Investigation of Catalyst-Transfer Condensation Polymerization for the Synthesis of *n*-Type π-Conjugated Polymer, Poly(2-dioxaalkylpyridine-3,6-diyl)

Yutaka Nanashima, Rena Shibata, Ryo Miyakoshi, Akihiro Yokoyama, Tsutomu Yokozawa

Department of Material and Life Chemistry, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-Ku, Yokohama 221-8686, Japan
Correspondence to: T. Yokozawa (E-mail: yokozt01@kanagawa-u.ac.jp)

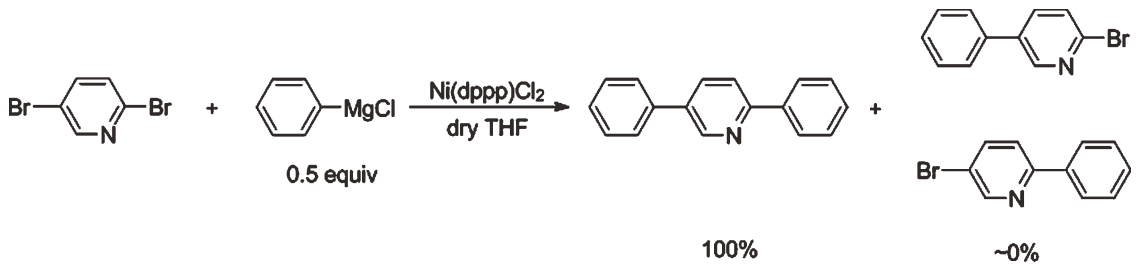
Received 13 April 2012; accepted 3 May 2012; published online
DOI: 10.1002/pola.26152

ABSTRACT: Kumada-Tamao coupling polymerization of 6-bromo-3-chloromagnesio-2-(3-(2-methoxyethoxy)propyl)pyridine **1** with a Ni catalyst and Suzuki-Miyaura coupling polymerization of boronic ester monomer **2**, which has the same substituted pyridine structure, with $^{t}Bu_3PPd$(*o*-tolyl)Br were investigated for the synthesis of a well-defined *n*-type π-conjugated polymer. We first carried out a model reaction of 2,5-dibromopyridine with 0.5 equivalent of phenylmagnesium chloride in the presence of Ni(dppp)Cl_2 and then observed exclusive formation of 2,5-diphenylpyridine, indicating that successive coupling reaction took place via intramolecular transfer of Ni(0) catalyst on the pyridine ring. Then, we examined the Kumada-Tamao polymerization of **1** and found that it proceeded homogeneously to afford soluble, regioregular head-to-tail poly(pyridine-2,5-diyl), poly(3-(2-(2-(methoxyethoxy)propyl)pyridine) (PMEPPy). However, the molecular weight distribution of the polymers obtained with several Ni and Pd catalysts was very broad, and the matrix-assisted laser desorption ionization time-of-flight mass spectra showed that the polymer had Br/Br and Br/H end groups, implying that the catalyst-transfer polymerization is accompanied with disproportionation. Suzuki-Miyaura polymerization of **2** with $^{t}Bu_3PPd$(*o*-tolyl)Br also afforded PMEPPy with a broad molecular weight distribution, and the tolyl/tolyl-ended polymer was a major product, again indicating the occurrence of disproportionation. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: catalysts; catalyst-transfer condensation polymerization; conjugated polymers; Kumada-Tamao coupling reaction; living polymerization; MALDI; *n*-type π-conjugated polymer; polypyridine

INTRODUCTION π-Conjugated polymers have received much attention because of their application in electronic devices such as thin-film transistors,[1] organic light-emitting diodes,[2] and photovoltaic cells.[3] Many π-conjugated polymers have been conventionally synthesized by step-growth polymerization, and therefore, it was difficult to control the molecular weight and to obtain polymers with low polydispersity.[4,5] However, the development of chain-growth condensation polymerization with a transition metal catalyst has made it possible to synthesize well-defined π-conjugated polymers.[6,7] We have proposed that this polymerization involves intramolecular catalyst transfer on the polymer backbone.[7] Kumada-Tamao catalyst-transfer condensation polymerization (KTCTCP) with a Ni catalyst yields well-defined poly(alkylthiophene)s,[8–16] polyfluorenes,[17,18] polyphenylenes,[19] and poly(*N*-alkylpyrrole)s,[18,20] as well as block copolymers[7] and gradient copolymers.[21]

However, KTCTCP has been limited to the polymerization of donor monomers for the synthesis of *p*-type π-conjugated polymers. The KTCTCP of acceptor monomers faces the following difficulties: (1) some electron-withdrawing groups such as carbonyl group in acceptor monomers cannot tolerate the conditions used for the formation of Grignard monomer; (2) the solubility of *n*-type π-conjugated polymers is generally lower than that of *p*-type ones because acceptor aromatics have stronger π–π stacking interaction than donor aromatics; and (3) the weaker π-donation of the *n*-type polymer backbone to Ni(0) catalyst may not sufficiently assist intramolecular catalyst transfer. Kiriy and coworkers have recently advanced this field and synthesized well-defined *n*-type π-conjugated copolymers by means of Suzuki-Miyaura coupling polymerization of a fluorene-benzothiadiazole monomer with a Pd catalyst[22] and by means of an unusual coupling polymerization of an anion radical of a thiophene-naphthalenediimide-thiophene monomer with a Ni catalyst,[23] both of which proceed in a chain-growth polymerization manner, presumably via a catalyst-transfer mechanism. To our knowledge, however, the KTCTCP of acceptor monomer



SCHEME 1 Model reaction of 2,5-dibromopyridine with a half equivalent of phenylmagnesium chloride in the presence of Ni(dppp)Cl_2.

consisting of a single arene structure has not been reported. We set out to explore the KTCTCP of simple acceptor monomers by focusing on the polymerization of pyridine monomers, which can be formed, without decomposition, from dihalopyridine with alkyl Grignard reagent.[24] The polymerization of 3-alkoxy-2-bromo-5-chloromagnesiopyridine unfortunately afforded a polymer insoluble in the reaction solvent, and we were not able to explore the KTCTCP.[25] On the other hand, the polymerization of 2-alkoxy-5-bromo-3-chloromagnesiopyridine proceeded via a catalyst-transfer polymerization mechanism to yield poly(2-(2-(2-methoxyethoxy)ethoxy)pyridine-3,5-diyl) (*m*-PMEEOPy) with well-defined molecular weight and narrow polydispersity.[26] However, this polypyridine, in which the repeat unit is connected at the 3,5-position, like the meta-positions in a benzene ring, is an nonconjugated polymer, and the electron-donating alkoxy group decreases the electron acceptor nature of the pyridine repeat unit. Accordingly, we should consider KTCTCP of para-substituted pyridine monomer bearing an alkyl side chain for the synthesis of well-defined *n*-type π-conjugated polymers. In this article, we report an investigation of the Kumada-Tamao coupling polymerization of 6-bromo-3-chloromagnesio-2-(3-(2-methoxyethoxy)propyl)pyridine **1** with a Ni catalyst to see whether the polymerization proceeds in a controlled manner via a catalyst-transfer polymerization mechanism. Furthermore, Suzuki-Miyaura coupling polymerization of boronic acid ester monomer **2**, having the same substituted pyridine structure, with ^{t}Bu$_3$PPd(*o*-tolyl)Br was also investigated to evaluate side reactions associated with this pyridine structure.

RESULTS AND DISCUSSION

Model Reaction

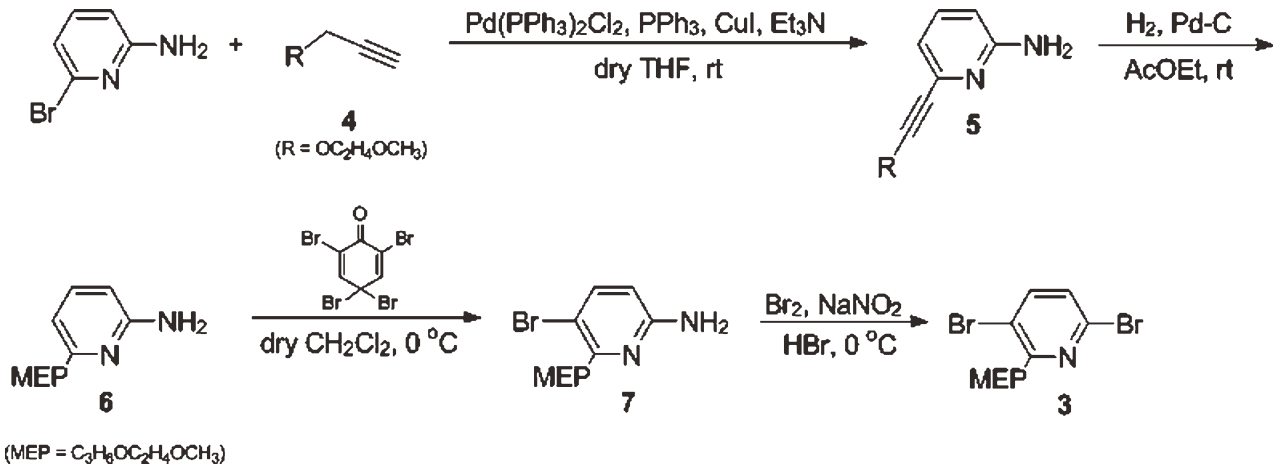
We first examined whether the Ni catalyst would intramolecularly walk on the acceptor pyridine ring between the para-positions by means of a model reaction, as we had done in our previous investigation of the KTCTCP of meta-substituted pyridine monomer.[26] Thus, 2,5-dibromopyridine was reacted with a half equivalent of phenylmagnesium chloride in the presence of a catalytic amount of Ni(dppp)Cl_2 [dppp = 1,3-bis(diphenylphosphino)propane] in tetrahydrofuran (THF) at ambient temperature. The products were analyzed by gas chromatography (GC), GC-mass spectroscopy (GC-MS), and ^{1}H NMR spectroscopy, and it turned out that 2,5-diphenylpyridine was quantitatively formed (Scheme 1). This result indicated that successive coupling reaction took place via intramolecular transfer of Ni(0) catalyst on the pyridine ring bearing no electron-donating alkoxy group, even though the π-donation ability of pyridine is weaker than that of donor monomers such as thiophene. Therefore, we expected that the polymerization of para-substituted pyridine monomer bearing an alkyl group would also proceed via a catalyst-transfer chain-growth polymerization mechanism to yield regioregular poly(pyridine-2,5-diyl) with well-defined molecular weight and low polydispersity.

Synthesis of Monomer Precursor

Poly(2-alkylpyridine-3,6-diyl)s were reported to be synthesized by means of Ni-catalyzed Kumada-Tamao coupling polymerization in THF under reflux,[24] but are not soluble in THF at ambient temperature.[27] We have found that dioxaalkyl and trioxaalkyl groups are effective for increasing the solubility of aromatic polyester[28] and polythiophene.[11] Therefore, we decided to examine the effect of introducing methoxyethoxypropyl (MEP) groups into polypyridine. Monomer precursor **3**, 3,6-dibromo-2-(3-(2-methoxyethoxy)propyl)pyridine, was synthesized as shown in Scheme 2. Sonogashira coupling reaction[29] of commercially available 2-amino-6-bromopyridine and 3-(2-methoxyethoxy)-1-propyne **4**, which was easily obtained by Williamson ether synthesis from 2-methoxyethanol and propargyl bromide, was carried out with Pd and copper catalysts, and the resulting 2-amino-6-(dioxaalkynyl)pyridine **5** was hydrogenated to afford 2-amino-6-MEP-pyridine **6**. The carbon adjacent to the MEP group location in **6** was selectively brominated with 2,4,4,6-tetrabromo-2,5-cyclohexadienone.[30] The amino group of the obtained **7** was converted to bromine by treatment with Br_2, HBr, and $NaNO_2$ to yield the monomer precursor **3**.

Polymerization from Dibromo Precursor 3

Monomer precursor **3** was converted to Grignard monomer **1** by treatment with 1 equivalent of isopropylmagnesium chloride (^{i}PrMgCl) in THF at room temperature for 24 h (conversion of **3** = 85%). It was confirmed by means of ^{1}H NMR and GC analysis that the bromine at the 3-position of **3** was exclusively converted to a chloromagnesio group. Polymerization of **1** was then carried out by the addition of several Ni and Pd catalysts to the reaction mixture (Scheme 3 and Table 1). First, Ni(dppp)Cl_2 was evaluated, because it is a suitable Ni catalyst for the synthesis of well-defined poly(3-hexylthiophene)[10] and *m*-PMEEOPy.[26] The polymerization



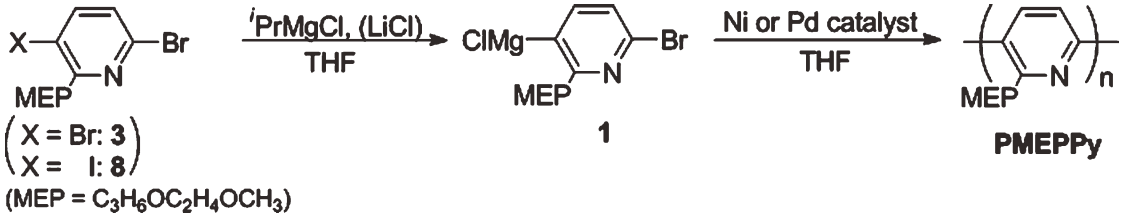
SCHEME 2 Synthesis of monomer precursor **3**.

proceeded smoothly at room temperature, and the conversion of **1** was 89% in 3 h. The obtained polymer had a very broad polydispersity, and pure poly(3-(2-(2-(methoxyethoxy)propyl)pyridine) (PMEPPy) was obtained by washing the crude product with methanol to remove low-molecular-weight oligomers (Fig. 1, entry 1). The obtained pure PMEPPy was readily soluble in common organic solvents, such as $CHCl_3$, CH_2Cl_2, and THF, as we had expected, but insoluble in hexane, diethyl ether, ethyl acetate, acetone, *N*,*N*-dimethylformamide, and methanol. The regioregularity was highly controlled as head-to-tail (HT) unit (Fig. 2). On the basis of assignment of the signals in the ^{1}H NMR spectrum of poly(2-hexylpyridine-3,6-diyl),[24] the α-CH_2 signal of the MEP group of the HT units of PMEPPy appeared at $\delta = 3.16$, whereas that of the head-to-head (HH) units appeared at $\delta = 2.68$ as a very small signal. The HT content of PMEPPy was estimated as higher than 97% from the integral ratio of the HT and HH signals. The UV–vis and photoluminescence spectra of PMEPPy in $CHCl_3$ are depicted in Figure 3. The absorption maxima (λ_{max}) and the photoluminescence maxima ($\lambda_{max\ em}$) are similar to those of poly(2-hexylpyridine-3,6-diyl).[31]

When Ni catalysts with different ligands, Ni(dppe)Cl_2 (dppe = 1,2-bis(diphenyl-phosphino)ethane) (entry 5) and Ni(dppf)Cl_2 (dppf = 1,1′-bis(diphenylphosphino)-ferrocene) (entry 6), were used, the products also showed broad polydispersity. Ni(dcpe)Cl_2 (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) (entry 7), Ni$(PPh_3)_2Cl_2$ (entry 8), and Ni$(Bu_3P)_2Cl_2$ (entry 9) resulted in low conversion of **1**, affording polymers with low molecular weight (entries 7–9) and broad polydispersity (entries 8 and 9). Pd catalysts were also not effective for obtaining polymers with low polydispersity (entries 10–13). As Ni(dppp)Cl_2 gave the highest molecular weight polymer, we further examined the polymerization with Ni(dppp)Cl_2 under various conditions. An increase in polymerization temperature from room temperature to 50 °C resulted in broader polydispersity (entry 2). Polymerization in the presence of LiCl[19,26] (entry 3) or dppp[20] (entry 4) also did not afford polymer with low polydispersity.

To examine the cause of the uncontrolled polymerization, the end groups of PMEPPy obtained by the polymerization of **3** with 1.0 equivalent of ^{i}PrMgCl and Ni(dppp)Cl_2 were analyzed by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry with dithranol (1,8-dihydroxy-9[10*H*]-anthracenone) as a matrix in the presence of potassium trifluoroacetate as a cationizing agent. As shown in Figure 4, the polymer provided three series of peaks. The major peaks are consistent with the values calculated by using the formula 193.1*n* (repeat unit) + 79.9 (Br) + 1.0 (H) + 39.1 (K^+), where *n* is the number of repeat units. Therefore, one of the end groups of the polymer is a bromine atom and the other is a hydrogen atom (designated as Br/H). Moreover, the other two series of minor peaks could be easily assigned to the K^+ adducts of Br/Br- and H/H-ended polymers.

It was reported that the MALDI-TOF mass spectra of poly(3-alkylthiophene)s with broad polydispersity, which were obtained by typical step-growth Ni-catalyzed polymerization



SCHEME 3 Polymerization of **1** for the synthesis of PMEPPy.

TABLE 1 Polymerization of **1** with various catalysts[a]

Entry	Cat.	Additive	Temp. (°C)	Time (h)	Conv. of 1(%)[b]	Crude Product $M_n(M_w/M_n)$[c]	Purified Product $M_n(M_w/M_n)$[c]	Regioregularity[d] (HT %)
1	$Ni(dppp)Cl_2$	–	rt	3	89	8400 (6.37)	16,800 (7.49)[e]	97
2		–	50	1	95	6650 (10.5)	–[f]	–[f]
3		LiCl[g]	rt	6	96	6000 (3.99)	–[f]	–[f]
4		dppp[h]	rt	1	78	4200 (12.3)	–[f]	–[f]
5	$Ni(dppe)Cl_2$	–	rt	3	78	3500 (7.86)	7,700 (3.48)[e]	98
6	$Ni(dppf)Cl_2$	–	rt	3	93	8500 (6.75)	13,500 (4.36)[e]	96
7	$Ni(dcpe)Cl_2$	–	rt	6	24	510 (1.03)	–[f]	–[f]
8	$Ni(PPh_3)_2Cl_2$	–	rt	6	73	1500 (4.78)	10,400 (1.97)	94
9	$Ni(Bu_3P)_2Cl_2$	–	rt	3	60	2100 (2.72)	6,100 (1.74)[i]	90
10	$Pd(dppp)Cl_2$	–	rt	6	39	710 (1.89)	–[f]	–[f]
11		–	50	6	85	1300 (2.17)	1,940 (1.89)[i]	76
12	$Pd(dppe)Cl_2$	–	50	6	98	2400 (1.96)	–[f]	–[f]
13	$Pd[(^tBu_3P)]_2$	–	50	6	20	1850 (6.91)	–[f]	–[f]

[a] Polymerization of **1** was carried out by treatment of **3** with 1.0 equiv of ^{i}PrMgCl, followed by addition of 1.8 mol % of Metal (ligand)Cl_2.
[b] Determined by GC.
[c] Estimated by GPC based on polystyrene standards (eluent: THF)
[d] Determined by ^{1}H NMR.
[e] Purified by washing with MeOH.
[f] Not determined.
[g] LiCl equimolar to **3**.
[h] Dppp equimolar to catalyst.
[i] Purified by HPLC.

of the corresponding chloromagnesio monomers, showed three kinds of end groups corresponding to Br/H, Br/Br, and H/H.[32] Therefore, one might suggest that the polymerization of **1** had proceeded via a step-growth polymerization mechanism. However, the molecular weight distribution of PMEPPy obtained by the polymerization of **1** with $Ni(dppp)Cl_2$ was very much broader than that of polymers obtained by step-growth polymerization, in which the molecular weight distribution theoretically approaches 2 at high conversion. Furthermore, the results of the model reaction indicated that the Ni catalyst has a propensity for intramolecular transfer on the pyridine ring. Accordingly, we consider that the formation of the Br/H, Br/Br, and H/H end groups of PMEPPy can be rationalized on the basis of catalyst-transfer polymerization accompanied with side reactions as follows (Scheme 4). The Br/H end is generally formed by catalyst-transfer polymerization: initiation from dibromo dimer, propagation via intramolecular transfer of the Ni catalyst to the polymer end group, and hydrolysis of the polymer-Ni(II)-Br end group with hydrochloric acid, leading to the H end group. However, the H end group might also be formed from the polymer-Ni-H complex, which is generated by β-hydride elimination of the polymer-Ni-^{i}Pr complex, because ^{i}PrMgCl remained in the reaction mixture; conversion of **3** to **1** with ^{i}PrMgCl was 85% [Scheme 4(A)]. The Ni(0) generated by reductive elimination from the polymer-Ni-H would be inserted into the C—Br bond of monomer **1** and/or of polymer with H/Br ends, followed by propagation and quenching with hydrochloric acid to afford polymer with H/H ends [Scheme 4(B,C)]. The Br/Br-ended polymers might be formed via disproportionation between Br/Ni(II)Br-ended polypyridines, followed by reductive elimination to afford coupled polymers

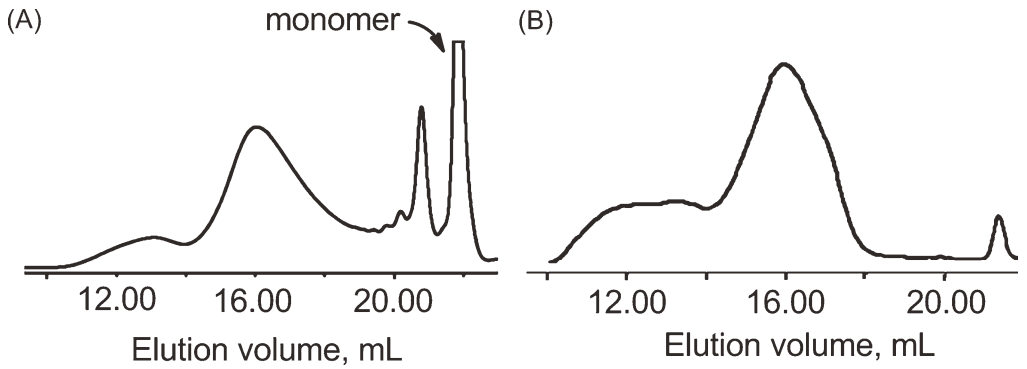


FIGURE 1 GPC profiles of PMEPPy obtained by the polymerization of **1**, formed by the reaction of **3** with 1.0 equivalent of ^{i}PrMgCl, with 1.8 mol % of $Ni(dppp)Cl_2$ at room temperature for 3 h: (A) crude product and (B) purified product obtained by washing with methanol.

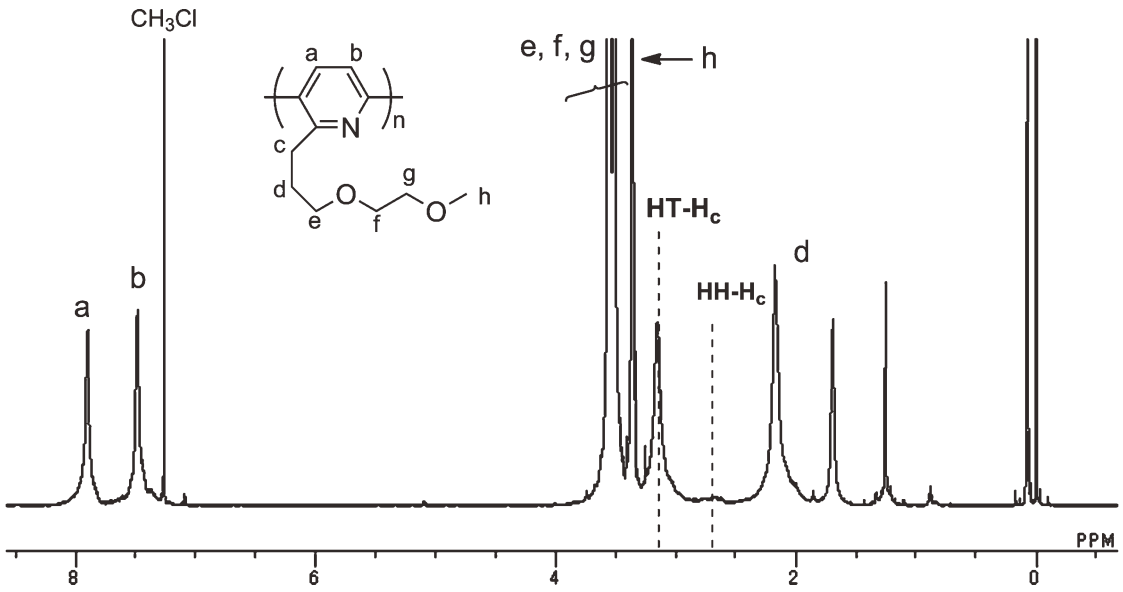


FIGURE 2 ^{1}H NMR spectrum of PMEPPy (M_n = 16,800, M_w/M_n = 7.49) in $CDCl_3$ at 25 °C.

[Scheme 4(D)]. The small peak in the higher molecular weight region in the gel permeation chromatography (GPC) elution curve of the obtained polymer could be due to this disproportionation product.

Polymerization from Bromiodo Precursor 8

If unreacted ^{i}PrMgCl does not remain in the reaction mixture, the complicated mechanisms described above would be simplified and it might be possible to establish a more precise polymerization mechanism of **1**. Therefore, we used 6-bromo-2-MEP-3-iodopyridine **8** as a monomer precursor instead of dibromo precursor **3**, hoping for quantitative generation of Grignard monomer **1** via a more facilitated magnesium-iodo exchange reaction. Indeed, the reaction of **8** with 1.0 equivalent of ^{i}PrMgCl in THF at 0 °C for 5 min quantitatively yielded Grignard monomer **1** (100% conversion of **8** as determined by analytical GC). The polymerization of **1** was then carried out at room temperature by the addition of 1.8 mol % of Ni(dppp)Cl_2 to the reaction mixture. However, the polymerization proceeded slowly, and the GPC profile of the products showed a very broad polydispersity [Fig. 5(A)]. This presumably arises from aggregation of Grignard monomer **1**, as in the case of the polymerization of *p*-phenylene monomer[19] and *m*-pyridine monomer.[26] Accordingly, the polymerization of **1** with Ni(dppp)Cl_2 was carried out in the presence of 1.0 equivalent of LiCl. This caused the polymerization to proceed more quickly; however, the molecular weight distribution of the obtained polymer was as broad as that of the polymer obtained from precursor **3** [Fig. 5(B)].

The MALDI-TOF mass spectrum of PMEPPy obtained at 1 h (M_n = 10,300, M_w/M_n = 4.35) contained one major series of peaks, corresponding to the K^+ adducts of the Br/Br-ended polymer, accompanied by two minor series of peaks (Fig. 6). The two minor series of peaks correspond to the K^+ adducts of PMEPPy with Br/H ends and the Na^+ adducts of PMEPPy

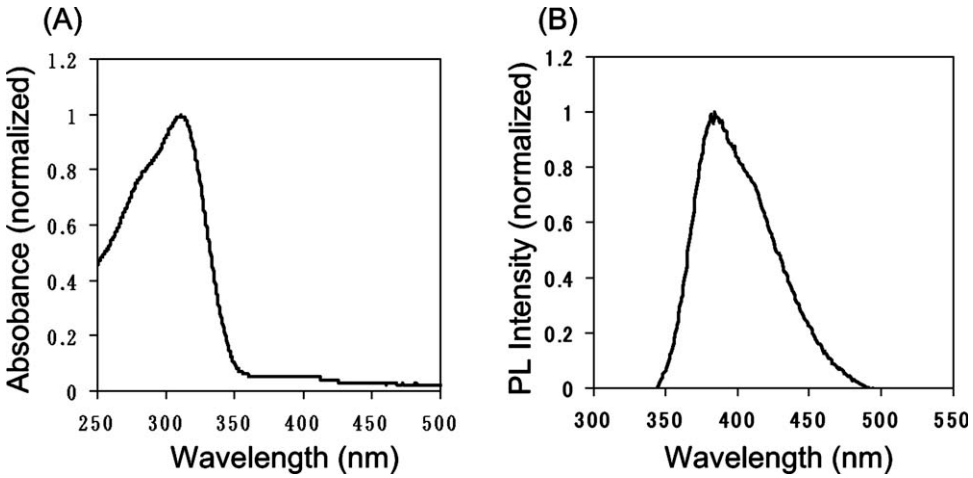


FIGURE 3 (A) UV–vis spectrum and (B) photoluminescence (PL) spectrum of PMEPPy in chloroform solution (~10^{-5} M).

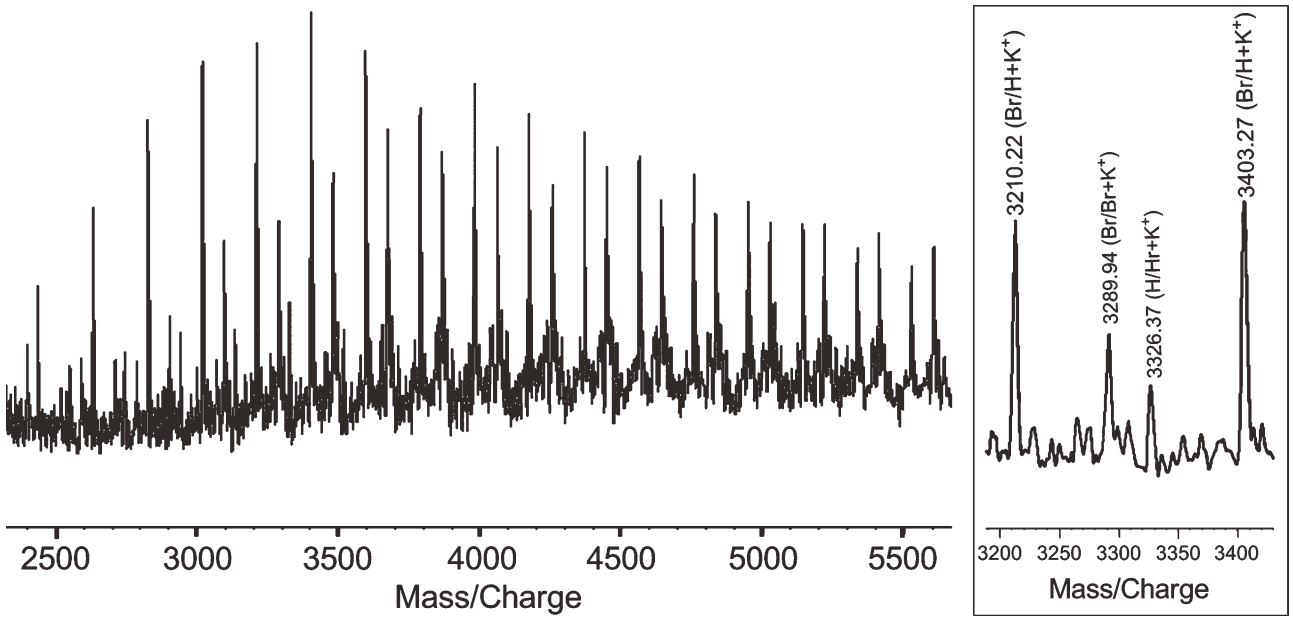
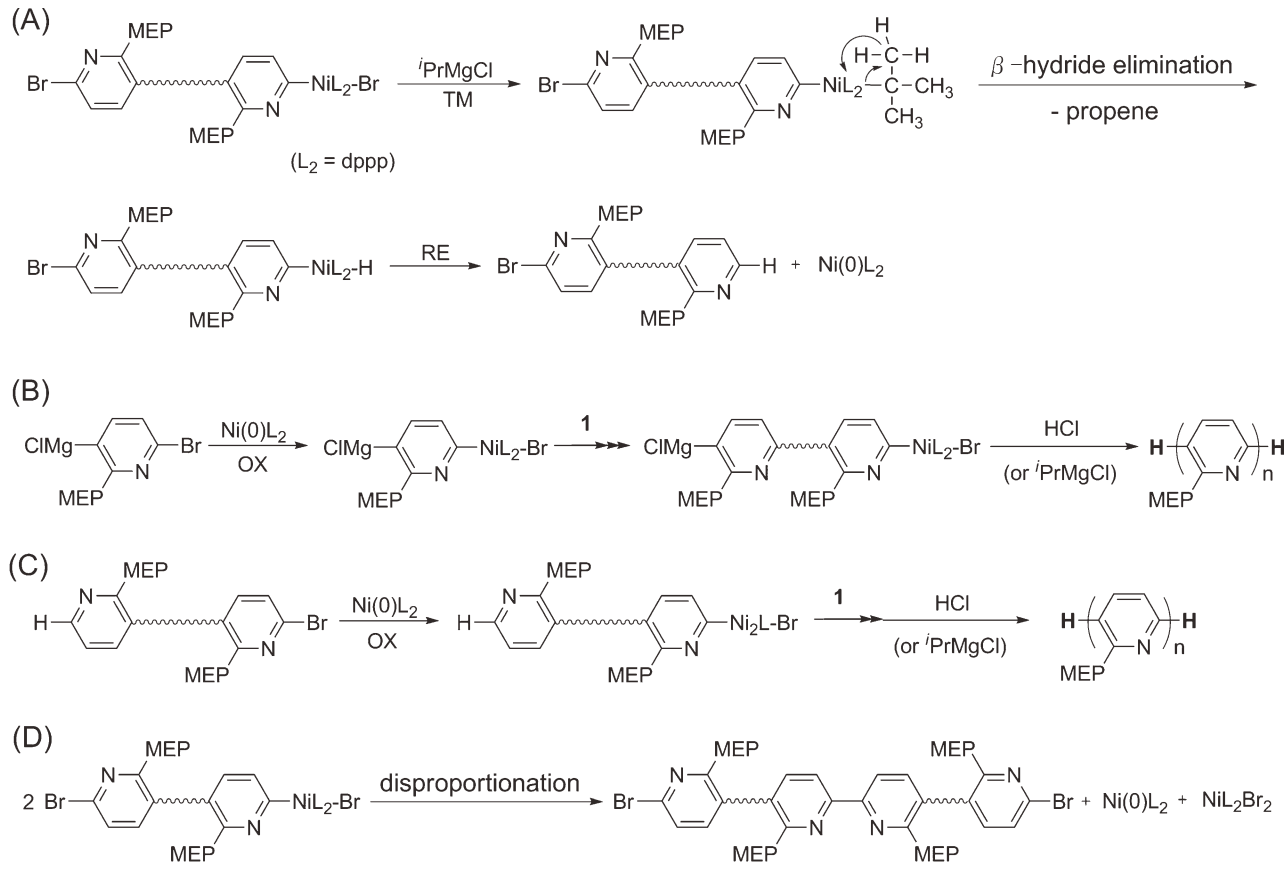


FIGURE 4 MALDI-TOF mass spectra of PMEPPy obtained by the polymerization of **1**, formed by the reaction of **3** with 1.0 equivalent of ^{i}PrMgCl, with 1.8 mol % of Ni(dppp)Cl_2 at room temperature for 1 h ($M_n = 5100$, $M_w/M_n = 3.14$).



TM = transmetalation, RE = reductive elimination, OX = oxidative addition

SCHEME 4 Proposed mechanism of production of (A) Br/H, (B and C) H/H and (D) Br/Br-ended PMEPPy by the polymerization of **1**, formed by the reaction of **3** with ^{i}PrMgCl, with Ni(dppp)Cl_2.

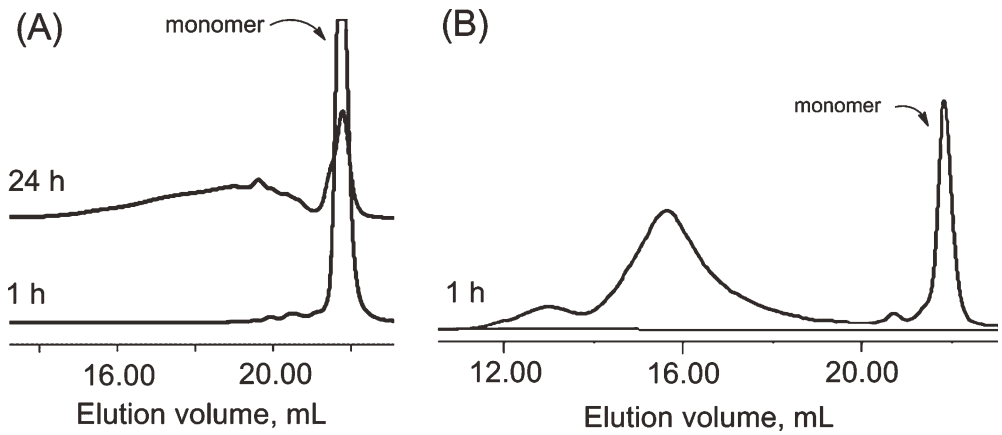


FIGURE 5 GPC profiles of PMEPPy obtained by the polymerization of **1**, formed by the reaction of **8** with 1.0 equivalent of ^{i}PrMgCl, with 1.8 mol % of Ni(dppp)Cl_2 (A) in the absence of LiCl at room temperature for 1 and 24 h (M_n = 1300, M_w/M_n = 4.49) and (B) in the presence of 1.0 equivalent of LiCl at room temperature for 1 h (M_n = 10,300, M_w/M_n = 4.35).

with Br/Br ends. Peaks due to H/H-ended polymers were not observed in this case, implying that the formation of the H/H-ended polymer involves the reaction of the polymer-Ni(II)-Br end group with residual ^{i}PrMgCl. Accordingly, the main product was PMEPPy with Br/Br ends, which was presumably formed via disproportionation, as discussed in the previous section.

We next followed the time course of the polymerization to clarify when PMEPPy with Br/Br ends was formed. The GPC profiles of the products showed two peaks from the beginning, and both peaks were shifted toward the higher molecular weight region with increasing reaction time [Fig. 7(A)]. In the MALDI-TOF mass spectra, the major peaks were always those of the Br/Br-ended polymers from the early stage to the final stage [Fig. 7(B)]. This result indicated that disproportionation occurred continually from the initial stage of polymerization. Thus, the polymerization of **1** with Ni(dppp)Cl_2 proceeds essentially via an intramolecular catalyst-transfer polymerization mechanism to afford PMEPPy with Br/H ends after hydrolysis of the polymer-Ni-Br complex; however, disproportionation reaction continually occurs to afford PMEPPy with Br/Br ends, as well as Ni(II) and Ni(0) complex, which can initiate the polymerization from **1** and insert into the terminal C—Br bond, followed by repropagation, respectively (Scheme 5). The tendency for occurrence of disproportionation in the polymerization of pyridine monomer **1**, in contrast to the absence of disproportionation in the KTCTCP of thiophene,[8] phenylene,[19] pyrrole,[20] and even 2-alkoxy-5-bromo-3-chloromagnesiopyridine[26] monomers, can presumably be attributed to coordination of the pyridine nitrogen adjacent to carbon-Ni-Br end to the Ni in

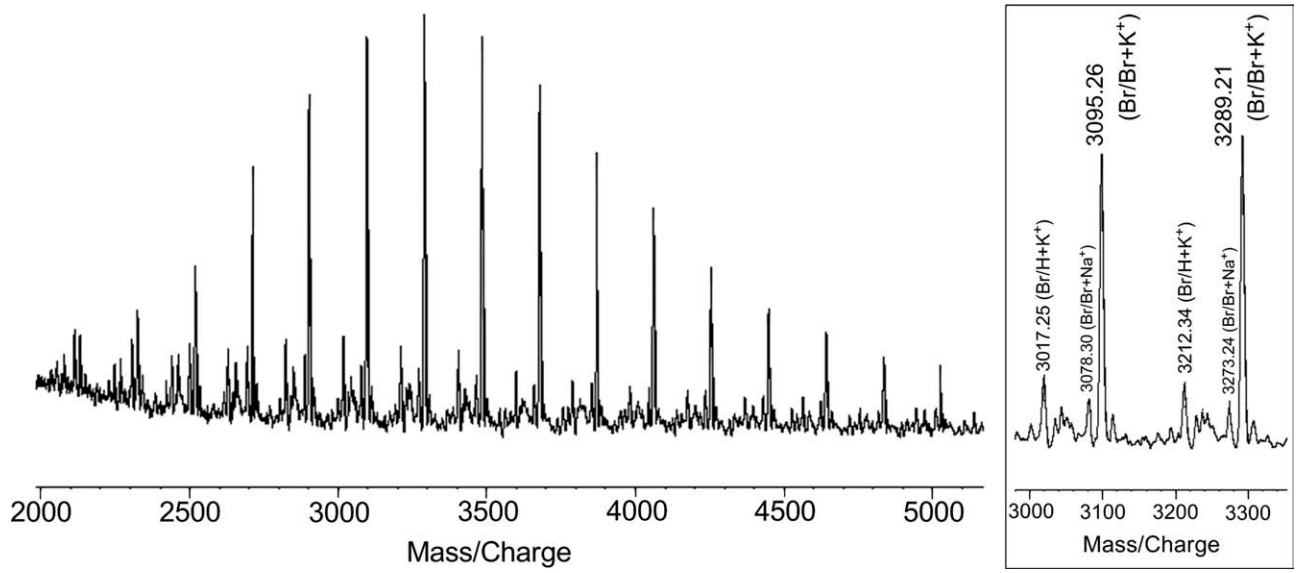


FIGURE 6 MALDI-TOF mass spectra of PMEPPy obtained by the polymerization of **1**, formed by the reaction of **8** with 1.0 equivalent of ^{i}PrMgCl, with 1.8 mol % of Ni(dppp)Cl_2 in the presence of 1.0 equivalent of LiCl at room temperature for 1 h (M_n = 10,300, M_w/M_n = 4.35).

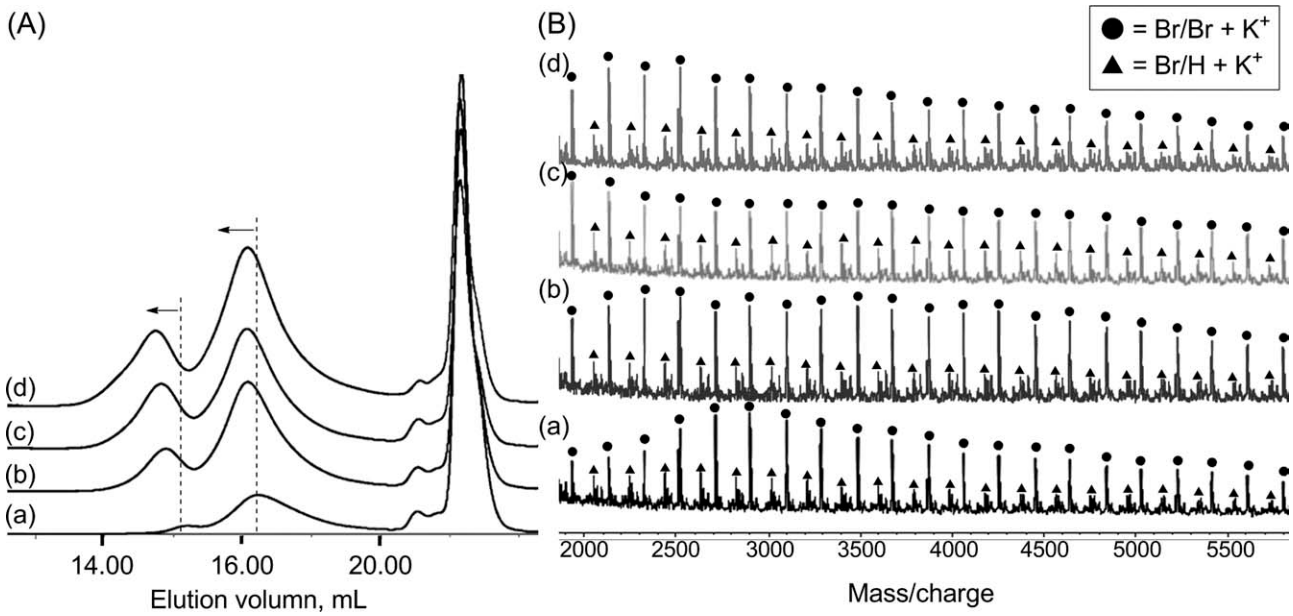


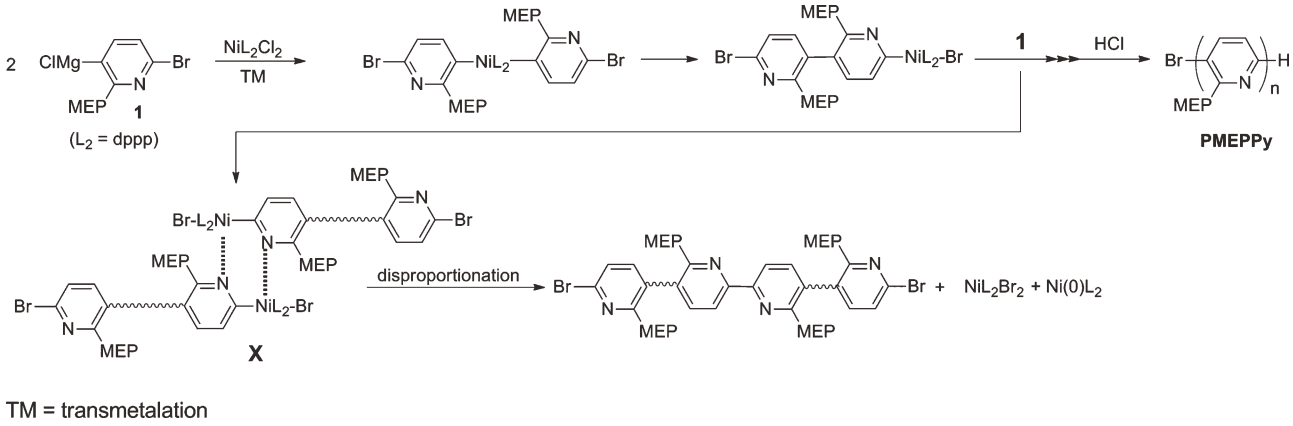
FIGURE 7 (A) GPC profiles and (B) MALDI-TOF mass spectra of PMEPPy obtained by the polymerization of **1**, formed by the reaction of **8** with 1.0 equivalent of ^{i}PrMgCl, with 1.8 mol % of Ni(dppp)Cl_2 in the presence of 1.0 equivalent of LiCl at room temperature for (a) 15 min (M_n = 8440, M_w/M_n = 2.16), (b) 30 min (M_n = 12,240, M_w/M_n = 3.13), (c) 45 min (M_n = 13,690, M_w/M_n = 3.79), and (d) 60 min (M_n = 13,100, M_w/M_n = 4.29).

another pyridine-Ni-Br end, as shown in complex X in Scheme 5.

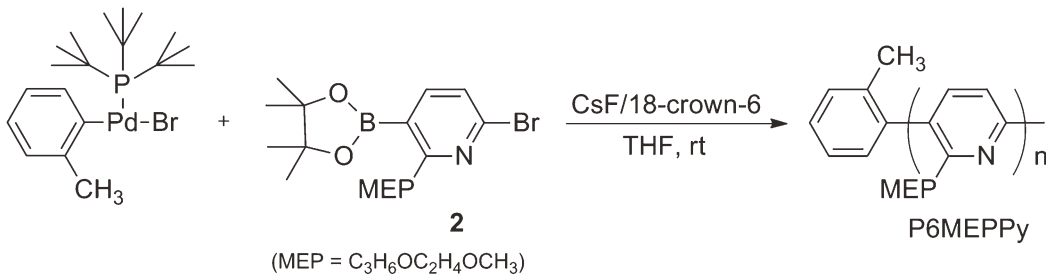
Suzuki-Miyaura Coupling Polymerization of 2

We speculated that disproportionation occurred in the Kumada-Tamao coupling polymerization of **1** because the nitrogen adjacent to carbon-Ni-Br coordinates to the Ni of another propagating end, that is, 6-bromopyridine monomers would be unsuitable for catalyst-transfer condensation polymerization, even though the catalyst can walk on the pyridine ring. We were next interested to see whether similar disproportionation would take place in the Suzuki-Miyaura coupling polymerization of a boronic ester monomer having the same pyridine structure with a Pd catalyst.

The corresponding pinacol boronate monomer **2** was synthesized from **3** by a standard method.[33] The polymerization of **2** with $^{t}Bu_3PPd$(*o*-tolyl)Br was carried out in the presence of CsF/18-crown-6 in THF containing a small amount of water at room temperature according to the Suzuki-Miyaura catalyst-transfer condensation polymerization protocols for the synthesis of poly(*p*-phenylene)[34] and polythiophene[35] (Scheme 6). The GPC profile of PMEPPy obtained up to 3 min had a relatively high molecular weight and a narrow molecular weight distribution; however, a peak in the low-molecular-weight region appeared at 5 min. After 15 min, the GPC showed a bimodal distribution, and then the two peaks merged into one broad peak at 24 h [Fig. 8(A)]. We also followed the polymerization by using MALDI-TOF mass spectrometry to check the polymer end groups [Fig. 8(B)]. The polymer obtained at 3 min had mainly tolyl groups at both ends, whereas the polymer with tolyl/Br ends became the main product at 15 min. The polymer obtained after 24



SCHEME 5 Proposed polymerization mechanism of **1**, formed by the reaction of **8** with ^{i}PrMgCl, with Ni(dppp)Cl_2.



SCHEME 6 Polymerization of **2** for the synthesis of PMEPPy.

h again had tolyl/tolyl ends. PMEPPy with tolyl/tolyl ends would have been formed via disproportionation. Consequently, it turns out that the unsatisfactory catalyst-transfer polymerization of **1** and **2** is due to disproportionation arising from the 6-bromopyridine structure of the monomers.

EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were obtained on JEOL ECA-500 and ECA-600 spectrometers. The internal standards for ^{1}H NMR spectra in $CDCl_3$ and DMSO-d_6 were tetramethylsilane (0.00 ppm) and the midpoint of CD_2H (2.50 ppm), respectively, and the internal standards for ^{13}C NMR spectra in $CDCl_3$ and DMSO-d_6 were the midpoints of $CDCl_3$ (77.0 ppm) and CD_3 (39.8 ppm), respectively. All melting points were measured with a Yanagimoto hot-stage melting point apparatus without correction. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh; Merck) with a specified solvent. Commercially available dehydrated THF (stabilizer-free; Kanto) and dehydrated dichloromethane (Kanto) were used as dry solvents. The conversion of monomer was determined by analytical GC performed on a Shimadzu GC-2010 gas chromatograph equipped with a Restek dimethypolylsiloxane fluid Rtx-1 column (15 m) and a flame ionization detector. GC mass spectra were obtained on a Shimadzu GC-MS-QP5050A with a Restek dimethypolylsiloxane fluid Rtx-1 column (30 m). The M_n and M_w/M_n values of polymers were measured on a Tosoh HLC-8020 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/Kratos AXIMA-CFR plus in the reflectron ion mode by use of a laser (λ = 337 nm). Dithranol was used as the matrix for the MALDI-TOF mass measurements. UV–vis spectra were measured on a Shimadzu UV-1800 spectrophotometer. Photoluminescence was measured on a Shimadzu RF-5300 spectrophotometer.

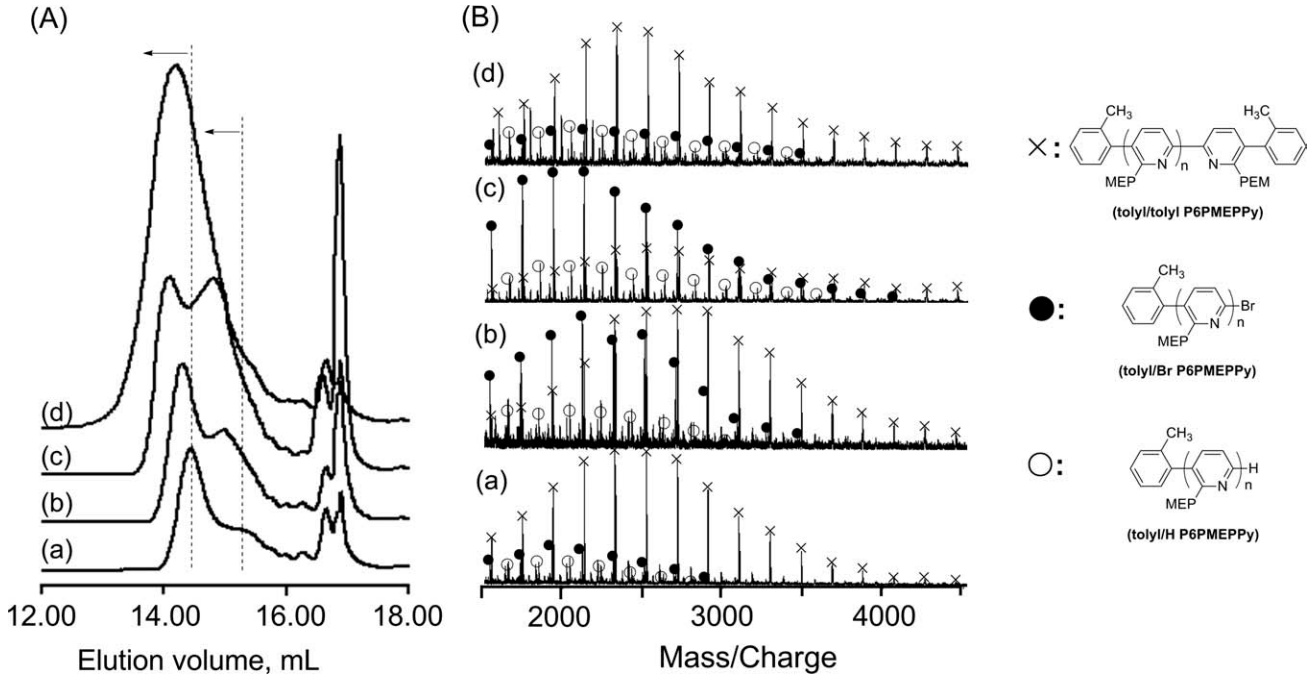


FIGURE 8 (A) GPC profiles and (B) MALDI-TOF mass spectra of PMEPPy obtained by the polymerization of **2** with 4.8 mol % of ^{t}Bu$_3$PPd(*o*-tolyl)Br at room temperature for (a) 3 min (M_n = 3550, M_w/M_n = 1.64), (b) 5 min (M_n = 3700, M_w/M_n = 1.72), (c) 15 min (M_n = 4100, M_w/M_n = 1.86), and (d) 24 h (M_n = 6000, M_w/M_n = 2.05).

Synthesis of 2,5-Diphenylpyridine

All glass apparatus were dried before use. The addition of reagents into a reaction flask and the withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. 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. 2,5-Dibromopyridine (0.477 g, 2.01 mmol) was placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (5.0 mL) was added into the flask via a syringe, and the mixture was stirred at 0 °C. To this mixture, phenylmagnesium chloride (2.0 M solution in THF, 2.2 mL, 4.40 mmol) was added via a syringe, and then a suspension of Ni(dppp)Cl_2 (5.9 mg, 0.0109 mmol, 0.54 mol %) in dry THF (5.0 mL) was added via a syringe at room temperature. After 3 h, the reaction was quenched with water, and the organic layer was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure by rotary evaporator, and the residue was purified by means of column chromatography (SiO_2, hexane/EtOAc = 8/1) to afford 2,5-diphenylpyridine as a pale yellow solid (0.270 g, 58%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.94 (d, J = 2.4 Hz, 1 H), 8.04 (d, J = 8.3 Hz, 2 H), 7.96 (dd, J = 2.4 and 8.3 Hz, 1 H), 7.82 (d, J = 8.3 Hz, 1 H), 7.63 (d, J = 8.3 Hz, 2 H), 7.52–7.48 (m, 4 H), 7.45–7.40 (m, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 156.2, 148.1, 139.0, 137.7, 135.1, 134.9, 129.1, 129.0, 128.8, 128.0, 127.0, 126.8, 120.3.

Model Reaction

All glass apparatus were dried before use. The addition of reagents into a reaction flask and the withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. 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. 2,5-Dibromopyridine (0.237 g, 1.00 mmol) and naphthalene (used as an internal standard for GC analysis, 25.9 mg, 0.20 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (5.0 mL) was added into the flask via a syringe, and the mixture was stirred at 0 °C. To this mixture, phenylmagnesium chloride (2.0 M solution in THF, 0.26 mL, 0.52 mmol) was added via a syringe, and then a suspension of Ni(dppp)Cl_2 (3.4 mg, 0.0063 mmol, 0.63 mol %) in dry THF (5.0 mL) was added via a syringe at room temperature. The reaction was allowed to proceed for 3 h followed by quenching in water. The organic layer was extracted with diethyl ether and subjected to GC and GC-MS analyses to determine the product composition and distribution.

Synthesis of 3-(2-Methoxyethoxy)-1-propyne (4)

A solution of 2-methoxyethanol (9.66 g, 126.9 mmol) in dry THF (150 mL) was mixed with a suspension of NaH (60% in oil, 6.02 g, 150 mmol), and the reaction mixture was stirred at 0 °C for 1 h under an argon atmosphere. A solution of propargyl bromide (16.75 g, 140.8 mmol) in dry THF (15 mL) was then added and stirring was continued at 0 °C for 4 h. The reaction was quenched with ice water, and the organic layer was extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure in a rotary evaporator, and the residue was purified by means of distillation (18 mmHg, 58.0–58.5 °C) to afford **4** as a colorless oil (10.08 g, 79%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.21 (d, J = 2.4 Hz, 2 H), 3.71–3.69 (m, 2 H), 3.59–3.57 (m, 2 H), 3.40 (s, 3 H), 2.40 (t, J = 2.4 Hz, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 79.5, 74.5, 71.6, 68.9, 59.0, 58.4.

Synthesis of 2-Amino-6-[3-(2-methoxyethoxy)-1-propynyl]pyridine (5)

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-Amino-6-bromopyridine (18.65 g, 107.8 mmol), triphenylphosphine (2.88 g, 11.0 mmol), cuprous iodide (2.03 g, 10.7 mmol), and bis(triphenylphosphine)palladium dichloride (3.78 g, 5.4 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (350 mL) was added into the flask via a syringe, and the mixture was stirred at room temperature. Next, triethylamine (22.0 mL, 158.5 mmol) and a solution of **3** (15.39 g, 129.4 mmol) in dry THF (22.0 mL) were added via a syringe, and stirring was continued at room temperature for 23 h. The reaction was quenched with aqueous 3 M HCl solution, and the aqueous layer was washed with dichloromethane and then made basic to around pH 14 with aqueous 10% NaOH solution. The organic layer was extracted with dichloromethane, and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure in a rotary evaporator, and the residue was purified by means of column chromatography (SiO_2, hexane/EtOAc = 4/1) to afford **5** as a pale brown oil (4.179 g, 68%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.38 (t, J = 7.7 Hz, 1 H), 6.83 (d, J = 7.2 Hz, 1 H), 6.46 (d, J = 8.2 Hz, 1 H), 4.56 (br s, 2 H), 4.43 (s, 2 H), 3.77–3.75 (m, 2 H), 3.60–3.59 (m, 2 H), 3.40 (s, 3 H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.1, 140.5, 137.8, 117.7, 108.7, 85.9, 84.0, 71.7, 69.1, 59.0, 58.9.

Synthesis of 2-Amino-6-[3-(2-methoxyethoxy) propyl]pyridine (6)

A mixture of 5% Pd/C (4.87 g, 5.0 mol %), **5** (4.18 g, 20.2 mmol), and ethyl acetate (200 mL) was stirred at room temperature for 4 h under a hydrogen atmosphere. The reaction mixture was filtered through Celite, and the filtrate was concentrated under vacuum. The residue was recrystallized from dichloromethane–hexane to give **6** as a white solid (7.81 g, 80%): mp = 64.9–66.1 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.32 (t, J = 7.7 Hz, 1 H), 6.51 (d, J = 7.5 Hz, 1 H), 6.31 (d, J = 7.9 Hz, 1 H), 4.38 (br s, 2 H), 3.59–3.57 (m, 2 H), 3.55–3.53 (m, 2 H), 3.50 (t, J = 6.7 Hz, 2 H), 3.39 (s, 3 H), 2.67 (t, J = 7.7 Hz, 2 H), 1.99 (quint, J = 7.2 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ =

160.3, 158.0, 138.0, 112.8, 105.7, 72.0, 70.8, 70.0, 59.0, 34.5, 29.4.

Synthesis of 6-Amino-3-bromo-2-[3-(2-methoxyethoxy) propyl]pyridine (7)

To a solution of **6** (7.71 g, 36.7 mmol) in dry dichloromethane (100 mL) at 0 °C, 2,4,4,6-tetrabromo-2,5-cyclohexadienone (17.5 g, 42.6 mmol) was slowly added. The mixture was stirred at 0 °C for 6 h. The reaction was quenched with aqueous 3 M HCl solution, and the aqueous layer was washed with dichloromethane and then made basic to around pH 14 with aqueous 10% NaOH solution. The organic layer was extracted with dichloromethane, and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure in a rotary evaporator, and the residue was recrystallized from dichloromethane–hexane to give **7** as a white solid (9.13 g, 86%): mp = 109.7–110.8 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.46 (d, J = 8.4 Hz, 1 H), 6.23 (d, J = 8.4 Hz, 1 H), 4.47 (br s, 2 H), 3.61–3.59 (m, 2 H), 3.57–3.53 (m, 4 H), 3.39 (s, 3 H), 2.82 (t, J = 7.2 Hz, 2 H), 1.99 (quint, J = 7.2 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.0, 156.9, 141.5, 108.5, 107.7, 72.0, 70.8, 69.9, 59.0, 33.7, 28.2.

Synthesis of 3,6-Dibromo-2-[3-(2-methoxyethoxy) propyl]pyridine (3)

A mixture of **7** (0.98 g, 3.39 mmol) and bromine (0.53 mL, 10.0 mmol) in aqueous 48% HBr solution (5.5 mL) was stirred at 0 °C for 0.5 h. An aqueous solution (3.0 mL) of $NaNO_2$ (0.72 g, 10.0 mmol) was added to the reaction mixture at 0 °C, and stirring was continued at 0 °C for 4 h. The resulting solution was neutralized with aqueous 10% NaOH solution and extracted with dichloromethane. The combined organic layers were washed with aqueous 10% $Na_2S_2O_3$ solution and water and dried over $MgSO_4$. The solvent was removed under reduced pressure in a rotary evaporator, and the residue was purified by means of column chromatography (SiO_2, hexane/EtOAc = 3/1) to afford **3** as a pale yellow oil (1.03 g, 86%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.2 Hz, 1 H), 7.18 (d, J = 8.2 Hz, 1 H), 3.61–3.59 (m, 2 H), 3.58–3.54 (m, 4 H), 3.39 (s, 3 H), 2.99 (t, J = 7.7 Hz, 2 H), 2.05 (quint, J = 7.7 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 161.5, 142.2, 139.7, 126.8, 120.3, 72.0, 70.5, 70.0, 59.1, 33.8, 27.9.

Synthesis of 6-Bromo-3-iodo-2-[3-(2-methoxyethoxy) propyl]pyridine (8)

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. Dibromopyridine **3** (3.54 g, 10.0 mmol) was placed in the flask, and the atmosphere in the flask was replaced with argon. Dry diethyl ether (30.0 mL) was added into the flask via a syringe, and the mixture was stirred at −78 °C. Then, *n*-butyl lithium (1.6 M in hexane, 7.5 mL, 12.0 mmol) was added via a syringe, and stirring was continued at −78 °C for 3 h. To this mixture, a solution of 1,2-diiodoethane (3.13 g, 11.1 mmol) in dry ether (20.0 mL) was added via a syringe. The mixture was stirred at room temperature for 1 h, then the reaction was quenched with water, and the organic layer was extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure by rotary evaporator, and the residue was purified by means of column chromatography (SiO_2, hexane/EtOAc = 4/1), followed by Kugelrohr distillation (0.04 mmHg, 110–115 °C) to afford **8** as a colorless oil (2.85 g, 71%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.2 Hz, 1 H), 7.03 (d, J = 8.2 Hz, 1 H), 3.61–3.60 (m, 2 H), 3.59–3.54 (m, 4 H), 3.39 (s, 3 H), 3.00 (t, J = 7.8 Hz, 2 H), 2.03 (quint, J = 7.8 Hz, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.2, 148.6, 141.2, 126.9, 94.4, 71.9, 70.4, 69.9, 59.1, 37.4, 28.3.

Synthesis of 6-Bromo-2-[3-(2-methoxyethoxy)propyl] pyridin-3-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2)

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. Dibromopyridine **3** (3.54 g, 10.0 mmol) was placed in the flask, and the atmosphere in the flask was replaced with argon. Dry diethyl ether (30.0 mL) was added into the flask via a syringe, and the mixture was stirred at −78 °C. Then, *n*-butyl lithium (1.6 M in hexane, 7.5 mL, 12.0 mmol) was added via a syringe, and stirring was continued at −78 °C for 3 h. To this mixture, a solution of triisopropyl borate (2.29 g, 12.2 mmol) in dry ether (10.0 mL) was added via a syringe. The mixture was stirred at room temperature for 2 h, then a solution of pinacol (1.61 g, 13.7 mmol) in dry ether (10.0 mL) was added, and after 5 min, acetic acid (0.60 mL, 10.5 mmol) was added. Stirring was continued at room temperature for 2 h. The reaction was quenched with water, and the organic layer was extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure in a rotary evaporator, and the residue was purified by means of Kugelrohr distillation (0.07–0.09 mmHg, 142–144 °C) to afford **2** as a colorless oil (2.56 g, 64%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.84 (d, J = 7.9 Hz, 1 H), 7.29 (d, J = 7.9 Hz, 1 H), 3.59–3.52 (m, 6 H), 3.38 (s, 3 H), 3.08 (t, J = 7.6 Hz, 2 H), 2.00–1.95 (m, 2 H), 1.34 (s, 12 H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 164.9, 146.0, 143.9, 124.6, 84.1, 71.9, 70.9, 69.6, 58.9, 34.2, 30.5, 24.7, 24.6.

Polymerization

Synthesis of HT-PMEPPy

Kumada-Tamao Coupling Polymerization. All glass apparatus were dried before use. The addition of reagents into a reaction flask and the withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. A round-bottomed flask equipped with a three-way stopcock containing lithium chloride (24.7 mg, 0.65 mmol) was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. Monomer precursor **8** (0.220 g, 0.55 mmol) was placed in the flask, and the

atmosphere in the flask was replaced with argon. Dry THF (2.6 mL) was added into the flask via a syringe, and the mixture was stirred at 0 °C. To this mixture, ^{i}PrMgCl (2.0 M solution in THF, 0.28 mL, 0.56 mmol) was added via a syringe, and stirring was continued at room temperature for 10 min (conversion of **8** to **1** was 100% by analytical GC). A suspension of Ni(dppp)Cl_2 (5.1 mg, 0.0094 mmol, 1.83 mol %) in dry THF (2.6 mL) was added via a syringe, and stirring was continued at room temperature. After 1 h, 5 M hydrochloric acid was added, and then the aqueous layer was made basic to around pH 14 with 10% aqueous NaOH. The mixture was extracted with dichloromethane, and the organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was washed well with methanol and collected by suction filtration to give HT-PMEPPy (M_n = 13,800, M_w/M_n = 5.71) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.90 (br s, 1 H), 7.49 (br s, 1 H), 3.57-3.51 (m, 6 H), 3.37 (s, 3 H), 3.16 (br s, 2 H) 2.17 (br s, 2 H).

Suzuki-Miyaura Coupling Polymerization. All glass apparatus were dried before use. The addition of reagents into a reaction flask and the withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. 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. Monomer **2** (40.0 mg, 0.100 mmol), dried CsF (68.6 mg, 0.452 mmol), and dried 18-crown-6 (215.1 mg, 0.814 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (7.5 mL) and distilled water (0.5 mL) were added into the flask via a syringe, and the mixture was degassed with argon. This mixture was added to a solution of $^{t}Bu_3$PPd(*o*-tolyl)Br (2.3 mg, 0.0048 mmol, 4.8 mol %) in dry THF (5.0 mL), degassed with argon, via a cannula, and the reaction mixture was stirred at room temperature. After 24 h, 5 M hydrochloric acid was added, and the aqueous layer was made basic to around pH 14 with 10% aqueous NaOH. The mixture was extracted with dichloromethane, and the organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give PMEPPy (M_n = 6000, M_w/M_n = 2.05).

CONCLUSIONS

The feasibility of Kumada-Tamao coupling polymerization of 6-bromo-3-chloromagnesio-2-(3-(2-methoxyethoxy)propyl)-pyridine **1** with a Ni catalyst as an extension of catalyst-transfer condensation polymerization for the synthesis of well-defined *n*-type π-conjugated polymers was investigated. We first demonstrated the occurrence of intramolecular transfer of Ni(0) catalyst on the pyridine ring by means of a model reaction of 2,5-dibromopyridine with 0.5 equivalent of phenylmagnesium chloride in the presence of Ni(dppp)Cl_2; this reaction afforded 2,5-diphenylpyridine exclusively. However, the Kumada-Tamao polymerization of **1** afforded polypyridine, PMEPPy, with very broad polydispersity with several kinds of Ni catalysts, including Ni(dppp)Cl_2. The MALDI-TOF mass spectra indicated that PMEPPy molecules with Br/Br and Br/H end groups were formed from the early stage to the final stage, implying that the polymerization proceeds via an intramolecular catalyst-transfer polymerization mechanism to afford PMEPPy with Br/H ends; however, disproportionation occurs to afford PMEPPy with Br/Br ends. The tendency for disproportionation in the polymerization of pyridine monomer **1** is presumably attributable to coordination of the nitrogen in the pyridine-Ni-Br end to the Ni in another pyridine-Ni-Br end. Suzuki-Miyaura coupling polymerization of pinacol boronate monomer **2** with a Pd catalyst was also accompanied with disproportionation. We are investigating catalyst-transfer condensation polymerization of other acceptor monomers, with the aim of synthesizing well-defined *n*-type π-conjugated polymers.

ACKNOWLEDGMENTS

This study was partially supported by a grant-in-aid (No. 21350067) for Scientific Research from Japan Society for the Promotion of Science and a Scientific Frontier Research Project Grant from the Ministry of Education, Science, Sports and Culture, Japan.

REFERENCES AND NOTES

1 Arias, A. C.; MacKenzie, J. D.; McCulloch, I.; Rivnay, J.; Salleo, A. *Chem. Rev.* **2010,** *110*, 3–24.

2 Grimsdale, A. C.; Chen, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2010,** *109*, 897–1091.

3 Li, C.; Liu, M.; Pschirer, N. G.; Baumgarten, M.; Müllen, K. *Chem. Rev.* **2010,** *110*, 6817–6855.

4 Babudri, F.; Farinola, G. M.; Naso, F. *J. Mater. Chem.* **2004,** *14*, 11–34.

5 Yamamoto, T. *Bull. Chem. Soc. Jpn.* **2010,** *83*, 431–455.

6 Yokozawa, T.; Yokoyama, A. *Chem. Rev.* **2009,** *109*, 5595–5619.

7 Yokozawa, T. In Conjugated Polymer Synthesis; Chujo, Y., Ed.; Wiley-CH: Weinheim, **2010;** pp 35–58.

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

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

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

11 Adachi, I.; Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Macromolecules* **2006,** *39*, 7793–7795.

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

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

14 Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008,** *41*, 1202–1214.

15 Beryozkina, T.; Senkovskyy, V.; Kaul, E.; Kiriy, A. *Macromolecules* **2008,** *41*, 7817–7823.

16 Tkachov, R.; Senkovskyy, V.; Komber, H.; Sommer, J.-U.; Kiriy, A. *J. Am. Chem. Soc.* **2010,** *132*, 7803–7810.

17 Huang, L.; Wu, S.; Qu, Y.; Geng, Y.; Wang, F. *Macromolecules* **2008,** *41*, 8944–8947.

18 Stefan, M. C.; Javier, A. E.; Osaka, I.; McCullough, R. D. *Macromolecules* **2009,** *42*, 30–32.

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

20 Yokoyama, A.; Kato, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2008,** *41*, 7271–7273.

21 Locke, J. R.; McNeil, A. J. *Macromolecules* **2010,** *43*, 8709–8710.

22 Elmalem, E.; Kiriy, A.; Huck, W. T. S. *Macromolecules* **2011,** *44*, 9057–9061.

23 Senkovskyy, V.; Tkachov, R.; Komber, H.; Sommer, M.; Heuken, M.; Voit, B.; Huck, W. T. S.; Kataev, V.; Petr, A.; Kiriy, A. *J. Am. Chem. Soc.* **2011,** *133*, 19966–19970.

24 Yamamoto, T.; Nakamura, T.; Fukumoto, H.; Kubota, K. *Chem. Lett.* **2001,** *30*, 502–503.

25 Nanashima, Y.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci. Part A: Polym. Chem.* **2012,** *50*, 1054–1061.

26 Nanashima, Y.; Yokoyama, A.; Yokozawa, T. *Macromolecules* **2012,** *45*, 2609–2613.

27 Miyatake, N.; Miyakoshi, R.; Yokoyama, A.; Yokozawa, T., unpublished work.

28 Iwashita, K.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci. Part A: Polym. Chem.* **2005,** *43*, 4109–4177.

29 Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975,** *16*, 4467–4470.

30 Dunn, A. D.; Currie, A.; Hayes, L. E. *J. Prakt. Chem.* **1989,** *3*, 369–374.

31 Fukumoto, H.; Kimura, R.; Sasaki, S.; Kubota, K.; Yamamoto, T. *J. Polym. Sci. Part B: Polym. Phys.* **2005,** *43*, 215–222.

32 Liu, J.; Loewe, R. S.; McCullough, R. D. *Macromolecules* **1999,** *32*, 5777–5785.

33 Bouillo, A.; Lancelot, J. C.; Collot, V.; Bovy, P. R.; Rault, S. *Tetrahedron* **2002,** *58*, 2885–2890.

34 Yokozawa, T.; Kohno, H.; Ohta, Y.; Yokoyama, A. *Macromolecules* **2010,** *43*, 7095–7100.

35 Yokozawa, T.; Suzuki, R.; Nojima, M.; Ohta, Y.; Yokoyama, A. *Macromol. Rapid Commun.* **2011,** *32*, 801–806.