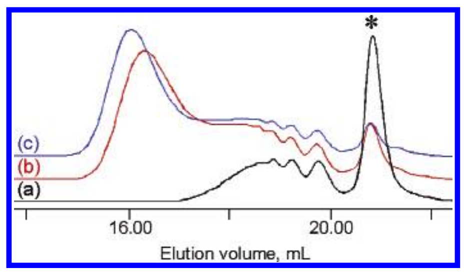


***Figure 1.*** GPC profiles of PPP, synthesized by the polymerization of **1** with 1.0 equiv of $^{i}$PrMgCl and 1.8 mol % Ni(dppe)$Cl_2$ in THF ($[\mathbf{1}]_0$ = 0.088 M) at room temperature. Polymerization time and conversion of **1** were (a) 5 min (34%), (b) 30 min (64%), and (c) 6 h (80%). The peak indicated by the asterisk is due to 1-bromo-2,5-dihexyloxybenzene formed by hydrolysis of **1**.



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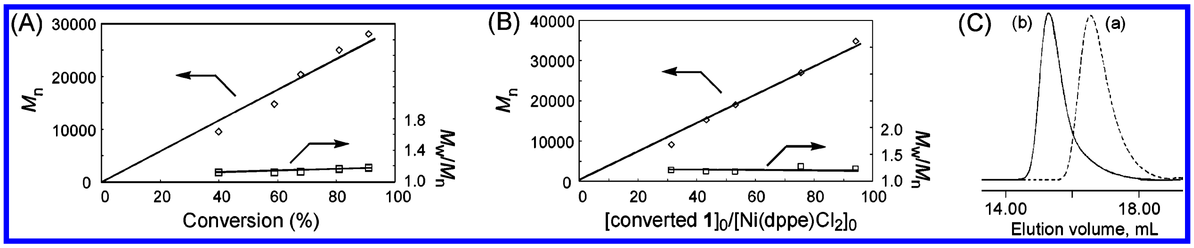


***Figure 2.*** (A) $M_n$ and $M_w/M_n$ values of PPP as a function of monomer conversion in the polymerization of **1** with 0.88 mol % of $Ni(dppe)Cl_2$ in THF at room temperature ($[\mathbf{1}]_0 = 0.080$ M). (B) $M_n$ and $M_w/M_n$ values of PPP, obtained with **1** and $Ni(dppe)Cl_2$ in THF at room temperature, as a function of the feed ratio of **1** to $Ni(dppe)Cl_2$ ($[\mathbf{2}]_0 = 0.10$ M). $[Ni(dppe)Cl_2]_0 = 0.7-3.0$ mM; conversion of $\mathbf{1} = 85-95\%$. (C) GPC profiles of the monomer addition experiment: (a) prepolymer ($[\mathbf{1}]_0/[Ni(dppe)Cl_2]_0 = 34$), conversion of $\mathbf{1} = 76\%$, $M_n = 8000$ and $M_w/M_n = 1.22$; (b) postpolymer ([remaining and added $\mathbf{1}]_0/[Ni(dppe)Cl_2]_0 = 49$), conversion of $\mathbf{1} = 80\%$, $M_n = 20400$ 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.[13] Accordingly, the polymerization of **1** with the above three Ni catalysts was carried out in the presence of 1 equiv of LiCl. When $Ni(dppp)Cl_2$ and $Ni(dppe)Cl_2$ 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 $Ni(dppf)Cl_2$ was used, LiCl was not effective (entry 6).

Since the polymerization of **1** with $Ni(dppe)Cl_2$ 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.[14] Furthermore, when the polymerization of **1** was carried out with various feed ratios of **1** to $Ni(dppe)Cl_2$, 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.[5] 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 $[\text{converted } \mathbf{1}]_0/[Ni(dppe)Cl_2]_0$ 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 $^1$H NMR spectrum of PPP. This material is available free of charge via the Internet at http://pubs.acs.org.

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