Polymer Chemistry

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Highly regioselective Pd/C-catalyzed direct arylation toward thiophene-based π-conjugated polymers

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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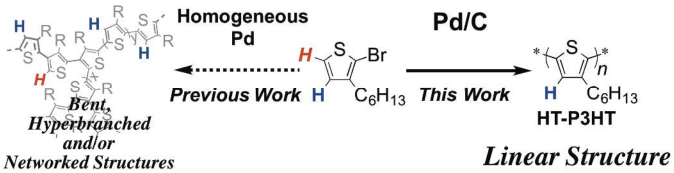
We have successfully developed an efficient and regioselective direct arylation polycondensation of thiophenes using Pd/C heterogeneous catalysts. The highly regioselective polycondensation of thiophene monomers was achieved under phosphine-free conditions, to give linear π-conjugated alternating copolymers with high molecular weight in high yield.

Recently, direct arylations of (hetero)aromatic C-H bonds have been attracted much attention as an important alternative for aryl C-C bond formation in organic chemistry. The various catalytic systems for the C-H bond transformations have been developed as an eco-friendly synthesis.[1-3] Among the metal-catalyzed direct arylations so far developed, palladium catalytic systems are quite common because of their high activity, selectivity, efficiency, and versatility. Many organic chemists devote their great efforts to developing novel Pd(0)-catalyzed direct arylations.[3] Heterogeneous palladium catalysts have various advantages such as reusability and stability. Pd/C is one of the most useful heterogeneous Pd catalysts for cross-coupling reactions. For example, a ligand-free Suzuki-Miyaura coupling reaction of aryl chlorides was achieved by use of Pd/C.[4] Thus heterogeneous Pd catalysts including Pd/C are becoming an important tool in organic chemistry. However, there are only a few reports on direct arylations using heterogeneous Pd catalysts. Glorius recently demonstrated a regioselective direct arylation of benzo[*b*]thiophenes with aryl chlorides catalyzed by a heterogeneous palladium on carbon.[5] Heterogeneous Pd catalysts have potential to progress highly efficient, green, and low-cost processes in both academic and industrial fields.[6]

Direct arylation polycondensations of (hetero)arenes are now becoming a significant synthetic tool for π-conjugated polymers with low residual metal content.[7,8] However, the direct arylation polycondensation using a heterogeneous catalytic system is undeveloped in the research area. It is noteworthy that an example of Pd/C-catalyzed (Suzuki-Miyaura, Stille, Mizoroki-Heck) cross-coupling polycondensations for π-conjugated polymers is reported by Li and Chen.[9] They proved that the efficiency of the Pd/C is comparable to that of homogeneous $Pd(PPh_3)_4$ catalyst, and showed that the advantage of much less Pd contamination in the resulting polymers leads to high performance electronics.

We report here a ligand-free direct arylation polycondensation using Pd/C toward thiophene-based π-conjugated polymers. The first report on the synthesis of poly(3-alkylthiophene-2,5-diyl) via direct arylation was reported by Lemaire.[10] The results of the polymerization with 2-iodo-3-alkylthiophene show low molecular weight, M_n up to ca. 3000. Ozawa reported an efficient approach to HT-P3HT with high molecular weight, M_n up to 30600, and high regioregularity, up to 98 %, by using Herrmann's catalyst, which is derived from $Pd(OAc)_2$ and $P(o\text{-tolyl})_3$, as a palladium source.[11] In general, direct arylation polycondensation with thiophenes does not easily give the linear π-conjugated polymers.[12,13] Monomer **1** has a reactive C-H bond at C5 and a less reactive one at C4 for direct arylation. The C-H arylation polycondensation of **1** occurs not only at the favorable 5-position but also at the unfavorable 4-position, so that bent and branched P3HT is obtained to some extent under general conditions (Scheme 1).[14] The regioselective and efficient direct arylation polycondensation of **1** is a challenging topic for synthesizing linear HT-P3HT. In this study, we succeeded in the synthesis of highly regioregular head-to-tail poly(3-hexylthiophene-2,5-diyl), HT-P3HT, from 2-bromo-3-hexylthiophene, **1**, by using Pd/C (Scheme 1).



Scheme 1 Previous results and this work of direct arylation polycondensation of 2-bromo-3-hexylthiophene, **1**.

The direct arylation polycondensation of **1** was run at 100-120 °C for 48 h in the presence of a Pd/C, palladium 10% on carbon (wetted with 55 % water) supplied by Tokyo Chemical Industry (TCI, P1785) Corporation. We first attempted the polycondensation in a gas-tight Schlenk tube under Ozawa's conditions (10 mol% of tris(*o*-methoxyphenyl)phosphine ligand, 1.0 equiv. of Cs_2CO_3, tetrahydrofuran (THF) as a solvent); 2.5 mol% of Pd/C were employed instead of Herrmann's catalyst. However, the molecular weight (M_n) and yield of the obtained polymer were very low (14% yield, M_n = 1600, M_w/M_n = 1.19). Our effort toward the optimization of the direct arylation polycondensation was next made based on the conditions for the synthesis of thiophene-based alternating copolymers reported by Kanbara.[12a] The polycondensation of **1** under the conditions [2.5 mol% of Pd/C, 1.0 equiv of pivalic acid, 3.0 equiv of K_2CO_3, *N,N*-dimethylacetoamide (DMAc)] proceeded to give P3HT in moderate yield, but the M_n value was not high (entry 1). The M_n increased up to 7800 when the polycondensation was carried out for longer times (entries 2 and 3). In contrast to the results using the Pd/C heterogeneous catalyst, $Pd(OAc)_2$, which is generally used for direct arylation polymerizations, yielded a large amount of insoluble products (entry 4).

To get more information about the reaction conditions, other solvents, such as toluene, THF, and *N*-methylpyrrolidone (NMP) were tested. When the polycondensation was carried out in toluene or THF, P3HT was not obtained (entries 5 and 6) at all. NMP was more efficient than DMAc. P3HT with a higher M_n value (11400) was obtained in good yield (entry 7). One half of the amount of Pd/C exhibited a slight decrease of the M_n value (entry 8). In general, Pd/C-catalyzed reactions do not use phosphine ligands.[4] However, addition of a ligand is expected to raise the reaction efficiency. A ligand employed for direct arylation polycondensations is tricyclohexylphosphonium tetrafluoroborate (PCy_3HBF_4).[12a] The polycondensation with PCy_3HBF_4 showed the increase of the molecular weight in both DMAc and NMP (entries 9 and 10). However, insoluble products were also formed during polymerization; the yield of P3HT decreased. The polycondensation in NMP at a high temperature of 120°C without phosphine ligand afforded P3HT with M_n of 16300 in high yield (entry 11).

Table 1 Pd-Catalyzed Direct Arylation Polycondensation of 2-Bromo-3-hexylthiophene, **1**

entry	solvent	[Pd]	time (h)	P3HT M_n [a] (kDa)	 M_w/M_n [a]	 HT (%) [b]	 yield (%) [c]
1	DMAc	**Pd/C**	48	5.7	1.36	94	52
2	DMAc	**Pd/C**	72	7.8	1.28	95	65
3	DMAc	**Pd/C**	96	7.8	1.32	96	71
4	DMAc	**$Pd(OAc)_2$**	48	5.0	1.52	70 [d]	< 3 [e]
5	toluene	**Pd/C**	48	-	-	-	0
6	THF	**Pd/C**	48	-	-	-	0
7	NMP	**Pd/C**	48	11.4	1.71	97	78
8	NMP	**Pd/C** [f]	48	9.0	1.74	95	80
9 [g]	DMAc	**Pd/C**	48	15.7	2.24	93	42 [e]
10 [g]	NMP	**Pd/C**	48	15.6	3.29	93	34 [e]
11 [h]	NMP	**Pd/C**	48	16.3	3.17	97	91
12	DMAc	**$Pd(OH)_2/C$**	48	14.8	3.20	96	99
13	NMP	**$Pd(OH)_2/C$**	48	18.9	3.01	96	99
14 [h]	NMP	**$Pd(OH)_2/C$**	48	19.3	2.29	89	38 [e]
15	NMP	**$Pd(OH)_2/C$**	18	18.4	3.11	97	99
16	NMP	**$Pd(OH)_2/C$** [f]	18	9.4	2.03	95	86
17	NMP	**$Pd(OH)_2/C$**	8	7.0	1.54	90	71
18	NMP	**$Pd(OAc)_2$**	8	6.7	2.80	66 [d]	10 [e]
19	NMP	**$Pd(OAc)_2$** [i]	8	5.4	1.89	60 [d]	6 [e]
20	NMP	**$Pd(OAc)_2$** [j]	18	-	-	-	<1 [e]

Conditions: 2-bromo-3-hexylthiophene (1.0 mmol), [Pd] (2.5 mol%), PivOH (1.0 mmol), K_2CO_3 (3.0 mmol), solvent (2.0 mL), 100°C, under argon. [a] Estimated by GPC measurements (eluent: THF, standard: polystyrene). [b] Estimated by ^1H NMR. [c] Insoluble in methanol. [d] Bent and branched structures were included. [e] A large amount of product insoluble in common organic solvents was obtained. [f] 1.25 mol%. [g] Tricyclohexylphosphonium tetrafluoroborate (10.0 mol%) was used as ligand. [h] 120 °C. [i] 5.0 mol%. [j] $Pd(OAc)_2$ (2.5 mol%) with five times amount of carbon.

Fagnou reported that Pearlman's catalyst, $Pd(OH)_2/C$, is a more effective Pd catalyst than Pd/C for direct arylation reactions.[15] The $Pd(OH)_2/C$ employed offers a homogeneous catalytic system by leaching of Pd into the solution at a high temperature (140°C). The polycondensation of **1** was conducted under the conditions of entry 7 by using a $Pd(OH)_2/C$ (2.5 mol% of Pd), palladium hydroxide 20% on carbon (wetted with 55% water) supplied by Tokyo Chemical Industry (TCI, P1528) Corporation. NMP gave better results than DMAc (entries 12 and 13). The M_n and yield of the obtained P3HT were high compared to the polycondensation using Pd/C (entries 7 and 13). A higher temperature (120°C) was problematic (entry 14). Although the M_n value of P3HT slightly increased (M_n = 19300), the yield was dropped to 38% and insoluble products appeared. High molecular weight P3HT (M_n = 18400, M_w/M_n = 3.11) was obtained quantitatively when the polymerization was carried out at 100 °C for 18 h in NMP (entry 15). The polycondensation with a lower loading of the $Pd(OH)_2/C$ (1.25 mol% of Pd) exhibited the decrease of the molecular weight (M_n = 9400, entry 16). The clearly different polymerization behavior of **1** was observed when the polycondensation was conducted with a homogeneous $Pd(OAc)_2$ catalyst (entry 18). The yield of P3HT was very low (10%) and large amount of insoluble products (55%) were yielded. This is probably due to the formation of the networked P3HT. Moreover the amount of the insoluble products (62%) increased with increasing of loading of $Pd(OAc)_2$ (entry 19). To verify the effectiveness of Pd/C as the palladium source, the polycondensation of **1** was carried out with a mixture of $Pd(OAc)_2$ and activated carbon (entry 20). A large amount of insoluble products was formed, similarly to the polycondensation using $Pd(OAc)_2$ (entry 18). This provides that regioselective direct arylation polycondensation occurs near activated carbons. Palladium from $Pd(OH)_2/C$ at 100°C may not leach (entry 13, 15-17), but leaching of active Pd species occurred at 120°C (entry 14). $Pd(OH)_2/C$ seems to behave as a heterogeneous-like catalyst under the condition (entry 13, 15-17). These results suggest that the carbon-supported Pd plays a crucial role for the regioselective direct arylation polycondensation of **1**.

Figure 1a shows the ^1H NMR spectra of P3HT synthesized by Grignard metathesis (GM) method (**$P3HT_{GM}$**: M_n = 26000, M_w/M_n = 1.36, HT (%) = 98, blue line) and the polymer (Table 1, entry 15) synthesized by our direct arylation (DA) method (**$P3HT_{DA}$**: red line). The regioregularity of P3HT was estimated from the integral ratios of two different α-methylene signals of the 3-hexyl group shown at 2.81 ppm (head-to-tail: *regioregular*) and 2.61 ppm (*regiorandom*). The **$P3HT_{DA}$** showed 97% head-to-tail regioregularity. Wang et al. reported an oxidative C-H homocoupling reaction of 2- or 3-substitued thiophenes by a Pd(II) catalyst.[14] Generally, Pd/C contains Pd(0) and a certain quantity of Pd(II). Introduction of tail-to-tail (TT) structure to the **$P3HT_{DA}$** might take place due to the oxidative C5-H homocoupling of **1** (Scheme S1a) by Pd(II) species in the Pd/C and $Pd(OH)_2/C$ used. No other α-methylene signals were observed. A sharp singlet signal attributed to C4-**H** was also observed in the aromatic region. The spectrum of the **$P3HT_{DA}$** was compatible with that of **$P3HT_{GM}$**. It is unlikely that the branched or bent structure[13a] formed by direct C4-H arylation of **1** was incorporated into **$P3HT_{DA}$**. On the other hand, the soluble **P3HT** with low HT regioregularity (66%) was obtained along with insoluble products by polymerization of **1** using $Pd(OAc)_2$ as a homogeneous catalyst (Table 1, entry 18). The ^1H NMR of the soluble **P3HT** showed a high integral ratio of α-methylene signal at 2.57 ppm (**b-P3HTa**, Figure S2a), probably due to the existence of the bent structure caused by direct C4-H arylation of **1**. Moreover, a new α-methylene signal was observed in the more upfield region of 2.30-2.20 ppm (Figure S1b) when the loading of $Pd(OAc)_2$ was doubled (Table 1 entry 19). It is known that the α-methylene signals of the branched P3HTs appear in more upfields.[13a] Thus the soluble P3HT seems to contain the bent and/or branched structures (**b-P3HTb**). Presumably, the obtained insoluble products are a cross-linked P3HT. Pd(OAc)$_2$, which is a common homogeneous catalyst for direct arylation polycondensations, caused some side reactions and incorporation of both branched and cross-linked structures into P3HT. It is conceivable that α,ω-dibromo-terminated telechelic oligo(3-hexylthiophene-2,5-diyl), Br-(**t-O3HT**)-Br, which was generated by Pd(II)-catalyzed oxidative C4-H coupling reaction of 2-bromo-3-hexylthiophene and/or the oligomers from **1**, would function as a cross-linker and react with C4-H bond of the thiophene ring of the propagating HT-P3HT polymer species, thus leading to the branched P3HT and finally to the insoluble P3HT network (Scheme S1b). The observed results with Pd/C and Pd(OAc)$_2$ indicate that the "heterogeneous Pd/C-catalyzed direct arylation polycondensation" is a highly selective and efficient polycondensation system for thiophene monomers.

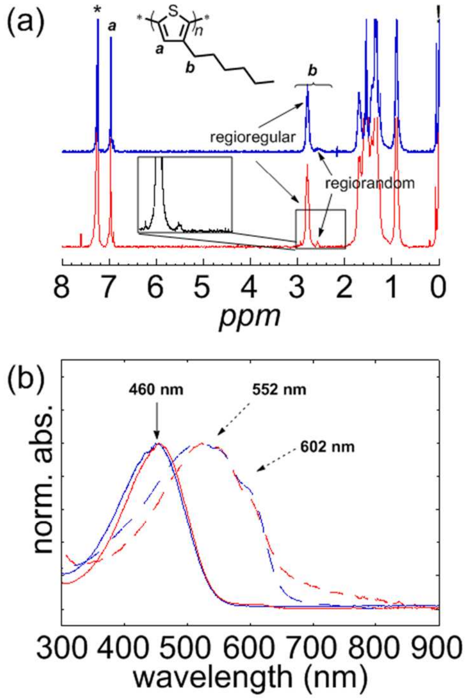
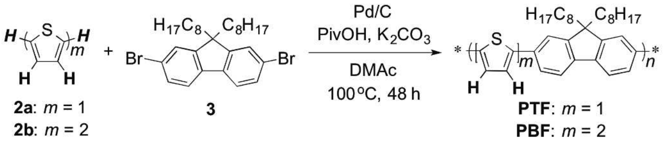


Fig. 1 (a) ^{1}H NMR spectra of **P3HT$_{\mathrm{DA}}$** (red line) and **P3HT$_{\mathrm{GM}}$** (blue line): Symbols, * and !, represent CHCl$_3$ and TMS, respectively. (b) UV-vis absorption spectra of **P3HT$_{\mathrm{DA}}$** (red line) and **P3HT$_{\mathrm{GM}}$** (blue line) in chloroform (solid line) and in film (dashed line) spin-coated from a toluene solution.

It is known that lack of linearity and the existence of branched structures of polythiophenes remarkably affect their optical properties in both solution and solid state.[13,16] The absorption spectra of **P3HT$_{\mathrm{DA}}$** and **P3HT$_{\mathrm{GM}}$** are displayed in Figure 1b. The spectrum of **P3HT$_{\mathrm{DA}}$** in chloroform is consistent with that of **P3HT$_{\mathrm{GM}}$**. In general, the bent (cross-conjugated) structure, that is, the C4-linked thiophene unit in P3HT, limits the mean-conjugation length. In addition, the C4-linked thiophene unit causes the steric repulsion between adjacent thiophene~~s~~ rings. Consequently, the spectra are blue-shifted.[13a,16] The existence of these bent and branched structure inhibits the formation of interdigitation, so that the absorption band does not exhibit significant red-shifts when its going from solution to film. The spectra of both **P3HT$_{\mathrm{DA}}$** and **P3HT$_{\mathrm{GM}}$** films showed large red-shifted absorption bands compared to those in chloroform. The large red-shifts of both the spectra would be derived from effective inter-polymer packing. Contrary to these linear HT-**P3HT**s, the absorption spectra of **b-P3HT**s [**b-P3HTa** (entry 18) and **b-P3HTb** (entry 19) in Table 1] showed blue-shifted bands ($\lambda_{\max}$ = 402 and 413 nm, respectively) compared to the linear **P3HT**s ($\lambda_{\max}$ = 460 nm) (Figure S2a). The fluorescence spectra of **b-P3HTa** and **b-P3HTb** in a dilute chloroform solution also showed blue-shifted band ($\lambda_{\max}$ = 569 and 571 nm, respectively) compared to those of **P3HT$_{\mathrm{DA}}$** and **P3HT$_{\mathrm{GM}}$** (Figure S2b). In addition, the absorption spectra of both **b-P3HTa** and **b-P3HTb** films did not show significant red-shifts because the branched structure decreases the crystallinity of P3HT (Figure S2a). The powder XRD pattern of the **P3HT$_{\mathrm{DA}}$** revealed its strong tendency to form a crystal structure in the film state (Figure S3). DSC trace of **P3HT$_{\mathrm{DA}}$** exhibited endothermic peaks at 221 and 238 °C, which are similar values to those of **P3HT$_{\mathrm{GM}}$** (227 and 240 °C) (Figure S4a). These results strongly also support that **P3HT$_{\mathrm{DA}}$** has a linear and highly regioregular head-to-tail structure.[17]

Thiophene has two reactive C-H bonds at the 2,5-positions and two less reactive C-H bonds at the 3,4-positions for direct arylation. To synthesis fully linear thiophene-based π-conjugated alternating copolymers, protected thiophene monomers such as 3,4-dimethylthiophene and 3,3',4,4'-tetramethylbithiophene should be employed. However, these protected thiophene units inhibit the extension of π-conjugation length and electronic communication of the polymers compared to unprotected thiophene units.[12b,18] Although poly([2,2'-bithiophene-5,5'-diyl]-*alt*-[9,9-dioctylfluorene-2,7-diyl]) (**PBF**) is a potential copolymer for high performance field effect transistor[19] and photovoltaics[20], no direct arylation polycondensation of 3,4-unprotected thiophenes has been achieved because of the lack of regioselectivity.[12] The Pd(OAc)$_2$-catalyzed polycondensation of bithiophene usually offers insoluble products because a cross-linking reaction occurs at the 3 and 4-positions. On the basis of the results of the Pd/C-catalyzed direct arylation polycondensation of **1**, we challenged the direct arylation polycondensation of 3,4-unprotected thiophenes (**2a** and **2b**) with 2,7-dibromo-9,9-dioctylfluorene (**3**) to expand our developed method to the synthesis of various types of π-conjugated alternating copolymers (Scheme 2, Table S2 and S3). After extensive screening of conditions, we found that the polycondensation of **2a** (1.1 equiv to **3**) with **3** gave poly([thiophene-2,5-diyl]-*alt*-[9,9-dioctylfluorene-2,7-diyl]) (**PTF**) with M_n of 6600 (M_w/M_n= 2.29) in 57% yield under the optimized conditions (Pd/C (2.5 mol% of Pd), PivOH, K$_2$CO$_3$, and DMAc). No insoluble polymeric product was obtained.[21] A 1.1-fold excess of thiophene is needed because of its low boiling point (84°C). Pd/C Catalyst was more effective than Pd(OH)$_2$/C catalyst in the case of unmodified thiophene (Table S2). Fagnou reported that dehalogenation of halogenated arenes slightly occurs as a side reaction by Pd(OH)$_2$/C catalyst in direct arylation reactions.[15] Debromination of **3** and/or the brominated end group of the propagating species may occur to terminate the polycondensation. In contrast to the polycondensation with Pd/C, Pd(OAc)$_2$-catalyzed polycondensation gave insoluble reddish black products (63% yield) and a soluble polymer in less than 1% yield. This is probably due to cross-linking reactions at the 3 and/or 4 position(s) of the thiophene units. 2,2'-Bithiophene (**2b**) has four hydrogen atoms at the 3,3',4,4'-positions. Undesirable C-H arylation may occur easily compared to thiophene **2a**. As expected, Pd(OAc)$_2$-catalyzed polycondensation of **2b** with **3** gave a large amount of insoluble reddish black products and a soluble polymer with M_n of 5900 (M_w/M_n= 1.87) in 7% yield. On the other hand, the Pd/C-catalyzed direct arylation polycondensation of **2b** with **3** gave the desired polymer, **PBF**, with M_n of 10900 (M_w/M_n= 3.02) in 73% yield. Insoluble polymeric product was not formed by the carbon-supported Pd-catalyzed direct arylation polycondensation.[21]



Scheme 2 Pd/C-Catalyzed direct arylation polycondensation between unprotected thiophenes, **2**, and 2,7-dibromo-9,9-dioctylfluorene, **3**.

To confirm the structures of the obtained **PTF** and **PBF**, structurally well-defined thiophene-fluorene alternating copolymers, **PTF$_{SC}$** and **PBF$_{SC}$**, were synthesized by Suzuki-Miyaura cross-coupling polymerization. The ^{1}H NMR spectra of **PTF** and **PBF** were compatible with those of **PTF$_{SC}$** and **PBF$_{SC}$** (Figure S5). These polymers showed aromatic signals attributed to the fluorene unit and the protons at 3,4-positions of the thiophene ring(s). To clarify whether the obtained **PTF** has a bent structure, poly([thiophene-3,4-diyl]-*alt*-[9,9-dioctylfluorene-2,7-diyl]) (**b-PTF**), which has a bent structure, was synthesized by Suzuki-Miyaura cross-coupling polymerization of 3,4-dibromothiophene with 9,9-dioctylfluorene-2,7-diboronic acid. The ^{1}H NMR spectrum of **b-PTF** showed characteristic signals of the fluorene ring at 7.11 (2H, *d*), 7.34 (2H, *s*), and 7.41 (2H, *d*) along with 7.16 (2H, *s*) of the thiophene ring, but these signals were not detected in the spectrum of **PTF** (Figure S5a). Moreover, **b-PTF** exhibited an α-methylene proton signal in the upfield region (1.68 ppm). However, such a signal was not detected in the spectrum of **PTF**. These results strongly supported that the structures of **PTF** and **PBF** are not bent but linear. The spectra of **PTF** and **PBF** in both chloroform and film were compatible with those of **PTF$_{SC}$** and **PBF$_{SC}$** (Figure S6). Therefore, the direct arylation polycondensation of *unprotected* thiophenes toward the synthesis of linear π-conjugated polymers was successfully achieved. It should be noted that the absorption spectra of the reported poly([3,3',4,4'-tetramethylnithiophene-5,5'-diyl]-*alt*-[9,9-dioctylfluorene-2,7-diyl]) shows an absorption maximum at 368 nm in chloroform (364 nm in film)[12b] whereas our **PBT** shows a lower energy band and bathochromic shift going from solution to film. The methyl protected-bithiophene monomers have been indispensable for the synthesis of linear alternating copolymers so far, but the protecting groups inhibit the extension of mean-conjugation length and effective packing (self-assembly) in solid state. Thus our synthetic method would apply to the synthesis of linear alternating π-conjugated copolymers for universal optoelectronic materials.

In conclusion, we have successfully demonstrated a Pd/C-catalyzed direct arylation (dehydrohalogenative) polycondensation of 2-bromo-3-hexylthiophene, giving linear and highly regioregular head-to-tail P3HT with high molecular weight. The high regioselectivity for the direct arylation of the thiophene ring made possible to carry out the polycondensation with thiophene and 2,2'-bithiophene, which have no protecting groups at 3,4-positions. Further studies on the selectivity are actively under way, and will be reported in due course.

Acknowledgement

One of the authors thanks Grant-in-Aid for Young Scientists (B), No. 24750116, for financial support. We thank Natsumi Kamiya in national defense academy for XRD measurement.

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† Electronic Supplementary Information (ESI) available: [details of experimental information, NMR spectra, UV-vis absorption spectra, Fluorescence spectra, powder XRD pattern, DSC traces, TGA results.]. See DOI: 10.1039/c000000x/

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