

Catalyst-transfer condensation polymerization for precision synthesis of π -conjugated polymers*

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Abstract: Catalyst-transfer condensation polymerization, in which the catalyst activates the polymer end-group, followed by reaction with the monomer and transfer of the catalyst to the elongated polymer end-group, has made it feasible to control the molecular weight, polydispersity, and end-groups of π -conjugated polymers. In this paper, our recent progress of Kumada–Tamao Ni catalyst-transfer coupling polymerization and Suzuki–Miyaura Pd catalyst-transfer coupling polymerization is described. In the former polymerization method, the polymerization of Grignard pyridine monomers was investigated for the synthesis of well-defined n-type π -conjugated polymers. *Para*-type pyridine monomer, 3-alkoxy-2-bromo-5-chloromagnesiopyridine, afforded poly(pyridine-2,5-diyl) with low solubility in the reaction solvent, whereas *meta*-type pyridine monomer, 2-alkoxy-5-bromo-3-chloromagnesiopyridine, yielded soluble poly(pyridine-3,5-diyl) with controlled molecular weight and low polydispersity. In Suzuki–Miyaura catalyst-transfer coupling polymerization, *t*-Bu₃PPd(Ph)Br was an effective catalyst, and well-defined poly(*p*-phenylene) and poly(3-hexylthiophene) (P3HT) were obtained by concomitant use of CsF/18-crown-6 as a base in tetrahydrofuran (THF) and a small amount of water.

Keywords: catalysis; catalysts; conjugated polymers; coupling reactions; Kumada; nickel; organic semiconductors; palladium catalyst-transfer; Suzuki.

INTRODUCTION

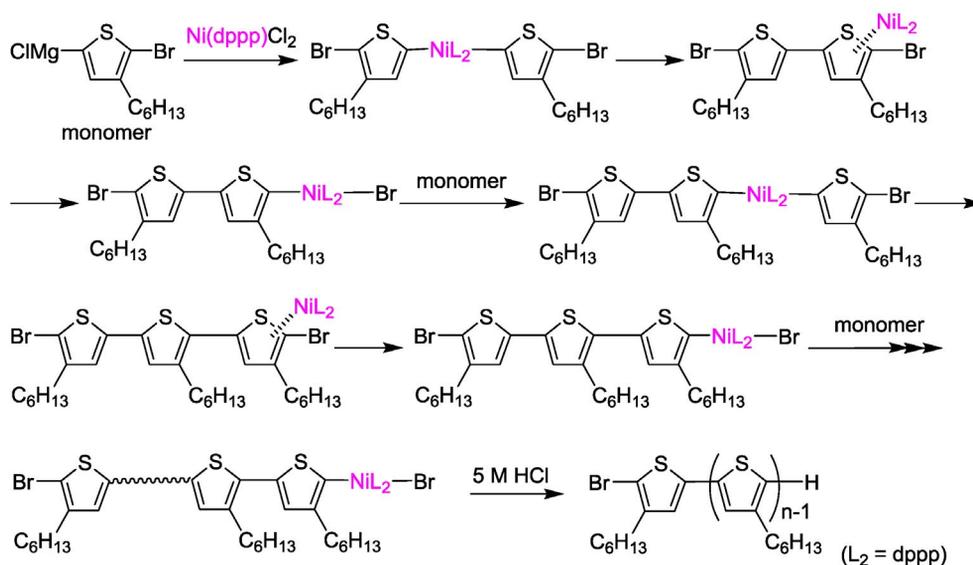
π -Conjugated polymers containing aromatic rings in the backbone are an attractive class of materials owing to their potential organic electronic materials and devices such as field effect transistors (FETs), organic light-emitting diodes (OLEDs), and photovoltaic cells. These polymers have generally been synthesized by condensation polymerization such as electrochemical polymerization [1] and metal-mediated polycondensation [2–4]. Therefore, the molecular weight of those polymers is generally difficult to control within narrow molecular weight distribution. However, uncontrolled molecular weight and broad molecular weight distribution do not stem inherently from the reaction type of condensation polymerization, i.e., condensation steps with elimination of a small molecule species, but from a polymerization mechanism for step-growth polymerization, in which all the end-groups of monomers and oligomers in the reaction mixture equally react with each other. Accordingly, if the mechanism of con-

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condensation polymerization could be converted from step-growth to chain-growth, π -conjugated polymers with defined molecular weight and narrow molecular weight distribution would be obtained.

This change of mechanism in condensation polymerization is evidently not impossible. We have developed chain-growth condensation polymerization and succeeded in synthesizing well-defined condensation polymers such as polyamides, polyethers, and polyesters. These polymerizations involve selective activation of the polymer end-groups as a result of differences in substituent effects between the monomer and the polymer [5,6]. Condensation polymerization with a catalyst can involve another mechanism for chain-growth condensation polymerization. That is catalyst-transfer mechanism, in which the catalyst activates the polymer end-group, followed by reaction with the monomer and transfer of the catalyst to the elongated polymer end-group, in a similar manner to biological condensation polymerization. We [7–9] and McCullough [10,11] have independently established this mechanism for the Ni-catalyzed condensation polymerization leading to poly(3-hexylthiophene) (P3HT). Thus, Ni(dppp)Cl₂ (dppp = 1,3-diphenylphosphinopropane) reacts with 2 equiv of Grignard thiophene monomer, and the coupling reaction occurs with concomitant generation of a zero-valent Ni complex. The Ni(0) complex does not diffuse to the reaction mixture but is inserted into the intramolecular C–Br bond. Another monomer reacts with this Ni, followed by the coupling reaction and transfer of the Ni catalyst to the next C–Br bond. Growth would continue in such a way that the Ni catalyst moves to the polymer end-group (Scheme 1).



Scheme 1

Since then, the catalyst-transfer condensation polymerization for poly(3-alkylthiophene)s (P3ATs) have been extensively developed. For example, block and gradient copP3ATs with different alkyl side chains and block copolymers of P3AT and vinyl polymers were synthesized [12,13]. External Ni-initiators [14–18] were formed and applied to the production of P3AT brushes from a substrate surface [14,16,19–21]. Furthermore, the mechanism has been thoroughly investigated [22–25]. We have investigated catalyst-transfer condensation polymerization for the synthesis of other π -conjugated polymers by not only Ni-catalyzed Kumada–Tamao coupling polymerization but also Pd-catalyzed Suzuki–Miyaura coupling polymerization. In this paper, our recent progress of study about catalyst-transfer condensation polymerization is described.

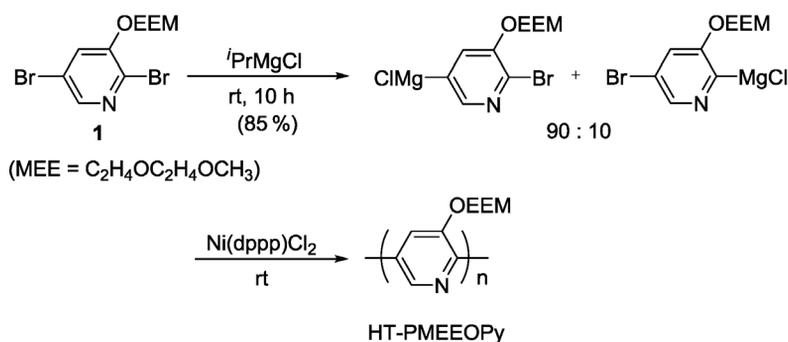
KUMADA–TAMAO COUPLING POLYMERIZATION

Kumada–Tamao catalyst-transfer condensation polymerization yields not only P3ATs but also poly(*p*-phenylene)s [26], poly(*m*-phenylene)s [27], poly(*N*-alkylpyrrole)s [28,29], polyfluorenes [29,30], and poly(bithienylmethylene)s [31] in a controlled manner. However, Kumada–Tamao catalyst-transfer condensation polymerization has been limited to the polymerization of donor monomers for the synthesis of p-type π -conjugated polymers. The polymerization of acceptor monomers has the following difficulties: (1) some electron-withdrawing groups such as carbonyl group in acceptor monomers are not tolerable 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 do; (3) the weaker π -donation of n-type polymer backbone to a Ni(0) catalyst may not sufficiently assist intramolecular catalyst transfer on the basis of the fact that well-defined π -conjugated block copolymers were obtained by the successive polymerization from a monomer with low π -donor ability to a monomer with high π -donor ability [28,32]. Kiri and Huck have recently advanced this field and synthesized well-defined n-type π -conjugated copolymers by unusual coupling polymerization of an anion radical of a thiophene-naphthalenediimide-thiophene monomer, generated from the corresponding dibromomonomer and zinc, with a Ni catalyst [33], which proceed in chain-growth polymerization manner presumably involving catalyst-transfer mechanism. However, the Kumada–Tamao catalyst-transfer condensation polymerization of acceptor monomer consisting of a single arene has not been reported. We have set out to explore the polymerization of simple acceptor monomers by focusing on the polymerization of pyridine monomers, which can be formed from dihalopyridine with alkyl Grignard reagent without decomposition of the monomer under this condition [34].

Poly(3-alkoxypyridine-2,5-diyl)

Polypyridine substituted with an *n*-alkoxy group is expected to have low solubility, because polyalkylpyridines are not soluble in general organic solvents such as THF, a reaction solvent for Kumada–Tamao coupling polymerization [34]. We have found that di- and trioxaalkyl groups are effective for increasing the solubility of aromatic polyester [35] and polythiophene [36]. Therefore, we decided to examine the effect of introducing methoxyethoxyethoxy (MEEO) groups into polypyridine [37].

Monomer precursor **1** was converted to a Grignard-type monomer by treatment with 1 equiv of isopropylmagnesium chloride (ⁱPrMgCl) in THF at room temperature for 10 h (conversion of **1** = 85 %). The bromine of **1** at the 5-position was predominantly, but not exclusively, converted to a chloromagnesium group. Polymerization of Grignard monomers, generated from **1** with ⁱPrMgCl, was carried out by addition of 1.8 mol % Ni(dppp)Cl₂ to the reaction mixture, as in the case of the polymerization of Grignard alkylthiophene monomers [7], but a yellow solid was unexpectedly precipitated within 1 h (Scheme 2). The obtained poly{3-(2-[2-(methoxyethoxy)ethoxy]pyridine-2,5-diyl)} (PMEEOPy) was soluble in halogenated solvents, such as dichloromethane and chloroform, although it was poorly soluble in THF, the polymerization solvent. The weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of PMEEOPy was as high as 25 000 and 1.33, respectively, as determined by means of gel permeation chromatography (GPC)-multiangle laser light scattering (MALLS) analysis in CHCl₃. The head-to-tail (HT) content of PMEEOPy was estimated to be 95 % by means of comparison of the ¹H NMR spectra with those of tail-to-tail (TT) and head-to-head (HH) model compounds.



Scheme 2

A solution of HT-PMEEOPy in CHCl₃ was found to emit blue light when the solution was irradiated with UV light at 254 nm. The UV–vis spectra of HT-PMEEOPy and HH-PMEEOPy, which was prepared by means of Yamamoto coupling polymerization of another monomer with Ni(COD)₂ (COD = 1,5-cyclooctadiene) [38], as well as a model compound of repeat unit **2**, 3-MEEO-pyridine, in CHCl₃ are depicted in Fig. 1A. The absorption maxima (λ_{\max}) of HT-PMEEOPy and HH-PMEEOPy were observed at 392 and 330 nm, respectively, i.e., at much longer wavelength than that of **2**. The λ_{\max} of HT-PMEEOPy is at 62 nm longer wavelength than that of HH-PMEEOPy, implying that the planarity of HT-PMEEOPy is higher than that of HH-PMEEOPy, resulting in a longer conjugation length. Figure 1B shows photoluminescence (PL) spectra of solutions of HT-PMEEOPy and HH-PMEEOPy in CHCl₃. The PL maxima ($\lambda_{\max \text{ em}}$) of HT-PMEEOPy and HH-PMEEOPy were observed at 440 and 414 nm upon irradiation at 392 and 330 nm, respectively.

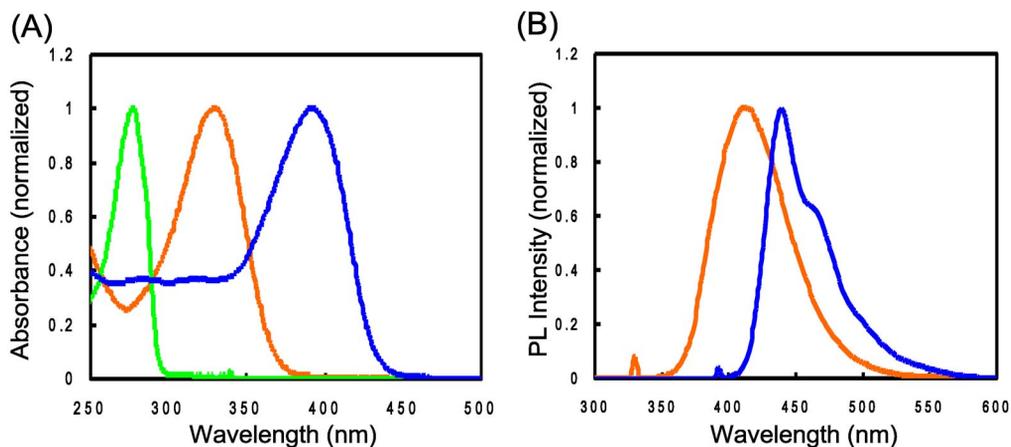


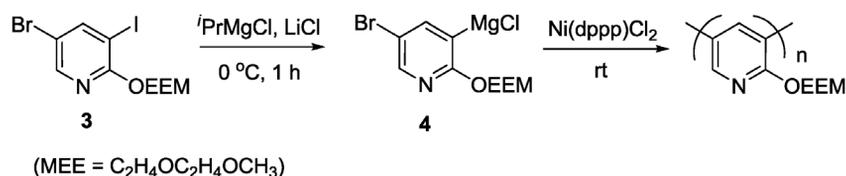
Fig. 1 (A) UV–vis spectra and (B) PL spectra of 3-MEEO-pyridine **2** as a model compound of repeat unit (green line), HH-PMEEOPy (orange line), and HT-PMEEOPy (blue line) in chloroform solution ($\sim 10^{-5}$ M).

Poly(2-alkoxypyridine-3,5-diyl)

Since PMEEOPy was precipitated during polymerization, we could not investigate the chain-growth polymerization behavior. Only if the polymer is soluble in the reaction solvent would we be able to establish whether this acceptor monomer unit undergoes Kumada–Tamao catalyst-transfer condensation polymerization. Therefore, we changed the polymerization position of this monomer unit from the 2,5-position (*para* type) to the 3,5-position (*meta* type) while retaining the same side chain (MEEO

group), although the obtained polypyridine, *m*-PMEEOPy, is not conjugated between the repeat units in the polymer [39].

We used 5-bromo-3-iodo-2-[2-(2-methoxyethoxy)ethoxy]pyridine (**3**) as a monomer precursor, which was quantitatively converted to a Grignard-type monomer **4** by treatment with 1.0 equiv of i PrMgCl in THF at 0 °C for 1 h. The polymerization of **4** was then carried out by addition of 1.8 mol % of Ni(dppp)Cl₂. However, the polymerization proceeded slowly (69 % conversion in 63 h), and the GPC profiles of the products showed a broad molecular weight distribution, although the peak shifted toward the higher-molecular-weight region with time. This polymerization behavior presumably arises from aggregation of Grignard monomer **4** due to coordination of the nitrogen of the pyridine ring to the magnesium. Accordingly, the polymerization of **4** with Ni(dppp)Cl₂ was carried out in the presence of LiCl (2 equiv to **4**) in a similar manner to the Kumada–Tamao catalyst-transfer condensation polymerization of *p*-phenylene monomer [26] (Scheme 3). As a result, the polymerization proceeded much faster, and the GPC chromatogram peak became narrow.



Scheme 3

When the M_n and M_w/M_n values of the crude *m*-PMEEOPy (without purification by precipitation or fractionation) were plotted against monomer conversion, the M_n value increased in proportion to conversion, and the M_w/M_n ratio was 1.34 or below over the whole conversion range (Fig. 2A), indicating chain-growth polymerization behavior. Furthermore, the M_n value also linearly increased in proportion to the feed ratio of monomer precursor **3** to the Ni catalyst (Fig. 2B). The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum of *m*-PMEEOPy obtained by polymerization for 5 min (conversion of **4** = 25 %, M_n = 4000, M_w/M_n = 1.34) contained one major series of peaks and one minor series of peaks (Fig. 3). The major peaks correspond to the Na⁺ adducts of *m*-PMEEOPy

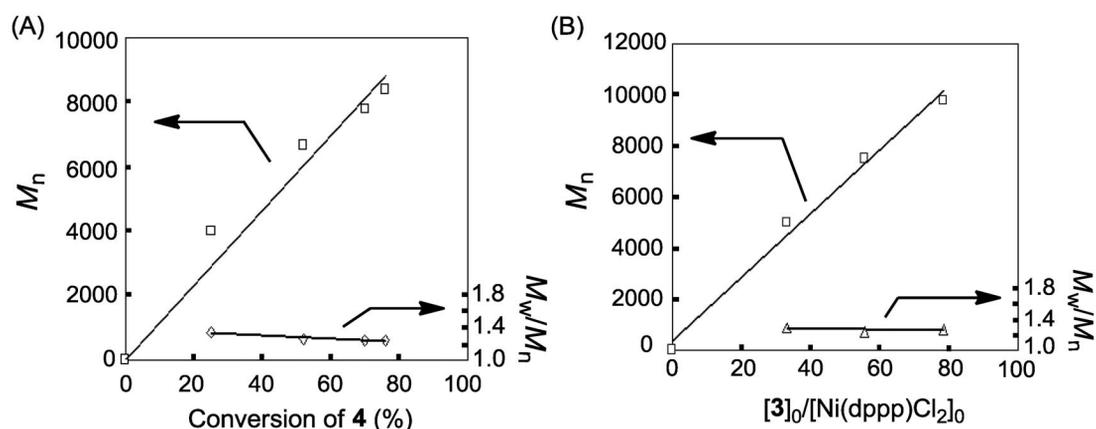


Fig. 2 (A) M_n and M_w/M_n values of *m*-PMEEOPy as a function of monomer conversion in the polymerization of **4** with 1.8 mol % of Ni(dppp)Cl₂ in the presence of 2.0 equiv of LiCl in THF ($[3]_0 = 0.1$ mol/L) at room temperature. (B) M_n and M_w/M_n values of *m*-PMEEOPy as a function of the feed ratio of **3** to Ni(dppp)Cl₂.

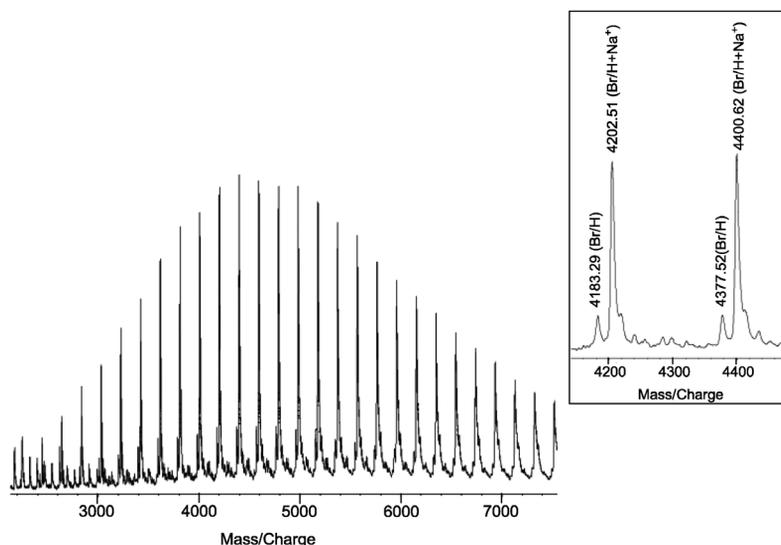
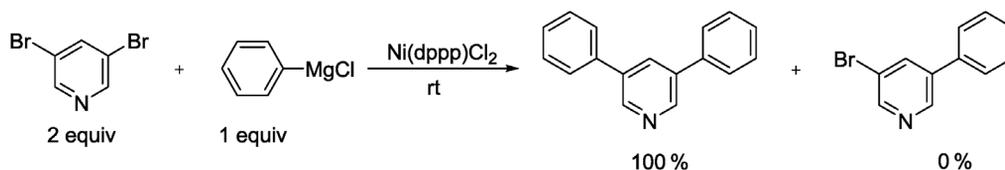


Fig. 3 MALDI-TOF mass spectra of *m*-PMEEOPy obtained by the polymerization of **4** with 1.8 mol % of Ni(dppp)Cl₂ in the presence of 2.0 equiv of LiCl in THF at room temperature for 5 min (conversion of **4** = 25 %, $M_n = 4000$, $M_w/M_n = 1.34$).

with bromine at one end and hydrogen at the other (designated as Br/H). For example, the 21-mer of this distribution is expected to produce a signal at m/z 195.2×21 (repeat unit) + 79.9 (Br) + 1.0 (H) + 23.0 (Na⁺) = 4203.1 Da, and indeed, a signal is observed at 4202.5 Da. The minor peaks correspond to *m*-PMEEOPy with Br/H ends. The polymerization behavior and the MALDI-TOF mass spectrum strongly support the involvement of a catalyst-transfer polymerization mechanism.

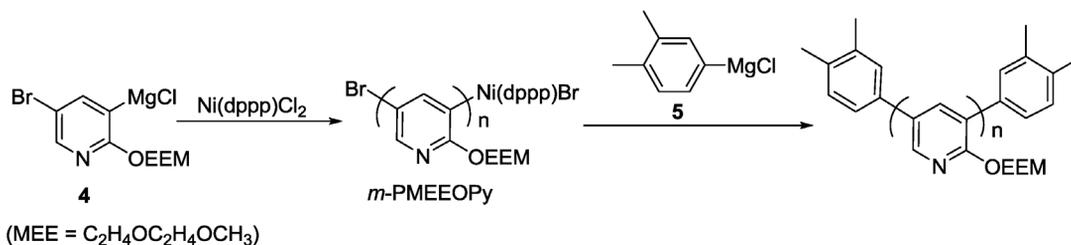
We further examined whether the Ni catalyst intramolecularly would move on the pyridine ring by means of a model reaction, as McCullough conducted in the investigation of the catalyst-transfer polymerization of thiophene monomer [10]. Thus, 3,5-dibromopyridine was reacted with half equiv of phenylmagnesium chloride in the presence of a catalytic amount of Ni(dppp)Cl₂ in THF at ambient temperature. The products were analyzed by gas chromatograph (GC), GC-mass spectrum (GC-MS), and ¹H NMR spectrum, and it turned out that only 3,5-diphenylpyridine was quantitatively formed (Scheme 4). This result indicated that successive coupling reaction took place via intramolecular transfer of Ni(0) catalyst on the pyridine ring, even though the π -donation ability of pyridine is weaker than that of donor monomers such as thiophene.



Scheme 4

Functionalization of the polymer end-groups was conducted by using Grignard reagent. Thus, **4** was polymerized with 1.99 mol % Ni(dppp)Cl₂ in the presence of 2.0 equiv of LiCl in THF at room temperature for 1 h (conversion of **4** = 80 %, $M_n = 7800$, $M_w/M_n = 1.22$), and then an excess of 3,4-dimethylphenylmagnesium chloride **5** (3,4-Me₂C₆H₃MgCl) was added to the reaction mixture

(Scheme 5). The mixture was stirred for a further 3 h, and then the reaction was quenched with 5 M HCl. End-group analysis of the obtained polymer ($M_n = 7870$, $M_w/M_n = 1.23$) was performed by MALDI-TOF MS (Fig. 4). The spectrum of an aliquot taken before addition of the Grignard reagent showed the peaks of the Na^+ cation adduct of *m*-PMEEOPy with Br/H end-groups and the non-cation adducts (Fig. 4A), whereas after the reaction with the Grignard reagent, the spectrum showed a new series of peaks, the values of which corresponded to Na^+ adducts of *m*-PMEEOPy with $\text{Me}_2\text{C}_6\text{H}_3/\text{Me}_2\text{C}_6\text{H}_3$ end-groups. Consequently, it turns out that aryl groups can be introduced at both ends of *m*-PMEEOPy by using the aryl Grignard reagent, as in the case of end-functionalization of P3ATs with Grignard reagents [9,40].



Scheme 5

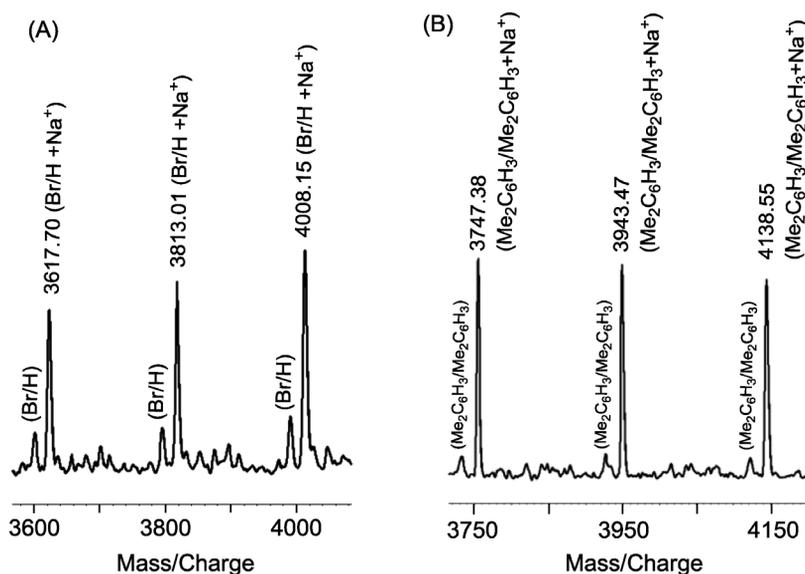
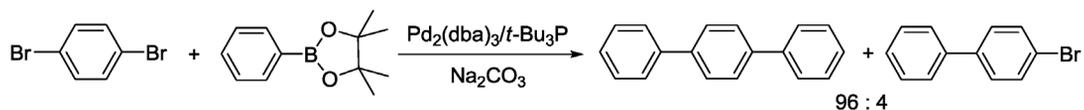


Fig. 4 MALDI-TOF mass spectra of *m*-PMEEOPy obtained by (A) the polymerization of **4** with 1.99 mol % of $\text{Ni}(\text{dppp})\text{Cl}_2$ in the presence of 2.0 equiv of LiCl in THF at room temperature for 1 h (conversion of **4** = 80 %, $M_n = 7800$, $M_w/M_n = 1.22$) and (B) subsequent reaction with 3,4-dimethylphenylmagnesium chloride ($M_n = 7870$, $M_w/M_n = 1.23$).

SUZUKI-MIYAUURA COUPLING POLYMERIZATION

Suzuki–Miyaura cross-coupling is widely used for organic synthesis and polymer synthesis because this reaction can be carried out in the presence of water and is less subject to steric hindrance of reagents and substrates. Therefore, we had started investigation of Suzuki–Miyaura catalyst-transfer condensation polymerization from model reactions: the Suzuki–Miyaura coupling reaction of dibromobenzenes

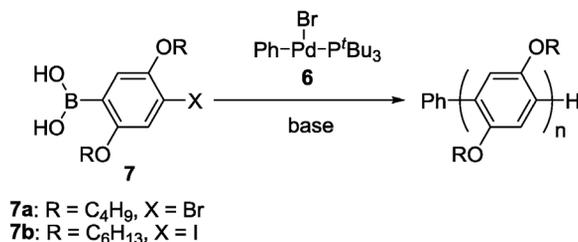
with phenylboronic acid ester with various Pd catalysts, and we found that *t*-Bu₃P was the best ligand to afford selectively diphenyl-substituted benzene via intramolecular transfer of the catalyst (Scheme 6) [41]. However, the same results that the Pd catalyst with *t*-Bu₃P ligand facilitates successive coupling reaction of dihaloarenes with boronic acids or esters were reported before our submission [42,43]. We then carried out the polymerization of a bromofluoreneboronic acid ester monomer with *t*-Bu₃PPd(Ph)Br (**6**), which had been a reported Pd complex [44], to obtain well-defined polyfluorenes via the catalyst-transfer mechanism [45]. This polymerization method was applied to the production of polyfluorene brushes from a substrate surface [46] and to the synthesis of hyperbranched polymers with 100 % degree of branching [47]. We have investigated the polymerization of other monomers leading to π -conjugated polymers.



Scheme 6

Poly(*p*-phenylene)s

In a preliminary study, the polymerization of bromophenylene boronic acid monomer **7a** with a Pd complex initiator **6** was attempted under the same conditions of the polymerization for polyfluorene using Na₂CO₃ as a typical base for Suzuki–Miyaura coupling reaction, but afforded polyphenylene with broad molecular weight distribution [45]. Therefore, we investigated the polymerization of iodo-phenylene boronic acid monomer **7b** with **6** under various conditions (Scheme 7) [48].



Scheme 7

The polymerization of **7b** with **6** ($[\mathbf{7b}]_0/[\mathbf{6}]_0 = 20$) was carried out by using various bases in THF at room temperature. We first used K₃PO₄. However, K₃PO₄ was not soluble in THF, and then **7b** remained unreacted even in 96 h. The obtained polymer had low molecular weight. When tetrabutylammonium fluoride (TBAF), which is soluble in THF, was used, **7b** remained and low-molecular-weight polymer was obtained. The use of CsF with a small amount of water for dissolving CsF gave similar results. However, addition of 18-crown-6 to the former reaction mixture accelerated the polymerization, and **7b** was consumed for 4 h. Furthermore, the molecular weight distribution became narrower up to 1.26. However, when the polymerization was carried out at higher monomer feed ratio ($[\mathbf{7b}]_0/[\mathbf{6}]_0 = 60$), the polydispersity became broad up to 1.84. The polymerization temperature was then decreased to 0 °C, resulting in narrower polydispersity ($M_w/M_n = 1.47$). Under this condition, the molecular weight of poly**7b** increased linearly in proportion to the conversion of **7b** while retaining low polydispersity ($M_w/M_n < 1.25$) in the polymerization at $[\mathbf{7b}]_0/[\mathbf{6}]_0 = 30$ (Fig. 5A). The molecular weight also proportionally increased by the $[\mathbf{7b}]_0/[\mathbf{6}]_0$ ratio up to 21 500 (Fig. 5B). Furthermore, MALDI-TOF mass spectra of the obtained poly**7b** showed that the polymer end-groups were controlled: a phenyl

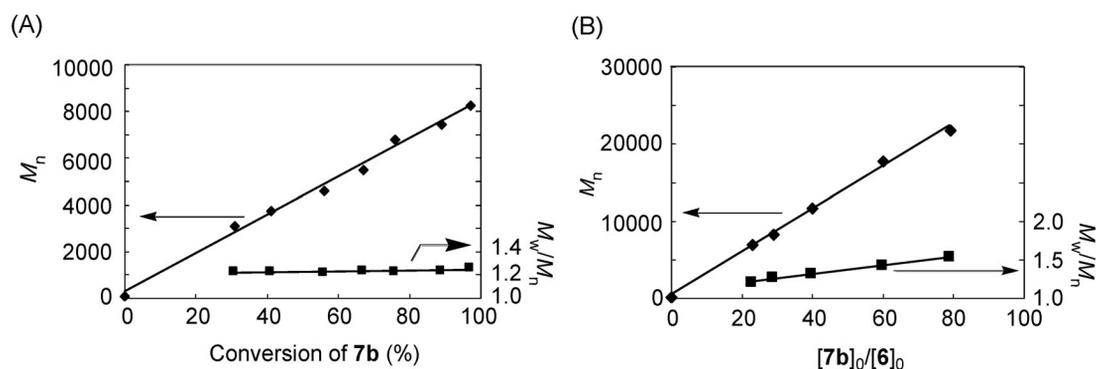


Fig. 5 M_n and M_w/M_n values of poly $7b$ as a function of (A) monomer conversion, obtained by the polymerization of $7b$ with 6 ($[7b]_0/[6]_0 = 30$), and (B) the feed ratio of $7b$ to 6 . All the polymerizations were carried out in the presence of 4 equiv of CsF and 8 equiv of 18-crown-6 in THF ($[7b]_0 = 8.0$ mM) and water (water/THF = 1/17 (v/v)) at 0 °C. M_n and M_w/M_n values were determined by GPC based on polystyrene standards.

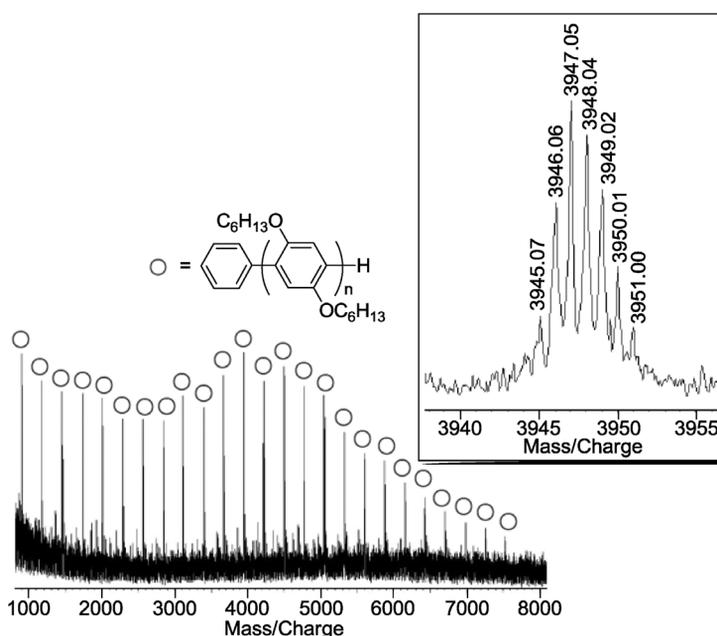
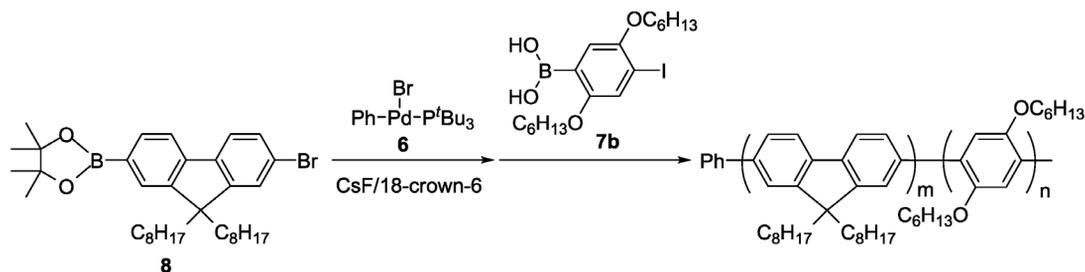


Fig. 6 MALDI-TOF mass spectra of the polymer obtained at $[7b]_0/[6]_0 = 20$.

group, derived from 6 , at one end and a hydrogen atom at the other end (Fig. 6). For example, the exact mass of a single isotope of the 14-mer with Ph/H is expected to produce a signal at 3944.99 Da, and in fact a signal was observed at 3945.07 Da, as shown in the magnified spectrum in Fig. 6. These results indicated that the polymerization of $7b$ also proceeds in a chain-growth polymerization manner via catalyst-transfer mechanism.

Since we have two monomers that undergo Suzuki–Miyaura catalyst-transfer condensation polymerization, block copolymer of polyfluorene and poly(*p*-phenylene) was synthesized. The fluorene monomer 8 was polymerized first in the presence of 5.0 mol % of 6 and CsF/18-crown-6 in THF containing a small amount of water at 0 °C to afford well-defined poly 8 ($M_n = 7300$, $M_w/M_n = 1.19$). Then 1.0 equiv of *p*-phenylene monomer $7b$ was added to the reaction mixture, and the second polymeriza-

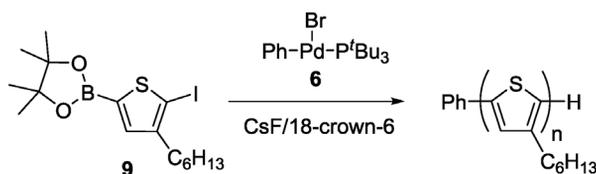
tion was conducted at the same temperature to afford the objective block copolymer with a narrow molecular weight distribution ($M_n = 13\,000$, $M_w/M_n = 1.29$) (Scheme 8). When the block copolymerization was carried out in reverse order, the polydispersity became broad ($M_w/M_n = 1.45$).



Scheme 8

Poly(3-hexylthiophene)

Suzuki–Miyaura coupling polymerizations leading to P3ATs were investigated [49–52], but well-controlled P3ATs have not been synthesized yet. Accordingly, thiophene monomer **9** was polymerized with **6** ($[9]_0/[6]_0 = 20$) under conditions similar to the case of poly(*p*-phenylene) (Scheme 9) [53]. The GPC chromatogram of the product shifted toward the higher-molecular-weight region with increasing reaction time, and monomer **9** was consumed in 24 h to afford P3HT with relatively low polydispersity ($M_w/M_n = 1.34$). The MALDI-TOF mass spectrum of P3HT, obtained after reaction for 24 h followed by quenching with 6 M HCl, contained only one series of peaks, which correspond to the polymer with a phenyl group at one end and a hydrogen atom at the other end (designated as Ph/H) (Fig. 7). For example, the exact mass of a single isotope of the 27-mer with Ph/H is expected to produce a signal at 4562.21 Da, and in fact a signal was observed at 4561.73 Da, as shown in the magnified spectrum in Fig. 7. Furthermore, the Ph/H end-groups were confirmed by the ^1H NMR spectrum, and the average value of degree of polymerization, estimated from the integral ratio of the repeat unit to the end-group, was 20, which agreed with the feed ratio. The MALDI-TOF mass spectrum of the product obtained at 15 min also contains one series of peaks due to P3HT with Ph/H, indicating that polymers with other end-groups, such as polymers from self-condensation of **9**, were not formed in the initial stage. Since the Ph and H end-groups are thought to be derived from the Ph group of **6** and the Pd complex end-group by quenching, respectively, the results of the MALDI-TOF mass spectra and the ^1H NMR spectrum of the obtained P3HT indicate that the polymerization of **9** with **6** involves the catalyst-transfer polymerization mechanism.



Scheme 9

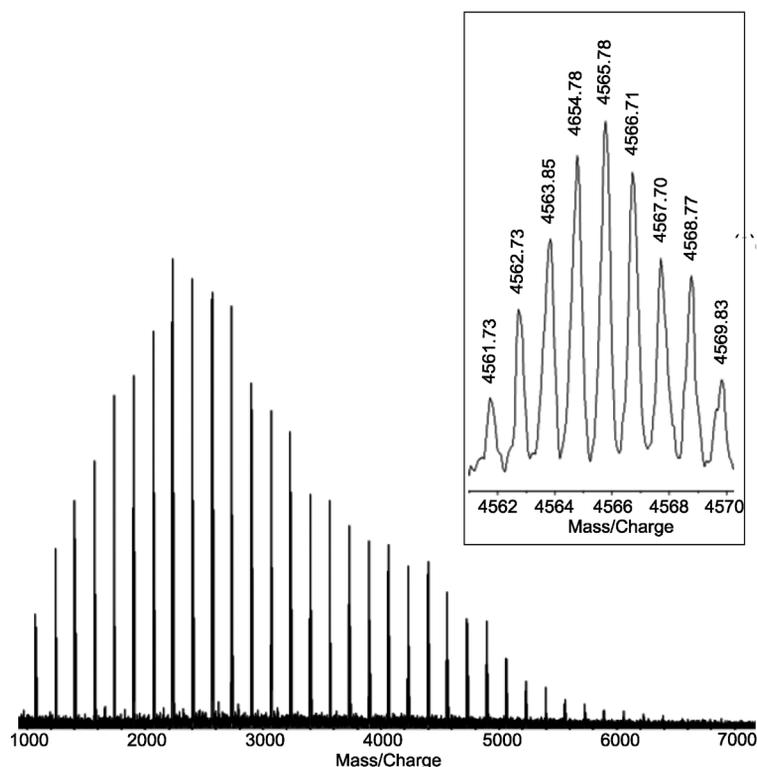


Fig. 7 MALDI-TOF mass spectra of the polymer obtained at $[9]_0/[6]_0 = 20$.

Regarding the regioregularity of P3HT, the ^1H NMR spectra showed only signals corresponding to head-to-tail, head-to-tail triad (designated as HT–HT), and other triad signals such as TT–HH, HT–HH, and TT–HT were not observed, as shown in Fig. 8 attached with the reported ^1H NMR spectrum of P3HT [54]. Therefore, the regioregularity is over 99 %, which suggests that no exchange reaction occurs between the boronic ester moiety and the iodine atom in monomer **9** in the polymerization with **6** at low temperature.

The polymerization of **9** with **6** was then carried out with various feed ratios ($[9]_0/[6]_0$) under the same polymerization conditions. The M_n values of the polymer increased linearly in proportion to $[9]_0/[6]_0$ until $[9]_0/[6]_0$ was 58, but the M_n value at $[9]_0/[6]_0 = 78$ was lower than the expected value. The polydispersity gradually increased with increasing $[9]_0/[6]_0$ ratio (Fig. 9), implying that side reactions took place in the case of polymerization at high $[9]_0/[6]_0$ ratio. Accordingly, the polymer obtained at $[9]_0/[6]_0 = 42$ was analyzed by means of MALDI-TOF MS. Again, the main series of peaks was due to the polymer with Ph/H, but another series of small peaks was also observed in the low m/z region. More detailed analysis of the by-product is required, but at least it can be said that P3HT without a Ph group derived from **6** is formed at a high $[9]_0/[6]_0$ ratio. This side reaction implies involvement of chain transfer of the catalyst to the monomer to some extent in the case of polymerization at a high $[9]_0/[6]_0$ ratio.

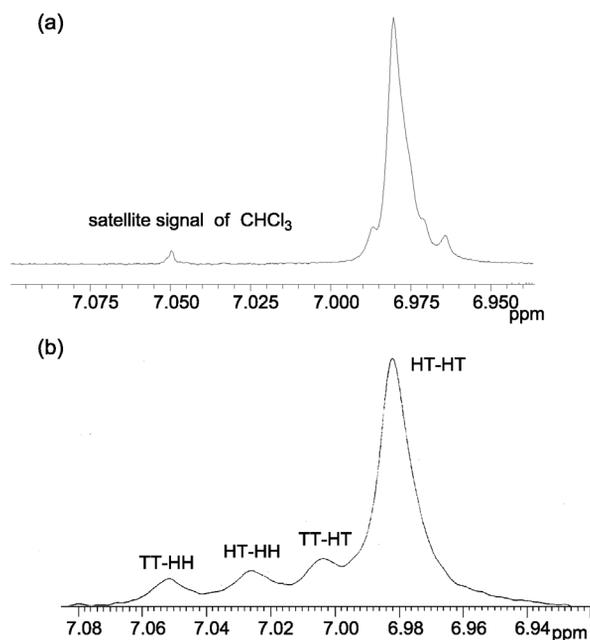


Fig. 8 (a) ^1H NMR spectrum of the polymer obtained at $[\mathbf{9}]_0/[\mathbf{6}]_0 = 20$; (b) ^1H NMR spectrum of P3HT in CDCl_3 , reported in ref. [38].

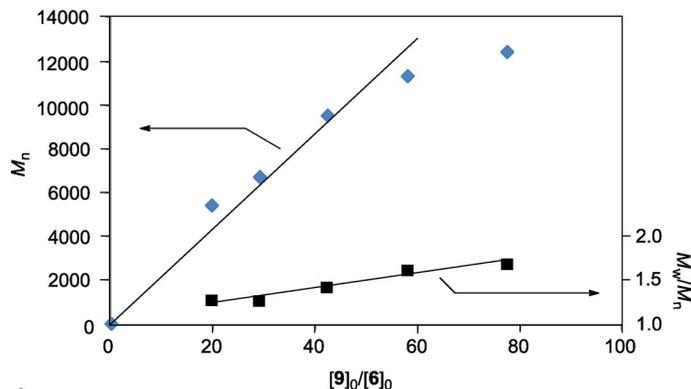
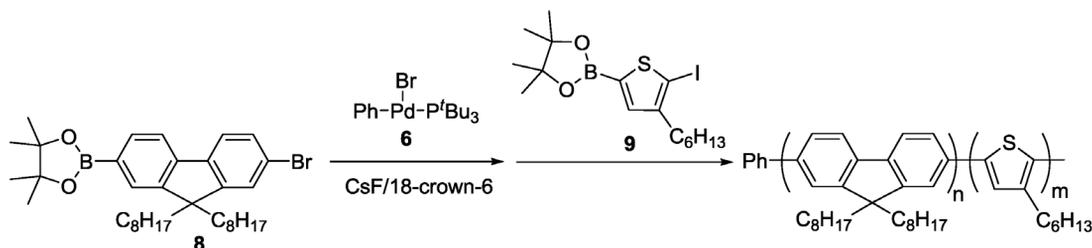


Fig. 9 M_n and M_w/M_n values of P3HT as a function of the feed ratio of **9** to **6**. M_n and M_w/M_n values were determined by GPC based on polystyrene standards.

We tried to synthesize block copolymers of P3HT and polyfluorene possessing a lower donor ability than P3HT. McCullough and co-workers have reported similar block copolymers synthesized by means of Kumada–Tamao coupling polymerization, in which thiophene Grignard monomer has to be added to the reaction mixture of polyfluorene as a prepolymer in the middle stage of polymerization before loss of the pseudo living polymerization character [55].

Because successive catalyst-transfer Suzuki–Miyaura coupling polymerizations should be conducted from a monomer with low π -donor ability to a monomer with high π -donor ability, as mentioned in the previous section [48], the fluorene monomer **8** was polymerized first in the presence of **6** ($[\mathbf{8}]_0/[\mathbf{6}]_0 = 20$) and CsF/18-crown-6 at 0°C for 4 h to afford well-defined polyfluorene (conversion of

8 = 99 %, $M_n = 10\,100$, $M_w/M_n = 1.37$). Then 1.0 equiv of thiophene monomer **9** was added to the reaction mixture, and the second polymerization was conducted at 0 °C for 72 h (Scheme 10). The GPC elution curve shifted toward the higher-molecular-weight region, and the obtained polymer showed $M_n = 14\,700$ and $M_w/M_n = 1.50$. These results indicate that the second monomer **9** was polymerized in a chain-growth polymerization manner from the polymer end group of the first polymer to yield diblock copolymer of polyfluorene and P3HT in almost quantitative yield. In the polymerization in the reverse order, surprisingly, the polymerization of **8** in the second stage hardly proceeded, and a large amount of **8** remained even 163 h after addition of **8** to the reaction mixture of P3HT as a prepolymer. The ^1H NMR spectrum of the product showed strong signals of the P3HT repeat unit and weak signals assignable to an oligofluorene segment attached to P3HT, which is different from the signals of the polyfluorene segment of polyfluorene-*b*-P3HT.



Scheme 10

CONCLUSION

We have expanded the variety of monomers for catalyst-transfer condensation polymerization leading to π -conjugated polymers. Poly(pyridine-3,5-diyl) was obtained in a controlled manner by means of Ni-catalyzed Kumada–Tamao coupling polymerization of 3-alkoxy-2-bromo-5-chloromagnesiopyridine, and well-defined poly(*p*-phenylene) and P3HT were obtained also by Pd-catalyzed Suzuki–Miyaura coupling polymerization of the corresponding boronic acid and boronic acid ester monomers. All π -conjugated block copolymers were further synthesized by successive polymerization of these different monomers in one pot. Future research efforts will be directed toward the development of catalyst-transfer condensation polymerization for the synthesis of well-defined block copolymers consisting of *p*- and *n*-type π -conjugated polymers and of well-defined, low-band-gap, donor–acceptor alternating π -conjugated polymers, both of which are promising organic electrical materials for photovoltaic devices.

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