Article

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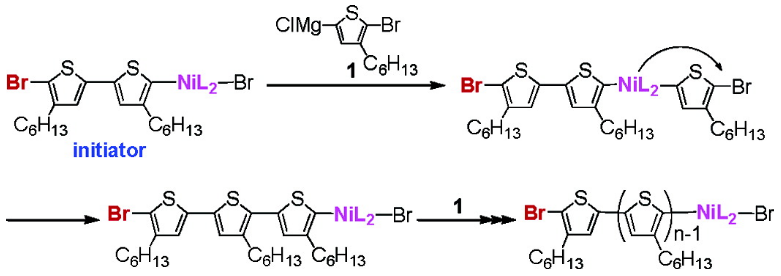

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Catalyst-Transfer Polycondensation. Mechanism of Ni-Catalyzed Chain-Growth Polymerization Leading to Well-Defined Poly(3-hexylthiophene)

Ryo Miyakoshi, Akihiro Yokoyama, and Tsutomu Yokozawa*

Contribution from the Department of Applied Chemistry, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

Received August 19, 2005; E-mail: yokozt01@kanagawa-u.ac.jp

Abstract: We studied the mechanism of the chain-growth polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene (**1**) with Ni(dppp)Cl_2 [dppp = 1,3-bis(diphenylphosphino)propane], in which head-to-tail poly(3-hexylthiophene) (HT-P3HT) with a low polydispersity is obtained and the M_n is controlled by the feed ratio of the monomer to the Ni catalyst. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra showed that the HT-P3HT uniformly had a hydrogen atom at one end of each molecule and a bromine atom at the other. The reaction of the polymer with aryl Grignard reagent gave HT-P3HT with aryl groups at both ends, which indicates that the H-end was derived from the propagating Ni complex. The degree of polymerization and the absolute molecular weight of the polymer could be evaluated from the ^1H NMR spectra of the Ar/Ar-ended HT-P3HT, and it was found that one Ni catalyst molecule forms one polymer chain. Furthermore, by reaction of **1** with 50 mol % Ni(dppp)Cl_2, the chain initiator was found to be a bithiophene−Ni complex, formed by a coupling reaction of **1** followed by insertion of the Ni(0) catalyst into the C−Br bond of the dimer. On the basis of these results, we propose that this chain-growth polymerization involves the coupling reaction of **1** with the polymer via the Ni catalyst, which is transferred intramolecularly to the terminal C−Br bond of the elongated molecule. We call this mechanism "*catalyst-transfer polycondensation*".

Introduction

Polycondensation is an important polymerization method for the synthesis of polyamides, polyesters, polyethers, and so on, which serve for production of fibers and as engineering plastics by virtue of their strong intermolecular forces. π-Conjugated polymers have received considerable attention with the development of the information technology industry and have also been synthesized by polycondensation. However, those polymers possess broad molecular weight distributions, because the polycondensation proceeds through a step-growth polymerization mechanism, in which all the end groups of monomers and oligomers in the reaction mixture equally react with each other. On the other hand, many natural polymeric materials are perfectly monodisperse macromolecules and are synthesized by the successive condensation of monomers with the polymer end group with the aid of selective activation by enzymes.[1−4] Especially in the biosynthesis of proteins, the overall process can be regarded as a kind of chain-growth polycondensation with catalyst transfer: that is, the polycondensation proceeds with the catalyst transferring to and activating only the elongated polymer end group.

We have developed an artificial chain-growth polycondensation without any catalyst.[5] The change of the substituent effect induced by bond formation of the monomer drives the reactivity of the polymer end group to become higher than that of the monomer, leading to chain-growth polycondensation. We have also investigated chain-growth polycondensation with a catalyst and found that the polycondensation of 2-bromo-5-chloromagnesio-3-hexylthiophene (**1**) with Ni(dppp)Cl_2 [dppp = 1,3-bis(diphenylphosphino)propane] proceeds via a chain-growth polymerization mechanism to yield head-to-tail poly(3-hexylthiophene)s (HT-P3HT) with low polydispersity and controlled molecular weight (Scheme 1).[6,7] In this paper, we deal with the mechanism of this chain-growth polycondensation and we show that the chain-growth mechanism involves selective intramolecular transfer of the catalyst to the polymer end group, resulting in the activation of only the polymer end group in a

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(1) For the biosynthesis of polypeptides, see (a) Weissbach, H.; Pestka, S. *Molecular Mechanism of Protein Biosynthesis*; Academic Press: New York, 1977. (b) Bermek, E. *Mechanism of Protein Synthesis. Structure−Function Relations, Control Mechanism, and Evolutionary Aspects*; Springer-Verlag: New York, 1985.

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(4) For the biosynthesis of *cis*-polyisoprene rubber, see (a) Light, D. R.; Dennis, M. S. *J. Biol. Chem.* **1989**, *254*, 18598. (b) Dennis, M. S.; Light, D. R. *J. Biol. Chem.* **1989**, *264*, 18608.

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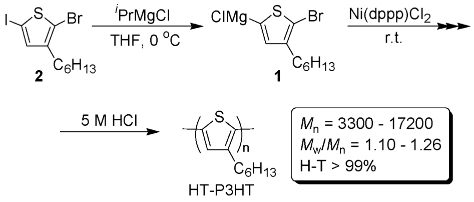
10.1021/ja0556880 CCC: $30.25

Scheme 1. Synthesis of Well-Defined HT-P3HT



manner similar to the biological polycondensations mentioned above. This is a novel mechanism of artificial chain-growth polycondensation and we call it "*catalyst-transfer polycondensation*." Although we[6] and McCullough and co-workers[8] have speculated that this was the mechanism, there have been no data to support it until now. Here, we used matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry and ^{1}H NMR spectroscopy to examine two types of HT-P3HT: one was obtained by quenching the polymerization with 5 M hydrochloric acid, and the other contained aryl groups at both ends of the polymer as a result of treatment of the polymerization mixture with aryl Grignard reagent. The results show that the propagating group is the Ni complex end of the polymer, and one polymer chain forms per single Ni catalyst molecule. Furthermore, the result of the reaction of **1** with 50 mol % Ni(dppp)Cl_2 demonstrated that a bithiophene−Ni−Br complex is the chain initiator.

Results and Discussion

Polymer Chain End. The polymerization of **1**, which was prepared in situ by the treatment of 2-bromo-3-hexyl-5-iodothiophene (**2**) with 1.0 equiv of isopropylmagnesium chloride at 0 °C for 1 h, was carried out in the presence of 1.60 mol % Ni(dppp)Cl_2 in tetrahydrofuran (THF) at room temperature for 6 h (conversion of **1** = 85%). Then the reaction mixture was quenched with 5 M hydrochloric acid and pure HT-P3HT (M_n = 9300, M_w/M_n = 1.10) was obtained after the crude product was washed with MeOH without use of a Soxhlet apparatus to remove low-molecular-weight fractions. The MALDI-TOF mass spectrum of the HT-P3HT obtained was taken with dithranol as a matrix in the absence of cationizing salt. Surprisingly, the mass spectrum contains only one series of peaks, indicating that each polymer molecule has the same end groups (Figure 1). Detailed analysis revealed that the *m*/*z* values can be accurately expressed as 166.3*n* (repeat unit) + 79.9 (Br) + 1.0 (H), where *n* is equal to the number of repeat units. Therefore, one end group of the polymer is a bromine atom and the other is a hydrogen atom (designated as Br/H). For example, the 30-mer of this distribution is expected to produce a signal at *m*/*z* 166.3 × 30 (repeat unit) + 79.9 (Br) + 1.0 (H) = 5069.9, and indeed, a signal is observed at 5069.80. The 30-mer with Br/Br ends and the 30-mer with H/H ends should afford signals at *m*/*z* 5148.8 and 4989.0, respectively, but these are not observed. On the other hand, it was reported that the MALDI-TOF mass spectra of poly(3-alkylthiophene)s with broad polydispersities, which were obtained by similar Ni-catalyzed polymerization of the corresponding chloromagnesio monomers, showed three kinds of end groups corresponding to Br/Br, Br/H, and H/H.[9] Since the H end group is thought to be derived from the magnesiochloride end group and/or the Ni complex end group by quenching, these poly(3-alkylthiophene)s with the Br/Br, Br/H, and H/H end groups seem to be produced by typical Ni-catalyzed step-growth polymerization. In our polymerization of **1** with Ni catalyst, however, the finding that the polymer has only the Br/H end groups and the fact that the polymerization proceeds in a chain-growth polymerization manner indicate that the polymerization is initiated by a single kind of molecule and propagated from a single kind of propagating group.

Even in our polymerization of **1**, however, the amount of Grignard reagent used to convert **2** into **1** strongly influenced the polymer end group and the molecular weight distribution of HT-P3HT. When 0.80 or 1.20 equiv of isopropylmagnesium chloride was used, the molecular weight distribution became broad (Figure 2a,d). On the other hand, HT-P3HT with a low polydispersity and a controlled molecular weight was obtained when 0.95 or 1.05 equiv of isopropylmagnesium chloride was used (Figure 2b,c). However, when 1.05 equiv of isopropylmagnesium chloride was used, the polymer end groups were no longer uniform (Figure 3). It is important to use 0.95−1.00

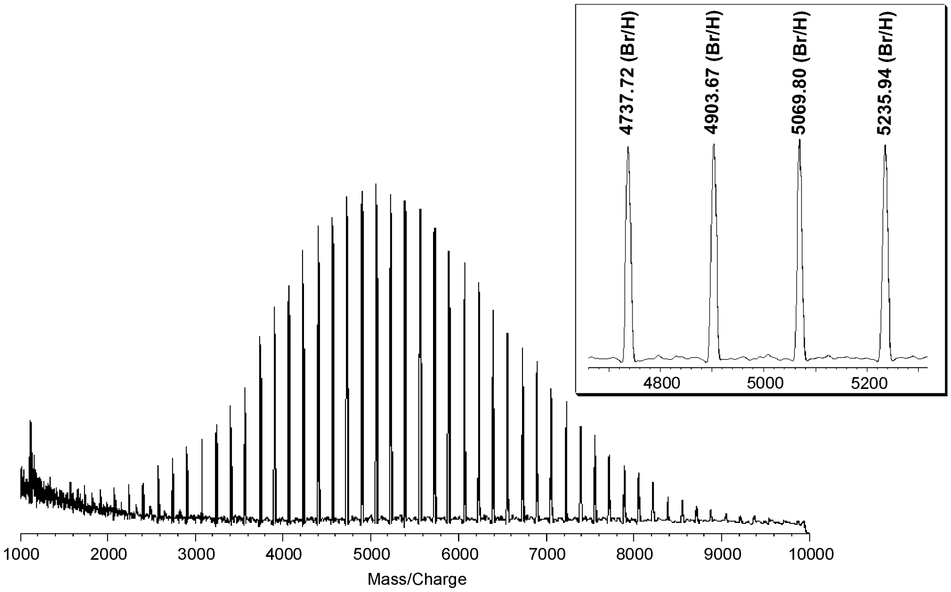


Figure 1. MALDI-TOF mass spectrum of HT-P3HT (M_n = 9300 and M_w/M_n = 1.10 determined by GPC).

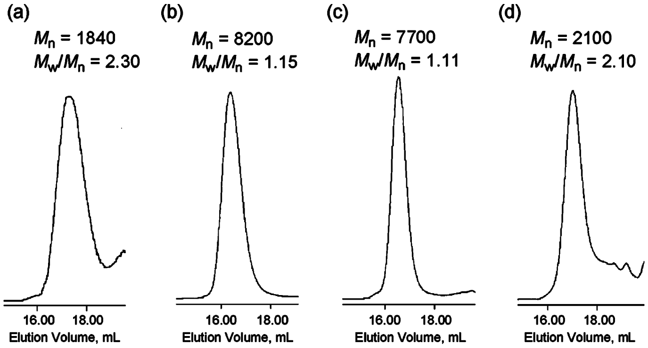


Figure 2. GPC profiles of HT-P3HT obtained by the polymerization of **2** with (a) 0.80 equiv, (b) 0.95 equiv, (c) 1.05 equiv, and (d) 1.20 equiv of ^{i}PrMgCl and 2.2 mol % Ni(dppp)Cl_2.

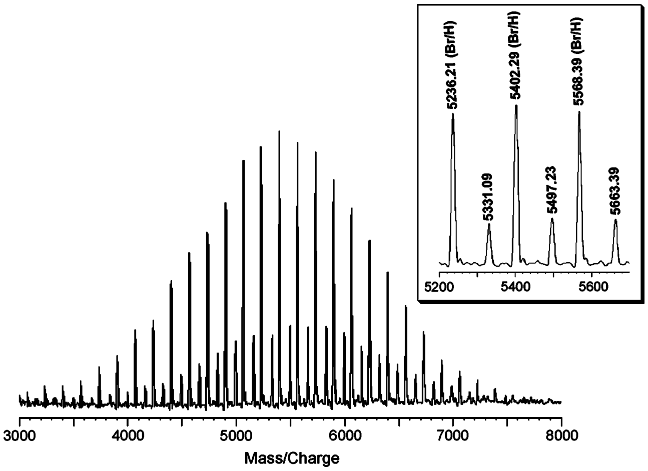
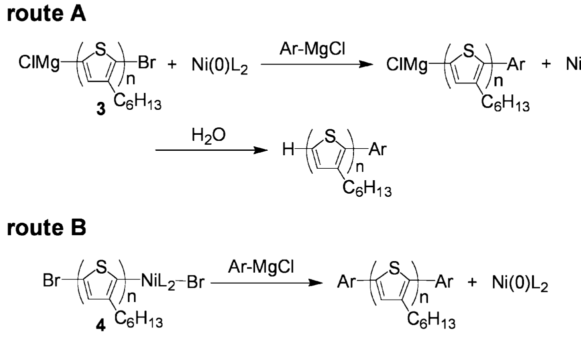


Figure 3. MALDI-TOF mass spectrum of HT-P3HT obtained by the polymerization of **2** with 1.05 equiv of ^{i}PrMgCl and 2.2 mol % Ni(dppp)-Cl_2.

Scheme 2. Two Possible Chain Ends of HT-P3HT before Quenching



equiv of the Grignard reagent to obtain HT-P3HT with a narrow molecular weight distribution and controlled chain ends.

Propagating Group. As mentioned in the previous section, the Br/H chain ends of HT-P3HT are consistent with two possible propagating groups: one is the magnesiochloride **3**, and the other is the Ni complex **4** (Scheme 2). We considered that the Ni complex was likely to be the propagating group because the coupling reaction between the polymers occurred slightly when the polymerization was quenched by water.[7] To identify the propagating group in the polymerization, arylmagnesium chloride was added to the reaction mixture at the last stage of polymerization. If the propagating group is magnesiochloride, the bromine of **3** will be replaced with the aryl group by virtue of the Ni catalyst, and quenching with water should afford HT-P3HT with H/Ar ends (route A). If the propagating group is the Ni complex on the other hand, the Ni complex will react with arylmagnesium chloride, and the coupling reaction will take place accompanied with release of Ni(0) catalyst by reductive elimination. Then the C−Br bond of **4** will undergo oxidative addition to this Ni(0), followed by similar coupling reaction to yield HT-P3HT with Ar/Ar ends (route B).

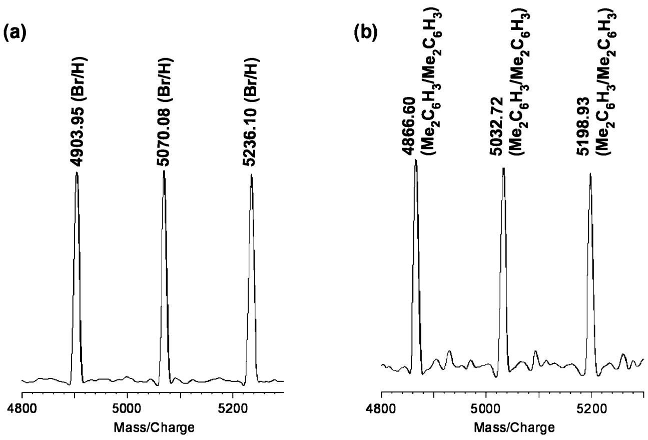


Figure 4. MALDI-TOF mass spectra of HT-P3HT obtained by (a) polymerization of **1** with 1.94 mol % Ni(dppp)Cl_2 for 30 min and (b) reaction with 3,4-dimethylphenylmagnesium chloride.

The polymerization of **1** was carried out in the presence of 1.94 mol % Ni(dppp)Cl_2 in THF at room temperature for 30 min (conversion of **1** = 74%; $M_n = 8400$, $M_w/M_n = 1.14$), and then an excess of 3,4-dimethylphenylmagnesium chloride (3,4-$Me_2C_6H_3MgCl$) was added to the reaction mixture. The mixture was stirred for 3 h, and then the reaction was quenched with water. End group analysis of the obtained polymer ($M_n = 8600$, $M_w/M_n = 1.16$) was performed by MALDI-TOF mass spectrometry (Figure 4). The spectrum contains only one series of peaks, the values of which correspond to HT-P3HT with $Me_2C_6H_3/Me_2C_6H_3$ end groups. For example, the 29-mer of this distribution is expected to produce a signal at m/z 166.3 × 29 (repeat unit) + 105.2 (3,4-dimethylphenyl group) + 105.2 (3,4-dimethylphenyl group) = 5033.1, and in fact a signal is observed at 5032.72. The polymer with the Br/H ends [166.3n (repeat unit) + 79.9 (Br) + 1.0 (H)] and that with the $Me_2C_6H_3$/H ends [166.3n (repeat unit) + 105.2 (3,4-dimethylphenyl group) + 1.0 (H)] are absent (neither m/z 4903.6 nor 4928.9 was detected in Figure 4b). This result indicates that the 3,4-dimethylphenyl group was introduced at both ends of the polymer, and that the propagating group of the polymer is the Ni complex.

A phenyl group was also quantitatively introduced at both ends by phenylmagnesium chloride. However, when *tert*-butylmagnesium chloride was used, the polymer with H/H end groups was obtained. This polymer may be formed from the polymer−Ni−H complex, which is generated by β-hydride elimination of the polymer−Ni−^{t}Bu complex. When isopropylmagnesium chloride was used, polymers with H/^{i}Pr and H/H

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

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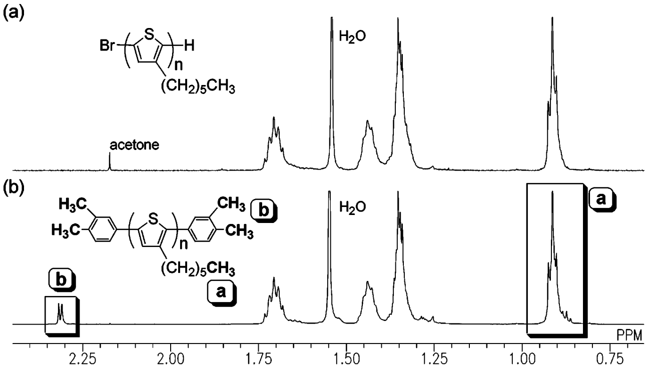

Figure 5. ^{1}H NMR spectra of HT-P3HT in $CDCl_3$ at 25 °C. (a) HT-P3HT obtained by polymerization of **1** with 1.94 mol % $Ni(dppp)Cl_2$ in THF at rt for 30 min, followed by quenching with 5 M hydrochloric acid. (b) HT-P3HT with $Me_2C_6H_3$/$Me_2C_6H_3$ end groups obtained by the addition of 3,4-dimethylphenylmagnesium chloride to the polymerization mixture, followed by stirring at rt for 3 h.

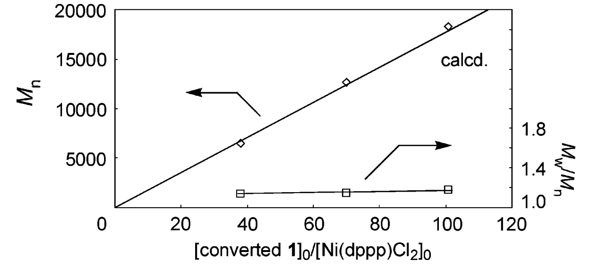

Figure 6. M_n and M_w/M_n values of HT-P3HT with Ar/Ar ends as a function of the molar ratio of converted **1** to $Ni(dppp)Cl_2$. M_n and M_w/M_n were determined by means of ^{1}H NMR spectroscopy and GPC, respectively.

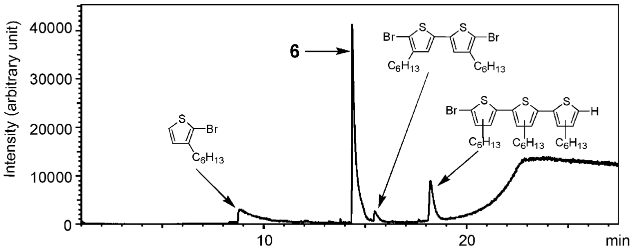

Figure 7. Gas chromatogram of reaction of **1** with 50 mol % $Ni(dppp)Cl_2$ at rt for 1 h.

end groups were obtained. McCullough and co-workers[10] reported similar results, but the introduction of aryl groups was not complete: polymers bearing Ar/Ar and Br/Ar end groups were obtained. The partial introduction of aryl groups would result from the formation of side reaction products during the polymerization of **1** as suggested by the termination reaction of polymerization[8] and the formation of Br/Br and H/H end group polymer obtained by the quenching of the polymerization before addition of aryl Grignard reagent,[9] both of which were not observed in our results. We tentatively speculated that the side reactions would be caused by an improper amount of Grignard reagent used to convert **2** into **1** as mentioned in the previous section and/or the insufficient purity of **2**.

Number of Polymer Molecules Formed per Ni Catalyst. On the basis of the above experiments, the average degree of polymerization (DP_n) and M_n can be determined from the ^{1}H NMR spectra. In the ^{1}H NMR spectra of HT-P3HT with $Me_2C_6H_3$/$Me_2C_6H_3$ end groups, the methyl proton signals of the dimethylphenyl groups at the two ends appeared at 2.32 and 2.31 ppm (Figure 5). Accordingly, on the basis of the integral ratio of the methyl proton signal **a** of the hexyl group in the repeat unit to the methyl signals **b** of the dimethylphenyl groups at the two ends, the DP_n and M_n were found to be 38 and 6500, respectively. Surprisingly, the feed ratio of the converted monomer **1** to the Ni catalyst in this polymerization was also 38. This result indicates that one Ni catalyst molecule forms one polymer chain and is in accordance with the result in the previous section that the propagating group of all the polymers is the Ni complex. Furthermore, when the polymerization was carried out with smaller amounts of the Ni catalyst, followed by reaction with 3,4-dimethylphenylmagnesium chloride, the M_n values determined similarly from the ^{1}H NMR spectra were in good agreement with the calculated values, assuming that one Ni catalyst molecule forms one polymer chain (Figure 6).

Initiator in the Reaction Mixture. Since the polymerization of **1** proceeds in a chain-growth polymerization manner and the M_n of the polymer is controlled by the feed ratio of **2** to the Ni catalyst despite the lack of addition of an initiator molecule, the chain initiator must be formed in situ via a reaction involving the Ni catalyst. According to the mechanism of the original coupling reactions between arylmagnesium halide and aryl halide in the presence of Ni(II) catalyst reported by Tamao et al.,[11] the Ni(II) is first reduced to Ni(0) by 2 equiv of arylmagnesium chloride, accompanied with the formation of aryl−aryl dimer, and then the generated Ni(0) starts the catalytic cycle of the coupling reaction. Therefore, in the polymerization of the Grignard monomer **1** in the presence of $Ni(dppp)Cl_2$, 2 equiv of **1** would react with $Ni(dppp)Cl_2$, followed by generation of the Ni(0) and the formation of a bithiophene having bromine atoms at each thiophene ring, which would be the initiator of this polymerization. To confirm this, **1** was reacted with 50 mol % $Ni(dppp)Cl_2$, and then the reaction mixture was quenched with 5 M hydrochloric acid and analyzed directly by GC/MS. The GC showed one main peak during 50−400 °C in the GC oven, with parent peaks at *m*/*z* 412 and 414 (Figure 7). This is consistent with the molecular weight value of 4,4′-dihexyl-5-bromo-2,2′-bithiophene (**6**) (MW = 412, 414). The tail-to-tail structure of **6** was determined from the two-dimensional heteronuclear multiple-bond correlation (HMBC) NMR spectrum[12] obtained after isolation of **6**. Other small peaks correspond to the quenched **1**, the bithiophene having two bromine atoms, and the terthiophene with H/Br ends on the basis of the *m*/*z* values. We thought at first that the bithiophene having two bromine atoms might be the initiator of the polymerization and would be detected by GC/MS. However, it was present in only a trace amount, and **6** was almost exclusively formed as a bithiophene. This result gives us important information about the polymerization mechanism. As described in the section on the propagating group, **6** would be obtained by hydrolysis of the nickel complex **5** with 5 M hydrochloric acid (Scheme 3). The formation of **5** indicates that the Ni(0), generated by the coupling reaction of **1**, is immediately inserted into one C−Br bond of the bithiophene having two bromine atoms. This insertion is thought to proceed intramolecularly without diffusion of the Ni(0), because the bithiophene without a bromine atom

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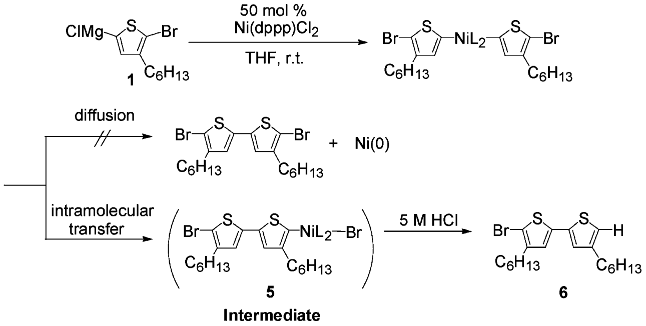
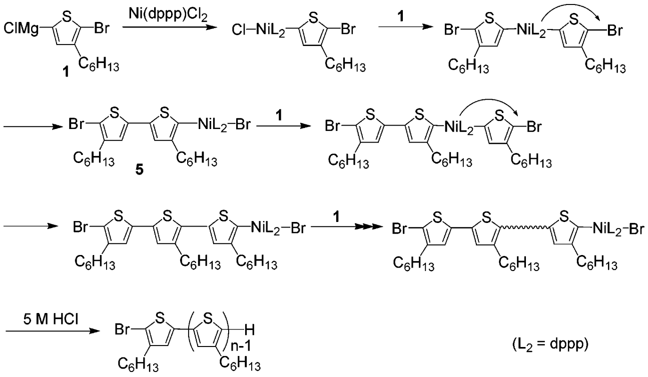
(12) See Supporting Information.

Scheme 3. Reaction of **1** with 50 mol % Ni(dppp)Cl$_2$



Scheme 4. Proposed Mechanism of Chain-Growth Polymerization of **1**



should be obtained in the intermolecular reaction of the bithiophene having two bromine atoms, even at 50 mol % Ni(0).

Proposed Mechanism of Chain-Growth Polymerization. In addition to the results in our previous paper that the polymerization of **1** proceeds in a chain-growth polymerization manner to yield HT-P3HT with low polydispersity and that the M_n is controlled by the feed ratio of **2** to the Ni catalyst,[6,7] we have now obtained further important results concerning the mechanism of this chain-growth polymerization of **1**: (1) the polymer end groups are uniform among molecules: one end group is a bromine atom and the other is a hydrogen atom; (2) the propagating end group is a Ni complex; (3) one Ni molecule forms one polymer chain; and (4) the chain initiator is **5** formed in situ via intramolecular transfer of Ni(0) after the coupling reaction. On the basis of these results, we believe that the mechanism illustrated in Scheme 4 is valid for the chain-growth polymerization of **1**. Thus, the polymerization is initiated by **5**, of which one molecule is generated per one Ni, and propagated by the coupling reaction between the polymer end group and monomer **1**, followed by the intramolecular transfer of the Ni(0) to the terminal C−Br bond to yield the polymer with Br/H ends after hydrolysis of the propagating Ni(II) complex. If the Ni(0) were inserted intermolecularly into the C−Br bond of the polymer end group, polymers with Br/Br and H/H end groups would be obtained, as well as the polymer with Br/H end groups. The molecular weight distribution would also become broader, because the coupling reaction would occur equally between all monomers and oligomers in a step-growth polymerization manner. However, these features are inconsistent with the observed results. A few other reactions involving similar intramolecular transfer of metal catalysts have recently been reported.[13−15] Consequently, the chain-growth polycondensation of **1** can be attributed not to the substituent effects seen in our chain-growth polycondensation[5] but rather to a specific reactivity of the Ni catalyst, which is transferred selectively to the elongated polymer propagating end. We call this type of polymerization "*catalyst-transfer polycondensation*." It should be noted that the mechanism of this catalyst-transfer polycondensation has conceptual similarity to that of the biosynthesis of biopolymers such as polypeptides,[1] in which the enzyme activates the polymer end group, followed by reaction with the monomer, and then moves to the end of the newly elongated polymer.

Conclusion

We have studied the mechanism of the chain-growth polymerization of **1**, affording HT-P3HT with defined molecular weight and low polydispersity. First, MALDI-TOF mass spectrometry showed that all the polymer molecules have the same end groups, that is, one bromine atom and one hydrogen atom. Subsequently, the propagating group, from which the H-end group is generated upon quenching, was determined to be a Ni complex from the result of the introduction of aryl groups at both ends with arylmagnesium chloride. Furthermore, ^{1}H NMR analysis of HT-P3HT with the Ar/Ar end groups allowed us to determine the average degree of polymerization and absolute molecular weight of the polymer, and it was found that one Ni catalyst molecule forms one polymer chain. Finally, the chain initiator was studied by the reaction of **1** with 50 mol % Ni(dppp)Cl$_2$, revealing that the initiator is the bithiophene formed by the coupling reaction of **1** accompanied with generation of the Ni(0) catalyst. On the basis of these results, we propose *catalyst-transfer polycondensation* as a new mechanism of chain-growth polycondensation. Thus, Ni(0) generated by the formation of the bithiophene is inserted intramolecularly into the C−Br bond of the bithiophene, and growth continues with the coupling reaction of **1** with the polymer end group, followed by the transfer of the Ni(0) to the terminal C−Br bond of the newly elongated monomer unit in a intramolecular fashion. We think that the catalyst-transfer polycondensation described here represents an important step forward from our chain-growth polycondensation, based on the change of substituent effects between monomer and polymer, and will be valuable for the synthesis of well-defined condensation polymers, including π-conjugated polymers. Studies of catalyst-transfer polycondensation for other conjugated polymers are currently in progress.

Experimental Section

2-Bromo-3-hexyl-5-iodothiophene (**2**) and 2-bromo-5-chloromagnesio-3-hexylthiophene (**1**) were prepared according to previously established procedures.[6] Isopropylmagnesium chloride (2.0 M solution in THF, Aldrich), 3,4-dimethylphenylmagnesium chloride (0.5 M solution in THF, Aldrich), phenylmagnesium chloride (2.0 M solution in THF, Aldrich), *tert*-butylmagnesium chloride (2.0 M solution in THF, TCI), [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (Ni(dppp)Cl$_2$, TCI), and dry tetrahydrofuran (THF, stabilizer-free, Kanto) were used as received without purification. Naphthalene, which was used

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as an internal standard for GC analysis, was purified by recrystallization from MeOH. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL ECA-600 with tetramethylsilane (TMS) as an internal standard. The M_n and M_w/M_n of polymers were measured on a Tosoh HLC-8020 gel-permeation chromatography (GPC) unit (eluent, THF; calibration, polystyrene standards) with two TSK-gel columns (2 × Multipore H_{XL}-M). MALDI-TOF mass spectra were recorded on a Shimadzu/Krotos Axima curved field reflectron (CFR) in the reflectron ion mode by use of a laser ($\lambda = 337$ nm). A sample solution of polymer and dithranol as a matrix was prepared in THF. Conversion of monomer was determined by analytical GC performed on a Shimadzu GC-14B gas chromatograph equipped with a GL Science dimethylsilicone fluid OV-101 column (3 m) and a flame ionization detector (FID), and analyses of conversion were carried out with naphthalene as an internal standard. GC mass spectra were obtained on a Shimadzu GCMS-QP5050A gas chromatograph−mass spectrometer with a Frontier Laboratories Ultra ALLOY capillary column UA$^+$-1(HT)-15M-0.1F.

All glass apparatus used for reactions was dried prior to use. Addition of reagents into the reaction flask and withdrawal of small aliquots of the reaction mixture for analysis were carried out via a syringe from the three-way stopcock under a stream of nitrogen.

General Procedure of Polymerization. A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. 2-Bromo-3-hexyl-5-iodothiophene **2** (373 mg, 1.00 mmol) and naphthalene (used as an internal standard for GC analysis; 56 mg, 0.044 mmol) were placed in the flask, and the atmosphere was replaced with argon. Into the flask was added dry THF (5.0 mL) via a syringe, and the mixture was stirred at 0 °C. To the mixture was added isopropylmagnesium chloride (2.0 M solution in THF, 0.50 mL, 1.0 mmol) via a syringe, and the mixture was stirred at 0 °C for 1 h. A suspension of Ni(dppp)Cl_2 (8.7 mg, 0.016 mmol, 1.60 mol %) in dry THF (5.0 mL) was added to the mixture via a syringe at 0 °C, and then the mixture was stirred at room temperature. After the reaction mixture had been stirred for 6 h (conversion = 85%), 5 M hydrochloric acid was added and the mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. To the residue was added MeOH. The insoluble material was washed well with MeOH and collected by suction filtration to give pure head-to-tail poly(3-hexylthiophene) ($M_n = 9300$, $M_w/M_n = 1.10$) as a purple solid (120 mg, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.98 (s, 1 H), 2.80 (t, $J = 7.7$ Hz, 2 H), 1.71 (quint, $J = 7.6$ Hz, 2 H), 1.48−1.38 (m, 2 H), 1.37−1.30 (m, 4 H), 0.91 (t, $J = 7.2$ Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.9, 133.7, 130.5, 128.6, 31.7, 30.5, 29.5, 29.3, 22.6, 14.1.

Reaction of Propagating Group with Grignard Reagent. A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. 2-Bromo-3-hexyl-5-iodothiophene **2** (373 mg, 1.00 mmol) and naphthalene (used as an internal standard for GC analysis; 36.1 mg, 0.282 mmol) were placed in the flask, and the atmosphere was replaced with argon. Into the flask was added dry THF (5.0 mL) via a syringe, and the mixture was stirred at 0 °C. To the mixture was added isopropylmagnesium chloride (2.0 M solution in THF, 0.50 mL, 1.0 mmol) via a syringe, and the whole was stirred at 0 °C for 1 h. A suspension of Ni(dppp)Cl_2 (10.5 mg, 0.0194 mmol, 1.94 mol %) in dry THF (5.0 mL) was added via a syringe at 0 °C, and the reaction mixture was stirred at room temperature. After 30 min, conversion of monomer and the M_n and M_w/M_n of the polymer formed were evaluated via a small aliquot of the reaction mixture, which was withdrawn via a syringe, quenched with 5 M hydrochloric acid, and extracted with Et_2O and then $CHCl_3$ (conversion = 74%, $M_n = 8400$, $M_w/M_n = 1.14$). Next, 3,4-dimethylphenylmagnesium chloride (0.5 M solution in THF, 1.5 mL, 0.8 mmol) was added to the reaction mixture via a syringe. Stirring was continued at room temperature for 6 h, and then water was added and the mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was washed well with MeOH and collected by suction filtration to give pure HT-P3HT with Ar/Ar ends ($M_n = 8600$, $M_w/M_n = 1.16$) as a purple solid (91.7 mg, 55%).

The reactions with various Grignard reagents (isopropylmagnesium chloride, phenylmagnesium chloride, and *tert*-butylmagnesium chloride) instead of 3,4-dimethylphenylmagnesium chloride were carried out similarly.

Identification of Initiator. A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. 2-Bromo-3-hexyl-5-iodothiophene **2** (373 mg, 1.00 mmol) was placed in the flask, and the atmosphere was replaced with argon. Into the flask was added dry THF (5.0 mL) via a syringe, and stirring was continued at 0 °C. To the mixture was added isopropylmagnesium chloride (2.0 M solution in THF, 0.50 mL, 1.0 mmol) via a syringe, and the mixture was stirred at 0 °C for 1 h. To a suspension of Ni(dppp)Cl_2 (271 mg, 0.500 mmol, 50 mol %) in dry THF (5.0 mL) was added the mixture via a syringe at 0 °C, and the whole was stirred at room temperature. After 1 h, a small aliquot of the reaction mixture was withdrawn for GC/MS analysis via a syringe, quenched with 5 M hydrochloric acid, and extracted with Et_2O. Then 5 M hydrochloric acid was added to the reaction mixture, and the whole was extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane) to give **6** as a pale yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.92 (d, $J = 1.4$ Hz, 1 H), 6.83 (br s, 1 H), 6.79 (m, 1 H), 2.56 (t, $J = 7.7$ Hz, 2 H), 2.52 (t, $J = 7.7$ Hz, 2 H), 1.64−1.56 (m, 4 H), 1.38−1.26 (m, 12 H), 0.92−0.86 (m, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.1, 142.8, 137.2, 136.4, 125.1, 124.2, 119.1, 107.3, 31.7, 31.6, 30.5, 30.3, 29.62, 29.58, 29.0, 28.9, 22.6, 14.1.

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Supporting Information Available: Whole view of Figure 4 and the two-dimensional HMBC NMR and ^{1}H NMR spectra of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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