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(Citation)
Polymer Journal,44(12):1209-1213

(Issue Date)
2012-12

(Resource Type)
journal article

(Version)
Accepted Manuscript

(URL)
https://hdl.handle.net/20.500.14094/90003950

Synthesis of π-conjugated poly(thienylenearylene)s with nickel-catalyzed C–H functionalization polycondensation

RUNNING HEAD: C–H functionalization polymerization

ABSTRACT

π-Conjugated polymers are synthesized by C–H, C–X polycondensation of 2-(4-haloaryl)thiophene monomers with a nickel catalyst and Knochel-Hauser base (TMPMgCl·LiCl). The C–H functionalization polycondensation reaction of a monobrominated monomer undergoes dehydrobrominative polymerization with an equimolar amount of TMPMgCl·LiCl and a catalytic amount of $NiCl_2$dppp to afford poly(2,5-thienylene-1,4-phenylene) and poly(2,5-thienylenepyridine-2,5-diyl) in reasonable yields. Polycondensation with triflate as a leaving group proceeds under similar conditions to afford poly(thienylenephenylene) in an excellent yield. Poly(benzodithiophene) is also found to be obtained by the reaction of the corresponding monobrominated benzodithiophene in the presence of a nickel catalyst bearing *N*-heterocyclic carbene (NHC) as a ligand.

KEYWORDS: polythiophene, C-H functionalization, conjugated polymer, nickel catalyst, benzodithiophene, Knochel-Hauser base.

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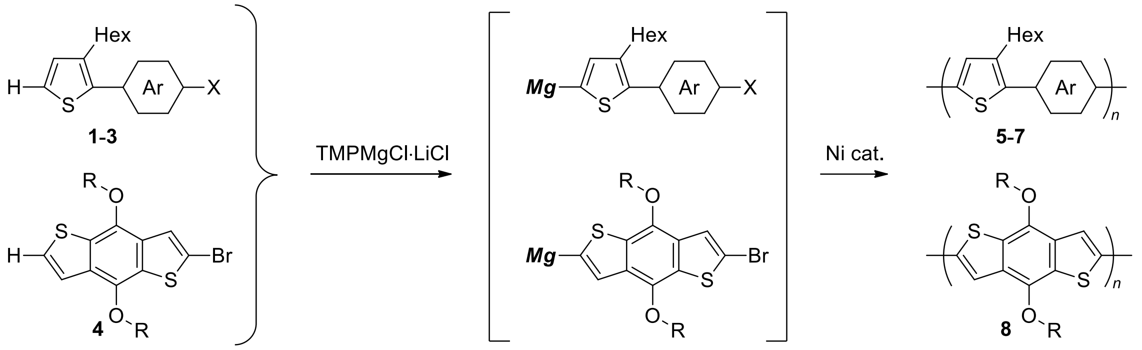
INTRODUCTION

π-Conjugated polymers have recently attracted considerable attention in materials science as advanced organic molecules such as organic TFT,[1] thin-film organic solar cell,[2] and conductive polymer materials.[3] In the context of the controlling of solid structures, and electrical and optical properties of these polymers as advanced materials, it has been important to form head-to-tail (HT)-type connections between monomer units.[4] In general, these regioregular π-conjugated polymers are synthesized by transition-metal-catalyzed cross-coupling reactions such as Suzuki-Miyaura,[5,6,7] and Migita-Kosugi-Stille coupling[8,9] reactions with main group organometallic comonomers.[10,11] However, these methods require the preliminary preparation of the corresponding organometallic monomer, which must be isolated and purified prior to the polymerization. Moreover, polycondensation using these reactions often require high reaction temperature and long reaction periods. Another synthetic approach introduced by McCullough[12] is that generation of metalated monomer using a halogen-magnesium exchange reaction with hindered alkyl Grignard reagents and following cross-coupling polymerization in the presence of a nickel catalyst, which is recognized as GRIM method. This protocol shows advantage for the synthesis of π-conjugated polymers in terms of decreasing the number of reaction steps and mild reaction conditions. Yamamoto and co-workers have recently reported that 2-(5-bromopyridine-2-yl)-3-hexyl-5-bromothiophene polymerize with the GRIM method through the regioselective magnesium-halogen exchange reaction, giving well-defined poly(thiophenepyridine).[13] In addition, Yokozawa and co-workers revealed that nickel-catalyzed polymerization using Kumada-Tamao-Corriu cross-coupling proceeds via a chain-growth polymerization mechanism to afford HT-poly(3-hexylthiophene) with low polydispersity and controlled molecular weight.[14,15,16] On the other hand, dehydrobrominative polycondensation is also a powerful method with superior atom efficiency. In particular, coupling reaction of relatively inert C–H bond of heteroaromatic compound with aryl halides in the presence of a palladium catalyst by direct C–H arylation is a highly efficient synthetic pathway. Takita, Ozawa, and their co-workers have developed polycondensation of 2-bromo-3-hexylthiophene using cesium carbonate as a base.[17] The use of Hermann’s catalyst and phosphine ligand with *o*-Me_2N substituents shows remarkable catalytic activity in this case. In addition, Kuwabara, Kanbara, and their co-workers recently reported synthesis of thiophene-based alternating copolymers via direct C–H arylation[18,19] applying Fagnou's protocol.[20] We have also reported that nickel-catalyzed dehydrobrominative polycondensation takes place by the deprotonation at the C–H bond of thiophene derivatives with Knochel-Hauser base, chloromagnesium 2,2,6,6-tetramethylpiperidide lithium chloride salt (TMPMgCl·LiCl).[21, 22] This method enables to undergo polymerization at lower reaction temperature within shorter polymerization periods.[23, 24, 25] During the course of our studies, our interest has been focused on the extention of the available monomer species. We herein describe C–H functionalization polymerization of 2-(4-haloarylated)thiophene derivatives leading to the synthesis of the corresponding formal alternating copolymer poly(thienylene-*alt*-arylene) and that of monobrominated benzodithiophene to afford poly(benzodithiophene) (Scheme 1).[26, 27]



Scheme 1.

EXPERIMENTAL PROCEDURE

General

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured on Varian Gemini 300. Unless noted, measurements were performed in a $CDCl_3$ solution. The chemical shifts were expressed in ppm with $CHCl_3$ (7.26 ppm for ^{1}H), $CDCl_3$ (77.0 ppm for ^{13}C), or tetramethylsilane (0 ppm for ^{1}H and ^{13}C) as internal standards. IR spectra were recorded on Bruker Alpha with an ATR attachment (Ge). High resolution mass spectra (HRMS) were measured by JEOL JMS-T100LP AccuTOF LC-Plus (DART-ESI) with a JEOL MS-5414DART attachment at Kobe University or JEOL JMS-700 MStation (FAB) at the Graduate School of Material Science, Nara Institute of Science and Technology. SEC (size exclusion chromatography) analyses were performed with a standard HPLC system equipped with a UV detector at 30 °C using $CHCl_3$ as an eluent with a Tosoh TSKgel GMH_{HR}-M at Kobe University or a Waters 150 CV at 140 °C using *o*-dichlorobenzene as an eluent at Hiroshima University. Molecular weights and molecular weight distributions were estimated on the basis of the calibration curve obtained by polystyrene standards. For thin layer chromatography (TLC) analyses throughout this work, Merck precorted TLC plates (silica gel 60 F254) were used.

Purification by HPLC with preparative SEC column (JAI-GEL-2H) was performed by JAI LC-9201. UV-vis spectra were measured by ALS SEC-2000 UV/VIS spectrometer with SEC-2000 DH. TMPMgCl·LiCl was prepared by the literature procedure[28] and stored in the freezer as 1.0 M THF solution. $NiCl_2$dppe and $NiCl_2$dppp were prepared according to the literature procedure.[29] Bistriflurometansulfonyl-1,4-dihydroxybenzene was prepared according to the literature procedure.[30] Other materials were purchased and used without further purification. Unless noted, all reactions were carried out under nitrogen atmosphere.

2-(4-Bromophenyl)-3-hexylthiophene (**1a**): To 100 mL Schlenk tube equipped with a magnetic stirring bar was added ^{i}PrMgBr (7.8 mL of 0.77 M THF solution, 6.0 mmol). To the solution was added 2-bromo-3-hexylthiophene (1.08 mL, 5.0 mmol) and stirring was continued at room temperature for 3 h. Then, 30 mL of THF, 1,4-dibromobenzene (0.68 mL, 6.0 mmol) and $PdCl_2(PPh_3)_2$ (175 mg, 0.25 mmol) were added successively to the resulting solution. The mixture was allowed to stir at 60 ºC for 24 h. After cooling to room temperature the mixture was quenched by hydrochloric acid (1.0 M, 1.0 mL). The solution was poured into the mixture of diethyl ether/water and two phases were separated. The aqueous phase was extracted with diethyl ether twice and the combined organic phase was dried over anhydrous sodium sulfate. Removal of the solvent left a crude oil, which was purified by chromatography on silica gel using hexane as an eluent to afford 1.21 g of **1a** as a pale yellow oil (73%). ^{1}H NMR δ 0.86 (t, *J* = 6.8 Hz, 3H), 1.18-1.32 (m, 6H), 1.50-1.65 (m, 2H), 2.61 (t, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 5.1 Hz, 1H), 7.23 (d, *J* = 5.1 Hz, 1H), 7.29 (dd, *J* = 8.5, 1.9 Hz, 2H), 7.52 (dd, *J* = 8.5, 1.9 Hz, 2H); ^{13}C NMR δ 14.0, 22.5, 28.6, 29.1, 30.9, 31.6, 121.4, 123.9, 129.5, 130.8, 131.5, 133.8, 136.3, 139.0; IR (ATR) 2954, 2925, 2855, 1487, 1465, 1072, 1010, 963, 821, 705, 687, 651 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{16}H_{20}BrS$ $[M+H]^+$: 323.0469; found: m/z 323.0468.

2-(5-Bromopyridine-2-yl)-3-hexylthiophene (**2**)**:** The titled compound was synthesized in a similar manner to the synthesis of **1a**. Monomer **2** was obtained as a pale yellow oil (66% yield). ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.21-1.39 (m, 6H), 1.58-1.70 (m, 2H), 2.86 (t, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 5.1 Hz, 1H), 7.30 (d, *J* = 5.1 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.81 (dd, *J* = 8.5, 2.4 Hz, 1H), 8.66 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR δ 14.0, 22.5, 29.1, 29.5, 30.3, 31.5, 118.0, 122.6, 125.9, 130.8, 136.3, 138.8, 141.5, 150.4, 152.0; IR (ATR) 2954, 2926, 2855, 1568, 1462, 1380, 1360, 1136, 1094, 1002, 880, 756, 723, 656 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{15}H_{19}BrNS$ $[M+H]^+$:

324.0422; found: m/z 324.0426.

2-(5-Bromothiophene-2-yl)-3-hexylthiophene (3): The titled compound was synthesized in a similar manner to the synthesis of 2-(4-bromophenyl)-3-hexylthiophene (**1a**). Monomer **3** was obtained as a pale yellow oil in 50% yield. ^{1}H NMR 0.88 (t, *J* = 6.8 Hz, 3H), 1.24-1.38 (m, 6H), 1.54-1.66 (m, 2H), 2.69 (t, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 3.8 Hz, 1H), 6.92 (d, *J* = 5.2 Hz, 1H), 7.01 (d, *J* = 3.8 Hz, 1H), 7.18 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR δ14.1, 22.6, 29.1, 29.1, 30.7, 31.6, 111.7, 124.2, 126.2, 129.5, 129.8, 130.1, 137.8, 140.2; IR (ATR) 2954, 2926, 2855, 1448, 1413, 970, 875, 834, 790, 758, 721, 692, 649 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{14}H_{18}BrS_2$ [M+H]$^+$: 329.0033; found: m/z 329.0033

2-(Triflurometansulfonyl-4-hydroxyphenyl)-3-hexylthiophene (**1b**): To 100 mL Schlenk tube equipped with a magnetic stirring bar was added EtMgCl (1.02 M in THF solution, 11.8 mL, 12 mmol). To the solution was added 2-bromo-3-hexylthiophene (2.15 mL, 10 mmol) and stirring was continued at 60 °C for 3 h. Then, 20 mL of THF, bistriflurometansulfonyl-1,4-dihydroxybenzene (3.94 g, 10.5 mmol) and $PdCl_2$dppf (408 mg, 0.5 mmol) were added successively. The mixture was allowed to stir at 60 ºC for 22 h. After cooling to room temperature the mixture was quenched by hydrochloric acid (1.0 M, 1.0 mL). The solution was poured into the mixture of diethyl ether/water and two phases were separated. The aqueous phase was extracted with diethyl ether twice and the combined organic phase was dried over anhydrous sodium sulfate. Removal of the solvent left a crude oil, which was purified by chromatography on silica gel using hexane as an eluent to afford 2.38 g of **1b** as a colorless oil (61%). ^{1}H NMR δ 0.86 (t, *J* = 7.1 Hz, 3H), 1.20-1.36 (m, 6H), 1.53-1.65 (m, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 6.99 (d, *J* = 5.2 Hz, 1H), 7.27 (d, *J* = 5.2 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR δ 13.9, 22.5, 28.6, 29.0, 30.9, 31.5, 118.8 (q, $J_{C\text{-}F}$ = 321 Hz), 121.4, 121.7, 124.5, 129.7, 131.0, 135.4, 139.6, 148.6; IR (ATR) 2929, 2857, 2360, 2341, 1498, 1425, 1249, 1210, 1140, 1016, 884, 840, 780, 753 cm^{-1}; HRMS (FAB+) Calcd for $C_{17}H_{19}F_3O_3S_2$ [M+H]$^+$: 392.0728; found: m/z 392.0728.

4,8-Di(2-ethylhexyloxy)benzo[1,2-b;3,4-b']dithiophene (**10**):[26] Benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione (1.1 g, 5 mmol), zinc powder (0.72 g, 11 mmol), and 15 mL of water were added to a 50 mL two neck flask. Then 3.0 g of NaOH was added to the mixture. The mixture was well stirred and heated to reflux for 1 h. Then, 1-bromo-2-ethylhexane (2.67 mL, 15 mmol) and a catalytic amount of tetrabutylammonium bromide (81 mg, 0.25 mmol) were added. The solution was poured to the mixture of diethyl ether/water and two phases were separated. The aqueous phase was extracted with diethyl ether twice and the combined organic phase was dried over anhydrous sodium sulfate. Removal of the solvent left a crude oil, which was purified by chromatography on silica gel using hexane as an eluent to afford 1.89 g of **10** as a colorless solid (85%). ^{1}H NMR δ 0.94 (t, J = 6.8 Hz, 6H), 1.01 (t, J = 7.4 Hz, 6H), 1.25-1.48 (m, 12H), 1.48-1.63 (m, 4H), 1.63-1.73 (m, 1H), 1.73-1.86 (m, 1H), 4.17 (d, J = 4.8 Hz, 4H), 7.36 (d, J = 5.6 Hz, 1H), 7.47 (d, J = 5.6 Hz, 1H).

2-Bromo-4,8-di(2-ethylhexyloxy)benzo[1,2-b;3,4-b']dithiophene (**4**): ^{n}BuLi in hexane (1.65 M, 0.34 mL, 0.6 mmol) was added dropwise to a solution of 4,8-di(2-ethylhexyloxy)benzo [1,2-b;3,4-b']dithiophene (**10**) (223 mg, 0.5 mmol) in THF (2 mL) at -78 °C and the reaction mixture was stirred for 2 h. 1,2-dibromoethane (51 μL, 0.6 mmol) was added in several portions to the solution at -78 °C over 10 min. Then the reaction mixture was stirred for 30 min. The mixture was quenched by hydrochloric acid (1.0 M, 1.0 mL). The solution was poured into the mixture of diethyl ether/water and two phases were separated. The aqueous phase was extracted with diethyl ether twice and the combined organic phase was dried over anhydrous sodium sulfate. Removal of the solvent left a crude oil, which was purified by chromatography on silica gel using hexane as an eluent to afford 175 mg of **4** as a light yellow oil (67%). ^{1}H NMR δ 0.76-1.07 (m, 12H), 1.15-1.70 (m, 16H), 1.70-1.85 (m, 4H), 4.13 (d, J = 5.5 Hz, 2H), 4.14 (d, J = 5.6 Hz, 2H), 7.38 (d, J = 5.6 Hz, 1H), 7.44 (s, 1H), 7.45 (d, J = 5.6 Hz, 1H); ^{13}C NMR δ 11.3, 14.1, 23.1, 23.1, 23.8, 29.2, 30.4, 40.6, 41.9, 76.0, 114.5, 120.2, 123.0, 126.1, 130.3, 130.7, 131.4, 143.6, 143.7; IR (ATR) 2958, 2927, 2871, 1521, 1441, 1355, 1247, 1182, 1031, 921, 822, 762, 711 cm^{-1}; HRMS (FAB+) Calcd for $C_{26}H_{37}BrO_2S_2$ [M]$^+$: 524.1418; found: m/z 524.1418.

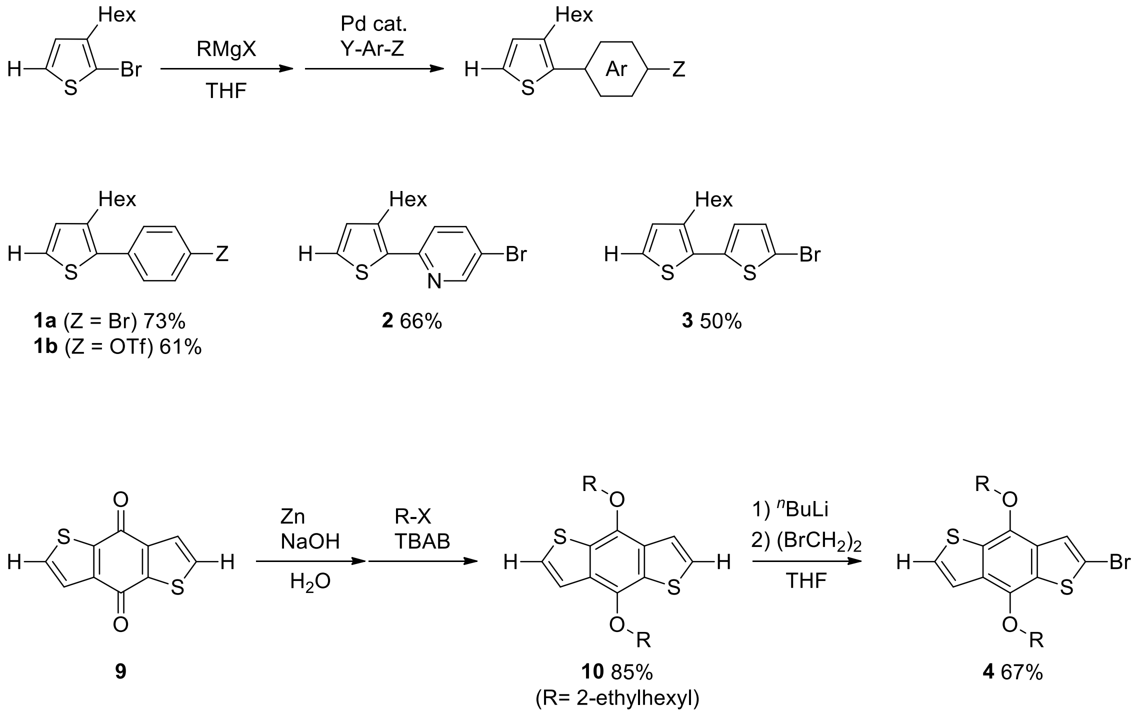
Poly(2-phenyl-3-hexylthiophene-5,4'-diyl) (**5**): To a solution of 1.0 M TMPMgCl·LiCl (0.5 mL, 0.5 mmol) in THF was added 2-(4-bromophenyl)-3-hexylthiophene (**1**: 0.5 mmol, 161 mg) dropwise at room temperature. After stirring at room temperature for 3 h, were successively added THF (4.5 mL) and $NiCl_2$dppp (5.2 mg, 0.01 mmol). The resulting mixture was allowed to stir at 25 °C for 24 h. Hydrochloric acid (1.0 M, 20 mL) and methanol (50 mL) were added to form precipitate. The mixture was filtered and the residue was washed with methanol repeatedly to leave yellow solid, which was dried under reduced pressure to afford 109 mg of **5** (89% yield). Molecular weight and molecular weight distribution were estimated by SEC analysis (eluent: *o*-dichlorobenzene) using polystyrene standards. SEC analysis showed M_n=22000 M_w/M_n=4.8. ^{1}H NMR δ 0.79-0.98 (m, 3H), 1.12-1.48 (m, 6H), 1.52-1.77 (m, 2H), 2.73 (t, J = 7.6 Hz, 2H), 7.28 (s, 1H), 7.51 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H).

Poly[2-(pyridine-2'-yl)-3-hexylthiophene-5,5'-diyl] (**6**): The titled compound was synthesized in a similar manner to the synthesis of poly(2-phenyl-3-hexylthiophene-5,4'-diyl) (**5**). The polymer **6** was obtained as an orange solid in 90% yield. (M_n=9500 M_w/M_n=2.8). ^{1}H NMR (trifluoroacetic acid-*d*) δ 0.26-0.47 (m, 3H), 0.68-1.02 (m, 6H), 1.17-1.42 (m, 2H), 2.30-2.60 (m, 2H), 7.36 (s, 1H), 7.80 (d, J = 7.1 Hz, 1H), 8.41 (d, J = 7.1 Hz, 1H), 8.74 (s, 1H) ; ^{13}C NMR (trifluoroacetic acid-*d*) δ 34.1, 43.7, 50.5, 50.9, 51.9, 52.8, 150.0, 150.6, 153.2, 154.2, 160.6, 161.7, 165.3, 167.1, 172.5.

Poly[4,8-di(2-ethylhexyloxy)benzo[1,2-b;3,4-b']dithiophene] (**8**): The titled compound was synthesized in a similar manner to the synthesis of poly(2-phenyl-3-hexylthiophene-5,4'-diyl) (**5**). The polymer **8** was obtained as an orange solid in 90% yield (M_n=51000 M_w/M_n=3.0). ^{1}H NMR δ 0.90 (t, J = 6.1 Hz, 6H), 0.95-1.81 (br m, 22H), 1.82-1.94 (br m, 4H), 4.00-4.29 (br m, 4H), 7.60 (br s, 1H).

RESULTS AND DISCUSSION

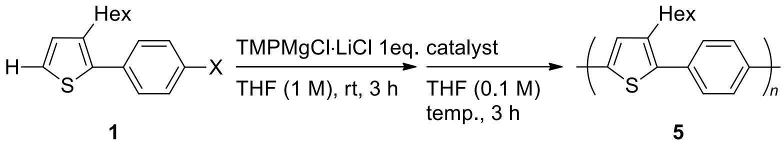
Synthesis of monomers **1**-**3** were carried out by the reaction of thienyl Grignard reagent and aryl halides with Kumada-Tamao-Corriu cross-coupling in the presence of a palladium catalyst. Generation of 3-hexyl-2-halomagnesio-thiophene was carried out with bromine-metal exchange reaction with ^{i}PrMgBr. The coupling reaction of the obtained thienyl Grignard reagent with 1,4-dibromobenzene proceeded smoothly in the presence of 5.0 mol% of $PdCl_2(PPh_3)_2$ as a catalyst to afford **1a** in 73% yield**.** The reaction of 5-bromo-2-iodopyridine, and 2,5-dibromothiophene similarly proceeded to afford corresponding products **2** and **3** in 66% and 50% yields, respectively. Although the coupling reaction with bistriflurometansulfonyl-1,4-dihydroxybenzene was examined in the presence of $PdCl_2(PPh_3)_2$ as a catalyst, we obtained the corresponding coupling product **1b** in only 22% yield, which would be due to the low activity of the palladium catalyst. The higher catalytic activity was achieved with 5.0 mol% of $PdCl_2$dppf (dppf: 1,1'-bis(diphenylphosphino)ferrocene), which afforded **1b** in 61% yield. Benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione was synthesized with Hou and Yang's procedure[31] in a 63% overall yield from thiophene-3-carboxylic acid. Quinone **9** was reduced by zinc powder in aqueous sodium hydroxide solution and following treatment of alkylbromide and catalytic amount of tetrabutylammonium bromide. The reaction with 2-ethylhexylbromide proceeded smoothly to afford alkylated products in 85% yield. We next examined the bromination reaction of benzodithiophene with *N*-bromosuccinimide (NBS). Unfortunately, benzodithiophene-4,8-dione **9** was obtained in this case, presumably due to the NBS promoted oxidative dealkylation.[32] Thus, the bromination reaction was carried out with proton abstruction reaction with *n*-butyl lithium and following treatment of 1,2-dibromoethane to afford monobrominated products **4** in 67% yield (Scheme 2).



Scheme 2.

We then studied polymerization reaction of bromide **1a** and triflate **1b** leading to head-to-tail type poly(thienylenephenylene). Table 1 summarizes the results. When the polymerization of 2-(4-bromophenyl)-3-hexylthiophene **1a** was carried out with an equimolar amount of TMPMgCl · LiCl and 3.0 mol% of $NiCl_2$dppp (dppp: 1,3-bis(diphenylphosphino)propane) at room temperature for 24 h, only 9% of polymer **5** was obtained. This result sharply contrasts to the polymerization with 2-bromo-3-hexylthiophene, which brought about excellent conversion at room temperature within 24 h, affording poly-3-hexylthiophene with M_n=23200 (M_w/M_n=1.35).[23] Drastic improvement was observed when the reaction was carried out in the presence of 2.0 mol% of $NiCl_2$dppp at 60 °C to afford the corresponding polymer in 87% yield. Since the obtained polymer was hardly soluble in $CHCl_3$, SEC analysis was performed at 140 °C using *o*-dichlorobenzene as an eluent. When the catalyst was switched to $NiCl_2(PPh_3)$IPr (IPr: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), which showed excellent catalytic activity in the polymerization of 2-chloro-3-hexylthiophene,[24] polymer **5** was obtained in 48% yield with low molecular weight (M_n=4470). Similar reaction with Pd-PEPPSI-SIPr[33, 34] afforded **5** in 35% yield with M_n =5190. Although polymerization reaction of triflate[35] **1a** in the presence of $NiCl_2$dppp proceeded at room temperature, 56% of oligomer was afforded. The reaction at the elevated temperature (60 °C) improved the yield to 99% (M_n = 28000).

Table 1.



entry	X	catalyst (mol%)	temp. (°C)	yield[b] (%)	M_n[c]	M_w/M_n[c]
1	-Br	$NiCl_2$(dppp) (3)	rt	9	4610	2.5
2	-Br	$NiCl_2$(dppp) (2)	60	89	5163[d]	6.8[d]
					22000[e]	4.8[e]
3	-Br	$NiCl_2$IPr(PPh_3) (2)	60	48	4470[d]	3.1[d]
4	-Br	Pd-PEPPSI-SIPr (2)	60	35	5190[d]	2.5[d]
5	-OTf	$NiCl_2$(dppp) (2)	rt	56	890	1.2
6	-OTf	$NiCl_2$(dppp) (2)	60	>99	5400[d]	1.5[d]
					28000[e]	6.9[e]

[a] The reaction was carried out with 0.5 mmol of **1a** or **1b** and 1.0 equiv. of TMPMgCl·LiCl in THF. [b] Isolated yield. [c] Unless otherwise specified, M_n and M_w/M_n values were estimated by SEC analyses using $CHCl_3$ as an eluent (30 °C). [d] SEC analyses were performed using soluble part of the polymers. [e] M_n and M_w/M_n values were estimated by SEC using *o*-dichlorobenzene as an eluent at 140 °C.

Fig 1 represents NMR spectra of 2-(4-bromophenyl)-3-hexylthiophene **1a**, and poly(thienylene-phenylene) **5** showing good agreement with the proposed structures. In the ^{1}H NMR spectrum of poly(thienylenephenylene), one proton signal at the β-position of the thienylene moiety was observed at 7.28 ppm and two proton signals on the phenylene moiety appeared at 7.51 ppm and 7.69 ppm, respectively.

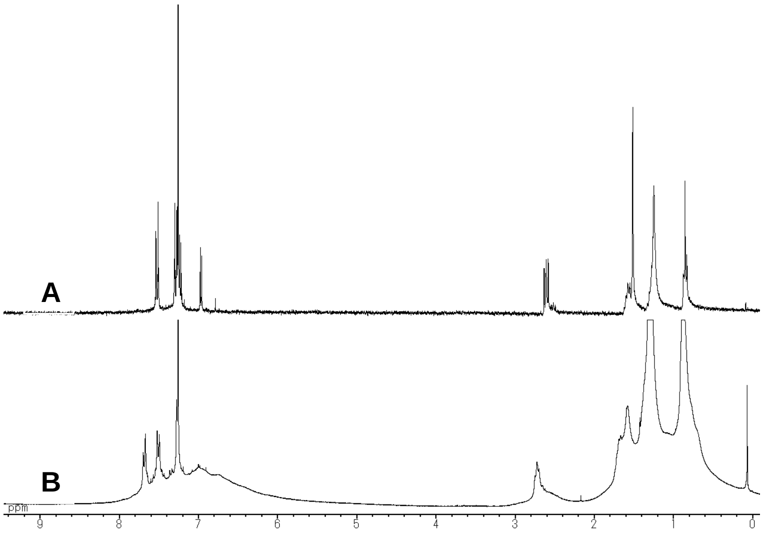
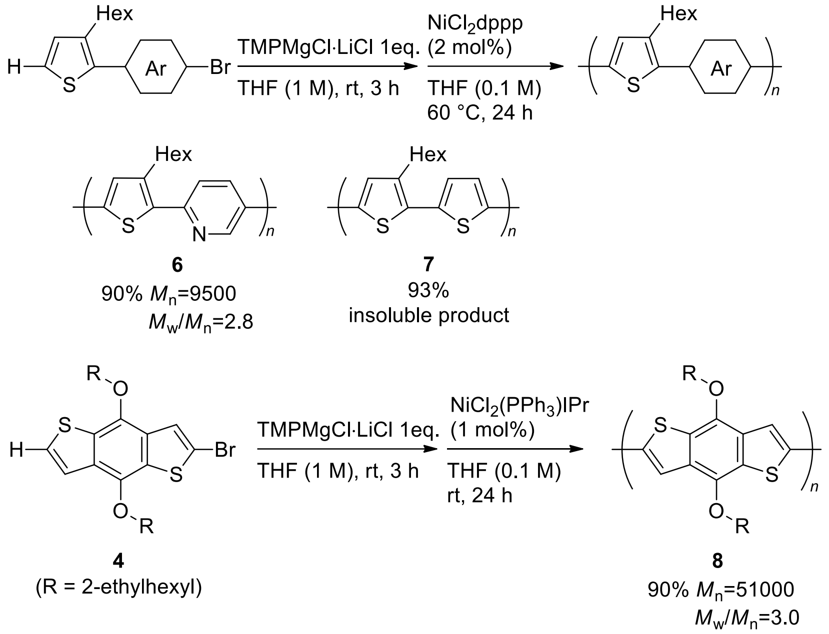


Figure 1. ^{1}H NMR spectra of 2-(4-bromophenyl)-3-hexylthiophene **1a** (A) and poly(thienylenephenylene) **5** (B)

Scheme 3 summarizes the polymerization of other monomers involving a 3-hexylthiophene moiety. The C–H functionalization polycondensation of 2-(5-bromopyridine-2-yl)-3-hexylthiophene **2** with Knochel-Hauser base catalyzed by 2.0 mol% of $NiCl_2$dppp gave polymer **6** in 90% yield with M_n=9500 (M_w/M_n=2.8). The obtained polymer was slightly soluble in $CHCl_3$, therefore, M_n and M_w/M_n values were estimated by SEC analysis using *o*-dichlorobenzene as an eluent at 140 °C. Polymerization of 2-(5-bromothiophene-2-yl)-3-hexylthiophene **3** also took place in a similar manner to afford highly insoluble polymer under similar conditions (2.0 mol% catalyst loading). The reaction of benzodithiophene **4** with TMPMgCl·LiCl and subsequent addition of a nickel catalyst bearing IPr ligand proceeded to afford the corresponding polymer in excellent yield. In the ^{1}H NMR spectra of polymer **5** and **6**, the thienyl-CH_2-C_5H_{11} protons was observed as a relatively simple signal, which supports the estimation of the regioregular structure of these polymers.



Scheme 3

Figure 2 summarizes UV-vis absorption spectra of polymers **5**, **6**, and **8** with a soluble part of the polymer in chloroform. The λ_{max} values were observed at 410 (**5**), 415 (**6**), 485 nm (**8**), respectively. It was found to shift to a shorter wavelength in the absorption peaks of **5** and **6** compared with that of poly(3-hexylthiophene) (ca. 450 nm), suggesting that less extended π-conjugation due to the rotation along with C–C bond between thienylene and arylene. On the other hand, remarkable shift to the longer wavelength was observed in the polymer **8** bearing a benzodithiophene moiety suggesting less twisted conformation of carbon–carbon bond between benzodithiophenes. The UV-vis peaks of **8** showed similar values in comparison with literature values of poly(4,8-Dihexyloxybenzo[1,2-b;3,4-b’]dithiophene-2,6-diyl) (λ_{max} = 450 nm).[36]

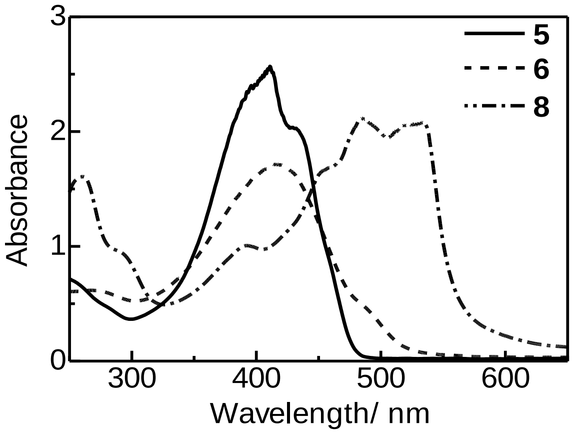


Figure 2. UV-vis absorption spectra of poly(thienylene phenylene) **5** (1 × 10^{-5} M), poly(thienylene pyridinylene) **6** (1 × 10^{-5} M), and poly(benzodithiophene) **8** (1 × 10^{-6} M) in $CHCl_3$.

CONCLUSION

In summary, nickel-catalyzed C–H functionalization polycondensation with Knochel-Hauser base afforded poly(thienylenephenylene), poly(thienylene pyridinylene), and poly(benzodithiophene). It was revealed that such polymers were obtained by C–H coupling under relatively mild reaction conditions with superior atom efficiency. Since the haloarylated thiophene monomers can be obtained by a simple cross-coupling reaction in a facile manner, the method is a potentially practical protocol for the preparation of formal poly(thienylene-*alt*-arylene)s.

ACKNOWLEDGEMENTS

This work was partially supported by KAKENHI (B) by Japan Society for the Promotion of Science (JSPS). A part of thiophene drivatives was kindly donated by Soken Chemical & Engineering Co. Ltd. The Authors thank Nara Institute of Science and Technology, Kyoto-Advanced Nanotechnology Network, supported by MEXT, Japan for measurements of high resolution mass spectra and Professor Takeshi Shiono of Hiroshima University for measurement of high temperature SEC.

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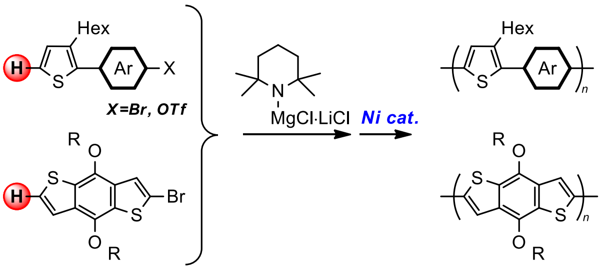
Figure legend

Figure 1. ^{1}H NMR spectra of 2-(4-bromophenyl)-3-hexylthiophene **1a** (A) and poly(thienylenephenylene) **5** (B)

Figure 2. UV-vis absorption spectra of poly(thienylene phenylene) **5** (1 × 10^{-5} M), poly(thienylene pyridinylene) **6** (1 × 10^{-5} M), and poly(benzodithiophene) **8** (1 × 10^{-6} M) in $CHCl_3$.

Graphical Abstract



π-Conjugated polymers are synthesized by C–H, C–X polycondensation of 2-(4-haloaryl)thiophene monomers with a nickel catalyst and Knochel-Hauser base (TMPMgCl·LiCl). The C–H functionalization polycondensation reaction of a monobrominated monomer undergoes dehydrobrominative polymerization with an equimolar amount of TMPMgCl·LiCl and a catalytic amount of $NiCl_2$dppp to afford poly(2,5-thienylene-1,4-phenylene) and poly(2,5-thienylenepyridine-2,5-diyl) in reasonable yields. Polycondensation with triflate as a leaving group proceeds under similar conditions to afford poly(thienylenephenylene) in an excellent yield. Poly(benzodithiophene) is also found to be obtained by the reaction of the corresponding monobrominated benzodithiophene in the presence of a nickel catalyst bearing *N*-heterocyclic carbene (NHC) as a ligand.