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Precision Synthesis of Poly(*N*-hexylpyrrole) and Its Diblock Copolymer with Poly(*p*-phenylene) via Catalyst-Transfer Polycondensation

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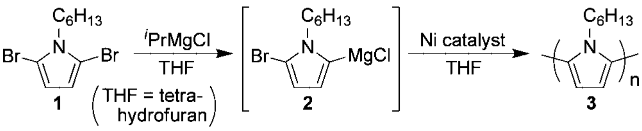
Well-defined block copolymers[1−3] and a dendronized polymer[4] containing head-to-tail poly(3-alkylthiophene)s (HT-PAT) have been synthesized via the Grignard metathesis method.[5] In their syntheses, the HT-PAT units were modified in several steps after the polymerization of thiophene monomers. Recently, we[6] and McCullough's group[7] have independently reported catalyst-transfer polycondensation which provides HT-PATs with uniform end structure, controlled molecular weight, and narrow polydispersity, and we have also reported catalyst-transfer polycondensation for the synthesis of well-defined poly(*p*-phenylene).[8] Because of living polymerization nature of catalyst-transfer polycondensation, one might think that it is easy to synthesize block copolymers composed of different conjugated polymers via successive addition of the corresponding monomers. However, one-pot synthesis in this manner has so far been applied only to the synthesis of diblock copolythiophenes with different side chains,[9,10] and block copolymers of different conjugated polymers have not been synthesized. Considering the reaction mechanism of catalyst-transfer polycondensation,[11] such a successive copolymerization should work well when the polymerization of each monomer proceeds with the same catalyst. Herein, we report that polycondensation of a Grignard-type *N*-hexylpyrrole monomer proceeds in a catalyst-transfer polymerization manner, and the best catalyst for the polymerization is Ni(dppe)Cl_2 (dppe = 1,2-bis(diphenylphosphino)ethane), which is the same catalyst as in the case of *p*-phenylene monomer.[8] We also found that the presence of additional dppe in the reaction mixture is crucial to control the polymerization precisely, and we developed a one-pot synthesis of diblock copolymer of poly(*N*-hexylpyrrole) and poly(*p*-phenylene). There are several reports on the organometallic polycondensation of N-substituted pyrrole monomer using nickel(II) acetylacetonate,[12] bis(1,5-cyclooctadiene)nickel(0),[13] or copper[14] as catalysts, but controlled polymerization has not been reported.

Scheme 1



We used 2,5-dibromo-1-hexylpyrrole (**1**) as a monomer precursor, which was converted to the Grignard-type monomer **2** by treatment with 0.96 equiv of isopropylmagnesium chloride in tetrahydrofuran (THF) at room temperature for 24 h. Then, the polymerization was carried out by addition of 1 mol % of a nickel catalyst to the reaction mixture (Scheme 1). When Ni(dppp)Cl_2 (dppp = 1,3-bis(diphenylphosphino)propane) was used as a catalyst in a similar manner to the case of polycondensation of hexylthiophene monomer[6] and the reaction was conducted at room temperature for 3 h, the polymerization proceeded smoothly and the conversion of **2** reached 85%. The gel permeation chromatography (GPC) profile of the product (Figure 1a) indicated formation of a polymeric product (M_n = 5.4×10^3 and $M_\mathrm{w}/M_\mathrm{n} = 1.26$, where M_n and M_w are number- and weight-average molecular weight, respectively) accompanied by low-molecular-weight oligomers at the elution volume between 19 and 21 mL. Polymerization with Ni(dppf)Cl_2 (dppf = 1,1′-bis(diphenylphosphino)ferrocene) gave almost the same results (Figure 1b). On the other hand, polymerization with Ni(dppe)Cl_2, which was the best catalyst for the catalyst-transfer polycondensation of *p*-phenylene monomer,[8] afforded the polymer with higher molecular weight and narrower polydispersity ($M_\mathrm{n} = 1.34 \times 10^4$, $M_\mathrm{w}/M_\mathrm{n} = 1.19$), though oligomeric byproduct were still formed (Figure 1c). When **2** was polymerized with Ni(dppe)Cl_2 at 0 °C, the formation of the byproduct decreased but was not completely suppressed. The gas chromatography−mass spectrometer (GC−MS) and ^{1}H NMR analyses revealed that several kinds of oligomers were formed, and we isolated 5,5′-dibromo-1,1′-dihexyl-2,2′-bipyrrole (**4**) as a major byproduct in 14% yield.[15] On the basis of the reaction mechanism of catalyst-transfer polycondensation,[11] **4** was thought to have been formed by intermolecular transfer of the nickel catalyst at the initial stage of polymerization. To suppress the formation of the oligomeric byproduct, we examined the effect of several additives and found that polymerization of **2** with 1 mol % of Ni(dppe)Cl_2 in the presence of 1 mol % of additional dppe at 0 °C gave good results without formation of byproduct (Figure 1d, $M_\mathrm{n} = 1.43 \times 10^4$, $M_\mathrm{w}/M_\mathrm{n} = 1.11$).[16]

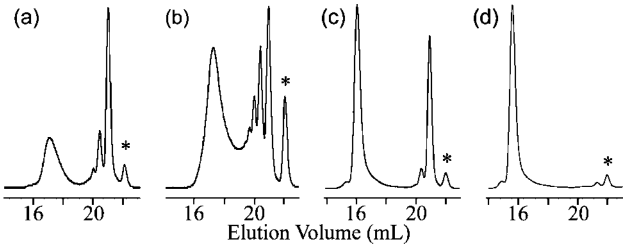


Figure 1. Gel permeation chromatography profiles of the products obtained by the polymerization of 2-bromo-5-chloromagnesio-1-hexylpyrrole (**2**) in tetrahydrofuran. The polymerization was carried out with 1 mol % of (a) Ni(dppp)Cl_2 (dppp = 1,3-bis(diphenylphosphino)propane) for 3 h (conversion of **2** = 85%), (b) Ni(dppf)Cl_2 (dppf = 1,1′-bis(diphenylphosphino)ferrocene) for 9 h (conversion of **2** = 90%), (c) Ni(dppe)Cl_2 (dppe = 1,2-bis(diphenylphosphino)ethane) for 2 h (conversion of **2** = 91%) at room temperature, and (d) 1 mol % of Ni(dppe)Cl_2 in the presence of 1 mol % of dppe at 0 °C for 32 h (conversion of **2** = 85%). The peaks marked with an asterisk are 2-bromo-1-hexylpyrrole, formed by the hydrolysis of unreacted **2** after quenching of the reaction mixture.

With the optimized reaction conditions to control the polymerization in hand, we investigated the nature of the chain-growth polymerization. We first examined the relationship between the conversion of the monomer **2** and the molecular weight of the polymer **3** obtained by the polymerization with 2.5 mol % of Ni(dppe)Cl_2 and 2.5 mol % of dppe and found that the molecular weight of **3** increased linearly in proportion to the conversion of **2** (Figure S1).[15] Furthermore, the molecular weight of the obtained polymer also increased linearly in proportion to the feed ratio of **2** to Ni(dppe)Cl_2 up to $M_\mathrm{n} = 1.43 \times 10^4$ (Figure

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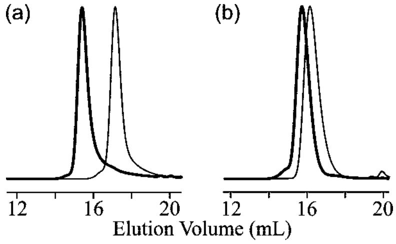
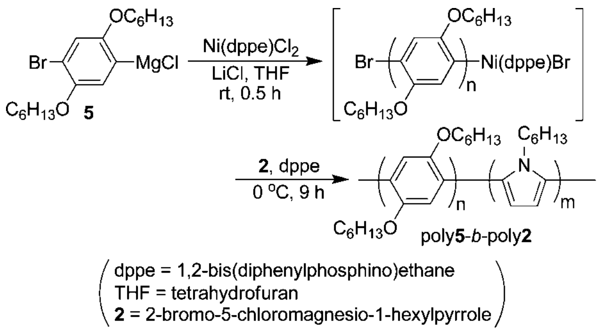


Figure 2. Gel permeation chromatography profiles of the polymer obtained by diblock copolymerization. (a) Poly(*N*-hexylpyrrole) (poly**2**) as a prepolymer (narrow line, $M_n = 5.5 \times 10^3$, $M_w/M_n = 1.20$) and poly(*N*-hexylpyrrole)-*b*-poly(2,5-dihexyloxy-*p*-phenylene) (poly**2**-*b*-poly**5**, bold line, $M_n = 1.78 \times 10^4$, $M_w/M_n = 1.38$). (b) Poly**5** as a prepolymer (narrow line, $M_n = 1.13 \times 10^4$, $M_w/M_n = 1.13$) and poly**5**-*b*-poly**2** (bold line, $M_n = 1.64 \times 10^4$, $M_w/M_n = 1.16$).

S2).[15] These linear relationships indicate that this polymerization indeed proceeded in a catalyst-transfer polymerization manner. The end groups of the polymer **3**, obtained by polymerization of **2** with 2.5 mol % of Ni(dppe)Cl_2 in the presence of 2.5 mol % of dppe, were analyzed by means of matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (Figure S3).[15] As expected from the reaction mechanism of the catalyst-transfer polycondensation,[11] the major peaks of the mass spectrum corresponded to the polymer with a bromine atom at one end and a hydrogen atom at the other end (designated as Br/H). However, the signals corresponding to Br/Br-ended polymers were also observed as minor peaks. Because the GPC elution curve of the obtained polymer showed a small shoulder at the higher-molecular-weight region (Figure 1d), the Br/Br-ended polymers might be formed via disproportionation reaction between the Br/Ni(II)Br-ended polypyrroles, followed by reductive elimination to afford the polymer-coupling product, as in the case of polymerization of the thiophene monomer quenched with water.[17]

We next tried to synthesize π-conjugated diblock copolymers via successive catalyst-transfer polycondensation of two monomers. Because the best catalyst for the polymerization of the pyrrole monomer **2** is Ni(dppe)Cl_2, which is also the best catalyst for the polymerization of the *p*-phenylene monomer, we studied block copolymerization of these monomers. The pyrrole monomer **2** was polymerized first in the presence of 2.5 mol % of Ni(dppe)Cl_2 and 2.5 mol % of dppe in THF at 0 °C for 8 h, to afford well-defined poly**2** (conversion of **2** = 78%, poly**2**: $M_n = 5.5 \times 10^3$ and $M_w/M_n = 1.20$). Then 1.0 equiv of *p*-phenylene monomer (1-bromo-4-chloromagnesio-2,5-dihexyloxybenene, **5**)[15] and 1.0 equiv of LiCl[8] were added to the reaction mixture, and the second polymerization was conducted at room temperature for 2 h. The conversion of **5** was 93%, and the GPC profiles of the obtained polymer showed $M_n = 1.78 \times 10^4$ and $M_w/M_n = 1.38$. From the first polymerization to the second one, the GPC elution curve shifted toward the higher-molecular-weight region, while retaining a narrow molecular weight distribution (Figure 2a). These results indicate that the polymerization of the second monomer **5** started from the terminal C−Ni group of the first polymer and proceeded in a chain-growth polymerization manner to yield the diblock copolymer poly**2**-*b*-poly**5**. However, the molecular weight distribution of the block copolymer obtained after the second polymerization was broader than that of the polymer obtained in the first stage. Because the GPC elution curve of the polymer obtained from the second polymerization showed tailing toward the lower-molecular-weight region, the broadening of the molecular weight distribution would be due to side reactions which terminated the progress of the second polymerization. We thought that the Br/Br-ended poly**2** mentioned above or the additional dppe, which was necessary to the chain-growth polymerization of **2**, might have disturbed the catalyst-transfer polycondensation of **5** in the second stage. Therefore, we examined the copolymerization in the reverse order (Scheme 2). The *p*-phenylene monomer **5** was polymerized first with 2.5 mol % of Ni(dppe)Cl_2 and 1.0 equiv of LiCl in THF at room temperature for 0.5 h to afford well-defined poly(*p*-phenylene) (conversion of **5** = 93%, poly**5**: $M_n = 1.13 \times 10^4$, $M_w/M_n = 1.13$). After the reaction mixture had cooled to 0 °C, 1.0 equiv of **2** and 2.5 mol % of dppe were added, and the second polymerization was carried out at 0 °C for 9 h. The conversion of the monomer **2** was 65%, and the GPC profiles of the obtained polymer showed the formation of well-defined diblock copolymer poly**5**-*b*-poly**2** with a narrow polydispersity ($M_n = 1.64 \times 10^4$ and $M_w/M_n = 1.16$). The integral ratios of the ^{1}H NMR spectrum indicated that the block copolymer contained the *p*-phenylene and pyrrole units in a ratio of 61.5/38.5.

Scheme 2



dppe = 1,2-bis(diphenylphosphino)ethane
THF = tetrahydrofuran
2 = 2-bromo-5-chloromagnesio-1-hexylpyrrole

In conclusion, we have demonstrated that polymerization of the *N*-hexylpyrrole monomer **2** with Ni(dppe)Cl_2 and dppe proceeds in a catalyst-transfer polymerization manner, that additional dppe plays a crucial role to suppress the formation of oligomeric byproduct, and that well-defined diblock copolymer composed of two π-conjugated polymers can be synthesized in one pot via successive catalyst-transfer polycondensation. This work has extended the scope of application of catalyst-transfer polymerization by employing ligand addition to control the polymerization as well as demonstrating one-pot synthesis of π-conjugated diblock copolymers. Further studies along this line are in progress.

Supporting Information Available: Experimental details, NMR spectra, and MALDI-TOF mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Iovu, M. C.; Jeffries-EL, M.; Sheina, E. E.; Cooper, J. R.; McCullough, R. D. *Polymer* **2005**, *46*, 8582–8586. (b) Li, B.; Sauvé, G.; Iovu, M. C.; Jeffries-EL, M.; Zhang, R.; Cooper, J.; Santhanam, S.; Schultz, L.; Revelli, J. C.; Kusne, A. G.; Kowalewski, T.; Snyder, J. L.; Weiss, L. E.; Fedder, G. K.; McCullough, R. D.; Lambeth, D. N. *Nano Lett.* **2006**, *6*, 1598–1602. (c) Iovu, M. C.; Craley, C. R.; Jeffries-EL, M.; Krankowski, A. B.; Zhang, R.; Kowalewski, T.; McCullough, R. D. *Macromolecules* **2007**, *40*, 4733–4735.

(2) Dai, C.-A.; Yen, W.-C.; Lee, Y.-H.; Ho, C.-C.; Su, W.-F. *J. Am. Chem. Soc.* **2007**, *129*, 11036–11038.

(3) Radano, C. P.; Scherman, O. A.; Stingelin-Stutzmann, N.; Müller, C.; Breiby, D. W.; Smith, P.; Janssen, R. A. J.; Meijer, E. W. *J. Am. Chem. Soc.* **2005**, *127*, 12502–12503.

(4) Watanabe, N.; Mauldin, C.; Fréchet, J. M. J. *Macromolecules* **2007**, *40*, 6793–6795.

(5) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250–253.

(6) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169–1171.

(7) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526–3528.

(8) Miyakoshi, R.; Shimono, K.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2006**, *128*, 16012–16013.

(9) Yokozawa, T.; Adachi, I.; Miyakoshi, R.; Yokoyama, A. *High Perform. Polym.* **2007**, *19*, 684–699.

(10) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649–8656.

(11) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542–17547.

(12) (a) Khoury, I.; Kovacic, P.; Gilow, H. M. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 395–400. (b) Kovacic, P.; Khoury, I.; Elsenbaumer, R. L. *Synth. Met.* **1983**, *6*, 31–38.

(13) (a) Yamamoto, T.; Zhou, Z.-H. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 833–839. (b) Kijima, M.; Abe, S.; Shirakawa, H. *Synth. Met.* **1999**, *101*, 61.

(14) Groenendaal, L.; Peerlings, H. W. I.; van Dongen, J. L. J.; Havinga, E. E.; Vekemans, J. A. J. M.; Meijer, E. W. *Macromolecules* **1995**, *28*, 116–123.

(15) See Supporting Information for details.

(16) A similar effect of an additional phosphine ligand on a metal ring-walking process has been reported recently: Zenkina, O.; Altman, M.; Leitus, G.; Shimon, L. J. W.; Cohen, R.; van der Boom, M. E. *Organometallics* **2007**, *26*, 4528–4534.

(17) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Macromol. Rapid Commun.* **2004**, *25*, 1663–1666.

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