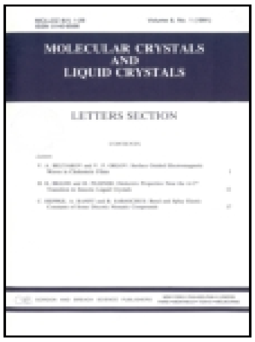

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Selectivity of Reaction Sites for Direct Arylation Polycondensation in Bithiophene Derivatives

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Direct arylation polycondensation has recently emerged as the method for the synthesis of π-conjugated polymers. In developing this methodology, site selectivity of the reacting C-H bonds is one of the most important issues. Herein, we investigate the direct arylation polycondensation of bithiophene and dialkylbithiophenes to assess site selectivity. We found that low temperature was a key factor for high selectivity in bithiophene, and that 4,4′-dicyclohexylbithiophene exhibited the highest selectivity among the tested dialkylbithiophenes reaction sites.

Keywords Conjugated polymer; direct arylation; site selectivity

Introduction

Direct arylation polycondensation has recently been applied to the synthesis of π-conjugated polymers [1–3] as a substitute for traditional cross-coupling polycondensation using the Suzuki-Miyaura or Migita-Kosugi-Stille coupling [4], and is advantageous because of fewer reaction steps and environment-friendly byproducts [5]. We have previously carried out polycondensation of 2,2′-bithiophene and 2,7-dibromo-9,9-dioctylfluorene, which afforded insoluble polymeric products in organic solvents owing to the formation of cross-linked structures [6]. The cross-linked structures could form from unexpected side reactions on the C-H bonds at β-position of bithiophene. In this work, we searched for conditions affording a high selectivity toward the α-position of bithiophene to avoid structural defects such as branching and/or cross-linking [7, 8]. In addition, we evaluated four kinds of dialkylbithiophenes in terms of selectivity.

Experimental

3,3′-Di(n-hexyl)bithiophene, 4,4′-di(n-hexyl)bithiophene [9], 3,3′-dicyclohexylbithiophene [10–12], and 4,4′-dicyclohexylbithiophene [9, 10] were prepared by similar methods to the literatures.

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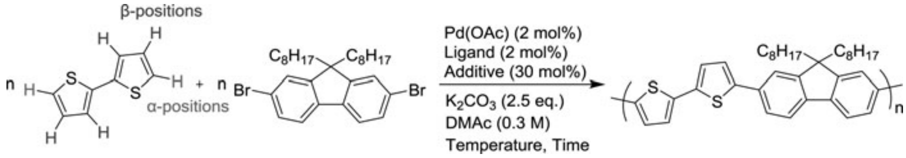
Table 1. Results of polycondensation of 2,2′-bithiophene with 2,7-dibromo-9,9-dioctylfluorene



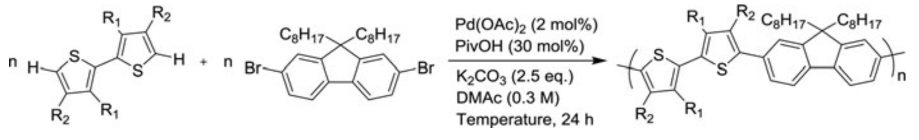
Entry	Ligand (2 mol%)	Additive (30 mol%)	Temperature (°C)	Time (h)	Yield (%)	Insoluble products	M_n (kDa)	M_w/M_n
1	none	PivOH	100	3	6	formed	9.4	2.28
2	none	PivOH	80	3	25	formed	11.1	2.25
3	none	PivOH	60	3	86	none	4.4	2.08
4	none	PivOH	60	24	61	formed	11.9	2.29
5	none	1-AdCOOH	60	24	48	formed	10.0	2.33
6	none	TFA	60	24	oligomer	-	-	-
7	$PCy_3 \cdot HBF_4$	PivOH	60	72	30	formed	10.0	2.26
8	$Ph_2P(CH_2)_2PPh_2$	PivOH	80	72	15	formed	7.4	2.13
9	$P(t\text{-}Bu)_3$	PivOH	80	72	52	formed	8.6	2.63
10	$P(2\text{-}furyl)_3$	PivOH	80	48	1	formed	8.4	1.54

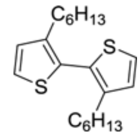
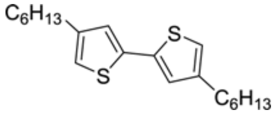
A mixture of $Pd(OAc)_2$ (2.25 mg, 0.010 mmol), pivalic acid (16.9 μL, 0.15 mmol), K_2CO_3 (173 mg, 1.25 mmol), 2,7-dibromo-9,9-dioctylfluorene (274 mg, 0.50 mmol), and 2,2′-bithiophene (83.1 mg, 0.50 mmol) was stirred in anhydrous dimethylacetamide (DMAc, 1.67 mL) for 24 h at 60°C under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into an aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH = 8). The suspension was stirred overnight at room temperature. The precipitate was separated by filtration and washed with 10% HCl solution, distilled water, methanol, and hexane. The precipitate was dissolved in $CHCl_3$, and the solution was filtered through a plug of Celite to remove insoluble material. Reprecipitation from $CHCl_3$/methanol gave polymer, described in Table 1, Entry 4, as a pale yellow solid in 61% yield. $M_n = 11\,900$, $M_w/M_n = 2.29$. ^1H NMR (400 MHz, $CDCl_3$): δ 0.66-0.76 (br, 4H), 0.76-0.83 (m, 6H), 0.99-1.23 (br, 20H), 1.99-2.10 (br, 4H), 7.21-7.36 (m, 4H), 7.55-7.74 (m, 6H).

Results and Discussion

Upon finding the appropriate conditions to afford high selectivity toward the α-position of bithiophene, we investigated polycondensation of 2,2′-bithiophene with 2,7-dibromo-9,9-dioctylfluorene under various conditions. In the case of the highly selective reaction, side reactions at the β-position of bithiophene do not proceed and cross-linked polymers are not formed, leading to a high yield of $CHCl_3$-soluble products. Table 1 shows the results of polycondensation under various conditions. First, the reactions at lower temperatures were investigated to suppress the reactions at the β-position (Table 1, Entries 1-3). A decrease in the reaction temperature improved the selectivity: the reactions at lower temperatures

Table 2. Results of polycondensation of di(*n*-hexyl)bithiophenes

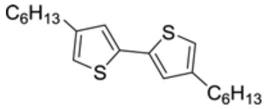
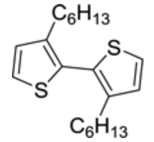
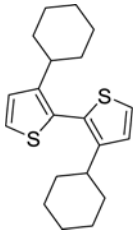
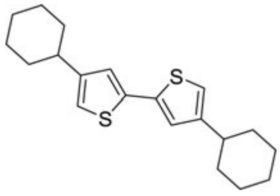


Entry	Monomer	Temperature (°C)	Yield (%)	Insoluble products	M_n (kDa)	M_w/M_n
1		60	90	none	16.3	1.91
2		70	99	none	33.4	4.15
3		60	95	none	16.4	2.25
4		70	89	none	16.6	1.79

afforded higher yields of the $CHCl_3$-soluble product. However, the molecular weight of the product decreased to 4.4 kDa at 60°C (Entry 3). To improve the molecular weight, polycondensation was carried out for 24 h (Entry 4). Whilst the yield slightly decreased (61%), the molecular weight significantly increased (11.9 kDa). Subsequently, the effect of the carboxylic acid additive in the catalytic system was examined [13]. Polycondensation with 1-adamantanecarboxylic acid (1-AdCOOH) or trifluoroacetic acid (TFA) (Entries 5 and 6) resulted in lower yields and molecular weights than that with pivalic acid (PivOH). Therefore, PivOH was determined to be the best additive for the reaction. To improve the selectivity, the effect of ligands was also evaluated. The addition of ligands with bulky alkyl groups such as PCy_3 and $Ph_2P(CH_2)_2PPh_2$ was expected to suppress reactions at the β-position of bithiophene because of the steric hindrance [14]. However, this phenomenon was not observed in this study (Entries 7-10).

With respect to the polycondensation of 2,2′-bithiophene, the reaction conditions listed in Entry 4 (Table 1) resulted in the highest selectivity. These conditions afforded a $CHCl_3$-soluble polymer with a molecular weight of 11.9 kDa and a yield of 61%. Based on these conditions, we investigated polycondensation of di(*n*-hexyl)bithiophenes (instead of unsubstituted bithiophene) to evaluate the effects of the alkyl chains on the yield and molecular weight. Polycondensation of 3,3′-di(*n*-hexyl)bithiophene afforded a $CHCl_3$-soluble polymer [15] with a molecular weight of 16.3 kDa and a yield of 90% (Table 2, Entry 1). These results were better than those obtained with unsubstituted bithiophene. Owing to the better results, the reaction temperature was increased to 70°C. Under these conditions, the molecular weight improved to 33.4 kDa without insoluble products (Entry 2), although the value of M_w/M_n increased. Polycondensation of 4,4′-di(*n*-hexyl)bithiophene, an isomer of 3,3′-di(*n*-hexyl)bithiophene, also afforded the corresponding polymer with a molecular weight of 16.4 kDa and a yield of 95% (Entry 3), which are comparable to the results for the 3,3′-analog. The reaction at 70°C did not improve the molecular weight (16.6 kDa)

Table 3. Results of polycondensation of dialkylbithiophenes for evaluating selectivity

Entry	Monomer	Temperature (°C)	Yield (%)	Insoluble products	M_n (kDa)	M_w/M_n
1		100	11	formed	32.4	3.01
2		100	36	formed	36.4	3.51
3		100	82	formed	14.9	6.04
4		100	96	none	20.0	4.15

despite the absence of insoluble products (Entry 4). The lower solubility of the 4,4′-di(*n*-hexyl)bithiophene-based polymer in the reaction solvent (DMAc) may suppress the positive effects of the reaction temperature. Consequently, the high yield and molecular weight of the di(*n*-hexyl)bithiophene-based polymer are presumably due to a decreased number of C-H bonds at the β-position. Additionally, the steric hindrance of the hexyl chains may reduce the side reactions.

At a higher temperature (100°C), the polycondensation of di(*n*-hexyl)bithiophenes led to formation of $CHCl_3$-insoluble products (Table 3, Entries 1 and 2). Alternatively, the introduction of bulky substituents such as cyclohexyl-groups suppressed the side reactions and induced the formation of soluble products (Entries 3 and 4). The polycondensation of 4,4′-dicyclohexylbithiophene at 100°C resulted in 96% yield without the formation of insoluble products. These results indicate that 4,4′-dicyclohexylbithiophene shows the highest selectivity among the four dialkylbithiophenes. The ^{1}H NMR spectrum of the polymer shows signals corresponding to the repeating units as well as the small signals at 2.6 and 6.8 ppm (Figure 1). The minor signals could be assigned to the terminal bithiophene unit. The relatively broad molecular weight distribution ($M_w/M_n = 4.15$) could be associated with a minor branched structure, which is undetectable by the ^{1}H NMR. Since the obtained polymer exhibited low solubility in DMAc, precipitation during polymerization would also account for the broad molecular weight distribution.

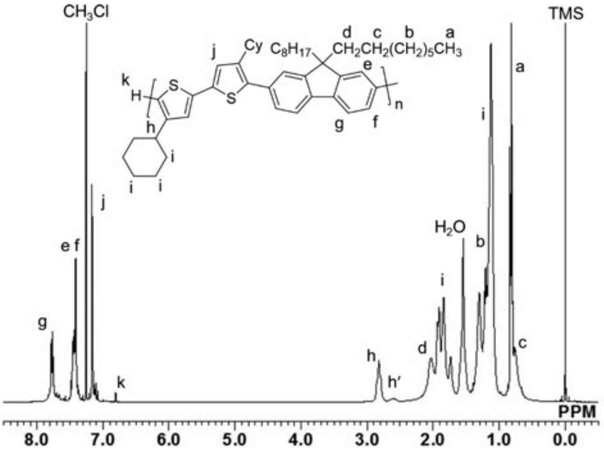


Figure 1. ^{1}H NMR spectrum of poly[2,7-(9,9-dioctylfluorene)-*alt*-5,5′-(4,4′-cyclohexyl-2,2′-bithiophene)]. The signals with k and h′ are assigned to the terminal unit.

Conclusion

In conclusion, we improved site selectivity in the polycondensation of bithiophene. In the case of unsubstituted bithiophene, lowering the reaction temperature improved the yield from 6 to 61% and the M_n from 9.4 to 11.9 kDa. In addition, this research reveals that 4,4′-dicyclohexylbithiophene has the highest selectivity among the four kinds of β-substituted bithiophenes.

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