ORIGINAL ARTICLE

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

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π -Conjugated polymers are synthesized by C–H and C–X polycondensation of 2-(4-haloaryl)thiophene monomers with a nickel catalyst, and the Knochel–Hauser base (TMPMgCl · LiCl (chloromagnesium 2,2,6,6-tetramethylpiperidide lithium chloride salt)). 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 NiCl₂dppp to produce poly(2,5-thienylene-1,4-phenylene) and poly(2,5-thienylenepyridine-2,5-diyl) with reasonable yields. Polycondensation with triflate as a leaving group proceeds under similar conditions to produce poly(thienylenephenylene) with an excellent yield. Poly(benzodithiophene) was also obtained from the reaction of the corresponding monobrominated benzodithiophene in the presence of a nickel-catalyst-bearing *N*-heterocyclic carbene as a ligand.

Polymer Journal (2012) 44, 1209–1213; doi:10.1038/pj.2012.89; published online 23 May 2012

Keywords: benzodithiophene; C–H functionalization; conjugated polymer; Knochel–Hauser base; nickel catalyst; polythiophene

INTRODUCTION

π -Conjugated polymers have recently attracted considerable attention in materials science as advanced organic molecules, such as organic thin-film transistors,¹ organic solar cells² and conductive polymer materials.³ With regard to the control of the solid structures, as well as the electrical and optical properties of these polymers for use as advanced materials, it has been important to form head-to-tail-type connections between monomer units.⁴ In general, these regioregular π -conjugated polymers are synthesized using transition-metal-catalyzed cross-coupling reactions, such as the Suzuki–Miyaura^{5–7} and Migita–Kosugi–Stille coupling^{8,9} reactions, with the main group organometallic comonomers.^{10,11} However, these methods require preliminary preparation of the corresponding organometallic monomer, which must be isolated and purified before the polymerization. Additionally, polycondensation using these reactions often requires high reaction temperatures and long reaction periods. Another synthetic approach introduced by McCullough and colleagues¹² is the generation of metalated monomers, using a halogen–magnesium exchange reaction with hindered alkyl Grignard reagents, followed by cross-coupling polymerization in the presence of a nickel catalyst, which is recognized as the grignard metathesis (GRIM) method. In addition, Yokozawa and co-workers^{13–15} revealed that cross-coupling proceeds via a chain-growth polymerization mechanism to yield head-to-tail poly(3-hexylthiophene) that has low polydispersity and a controlled molecular weight. These protocols show advantages for the synthesis of π -conjugated polymers in terms of decreasing the number of reaction steps and

mild reaction conditions. Yamamoto and co-workers¹⁶ have also reported that 2-(5-bromopyridine-2-yl)-3-hexyl-5-bromothiophene polymerizes with the grignard metathesis (GRIM) method through the regioselective magnesium–halogen exchange reaction, yielding the well-defined poly(thiophenepyridine). Additionally, dehydrobrominative polycondensation is a powerful method that exhibits superior atom efficiency. In particular, the coupling reaction of the relatively inert C–H bond of heteroaromatic compounds with aryl halides in the presence of a palladium catalyst by direct C–H coupling is a highly efficient synthetic pathway. Takita, Ozawa, and their co-workers¹⁷ have developed the polycondensation of 2-bromo-3-hexylthiophene using cesium carbonate as a base. The use of Hermann's catalyst with an appropriate phosphine ligand has been shown to be key for the remarkable catalytic activity that results in successful polymerization. In addition, Kuwabara, Kanbara, and their co-workers^{18,19} recently reported the synthesis of thiophene-based alternating copolymers through direct C–H coupling by 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 the thiophene derivatives with the Knochel–Hauser base and chloromagnesium 2,2,6,6-tetramethylpiperidide lithium chloride salt (TMPMgCl · LiCl).^{21,22} This method enables the polymerization to occur at lower reaction temperatures within shorter polymerization times.^{23–25} During the course of our studies, our interest has been focused on extending the available monomer species. We herein describe the C–H functionalization polymerization of 2-(4-haloaryl)-thiophene derivatives, leading to the synthesis of the

Scheme 1

corresponding formal alternating copolymer poly(thienylene-alt-arylene) and that of monobrominated benzodithiophene to afford poly(benzodithiophene) (Scheme 1).^{26,27}

EXPERIMENTAL PROCEDURE

General

¹H nuclear magnetic resonance (NMR; 300 MHz) and ¹³C NMR (75 MHz) spectra were measured on a Varian Gemini 300 (Varian Japan, Tokyo, Japan). Unless noted, the measurements were performed in a CDCl₃ solution. The chemical shifts were expressed in p.p.m. with CHCl₃ (7.26 p.p.m. for ¹H), CDCl₃ (77.0 p.p.m. for ¹³C), or tetramethylsilane (0 p.p.m. for ¹H and ¹³C) as internal standards. Infra-red (IR) spectra were recorded on a Bruker Alpha with an attenuated total reflectance (ATR) attachment (Ge). High-resolution mass spectra (HRMS) were measured on a JEOL JMS-T100LP AccuTOF LC-Plus (DART-ESI; JEOL, Tokyo, Japan) with a JEOL MS-5414DART attachment at Kobe University, or a 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 using a standard high-performance liquid chromatography system equipped with a ultraviolet (UV) detector at 30 °C using CHCl₃ as an eluent with a Tosoh TSKgelGMH_{HR}-M (Tosoh, Tokyo, Japan) at Kobe University, or a Waters 150 CV (Nihon Waters K. K., Tokyo, Japan) at 140 °C using *o*-dichlorobenzene as an eluent at Hiroshima University. Molecular weights and molecular weight distributions were estimated from the calibration curves obtained using polystyrene standards. For the thin-layer chromatography analyses throughout this work, Merck precoated thin-layer chromatography plates (silica gel 60 F254, E. Merck, Tokyo, Japan) were used. High-performance liquid chromatography purifications using preparative SEC columns (JAI-GEL-2H) were performed using a JAI LC-9201 (JAI, Tokyo, Japan). UV-vis spectra were measured on an ALS SEC-2000 UV/VIS spectrometer with a SEC-2000 DH (BAS, Tokyo, Japan). TMPMgCl·LiCl was prepared using the procedure reported in the literature²⁸ and then stored in a freezer as a 1.0 M tetrahydrofuran (THF) solution. NiCl₂dpppe and NiCl₂dppp were prepared according to the procedure reported in the literature.²⁹ Bistrifluoromethylsulfonfyl-1,4-dihydroxybenzene was prepared according to the procedure reported in the literature.³⁰ Other materials were purchased and used without further purification. Unless noted, all reactions were performed under a nitrogen atmosphere.

2-(4-Bromophenyl)-3-hexylthiophene (1a)

ⁱPrMgBr (7.8 ml of 0.77 M THF solution, 6.0 mmol) was added to a 100 ml Schlenk tube equipped with a magnetic stirring bar. Then, 2-bromo-3-hexylthiophene was added to the solution (1.08 ml, 5.0 mmol), and stirring was maintained at room temperature for 3 h. Then, 30 ml of THF, 1,4-dibromobenzene (0.68 ml, 6.0 mmol) and PdCl₂(PPh₃)₂ (175 mg, 0.25 mmol) were successively added to the resulting solution. The mixture was allowed to stir at 60 °C for 24 h. After cooling to room temperature, the mixture was quenched with hydrochloric acid (1.0 M, 1.0 ml). The solution was poured into a mixture of diethyl ether/water, and the two phases were then separated. The aqueous phase was extracted with diethyl ether twice, and the combined organic phase was dried over anhydrous sodium sulfate. The removal of the solvent left a crude oil, which was purified by chromatography on silica gel using hexane as an eluent to yield 1.21 g of **1a** as a pale yellow oil (73%). ¹H NMR δ 0.86 (t, *J* = 6.8 Hz, 3 H), 1.18–1.32 (m, 6 H), 1.50–1.65 (m, 2 H), 2.61

(t, *J* = 7.8 Hz, 2 H), 6.97 (d, *J* = 5.1 Hz, 1 H), 7.23 (d, *J* = 5.1 Hz, 1 H), 7.29 (dd, *J* = 8.5, 1.9 Hz, 2 H), 7.52 (dd, *J* = 8.5, 1.9 Hz, 2 H); ¹³C 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 +). Calculated for C₁₆H₂₀BrS [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). ¹H NMR δ 0.88 (t, *J* = 6.7 Hz, 3 H), 1.21–1.39 (m, 6 H), 1.58–1.70 (m, 2 H), 2.86 (t, *J* = 7.8 Hz, 2 H), 6.97 (d, *J* = 5.1 Hz, 1 H), 7.30 (d, *J* = 5.1 Hz, 1 H), 7.41 (d, *J* = 8.5 Hz, 1 H), 7.81 (dd, *J* = 8.5, 2.4 Hz, 1 H), 8.66 (d, *J* = 2.4 Hz, 1 H); ¹³C 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 +). Calculated for C₁₅H₁₉BrNS [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 with a 50% yield. ¹H NMR 0.88 (t, *J* = 6.8 Hz, 3 H), 1.24–1.38 (m, 6 H), 1.54–1.66 (m, 2 H), 2.69 (t, *J* = 7.9 Hz, 2 H), 6.84 (d, *J* = 3.8 Hz, 1 H), 6.92 (d, *J* = 5.2 Hz, 1 H), 7.01 (d, *J* = 3.8 Hz, 1 H), 7.18 (d, *J* = 5.2 Hz, 1 H); ¹³C NMR δ 14.1, 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 +). Calculated for C₁₄H₁₈BrS₂ [M + H]⁺: 329.0033; found: *m/z* 329.0033.

2-(Trifluoromethylsulfonfyl-4-hydroxyphenyl)-3-hexylthiophene (1b)

EtMgCl (1.02 M in the THF solution, 11.8 ml, 12 mmol) was added to a 100-ml Schlenk tube equipped with a magnetic stirring bar. Then, 2-bromo-3-hexylthiophene (2.15 ml, 10 mmol) was added to the solution, and stirring was maintained at 60 °C for 3 h. Then, 20 ml of THF, bistrifluoromethylsulfonfyl-1,4-dihydroxybenzene (3.94 g, 10.5 mmol) and PdCl₂dppf (408 mg, 0.5 mmol) were successively added. The mixture was allowed to stir at 60 °C for 22 h. After cooling to room temperature, the mixture was quenched with hydrochloric acid (1.0 M, 1.0 ml). The solution was poured into a mixture of diethyl ether/water, and the two phases were then separated. The aqueous phase was extracted with diethyl ether twice, and the combined organic phase was dried over anhydrous sodium sulfate. The removal of the solvent left a crude oil, which was purified by chromatography on silica gel, using hexane as an eluent to yield 2.38 g of **1b** as a colorless oil (61%). ¹H NMR δ 0.86 (t, *J* = 7.1 Hz, 3 H), 1.20–1.36 (m, 6 H), 1.53–1.65 (m, 2 H), 2.62 (t, *J* = 7.7 Hz, 2 H), 6.99 (d, *J* = 5.2 Hz, 1 H), 7.27 (d, *J* = 5.2 Hz, 1 H), 7.31 (d, *J* = 8.8 Hz, 2 H), 7.49 (d, *J* = 8.8 Hz, 2 H); ¹³C NMR δ 13.9, 22.5, 28.6, 29.0, 30.9, 31.5, 118.8 (q, *J*_{C-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 +). Calculated for C₁₇H₁₉F₃O₃S₂ [M + H]⁺: 392.0728; found: *m/z* 392.0728.

4,8-Di(2-ethylhexyloxy)benzo[1,2-*b*:3,4-*b'*]dithiophene (10)

²⁶Benzo[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 into a mixture of diethyl ether/water, and the two phases were then separated. The aqueous phase was extracted with diethyl ether twice, and the combined organic phase was dried over anhydrous sodium sulfate. The removal of the solvent left a crude oil, which was purified by chromatography on silica gel, using hexane as an eluent to yield 1.89 g of **10** as a colorless solid (85%). ^1H 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**)

$n\text{BuLi}$ 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 the course of 10 min. The reaction mixture was then stirred for 30 min. The mixture was quenched with hydrochloric acid (1.0 M, 1.0 ml). The solution was poured into a mixture of diethyl ether/water, and the two phases were then 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 yield 175 mg of **4** as a light yellow oil (67%). ^1H 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+). Calculated for $\text{C}_{26}\text{H}_{37}\text{BrO}_2\text{S}_2$ [$\text{M}]^+$: 524.1418; found: m/z 524.1418.

Poly(2-phenyl-3-hexylthiophene-5,4'-diyl) (**5**)

2-(4-bromophenyl)-3-hexylthiophene (**1**; 0.5 mmol, 161 mg) was added dropwise to a solution of 1.0 M $\text{TMPMgCl} \cdot \text{LiCl}$ (0.5 ml, 0.5 mmol) in THF at room temperature. After stirring at room temperature for 3 h, THF (4.5 ml) and NiCl_2dppp (5.2 mg, 0.01 mmol) were successively added to the solution. 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 the precipitate. The mixture was filtered, and the residue was repeatedly washed with methanol to yield a yellow solid, which was dried under reduced pressure to yield 109 mg of **5** (89% yield). The molecular weight and molecular weight distribution were estimated by SEC analysis (eluent: *o*-dichlorobenzene) using polystyrene standards. The SEC analysis showed $M_n = 22000$ $M_w/M_n = 4.8$. ^1H 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**). Polymer **6** was obtained as an orange solid with a 90% yield. ($M_n = 9500$ $M_w/M_n = 2.8$). ^1H 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**). Polymer **8** was obtained as an orange solid with a 90% yield ($M_n = 51000$ $M_w/M_n = 3.0$). ^1H 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

The synthesis of monomers **1–3** were performed from the reaction of the thienyl Grignard reagent and aryl halides with Kumada–Tamao–Corriu cross-coupling in the presence of a palladium catalyst. The generation of 3-hexyl-2-halomagnesio-thiophene was performed using the bromine–metal exchange reaction with $^i\text{PrMgBr}$. The coupling reaction of the obtained thienyl Grignard reagent with 1,4-dibromobenzene proceeded smoothly in the presence of 5.0 mol% of $\text{PdCl}_2(\text{PPh}_3)_2$ as a catalyst to afford **1a** with a 73% yield. The reaction of 5-bromo-2-iodopyridine and 2,5-dibromothiophene proceeded similarly to afford products **2** and **3** with 66 and 50% yields, respectively. Although the coupling reaction with bistrifluoromethylsulfonyl-1,4-dihydroxybenzene was examined in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$ as a catalyst, we obtained the corresponding coupling product **1b** with only a 22% yield, which would be because of the low activity of the palladium catalyst. Higher catalytic activity was achieved with 5.0 mol% of PdCl_2dppf (dppf: 1,1'-bis(diphenylphosphino)ferrocene), which afforded **1b** with a 61% yield. Benzo[1,2-b:4,5-b']dithiophene-4,8-dione was synthesized using Hou and Yang's procedure,³¹ with a 63% overall yield from thiophene-3-carboxylic acid. Quinone **9** was reduced by zinc powder in an aqueous sodium hydroxide solution, and then treated with alkylbromide and a catalytic amount of tetrabutylammonium bromide. The reaction with 2-ethylhexylbromide proceeded smoothly to afford alkylated

Scheme 2

Table 1 Polymerization of **1** with TMPMgCl · LiCl and catalyst^a

Entry	X	Catalyst (mol%)	Temperature (°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

Abbreviations: RT, room temperature; SEC, size exclusion chromatography; PEPPSI, pyridine-enhanced precatalyst preparation stabilization and initiation; SiPr, 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene; TMPMgCl LiCl, chloromagnesium 2,2,6,6-tetramethylpiperide lithium chloride salt.

^aThe reaction was carried out with 0.5 mmol of **1a** or **1b**, and 1.0 equivalent of TMPMgCl · LiCl in THF.

^bIsolated yield.

^cUnless otherwise specified, M_n and M_w/M_n values were estimated by SEC analyses using CHCl₃ as an eluent (30 °C).

^dSEC analyses were performed using soluble part of the polymer.

^eM_n and M_w/M_n values were estimated by SEC using *o*-dichlorobenzene as an eluent at 140 °C.

products with an 85% yield. We then examined the bromination reaction of benzodithiophene with *N*-bromosuccinimide (NBS). Unfortunately, benzodithiophene-4,8-dione **9** was obtained in this case, presumably because the NBS promoted oxidative dealkylation.³² Therefore, the bromination reaction was performed with the proton abstraction reaction using *n*-butyl lithium and then treated with 1,2-dibromoethane to afford monobrominated products **4** with a 67% yield (Scheme 2).

We then studied the polymerization reaction of bromide **1a** and triflate **1b** that resulted in the head-to-tail type poly(thienylene-phenylene). Table 1 summarizes the results. When the polymerization of 2-(4-bromophenyl)-3-hexylthiophene **1a** was performed using an equimolar amount of TMPMgCl LiCl and 3.0 mol% of NiCl₂dppp (dppp: 1,3-bis(diphenylphosphino)propane) at room temperature for 24 h, only 9% of polymer **5** was obtained. This result sharply contrasts 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 A drastic improvement was observed when the reaction was performed in the presence of 2.0 mol% of NiCl₂dppp at 60 °C to afford the corresponding polymer with an 87% yield. Because the obtained polymer was hardly soluble in CHCl₃, SEC analysis was performed at 140 °C using *o*-dichlorobenzene as an eluent. When the catalyst was switched to NiCl₂(PPh₃)IPr (IPr: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), which showed excellent catalytic activity during the polymerization of 2-chloro-3-hexylthiophene,²⁴ polymer **5** was obtained with a 48% yield and low molecular weight (M_n = 4470). The similar reaction with Pd-PEPPSI-SiPr (pyridine-enhanced precatalyst preparation stabilization and initiation–1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene)³³ afforded **5** with a 35% yield and M_n = 5190. Although the polymerization reaction of triflate³⁴ **1b** in the presence of NiCl₂dppp proceeded at room temperature, only 56% of the oligomer was obtained. Performing the reaction at elevated temperature (60 °C) improved the yield to 99% (M_n = 28000).

Figure 1 presents the NMR spectra of 2-(4-bromophenyl)-3-hexylthiophene **1a** and poly(thienylene-phenylene) **5**, and shows good agreement with the proposed structures. Although it is difficult to estimate the regioregularity from ¹H NMR because of the broadening of signals, polymerization would occur between the C–H bond and C–Br(OTf) bond, resulting in the corresponding regioregular polymer. In the ¹H NMR spectrum of poly(thienylene-phenylene), one

Figure 1. ¹H NMR spectra of 2-(4-bromophenyl)-3-hexylthiophene **1a** (a) and poly(thienylene-phenylene) **5** (b). **Scheme 3**

proton signal at the β-position of the thienylene moiety was observed at 7.28 p.p.m., and two proton signals from the phenylene moiety appeared at 7.51 and 7.69 p.p.m.

Scheme 3 summarizes the polymerization of other monomers containing a 3-hexylthiophene moiety. The C–H functionalization polycondensation of 2-(5-bromopyridine-2-yl)-3-hexylthiophene **2** with the Knochel–Hauser base catalyzed by 2.0 mol% of NiCl₂dppp produced polymer **6** with a 90% yield and M_n = 9500 (M_w/M_n = 2.8). The obtained polymer was slightly soluble in CHCl₃; therefore, the M_n and M_w/M_n values were estimated from the SEC analysis using *o*-dichlorobenzene as an eluent at 140 °C. Polymerization of 2-(5-bromothiophen-2-yl)-3-hexylthiophene **3** also occurred in a similar manner to produce a highly insoluble polymer under similar conditions (2.0 mol% catalyst loading). The reaction of benzodithiophene **4** with TMPMgCl LiCl and the subsequent addition of a nickel catalyst bearing an IPr ligand proceeded to produce the corresponding polymer in excellent yield. In the ¹H NMR spectra of polymer **5** and **6**, the thienyl-CH₂-C₅H₁₁ protons was observed as a relatively simple signal, which supports the estimation of the regioregular structure of these polymers.

Figure 2 presents the 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. The

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 .

absorption peaks of **5** and **6** shifted to a shorter wavelength compared with that of poly(3-hexylthiophene) (approximately 450 nm), suggesting less extended π -conjugation because of the rotation along the C–C bond between thienylene and arylene. However, a remarkable shift to a longer wavelength was observed in polymer **8** that bears a benzodithiophene moiety, which suggests a less twisted conformation of the carbon–carbon bond between the benzodithiophenes. The peaks in the UV-vis spectrum of **8** showed similar values in comparison with the values reported in the literature for poly(4,8-Dihexyloxybenzo[1,2-b;3,4-b']dithiophene-2,6-diyl) ($\lambda_{\text{max}} = 450 \text{ nm}$).³⁵

CONCLUSIONS

In summary, the nickel-catalyzed C–H functionalization polycondensation with the Knochel–Hauser base produced poly(thienylene-phenylene), poly(thienylene pyridinylene) and poly(benzodithiophene). These polymers were obtained by C–H coupling under relatively mild reaction conditions with superior atomic efficiency. Because the haloarylated thiophene monomers can be obtained from a simple cross-coupling reaction in a facile manner, this 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 the Japan Society for the Promotion of Science (JSPS). Thiophene derivatives were partly donated by Soken Chemical & Engineering Co. Ltd. We thank the 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 the Hiroshima University for measurement of high-temperature SEC.

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