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Microwave-Assisted Polycondensation via Direct Arylation of 3,4-Ethylenedioxythiophene with 9,9-Dioctyl-2,7-dibromofluorene

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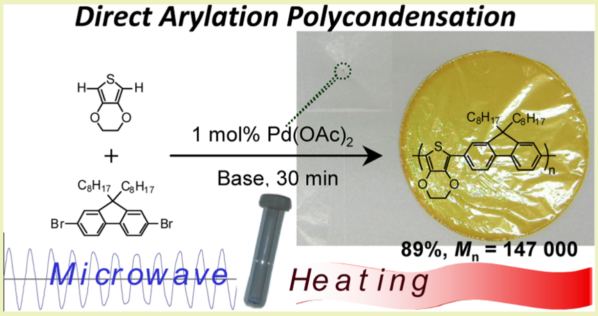
Supporting Information



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 compounds[14] 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, KOPiv (175 mg, 1.3 mmol), 3,4-ethylenedioxythiophene (53.4 μL, 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

Received: February 25, 2013
Revised: April 16, 2013
Published: May 7, 2013

dx.doi.org/10.1021/sc4000576 | *ACS Sustainable Chem. Eng.* 2013, 1, 878−882

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 H-$(C_{35}H_{44}O_2S)_{140}$-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).

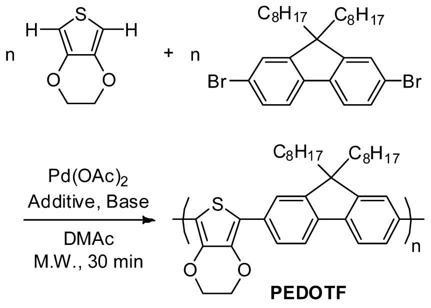
Table 1. Microwave-Assisted Polycondensation for Synthesis of PEDOTF[a]

entry	base	additive	temp. (°C)	M_n[b]	M_w/M_n[b]	yield (%)[c]
1[d]	K_2CO_3	1-$AdCO_2H$	100	39 000	2.24	89
2	K_2CO_3	1-$AdCO_2H$	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

[a] Reactions for 30 min were carried out using $Pd(OAc)_2$ (1.0 mol %), additive (30 or 0 mol %), and base (2.5 equiv) in DMAc (0.3 M). [b] Estimated by GPC calibrated on polystyrene external standards. [c] The products were obtained by reprecipitation from chloroform/methanol. [d] The 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 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]

Scheme 1. Microwave-Assisted Polycondensation for Synthesis of PEDOTF



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 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

Table 2. Detailed Examinations of Microwave-Assisted Polycondensation[a]

entry	conc. (M)	$Pd(OAc)_2$ (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

[a] Reactions were carried out using $Pd(OAc)_2$ and KOPiv (2.5 equiv) in DMAc for various reaction conditions. [b] Estimated by GPC calibrated on polystyrene external standards. [c] The products were obtained by reprecipitation from chloroform/methanol. [d] Result after washing the product in entry 3 with DMF. [e] The reaction under conventional heating.

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 $Pd(OAc)_2$ 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 $Pd(OAc)_2$ 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 $Pd(OAc)_2$ 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 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).

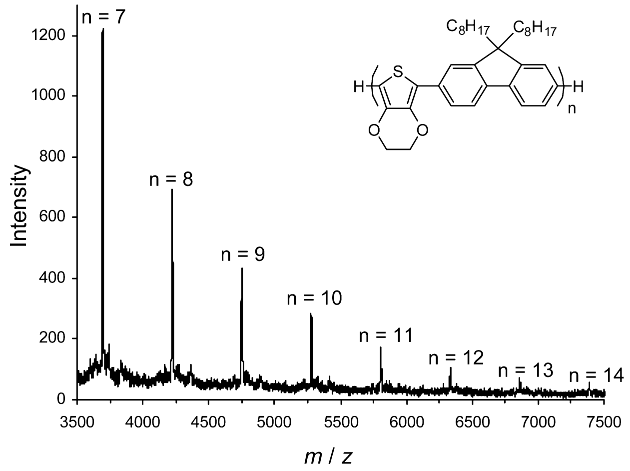
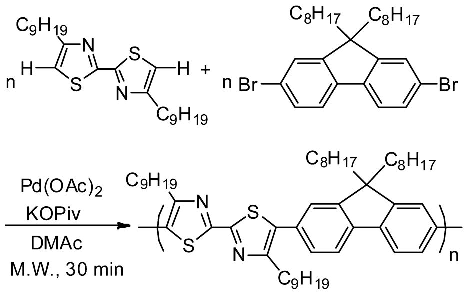


Figure 1. MALDI-TOF-MS spectrum of PEDOTF (Table 2, entry 2).

To expand the application range of this method, direct arylation polycondensation of 4,4′-dinonyl-2,2′-bithiazole[29] 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 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.

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



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.

ACKNOWLEDGMENTS

The authors thank the Chemical Analysis Center of the University of Tsukuba for the measurements of elemental analyses and MALDI-TOF-MS. The authors also thank Prof. T. Koizumi and the Center for Advanced Materials Analysis, Technical Department, Tokyo Institute of Technology for the measurements of halogen/sulfur elemental analyses. This work was partly supported by the Collaborative Research Program of Institute for Chemical Research, Kyoto University, and the Industrial Technology Research Grant Program in 2011 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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-$AdCO_2H$, 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

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