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Linear-selective Cross-coupling Polymerization of Branched Oligothiophene by Deprotonative Metalation and Cross-coupling

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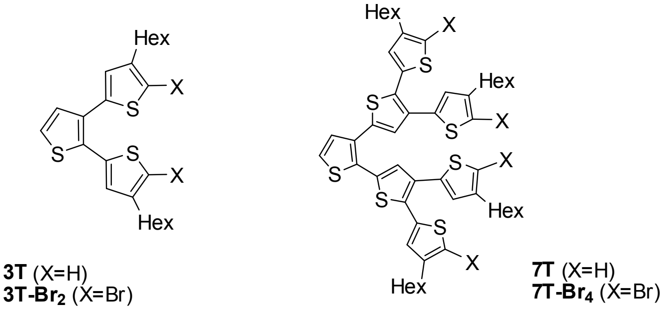
Brominated oligothiophene with a branched structure was subjected to deprotonative metalation with the bulky magnesium amide chloromagnesium 2,2,6,6-tetramethylpiperidine-2-yl lithium chloride salt (TMPMgCl·LiCl), which is recognized as Knochel-Hauser base. The thus metalated oligothiophene was polymerized in the presence of a nickel(II) NHC (*N*-heterocyclic carbene) complex to afford polymers of M_n of 4400 to 44000, which correspond well to the monomer feed/catalyst loading ratio. Analysis by MALDI-TOF MS suggests formation of a linear polymer with oligothiophene as the monomer. Polymerization of 7-mer (**7T**-Br_4) also affords polythiophene of a similar structure.

Polythiophenes obtained by transition-metal-catalyzed cross coupling polymerization are of great interest in materials science as well as polymer synthesis.[1,2] Regioregular head-to-tail-type poly(3-hexylthiophene) (HT-P3HT) shows particularly interesting properties as materials and is employed in a wide range of optoelectronic devices such as photovoltaic cells,[3] organic semiconductors,[4] and conductive thin films.[5] Oligo and polythiophenes with branched structures also attract attention and a wide range of such compounds have been designed and synthesized to date.[6] We recently described the highly efficient preparation of oligothiophene dendrimers in a stepwise manner, in which extension of each generation is concisely achieved in a single step.[7] Several branched oligothiophenes such as **3T**, **7T** were shown to be prepared with high efficiencies. It was also shown that such dendrimers were regioselectively halogenated to afford multiply halogenated branched oligomers. (Chart 1)



3T (X=H)
3T-Br$_2$ (X=Br)

7T (X=H)
7T-Br$_4$ (X=Br)

Chart 1 Oligothiophene dendrimers

Our interest turned to cross coupling polymerization of the thus formed branched halothiophenes, in which preference for linear[8] or divergent propagation[9] would be of particular interest. Herein, we report that deprotonative polymerization of multiply brominated oligothiophene dendrimers furnishes linear polymers and the remaining carbon-bromine bond in the polymer side chains can be successfully transformed.

Preparation of monomer precursor (**1a**) was performed according to our previously reported method that described the nickel catalyzed cross coupling reaction of 2,3-dibromothiophene with regioselectively metalated 3-hexylthiophene.[7] The obtained branched terthiophene **3T** was selectively brominated by careful treatment with two equivalents of *N*-bromosuccinimide. Polymerization of **1a** was carried out with 1.2 equivalents of Knochel-Hauser base (chloromagnesium 2,2,6,6-tetramethylpiperidine lithium

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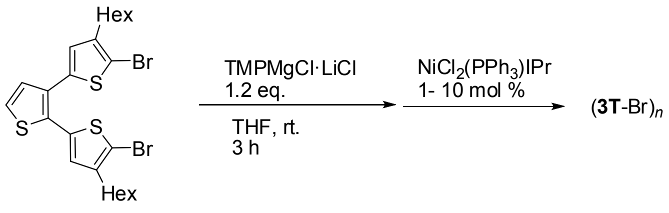
chloride salt: TMPMgCl·LiCl)[10] at room temperature for 3 h followed by addition of a nickel catalyst.[11]



3T-Br$_2$ **(1a)**

Scheme 1 Polymerization of **3T**-Br$_2$ (**1a**) with NiCl$_2$(PPh$_3$)IPr

When the reaction of **1a** was carried out with 1.0 mol % nickel *N*-heterocyclic carbene (NHC) complex NiCl$_2$(PPh$_3$)IPr (IPr: *N*,*N*'-(2,6-diisopropylphenyl)imidazolium) in THF as shown in Scheme 1, rapid polymerization took place and the color change of the solution turned dark orange after stirring for 2 h. Termination of the polymerization with HClaq/MeOH resulted in formation of crude polymer solid. The obtained polymer was found to be highly soluble in organic solvents and SEC analysis showed M_n = 44000 (PDI = 1.30). The reaction was carried out under several conditions as summarized in Table 1, revealing that increasing the loading of catalyst (1-10 mol %) afforded polymers with lower molecular weight (entry 1-6). MALDI-TOF mass spectrometry (MS) of the polymer of entry 6 (M_n = 4350 by SEC) revealed a repeating unit of M/Z = 493.06 as shown in Fig. 1. suggesting the structure of (**3T**-Br)$_n$ and end groups composed of H/H (minor) and H/Br (major). The average molecular weight corresponded reasonably well with the monomer feed/ catalyst loading ratio (e.g. theoretical M = 49300 for 1 mol % Ni catalyst in entry 1). The above results suggest that linear polymers composed of monobrominated **3T** as a repeating unit are obtained in the polymerization reaction. Additionally, unless the organometallic monomer is completely consumed, a nickel species that is capable of incorporating additional monomer exists at the polymer end. Use of NiCl$_2$dppp also led to polymerization although a longer reaction period was found to be necessary. (entry 7) However, prolonged reaction with NiCl$_2$dppe or the Ni NHC complex[12,13] resulted in gelation. (entries 2 and 8) The reaction with Pd-PEPPSI as a catalyst also resulted in polymerization, albeit much more slowly (entry 9) and polymerization took place with slightly inferior efficiency when catalyzed by Pd(tBu$_3$P)$_2$ (entry 10). Although deprotonation with a lithium amide such as LDA followed by metal exchange with Mg^{2a,14} or Zn^{2a,15} ion might be an alternative choice to give a similar metalated species (monomer), it should be pointed out that the metalation protocol used here was achieved in a single step at room temperature.

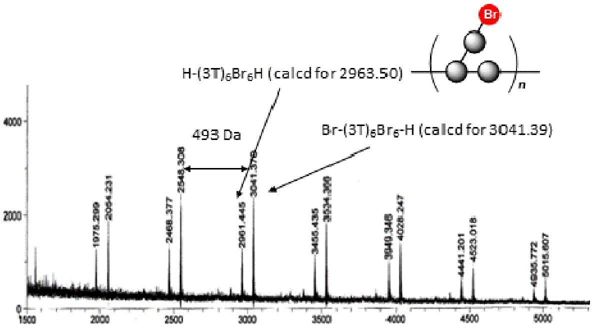


Fig. 1 MALDI-TOF mass spectrum of the polymerization product of **1a** (Table 1, entry 6)

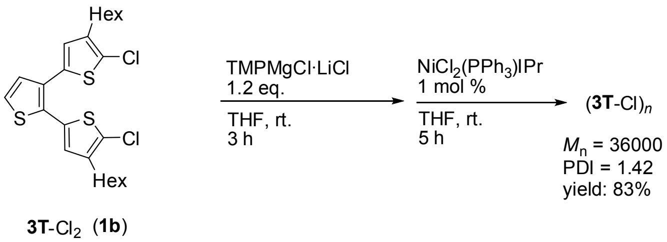
Table 1 Polymerization of **1a** with TMPMgCl·LiCl followed by nickel or palladium[a]

entry	catalyst (mol %)	time h	yield[b] %	M_n (M_{theor})[c]	PDI
1	NiCl$_2$(PPh$_3$)IPr (1.0)	2	98 (99)	44000 (49300)	1.30
2	(1.0)	24	gel[d]	--	--
3	(2.0)	2	88 (92)	21000 (24700)	1.20
4	(3.0)	2	93 (95)	15700 (16400)	1.23
5	(4.0)	2	80 (96)	13000 (12400)	1.23
6	(10.0)	2		4400 (4900)	1.12
7	NiCl$_2$dppp (1.0)	24	77 (89)	55000	1.56
8	NiCl$_2$dppe (1.0)	24	gel[d]	--	--
9	PdPEPPSI-SIPr (1.0)	70	83 (93)	28700	1.58
10	Pd(tBu$_3$P)$_2$ (1.0)	24	51 (86)	11000	1.93

[a] Polymerization was carried out with 1.2 equiv TMPMgCl·LiCl in 3 mL THF with **1a** (0.3 mmol) stirring at room temperature for 2 h followed by addition of NiCl$_2$(PPh$_3$)IPr. [b] Conversion of monomer (%) is shown in parentheses. [c] The theoretical molecular weight based on the monomer/catalyst feed ratio given in parentheses. [d] Insoluble materials were formed in the polymerizing solution.

Measurement of viscosity also supports that the polymerization reaction proceeds in a linear-selective manner, while divergent polymerization leading to hyperbranched polymer hardly occurs. The relationship between viscosity η and M_n can be expressed as, $\eta = K(M_n)^{\alpha}$ where K and α are constants based on the polymer properties; it has been suggested that an ideal linear polymer has an α value of ca. 0.5 while that of branched polymer is much smaller. Measurement of the viscosity of (**3T**-Br)$_n$ revealed that it had an α 0.88, which supports it being a linear polymer. Hwoever, Luscombe recently reported the synthesis of a hyperbranched polymer composed of branched oligothiophene, for which the α value is described as 0.19-0.31.[9c] Furthermore, calculation of the α value of oligothiophene dendrimers 3T, 7T, and 15T showed ca. α = 0.20. These results strongly suggest that the structure of (**3T**-Br)$_n$ prepared by nickel-catalyzed polymerization is linear despite the presence of two possible reactive carbon-bromine bonds.

The deprotonative polymerization was found to take place also with the chloride analog **3T**-Cl$_2$ (**1b**) under similar conditions to afford (**3T**-Cl)$_n$ smoothly as shown in Scheme 2.[16] The average molecular weight of the obtained polymer again agreed with the catalyst loading/monomer feed ratio with M_n = 36000 and with a PDI of 1.42.



Scheme 2 Polymerization of **3T**-Cl$_2$ (**1b**) with NiCl(PPh$_3$)IPr

We next turned our attention to the molecular structure of the obtained polymer. Linear polymerization could proceed in two alternative manners either α-α conjugation leading to **A** of Figure 2 or α-β conjugation to afford **B**. According to the UV-vis spectrum of (**3T**-Br)$_n$ exhibiting a λ_{max} of 432 nm, the structure of (**3T**-Br)$_n$ is most likely to involve linear α-α conjugation **A**. We thus prepared the two monochlorinated **3T**s **2** and **3**, and these chlorothiophenes were polymerized. The reaction of **2** proceeded similarly to that of **3T**-Cl$_2$ (**1b**) with deprotonation by the Knochel-Hauser base and following treatment with Ni-NHC catalyst (1 mol %)[16] afforded α-α conjugated polymer **A'** (65% yield; M_n = 22600; PDI = 1.75). The regioisomer chloride **3** also reacted under similar conditions, although with a reduced polymerization efficiency (48% yield; M_n = 11000; PDI = 1.09) suggesting that catalyst transfer through unlikely bond alternation toward α-β conjugation took place less smoothly. The regioisomers **A'** and **B'** were then treated with NBS to afford the brominated polymers **A** and **B**, respectively, whose ^{1}H NMR spectra are shown in Fig. 3 (b) and (a). Comparing these NMR spectra with that of (**3T**-Br)$_n$ reveals that the spectrum of brominated polymer **A** from α-α conjugated polymer **A'** is almost identical to that of (**3T**-Br)$_n$ and that signals assigned as α-β conjugation of **B** are observed at an intensity of less than 1:20. The M_n value of the linear polymer **A** from **A'** as estimated by SEC also showed reasonable correspondence with that based on viscosity measurement, which was interpolated from the calculated slope of (**3T**-Br)$_n$ (α = 0.88).[8b] These results further support the hypothesis that polymerization of **1a** would be linear because of preferential selective α-α conjugation via nickel-catalyzed cross coupling.

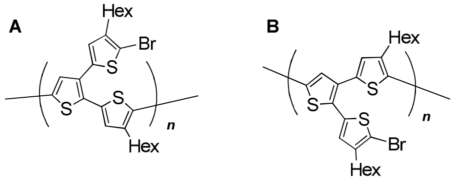
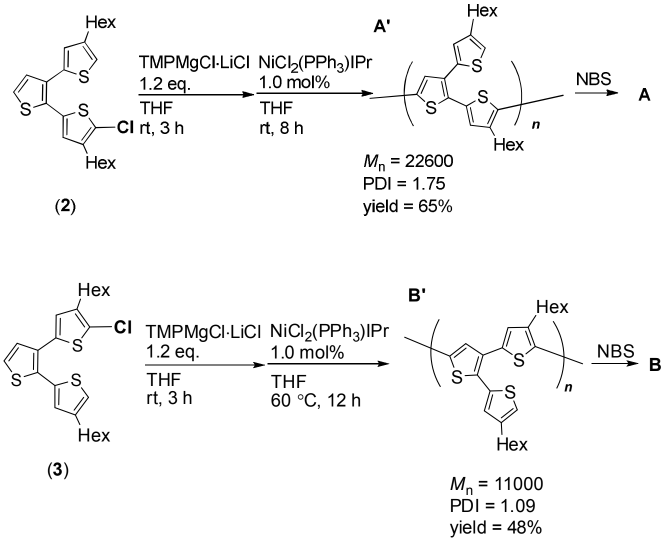


Fig. 2 α-α and α-β conjugated polymer



Scheme 3 Polymerization of monochlorinated **3T 2** and **3** with NiCl$_2$(PPh$_3$)IPr

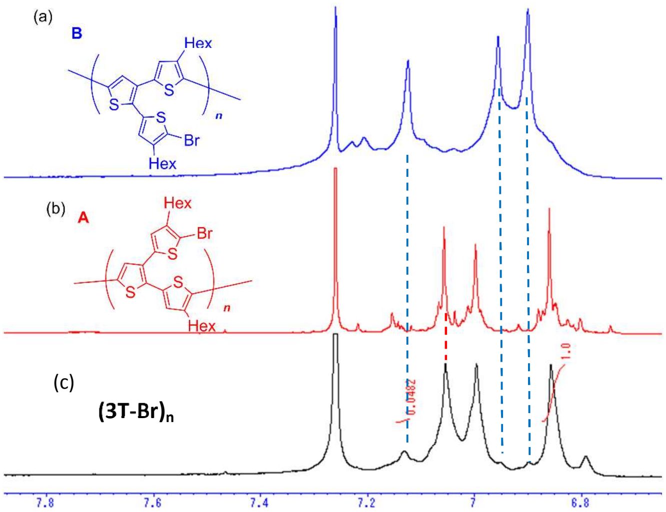
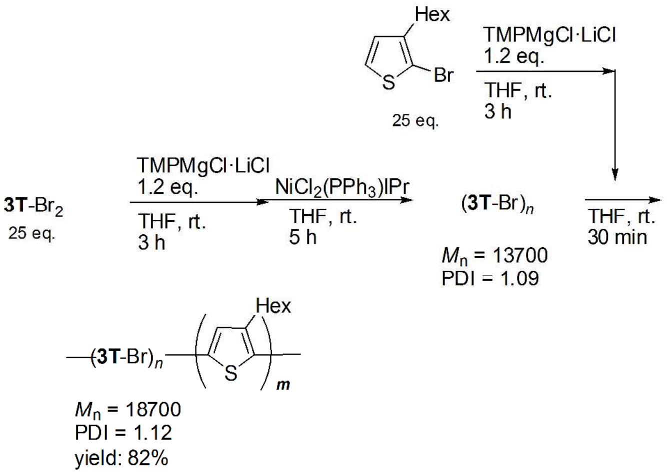


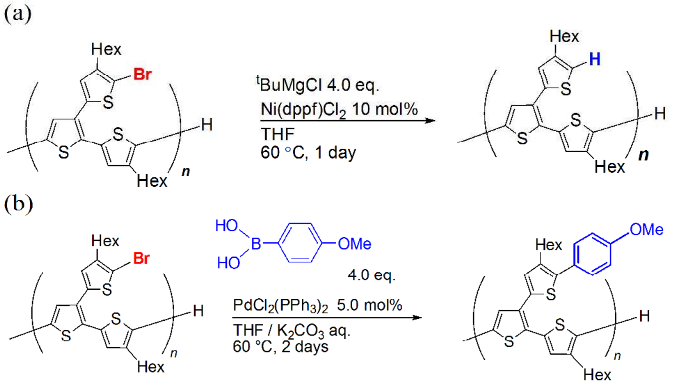
Fig. 3 ^{1}H NMR spectra of polymer **A** and **B** and the reduction product from (**3T**-Br)$_n$

We next performed copolymerization of **3T**-Br$_2$ with 2-bromo-3-hexylthiophene. After the polymerization of **3T**-Br$_2$ (25 equiv relative to Ni catalyst) with TMPMgCl·LiCl and NiCl$_2$(PPh$_3$)IPr at room temperature for 2 h (M_n = 13700; PDI = 1.09; M_{theor} = 12300), metalated thiophene (25 equiv), which was also formed in situ by the reaction of 2-bromo-3-hexylthiophene and TMPMgCl·LiCl, was added to the initial polymerization mixture. Further stirring of the reaction mixture afforded block copolymer. SEC profile clearly showed a shift of the peak of the initial polymer toward a higher molecular weight (M_n = 18700; PDI = 1.12; M_{theor} = 16500).



Scheme 4 Synthesis of block copolymer

Since the obtained linear polymer bears a bromo group at each side chain, functionalization of the carbon-bromine bonds was examined. Reductive transformation of (**3T**-Br)$_n$ proceeded with *t*BuMgCl as a reducing agent in the presence of NiCl$_2$dppf as a catalyst.[17] Treatment of the polymer in THF under reflux for 1 day formed the debrominated product as shown in Scheme 5(a). MALDI-TOF MS clearly identified the repeating unit of **3T**-H (416.7 Da), as shown in Fig. 4(a). Transformation of the carbon-bromine bond of (**3T**-Br)$_n$ was also carried out with arylboronic acid 4-MeOC$_6$H$_4$B(OH)$_2$ in the presence of palladium catalyst PdCl$_2$(PPh$_3$)$_2$ (Scheme 5b).[18] Reaction at 60 °C for 2 days resulted in complete conversion to the arylated polymer and measurement by MALDI-TOF-MS showed reasonable agreement with the repeating arylterthiophene. (Fig. 4b)



Scheme 5 (a) Reductive transformation of (**3T**-Br)$_n$ with *t*BuMgCl; (b) arylation by Suzuki-Miyaura coupling

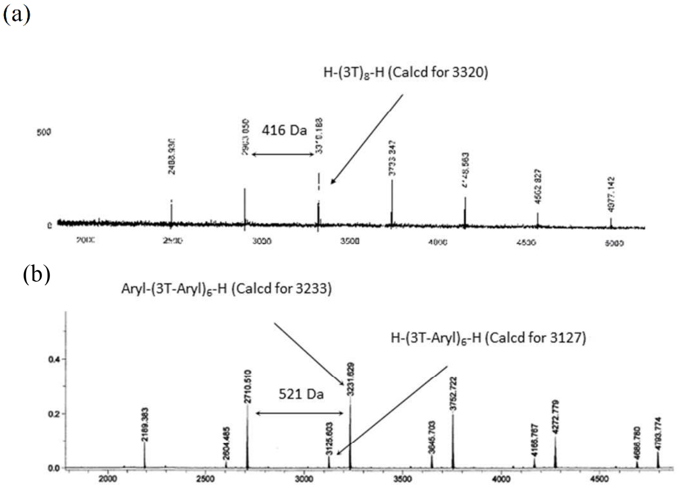
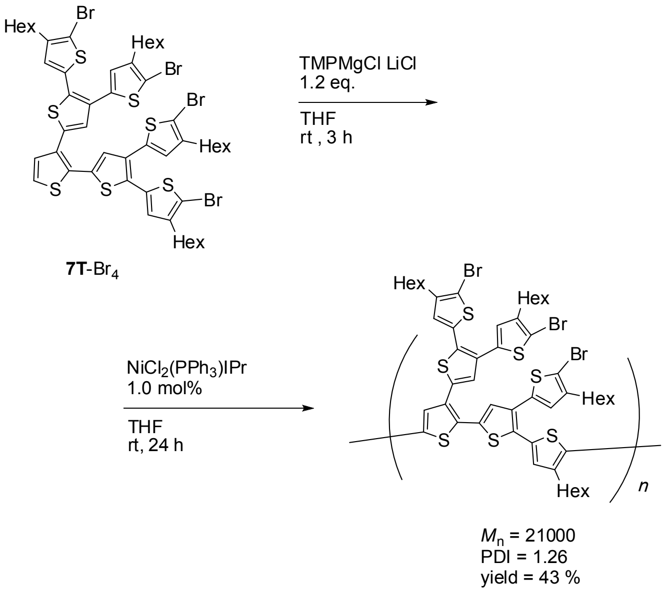


Figure 4 MALDI-TOF mass spectra of (a) debrominated; and (b) arylated polymers

Polymerization of an oligothiophene dendrimer composed of seven thiophene units with four bromo groups at the 2-position was also carried out under similar conditions.[7] When the reaction was performed with 1 mol % nickel catalyst, (**7T**-Br$_3$)$_n$ was obtained in a slightly lower yield (43%) because of difficulties in effective deprotonation with TMPMgCl. The produced polymer had M_n and PDI of 21000 and 1.75 (M_{theor} = 52000), respectively, as shown in Scheme 6.



Scheme 6 Polymerization of **7T**-Br$_4$

Conclusions

We have shown that oligothiophene dendrimers bearing multiple carbon-bromine bonds suitable for use as monomers in cross-coupling polymerization. It was revealed that the monomer underwent selective linear polymerization, which was confirmed by MALDI-TOF MS analysis, while hyperbranched polythiophene was not obtained despite the presence of two polymerizable bromine functionalities. The molecular weight of the product polymer was controllable by adjusting the ratio of monomer feed/catalyst loading suggesting that catalyst-transfer-type cross-coupling polycondensation^2 took place. Because the produced polymer bears carbon-bromine bond in its side chains, further functionalizations through reduction and palladium-catalyzed arylation by transition metal catalysis were demonstrated. Poly(oligothiophene dendrimer) formed by linear polymerization is a novel class of structure with extended π-conjugation; thus, we anticipate its application towards new materials.

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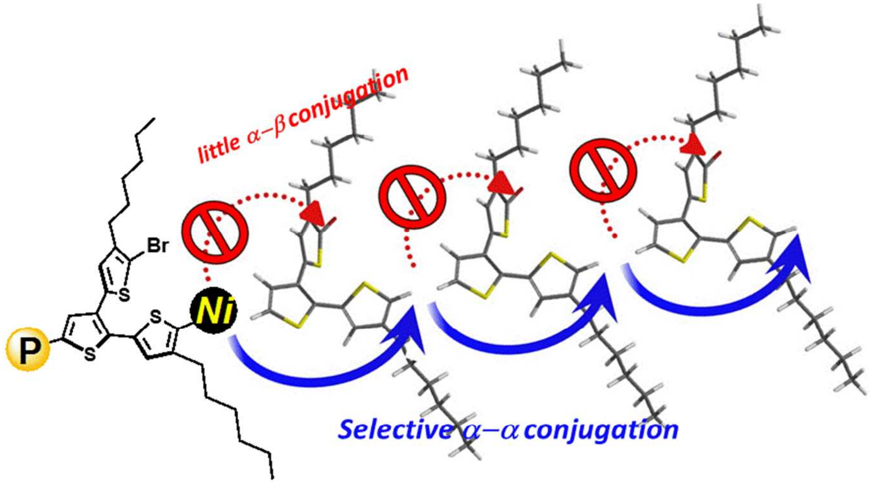
little α−β conjugation
Br
S
S
S
P
Ni
Selective α−α conjugation