

1 **Selectivity of reaction sites for direct arylation polycondensation in**
2 **bithiophene derivatives**

3 YOHEI FUJIE, JUNPEI KUWABARA, AND TAKAKI KANBARA*

4 Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), Graduate
5 School of Pure and Applied Sciences, University of Tsukuba, Japan

6 *Corresponding author. Tel.: +81-29-853-5066, Fax: +81-29-853-4490, E-mail:
7 kanbara@ims.tsukuba.ac.jp

8
9 **Keywords** Conjugated polymer; direct arylation; site selectivity

10
11 **ABSTRACT**

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

19
20 **Running head:** *Site selectivity of the C-H bonds in direct arylation polycondensation*

21
22 **INTRODUCTION**

23 Direct arylation polycondensation has recently been applied to the synthesis of
24 π -conjugated polymers [1-3] as a substitute for traditional cross-coupling
25 polycondensation using the Suzuki-Miyaura or Migita-Kosugi-Stille coupling [4], and is
26 advantageous because of fewer reaction steps and environment-friendly byproducts [5].
27 We have previously carried out polycondensation of 2,2'-bithiophene and
28 2,7-dibromo-9,9-dioctylfluorene, which afforded insoluble polymeric products in
29 organic solvents owing to the formation of cross-linked structures [6]. The cross-linked
30 structures could form from unexpected side reactions on the C-H bonds at β -position of
31 bithiophene. In this work, we searched for conditions affording a high selectivity toward
32 the α -position of bithiophene to avoid structural defects such as branching and/or
33 cross-linking [7,8]. In addition, we evaluated four kinds of dialkylbithiophenes in terms
34 of selectivity.

35
36 **EXPRIMENTAL**

1 3,3'-Di(*n*-hexyl)bithiophene, 4,4'-di(*n*-hexyl)bithiophene [9],
2 3,3'-dicyclohexylbithiophene [10-12], and 4,4'-dicyclohexylbithiophene [9,10] were
3 prepared by similar methods to the literatures.

4 A mixture of Pd(OAc)₂ (2.25 mg, 0.010 mmol), pivalic acid (16.9 μL, 0.15 mmol),
5 K₂CO₃ (173 mg, 1.25 mmol), 2,7-dibromo-9,9-dioctylfluorene (274 mg, 0.50 mmol),
6 and 2,2'-bithiophene (83.1 mg, 0.50 mmol) was stirred in anhydrous dimethylacetamide
7 (DMAc, 1.67 mL) for 24 h at 60 °C under nitrogen atmosphere. After cooling to room
8 temperature, the mixture was poured into an aqueous solution of
9 ethylenediaminetetraacetic acid disodium salt (pH = 8). The suspension was stirred
10 overnight at room temperature. The precipitate was separated by filtration and washed
11 with 0.1 M HCl solution, distilled water, methanol, and hexane. The precipitate was
12 dissolved in CHCl₃, and the solution was filtered through a plug of Celite to remove
13 insoluble material. Reprecipitation from CHCl₃/methanol gave polymer, described in
14 Table 1, Entry 4, as a pale yellow solid in 61% yield. $M_n = 11\,900$, $M_w/M_n = 2.29$. ¹H
15 NMR (400 MHz, CDCl₃): δ 0.66-0.76 (br, 4H), 0.76-0.83 (m, 6H), 0.99-1.23 (br, 20H),
16 1.99-2.10 (br, 4H), 7.21-7.36 (m, 4H), 7.55-7.74 (m, 6H).

17 18 **RESULTS AND DISCUSSION**

19 Upon finding the appropriate conditions to afford high selectivity toward the α-position
20 of bithiophene, we investigated polycondensation of 2,2'-bithiophene with
21 2,7-dibromo-9,9-dioctylfluorene under various conditions. In the case of the highly
22 selective reaction, side reactions at the β-position of bithiophene do not proceed and
23 cross-linked polymers are not formed, leading to a high yield of CHCl₃-soluble products.
24 Table 1 shows the results of polycondensation under various conditions. First, the
25 reactions at lower temperatures were investigated to suppress the reactions at the
26 β-position (Table 1, Entries 1-3). A decrease in the reaction temperature improved the
27 selectivity: the reactions at lower temperatures afforded higher yields of the
28 CHCl₃-soluble product. However, the molecular weight of the product decreased to 4.4
29 kDa at 60 °C (Entry 3). To improve the molecular weight, polycondensation was carried
30 out for 24 h (Entry 4). Whilst the yield slightly decreased (61%), the molecular weight
31 significantly increased (11.9 kDa). Subsequently, the effect of the carboxylic acid
32 additive in the catalytic system was examined [13]. Polycondensation with
33 1-adamantanecarboxylic acid (1-AdCOOH) or trifluoroacetic acid (TFA) (Entries 5 and
34 6) resulted in lower yields and molecular weights than that with pivalic acid (PivOH).
35 Therefore, PivOH was determined to be the best additive for the reaction. To improve
36 the selectivity, the effect of ligands was also evaluated. The addition of ligands with

1 bulky alkyl groups such as PCy₃ and Ph₂P(CH₂)₂PPh₂ was expected to suppress
2 reactions at the β-position of bithiophene because of the steric hindrance [14]. However,
3 this phenomenon was not observed in this study (Entries 7-10).

4 With respect to the polycondensation of 2,2'-bithiophene, the reaction conditions listed
5 in Entry 4 (Table 1) resulted in the highest selectivity. These conditions afforded a
6 CHCl₃-soluble polymer with a molecular weight of 11.9 kDa and a yield of 61%. Based
7 on these conditions, we investigated polycondensation of di(*n*-hexyl)bithiophenes
8 (instead of unsubstituted bithiophene) to evaluate the effects of the alkyl chains on the
9 yield and molecular weight. Polycondensation of 3,3'-di(*n*-hexyl)bithiophene afforded a
10 CHCl₃-soluble polymer [15] with a molecular weight of 16.3 kDa and a yield of 90%
11 (Table 2, Entry 1). These results were better than those obtained with unsubstituted
12 bithiophene. Owing to the better results, the reaction temperature was increased to 70 °C.
13 Under these conditions, the molecular weight improved to 33.4 kDa without insoluble
14 products (Entry 2), although the value of M_w/M_n increased. Polycondensation of
15 4,4'-di(*n*-hexyl)bithiophene, an isomer of 3,3'-di(*n*-hexyl)bithiophene, also afforded the
16 corresponding polymer with a molecular weight of 16.4 kDa and a yield of 95% (Entry
17 3), which are comparable to the results for the 3,3'-analog. The reaction at 70 °C did not
18 improve the molecular weight (16.6 kDa) despite the absence of insoluble products
19 (Entry 4). The lower solubility of the 4,4'-di(*n*-hexyl)bithiophene-based polymer in the
20 reaction solvent (DMAc) may suppress the positive effects of the reaction temperature.
21 Consequently, the high yield and molecular weight of the di(*n*-hexyl)bithiophene-based
22 polymer are presumably due to a decreased number of C-H bonds at the β-position.
23 Additionally, the steric hindrance of the hexyl chains may reduce the side reactions.

24 At a higher temperature (100 °C), the polycondensation of di(*n*-hexyl)bithiophenes led
25 to formation of CHCl₃-insoluble products (Table 3, Entries 1 and 2). Alternatively, the
26 introduction of bulky substituents such as cyclohexyl-groups suppressed the side
27 reactions and induced the formation of soluble products (Entries 3 and 4). The
28 polycondensation of 4,4'-dicyclohexylbithiophene at 100 °C resulted in 96% yield
29 without the formation of insoluble products. These results indicate that
30 4,4'-dicyclohexylbithiophene shows the highest selectivity among the four
31 dialkylbithiophenes. The ¹H NMR spectrum of the polymer shows signals
32 corresponding to the repeating units as well as the small signals at 2.6 and 6.8 ppm
33 (Figure 1). The minor signals could be assigned to the terminal bithiophene unit. The
34 relatively broad molecular weight distribution ($M_w/M_n = 4.15$) could be associated with
35 a minor branched structure, which is undetectable by the ¹H NMR. Since the obtained
36 polymer exhibited low solubility in DMAc, precipitation during polymerization would

1 also account for the broad molecular weight distribution.

2 **CONCLUSION**

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

9 **REFERENCES**

10 [1] Okamoto, K., Zhang, J., Housekeeper, J. B., Marder, S. R., & Luscombe, C. K.
11 (2013). *Macromolecules*, *46*, 8059.

12 [2] Wang, Q., Takita, R., Kikuzaki, Y., & Ozawa, F. (2010). *J. Am. Chem. Soc.*, *132*,
13 11420.

14 [3] Lu, W., Kuwabara, J., & Kanbara, T. (2011). *Macromolecules*, *44*, 1252.

15 [4] Bryan, Z. J. & McNeil, A. J. (2013). *Macromolecules*, *46*, 8395.

16 [5] Kuwabara, J., Yasuda, T., Choi, S. J., Lu, W., Yamazaki, K., Kagaya, S., Han, L., &
17 Kanbara, T. (2014). *Adv. Funct. Mater.*, *24*, 3226.

18 [6] Fujinami, Y., Kuwabara, J., Lu, W., Hayashi, H., & Kanbara, T. (2012). *ACS Macro*
19 *Lett.*, *1*, 67.

20 [7] Kuwabara, J., Nohara, Y., Choi, S. J., Fujinami, Y., Lu, W., Yoshimura, K., Oguma,
21 J., Suenobu, K., & Kanbara, T. (2013). *Polym. Chem.*, *4*, 947.

22 [8] Rudenko, A. E., Wiley, C. A., Tannaci, J. F., & Thompson, B. C. (2013). *J. Polym.*
23 *Sci., Part A: Polym. Chem.*, *51*, 2660.

24 [9] Zhang, M., Fan, H., Guo, X., Yang, Y., Wang, S., Zhang, Z., Zhang, J., Zhan, X., &
25 Li, Y. (2011). *J. Poly. Sci. A: Poly. Chem.*, *49*, 2746.

26 [10] Cui, C., Sun, Y., Zhang, Z., Zhang, M., Zhang, J., & Li, Y. (2012). *Macromol.*
27 *Chem. Phys.*, *213*, 2267.

28 [11] Whelligan, D. K., Solanki, S., Taylor, D., Thompson, D. W., Cheung, K. J., Boxall,
29 K., Mas-Droux, C., Barillari, C., Burns, S., Grummitt, C. G., Collins, I., Montfort, R. L.
30 M., Aherene, G. W., Bayliss, R., & Hoelder, S. (2010). *J. Med. Chem.*, *53*, 7682.

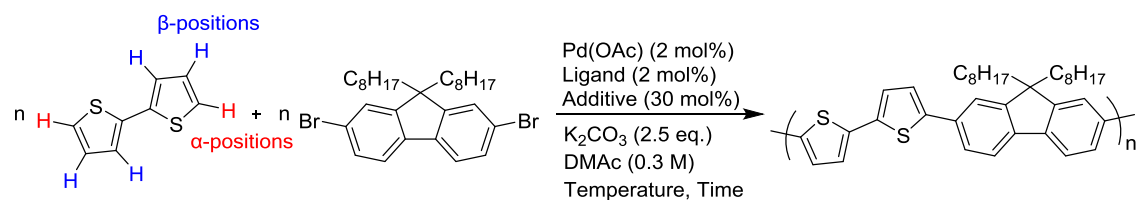
31 [12] Bongini, A., Barbarella, G., Favaretto, L., Sotgiu, G., Zambianchi, M., & Casarini,
32 D. (2002). *Tetrahedron*, *58*, 10151.

33 [13] Lafrance, M. & Fagnou, K. (2006). *J. Am. Chem. Soc.*, *128*, 16496.

34 [14] Ueda, K., Yanagisawa, S., Yamaguchi, J., & Itami, K. (2010). *Angew. Chem. Int.*
35 *Ed.*, *49*, 8946.

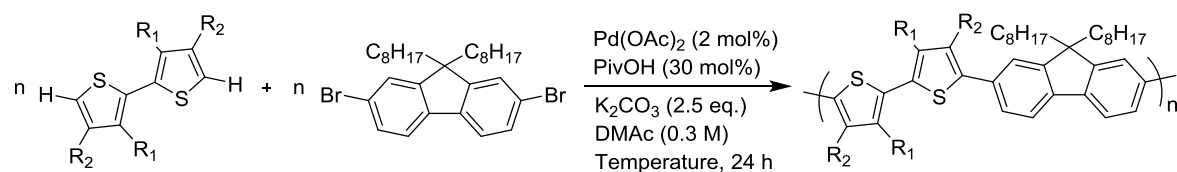
36 [15] Chen, H., He, M., Pei, J., & Liu, B. (2002). *Anal. Chem.*, *74*, 6252.

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 ·HBF ₄	PivOH	60	72	30	formed	10.0	2.26
8	Ph ₂ P(CH ₂) ₂ PPh ₂	PivOH	80	72	15	formed	7.4	2.13
9	P(<i>t</i> -Bu) ₃	PivOH	80	72	52	formed	8.6	2.63
10	P(2-furyl) ₃	PivOH	80	48	1	formed	8.4	1.54

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

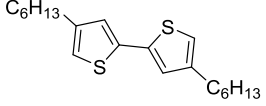
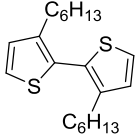
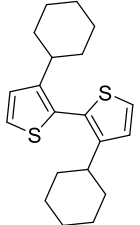
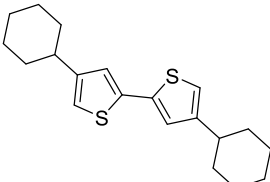


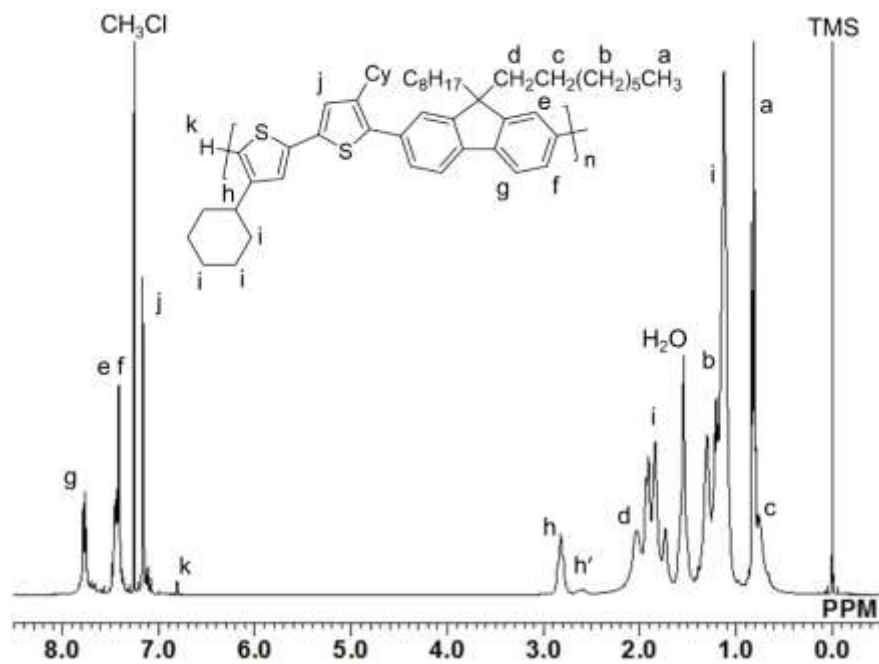
Entry	Monomer	Temperature (°C)	Yield (%)	Insoluble products	M_n (kDa)	M_w/M_n
1		60	90	none	16.3	1.91
2		70	99	none	33.4	4.15
3		60	95	none	16.4	2.25
4		70	89	none	16.6	1.79

1

2

3 **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



4

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