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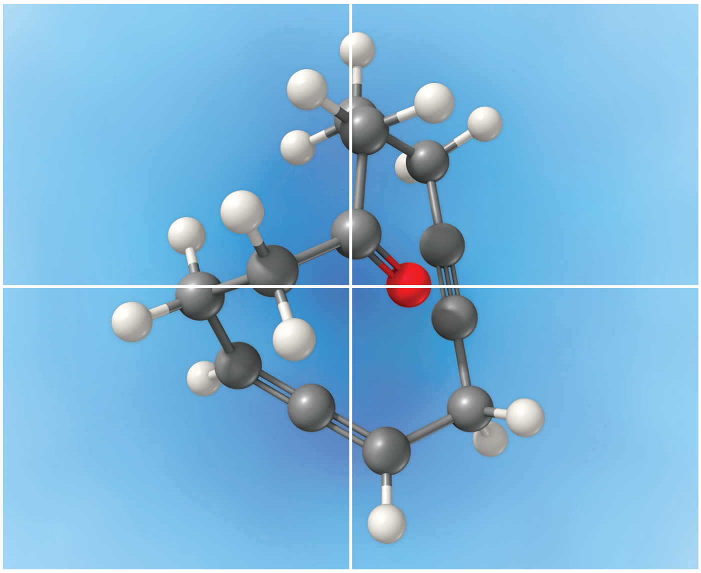

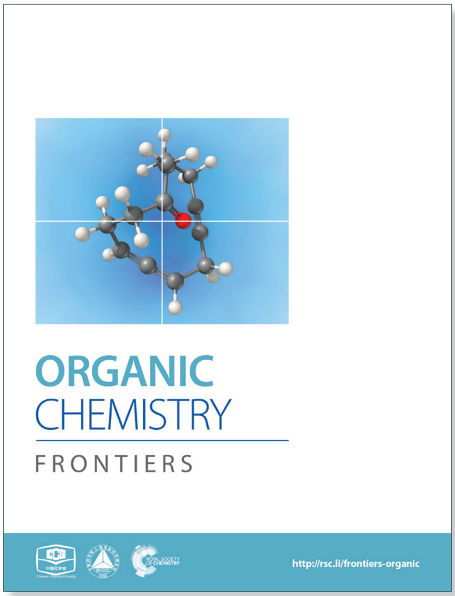

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Polythiophene Synthesis via Halogen Dance†

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Polymerization of 2,4-dibromo-3-hexyl-5-lithiated thiophene that is formed by deprotonation of 2,5-dibromo-3-hexylthiophene with LDA and following halogen dance takes place in the presence of nickel(II) or palladium(II) catalyst to afford poly(3-bromo-4-hexylthiophen-2,5-diyl).

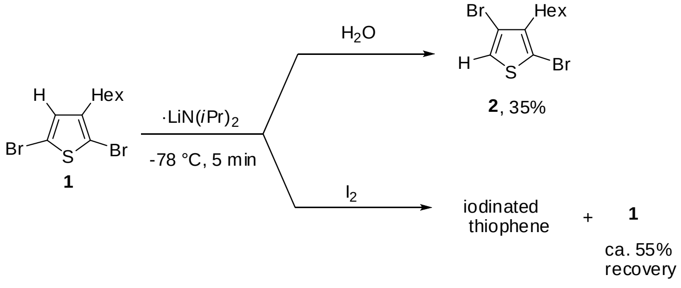
Introduction

Polythiophenes recently attract much attention as materials for a variety of electronic devices.[1] Development of a facile method for the preparation of polythiophenes is of particular interest in organic and organometallic chemistry as well as polymer synthesis. Cross coupling of metalated thiophenes with thienyl halides in the presence of a transition metal catalyst is one of the most practical preparative method to form the thiophene-thiophene bond leading to polythiophenes and various types of polythiophenes are indeed synthesized by cross coupling methodology.[2] In particular, the reaction of 2-halo-5-metalated thiophene, which is in situ formed by the reaction of the corresponding 2,5-dihalothiophene developed by Rieke, McCullough, and Yokozawa, is extensively studied to afford poly(3-substituted thiophen-2,5-diyl)s with remarkably excellent head-to-tail regioregularity in controllable manners of molecular weight and molecular weight distribution based on the amount of catalyst loading.[3]

On the other hand, we have been engaged in the development of transition metal-catalyzed coupling reactions, in which coupling at the C-H bond of heteroaromatic compounds has been of our particular concern.[4] We have recently developed several polymerization of thiophene derivatives that occur by the condensation at the C-H and C-X bonds leading to polythiophenes, where deprotonative metalation of halothiophene has played important role for the successful polymerization.[5] Accordingly, development of a new class of metalation protocols for heteroaromatic compounds is highly important in the synthesis of π-conjugated polymers. Concerning the polythiophene synthesis organomagnesium (Grignard reagents), zinc, boron, and tin reagents have been mainly employed as a metallic species.[2-5] In addition to the above metals, we have shown organolithium species of thiophene derivatives, indeed, can be available for nickel(II)-catalyzed polythiophene synthesis and lithiation was performed by deprotonation at the C-H bond or lithium-halogen exchange at the carbon-halogen bond.[6] Among lithiation of (hetero)aromatic compounds an alternative choice also for the formation of organolithium species is halogen dance, which occurs intra- or intermolecular halogen-lithium exchange.[7] In our preliminary communication on Murahashi coupling polymerization of thiophene derivatives with organolithium species, we have partially described that organolithium of thiophene formed by halogen dance can also be served as an organometallic monomer for polythiophene synthesis,[6] however, little studies on the detail has been discussed. Herein we report halogen dance of thiophene derivatives toward the formation of lithiated monomer, polymerization of the thus formed metalated species, and transformation of the polythiophene formed through halogen dance.

Results and discussion

First, we studied the optimum condition of halogen dance with 2,5-dibromo-3-hexylthiophene (**1**) as shown in Scheme 1. Deprotonation of **1** at the 4-position was carried out with LDA(lithium diisopropylamide: LiN*i*Pr$_2$) at -78 ℃. After stirring for 5 min, progress of halogen dance was confirmed by treatment of H_2O to obtain 35% of 2,4-dibromo-3-hexylthiophene (**2**). Since the progress of deprotonation under similar conditions was also found to be ca. 45%, which was confirmed by treatment of deprotonated mixture with iodine to observe unreacted ca. 55% of **1**, these results suggested that the lithiated species at the 4-position was mostly rearranged into 5-lithio-4-brominated thiophene at -78 ℃ through halogen dance.



Scheme 1. Deprotonation of **1** with LDA

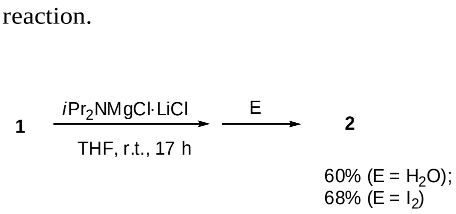
Halogen dance under several conditions was then examined as summarized in Table 1. When **1** was treated with 1.1 equivalents of LDA at 0 ℃ and room temperature for 5 min, 90%, respectively, of **2** was obtained by treatment of water. On the other hand, deprotonation with LTMP (lithium 2,2,6,6-tetramethylpiperidide) was found slower to observe conversion to **2** in only 75% after stirring at room temperature for 30 min whereas further reaction to 4 h improved the reaction to 81%. The reaction of **1** with Cy_2NLi (lithium dicyclohexylamide) underwent halogen dance smoothly to observe, after treatment of water, conversion to **2** in 85% (30 min) and 96% (5 h), respectively. It was also found that the reaction of **1** with lithium diethylamide (Et_2NLi) at room temperature for 30 min resulted in 85% conversion. By contrast, LHMDS (lithium hexamethyldisilazide) was found to hardly deprotonate **1** at room temperature for 30 min. Conditions at 60 ℃ for 24 h were required to afford **2** in 77% conversion.

Table 1. Halogen dance of **1** with lithium amide.[a]

Lithiumamide	Temp(℃)	Time	Conversion to **2** (%)[b]
LDA[c]	-78	5 min	35
	0	5 min	90
	r.t.	5 min	90
LTMP[d]	r.t.	30 min	75
	r.t.	4 h	81
Cy_2NLi[e]	r.t.	30 min	85
	r.t.	5 h	96
Et_2NLi	r.t.	30 min	85
LHMDS[f]	r.t.	30 min	0
	60	24 h	77

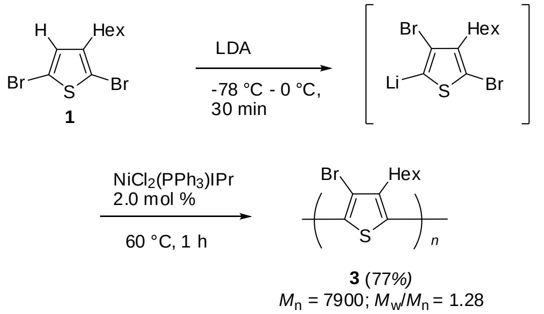
[a] The reaction was carried out with **1** (0.5 mmol) and 1.1 equiv. of lithiumamide in THF. [b] Confirmed by ^1H NMR after quenching the crude reaction mixture with water. [c] Lithium diisopropylamide [d] Lithium 2,2,6,6-tetramethylpiperidide [e] Lithium dicyclohexylamide [f] Lithium hexamethyldisilazide

Halogen dance with magnesium amide was also studied. When the reaction of **1** was examined with Knochel-Hauser base[8] TMPMgCl·LiCl (chloromagnesium-2,2,6,6-tetramethylpiperidide lithium chloride salt), halogen dance hardly took place at room temperature for 3 h. However, the reaction with $i\text{Pr}_2\text{NMgCl}\cdot\text{LiCl}$ (1.2 equiv) resulted in ca. 60% halogen dance, which was confirmed by quenching with water to afford **2**. Since treatment with iodine suggested the amount of deprotonation was 68%, most of the metalated thiophene magnesium species induced halogen dance. Although the reaction of $i\text{Pr}_2\text{NMgCl}\cdot\text{LiCl}$ at the elevated temperature (60 ℃) was also examined, it was found to observe little improvement of the reaction.



Scheme 2. Attempted halogen dance of **1** with $i\text{Pr}_2\text{NMgCl}\cdot\text{LiCl}$

With the studied reaction conditions of halogen dance, polymerization of the thus obtained lithiated thiophene species was carried out. After 2,5-dibromothiophene **1** was added to a THF solution of LDA at -78 ℃, the reaction mixture was gradually raised to 0 ℃ over 30 min to induce halogen dance. Then, 2.0 mol % of nickel catalyst bearing *N*-heterocyclic carbene (NHC) ligand $\text{NiCl}_2(\text{PPh}_3)\text{IPr}$[9] was added to the resulting mixture and stirring was continued at 60 ℃ for 1 h to afford polymer **3** in 77% isolated yield. SEC analysis revealed to show M_n=7900 (M_w/M_n = 1.28). (Scheme 3)



Scheme 3. Halogen dance polymerization of **1** with LDA

Figure 1 shows ^1H NMR spectrum of the obtained polymer indicating the proton signal observed at 6.8 ppm disappeared. Broadening of alkyl signals corresponding to the substituent at the 3-position also support polymer formation. In addition, elemental analysis of the obtained polythiophene indicated bromine contents of 32.83% showing good correspondence to $Br(C_{10}H_{13}BrS)_{32}H$ (33.27%). The result suggests the monomer unit of **3** contains bromine atom. In contrast with poly(3-hexylthiophen-2,5-diyl), the polymer bearing a bromine atom at the 4-position **3** was found to be highly soluble in organic solvents such as THF, chloroform, and hexane. The results suggest that π-conjugation between the thiophene rings in the polymer chain is less extended.

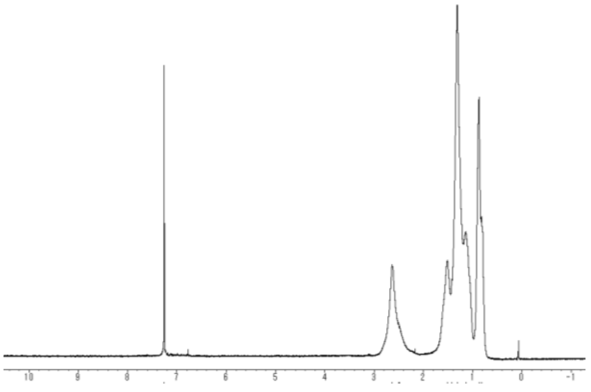


Figure 1. ^1H NMR spectrum ($CDCl_3$) of **3**

Table 2. Halogen dance polymerization of **1**.[a]

entry	Halogen dance (Temp, Time)	Catalyst (mol %)	Polymerization Temp(℃), time (h)	Yield (%)	M_n [b]	M_w/M_n [b]
1	LDA (0, 30 min)	$NiCl_2(PPh_3)IPr$[c] (2.0)	60, 1	77	7900	1.28
2	LDA (0, 30 min)	$NiCl_2(PPh_3)IPr$[c] (1.3)	r.t., 1	78	5100	1.45
3	LDA (r.t., 2 h)	$NiCl_2$dppp (2.0)	60, 24	44	1200	
4	LDA (r.t., 3.5 h)	$NiCl_2$dppf (2.0)	60, 24	62	1100	
5	LDA (r.t., 2 h)	Umicore CX31[d] (5.0)	60, 24	43	4400	3.36
6	LDA (r.t., 2 h)	Umicore CX32[e] (5.0)	60, 24	56	6000	3.48
7	LDA (0, 30 min)	PEPPSI-SIPr[f] (1.3)	r.t., 72	67	7700	1.66
8	Cy_2NLi (r.t., 5 h)	$NiCl_2(PPh_3)IPr$ (1.0)	60, 24	72	10100	1.61
9	Cy_2NLi (r.t., 5 h)	$NiCl_2(PPh_3)IPr$ (1.0)	r.t., 24	41	6700	1.56
10	Cy_2NLi (r.t., 5 h)	PEPPSI-SIPr[f] (1.0)	r.t., 24	53	6100	1.57
11	LTMP (r.t., 8 h)	PEPPSI-SIPr[f] (1.0)	r.t., 24	72	5600	1.54

[a] The reaction was carried out with **1** (0.5 mmol) and 1.1 equiv. of lithiumamide in THF for the metalation and 1.0-5.0 mol % of catalyst was employed for the polycondensation. [b] M_n and M_w/M_n values were estimated by SEC analysis using $CHCl_3$ as an eluent. [c] IPr: 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene [d] [1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]chloro[3-phenylallyl]palladium(II) [e] [1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]chloro[3-phenylallyl]palladium(II) [f] (1,3-Bis(2,6-diisopropylphenyl)imidazolidene) (3-chloropyridyl)palladium(II) dichloride

Table 2 represents halogen dance polymerization of **1** under several conditions. Compared with the polymerization conditions shown in Scheme 3 (entry 1), it was found that polymerization with $NiCl_2(PPh_3)IPr$ also proceeded at room temperature in 78% yield (M_n=7900; M_w/M_n = 1.28) (entry 2). On the other hand, other nickel catalysts bearing bidentate phosphine ligands dppp and dppf was less effective to afford oligomers with inferior yields. (entry 3,4) Considering that nickel catalysts bearing bidentate phosphines effectively undergo polymerization of 3-hexylthiophene, polymerization to afford **5** would be less reactive because of steric effect of the bromine substituent. A palladium catalyst was also found to undergo polymerization when NHC is employed as a ligand.[10] Use of palladium catalysts bearing NHC ligands (Umicore CX31 and CX32)[11] induced polymerization to afford **3** of slightly higher molecular weights although the molecular weight distribution was much broader (entry 5,6). However, polymeization with PEPPSI[12]-SIPr at room temperature afforded **3** of higher molecular weight (entry 7). The lithiated monomer via halogen dance with Cy_2NLi and LTMP was also found to afford polymer **3** smoothly. (entry 8-11)

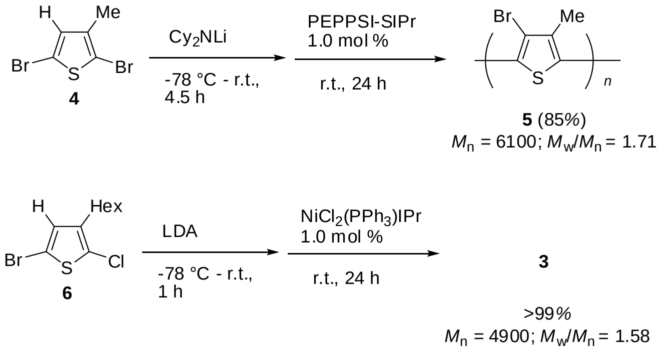
Table 3 summarizes the result on the relationship of molecular weight with catalyst loading in the halogen dance polymerization. It was found that molecular weight of **3** increased as the amount of catalyst loading decreased. However, the molecular weight was found much inferior to the theoretical line based on the ideal living polymerization.

Table 3. Halogen dance polymerization of **1**.[a]

1/Ni cat.	Yield, %	M (theor.)[b]	M_n	M_w/M_n
33	65	8200	2800	1.22
50	61	12300	3300	1.28
67	78	16300	4400	1.42
100	72	24500	10100	1.61

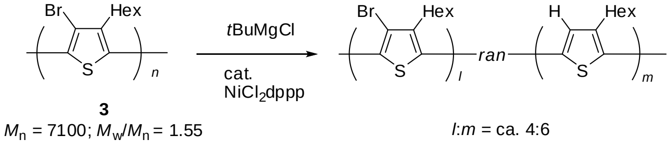
[a] The reaction was carried out with **1** and 1.1 equiv. of Cy_2NLi in THF for halogen dance (-78 ℃ - r.t. over 5 h) and 1.0-3.0 mol% of $NiCl_2(PPh_3)IPr$ was employed for the polymerization. [b] Theoretical molecular weight based on the ration of **1**/nickel catalyst at the 100% conversion. [c] M_n and M_w/M_n values were estimated by SEC analysis using $CHCl_3$ as an eluent.

A thiophene derivative bearing a methyl substituent at the 3-position was also subjected to halogen dance polymerization. The reaction of 2,5-dibromo-3-methylthiophene **4** was treated with lithium dicyclohexylamide at -78 ℃ and then gradually raised to room temperature over 4.5 h. Addition of palladium catalyst PEPPSI-SIPr (1.0 mol %) at room temperature induced polymerization in a similar manner to the case of **1** to afford the corresponding polymer **5** in 85% yield after stirring for 24 h. (M_n = 6100, M_w/M_n = 1.71) The reaction of chlorothiophene was also performed with 5-bromo-2-chloro-3-hexylthiophene (**6**). Treatment of **6** with LDA and following addition of $NiCl_2(PPh_3)IPr$ (1.0 mol %) resulted in polymerization at room temperature for 24 h to afford the corresponding polymer **3** in a quantitative yield. (M_n = 4900, M_w/M_n = 1.58). These results are depicted in Scheme 4.



Scheme 4. Halogen dance polymerization of **4** and **6**

Transformation of polymer **3** obtained by halogen dance polymerization was subjected to transformation. Since it is interesting that polymerization of 2,5-dihalo-3-alkylthiophene gives polymers of different structures by switching the metalation protocol. Usual GRIM (Grignard metathesis)[3] metalation and the following transition-metal-catalyzed polycondensation gives poly(3-alkylthiophen-2,5-diyl) whereas halogen dance is shown to lead to poly(3-alkyl-4-bromo-thiophen-2,5-diyl). We envisaged that the obtained polymer by halogen dance would be transformed by reduction of the bromine atom toward poly(3-alkylthiophen-2,5-diyl). Accordingly, the polymer obtained by halogen dance (M_n =7100; M_w/M_n = 1.55) was treated with *t*BuMgCl (2.0 equiv.) in the presence of $NiCl_2$dppp at room temperature for 24 h. Measurement of ^{1}H NMR spectrum revealed that a new signal at ca. 7 ppm, which is identical with the methine proton of the thiophene ring of P3HT appeared. Comparison of the integral value with that of the CH_2 signal of hexyl group adjacent to the thiophene ring suggested ca. 60% of bromine atom was reduced to hydrogen. The color of polymer was changed from yellow to dark purple. Measurements of UV-vis spectra of **3** and the transformed polymer (λ_{max} shifted to 357 nm to 376 nm) also suggested extended π-conjugation increased close to that of P3HT (λ_{max} = ca. 450 nm).



Scheme 5. Transformation of **3**

Conclusion

In conclusion, we have shown a new class of polymerization with organolithium species of a thiophene derivative, which was generated by halogen dance of 2,5-dihalo-3-alkylthiophene by treatment with lithium amide. The reaction afforded polythiophene bearing bromine atom as a substituent of the thiophene ring. The reaction was found to proceed in the presence of nickel(II) or palladium(II) catalyst via cross coupling polycondensation of organolithium. Debromination of the obtained polymer increased to the contents of extended π-conjugation. If a proper halogen dance is designed in not only thiophene ring but also another class of aromatic rings, this strategy enhances variety of halogen-containing polymer materials, which allow wide range of organic transformation reactions.

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Notes and references

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† This paper is dedicated to Professor Max Malacria upon cerebration of his 65th birthday.

Electronic Supplementary Information (ESI) available: Experimental details and spectroscopic data. See DOI: 10.1039/b000000x/

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10 Attempted reaction with Pd(tBu_3P)$_2$, which was shown to induce several polymerization of (hetero)arylenes,[3, 5-7] resulted in giving little polymerization.

11 [1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene]chloro[3-phenylallyl]palladium(II): (CX31) and [1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene]chloro[3-phenylallyl]palladium(II) (CX32), respectively. Y. Horiguchi, S. P. Nolan, *J. Synth. Org. Chem. Jpn.* 2009, **67**, 653.

12 PEPPSI: Pyridine-enhanced precatalyst preparation stabilization and initiation, (1,3-Bis(2,6-diisopropylphenyl)imidazolidene) (3-chloropyridyl) palladium(II) dichloride. (a) C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson and M. G. Organ, *Chem. Eur. J.* 2006, **12**, 4743. (b) M. G. Organ, S. Calimisiz, M. Sayah, K. H. Hoi and A. J. Lough, *Angew. Chem., Int. Ed.* 2009, **48**, 2383.