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Synthesis of Donor-Acceptor Conjugated Polymers Based on Benzo[1,2-*b*:4,5-*b′*]dithiophene and 2,1,3-Benzothiadiazole via Direct Arylation Polycondensation: Toward Efficient C-H Activation in Nonpolar Solvents

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ABSTRACT

This article describes synthesis of donor–acceptor (D–A) type copolymers based on benzo[1,2-*b*:4,5-*b′*]dithiophene and 2,1,3-benzothiadiazole via direct-arylation cross-coupling polycondensation. To achieve high performance polymerization, we have systematically investigated the reaction factors including catalysts, solvents, ligands, bases, additives, concentration of reactants and phase transfer agents. In particular, 1,2-dimethylbenzene (ODMB), as a nonpolar high boiling point solvent, is a superior medium to perform this direct-arylation polymerization. In this nonpolar aromatic solvent, $Pd_2dba_3/(o\text{-}MeOPh)_3P$, accompanied with a base of potassium carbonate and an additive of pivalic acid, serves as an efficient catalyst system to obtain high-quality polymers. Our optimized condition gave the polymer with a weight-average molecular weight (M_w) as high as 60 kg/mol in nearly quantitative yield and excellent C-H selectivity.

Keywords: direct-arylation; benzothiadiazole; benzodithiophene; conjugated polymers; organic semiconductors

INTRODUCTION

Conjugated polymers (CPs), due to their excellent optical and electronic properties, have attracted tremendous interest in the past decades from both academic and industrial fields. The so-called D-A conjugated polymers containing alternating electron-rich and electro-deficient units are particularly attractive due to the facile tunability of the electronic structures in their conjugated backbones and consequent optoelectronic properties of the polymers.[1-6] To date, most of D–A conjugated polymers have been synthesized by classic Stille coupling polycondensation or Suzuki coupling polycondensation.[7-9] But these reactions show disadvantages such as the necessity of prefunctionizing monomers (arylstannanes or arylboron derivatives) using flammable and nonstable butyllithium. Other issues, particularly for Stille coupling, include the difficulty of purifying arylstannane monomers and the formation of toxic byproducts. To synthesize conjugated polymers via an economically efficient, safe and environment-friendly approach, special attention has been paid to carbon–hydrogen (C-H) direct arylation cross-coupling reaction. [9-12]

The protocols of C-H direct arylation towards synthesis of conjugated polymers have usually been borrowed from what has been learned in synthesis of small organic molecules for pharmaceutics.[13-14] For example, Fagnou et al. explored an effective synthetic protocol, which involves palladium acetate ($Pd(OAc)_2$) as a catalyst, *N,N*-dimethylacetamide (DMAc) as a solvent, potassium carbonate (K_2CO_3) as a base and pivalic acid (PivOH) as an additive, for direct arylation of aromatic compounds.[15-16] This synthetic protocol has been successfully applied to the synthesis of many conjugated polymers.[17-29] The catalyst $Pd(OAc)_2$ is particularly efficient in highly polar solvents such as DMAc, in which most low polar or nonpolar conjugated polymers show limited solubility. Therefore, highly polar solvents are not ideal reaction media for synthesis of conjugated polymers, particularly for those decorated with hydrophobic alkyl side chains.

Very recently, there has been some progress on exploring low polar or nonpolar solvents as the reaction media for synthesis of conjugated polymers. For instance, Ozawa et al. used tetrahydrofuran (THF) instead of highly polar solvents to synthesize poly(3-hexylthiophene-2,5-diyl) (P3HT), to ensure the solubility of the resulting polymers during polymerization.[30] Herrmann's catalyst (*trans*-Di-*μ*-acetatobis[2-[bis(2-methylphenyl)phosphine]benzyl]dipalladium), in the presence of an appropriate ligand, was proven an effective catalyst in this reaction system to afford high-molecular-weight P3HT with high regioregularity (98%), whereas the reaction catalyzed with $Pd(OAc)_2$ in the same solvent was not reproducible and frequently provided low molecular weight products. Later, Leclerc et al. utilized this reaction condition with modifications to synthesize a series of D-A type conjugated polymers.[31-36] The reaction was typically performed with heating at 120 °C. The overheated solvent (THF) and the necessity of using a sealed and pressurized reaction container, however, may compromise the reproducibility of the polymerization and raise the cost as well as safety concerns for performing and scaling up the synthesis. In addition, some monomers cannot be polymerized in THF with Herrmann's catalyst.[36] More recently, Ozawa et al. reported another efficient catalytic system based on tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct ($Pd_2(dba)_3 \cdot CHCl_3$) for polycondensation of 2,7-dibromo-9,9-dioctylfluorene and 1,2,4,5-tetrafluorobenzene.[37] This catalytic system was sufficiently reactive in THF and in toluene to afford the polyphenylene derivative with high molecular weight in high yield.

Despite these recent advances, little study has been carried out in exploring high boiling point nonpolar solvents for efficient synthesis of conjugated polymers via direct arylation polycondensation. Even less has been understood with reaction factors that affect the direct arylation polycondensation in nonpolar solvents.

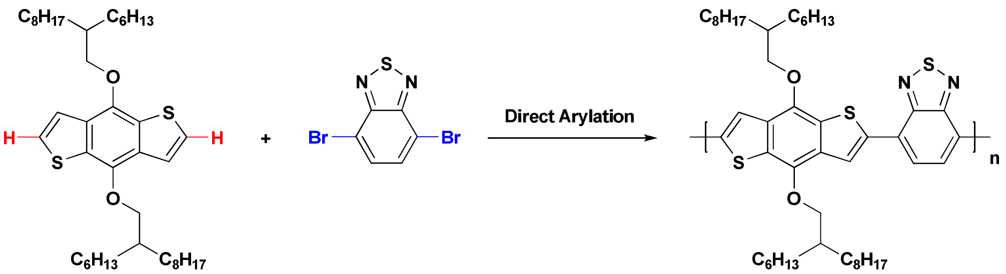
In this article, we report such a direct arylation polycondensation system. Our target polymer, denoted as **PBDTBT**, consists of alternating benzo[1,2-*b*:4,5-*b*′]dithiophene (**BDT**) as electron donor (D) and 2,1,3-benzothiadiazole (**BT**) as the electron acceptor (A). Both **BDT** and **BT** have been among the most popular building blocks in a variety of D-A conjugated polymer semiconductors.[1-6,38-47] Two long branched 2-hexyldecyloxy groups were introduced to **BDT** segment to afford good solubility of **PBDTBT** in a variety of solvents.

To optimize the polymerization of **BDT** and **BT** under the scheme of direct arylation, we have systematically examined a broad range of factors, including a series of low polar or nonpolar solvents, catalysts, ligands, bases, additives, reactant concentrations and phase transfer agents. Our optimized condition of direct arylation gives high molecular weight **PBDTBT** in nearly quantitative yield with good regioregularity.

RESULTS AND DISCUSSION

Scheme 1 shows the synthetic route to the polymer **PBDTBT** via palladium-catalyzed direct arylation coupling reaction between monomers 4,8-Di(2-hexyldecyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (**HDBDT**) and 4,7-Dibromobenzothiadiazole (**BrBT**). The following sections describe our systematic study of the factors that influence this direct arylation polymerization.

Scheme 1. Synthetic Route to the Polymer **PBDTBT**.



Effect of Catalysts: Palladium(0) (Pd(0)) usually serves as the major active species in most of palladium-catalyzed cross-coupling reactions. However, due to the labile characteristics, the Pd(0) complexes usually need to be reduced *in situ* from palladium(II) (Pd(II)) complexes and manifolded with varying coordination shells to form reactive species.[48-49] So the chemical characteristics of palladium catalysts, also known as catalytic precursors, are important to determine their activity in a cross-coupling reaction. We examined activities of different palladium complexes for polymerizing **HDBDT** and **BrBT**. As shown in **Table 1**, the polymerization using Herrmann's catalyst in THF resulted in **PBDTBT** with a low number-average molecular weight (M_n) of 4.1 kg/mol, indicating that the activity of Herrmann's catalyst is not sufficient to activate the C-H bonds at the positions of 2- and 6- of **BDT** to form high molecular weight polymers. As can be expected, **PBDTBT** prepared using $Pd(OAc)_2$ in DMAc precipitated from the reaction system in the process of polymerization and formed metallic luster polymer pellets. The solubility limitation of the resulting polymer in DMAc blocked the further growth of polymer chains, especially for the molecules surrounded by others in the precipitated particles. As a result, using DMAc as reaction medium gave the polymer **PBDTBT** with a relatively high polydispersity index (PDI) of 2.9. Compared with $Pd(OAc)_2$ in DMAc, Pd_2dba_3 catalyst in THF led to similar weight-average molecular weight (M_w), but improved M_n with a relatively low PDI of 2.0.

Table 1. Polymerization results of **HDBDT** and **BrBT** in different catalyst systems[a].

Entry	Catalyst	Ligand	Solvent	Base	Yield (%)	M_n (kg/mol)	M_w (kg/mol)	PDI
1	$Pd(OAc)_2$	$PCy_3 \cdot HBF_4$	DMAc	K_2CO_3	98	11.0	32.2	2.9
2	Herrmann's Catalyst	(o-MeOPh)$_3$P	THF	Cs_2CO_3	88	4.1	9.8	2.4
3	Pd_2dba_3	(o-MeOPh)$_3$P	THF	Cs_2CO_3	99	16.0	32.8	2.0

[a] **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were polymerized in solvent (1 mL), in the presence of catalyst (5 mol %), ligand (10 mol %), base (0.6 mmol) and PivOH (0.06 mmol), at 100 °C for 24 h.

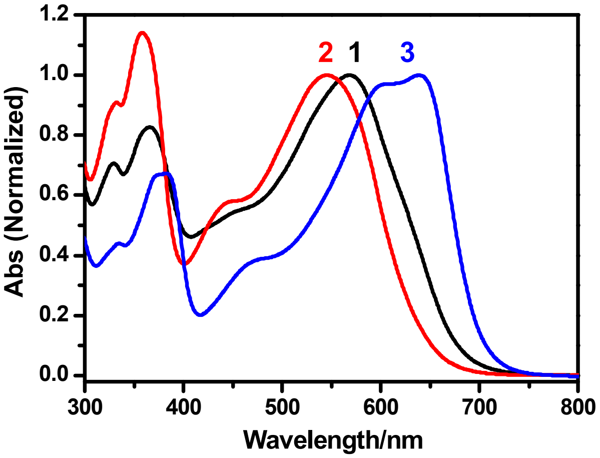
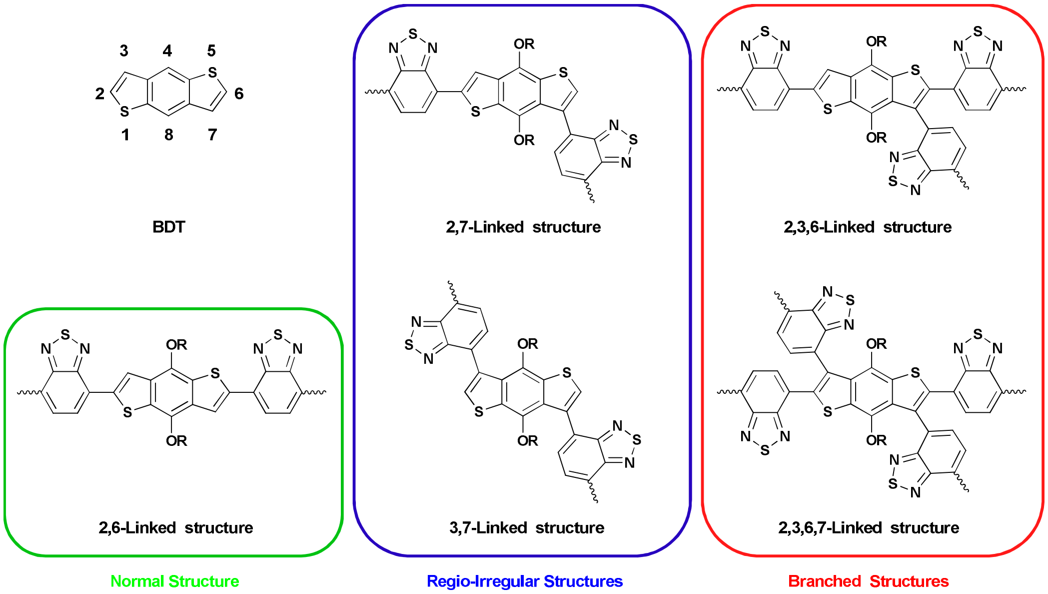


Figure 1. Absorption spectra of chloroform solutions of **PBDTBTs** synthesized with different catalysts: **Line 1**, **2**, **3** corresponding to the polymers synthesized under the condition shown in **Entry 1**, **2**, **3**, respectively, in **Table 1**.

To further compare the polymers prepared using these different catalytic systems, absorption spectra of the polymers were collected (**Figure 1**). As expected, **PBDTBT** synthesized using Herrmann's catalyst/THF, due to its much lower molecular weight, shows an absorption peak at a shorter wavelength (545 nm) than those of other two polymers synthesized using $Pd(OAc)_2$/DMAc (568 nm) and Pd_2dba_3/THF (638 nm), respectively. Surprisingly, the polymers synthesized using $Pd(OAc)_2$/DMAc and Pd_2dba_3/THF, respectively, despite their similar M_w, show much different optical absorption properties. The latter shows an absorption peak and the onset at longer wavelengths, corresponding to a longer average conjugation length. The average conjugation length of CPs is determined by maximum effective conjugation length, degree of polymerization (molecular weight) and structural defects.[4] Here, the difference of conjugation length between **PBDTBTs** prepared with $Pd(OAc)_2$/DMAc and Pd_2dba_3/THF, respectively, might be mainly attributed to the structural defects, which is further discussed in the final section (**Optical Properties**). The possible structural defects in **PBDTBTs** prepared by direct arylation polymerizations are shown in **Scheme 2**.

Scheme 2. Possible structural defects in **PBDTBTs** prepared by direct arylation polymerizations.



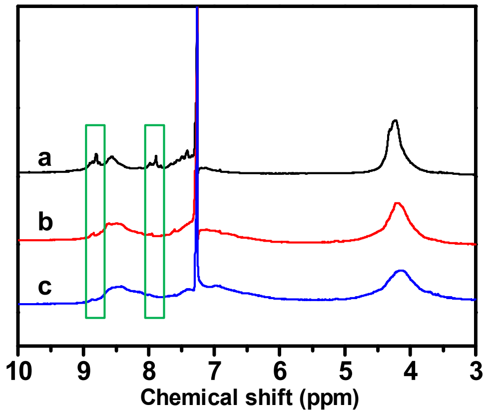


Figure 2. ^{1}H-NMR spectra of **PBDTBTs** synthesized under different conditions: **Line a**, **b** corresponding to the polymers synthesized under the condition shown in **Entry 1**, **3** in **Table 1**, respectively; **Line c** corresponding to the polymer synthesized under the optimized condition in ODMB (**Entry 1**, **Table 5**).

To obtain more information about the molecular structures of **PBDTBTs** synthesized using $Pd(OAc)_2$/DMAc and Pd_2dba_3/THF, ^{1}H-NMR spectra of these polymers were collected. As highlighted with green rectangles in **Figure 2**, marked regio-irregular sequences peaks around 7.9 and 8.8 ppm are observed in the spectrum (**Line a**) of **PBDTBT** synthesized using $Pd(OAc)_2$/DMAc. These two peaks may be assigned to the protons of 6-unsubstitute benzo[1,2-*b*:4,5-*b′*]dithiophene and protons at 5 and 6 positions of benzothiodiazole which linked on the 3 and/or 7 positions of BDT, respectively, as shown in **Scheme 2**. In contrast, only negligible peaks exist in those regions for the polymer synthesized using Pd_2dba_3/THF (**Line b**).

All of the results described above indicate that Pd_2dba_3 is a superior catalyst in THF, compared to Herrmann's catalyst in the same solvent and $Pd(OAc)_2$ in DMAc for direct arylation polymerization of **HDBDT** and **BrBT**. Therefore, in the following sections, we focus on Pd_2dba_3 catalyst and discuss how other factors influence the direct arylation polymerization.

Effect of Solvents: For most reactions involving C-H direct arylation coupling, transition-metal based catalysts, largely $Pd(OAc)_2$, show relatively higher reactivity in polar solvents than in nonpolar ones. Nevertheless, the influence of solvents on direct arylation still remains complex, as other factors also affect the polymerization result. To explore solvents appropriate for the Pd_2dba_3-catalyzed direct arylation polymerization, we systematically studied this polymerization in a variety of solvents, including THF, 1,4-dioxane (DIO), anisole (methoxybenzene, MOB), toluene (methylbenzene, MB), xylene (dimethylbenzene, DMB), mesitylene (1,3,5-trimethylbenzene, TMB), ODMB and tetrahydronaphthalene (THN). The chemical structures of the solvents used in the direct arylation polymerizations are summarized in **Scheme 3**. As shown in **Table 2**, the common low polar or nonpolar ether and arene solvents can serve as the reaction media for efficient Pd_2dba_3-catalyzed direct arylation. Interestingly, all of the tested solvents give the polymers with rather high yield (≥ 95%) but quite different molecular weights. Although no clear relationship between polarity of the reaction solvent and molecular weight of the resulting polymers can be concluded from these experiments, the ether solvents with higher polarity than the arene solvents tend to give polymers with higher molecular weights. In addition, it appears that some extremely high boiling point solvents (e.g. TMB and THN) are unfavorable to the Pd_2dba_3-catalyzed polymerization.

It is worthwhile to note that, in ODMB, the polymerization gives comparable result to that in THF, indicating that ODMB is a promising reaction medium for Pd_2dba_3-catalyzed coupling polymerization. As mentioned in **INTRODUCTION**, most of direct arylation polymerizations for synthesis of conjugated polymers have been carried out in high-boiling-point, highly polar solvents such as DMAc, in which high-molecular-weight polymer products often show limited solubility. In contrast, ODMB described above is a nonpolar aromatic solvent with a boiling point of 144.4 ^{o}C. Based on the “like dissolves like” principle, ODMB should possess good solubility for aromatic compounds, particularly for nonpolar and low polar molecules. Therefore, ODMB should be favorable for synthesis of a broad range of conjugated polymers. In addition, the significantly higher boiling point of ODMB than that of

THF allows the polymerization to be readily performed at ambient pressure.

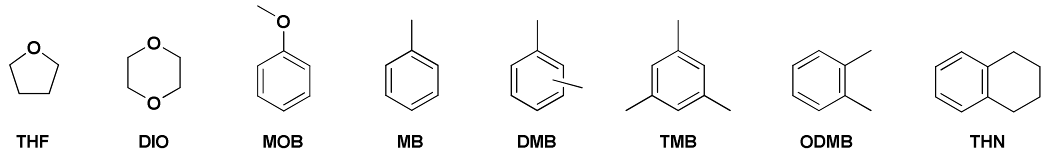
Table 2. Effect of solvent on polymerization of **HDBDT** and **BrBT**[a,b].

Entry	Solvent	Boiling point (°C)	Dielectric constant	Dipole moment (10^{-10} C·m)	Yield (%)	M_n (kg/mol)	M_w (kg/mol)	PDI
1	THF	66	7.58	5.67	99	16.0	32.8	2.0
2	DIO	101.3	2.209	1.50	97	14.1	31.0	2.2
3	MOB	153.7	4.33	4.00	96	13.2	23.7	1.8
4	MB	110.6	2.24	1.23	99	13.6	24.3	1.8
5	DMB	137-140	-	-	96	11.3	22.5	2.0
6	TMB	164.7	2.279	0.23	95	6.8	11.9	1.7
7	ODMB	144.4	2.266	1.47	98	14.2	31.1	2.2
8	THN	207.6	2.733	1.33	95	5.2	8.2	1.6

[a] The physical properties of the solvents were from reference 50.

[b] **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were polymerized in solvent (1 mL), in the presence of Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), Cs_2CO_3 (0.6 mmol) and PivOH (0.06 mmol), at 100 °C for 24 h.

Scheme 3. Chemical structures and abbreviations of solvents used in the direct arylation polymerizations.



Effect of Ligands: Tris(2-methoxyphenyl)phosphine ((*o*-MeOPh)$_3$P) served as an exceptionally effective ligand for Pd_2dba_3-catalyzed coupling copolymerization of **HDBDT** and **BrBT** in ODMB. There was no polymerization, however, when (*o*-MeOPh)$_3$P was absent or replaced with other ligands, such as triphenylphosphane (Ph_3P), tris(2-methylphenyl)phosphine ((*o*-Tol)$_3$P) and tri-*t*-butyl phosphine ((*t*-Bu)$_3$P). The coordinating ability of ortho-methoxy groups may play a particularly important role in the high efficiency of (*o*-MeOPh)$_3$P in the polymerization.[37]

Effect of Bases: The presence of a base is necessary in transition metal catalyzed coupling reaction to promote the efficiency of the catalysts and increase the yield of the products. The role of a base is not only to abstract protons and neutralize acids introduced and/or produced in the reaction system, but also to activate the catalysts and facilitate regeneration of the reactive species. The performance of bases in reactions is determined by many factors, including the intrinsic factors such as basicity, nucleophilicity, and steric hindrance, as well as the extrinsic factors such as solubility, ionization ability, aggregation state, and coordination ability.

The results of copolymerization of **HDBDT** and **BrBT** in presence of different bases are summarized in **Table 3**. Carbonates were examined firstly, due to their wide use in previous direct arylation polymerizations. Among the tested carbonates, potassium carbonate (K_2CO_3) gave optimal results; cesium carbonate (Cs_2CO_3) showed an acceptable polymerization result; sodium carbonate (Na_2CO_3) was ineffective, only giving trace oligomer/polymer; calcium carbonate ($CaCO_3$) and barium carbonate ($BaCO_3$) did not give any oligomer/polymer at all after a brief purification procedure.

The performance of carbonates should be related to their basicity and solubility. Solubility of the carbonates, both in typical solvents[51-52] and water, follows an order of $Cs_2CO_3 > K_2CO_3 > Na_2CO_3 > CaCO_3 \approx BaCO_3$. In Pd-catalyzed cross-coupling reaction, it is important to maintain a reasonable concentration of basic anions in the reaction system.[53] We speculate that the concentration of carbonate from K_2CO_3 in ODMB at the polymerization temperature (i.e. 100 ^oC) should be at a favorable level, compared to other carbonates, for the direct arylation polymerization of **HDBDT** and **BrBT**.

As K_2CO_3 showed better performance than other metal carbonates in the direct arylation polymerization, we further tested potassium bases with other anions. The polymerization results are shown in **Table 3**. Potassium phosphate (K_3PO_4) is also an effective base, outranked only by K_2CO_3. Compared to K_3PO_4, potassium acetate

(KOAc) gives polymer products with a lower reaction yield and a lower M_n, which may be caused by its weak alkaline and less effective coordination with reactive catalytic centers. When potassium tert-butoxide (*t*-BuOK) was added to the polymerization system, the reaction mixture turned to dark brown while being heated in an oil bath. This phenomenon suggested that some reagents were decomposed or some side reactions occurred in the presence of such a strong base.

Finally, organic bases such as triethylamine (TEA), diisopropylethylamine (DIPEA), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and triethylenediamine (TEDA) were tested in the copolymerization of **HDBDT** and **BrBT**. But none of them resulted in formation of polymer products. The presence of organic bases may lead to debromination of dibromobenzothiadiazole as a main reaction[54] and consequently interfere with the polymerization.

As K_2CO_3 showed the best performance among all of the bases tested above, we further optimized the equivalence of K_2CO_3 (**Entries 2**, **13**, **14** and **15**, **Table 3**) in the reaction mixtures. With the increase of K_2CO_3 from 2 to 5 equivalents, the molecular weight of the resulting polymers increased gradually. Further increase of the amount of K_2CO_3 to 10 equivalents, the molecular weight of the resulting polymers cannot be further improved.

Table 3. Effect of bases on polymerization of **HDBDT** and **BrBT**[a].

Entry	Base	Yield (%)	M_n (kg/mol)	M_w (kg/mol)	PDI
1	Cs_2CO_3 (3 eq)	98	14.2	31.1	2.2
2	K_2CO_3 (3 eq)	98	19.5	46.5	2.4
3	Na_2CO_3 (3 eq)	trace	-	-	-
4	$CaCO_3$ (3 eq)	0	-	-	-
5	$BaCO_3$ (3 eq)	0	-	-	-
6	K_3PO_4 (3 eq)	96	18.0	39.7	2.2
7	KOAc (3 eq)	85	5.4	8.5	1.6

8	*t*-BuOK (3 eq)	0	-	-	-
9	TEA (3 eq)	0	-	-	-
10	DIPEA (3 eq)	0	-	-	-
11	DBU (3 eq)	0	-	-	-
12	TEDA (3 eq)	0	-	-	-
13	K_2CO_3 (2 eq)	97	18.6	42.8	2.3
14	K_2CO_3 (5 eq)	98	22.0	54.4	2.5
15	K_2CO_3 (10 eq)	97	20.2	47.3	2.3

[a] **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were polymerized in ODMB (1 mL), in the presence of Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), base and PivOH (0.06 mmol), at 100 °C for 24 h.

Effect of Additives: Carboxylate additives play an important role in transition metal catalyzed direct arylation reaction. It has been proposed that C-H bond transformations assisted by carboxylates proceed via a mechanism in which metalation takes place via a concerted base-assisted deprotonation.[55] Fagnou et al. proved that the pivalate anion is a key component in cleaving of C-H bond by lowering the cleavage energy of C-H bond and acting as a catalytic proton shuttle from unactivated substrate to the stoichiometric carbonate base.[15] In addition, DIPEA as an alternative to carboxylates shows improved selectivity in some cases.[56]

The effect of additives on the Pd_2dba_3-catalyzed copolymerization of **HDBDT** and **BrBT** in ODMB is summarized in **Table 4**. Surprisingly, the Pd_2dba_3-catalyzed polymerization was quenched upon addition of DIPEA as an additive. The presence of DIPEA may result in debromination of bromide monomer and thus quenches the coupling reaction.[54] In contrast to DIPEA, the addition of PivOH to the reaction mixture did promote the coupling copolymerization. For example, the addition of 0.5 equivalent (*vs*. the monomer) PivOH resulted in a more than 6-fold increase of molecular weight of the formed polymer, compared to that of the polymer synthesized without PivOH. In addition, this increase of molecular weight was accompanied by an increase of the reaction yield from 68% to 98%. Further increase of the amount of PivOH up to 1 equivalent (*vs*. the monomer) did not lead to significant improvement of the polymerization (**Entry 5**, **Table 4**).

Table 4. Effect of additives on polymerization of **HDBDT** and **BrBT**[a].

Entry	Additive	Yield (%)	M_n (kg/mol)	M_w (kg/mol)	PDI
1	none	68	3.4	7.7	2.3
2	PivOH (0.3 eq)	98	19.5	46.5	2.4
3	DIPEA (0.3 eq)	0	-	-	-
4	PivOH (0.5 eq)	98	21.9	53.6	2.4
5	PivOH (1 eq)	97	21.1	51.0	2.4

[a] **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were polymerized in ODMB (1 mL), in the presence of Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 (0.6 mmol) and additive, at 100 °C for 24 h.

Effect of Reactant Concentration: Under the optimized reaction condition (**Entry 1** in **Table 5**), after several hours of polymerization, the resulting polymers precipitated from the reaction mixture occasionally onto the inner surface of the reaction vessel, producing a metallic luster "conjugated polymer mirror" on the inner vessel surface. One possible reason for the early precipitation of polymer products during the reaction can be the very high concentration (> 160 mg/ml) of the formed polymers in the reaction medium. The precipitation of polymers from the concentrated reaction medium may limit the formation of the high molecular weight polymers. To resolve the issue of the precipitation, we added extra solvent of ODMB to dilute the reaction mixture. The polymerization results at different concentrations are summarized in **Table 5**. Unfortunately, the dilution of the reaction mixture slowed down the polymerization significantly. Although the yield of the reaction was little affected upon dilution of the reaction mixture, the average molecular weight of the polymer products fell gradually with the decrease of the reactant concentration from 0.2 to 0.05 M.

Table 5. Effect of reactant concentrations on polymerization of **HDBDT** and **BrBT**[a].

Entry	Concentration	Yield (%)	M_n (kg/mol)	M_w (kg/mol)	PDI
1	0.2 M	98	24.5	60.1	2.4
2	0.1 M	99	19.5	45.0	2.3
3	0.05 M	97	13.8	26.6	1.9

[a] **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were polymerized in ODMB (1, 2, or 4 mL), in the presence of Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 (1 mmol) and PivOH (0.1 mmol), at 100 °C for 24 h.

Effect of Phase Transfer Agents: As discussed above, pivalic acid has been proven to be one of the most effective additives to enhance the reactivity of C-H bonds. Thompson et al. proposed that the *in situ* generated carboxylate anions acted as a soluble organic base to promote the reaction.[9] From this point of view, it appears that increasing the solubility of inorganic base (e.g. K_2CO_3) in a reaction system might benefit direct arylation cross-coupling. Phase transfer agents (PTAs) have been widely used in heterogeneous reactions to facilitate the migration of inorganic base from an aqueous phase or a solid state into an organic phase where reaction occurs. Here, we studied the effect of a series of PTAs, including 1,4,7,10,13,16-hexaoxacyclooctadecane (18-Crown-6), aliquat 336, tetra-*n*-butylaminium bromide (TBAB), tetra-*n*-butylammonium fluoride (TBAF), and tetra-*n*-butylammonium hexafluorophosphate (TBAPF6) on the direct arylation polymerization in ODMB. The results (**Table 6**) appeared too scattering to reach a clear conclusion. While the addition of 18-Crown-6 or TBAPF6 or distilled water gave polymers with relatively low molecular weights; quaternary ammonium salts associated with simple anions (i.e. halide ions, including chloride ion in aliquat 336, bromide ion in TBAB and fluoride ion in TBAF, respectively) nearly quenched the polymerization. This effect might be caused by these extra anions from PTAs (if any) and inorganic base solubilized by PTAs, that may block the free coordination sites of low-ligated Pd(0) complexes, which is necessary for the turnover of the catalyst.[53] As a result, the reactions were slowed down or even quenched.

Table 6. Effect of phase transfer agents on polymerization of **HDBDT** and **BrBT**.

Entry	PTA	Yield (%)	M_n (kg/mol)	M_w (kg/mol)	PDI
1	none	99	19.5	45.0	2.3
2	18-Crown-6	96	10.2	16.7	1.6
3	Aliquat 336	trace	-	-	-
4	TBAB	trace	-	-	-
5	TBAF	trace	-	-	-
6	TBAPF6	99	16.8	35.9	2.1
7	Water (0.4 ml)	99	9.2	15.7	1.7

[a] **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) were polymerized in ODMB (2 mL), in the presence of Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 (1 mmol), PivOH (0.1 mmol) and PTA (0.06 mmol), at 100 °C for 24 h.

Optical Properties:

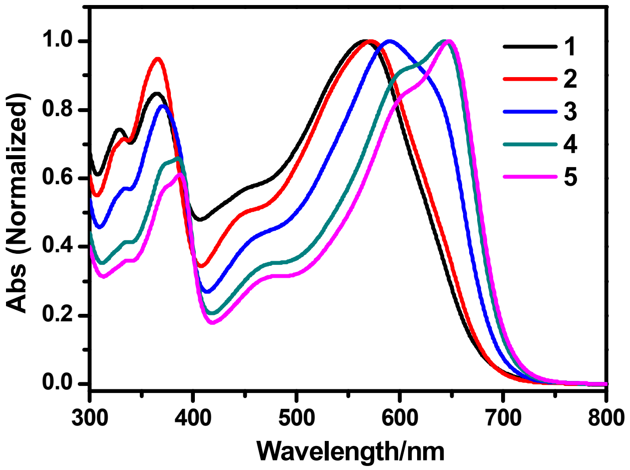


Figure 3. Absorption spectra of chloroform solutions of **PBDTBT** synthesized under different conditions: the **Lines 1-5** corresponding to the polymers **Entry 1-5** listed in **Table 7** with the same sequence.

We further studied the optical properties of the polymers synthesized under different conditions of direct arylation polymerizations described above. The absorption spectra of some representative polymers with different molecular weights synthesized in ODMB are presented in **Figure 3**. **PBDTBT** synthesized using $Pd(OAc)_2$/DMAc is also included for comparison. **Table 7** summarizes the optical data, including the absorption peak wavelengths (λ_{abs}), the onset-absorption wavelengths (λ_{onset}), and the full width at half maximum absorption (FWHM) of the polymers.

Table 7. Optical properties of **PBDTBT** synthesized under different polymerization conditions.

Entry	M_n/M_w (kg/mol)	Polymerization Condition	λ_{abs} in $CHCl_3$ (nm)	λ_{onset} in $CHCl_3$ (nm)	FWHM (nm)
1	11.0/32.2	$Pd(OAc)_2$/DMAc[a]	329, 365, 567	678	210
2	5.4/8.5	$Pd_2(dba)_3$/ODMB[b]	333, 366, 572	685	185
3	9.2/15.7	$Pd_2(dba)_3$/ODMB[c]	334, 370, 590	691	163
4	16.8/35.9	$Pd_2(dba)_3$/ODMB[d]	336, 385, 643	699	139
5	24.5/60.1	$Pd_2(dba)_3$/ODMB[e]	337, 387, 648	702	128

Details of the polymerizations: [a]DMAc (1 mL), $Pd(OAc)_2$ (5 mol %), $PCy_3 \cdot HBF_4$ (10 mol %), K_2CO_3 (0.6 mmol) and PivOH (0.06 mmol); [b]ODMB (1 mL), Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), KOAc (0.6 mmol) and PivOH (0.06 mmol); [c]ODMB (2 mL), Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 (1 mmol), PivOH (0.1 mmol) and water (0.4 ml); [d]ODMB (2 mL), Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 (1 mmol), PivOH (0.1 mmol) and TBAPF6 (0.06 mmol); [e]ODMB (1 mL), Pd_2dba_3 (5 mol %), (*o*-MeOPh)$_3$P (10 mol %), K_2CO_3 (1 mmol) and PivOH (0.1 mmol). All of these polymerizations were carried out with **HDBDT** (0.2 mmol) and **BrBT** (0.2 mmol) at 100 °C for 24 h.

As expected, for the polymers synthesized in ODMB, gradual bathochromic shifts of both the absorption peak and the onset of absorption were observed with the increase of the molecular weight, accompanied by a decrease of the FWHM. The **PBDTBT** prepared using $Pd(OAc)_2$/DMAc (**Line 1**) showed a slight hypsochromic shift in its absorption spectrum, compared with **PBDTBT** synthesized using Pd_2dba_3/ODMB and with a much lower molecular weight (**Line 2**). In other words, the conjugation length of **PBDTBT** prepared using $Pd(OAc)_2$/DMAc with M_n/M_w of 11.0/32.2 kg/mol, was even inferior to that of **PBDTBT** polymerized in ODMB with M_n/M_w of 5.4/8.5 kg/mol. These results imply that some structural defects, presumably caused by the relatively poor regioselectivity in the polymerization, may exist in the polymer prepared using $Pd(OAc)_2$/DMAc.[9,11,22,23,27]

To further probe the structure of the polymers synthesized in ODMB, ^{1}H-NMR spectrum of a representative **PBDTBT** prepared under the optimized reaction condition (**Entry 1** in **Table 5**) was collected and the result is presented in **Figure 2** for comparison. A close inspection of the NMR spectrum reveals only slight distortion without any distinguishable peaks in the regions around 8.8 and 7.9 ppm. This result further suggests that the relatively poor C-H regioselectivity observed in $Pd(OAc)_2$-catalyzed polymerization in DMAc was suppressed in the Pd_2dba_3-catalyzed polymerization in ODMB.

In addition, the **PBDTBT** that we synthesized here via direct arylation polymerization in ODMB (**Line 3** and **4**) shows similar or even red-shifted absorption compared with the same type of polymer with similar M_n but synthesized via Stille coupling by other research groups.[40-41] Again, these results suggest the good regioregularity of the polymers synthesized via Pd_2dba_3-catalyzed direct arylation polymerization in ODMB.

CONCLUSION

D-A type conjugated polymers based on **BDT** and **BT** have been synthesized by direct-arylation polycondensation. We have systematically investigated the reaction parameters, including catalysts, ligands, solvents, bases, additives and concentrations, and studied how each factor influences the direct arylation polycondensation. ODMB as a nonpolar and high-boiling-point solvent is a promising reaction medium to perform the direct-arylation polymerization. An optimized condition of reacting 0.2 M of **HDBDT** and stoichiometric **BrBT** with 5 mol % of Pd_2dba_3, 10 mol % of (o-MeOPh)$_3$P, 5 equivalents of K_2CO_3, 0.5 equivalents of PivOH in ODMB gives **PBDTBT** with a weight average molecular weight of 60 kg/mol in almost quantitative yield and good regioselectivity. We expect that the knowledge that we learn from this system of direct arylation polymerization will be useful for economically efficient and environment-green synthesis of a broad scope of conjugated polymers for applications such as optoelectronic devices, sensing and bioimaging.

EXPERIMENTAL SECTION

Materials. HDBDT was synthesized according to the procedure described in a previous report[44]. **BrBT** and other reagents, solvents were commercial grade and used as received without further purification. All reactions were performed under nitrogen atmosphere.

Measurements and Characterization. The number-average molecular weights (M_n), weight-average molecular weights (M_w) and polydispersity index (PDI, M_w/M_n) of the polymers were measured with gel permeation chromatography (GPC) from Agilent 1260 Infinity system at 30 °C, with polystyrenes as reference standard and THF as an eluent. All new compounds were characterized by nuclear magnetic resonance spectra (NMR). The NMRs were recorded on a Bruker AV 300 spectrometer at room temperature. UV-Vis absorption spectra were recorded on a Shimadzu spectrometer model UV-2450. Absorption spectra measurements of the polymer solutions were carried out in chloroform at room temperature.

General Procedures of Polymerization. In a glove box, **HDBDT** (0.2 mmol), **BrBT** (0.2 mmol), catalyst (10 μmol), ligand (20 μmol), base, additive(s) and solvent were added in a reaction vial with a magnetic stirring bar. The vial was sealed with a rubber cap and then removed from the glove box. The vial was heated in a 100 ^{o}C oil bath for 24 hours. After being cooled to room temperature, the reaction mixture was diluted with 30 ml of chloroform and then filtered to remove the insoluble species. The filtrate was concentrated and added dropwise to 100 mL of ethanol, filtered through a Soxhlet thimble, and then subjected to Soxhlet extraction with methanol and chloroform sequentially. The chloroform fraction was concentrated and precipitated into 100 mL of ethanol. The precipitates were collected by filtration and dried under vacuum for one day to yield the target polymer.

When purifying the reaction mixtures from different batches of polymerizations, we tried to remove unreacted starting materials and low molecular weight organic and inorganic impurities and collect all the resulting polymers and oligomers present in final products in order to completely compare the polymerizations under different reaction conditions.

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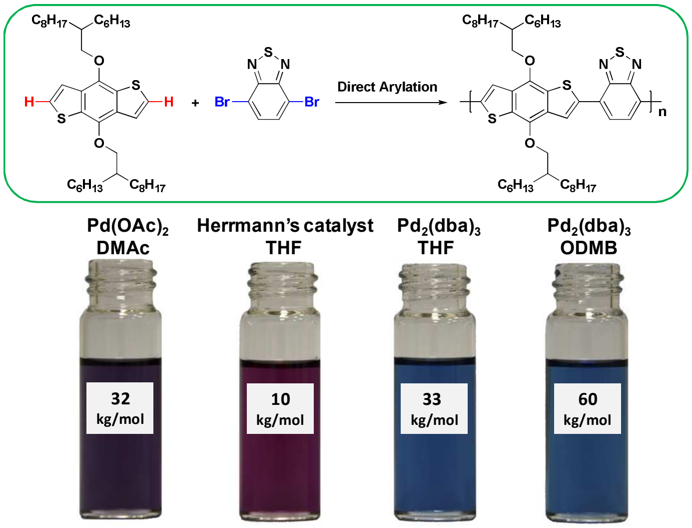
For Table of Contents Only

Synthesis of Donor-Acceptor Conjugated Polymers Based on Benzo[1,2-*b*:4,5-*b′*]dithiophene and 2,1,3-Benzothiadiazole via Direct Arylation Polycondensation: Toward Efficient C-H Activation in Nonpolar Solvents

Xiaochen Wang, Mingfeng Wang



1,2-Dimethylbenzene, as a nonpolar high boiling point solvent, has been discovered to be a superior medium to perform direct-arylation polymerization.