

ORIGINAL ARTICLE

Direct arylation polycondensation for the synthesis of bithiazole-based conjugated polymers and their physical properties

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The reaction conditions for direct arylation polycondensation were investigated for the synthesis of bithiazole-based conjugated polymers, which have been difficult to synthesize under previous conditions owing to the low solubility of the product in the reaction solvent. The investigation revealed that the reaction with the Pd(PCy₃)₂ precatalyst and *N,N*-diethylpropanamide (that is, reaction solvent) afforded three types of the bithiazole-based conjugated polymers with high molecular weights. These conditions also effectively suppressed the formation of structural defects, such as a non-alternating structure caused by homocoupling. The structure–property relationships of the obtained polymers were evaluated based on their absorption properties, energy levels, crystallinity and semiconducting properties. The highest occupied molecular orbital/lowest unoccupied molecular orbital levels reasonably reflect their chemical structure. The high crystallinity of the polymers was confirmed by X-ray diffraction analysis. These polymers tend to aggregate even in the solution state. Control of the aggregation characteristics was a key factor for increasing the power conversion efficiency of the organic photovoltaic devices that were fabricated from the polymers. This study expanded the application range of direct arylation polycondensation for the preparation of crystalline polymer materials.

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INTRODUCTION

Bithiazole derivatives are attractive aromatic units for optoelectronic materials owing to their planar structure, electron acceptor properties and strong intermolecular interactions.¹ Bithiazole-based small molecules serve as high-performance n-type semiconducting materials for organic field-effect transistors.² π -Conjugated polymers bearing bithiazole units have also been reported as n-type semiconducting materials³ as well as p-type semiconducting materials for organic field-effect transistors^{4,5} and organic photovoltaics (OPVs).^{1,6–8} Owing to the weak acceptor property of bithiazole units, bithiazole-based polymers have lower highest occupied molecular orbital (HOMO) levels than the corresponding thiophene-based polymers. The low HOMO level of the bithiazole-based polymer affords several advantages in terms of air stability and electron transport properties.^{1,3–5} In addition, intermolecular interactions between the S and N atoms suggest that the bithiazole-based polymers may have strong interchain interactions, which result in aggregation properties and high crystallinity.

These bithiazole-based polymers have been primarily synthesized via polycondensation using cross-coupling reactions, such as the Migita–Kosugi–Stille and Suzuki–Miyaura coupling reactions.^{1,9,10} However, the instability of the stannylated bithiazole monomer has led to the formation of a low molecular weight polymer.^{3,11} In recent years, polycondensation using a direct C–H arylation reaction was

developed as an alternative method for the synthesis of conjugated polymers.^{12–18} Because direct arylation polycondensation does not require organometallic monomers, this new method can avoid the preparation of stannylated monomers, which require caution in handling and have problems associated with instability. In fact, direct arylation polycondensation of bithiazole-based monomers has afforded a series of conjugated polymers with high molecular weights.^{19–22} In some cases, only low molecular weight polymers were obtained owing to the low solubility of the target polymers in the reaction solvent (that is, *N,N*-dimethylacetamide (DMAc)).^{21,22} To overcome this issue, investigation of the reaction conditions was the primary objective of this study. In addition, we evaluated the accuracy of the repeating structures of the polymers that were synthesized under the established reaction conditions. Finally, the structure–property relationships of the polymers were investigated based on their absorption properties, energy levels, crystallinity and semiconducting properties to provide insight into the bithiazole-based polymers.

EXPERIMENTAL PROCEDURE

Materials

Pd(OAc)₂, chlorobenzene (CB), 1,8-diiodooctane (DIO) and other chemicals were received from commercial suppliers and used without further purification. Pd(PCy₃)₂ was purchased from Aldrich (St Louis, MO, USA) and stored under

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N_2 atmosphere at 0 °C. Anhydrous DMAc was purchased from Kanto Chemical (Tokyo, Japan) and used as a dry solvent. *N,N*-diethylpropanamide was dried over molecular sieves and degassed by freeze–pump–thaw cycles prior to use. 4,4'-Bis(2-octyldodecyl)-2,2'-bithiazole,²¹ 5,5'-dibromo-2,2'-bithiazole,²³ 4,4'-dinonyl-2,2'-bithiazole²⁴ and 2,6-dibromo-4,8-bis(2-octyldodecyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene²⁵ were prepared according to previously reported methods. The synthesis of 2,6-dibromo-4,8-bis(2-octyldodecyl)benzo[1,2-*b*:4,5-*b'*]dithiophene is described in Supplementary Information. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, CLEVIOS P VP AI 4083) was purchased from Heraeus (Hanau, Germany). PC₇₀BM (purity 99%) was purchased from Solenne (Groningen, The Netherlands).

General measurements and characterization

The nuclear magnetic resonance (NMR) spectra were recorded on AVANCE-400 and AVANCE-600 NMR spectrometers (Bruker, Karlsruhe, Germany). Gel permeation chromatography (GPC) measurements were conducted using a prominence GPC system (SHIMADZU, Kyoto, Japan) that was equipped with polystyrene gel columns using $CHCl_3$ as the eluent after calibration with polystyrene standards (40 °C). The high-temperature GPC measurements (140 °C) were conducted using a HLC-8321 GPC/HT (TOSOH, Tokyo, Japan) with *o*-dichlorobenzene (*o*-DCB) as the eluent after calibration with polystyrene standards. The matrix-assisted laser desorption/ionization mass (MALDI-TOF-MS) spectra were recorded on a MALDI TOF/TOF 5800 (AB SCIEX, Framingham, MA, USA) in linear mode using dithranol as the matrix. The ultraviolet-visible (UV-Vis) absorption spectra were recorded on a V-630 spectrometer (JASCO, Tokyo, Japan). The X-ray diffraction (XRD) patterns were recorded at 298 K on a MultiFlex X-ray diffractometer with a $CuK\alpha$ radiation source (Rigaku, Tokyo, Japan). The HOMO energy levels were estimated by photoelectron yield spectroscopy using an AC-3 spectrometer (Riken Keiki, Tokyo, Japan). The atomic force microscopic images were obtained using Nanoscope (SII Nano Technology Inc., Tokyo, Japan). The thermal properties were measured on an EXSTAR TG/DTA6300 instrument (Hitachi High-Technologies Corporation, Tokyo, Japan). The density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d) level with the Gaussian09 Rev. D.01 program (Gaussian, Inc., Wallingford, CT, USA). All of the manipulations for the reactions were performed under a nitrogen atmosphere using a glove box or standard Schlenk techniques. The NMR spectra and TGA curves are shown in Supplementary Figures S7–S14.

Synthesis of P1

A mixture of $Pd(PCy_3)_2$ (6.6 mg, 0.010 mmol), 1-adamantanecarboxylic acid (10.6 mg, 0.059 mmol), K_2CO_3 (67.2 mg, 0.49 mmol), 5,5'-dibromo-2,2'-bithiazole (63.9 mg, 0.20 mmol) and 4,4'-di(2-octyldodecyl)-2,2'-bithiazole (143 mg, 0.20 mmol) was stirred in *N,N*-diethylpropanamide (2.0 ml) at 100 °C for 48 h under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into an aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH = 8). The suspension was stirred for 1 h at room temperature. The precipitates were separated by filtration and washed with a 10% HCl solution, distilled water, methanol and hexane. The remaining solid was extracted with $CHCl_3$ by sonication and stirring at room temperature. The solution was filtered, concentrated and reprecipitated into methanol. The precipitates were collected by filtration and dried under reduced pressure. **P1** was isolated as a dark red solid in 43% yield as a hexane-insoluble and $CHCl_3$ -soluble fraction. $M_n = 35\,000$, $M_w/M_n = 3.21$. 1H NMR (600 MHz, $C_2D_2Cl_4$, 373 K): δ 7.94 (s, 2H), 2.89 (br, 4H), 2.05 (m, 2H), 1.43–1.18 (br, 64H), 0.85 (m, 12H). $^{13}C\{^1H\}$ NMR (150 MHz, $C_2D_2Cl_4$, 373 K): δ 161.36, 159.11, 156.92, 143.56, 131.03, 124.25, 38.35, 35.48, 34.31, 34.09, 32.06, 30.16, 29.79, 29.74, 29.43, 26.95, 22.76, 14.11 (8 signals of the alkyl group were overlapped). Anal. Calcd. for $C_{52}H_{84}N_4S_4$: C, 69.90; H, 9.48; N, 6.27; S, 14.35; Br, 0.00. Found: C, 69.05; H, 9.86; N, 6.32; S, 14.42; Br, 0.14.

Synthesis of P2

A mixture of $Pd(PCy_3)_2$ (5.0 mg, 0.0075 mmol), 1-adamantanecarboxylic acid (8.1 mg, 0.045 mmol), K_2CO_3 (51.8 mg, 0.38 mmol), 2,6-dibromo-4,8-bis(2-octyldodecyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (141.2 mg, 0.15 mmol) and 4,4'-dinonyl-2,2'-bithiazole (63.1 mg, 0.15 mmol) in *N,N*-diethylpropanamide

(1.5 mL) was stirred at 100 °C for 48 h under a nitrogen atmosphere. Then a solution of 4,4'-dinonyl-2,2'-bithiazole (31.5 mg, 0.075 mmol) in *N,N*-diethylpropanamide (1.5 mL) was added to the reaction mixture. After the reaction proceeded at 100 °C for 24 h, **P2** was isolated as a hexane-insoluble and $CHCl_3$ -soluble fraction in 51% yield by the same purification procedure that was used for **P1**. $M_n = 47\,000$, $M_w/M_n = 3.61$. 1H NMR (600 MHz, $C_2D_2Cl_4$, 373 K): δ 7.58 (s, 2H), 4.26 (br, 4H), 3.07 (br, 4H), 1.97–1.82 (br, 4H), 1.65 (br, 2H), 1.57–1.17 (m, 88H) 0.86 (m, 18H). $^{13}C\{^1H\}$ NMR (150 MHz, $C_2D_2Cl_4$, 373 K): δ 159.01, 156.50, 144.59, 133.38, 132.30, 130.08, 128.14, 120.64, 77.17, 39.81, 32.05, 31.91, 30.89, 30.28, 29.84, 29.78, 29.71, 29.68, 29.56, 29.44, 27.35, 22.75, 14.09 (14 signals of the alkyl group were overlapped). Anal. Calcd. for $C_{74}H_{122}N_2O_2S_4$: C, 74.07; H, 10.25; N, 2.33; S, 10.69; Br, 0.00. Found: C, 72.94; H, 10.43; N, 2.45; S, 10.56; Br, 0.11.

Synthesis of P3

P3 was synthesized using the same procedure as that used for **P2** on a 0.18 mmol scale with 2,6-dibromo-4,8-bis(2-octyldodecyl)benzo[1,2-*b*:4,5-*b'*]dithiophene (163.9 mg, 0.18 mmol) rather than 2,7-dibromo-4,8-bis(2-octyldodecyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene. **P3** was isolated as a hexane-insoluble and $CHCl_3$ -soluble fraction in 85% yield. $M_n = 49\,000$, $M_w/M_n = 4.61$. 1H NMR (600 MHz, $C_2D_2Cl_4$, 373 K): δ 7.57 (s, 2H), 3.09 (br, 8H), 2.13 (br, 2H), 1.90 (br, 4H), 1.53–1.15 (m, 88H), 0.855 (m, 18H). $^{13}C\{^1H\}$ NMR (150 MHz, $C_2D_2Cl_4$, 373 K): δ 158.83, 156.18, 139.11, 137.59, 133.22, 128.81, 128.65, 122.50, 39.22, 38.86, 34.77, 32.05, 30.99, 30.20, 29.78, 29.73, 29.69, 29.59, 29.43, 27.12, 22.75, 14.08 (15 signals of the alkyl group were overlapped). Anal. Calcd. for $C_{74}H_{122}N_2S_4$: C, 76.09; H, 10.53; N, 2.40; S, 10.98; Br, 0.00. Found: C, 75.40; H, 10.88; N, 2.39; S, 11.33; Br, 0.00.

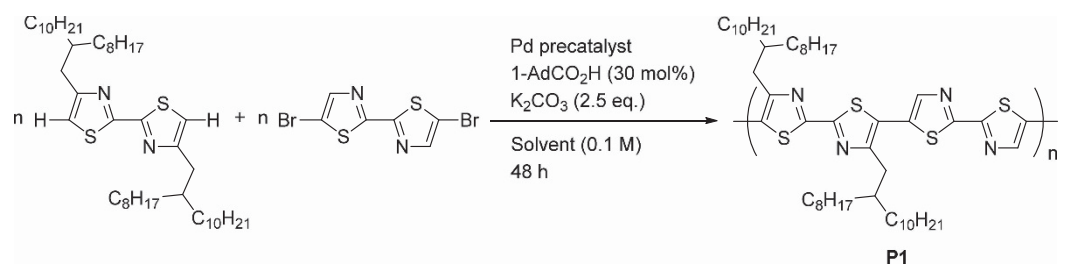
Fabrication and characterization of OPV cells

The OPV cells were fabricated in the following configuration: ITO/PEDOT:PSS/bulk heterojunction (BHJ) layer/LiF/Al. The patterned ITO (conductivity: 10 Ω per square) glass was pre-cleaned in an ultrasonic bath containing acetone and ethanol and then treated in an ultraviolet-ozone chamber. A thin layer (40 nm) of PEDOT:PSS was spin-coated onto the ITO at 3000 r.p.m. and air-dried at 110 °C for 10 min on a hot plate. Then the substrate was transferred to a N_2 -filled glove box where it was re-dried at 110 °C for 10 min on a hot plate. A CB solution (3% DIO) consisting of **P2** and PC₇₀BM blended in a 1:2 or 1:4 ratio was subsequently spin-coated onto the PEDOT:PSS surface to form the BHJ layer. The substrates with the BHJ layers were dried for 10 min at 110 °C for the film spin-casted from the CB solution. Then LiF (1 nm) and Al (80 nm) were deposited onto the active layer by conventional thermal evaporation at a chamber pressure lower than 5×10^{-4} Pa, which provided the devices with an active area of 5×2 mm². The thicknesses of the BHJ and PEDOT:PSS layers were measured using an automatic microfigure measuring instrument (SURFCORDER ET200, Kosaka Laboratory, Ltd., Tokyo, Japan). The current density–voltage (J – V) curves were measured using an ADCMT 6244 DC voltage current source/monitor under AM 1.5 solar-simulated light irradiation (100 mW cm⁻²) (OTENTO-SUN III, Bunkoh-Keiki Co., Ltd., Tokyo, Japan). The external quantum efficiency (EQE) and the internal quantum efficiency (IQE) were measured using an SM-250 system (Bunkoh-Keiki Co., Ltd.) with an integrating sphere to determine the reflectance (R) of the BHJ OPVs to estimate $IQE = EQE/(1-R)$.

RESULTS AND DISCUSSION

Optimization of reaction conditions

To investigate the synthetic conditions for a conjugated polymer with low solubility, direct arylation polycondensation of 4,4'-bis(2-octyldodecyl)-2,2'-bithiazole with 5,5'-dibromo-2,2'-bithiazole was selected as the target reaction. The corresponding polymer (**P1**) is expected to have a low solubility in polar solvents owing to its planar structure and the interchain interactions of the bithiazole units (Table 1).^{26,27} Under the previously reported conditions using DMAc,^{19–22} only oligomeric products were obtained, as expected (Entry 1, Table 1). In Entry 2, a reaction at a higher temperature (120 °C) was conducted to increase the reaction rate and amount of dissolved polymer during the

Table 1 Results of polycondensation reactions^a


Entry	Catalyst	Temp., °C	Solvent ^b	Hexane soluble part ^c		CHCl ₃ soluble part ^d	
				Yield, %	M _n ^e (M _w /M _n)	Yield, %	M _n ^e (M _w /M _n)
1	Pd(OAc) ₂ ^f	100	DMAc	79	2700 (1.19)		
2	Pd(PAr ₃) ₃ ^g	120	DMAc	86	6000 (1.88)		
3	Pd(PAr ₃) ₃ ^g	120	DMAc/ <i>m</i> -xylene ^h	77	5300 (2.28)		
4	Pd(PAr ₃) ₃ ^g	120	DEPA	20	6000 (2.52)	62	17 000 (2.86)
5	Pd(P <i>t</i> -Bu ₃) ₂	120	DEPA	99	12 000 (2.80)		
6	Pd(PCy ₃) ₂	120	DEPA	52	11 000 (3.34)	44	26 000 (3.01)
7	Pd(PCy ₃) ₂	100	DEPA	42	18 000 (2.85)	43	35 000 (3.21)
8	Pd(PCy ₃) ₂	90	DEPA	57	19 000 (1.40)		

^aReactions were conducted using a Pd precatalyst (5 mol%), 1-AdCOOH (30 mol%), and K₂CO₃ (2.5 equiv).

^bDMAc = *N,N*-dimethylacetamide. DEPA = *N,N*-diethylpropanamide.

^cMethanol-insoluble and hexane-soluble fraction.

^dHexane-insoluble and CHCl₃-soluble fraction.

^eEstimated by GPC calibrated with polystyrene standards using CHCl₃ as an eluent at 40 °C.

^f2 mol% of Pd precatalyst.

^gPAr₃ = tris[3,5-bis(trifluoromethyl)phenyl]phosphine.

^h1:1 mixture of DMAc and *m*-xylene.

reaction. In this reaction, a Pd(0) precatalyst with phosphine ligands was used to stabilize the Pd catalyst at high temperatures rather than using the reported phosphine-free catalyst.¹³ The molecular weight of the obtained polymer increased to 6000 (Entry 2) but the product was still soluble in hexane at room temperature. The addition of an aromatic solvent (that is, *m*-xylene) did not improve the molecular weight (Entry 3). Upon changing the solvent from DMAc to *N,N*-diethylpropanamide, the reaction afforded a hexane-insoluble product (62%), which is a relatively high molecular weight fraction (Entry 4). With regards to the Pd(0) precatalyst, Pd(PCy₃)₂ was a suitable precursor for this reaction (Entries 4–6). In *N,N*-diethylpropanamide, reaction at 100 °C provided a high molecular weight polymer with M_n = 35 000 (Entry 7). A reaction temperature of 90 °C was insufficient for the formation of a high molecular weight polymer (Entry 8). Based on these results, the reaction conditions used for Entry 7 were determined to be the most suitable for the synthesis of **P1** in a polar solvent. PCy₃ has been reported to be an efficient supporting ligand for Pd catalysts in direct arylation reactions.²⁸ The use of a Pd(0) precursor (that is, Pd(PCy₃)₂) rather than a Pd(II) precursor may lead to a high initiation efficiency in the catalysis.²⁹ *N,N*-diethylpropanamide exhibited better solubilizing properties to **P1** than DMAc at 100 °C, which was most likely due to the additional methylene moieties in *N,N*-diethylpropanamide (Supplementary Figure S1). The high solubilizing property of *N,N*-diethylpropanamide to **P1** results in the formation of a high molecular weight polymer. Rudenko and Thompson³⁰ also reported that *N,N*-diethylpropanamide was available in the synthesis of poly(3-hexylthiophene) using a direct arylation reaction. Toluene was not an appropriate solvent for this reaction system (Supplementary Table S1) even though toluene was utilized for direct arylation polycondensation of several

electron-deficient monomers.^{31,32} A high-temperature GPC measurement (140 °C) for the sample obtained from Entry 7 revealed a lower molecular weight (M_n = 22 000) than that obtained at 40 °C (M_n = 35 000). This observation indicates aggregation of **P1** at approximately room temperature. The aggregation behavior was evaluated by UV-Vis absorption spectroscopy, as described later.

Characterization of the polymer structure

The structure of **P1** was evaluated using ¹H NMR and MALDI-TOF-MS. Figure 1 shows the ¹H NMR spectrum of **P1** that was obtained from Entry 7 in Table 1. In addition to the signals corresponding to the repeating unit (7.94, 2.89 and 2.05 p.p.m.), signals corresponding to the terminal 4,4'-bis(2-octyldecyl)bithiazole unit were observed at 6.94, 2.75 and 1.84 p.p.m. The small signal at 8.01 p.p.m. can be assigned to the linkage of the non-substituted bithiazole unit, which was estimated from the chemical shift of 5,5'-bithiazole.³³ The non-alternating structure was caused by a homocoupling reaction of the C-Br moieties in 5,5'-dibromo-2,2'-bithiazole, which is a common side reaction in direct arylation polycondensations.^{34–36} The signal intensity corresponding to the homocoupling defect depends on the reaction conditions (Supplementary Figure S2). The polymer from Entry 7 exhibited a relatively small amount of defects compared with those from Entries 4 and 6 (Table 1). These results indicate that the use of PCy₃ and a low reaction temperature suppress the side reaction. In direct arylation, the homocoupling reaction of aryl-Pd intermediates is considered to occur via the transmetalation of aryl-Pd intermediates after oxidative addition of the arylbromide.^{29,37} PCy₃ may suppress the undesired transmetalation of the intermediates owing to its bulkiness and strong coordination ability. By evaluating the side reaction, the MALDI-TOF-MS results exhibited similar trends to the results from

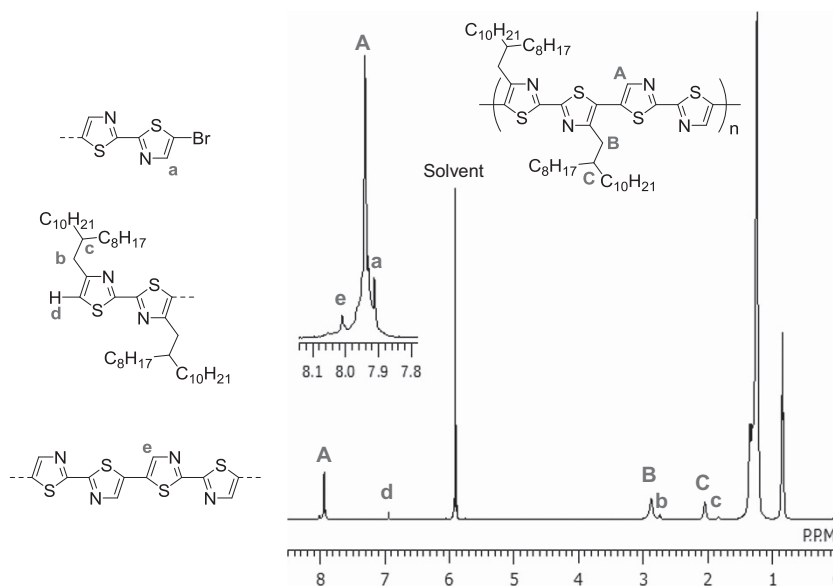
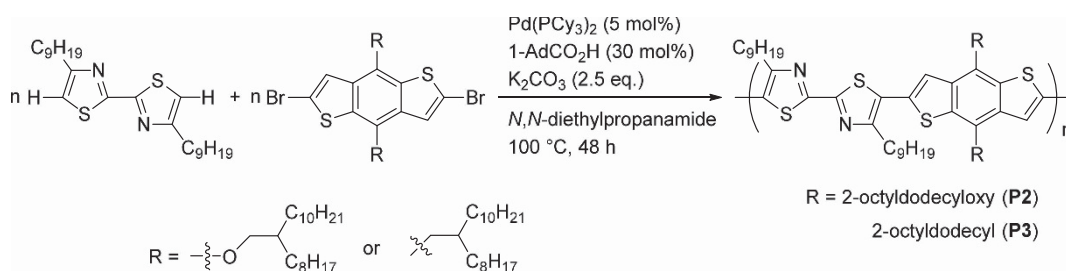


Figure 1 ^1H NMR spectrum of **P1** (Entry 7 in Table 1) (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K). A full color version of this figure is available at *Polymer Journal* online.

Table 2 Synthesis of **P2** and **P3**



Polymer	R	Hexane soluble part ^a		CHCl_3 soluble part ^b		
		Yield, %	M_n^c (M_w/M_n)	Yield, %	M_n^c (M_w/M_n)	M_n^d (M_w/M_n)
P2	2-Octyldodecyloxy	24	22 000 (2.11)	51 ^e	47 000 (3.61)	28 000 (2.49)
P3	2-Octyldodecyl	10	15 000 (1.30)	85	49 000 (4.61)	28 000 (2.49)

^aMethanol-insoluble and hexane-soluble fraction.

^bHexane-insoluble and CHCl_3 -soluble fraction.

^cEstimated by GPC calibrated with polystyrene standards using CHCl_3 as an eluent at 40 °C.

^dEstimated by GPC calibrated with polystyrene standards using *o*-DCB as an eluent at 140 °C.

^eInsoluble products in CHCl_3 were also obtained.

^1H NMR. The mass spectrum of the polymer from Entry 7 exhibited relatively low intensity peaks that corresponded to the defect structure (Supplementary Figure S3). The structure from the C-H/C-H homocoupling was also detected in the mass spectrum even though the ^1H NMR spectrum did not indicate the presence of this structure, which was most likely due to signals overlapping with those of the terminal structures.

Synthesis of donor–acceptor (D–A) polymers

Based on the established reaction conditions, bithiazole-based D–A polymers were synthesized via direct arylation of 4,4'-dinonyl-2,2'-bithiazole with dibromobenzodithiophene derivatives to confirm the

application range of the reaction conditions (Table 2). 2-Octyldodecyloxy- and 2-octyldodecyl-substituted dibromobenzodithiophenes were selected for preparation of D–A polymers with different electronic properties. Both of the reactions with 2-octyldodecyloxy- and 2-octyldodecyl-substituted dibromobenzodithiophenes afforded high molecular weight polymers (**P2** and **P3**) in reasonable yields. For 2-octyldodecyloxy-substituted dibromobenzodithiophene, a small amount of CHCl_3 -insoluble products was obtained, which was most likely due to the low solubility caused by stronger interchain D–A interactions. Previous reports have demonstrated that a polycondensation reaction using Stille cross-coupling can afford an analogous polymer to **P2** with a molecular weight of 7000.⁷ The higher molecular

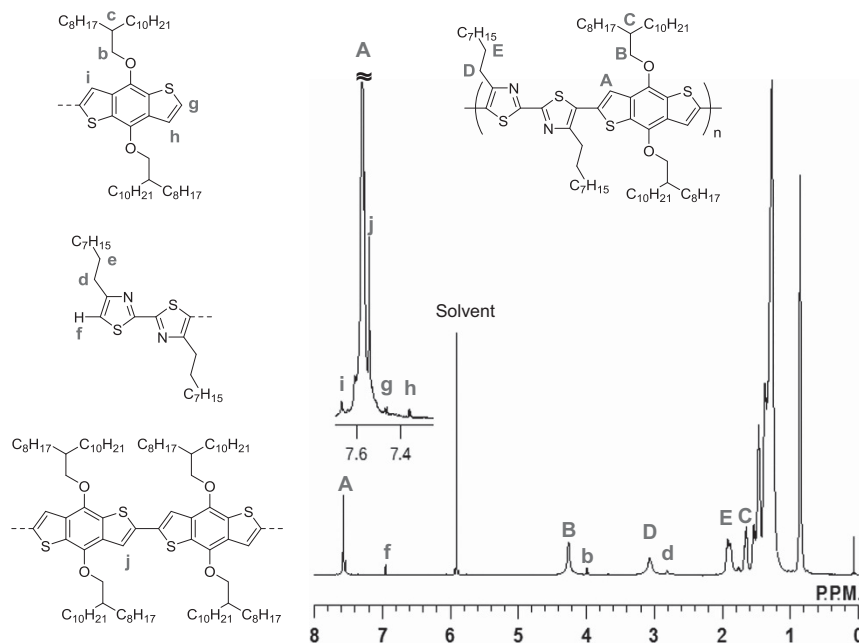


Figure 2 ^1H NMR spectrum of **P2** (600 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K). A full color version of this figure is available at *Polymer Journal* online.

weight of **P2** confirms that the established reaction conditions are useful for the synthesis of D–A polymers. Recently, Wakioka *et al.*³⁸ reported the direct arylation polycondensation of a bithiazole monomer in tetrahydrofuran using their original catalytic system. Because this reaction also afforded a high molecular weight polymer, tetrahydrofuran is another option for the synthesis of bithiazole-based polymers.

The ^1H NMR spectrum of **P2** contains relatively small signals for the terminal bithiazole structure compared with that for **P1** owing to the high molecular weight of **P2** (Figure 2). Three signals corresponding to the debrominated benzodithiophene terminal were observed at 7.67, 7.46 and 7.36 p.p.m. with a reasonable coupling pattern. The homocoupled structure of the benzodithiophene unit was also detected at 7.54 p.p.m. with a low intensity signal.³⁹ In **P3**, similar signal patterns were observed in the ^1H NMR spectrum (Supplementary Figure S4). The MALDI-TOF-MS spectra indicated that alternative structures were dominant in both **P2** and **P3** (Supplementary Figures S5 and S6).

Absorption properties

The absorption maxima of **P1–P3** appeared at approximately 500 nm in the solution state (Figures 3a–c and Table 3). These absorption bands are associated with shoulders in a longer wavelength region. The shoulders may result from aggregation of the polymer in solution because time-dependent (TD)-DFT calculations for model compounds of **P1–P3** did not predict transitions in the long wavelength region (Figure 4). The aggregation hypothesis is also supported by enhancement of the shoulder bands in the film state. To investigate the aggregation behavior, variable temperature absorption spectra were measured from 30 to 80 °C (Figures 3d–f). These spectra exhibited blue shifts of the absorption at high temperatures, which confirms the dissociation of aggregates.⁴⁰ The shapes of the absorption spectra at 80 °C are in good agreement with those of the estimated absorption spectra that were predicted using TD-DFT calculations (Figure 4). At 80 °C, **P1–P3** possess similar absorption maxima even though **P2** and **P3** were expected to exhibit long-wavelength

absorption compared with that of **P1** owing to the D–A structures of **P2** and **P3**. The weak acceptor property of the bithiazole unit may result in a small contribution from charge transfer absorption.²¹ Indeed, the TD-DFT calculations predicted a large contribution from a $\pi\text{-}\pi^*$ transition from the HOMO to the lowest unoccupied molecular orbital (LUMO) in each polymer rather than a charge transfer transition (Figure 4).

Physical properties

The physical properties of **P1–P3** are summarized in Table 4. Despite the similar absorption properties and band gaps in **P1–P3**, the energy levels reasonably reflect their chemical structures (Supplementary Figure S17).^{21,41} The results from photoelectron yield spectroscopy indicated that **P1** had a lower HOMO level than those of **P2** and **P3** owing to the acceptor–acceptor structure of **P1**. The presence of an electron-donating oxygen atom in the side chain of **P2** contributes to a slightly higher HOMO level compared with that of **P3**. To evaluate the crystallinity of the film state, X-ray diffraction analysis was performed on **P1–P3** before and after annealing at 200 °C (Figure 5, Table 4). In all of the polymers, the annealing treatments sharpened the diffraction peaks. After annealing, **P1** exhibited diffraction peaks that corresponded to a lamellar structure up to the fourth order. A diffraction peak corresponding to a $\pi\text{-}\pi$ stacking structure was not detected. Similar diffraction patterns were reported in bithiazole-rich conjugated polymers.^{4,5,27} In contrast, **P2** exhibited a strong diffraction peak in the high-angle region ($2\theta = 23.20^\circ$), corresponding to a $\pi\text{-}\pi$ stacking structure. The lamellar diffraction peak was relatively small (3.67°). In addition, a diffraction peak at 5.69° ($d = 15.51 \text{ \AA}$) was detected with a second-order diffraction at 11.17° . Because the distance of the repeating unit of **P2** was estimated to be 15.9 \AA using DFT calculations, these diffractions may result from a periodic structure in the main chain direction. Similar observations have been previously reported.^{42,43} **P3** exhibited diffractions from both lamellar and stacking structures.

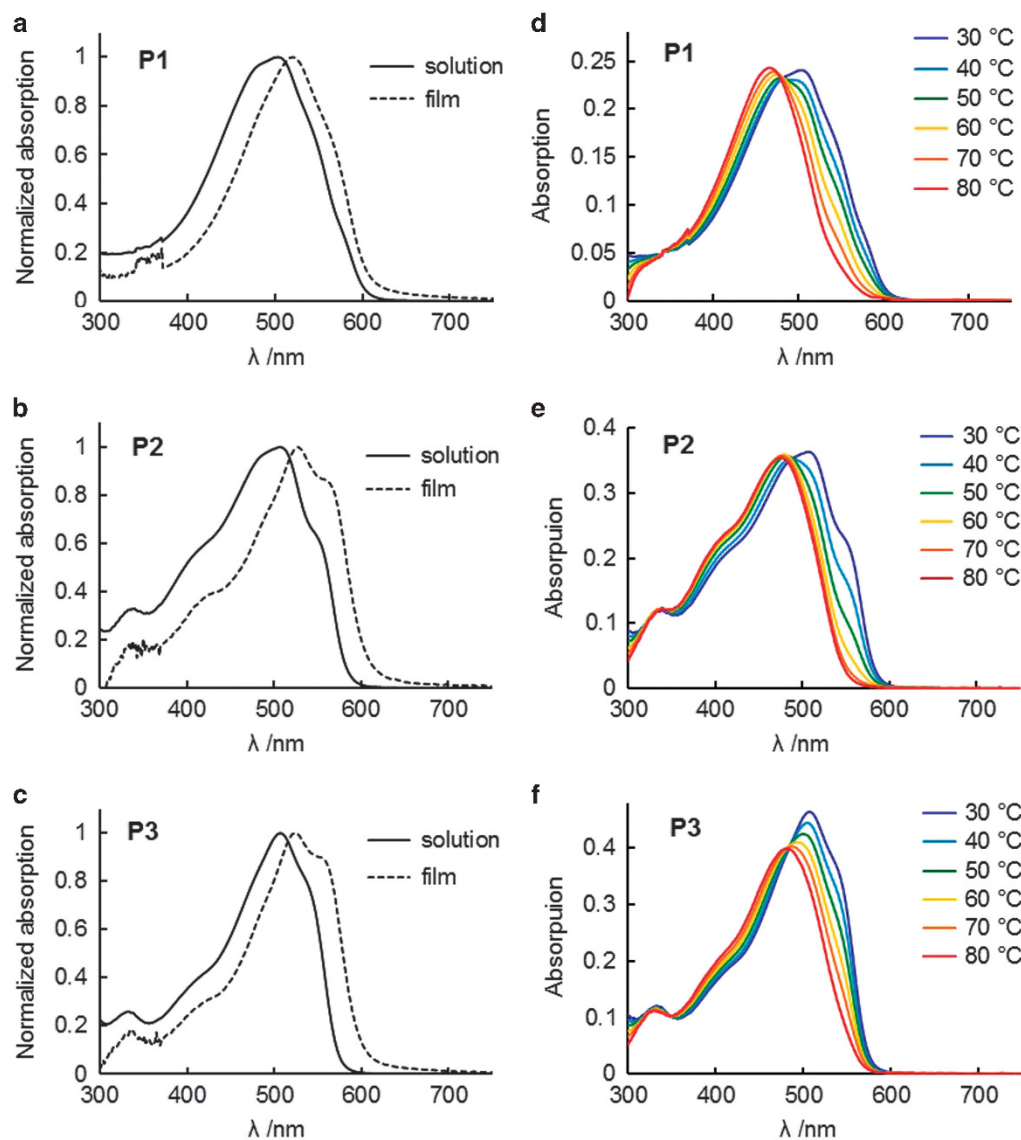


Figure 3 (a–c) UV-Vis absorption spectra of **P1–P3** in the solution state (toluene, 30 °C, 1.0×10^{-5} M) and the film state. (d–f) Variable temperature absorption spectra of **P1–P3** in toluene (30–80 °C, 1.0×10^{-5} M).

Table 3 Absorption properties

Polymer	Solution ^a		Calculation ^b		Film
	λ_{\max} , nm at		λ_{\max} , nm	λ_{\max} , nm	λ_{onset}^c , nm
	30 °C	80 °C			
P1	504	466	517	520	602
P2	507	476	498	527	603
P3	507	480	505	523	600

^aIn toluene (1.0×10^{-5} M).

^bCalculated using TD-DFT.

^cAbsorption onset.

OPV characteristics

Because the energy levels of **P2** and **P3** looked promising, these polymers were evaluated as BHJ OPV materials. The BHJ OPVs were fabricated with PC₇₀BM as the acceptor material and blend ratios of 1:2

or 1:4 using various solvents (Table 5 and Supplementary Table S2). The OPV with **P2**:PC₇₀BM at a 1:4 mixing ratio using CB as the solvent yielded a power conversion efficiency (PCE) of 0.51% (Entry 1, Table 5). This PCE increased to 1.03% upon addition of 3% DIO in the CB solvent (Entry 2, Supplementary Figure S15). The surface morphology of the active layers was evaluated using atomic force microscopy (Figure 6). In contrast to the smooth surface of **P2** (Figure 6a), the surface of the BHJ film with **P2** and PC₇₀BM was rough, indicating substantial phase separation (Figure 6b). The pronounced phase separation reduced the heterojunction interface area for exciton dissociation, which led to the low J_{sc} of BHJ OPVs. Because the addition of 3% DIO in the CB solvent decreased the domain size (Figure 6c), the increase in PCE most likely resulted from improvement in phase separation. **P3** exhibited a trend similar to that of **P2** (Supplementary Figure S16). Owing to the strong intermolecular interactions of the bithiazole units, control of the aggregation behavior is crucial for improvement of PCE in the bithiazole-based polymer materials.

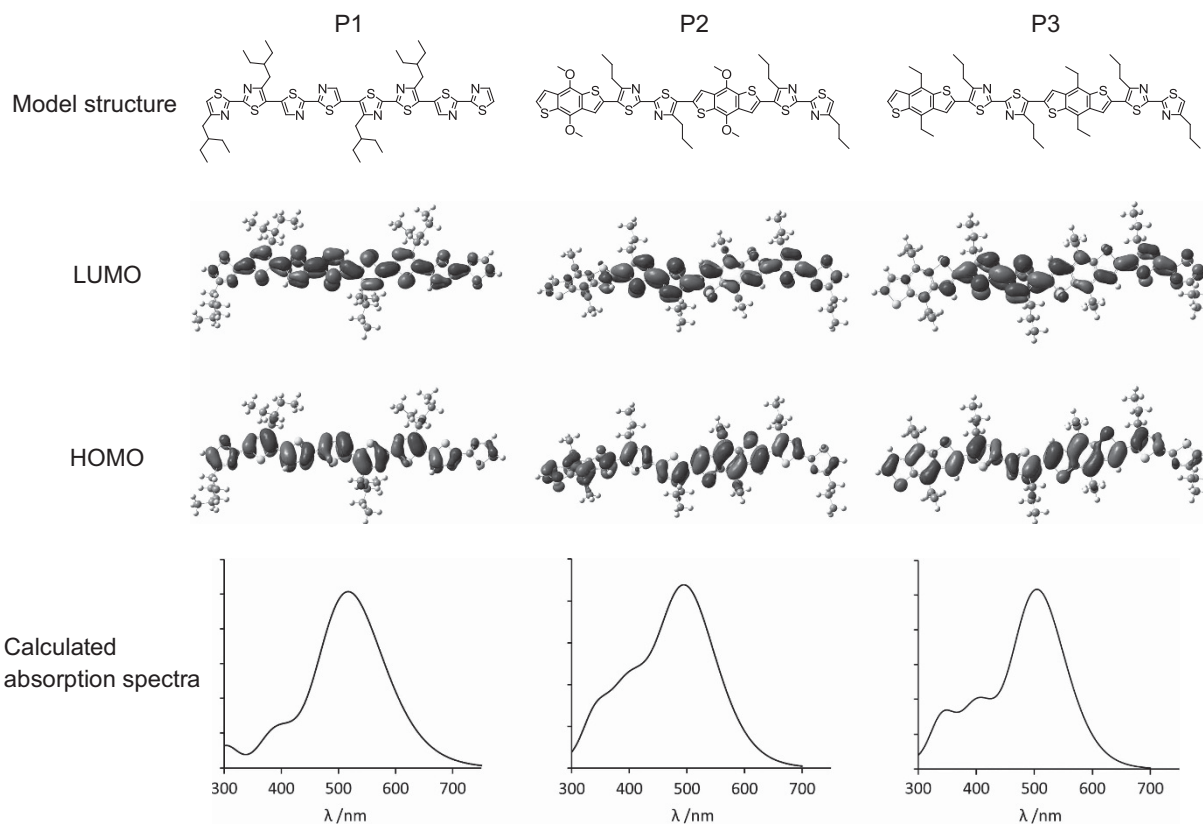


Figure 4 HOMO and LUMO distribution of model compounds for **P1–P3** along with the calculated absorption spectra obtained from TD-DFT calculations. A full color version of this figure is available at *Polymer Journal* online.

Table 4 Physical properties

Polymer	E_g^{opta} , eV	$HOMO^b$, eV	$LUMO^c$, eV	T_{d5}^d , °C	Diffraction peak (2θ) ^e
P1	2.06	−5.99	−3.93	405	4.17, 8.34, 12.52, 16.87
P2	2.06	−5.40	−3.34	312	3.67, 5.69, 11.17, 23.20
P3	2.07	−5.49	−3.42	410	3.61, 5.60, 7.15, 22.33

Abbreviations: HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

^aOptical band gap from the absorption onset in the film state.

^bHOMO from photoelectron yield spectroscopy.

^c $LUMO = HOMO + E_g^{opt}$.

^dThe 5% weight-loss temperatures under an inert atmosphere.

^eDiffraction peaks from XRD after annealing at 200 °C.

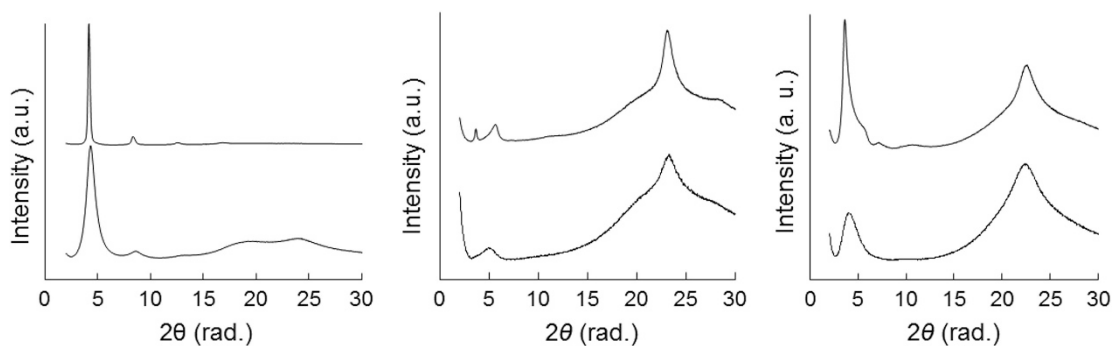


Figure 5 X-ray diffraction patterns of **P1–P3** before (bottom) and after annealing (top).

Table 5 OPV characteristics^a

Entry	Polymer	Solvent ^b	Thickness, nm	J_{sc} , mAcm^{-2}	V_{oc} , V	FF	PCE, %
1	P2	CB	88	1.55 ± 0.04	0.78 ± 0.03	0.425 ± 0.006	0.51 ± 0.04
2	P2	CB+DIO 3%	87	2.99 ± 0.12	0.75 ± 0.03	0.46 ± 0.01	1.03 ± 0.05
3	P3	CB	78	0.98 ± 0.09	0.70 ± 0.04	0.39 ± 0.08	0.28 ± 0.09
4	P3	CB+DIO 3%	80	2.40 ± 0.09	0.67 ± 0.03	0.45 ± 0.02	0.74 ± 0.07

Abbreviations: FF, fill factor; OPV, organic photovoltaic.

^aThe average values with s.d.s. were calculated from the results of three or more OPV samples. OPV configuration: ITO/PEDOT:PSS (40 nm)/P2-P3:PC₇₀BM (1:4)/LiF (1 nm)/Al (80 nm).

^bChlorobenzene (CB) and 1,8-diodooctane (DIO).

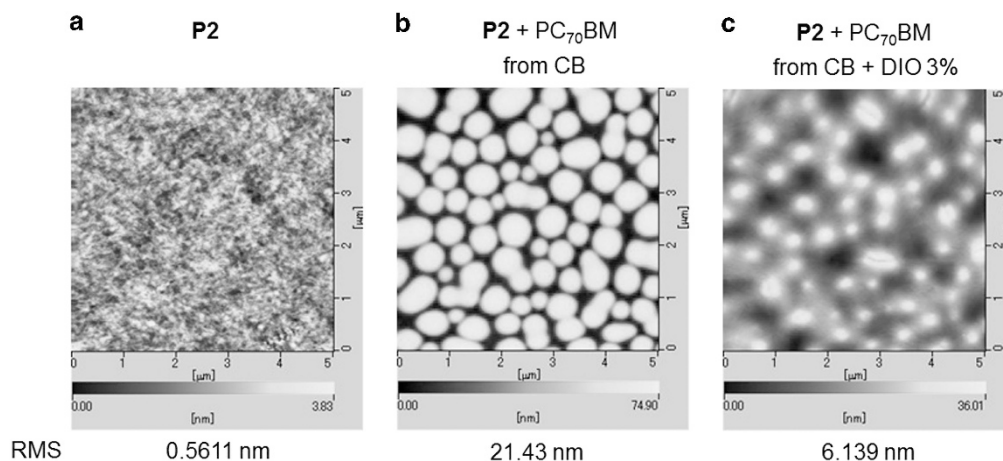


Figure 6 AFM images ($5 \times 5 \mu\text{m}^2$) of (a) P2, (b) P2:PC₇₀BM (1:4) from CB solution, and (c) P2:PC₇₀BM (1:4) from CB+DIO 3% solution with the root mean square (RMS) roughness values. A full color version of this figure is available at *Polymer Journal* online.

CONCLUSION

The investigation of the reaction conditions of the direct arylation polycondensation led to the successful synthesis of bithiazole-based crystalline polymers with low solubilities. The choice of a suitable solvent (that is, *N,N*-diethylpropanamide) facilitated smooth coupling reactions along with the prevention of precipitation of the growing polymers as the reaction progressed. The bithiazole-based polymer exhibited aggregation even in the dilute solution state (1×10^{-5} M). This aggregation behavior produced high crystallinity, which was confirmed by the X-ray diffraction analysis. Control of aggregation is a key factor for increasing the PCE of the BHJ OPVs with bithiazole-based conjugated polymers. This study expanded the application range of direct arylation polycondensation for the preparation of various crystalline polymers with low solubilities. In addition, the detailed investigation of the structure–property relationships provides insight into the molecular design of conjugated polymer materials.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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