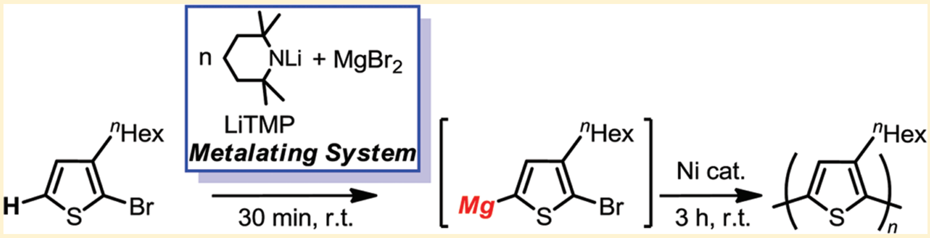
ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

Studies on the Generation of Metalating Species Equivalent to the Knochel–Hauser Base in the Dehydrobrominative Polymerization of Thiophene Derivatives

Shunsuke Tamba, Shinobu Mitsuda, Fujimaru Tanaka, Atsushi Sugie, and Atsunori Mori*

Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan

S Supporting Information

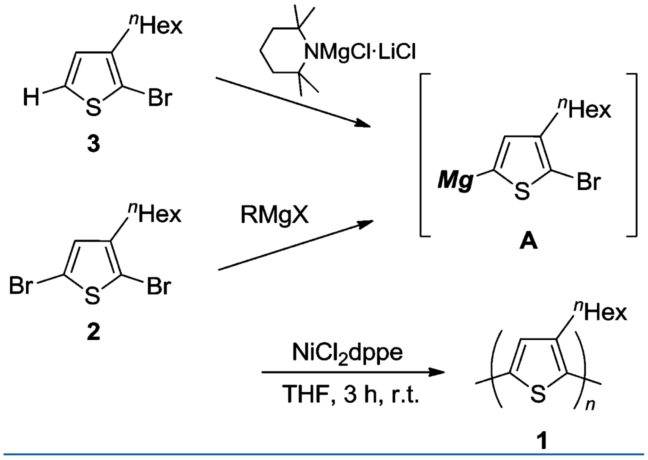


ABSTRACT: Dehydrobrominative polycondensation of 2-bromo-3-hexylthiophene proceeded with TMPMgBr·LiBr and $(TMP)_2Mg\cdot 2LiBr$, formed by LiTMP and $MgBr_2$, which was found to serve as a surrogate of the Knochel–Hauser base TMPMgCl·LiCl, and head-to-tail-type regioregular poly(3-hexylthiophene) was obtained with high efficiency. The regioregular poly(3-hexylthiophene) was also found to be obtained by one-shot addition of 2-bromo-3-hexylthiophene as a monomer, magnesium amide, and a nickel catalyst, suggesting that complete formation of metalated thiophene species is not an essential requisite for the successful polymerization with a nickel catalyst. This method was employed for the preparation of tolyl-terminated polythiophene by an aryl group with narrow molecular weight distribution using (*o*-tolyl)NiCldppp as a catalyst.

INTRODUCTION

Polythiophenes have attracted much attention in materials science. In particular, polythiophenes that are controlled as head-to-tail-type (HT) regioregularity form a highly planar structure with extended π conjugation and show remarkable physical properties as materials such as organic TFT,[1] thin-film organic solar cells,[2] and conductive polymer materials.[3] Head-to-tail-type poly(3-hexylthiophene) (**1**; HT-P3HT) has been generally synthesized by dehalogenative ($-X_2$) polycondensation from 2,5-dibromo-3-hexylthiophene (**2**), which was developed by Rieke,[4] McCullough,[5] and Yokozawa,[6] with a Grignard reagent in the presence of a nickel or palladium catalyst.[7] On the other hand, dehydrobrominative (−HBr) polycondensation, which employs 2-bromo-3-hexylthiophene (**3**) as a monomer precursor, is also a powerful method and shows advantages in terms of atom efficiency. McCullough reported generation of metalated thiophene monomer using deprotonation with lithium diisopropylamide (LDA) following metal exchange with $ZnCl_2$, which was the first report to synthesize HT-P3HT (**1**) with 2-bromo-3-hexylthiophene with a nickel catalyst.[8] Recently, Takita, Ozawa, and their co-workers developed the palladium-catalyzed polymerization of **3** leading to HT-P3HT by utilizing a palladium-catalyzed C–H arylation reaction.[9] However, these polymerization reactions required low temperature for lithiation and the following metal exchange to zinc or extremely high temperature was necessary for the polymerization by palladium catalysis. We have also reported that C–H functionalization polycondensation takes place with **3** and related compounds under mild conditions using the Knochel–Hauser base, chloromagnesium 2,2,6,6-tetramethylpiperidide lithium salt (TMPMgCl·LiCl) to generate the metalated species **A**. as shown in Scheme 1. and polymerization took place in the presence of a nickel(II) catalyst to afford highly regioregular poly-3-substituted thiophenes with high efficiency.[10] During the course of our studies on the development of efficient

Scheme 1



Received: December 5, 2011
Published: March 12, 2012

polymerization processes, our interest has been focused on the development of a new class of metalating species that is equivalent to Knochel–Hauser base[11] (magnesium amide) at the C–H bond of thiophene. We herein describe that several metalating reagents and the metalating protocols are found to be equally effective for polythiophene synthesis.[12]

■ RESULTS AND DISCUSSION

We first examined the use of lithium 2,2,6,6-tetramethylpiperidide (LiTMP) and magnesium bromide, which would form TMPMgBr·LiBr, as shown in Scheme 2.[13] Table 1 summarizes the results. The reaction of TMPH with *n*-butyllithium at 0 °C in anhydrous THF and then addition of magnesium bromide, which was formed in situ by the reaction of Mg and 1,2-dibromoethane in diethyl ether, was performed and the reaction mixture thus obtained was subjected to the polymerization of 2-bromo-3-hexylthiophene (**3**) in the presence of 1.0 mol % of $NiCl_2dppe$. The polymerization reaction took place similarly to the case of that with Knochel–Hauser base to afford the corresponding polymer **1** in 52% yield (M_n = 14 000, M_w/M_n = 1.49) (entry 1). The result suggests that magnesium amide generated by lithium amide and a magnesium salt also forms metalating species and is equally as effective as the Knochel–Hauser base. We next examined the polymerization performance of $Mg(TMP)_2$,[14] which was generated by the reaction of 2 equiv of LiTMP and $MgBr_2·Et_2O$. The obtained species also underwent polymerization to afford the polymer **1** in excellent yield and reasonable molecular weight with relatively narrow molecular weight distribution (entry 2). It was also found that **1** was obtained in 93% yield when 2 equiv of monomer **3** was employed toward $Mg(TMP)_2$, suggesting that both amides on the magnesium atom were utilized for the metalation of **3** (entry 3). The use of 0.5 equiv of the magnesium ate complex $[(TMP)_3Mg]Li$,[15] which was generated by the reaction of 3LiTMP and $MgBr_2·Et_2O$, toward **3** was found to give the polymer **1** in 72% yield (M_n = 13 500, M_w/M_n = 1.72) (entry 4). On the other hand, polymerization with equimolar amounts of $[(TMP)_3Mg]Li$ and **3** resulted in no polymerization under similar conditions (entry 5). The result can be explained by the fact that the organometallic species thought to be formed as $[Thienyl–Mg(TMP)_2]Li$, which was confirmed by the reaction with iodine leading to the corresponding iodothiophene in 94% yield, involves difficulties in further transmetalation to nickel due to the steric effect of two hindered TMP groups. Polymerization of **3** with 0.33 equiv of $[(TMP)_3Mg]Li$ through $[(Thienyl)_3Mg]Li$ with $NiCl_2dppe$ as a catalyst afforded P3HT (**1**) in only 19% yield; in contrast, the palladium-catalyzed cross-coupling of $[(Thienyl)_3Mg]Li$ with an aryl halide was reported to take place (entry 6).[15c] The reaction with the metalating system of zinc in place of magnesium using 1:1 LiTMP and $ZnEt_2$, by which $[TMPZnEt_2]Li$ would be formed, also resulted in no reaction (entry 7). Although polymerization with an ate complex of zinc has been unsuccessful,[16] metalation of 2-bromo-3-hexylthiophene (**3**) was also found to take place. Treatment of the metalated species $[TMPZnEt_2]Li$ with iodine at room temperature for 30 min in THF afforded the corresponding iodide 2-bromo-3-hexyl-5-iodothiophene in 98% yield.

Scheme 2

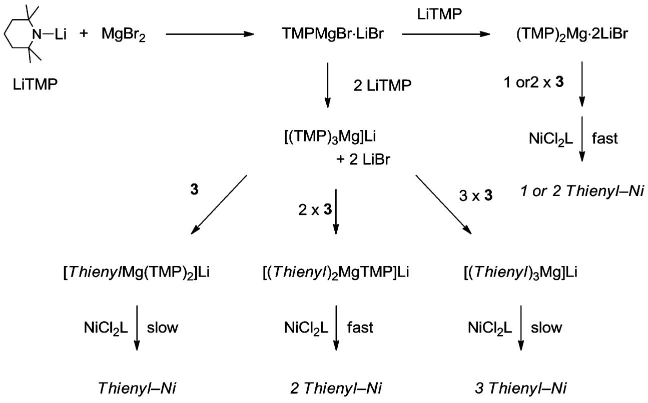
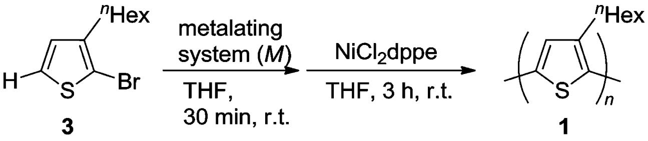


Table 1. Polymerization of 2-Bromo-3-hexylthiophene (3) with Various Metalating Reagents[a]

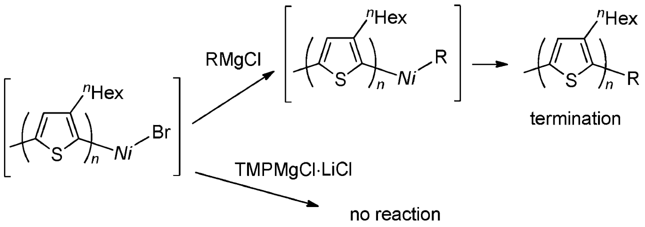


entry	metalating system (M)	3/M (mol/mol)	yield[b] (%)	M_n[c]	M_w/M_n[c]
1	TMPLi + $MgBr_2$	1.0	52	14 000	1.49
2	2TMPLi + $MgBr_2$	1.0	>99	19 000	1.69
3	2TMPLi + $MgBr_2$	2.0	93	12 100	1.64
4	3TMPLi + $MgBr_2$	2.0	72	13 500	1.72
5	3TMPLi + $MgBr_2$	1.0	0		
6	3TMPLi + $MgBr_2$	3.0	19	4 600	1.34
7	TMPLi + $ZnEt_2$	1.0	0		

[a]The reaction was carried out with **3** and metalating reagent in THF for the metalation, and 1.0 mol % of nickel catalyst was employed for the polycondensation. [b]Isolated yield. [c]M_n and M_w/M_n values were estimated by SEC analysis using $CHCl_3$ as an eluent.

Concerning the metalated species of 3-substituted thiophenes, it is also intriguing to know if a one-shot procedure, in which the addition of necessary substrate, reagents, and the catalyst is carried out simultaneously, can be achieved. However, it is well-known that complete consumption of the alkyl Grignard reagent RMgX leading to the metalated thiophene is necessary prior to polymerization with a nickel catalyst in the debrominative polycondensation of 2,5-dibromo-3-substituted thiophene **2**. Otherwise, the remaining RMgX serves as a terminating agent of the propagating Ni–Br polymer end to afford the alkylated polymer end via formation of the Ni–alkyl bond and thus induces immediate reductive elimination[5e,6b] (Scheme 3).

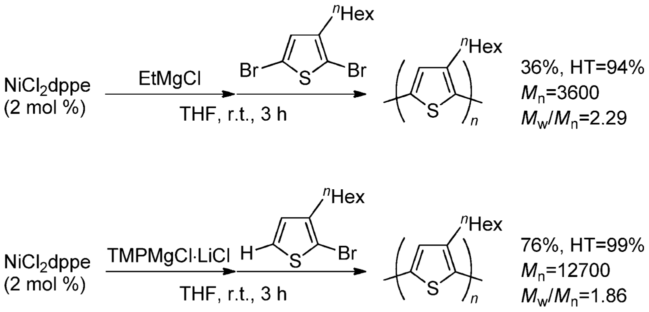
Scheme 3



Accordingly, synthesis of HT-P3HT by the established GRIM (Grignard metathesis) method with **2** has been generally carried out by **2** and RMgX to give **A** of Scheme 1 and the following addition of a nickel catalyst. It has also been necessary to form the similar intermediate **A** in the deprotonation of 2-bromo-3-hexylthiophene (**3**) with a lithium amide such as LDA prior to metal exchange with a zinc salt.[17] On the other hand, complete deprotonation with magnesium amide prior to nickel-catalyzed polymerization may not be required, since the magnesium amide $R_2NMgX(\cdot LiCl)$ is potentially inert to thienyl−Ni−X species, which is the propagating end of the polymer.

When the polymerization by GRIM was carried out by the addition of 2,5-dibromo-3-hexylthiophene (**2**) to a mixture of an equimolar amount of ethyl magnesium chloride and 2.0 mol % of $NiCl_2dppe$, only 36% of P3HT (**1**) was obtained with a much lower M_n of 3600 (M_w/M_n = 2.29), suggesting termination by the remaining Grignard reagent.[18] The result is in sharp contrast to the one-shot polymerization with the nickel catalyst, TMPMgCl·LiCl, and 2-bromo-3-hexylthiophene (**3**), which brought about excellent conversion at room temperature within 3 h, affording the polymer **1** with M_n = 12 700 (M_w/M_n = 1.86) (Scheme 4).

Scheme 4



We also examined the one-shot polymerization reaction of the monomer **3**, which was carried out by the addition of a magnesium amide species to the mixture of **3** and a nickel catalyst. As summarized in Table 2, the polymerization of 2-bromo-3-hexylthiophene (**3**) was carried out with an equimolar amount of Knochel−Hauser base at 25 °C for 3 h in the presence of 2.0 mol % of $NiCl_2dppp$. The corresponding HT-P3HT was obtained in 90% yield with M_n = 10 500 (M_w/M_n = 1.84) and an HT selectivity of 98% (entry 1). The use of $NiCl_2dppe$ as a catalyst improved M_w/M_n to 1.54. However, the molecular weight of the polymer was slightly lower (M_n = 5400, entry 2). The reaction with NiCl(*o*-tolyl)dppp, which was generated by $NiCl(o\text{-tolyl})(PPh_3)_2$ and DPPP in situ, resulted to afford the tolyl-terminated P3HT in 70% yield with M_n = 9500 and the remarkably narrow M_w/M_n = 1.14[19] (entry 3). It was also found that the addition of the related base prepared with LiTMP and $MgBr_2$ to a mixture of **3** and NiCl(*o*-tolyl)dppp similarly afforded HT-P3HT (entry 4). Figure 1 shows the ^1H NMR spectrum of the tolyl-terminated polymer using TMPMgCl·LiCl as a base, in which the methyl group derived from the terminal tolyl group was clearly observed. The average degree of polymerization was estimated to be ca. 59 (M_n = 9900) by the calculation of the integration ratio of the methyl (tolyl) and the methylene (thiophene side chain) protons.

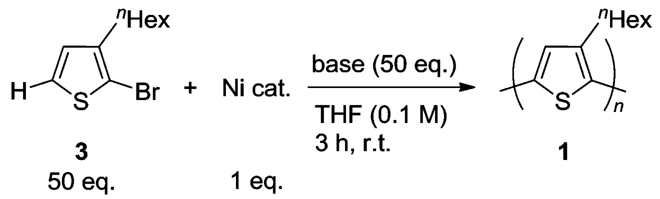
■ CONCLUSION

In conclusion, we have successfully generated a thienyl metallic species, which is a precursor of the corresponding regioregular polythiophene, by the reaction of LiTMP and $MgBr_2$. The presumably formed metalating agent TMPMgBr·LiBr exhibited reactivity similar to that of the Knochel−Hauser base (TMPMgCl·LiCl) for the proton abstraction at the C−H bond of thiophene derivatives, and the thienyl metal species thus obtained underwent polymerization. Another metalating species, $(TMP)_2Mg$, was also found to be available for the metalation and further polymerization. These metalating agents can be generated by the common chemicals BuLi, secondary amine, and $MgBr_2$ (Mg and $(CH_2Br)_2$), suggesting a facile preparation method for regioregular polythiophene. It is also remarkable that magnesium amide does not serve as a poisoning agent for the dehydrobrominative polymerization of thiophene, which is in marked contrast with the fact that the remaining alkyl Grignard reagent induces undesired termination of GRIM polymerization (debrominative polythiophene synthesis); thus, complete conversion toward thienyl magnesium species is not necessary, allowing the polymerization procedure in a one-shot manner.

■ EXPERIMENTAL SECTION

General Methods. All the reactions were carried out under a nitrogen atmosphere. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured on a Varian Gemini 300 instrument as $CDCl_3$ solutions. The chemical shifts were expressed in ppm with $CHCl_3$ (7.26 ppm for ^1H) or $CDCl_3$ (77.0 ppm for ^{13}C) as internal standards. SEC (size exclusion chromatography) analyses were performed with a standard HPLC system equipped with a UV detector using $CHCl_3$ as eluent with a Tosoh TSKgel GMH_{HR}-M. Molecular weights and molecular weight distributions were estimated on the basis of the calibration curve obtained by six polystyrene standards (M_n = 2630−355 000). TMPMgCl·LiCl was prepared by following the literature procedure[20] and stored in the freezer as a 1.0 M THF solution.

Table 2. One-Shot Polymerization with Knochel−Hauser Base[a]



entry	Ni cat.	base	yield[b] (%)	M_n,[c] M_w/M_n[c]	HT[d] (%)
1	$NiCl_2dppp$	TMPMgCl·LiCl	90	10 500, 1.84	98
2	$NiCl_2dppe$	TMPMgCl·LiCl	87	5 400, 1.58	96
3	$NiCl(o\text{-tolyl})(PPh_3)_2$ + DPPP	TMPMgCl·LiCl	70	9 500, 1.14	99
4	$NiCl(o\text{-tolyl})(PPh_3)_2$ + DPPP	2LiTMP+ $MgBr_2$	81	15 000, 1.33	99

[a]The reaction was carried out with 1.0 mmol of **3**, 1.0 equiv of metalating reagent, and 2.0 mol % of nickel catalyst in 10 mL of THF at room temperature for 3 h. [b]Isolated yield. [c]M_n and M_w/M_n values were estimated by SEC analysis using $CHCl_3$ as an eluent. [d]HT selectivity was estimated by ^1H NMR analysis.

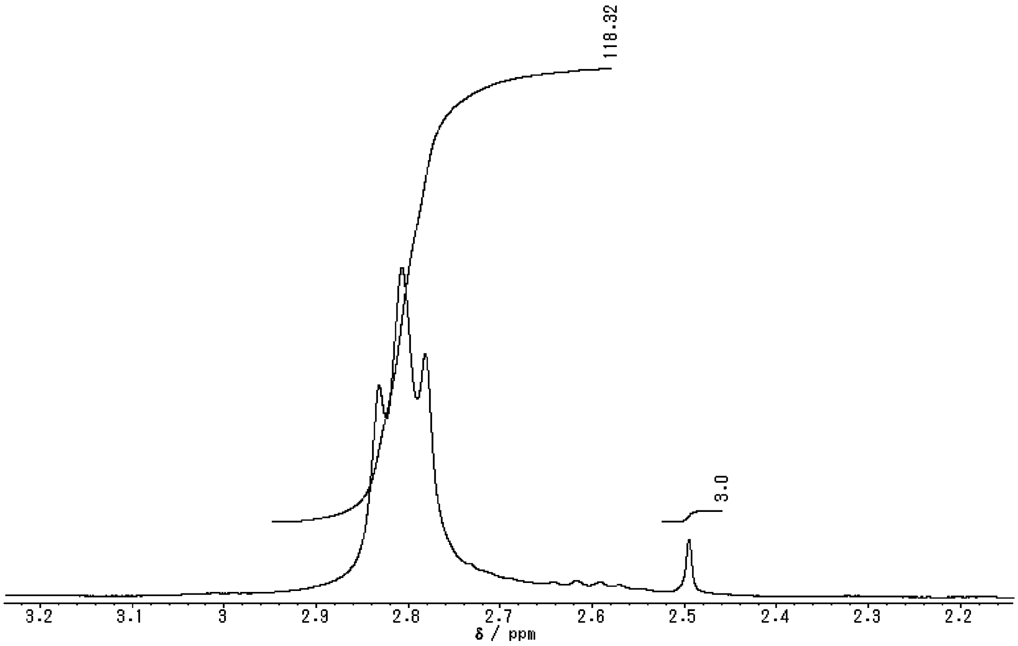


Figure 1. ^{1}H NMR spectrum of tolyl-terminated P3HT using TMPMgCl·LiCl as a base (Table 2, entry 3), with protons of Thienyl−CH_2−C_5H_{11} (left) and CH_3−C_6H_4− (right) being shown.

$NiCl_2dppe$[21] and NiCl(*o*-tolyl)$(PPh_3)_2$[19a] were prepared according to the literature procedures. $MgBr_2·Et_2O$[22] and $[ZnEt_2(TMP)]Li$[16b] were prepared according to the literature procedures. Other materials were purchased and used without further purification.

Polymerization of 2-Bromo-3-hexylthiophene with LiTMP/$MgBr_2$ in the Presence of $NiCl_2dppe$. ^{n}BuLi in hexane (1.65 M, 0.6 mL, 1.0 mmol) was added dropwise to a solution of TMPH (200 μL, 1.2 mmol) in THF (1 mL) at −78 °C, and the reaction mixture was stirred at 0 °C for 0.5 h. $MgBr_2·Et_2O$ (0.5 mmol) was added in several portions to the solution of the formed LiTMP at 0 °C over 10 min. Then the reaction mixture was stirred at 0 °C for 2 h to produce a solution of $(TMP)_2Mg$ in THF. Subsequently, 2-bromo-3-hexylthiophene (**3**; 200 μL, 1.0 mmol) was added dropwise to the solution of the formed $(TMP)_2Mg$ at room temperature. After the mixture was stirred at 25 °C for 0.5 h, THF (8 mL) and $NiCl_2dppe$ (5.2 mg, 0.01 mmol) were successively added. The resulting mixture was stirred at 25 °C for 3 h. Hydrochloric acid (1.0 M, 20 mL) and methanol (50 mL) were added to form a precipitate. The mixture was filtered, and the residue was washed with methanol repeatedly to leave a dark purple solid, which was dried under reduced pressure to afford 156 mg of poly(3-hexylthiophene) (**1**; 93%, M_n = 12 100, M_w/M_n = 1.64). The regioregularity was estimated by ^{1}H NMR analysis (thienyl-CH_2 signals) at the δ 2.80 (H-T) and δ 2.60 (H−H) signals (H-T regioregularity 98%). ^{1}H NMR (300 MHz): δ 0.92 (t, *J* = 6.6 Hz, 3H), 1.20−1.52 (m, 6H), 1.60−1.80 (m, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 6.98 (s, 1H). ^{13}C NMR (75 MHz): δ 14.1, 22.7, 29.3, 29.5, 30.5, 31.7, 128.6, 130.5, 133.7, 139.9.

General Procedure for the One-Shot Polymerization of 2-Bromo-3-hexylthiophene. In a 50 mL two-neck flask equipped with a magnetic stirring bar were added NiCl(*o*-tolyl)$(PPh_3)_2$ (14 mg, 0.02 mmol), 2-bromo-3-hexylthiophene (**3**; 200 μL, 1.0 mmol), DPPP (8 mg, 0.02 mmol), and anhydrous THF (9 mL). After the mixture was stirred at 25 °C for 5 min 1.0 M TMPMgCl·LiCl (1.0 mL, 1.0 mmol) was successively added in THF dropwise at room temperature. The resulting mixture was stirred at 25 °C for 3 h. Hydrochloric acid (1.0 M, 20 mL) and methanol (50 mL) were added to form a precipitate. The mixture was filtered, and the residue was washed with methanol repeatedly to leave a dark purple solid, which was dried under reduced pressure to afford 117 mg of poly(3-hexylthiophene) (**1**; 70%, M_n = 9500, M_w/M_n = 1.14, H-T regioregularity 99%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving NMR spectra of head-to-tail-type poly (3-hexylthiophene) and that of end-functionalized P3HT with a tolyl group. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: amori@kobe-u.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by KAKENHI (B) by the Japan Society for the Promotion of Science (JSPS). We thank Shuji Okamoto and Hikaru Meguro of Soken Chemical & Engineering Co., Ltd. for their kind donation of thiophene monomers.

■ REFERENCES

(1) (a) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741. (b) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, W. W.; Herwig, P.; deLeeuw, D. M. *Nature* **1999**, *401*, 685. (c) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C.-S.; Ree, M. *Nat. Mater.* **2006**, *5*, 197. (d) Woo, C. H.; Thompson, B. C.; Kim, B. J.; Toney, M. F.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2008**, *130*, 16324.

(2) (a) Roncali, J. *Chem. Rev.* **1997**, *97*, 173. (b) Günes, S.; Neugebauer, H.; Sarisiftci, N. S. *Chem. Rev.* **2007**, *107*, 1324. (c) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*, 5868.

(3) (a) Chen, F.; Mehta, P. G.; Takiff, L.; McCullough, R. D. *J. Mater. Chem.* **1996**, *6*, 1763. (b) Gangopadhyay, P.; Koeckelberghs, G.; Persoons, A. *Chem. Mater.* **2011**, *23*, 516. (c) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537. (d) Grimsdale, A. C.;

Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897.

(4) (a) Chen, T. A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087. (b) Chen, T.-A.; O'Brien, R. D.; Rieke, R. D. *Macromolecules* **1993**, *26*, 3462. (c) Chen, T. A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233. (d) Wu, X.; Chen, T.-A.; Rieke, R. D. *Macromolecules* **1996**, *29*, 7671.

(5) (a) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250. (b) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526. (c) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649. (d) Jeffries-El, M.; Sauvé, G.; McCullough, R. D. *Macromolecules* **2005**, *38*, 10346. (e) Stefan, M. C.; Javier, A. E.; Osaka, I.; McCullough, R. D. *Macromolecules* **2009**, *42*, 30.

(6) (a) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169. (b) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542. For a review, see: (c) Yokozawa, T.; Yokoyama, A. *Chem. Rev.* **2009**, *109*, 5595.

(7) For selected reviews, see: (a) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93. (b) Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202.

(8) (a) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, *1*, 70. (b) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904.

(9) (a) Wang, Q.; Takita, R.; Kikuzaki, T.; Ozawa, F. *J. Am. Chem. Soc.* **2010**, *132*, 11420. See also: (b) Hassan, J.; Shultz, E.; Gozzi, C.; Lemaire, M. *J. Mol. Catal. A: Chem.* **2003**, *195*, 125.

(10) (a) Tamba, S.; Tanaka, S.; Okubo, Y.; Okamoto, S.; Meguro, H.; Mori, A. *Chem. Lett.* **2011**, *40*, 398. (b) Tamba, S.; Shono, K.; Sugie, A.; Mori, A. *J. Am. Chem. Soc.* **2011**, *133*, 9700. (c) Tanaka, S.; Tamba, S.; Tanaka, D.; Sugie, A.; Mori, A. *J. Am. Chem. Soc.* **2011**, *133*, 16734. For a review, see: (d) Mori, A. *J. Synth. Org. Chem. Jpn.* **2011**, *69*, 1202.

(11) (a) Krasovskiy, A.; Krasovskaya, V.; Knochel, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 2958. (b) Lin, W.; Baron, O.; Knochel, P. *Org. Lett.* **2006**, *8*, 5673. (c) Clososki, G. C.; Rohbogner, C. J.; Knochel, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 7681. (d) Rohbogner, C. J.; Clososki, G. C.; Knochel, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 1503. (e) Stoll, A. H.; Knochel, P. *Org. Lett.* **2008**, *10*, 113. (f) Mosrin, M.; Knochel, P. *Org. Lett.* **2008**, *10*, 2497. (g) Piller, F. M.; Knochel, P. *Org. Lett.* **2009**, *11*, 445. (h) Hauser, C. R.; Walker, H. G. *J. Am. Chem. Soc.* **1947**, *69*, 295. (i) Frostick, F. C.; Hauser, C. R. *J. Am. Chem. Soc.* **1949**, *71*, 1350. (j) Eaton, P. E.; Lee, C.-H.; Xiong, Y. *J. Am. Chem. Soc.* **1989**, *111*, 8016.

(12) For selected reviews, see: (a) Haag, B.; Mosrin, M.; Ila, H.; Malakhov, V.; Knochel, P. *Angew. Chem., Int. Ed.* **2011**, *50*, 9794. (b) Mulvey, R. E. *Organometallics* **2006**, *25*, 1060. (c) Mulvey, R. E.; Mongin, F.; Uchiyama, M.; Kondo, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 3802.

(13) Garcalvarez, P.; Graham, D. V.; Hevia, E.; Kennedy, A. R.; Klett, J.; Mulvey, R. E.; O'Hara, C. T.; Weatherstone, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 8079.

(14) (a) Eaton, P. E.; Xiong, Y.; Gilardi, R. *J. Am. Chem. Soc.* **1993**, *115*, 10195. (b) Clososki, G. C.; Rohbogner, C. J.; Knochel, P. *Angew. Chem.* **2007**, *119*, 7825;(c) *Angew. Chem., Int. Ed.* **2007**, *46*, 7681.

(15) (a) Awad, H.; Mongin, F.; Trécourt, F.; Quéguiner, G.; Marsais, F.; Blanco, F.; Abarca, B.; Ballesteros, R. *Tetrahedron Lett.* **2004**, *45*, 6697. (b) Awad, H.; Mongin, F.; Trécourt, F.; Quéguiner, G.; Marsais, F. *Tetrahedron Lett.* **2004**, *45*, 7873. (c) Bayh, O.; Awad, H.; Mongin, F.; Hoarau, C.; Trécourt, F.; Quéguiner, G.; Marsais, F.; Blanco, F.; Abarca, B.; Ballesteros, R. *Tetrahedron* **2005**, *61*, 4779.

(16) (a) Uchiyama, M.; Matsumoto, Y.; Nobuto, D.; Furuyama, T.; Yamaguchi, K.; Morokuma, K. *J. Am. Chem. Soc.* **2006**, *128*, 8748−8750. (b) Kondo, Y.; Morey, J. M.; Morgan, J. C.; Naka, H.; Nobuto, D.; Raithby, P. R.; Uchiyama, M.; Wheatley, A. E. H. *J. Am. Chem. Soc.* **2007**, *129*, 12734. (c) L'Helgoual'ch, J.-M.; Seggio, A.; Chevallier, F.; Yonehara, M.; Jeanneau, E.; Uchiyama, M.; Mongin, F. *J. Org. Chem.* **2008**, *73*, 177. (d) Clegg, W.; Conway, B.; Hevia, E.; McCall, M. D.; Russo, L.; Mulvey, R. E. *J. Am. Chem. Soc.* **2009**, *131*, 2375.

(17) Lohwasser, R. H.; Thelakkat, M. *Macromolecules* **2011**, *44*, 3388.

(18) A lower H-T regioregularity (89%) was observed when ^{i}PrMgCl·LiCl was employed instead of EtMgCl (40% yield, M_n = 5200, M_w/M_n = 1.82). See also: (a) Wu, S.; Huang, L.; Tian, H.; Geng, Y.; Wang, F. *Macromolecules* **2011**, *44*, 7558. (b) Lamps, J.-P.; Catala, J.-M. *Macromolecules* **2011**, *44*, 7962.

(19) For selected examples of end-group functionalization, see: (a) Lanni, E. L.; McNeil, A. J. *Macromolecules* **2010**, *43*, 8039. (b) Bronstein, H. A.; Luscombe, C. K. *J. Am. Chem. Soc.* **2009**, *131*, 12894. (c) Smeets, A.; Willot, P.; Winter, J. D.; Gerbaux, P.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2011**, *44*, 6017. (d) Senkovskyy, V.; Sommer, M.; Tkachov, R.; Komber, H.; Huck, W. T. S.; Kiriy, A. *Macromolecules* **2010**, *43*, 10157. (e) Doubina, N.; Paniagua, S. A.; Soldatova, A. V.; Jen, A. K. Y.; Marder, S. R.; Luscombe, C. K. *Macromolecules* **2011**, *44*, 512. (f) Smeets, A.; Van den Bergh, K.; Winter, J. D.; Gerbaux, P.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2009**, *42*, 7638.

(20) Do, H.-Q.; Daugulis, O. *J. Am. Chem. Soc.* **2009**, *131*, 17052.

(21) Booth, G.; Chatt, J. *J. Chem. Soc.* **1965**, 3239.

(22) Black, T. H.; McDermott, T. S.; Brown, G. A. *Tetrahedron Lett.* **1991**, *32*, 6501.