

Facile Synthesis of Fluorene-based π -Conjugated Polymers via Sequential Bromination/Direct Arylation Polycondensation

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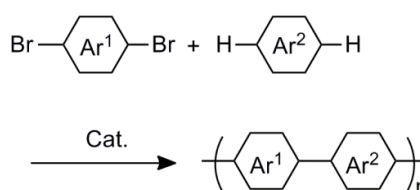
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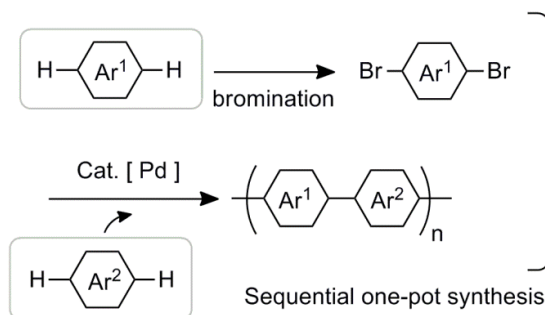
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Catalytic direct arylation of aromatic compounds via cleavage of C-H bonds has attracted increasing attention as a simple synthetic method that helps eliminate prior preparations of organometallic reagents.¹⁻⁶ Recently, several groups have attempted to utilize this reaction in polycondensation for the synthesis of π -conjugated polymers that are considered promising materials for optoelectronic devices such as organic photovoltaic cells, field effect transistors, and light emitting diodes (Scheme 1 (a)).⁷⁻¹⁶ However, this polycondensation reaction still requires prior preparation of dihalogenated aromatic monomers as coupling partners: Introduction of C-Br groups into the corresponding aromatic compounds and purification of the dibrominated aromatic monomers would involve extra synthetic steps. These observations prompted our interest in the facile synthesis of π -conjugated polymers via sequential bromination and direct arylation polycondensation (Scheme 1 (b)); this protocol enables the use of each aromatic monomer without pre-introduction of reactive C-Br bonds as well as organometallic functional groups. We thus explored an efficient bromination reaction and employed it for the bromination of arenes with quaternary ammonium tribromide; the reaction proceeded smoothly under mild conditions, giving the desired bromoarenes in good yields.¹⁷⁻²² 9,9-Dioctylfluorene is an appropriate targeting monomer because 2,7-dibromo-9,9-dioctylfluorene possesses good

(a) Direct arylation polycondensation



(b) This work: Sequential bromination / Direct arylation polycondensation



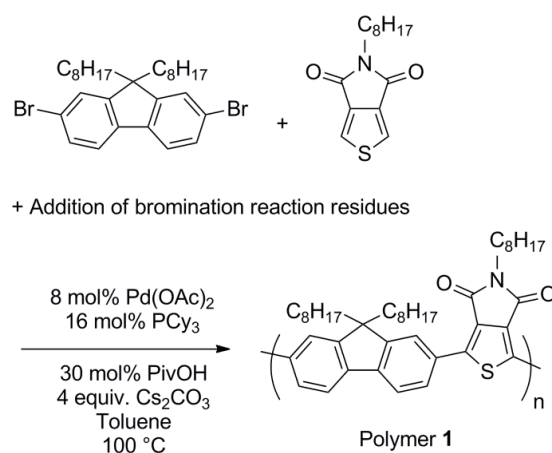
Scheme 1. Schematic illustrations of sequential bromination and direct arylation polycondensation.

reactivity toward the direct arylation polycondensation and high selectivity against side reactions; accordingly, a variety of fluorene-based π -conjugated polymers have been synthesized.^{15,23-32} We herein report the synthesis of fluorene-based π -conjugated polymers via sequential bromination of 9,9-dioctylfluorene and Pd-catalyzed direct arylation polycondensation.

The following two conditions must be satisfied for sequential bromination and Pd-catalyzed direct arylation polycondensation. Each reaction should efficiently proceed, and residues and/or byproducts originating from the bromination reaction step should have negligible impact on the successive polycondensation step. For instance, bromination of aromatic compounds has been generally carried out with bromine or *N*-bromosuccinimide (NBS);³³⁻³⁵ however, the residual bromine and/or the produced byproducts such as succinimide are considered to inhibit the following direct arylation. In contrast, bromination with benzyltrimethylammonium tribromide (BTMA Br₃)¹⁶⁻¹⁸ was expected to be preferable for our protocol; the solid brominating agent allows for accurate stoichiometric reaction, and benzyltrimethylammonium bromide (BTMA Br), a byproduct of the bromination, does not inhibit the successive polycondensation step because tetraalkylammonium halides have been often used as a phase transfer catalyst in polycondensation processes.^{7,12,36-38} Therefore, we began our investigation with dibromination of 9,9-dioctylfluorene using a stoichiometric amount of BTMA Br₃. According to the literature,¹⁶ the reaction gave 2,7-dibromo-9,9-dioctylfluorene in excellent isolated yield (98%) in the presence of ZnCl₂, which served as a Lewis acid,¹⁷ and acetic acid, and only a trace amount of mono-brominated product was

observed. In addition, the reaction smoothly proceeded in the absence of acetic acid and the dibrominated product was isolated in good yield (98%, Scheme S1, Supporting Information); consequently, we adopted the reaction conditions in the absence of acetic acid.

Subsequently, to assess whether the presence of the conserved residues of the bromination reaction considerably affected the following polycondensation process or not, Pd-catalyzed direct arylation polycondensation of 5-octylthieno[3,4-*c*]pyrrole-4,6-dione (TPD) with the isolated pure 2,7-dibromo-9,9-dioctylfluorene was conducted in the presence of some additives (Scheme 2). Table 1



Scheme 2. Direct arylation polycondensation in the presence of byproduct of bromination reaction.

Table 1. Results of direct arylation polycondensation of 2,7-dibromo-9,9-dioctylfluorene with TPD in the presence of additive^{a)}

Entry	Additive (equiv.)	Reaction time / h	Yield ^{b)} / %	M_n ^{c)}	M_w/M_n ^{c)}
1	-	24	96	129200	2.60
2	Succinimide (2)	24 (240)	0 (0)	-	-
3	BTMA Br (2)	24	95	89500	2.32
4	BTMA Br (2) / ZnCl ₂ (2.5)	48	95	50500	2.33

^{a)} Reactions were carried out at 100 °C in toluene (2.5 mL) for 0.50 mmol scale using Pd(OAc)₂ (8 mol%), PCy₃ (16 mol%), PivOH (30 mol%) and Cs₂CO₃ (4 equiv.); ^{b)} The products were obtained by reprecipitation from CHCl₃/CH₃OH; ^{c)} Estimated by GPC calibrated on polystyrene standards.

summarizes the results of the polycondensation. According to a previous report,²³ a control experiment without the additive smoothly proceeded and gave the corresponding polymer (Polymer 1) in good yield (entry 1). In contrast, the addition of succinimide did not give the polymeric product even after a prolonged reaction (entry 2), indicating that the byproduct of bromination with NBS prohibited direct arylation, presumably due to the formation of palladium-succinimide complex,³⁹ which may deactivate the catalytic system. Alternatively, the polycondensation reaction proceeded smoothly in the presence of BTMA Br (entry 3); Wang *et al.* have elaborated on positive and negative effects of the addition of phase transfer agents on the direct arylation polycondensation.³⁶ The addition of zinc chloride slightly reduced the catalytic activity, but increasing the reaction time to 48 h afforded the polymeric product (entry 4).

Based on these observations, we finally examined the sequential Pd-catalyzed direct arylation polycondensation; the bromination reaction mixture was used without purification for the successive polycondensation (Scheme 3 (a)). The sequential protocol gave Polymer 1 with a molecular weight of 34,500, in 80% yield. Polymer 1 obtained from the sequential protocol was characterized by NMR spectroscopy, Matrix Assisted Laser

Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF-MS), and elemental analysis. As shown in Figure 1, the ¹H NMR spectrum of Polymer 1 prepared via the sequential protocol essentially agrees with that of the polymer obtained from the isolated pure 2,7-dibromo-9,9-dioctylfluorene. Each ¹H NMR signal can be assigned to the repeating unit; the integral ratios of the signals agree with the assignments and are consistent with the alternating structure of the polymer. All ¹³C{¹H}

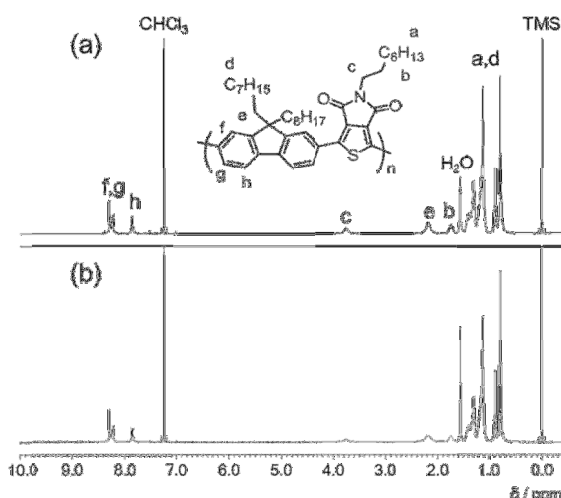
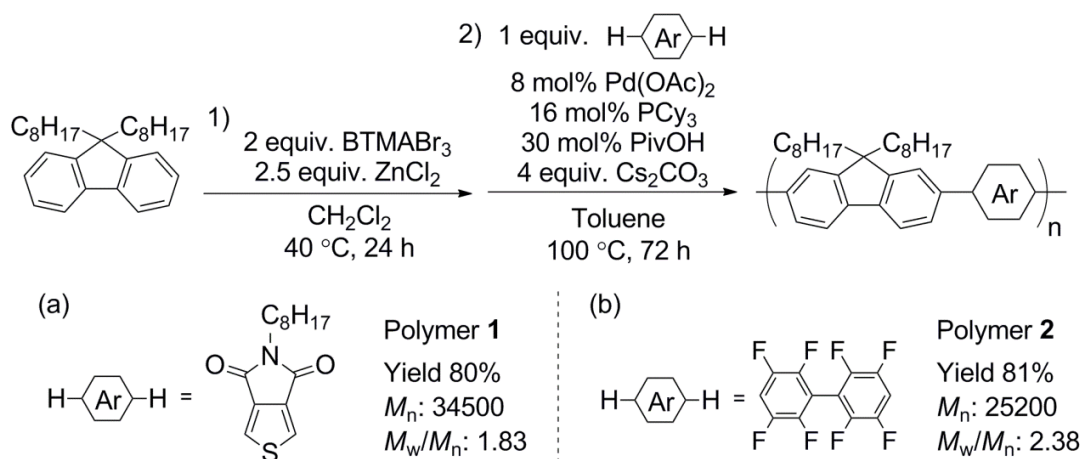


Figure 1. ¹H NMR spectra of Polymer 1 (400 MHz, in CDCl₃). (a) Synthesized via sequential protocol (Scheme 3 (a)) and (b) synthesized from the isolated 2,7-dibromo-9,9-dioctylfluorene (Scheme 2, Table 1, Entry 1).



Scheme 3. Sequential bromination of 9,9-dioctylfluorene and direct arylation polycondensation with (a) TPD and (b) 2,2',3,3',5,5',6,6'-octafluorobiphenyl.

NMR signals are also assignable to the carbons in the recurring unit (Figure 1S, supporting information). The MS spectrum exhibits peaks at regular intervals in the measurable molecular weight range, corresponding to the structure of the linked fluorene and TPD units (Figure S2, supporting information). The absorption spectra of the obtained polymers are also essentially identical (Figure S3, Supporting Information), and the optical bandgap is determined to be 2.45 eV. Consequently, the difference in the synthetic protocols does not affect the chemical structure and optical properties of the polymers.

The sequential protocol was further demonstrated by the polycondensation of 9,9-dioctylfluorene with 2,2',3,3',5,5',6,6'-octafluorobiphenyl (Scheme 3 (b)); the direct arylation polycondensation of the isolated pure 2,7-dibromo-9,9-dioctylfluorene and 2,2',3,3',5,5',6,6'-octafluorobiphenyl gave the corresponding polymer with a molecular weight of 43,200 in 95% yield.²⁶ The sequential protocol afforded the corresponding polymer (Polymer 2) with a molecular weight of 25,200 in 81% yield. The NMR and absorption spectra essentially agreed with those in previous reports (Figure S5-7, 9, Supporting Information).²⁶ These results were consistent with the trend observed in the synthesis of Polymer 1.

In summary, the synthesis of fluorene-based π -conjugated polymers via sequential bromination and direct arylation was demonstrated. Bromination of 9,9-dioctylfluorene using BTMA Br₃ efficiently proceeded and barely inhibited the following direct arylation polycondensation, successfully giving π -conjugated polymers. Currently, the polycondensation reaction conditions are very specific towards the targeting monomer being electron-poor, and established conditions would be required for the electron-rich one.²³ However, this is the first example of the facile synthesis of π -conjugated polymers in a one-pot fashion, without the need for prior preparation

and purification of dibrominated aromatic monomers as well as organometallic monomers, and the bromination reaction using BTMA Br₃ is also available to other aromatic compounds such as thiophene^{21,22} and carbazole derivatives (Scheme S2, Supporting Information). Therefore, the fundamental findings described here should present new insights for the synthesis of π -conjugated semiconducting materials using the step-economical protocol. Further studies, including availability of the synthetic protocol for other aromatic monomers and evaluation of electrical properties of the polymers are currently underway in our laboratory.

EXPERIMENTAL

Sequential bromination of 9,9-dioctylfluorene and Pd-catalyzed direct arylation polycondensation with 5-octylthieno[3,4-c]pyrrole-4,6-dione

A catalyst solution was prepared in advance using the following procedure: a mixture of PCy₃ (239 mg, 0.852 mmol), Pd(OAc)₂ (95.7 mg, 0.426 mmol), and anhydrous toluene (4.25 mL) was stirred at room temperature overnight under nitrogen atmosphere. The resulting mixture was used as a catalyst solution (PCy₃: 0.200 mol/L, Pd(OAc)₂: 0.100 mol/L).

A mixture of dried ZnCl₂ (170 mg, 1.25 mmol), 9,9-dioctylfluorene (195 mg, 0.500 mmol), anhydrous dichloromethane (2 mL), and BTMA Br₃ (390 mg, 1.00 mmol) was stirred for 24 h at 40 °C under nitrogen atmosphere. After the mixture was cooled to room temperature, anhydrous toluene (1 mL) and Cs₂CO₃ (652 mg, 2.00 mmol) were added and stirred for 1 h. Then, TPD (133 mg, 0.500 mmol), catalyst solution (0.400 mL including Pd(OAc)₂ (0.0400 mmol) and PCy₃ (0.0800 mmol)), pivalic acid (PivOH) (0.0169 mL, 0.150 mmol), and anhydrous toluene (1.1 mL) were added to the mixture. The resulting mixture was stirred at 100 °C for 72 h. After cooling to room temperature, the mixture was diluted with CHCl₃ (100 mL) and then washed with 1 M HCl

solution (50 mL × 3), 0.1 M ethylenediaminetetraacetic acid disodium salt (pH 8) (50 mL × 3), and distilled water (50 mL × 3). The organic layer was dried over sodium sulfate and filtered through a Celite plug. The solution was concentrated under reduced pressure and precipitated in CH₃OH. The polymer deposit was washed with CH₃OH and hexane. The solid was reprecipitated from CHCl₃ / CH₃OH, giving poly[(9,9-dioctylfluorene-2,7-diyl)-(5-octylthieno[3,4-c]pyrrole-4,6-dione-1,3-diyl)] (Polymer **1**) as a yellow solid in 80% yield ($M_n = 34500$, $M_w/M_n = 1.83$). ¹H NMR(400 MHz, CDCl₃): δ 8.20-8.31 (m, 4H), 7.86 (d, $J = 8.0$ Hz, 2H), 3.75 (br, 2H), 2.18 (br, 4H), 1.74 (br, 2H), 0.60-1.47 (m, br 43H). ¹³C{¹H} NMR(150 MHz, CDCl₃): δ 163.1, 152.4, 145.2, 142.2, 130.5, 130.2, 127.4, 122.8, 120.6, 55.8, 40.1, 38.7, 31.8, 30.0, 29.3, 29.2, 28.6, 27.1, 23.93, 22.7, 22.6, 14.1. Anal. calcd. for C₄₃H₅₇NO₂S: C 79.21, H 8.81, N 2.15; found C 78.99, H 8.61, N 2.27.

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GRAPHICAL ABSTRACT

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TITLE

Facile Synthesis of Fluorene-based π -Conjugated Polymers via Sequential Bromination/Direct Arylation Polycondensation

TEXT

The synthesis of fluorene-based π -conjugated polymers via sequential bromination and Pd-catalyzed direct arylation polycondensation was demonstrated; the protocol allows dual functionalization of each aromatic monomer in one-pot fashion. This synthetic protocol afforded the corresponding polymers with high molecular weights in good yields (up to yield 80%, M_n 34500).

GRAPHICAL ABSTRACT FIGURE

