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Polycondensation of Dibromofluorene Analogues with Tetrafluorobenzene via Direct Arylation

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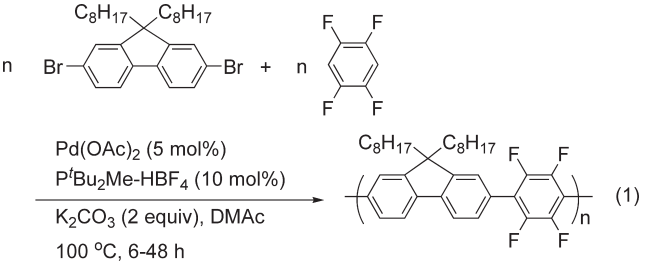
Supporting Information

π-Conjugated polymers have attracted considerable attention as important materials because of their wide application to next-generation flexible electronic devices such as organic thin-film solar cells and organic electroluminescence devices (OLEDs).[1−5] Conventionally, many π-conjugated polymers were synthesized by polycondensation using transition-metal-catalyzed cross-coupling reactions such as Suzuki−Miyaura coupling and Migita−Kosugi−Stille coupling.[6−11] Although these methods are effective for the synthesis of a variety of π-conjugated polymers, they require the preparation of bifunctional organoboron or organotin compounds as monomers. Moreover, the polycondensation produces a stoichiometric amount of toxic byproduct such as organostannyl compounds. Therefore, the development of a convenient and environmentally friendly method of synthesizing π-conjugated polymers is highly desirable.

In recent years, catalytic dehydrohalogenative cross-coupling reactions of nonpreactivated arenes with aryl halides, so-called direct arylation, have been developed.[12−18] In terms of the prior preparation of organometallic monomers and the treatment of toxic byproduct, polycondensation by direct arylation is superior to conventional methods based on a cross-coupling reaction (Scheme 1). Recently, Ozawa and co-workers successfully synthesized poly(3-alkylthiophene)s with high molecular weight and high regioregularity via direct arylation.[19] However, polycondensation through direct arylation has rarely been reported.[19−21] We focused on the Pd-catalyzed direct arylation of pentafluorobenzene with aryl halides because the acidic C−H bond owing to the fluorine substituents enables effective direct arylation, giving the coupling products with excellent yields.[16−18] Herein we report the polycondensation of 1,2,4,5-tetrafluorobenzene with 2,7-dibromo-9,9-dioctylfluorene or 3,6-dibromo-*N*-octadecylcarbazole via direct arylation. This work expands the range of methods for the synthesis of π-conjugated polymers.

The polycondensation of 1,2,4,5-tetrafluorobenzene with 2,7-dibromo-9,9-dioctylfluorene was carried out in the presence of $Pd(OAc)_2$ (5 mol %), a phosphine ligand (10 mol %), and K_2CO_3 (2 equiv) in dimethylacetamide (DMAc) for 6−48 h (eq 1). Under the conditions, high-molecular-weight poly[(9,9-dioctylfluorene-2,7-diyl)-(2,3,5,6-tetrafluoro-1,4-phenylene)] (PDOF-TP) was obtained in a single step (M_n = 17 600−31 500).[22] To determine the appropriate polymerization conditions, the polycondensation of 1,2,4,5-tetrafluorobenzene with 2,7-dibromo-9,9-dioctylfluorene was carried out under various conditions. Table 1 summarizes the results of the polycondensation. In terms of the ligand of the catalytic system, P^tBu_2Me-HBF_4 is effective for polycondensation, whereas the catalytic system without added phosphine ligand or with P^tBu_3-HBF_4 and 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (S-Phos) did not promote the reaction (entries 1−4). Since a reduced amount of the Pd catalyst (2.5 mol %) gave a low yield of the products, 5 mol % of the catalyst is essential for the polymerization (entry 5). The effect of the solvent was also examined for toluene, 1,2-dichlorobenzene, DMF, and DMAc, which have often been used as solvents for palladium-catalyzed direct arylation.[12−18] Although the polycondensation proceeded in DMAc and DMF (entries 1 and 6), no polymeric product was obtained in toluene or 1,2-dichlorobenzene (entries 7 and 8). Considering the yield and molecular weight of the polymer, DMAc is the best solvent for this polymerization. The polycondensation for 6 h gave PDOF-TP with a high molecular weight of 17 600 and a high yield of 82% (entry 1).[23,24] The molecular weight of the polymer reached 27 300 when the reaction time was increased to 24 h (entries 9 and 10). However, the molecular weight of the polymer only slightly increased after 24 h (entry 11), presumably due to the precipitation of polymeric products from the reaction media and the deactivation of the Pd catalyst by prolonged heating.



(1)

In general, a high concentration of monomer is favorable for polycondensation, whereas a π-conjugated polymer is often precipitated out from solution at a high concentration during a reaction, which prevents a smooth polymerization.[25,26] Therefore, the concentration of monomer is a crucial factor for the synthesis of a π-conjugated polymer. Table 2 shows the effect of the concentration of the monomers. The molecular weight of the polymer increased with decreasing concentration of the

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Scheme 1. Schematic Representatives of Conventional Polycondensations by Cross-Coupling Reaction and a Novel Polycondensations by a Direct Arylation

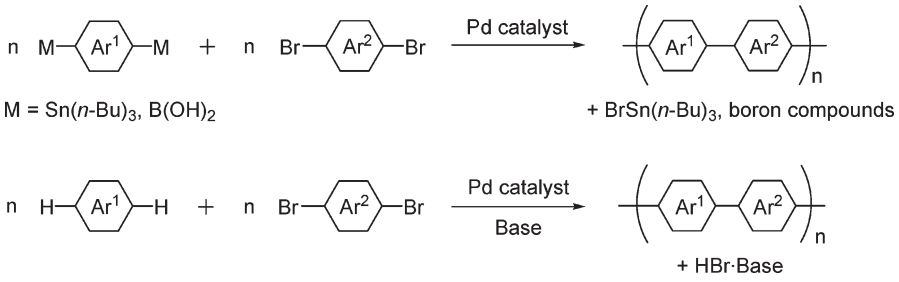

Table 1. Polycondensation of 1,2,4,5-Tetrafluorobenzene with 2,7-Dibromo-9,9-dioctylfluorene[a]

entry	ligand	solvent	time (h)	M_n[b]	M_w/M_n[b]	DP[c]	yield (%)[d]
1	P^tBu_2Me-HBF_4	DMAc	6	17 600	2.68	33	82
2	none	DMAc	6				0
3	P^tBu_3-HBF_4	DMAc	6				0
4	S-Phos	DMAc	6				0
5[e]	P^tBu_2Me-HBF_4	DMAc	6	9 400	1.45	18	26
6	P^tBu_2Me-HBF_4	DMF	6	14 400	2.10	27	53
7	P^tBu_2Me-HBF_4	1,2-dichlorobenzene	6				0
8	P^tBu_2Me-HBF_4	toluene	6				0
9	P^tBu_2Me-HBF_4	DMAc	12	20 200	2.87	38	79
10	P^tBu_2Me-HBF_4	DMAc	24	27 300	3.53	50	79
11	P^tBu_2Me-HBF_4	DMAc	48	30 800	2.24	57	74

[a] Reactions were carried out at 100 °C using $Pd(OAc)_2$ (5 mol %), ligand (10 mol %), and K_2CO_3 (2 equiv) in a concentration of 1 M. [b] Estimated by GPC calibrated on polystyrene standards. [c] The average degree of polymerization were calculated from GPC data and molecular weight of the repeating unit. [d] The products were obtained by reprecipitation from $CHCl_3$/MeOH. [e] $Pd(OAc)_2$ (2.5 mol %) and P^tBu_2Me-HBF_4 (5 mol %).

monomers from 2 to 0.5 M (entries 1−3). Then the molecular weight and yield of the polymer markedly decreased at a concentration of less than 0.5 M (entries 4 and 5). Therefore, 0.5 M is a suitable concentration of the monomers in this polymerization. On the basis of these results, the optimal reaction time and concentration are 24 h and 0.5 M, respectively. Under the optimal conditions, the polycondensation gave a polymer with a molecular weight of 31 500 (entry 6), higher than that of the polymer prepared by polycondensation via Suzuki−Miyaura coupling (M_n = 3200).[23]

The structure of the repeating unit of PDOF-TP was completely identified by ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra (see Supporting Information).[22] The spectra were characterized by comparison with the model compound 2,7-bis(2,3,5,6-tetrafluorophenyl)-9,9-dioctylfluorene, which was synthesized by the reaction of 2,7-dibromo-9,9-dioctylfluorene and an excess amount of 1,2,4,5-tetrafluorobenzene. Note that no characteristic signal of the terminal tetrafluorophenyl unit appears in the ^1H or ^{19}F NMR spectra of PDOF-TP. To gain detailed information on the terminal unit, MALDI-TOF-MASS was measured using dithranol as a matrix.[27] The main peaks of the spectrum correspond to a polymer with two Br terminals (Figure S-13). The spectrum indicates that the mass of the repeating unit is 536, which is in accord with the calculated mass of a unit of (9,9-dioctylfluorene-2,7-diyl)-(2,3,5,6-tetrafluoro-1,4-phenylene). The elemental analysis of PDOF-TP with an M_n of 27 300 (DP = 50) was in accord with the calculated value for the molecular formula Br-$(C_{35}H_{40}F_4)_{50}$-$C_{29}H_{40}$Br.[22]

Table 2. Effect of Reaction Concentration on Polycondensation of 1,2,4,5-Tetrafluorobenzene with 2,7-Dibromo-9,9-dioctylfluorene[a]

entry	concentration (M)	time (h)	M_n[b]	M_w/M_n[b]	DP[c]	yield (%)[d]
1	2	6	10 200	2.44	19	74
2	1	6	17 600	2.68	33	82
3	0.5	6	26 700	3.11	50	83
4	0.25	6	12 900	1.92	24	59
5	0.01	6				0
6	0.5	24	31 500	3.45	59	81

[a] Reactions were carried out at 100 °C using $Pd(OAc)_2$ (5 mol %), P^tBu_2Me-HBF_4 (10 mol %), and K_2CO_3 (2 equiv) in DMAc. [b] Estimated by GPC calibrated on polystyrene standards. [c] The average degree of polymerization was calculated from GPC data and molecular weight of the repeating unit. [d] The products were obtained by reprecipitation from $CHCl_3$/MeOH.

The same reaction protocol made it possible to achieve the polycondensation of 1,2,4,5-tetrafluorobenzene with 3,6-dibromo-*N*-octadecylcarbazole. The reaction yielded the new polymer poly[(*N*-octadecylcarbazole-3,6-diyl)-(2,3,5,6-tetrafluoro-1,4-phenylene)] (POC-TP) in 78% yield as a precipitate in methanol. The low-molecular-weight fraction (M_n = 2500) was removed by washing with $CHCl_3$. Then, a polymer with a high molecular weight, M_n = 8300 (M_w/M_n = 1.7), was obtained in 66% yield (eq 2). The molecular weight of POC-TP was measured by high-temperature GPC with 1,2-dichlorobenzene

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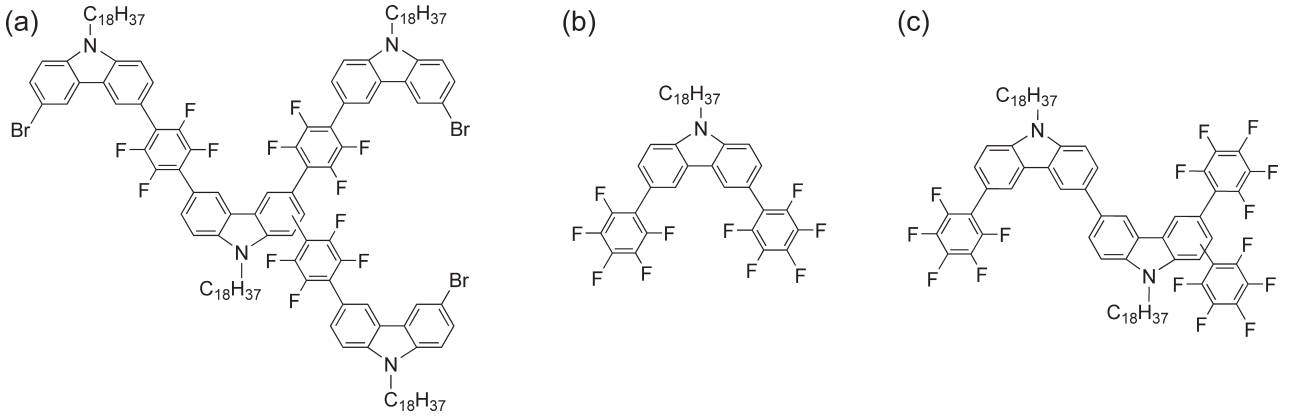
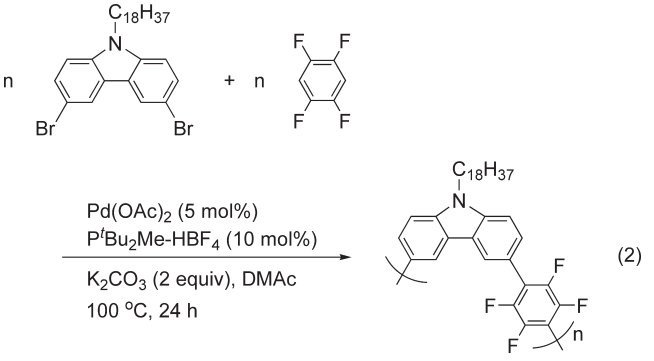


Figure 1. Proposed structures from the results of MALDI-TOF-MASS. (a) One of the structures in PDOF-TP. (b) The main product of the model reaction. (c) One of the minor products of the model reaction.

as an eluent at 140 °C because the polymer is insoluble in $CHCl_3$, THF, and DMF at room temperature.



(2)

The ^1H NMR, $^{13}C\{^1H\}$ NMR, and ^{19}F NMR spectra suggest the repeating structure of POC-TP shown in eq 2 (Figures S-7—S-9). However, the result of MALDI-TOF-MASS indicates the formation of a branching structure (Figure S-14). A typical mass number in the oligomeric region is 2354, corresponding to $C_{138}H_{171}Br_3F_{12}N_4$. This formula indicates the existence of three Br-substituted carbazole groups in the polymer chain. The tentative structure is proposed in Figure 1a. The formation of the structure requires an oxidative cross-coupling reaction between the C—H bonds in carbazole and tetrafluorobenzene moieties.[28] We examined a controlled model reaction to clarify the possibility of an unfavorable coupling reaction. The Pd-catalyzed coupling reaction of 3,6-dibromo-*N*-octadecylcarbazole with 2 equiv of pentafluorobenzene gave 3,6-bis(pentafluorophenyl)-*N*-octadecylcarbazole in 81% yield (Figure 1b) and a mixture of several minor products in 5% yield. The MALDI-TOF-MASS of the minor products exhibits m/z = 1334 (Figure S-15), corresponding to $C_{78}H_{85}F_{15}N_2$ (Figure 1c). This result indicates the occurrence of homo-coupling reactions between two C—Br groups and an oxidative coupling reaction between C—H groups in carbazole and tetrafluorobenzene.[28] From the results of the model reaction, the polycondensation of 3,6-dibromo-*N*-octadecylcarbazole and tetrafluorobenzene involves unexpected C—H bond activation, resulting in the branching structure. At the late stage of the polymerization, this reaction is likely to give a cross-linking structure. The low solubility of POC-TP is presumably due to the cross-linking structure. In the case of the polymerization of 2,7-dibromo-9,9-dioctylfluorene with 1,2,4,5-tetrafluorobenzene, the branching structure was minor, which was confirmed by MALDI-TOF-MASS. The result of the model reaction also supports the low probability of the side reaction.[29]

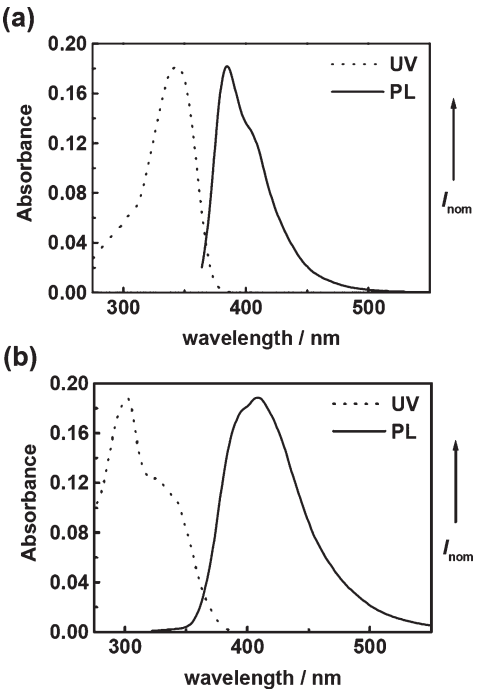


Figure 2. Absorption and photoluminescence spectra of PDOF-TP and POC-TP in solution state: (a) PDOF-TP in $CHCl_3$; (b) POC-TP in $Cl_2CHCHCl_2$.

Owing to their high molecular weight, free-standing films of PDOF-TP and POC-TP can be fabricated by a solution-casting method. The films and the solution of the polymers exhibited blue fluorescence in solution and film states. Figure 2a shows the maximum emission wavelength of PDOF-TP in solution of 385 nm, whose quantum yield is 66% at room temperature in air, which is higher than that of the PDOF-TP synthesized by a Suzuki—Miyaura coupling reaction.[23] The POC-TP exhibited emission at 410 nm with low intensity (Φ = 4.3%) in solution.

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In summary, a novel and effective polycondensation reaction via direct arylation was developed to successfully obtain high-molecular-weight poly[(9,9-dioctylfluorene-2,7-diyl)-(2,3,5,6-tetrafluoro-1,4-phenylene)] and poly[(*N*-octadecylcarbazole-3,6-diyl)-(2,3,5,6-tetrafluoro-1,4-phenylene)]. Since this method does not require the preparation of bifunctional organometallic reagents such as organoboron and organotin compounds, the π-conjugated polymers can be synthesized via a simple pathway. In addition, the byproducts of the polycondensation are KBr, CO_2, and H_2O, which are easily removed from the polymer. The benefits of the simple purification process are very important in the case of forming materials requiring high purity such as those used in OLEDs. To expand the range of use of this synthetic method, further studies including examinations using various aromatic monomers are in progress.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Typical polymeization conditions. A mixture of $Pd(OAc)_2$ (11.2 mg, 0.050 mmol), $P^tBu_2Me\text{-}HBF_4$ (24.8 mg, 0.1 mmol), 2,7-dibromo-9,9-dioctylfluorene (548 mg, 1.0 mmol), 1,2,4,5-tetrafluorobenzene (112 μL, 1.0 mmol), and K_2CO_3 (276 mg, 2.0 mmol) was stirred in anhydrous dimethylacetamide (1.0 mL) for 24 h at 100 °C under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into aqueous solution of ethylenediaminetetraacetic acid tetrasodium salt (EDTA·4Na). The suspension was stirred for 1 h at room temperature. The precipitate was separated by filtration and washed with 1 M HCl solution, distilled water, MeOH, and hexane. The gray solid was dissolved in $CHCl_3$, and the solution was filtered through a plug of Celite to remove insoluble material. A reprecipitation from $CHCl_3$/MeOH gave a gray solid of poly[(9,9-dioctylfluorene-2,7-diyl)-(2,3,5,6-tetrafluoro-1,4-phenylene)] (PDOF-TP) in a 79% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (2H, d, J = 8.0 Hz), 7.56 (4H, br), 2.08 (4H, br), 1.12 (20H, br), 0.83 (10H, m). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.5, 145.5−143.2 (d, J_{C-F} = 235.8 Hz), 141.2 (m), 129.2, 126.6, 125.1, 120.2, 119.9 (m), 55.6, 40.1, 31.8, 29.9, 29.2, 23.9, 22.6, 14.0. ^{19}F NMR (377 MHz, $CDCl_3$): δ −140.5 (s). Anal. Calcd. for Br-$(C_{35}H_{40}F_4)_{50}$-$C_{29}H_{40}$Br: C, 78.03; H, 7.51. Found: C, 77.95; H, 7.60. M_n = 27 300, M_w/M_n = 3.53.
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(29) The similar model reaction of 2,7-dibromo-9,9-dioctylfluorene with 2 equiv of pentafluorobenzene gave 2,7-bis(pentafluorophenyl)-9,9-dioctylfluorene in 98% yield, without formation of the minor products from an oxidative coupling reaction between C−H groups.