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Importance of the Order of Successive Catalyst-transfer Condensation Polymerization in the Synthesis of Block Copolymers of Polythiophene and Poly(*p*-phenylene)

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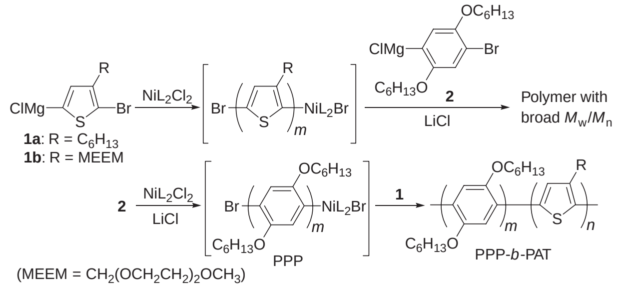
Successive catalyst-transfer condensation polymerization of a Grignard-type phenylene monomer and then a thiophene monomer with a Ni catalyst yields well-defined block copolymers of poly(*p*-phenylene) and polythiophene, but the reverse order of polymerization results in polymers with broad molecular weight distribution.

π-Conjugated polymers are key materials in the development of organic electronic materials and devices, such as field effect transistors (FETs)[1] and light-emitting diodes (LEDs).[2] Considering that LEDs are composed of two or three kinds of π-conjugated homopolymers with different electronic properties, block copolymers consisting of different π-conjugated polymers could have many applications; for example, the use of various combinations and ratios of π-conjugated monomers should enable fine tuning of target properties. However, practical synthetic methods for block copolymers of π-conjugated polymers have not been established.[3] We have recently developed catalyst-transfer condensation polymerization that yields well-defined π-conjugated polymers in a living polymerization fashion.[4] Therefore, successive application of this polymerization method is expected to be a convenient and practical approach to π-conjugated block copolymers, as block copolymers of vinyl monomers or cyclic monomers can be synthesized by conventional living polymerizations. In successive catalyst-transfer condensation polymerization, however, it has not been clarified which monomer should be polymerized first for successful production of the block copolymers, or whether the order of polymerization is unimportant. Herein we investigated the synthesis of block copolymers of poly(3-alkylthiophene) (PAT) and poly(*p*-phenylene) (PPP) by the successive catalyst-transfer condensation polymerization of monomers **1**[5] and **2**[6] with a Ni catalyst. We show that the order of polymerization is crucial for the synthesis of well-defined block copolymers consisting of different π-conjugated polymers (Scheme 1).

In the synthesis of block copolymers of poly(3-hexylthiophene) (PHT) and PPP, we first conducted the polymerization of **1a**, followed by the postpolymerization of **2**. As a catalyst, we used Ni(dppp)Cl_2 [dppp = 1,3-bis(diphenylphosphino)propane], which is the most suitable catalyst for the prepolymerization of **1a**,[5a–5c] although Ni(dppe)Cl_2 [dppe = 1,2-bis(diphenylphosphino)ethane] is the best for the postpolymerization of **2**.[6] Monomers **1a** and **2** were generated in situ by the reaction of the corresponding bromoiodo precursors with *i*-PrMgCl.[7] When a solution of **2** was added to the reaction mixture of PHT as a prepolymer, LiCl equimolar to **2** was added simultaneously with **2**, as in the case of homopolymerization of **2**.[6] The GPC elution curves of PHT as a prepolymer and PHT-*b*-PPP as a postpolymer are shown in Figure 1a. PHT possessed a low polydispersity ($M_w/M_n = 1.15$), whereas the block copolymer showed a broad molecular weight distribution ($M_w/M_n = 2.36$). The uncontrolled postpolymerization might have been due to the effect of the order of polymerization or the use of an unsuitable catalyst for the postpolymerization. Successive block copolymerization was then carried out in the reverse order. Monomer **2** was polymerized with the same catalyst, Ni(dppp)Cl_2, in the presence of LiCl at ambient temperature for 1 h ($M_n = 7800$, $M_w/M_n = 1.28$), followed by the postpolymerization of **1a** equimolar to **2**. Contrary to the block copolymerization initially examined, the block copolymer obtained in this case possessed a narrow molecular weight distribution ($M_n = 19400$, $M_w/M_n = 1.24$) (Figure 1b). When Ni(dppe)Cl_2 was used instead of Ni(dppp)Cl_2, a block copolymer with a low polydispersity was again obtained by employing this polymerization order ($M_n = 16200$, $M_w/M_n = 1.27$) (Figure 1c). These results imply that



Scheme 1.

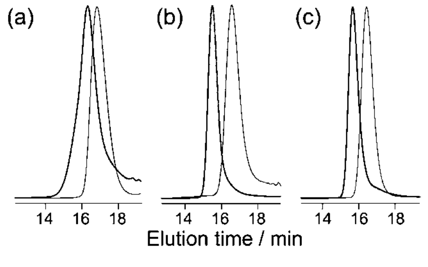


Figure 1. GPC elution curves of prepolymer (narrow line) and block copolymer as a postpolymer (bold line) obtained by block copolymerization of **1a** and **2** with a Ni catalyst: (a) polymerization of **1a** (conversion = 77%) followed by **2** (conversion = 73%) with Ni(dppp)Cl_2: PHT ($M_n = 7300$, $M_w/M_n = 1.15$) and PHT-*b*-PPP ($M_n = 5600$, $M_w/M_n = 2.36$); (b) polymerization of **2** (conversion = 67%) followed by **1a** (conversion = 91%) with Ni(dppp)Cl_2: PPP ($M_n = 7800$, $M_w/M_n = 1.28$) and PPP-*b*-PHT ($M_n = 19400$, $M_w/M_n = 1.24$); (c) polymerization of **2** (conversion = 73%) followed by **1a** (conversion = 93%) with Ni(dppe)Cl_2: PPP ($M_n = 10900$, $M_w/M_n = 1.11$) and PPP-*b*-PHT ($M_n = 16200$, $M_w/M_n = 1.27$).

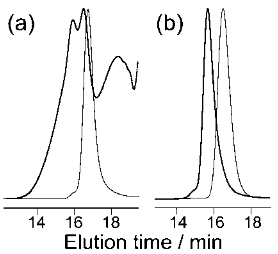


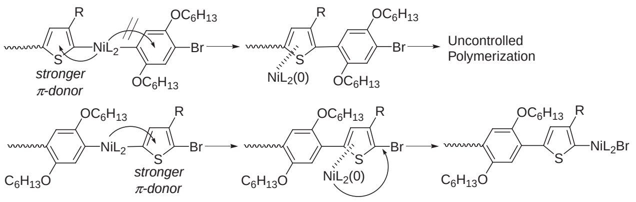
Figure 2. GPC elution curves of prepolymer (narrow line) and postpolymer (bold line) obtained by block copolymerization of **1b** and **2** with Ni(dppe)Cl_2: (a) polymerization of **1b** (conversion = 93%) followed by **2** (conversion = 100%): PMEEMT ($M_n = 7500$, $M_w/M_n = 1.16$) and the postpolymer ($M_n = 3100$, $M_w/M_n = 4.20$); (b) polymerization of **2** (conversion = 69%) followed by **1b** (conversion = 100%): PPP ($M_n = 10500$, $M_w/M_n = 1.10$) and PPP-*b*-PMEEMT ($M_n = 17600$, $M_w/M_n = 1.21$).

controlled block copolymerization may be governed by the order of polymerization rather than the catalyst.

We next studied the block copolymerization of **1b** and **2**, because the most suitable Ni catalyst for the polymerization of both **1b**[5d] and **2** is the same: Ni(dppe)Cl_2. The successive polymerization of **1b** and then **2** was first carried out with Ni(dppe)Cl_2. Although poly{3-[2-(2-methoxyethoxy)ethoxy]methylthiophene} (PMEEMT) as a prepolymer possessed a narrow molecular weight distribution ($M_w/M_n = 1.16$), the GPC elution curve of the postpolymer showed multimodal peaks (Figure 2a). In the reverse order of polymerization, however, both PPP as a prepolymer and PPP-*b*-PMEEMT as a postpolymer had narrow molecular weight distributions ($M_w/M_n = 1.10$ and 1.21, respectively), and the GPC elution curve of the prepolymer was clearly moved to the higher molecular weight region (Figure 2b). Consequently, it turns out that the order of polymerization is crucial for the synthesis of well-defined block copolymers consisting of different π-conjugated polymers. In the synthesis of the block copolymers of PAT and PPP, the PPP segment needs to be prepared first, followed by elongation of the PAT segment.

Successful block copolymerization of **2** and then **1** may be accounted for by the π-donor ability of PAT and PPP because the π-electrons of the polymers are considered to assist the transfer of the Ni catalyst in catalyst-transfer polymerization.[6,8] When **2** is added to the reaction mixture of PAT as a prepolymer, the Ni catalyst would be difficult to move to the terminal C–Br bond of the phenylene ring of the elongated **2** unit, because the thiophene ring has stronger π-donor ability than the phenylene ring.[9] On the other hand, when **1** is added to PPP as a prepolymer, the Ni catalyst would smoothly move to the C–Br bond of the thiophene ring with stronger π-donor ability (Scheme 2).

In conclusion, we have demonstrated that the order of polymerization is important for the synthesis of well-defined block copolymers of different π-conjugated polymers via catalyst-transfer condensation polymerization. The successive polymerizations should be conducted from a monomer with low π-donor ability to a monomer with high π-donor ability. This result is similar to that for block copolymerization via anionic living polymerization; for example, polystyryl carbanion initiates the polymerization of methyl methacrylate, but the reverse does not occur. Our finding should be helpful for the efficient synthesis of a variety of well-defined block copolymers of π-conjugated polymers by means of catalyst-transfer condensation polymerization. Experiments along this line are in progress.



Scheme 2.

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9 The π-donor ability of PHT, PMEEMT, and PPP was estimated by calculation (AM1, WinMOPAC 3.9) of the electronegativity of 3-hexylthiophene (Q = −0.116), 3-MEEMthiophene (Q = −0.113), and 1,4-dihexyloxybenzene (Q = −0.104), respectively.

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