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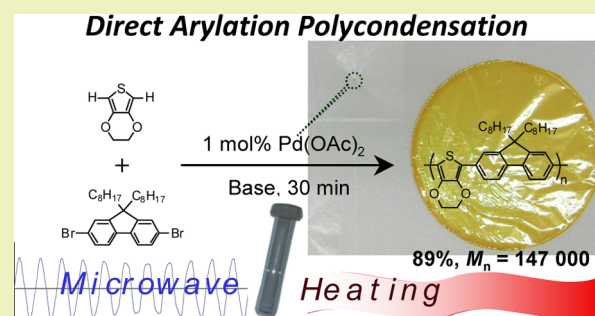
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S Supporting Information

ABSTRACT: For synthesis of π -conjugated polymers, polycondensation via direct arylation reactions of C–H bonds in aromatic monomers with dibromo-arylenes has attracted increasing attention as a simple synthetic method in which the preparation of organometallic reagents is unnecessary. To develop direct arylation polycondensation for practical use in the synthesis of optoelectronic polymer materials, microwave-assisted reactions were investigated and optimized in terms of a kind of base, concentration, reaction time, and amount of catalyst. Under the optimized conditions, the microwave-assisted direct arylation of 3,4-ethylenedioxythiophene with dibromofluorene for 30 min with catalyst (1 mol %) gave the corresponding polymer with an extremely high molecular weight up to 147 000. The high molecular weight of the polymer enables formation of a large and flexible self-standing film, leading to an advantage in fabricating organic thin-film devices. The elemental analysis and MALDI-TOF-MS reveal that the polymer has high purity and no bromo- and metallo-terminals. Because only microwave-assisted direct arylation provided these features in the polymer, the present method is superior to conventional methods. Therefore, microwave-assisted polycondensation via direct arylation methodology lends itself well to practical application using inherent product from economical and environmental points of view for the synthesis of pure optoelectronic materials.

KEYWORDS: Microwave heating, Direct arylation, Polycondensation, Conjugated polymer, Highly pure polymer



■ INTRODUCTION

Direct arylation of C–H bonds in aromatic compounds with aryl halides have attracted increasing attention as a simple synthetic method in which the preparation of organometallic reagents is unnecessary.^{1,2} Recently, several groups have attempted to apply this method to the synthesis of π -conjugated polymers that are considered to be promising materials for optoelectronic devices such as organic thin-film solar cells.^{3–13} We reported polycondensation reactions of thiophene derivatives with dibromoarylenes via direct arylation using palladium acetate (Pd(OAc)₂) without phosphine ligands.^{10,11} This methodology has several advantages from economical and environmental points of view: the corresponding polymers were obtained in fewer overall reaction steps and without the formation of a stoichiometric amount of toxic metal-containing waste such as organostannyl compounds from organometallic reagents. This method allows for the preparation of highly pure polymer materials owing to the absence of contamination by phosphine compounds¹⁴ and metals.¹⁵ These types of contaminants are a common problem in the preparation of polymer materials for optoelectronic devices.¹⁶ Alternatively, the application of microwave heating is known to accelerate organic reactions including direct arylation.^{17–19} Therefore, microwave-assisted direct arylation is expected to provide further sophistication to direct arylation polycondensation

for practical use in the synthesis of optoelectronic polymer materials.²⁰ Herein, we report a highly efficient direct arylation polycondensation using microwave heating, which results in shorter reaction times and increased molecular weight of the obtained conjugated polymers.

■ EXPERIMENTAL SECTION

A typical procedure for the microwave-assisted polycondensation reaction of 3,4-ethylenedioxythiophene with 2,7-dibromo-9,9-dioctylfluorene is as follows (Table 2, entry 2 in the main text).

Pd(OAc)₂ (1.1 mg, 0.0050 mmol) and 2,7-dibromo-9,9-dioctylfluorene (274 mg, 0.50 mmol) were weighed in air and placed in a 10 mL microwave vessel contained with a magnetic stir bar. The vessel was transferred to a glovebox under nitrogen atmosphere. Then, KO₂Piv (175 mg, 1.3 mmol), 3,4-ethylenedioxythiophene (53.4 μ L, 0.50 mmol), and degassed DMAc (2.5 mL) were added. The vessel was sealed with a septum and removed from the glovebox. The sealed vessel was then placed in the microwave reactor and heated at 80 °C for 30 min. After cooling to room temperature, an aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH 8) was added. The suspension was stirred 2 h at room temperature. The precipitate was separated by filtration and washed with 0.1 M HCl solution, distilled

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water, MeOH, and hexane. The precipitate was dissolved in CHCl_3 , and the solution was filtered through Celite to remove insoluble materials. A reprecipitation from chloroform/methanol gave polymer as a pale yellow solid in 99% yield. GPC: $M_n = 74\,000$, $M_w/M_n = 2.66$. ^1H NMR (400 MHz, CDCl_3): δ 7.82 (d, $J = 8$ Hz, 2H), 7.71–7.70 (m, 4H), 4.45 (s, 4H), 2.06 (br, 4H), 1.22–1.10 (m, 20H), 0.82–0.80 (m, 6H), 0.76 (br, 4H). Elemental analysis: calcd (%) for $\text{H}-(\text{C}_{35}\text{H}_{44}\text{O}_2\text{S})_{140}-\text{H}$: C 79.50, H 8.39, S 6.06, Br 0.00%. Found: C 79.45, H 8.34, S 6.16, Br 0.00%.

RESULTS AND DISCUSSION

Recently, we reported the optimization of reaction conditions for direct arylation polycondensation of 3,4-ethylenedioxythiophene with 9,9-dioctyl-2,7-dibromofluorene under conventional heating, thereby yielding poly[(3,4-ethylenedioxythiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (PEDOTF).²¹ Under the optimized conditions, the reaction gave PEDOTF with a molecular weight of 39 000 in 89% yield after 6 h (Table 1, entry 1).

Table 1. Microwave-Assisted Polycondensation for Synthesis of PEDOTF^a

entry	base	additive	temp. (°C)	M_n^b	M_w/M_n^b	yield (%) ^c
1 ^d	K_2CO_3	1-AdCO ₂ H	100	39 000	2.24	89
2	K_2CO_3	1-AdCO ₂ H	100	15 000	1.87	98
3	K_2CO_3	PivOH	100	20 000	2.11	98
4	K_2CO_3	AcOH	100	23 000	2.49	94
5	KOAc		100	28 000	2.07	97
6	KOPiv		100	48 000	2.26	99
7	KOPiv		80	56 000	2.51	99
8	KOPiv		60	24 000	1.92	94

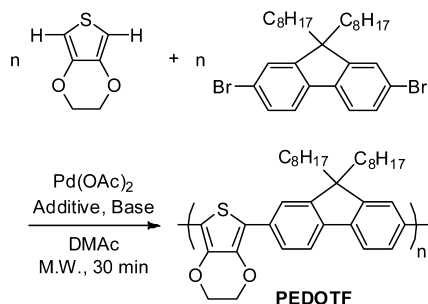
^aReactions for 30 min were carried out using $\text{Pd}(\text{OAc})_2$ (1.0 mol %), additive (30 or 0 mol %), and base (2.5 equiv) in DMAc (0.3 M).

^bEstimated by GPC calibrated on polystyrene external standards. ^cThe products were obtained by reprecipitation from chloroform/methanol.

^dThe results of the reaction for 6 h under conventional heating shown in ref 21.

The investigation into the microwave-assisted reaction began with the polycondensation reaction under the same conditions except for the reaction time (30 min) (Scheme 1). The reaction

Scheme 1. Microwave-Assisted Polycondensation for Synthesis of PEDOTF



gave PEDOTF with a molecular weight of 15 000 in 98% yield (Table 1, entry 2). The reactions with pivalic acid (PivOH) or acetic acid (AcOH) showed similar results to those with 1-adamantanecarboxylic acid (AdCO_2H) (entries 3 and 4). Interestingly, the use of potassium acetate (KOAc), instead of the combination of carboxylic acids and K_2CO_3 , resulted in a

higher molecular weight (entry 5). In addition, potassium pivalate (KOPiv) proved to be a more effective base than KOAc in terms of the molecular weight of the obtained polymer (48 000) (entry 6). These results indicate that potassium carboxylates are efficient bases for the polycondensation reaction under microwave heating. The choice of potassium carboxylate affects the polycondensation reaction because potassium carboxylate serves as not only a base but also as a carboxylato ligand, assisting in the deprotonation of a C–H bond.^{22–25}

To assess the effect of the reaction temperature, polycondensation reactions with KOPiv at various temperatures were conducted (Table 1). In the case of the reactions with KOPiv, 80 °C is a suitable reaction temperature, yielding PEDOTF with a high molecular weight of 56 000 (entries 6–8). The results of the multiple experiments under the conditions in entries 6 and 7 demonstrated good repeatability of the reaction (Table S2, Supporting Information).

Various fundamental parameters in the reaction conditions were investigated to gain some insight into the microwave-assisted polycondensation (Table 2). A high concentration of

Table 2. Detailed Examinations of Microwave-Assisted Polycondensation^a

entry	conc. (M)	$\text{Pd}(\text{OAc})_2$ (mol %)	time (min)	M_n^b	M_w/M_n^b	yield (%) ^c
1	0.3	1.0	30	56 000	2.51	99
2	0.2	1.0	30	74 000	2.66	99
3	0.1	1.0	30	77 000	5.73	99
4 ^d	0.1	1.0	30	147 000	2.89	89
5	0.05	1.0	30	36 000	3.54	99
6	0.2	2.0	30	71 000	3.40	99
7	0.2	0.50	30	48 000	2.71	98
8	0.2	0.10	30	21 000	2.08	96
9	0.2	1.0	20	65 000	2.44	99
10	0.2	1.0	5	45 000	2.65	97
11 ^e	0.2	1.0	30	25 000	1.85	96

^aReactions were carried out using $\text{Pd}(\text{OAc})_2$ and KOPiv (2.5 equiv) in DMAc for various reaction conditions. ^bEstimated by GPC calibrated on polystyrene external standards. ^cThe products were obtained by reprecipitation from chloroform/methanol. ^dResult after washing the product in entry 3 with DMF. ^eThe reaction under conventional heating.

monomer in solution generally increases the reaction rate; however, a π -conjugated polymer often precipitates from solution at high concentrations, which prevents a smooth polymerization.^{5,26} Therefore, the reactions under various concentrations of monomers were carried out to determine the effect on the polycondensation (Table 2, entries 1–3, 5). The molecular weight of PEDOTF increased on decreasing the concentration of the monomers from 0.3 to 0.1 M (entries 1–3). Then, the molecular weight and yield of PEDOTF drastically decreased at concentrations <0.1 M (entry 5). The reaction at concentrations of 0.1 M also resulted in an increased molecular weight distribution (5.73). The large molecular weight distribution is not caused by aggregation of the polymer in chloroform used for the GPC measurement because GPC trace is independent of a sample concentration (Supporting Information). The large molecular weight distribution is due to the polymer residues of relatively low molecular weight, which cannot be removed by simple reprecipitation owing to their molecular weight of about 2 000 (Figure S1, Supporting

Information). The residual low-molecular-weight fractions could be removed by washing with *N,N'*-dimethylformamide (DMF) at around 90 °C, giving PEDOTF with a molecular weight of 147 000 ($M_w/M_n = 2.89$) in 89% yield (entry 4).²⁷

The dependence on the amount of Pd precatalyst was also investigated (entries 6–8). The polycondensation reaction with 2.0 mol % of $\text{Pd}(\text{OAc})_2$ gave PEDOTF with a molecular weight of 71 000 in 99% yield (entry 6). This result is comparable to that with 1.0 mol % catalyst (entry 2). Decreasing the catalyst loading to <1.0 mol % resulted in a decreasing molecular weight and low yield of PEDOTF (entries 2, 7 and 8). Alternatively, it is notable that the polycondensation reaction with only 0.1 mol % of $\text{Pd}(\text{OAc})_2$ gave PEDOTF with a molecular weight of 21 000 in 96% yield (entry 8). Thus, microwave heating is able to decrease the amount of catalyst needed for the polycondensation reaction.

Finally, reaction time was investigated under the optimized conditions: 1.0 mol % of $\text{Pd}(\text{OAc})_2$ and KOPIV in DMAc (0.2 M) (entries 2, 9, and 10). Although the molecular weight of PEDOTF decreased with decreasing reaction time, PEDOTF with a molecular weight of 45 000 was obtained after 5 min (entry 10). These results indicate that most of the C–C bond formation occurs within 5 min. The reaction under conventional heating for 30 min gave PEDOTF with relatively low molecular weight (25 000) (entry 11), although the conditions (except for the heating method) were the same as that of the reaction in entry 2. Therefore, the extremely short reaction time of the direct arylation polycondensation is a prominent feature of the microwave heating.²⁸ As described above, a detailed examination of reaction conditions clarified the correlation between reaction parameters and the polycondensation reaction.

The MALDI-TOF-MS spectrum of PEDOTF exhibited peaks at regular intervals, corresponding to the structure of linked EDOT and fluorene, and those terminals without Br group (Figure 1).²¹ The extremely high efficiency of this

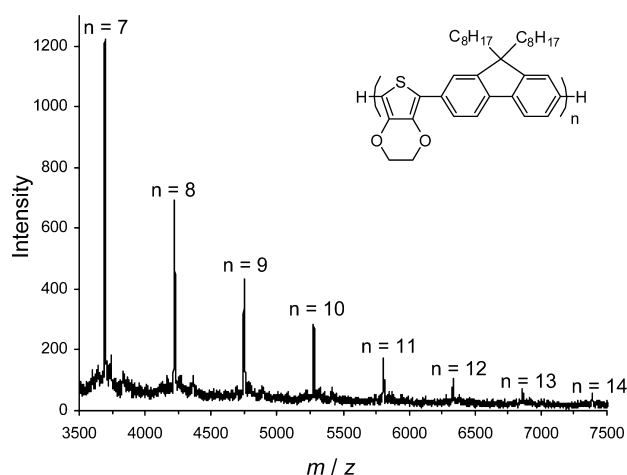


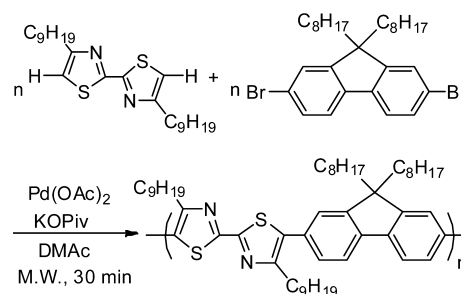
Figure 1. MALDI-TOF-MS spectrum of PEDOTF (Table 2, entry 2).

reaction under microwave heating is likely to provide full consumption of the C–Br moiety by direct arylation and a minor dehalogenation reaction. In contrast, the MALDI-TOF-MS spectrum of the sample from the reaction under conventional heating exhibited the existence of Br groups due to an incomplete reaction (Figure S2, Supporting Information). The MALDI-TOF-MS spectrum in Figure 1 also shows a

linear structure without branching caused by a side reaction at the C–H bond in the fluorene unit. This result shows a high selectivity for C–H bonds in the direct arylation polycondensation. This reaction has advantages on no contamination from Sn, B, or P impurities in the obtained polymer. In addition, the microwave-assisted reaction allows reduced loading of the Pd catalyst, leading to potentially lower residual Pd impurities in the polymer materials. Indeed, the high purity of the obtained polymer was confirmed by elemental analysis. The analytical data matched well with the calculated values, even though the polymer was purified by simple reprecipitation and washing (Supporting Information).

To expand the application range of this method, direct arylation polycondensation of 4,4'-dinonyl-2,2'-bithiazole²⁹ with 2,7-dibromo-9,9-dioctylfluorene was conducted using the optimized conditions for the synthesis of PEDOTF under microwave heating (Scheme 2). The reaction at 80 °C gave

Scheme 2. Microwave-Assisted Direct Arylation Polycondensation of 4,4'-Dinonyl-2,2'-Bithiazole with 2,7-Dibromo-9,9-Dioctylfluorene



poly[(4,4'-dinonyl-2,2'-bithiazole-5,5'-diyl)-(9,9-dioctylfluorene-2,7-diyl)] with a molecular weight of 20 000 in 94% yield. In addition, the reaction at 100 °C gave the corresponding polymer with a molecular weight of 48 000 in 99% yield (Table S6, Supporting Information). These results suggest that the reaction of 4,4'-dinonyl-2,2'-bithiazole requires a higher temperature than that of EDOT. Because the reaction under conventional heating required 3 h for achieving similar molecular weight (46 000), microwave heating also enabled shortened reaction times for this polycondensation reaction.

CONCLUSION

In conclusion, direct arylation polycondensation under microwave heating allows reduced loading of the Pd catalyst, leading to economical benefit and potentially lower residual Pd impurities in the polymer materials. In terms of environmental aspects, this reaction has advantages of no production of Sn, B, or P compounds as byproducts. This methodology lends itself well to practical application for the synthesis of optoelectronic materials because of the large molecular weight of the polymer, high purity, and shortened reaction times.

ASSOCIATED CONTENT

Supporting Information

Experimental details, full experimental results, MALDI-TOF-MS spectra, ¹H NMR spectra, GPC trace, and elemental analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

EDOT, ethylenedioxythiophene; PEDOTF, poly[(3,4-ethylenedioxythiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)]; Pd(OAc)₂, palladium acetate; DMAc, *N,N'*-dimethylacetamide; PivOH, pivalic acid; AcOH, acetic acid; 1-AdCO₂H, 1-adamantane carboxylic acid; KOAc, potassium acetate; KOPiv, potassium pivalate; DMF, *N,N'*-dimethylformamide; *M*, molar concentration; *M_w*, weight-average molecular weight; *M_n*, number average molecular weight; GPC, gel permeation chromatography; NMR, nuclear magnetic resonance; MALDI-TOF-MS, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry

■ REFERENCES

- (1) Ackermann, L.; Vicente, R.; Kapdi, A. R. Transition-metal-catalyzed direct arylation of (hetero)arenes by C–H bond cleavage. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792–9826.
- (2) Bellina, F.; Rossi, R. Recent advances in the synthesis of (hetero)aryl-substituted heteroarenes via transition metal-catalyzed direct (hetero)arylation of heteroarene C–H bonds with aryl halides or pseudohalides, diaryliodonium salts, and potassium aryltrifluoroborates. *Tetrahedron* **2009**, *65*, 10269–10310.
- (3) Kumar, A.; Kumar, A. Single step reductive polymerization of functional 3,4-propylenedioxythiophenes via direct C–H arylation catalyzed by palladium acetate. *Polym. Chem.* **2010**, *1*, 286–288.
- (4) Wang, Q.; Takita, R.; Kikuzaki, Y.; Ozawa, F. Palladium-catalyzed dehydrohalogenative polycondensation of 2-bromo-3-hexylthiophene: An efficient approach to head-to-tail poly(3-hexylthiophene). *J. Am. Chem. Soc.* **2010**, *132*, 11420–11421.
- (5) Lu, W.; Kuwabara, J.; Kanbara, T. Polycondensation of dibromofluorene analogues with tetrafluorobenzene via direct arylation. *Macromolecules* **2011**, *44*, 1252–1255.
- (6) Lu, W.; Kuwabara, J.; Iijima, T.; Higashimura, H.; Hayashi, H.; Kanbara, T. Synthesis of π -conjugated polymers containing fluorinated arylene units via direct arylation: Efficient synthetic method of materials for OLEDs. *Macromolecules* **2012**, *45*, 4128–4133.
- (7) Berrouard, P.; Najari, A.; Pron, A.; Gendron, D.; Morin, P.-O.; Pouliot, J.-R.; Veilleux, J.; Leclerc, M. Synthesis of 5-alkyl[3,4-*c*]thienopyrrole-4,6-dione-based polymers by direct heteroarylation. *Angew. Chem., Int. Ed.* **2012**, *51*, 2068–2071.
- (8) Wang, D. H.; Pron, A.; Leclerc, M.; Heeger, A. J. Additive-free bulk-heterojunction solar cells with enhanced power conversion efficiency, comprising a newly designed selenophene-thienopyrrolo-dione copolymer. *Adv. Funct. Mater.* **2013**, *23*, 1297–1304.
- (9) Tamba, S.; Shono, K.; Sugie, A.; Mori, A. C–H functionalization polycondensation of chlorothiophenes in the presence of nickel catalyst with stoichiometric or catalytically generated magnesium amide. *J. Am. Chem. Soc.* **2011**, *133*, 9700–9703.
- (10) Fujinami, Y.; Kuwabara, J.; Lu, W.; Hayashi, H.; Kanbara, T. Synthesis of thiophene- and bithiophene-based alternating copolymers via Pd-catalyzed direct C–H arylation. *ACS Macro Lett.* **2012**, *1*, 67–70.
- (11) Kuwabara, J.; Nohara, Y.; Choi, S. J.; Fujinami, Y.; Lu, W.; Yoshimura, K.; Oguma, J.; Suenobu, K.; Kanbara, T. Direct arylation polycondensation for the synthesis of bithiophene-based alternating copolymers. *Polym. Chem.* **2013**, *4*, 947–953.
- (12) Kowalski, S.; Allard, S.; Scherf, U. Synthesis of poly(4,4-dialkyl-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-*alt*-2,1,3-benzothiadiazole) (PCPDTBT) in a direct arylation scheme. *ACS Macro Lett.* **2012**, *1*, 465–468.
- (13) Chang, S.-W.; Waters, H.; Kettle, J.; Kuo, Z.-R.; Li, C.-H.; Yu, C.-Y.; Horie, M. Pd-catalyzed direct arylation polymerisation for synthesis of low-bandgap conjugated polymers and photovoltaic performance. *Macromol. Rapid Commun.* **2012**, *33*, 1927–1932.
- (14) Goodson, F. E.; Wallow, T. I.; Novak, B. M. Mechanistic studies on the Aryl–Aryl interchange reaction of ArPdL₂I (L = triarylphosphine) complexes. *J. Am. Chem. Soc.* **1997**, *119*, 12441–12453.
- (15) Park, J. K.; Jo, J.; Seo, J. H.; Moon, J. S.; Park, Y. D.; Lee, K.; Heeger, A. J.; Bazan, G. C. End-capping effect of a narrow bandgap conjugated polymer on bulk heterojunction solar cells. *Adv. Mater.* **2011**, *23*, 2430–2435.
- (16) Kettle, J.; Horie, M.; Majewski, L. A.; Saunders, B. R.; Tuladhar, S.; Nelson, J.; Turner, M. L. Optimisation of PCPDTBT solar cells using polymer synthesis with Suzuki coupling. *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 2186–2193.
- (17) Kappe, C. O. Controlled microwave heating in modern organic synthesis. *Angew. Chem., Int. Ed.* **2004**, *43*, 6250–6284.
- (18) Baghbanzadeh, M.; Pilger, C.; Kappe, C. O. Palladium-catalyzed direct arylation of heteroaromatic compounds: Improved conditions utilizing controlled microwave heating. *J. Org. Chem.* **2011**, *76*, 8138–8142.
- (19) Sharma, A.; Vacchani, D.; Van der Eycken, E. Developments in direct C–H arylation of (hetero)arenes under microwave irradiation. *Chem.—Eur. J.* **2013**, *19*, 1158–1168.
- (20) Abdo, N. I.; El-Shehaw, A. A.; El-Barbary, A. A.; Lee, J.-S. Palladium-catalyzed direct C–H arylation of thieno[3,4-*b*]pyrazines: Synthesis of advanced oligomeric and polymeric materials. *Eur. J. Org. Chem.* **2012**, 5540–5551.
- (21) Yamazaki, K.; Kuwabara, J.; Kanbara, T. Detailed optimization of polycondensation reaction via direct C–H arylation of ethylenedioxythiophene. *Macromol. Rapid Commun.* **2013**, *34*, 69–73.
- (22) Lapointe, D.; Fagnou, K. Overview of the mechanistic work on the concerted metallation–deprotonation pathway. *Chem. Lett.* **2010**, *39*, 1118–1126.
- (23) Liégault, B.; Lapointe, D.; Caron, L.; Vlassova, A.; Fagnou, K. Establishment of broadly applicable reaction conditions for the palladium-catalyzed direct arylation of heteroatom-containing aromatic compounds. *J. Org. Chem.* **2009**, *74*, 1826–1834.
- (24) Roger, J.; Požgan, F.; Doucet, H. Ligand-less palladium-catalyzed direct 5-arylation of thiophenes at low catalyst loadings. *Green Chem.* **2009**, *11*, 425–432.
- (25) Dong, J. J.; Roy, D.; Roy, R. J.; Ionita, M.; Doucet, H. Palladium-catalyzed C2 or C5 direct arylation of 3-substituted thiophenes with aryl bromides. *Synthesis* **2011**, *21*, 3530–3546.
- (26) Sokolov, L. B. Polycondensation in Solution. In *Synthesis of Polymers by Polycondensation*, 1st ed.; Israel Program for Scientific Translations: Jerusalem, 1968; Chapter 4, pp 87–116.
- (27) Recently, Ozawa et al. reported direct arylation polycondensation giving a high-molecular-weight conjugated polymer. Wakioka, M.;

Kitano, Y.; Ozawa, F. A highly efficient catalytic system for polycondensation of 2,7-dibromo-9,9-dioctylfluorene and 1,2,4,5-tetrafluorobenzene via direct arylation. *Macromolecules* **2013**, *46*, 370–374.

(28) The high molecular weight of PEDOTF under microwave heating is probably caused by rapid and uniform heating of the reaction media by microwave. See ref 17.

(29) Lu, W.; Kuwabara, J.; Kanbara, T. Synthesis of 4,4'-dinonyl-2,2'-bithiazole-based copolymers via Pd-catalyzed direct C–H arylation. *Polym. Chem.* **2012**, *3*, 3217–3219.