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Palladium-Catalyzed Dehydrohalogenative Polycondensation of 2-Bromo-3-hexylthiophene: An Efficient Approach to Head-to-Tail Poly(3-hexylthiophene)

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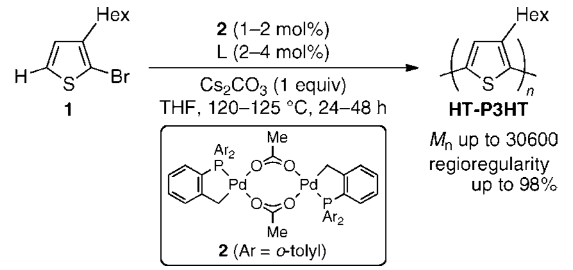
Abstract: Dehydrohalogenative polycondensation of 2-bromo-3-hexylthiophene was successful with Herrmann's catalyst and tris(2-dimethylaminophenyl)phosphine as catalyst precursors, giving head-to-tail poly(3-hexylthiophene) (HT-P3HT) with high molecular weight (M_n = 30 600, M_w/M_n = 1.60) and high regioregularity (98%) in almost quantitative yield (99%).

Poly(3-alkylthiophene)s (P3ATs) are among the most promising π-conjugated polymers for the development of flexible electronic devices such as organic field-effect transistors, organic light-emitting diodes, and solar cells.[1] It has been documented that their physical properties are strongly affected by the regioregularity of the thiophene units, and head-to-tail (HT) polymers are superior to head-to-head (HH) and regiorandom isomers in terms of characteristics including electrical conductivity, light-emitting ability, and field-effect mobility.[2] Such head-to-tail regioregular P3ATs (HT-P3ATs) were first synthesized in 1992 by polycondensation based on nickel-catalyzed cross-coupling reactions using organometallic reagents of magnesium and zinc,[3] and later the catalytic systems were remarkably improved to be capable of chain-growth polymerization leading to HT-P3ATs with extremely narrow molecular weight distributions.[4]

In synthetic organic chemistry, catalytic dehydrohalogenative coupling of heteroarenes with aryl halides (so-called direct arylation) has recently attracted a great deal of attention as an alternative to conventional cross-coupling reactions.[5] This new class of cross-coupling processes, which does not require prepreparation of organometallic reagents, should be of benefit to polymer synthesis with respect to reduced waste generation and fewer reaction steps. Pioneering work in this area was carried out by Lemaire and co-workers,[6] who attempted the dehydrohalogenative polycondensation of 2-halo-3-alkylthiophenes. While the product obtained was only an oligomer ($M_n \approx 3000$), the regioregularity was determined to be ~90%. Herein we disclose a highly efficient palladium catalyst that successfully converts 2-bromo-3-hexylthiophene (**1**) into head-to-tail regioregular poly(3-hexylthiophene) (HT-P3HT) with high molecular weight (M_n up to 30 600) and high regioregularity (up to 98%) (Scheme 1).

Polycondensation of **1** was examined in tetrahydrofuran (THF) in the presence of Cs_2CO_3 (1 equiv) and a palladium catalyst (1−2 mol %) generated in situ from a palladium source and a tertiary phosphine ligand (L). To ensure the solubility of P3HT during polymerization, THF was chosen as the solvent instead of *N*,*N*-dimethylformamide (DMF) or *N*,*N*-dimethylacetamide (DMA), which are the polar solvents generally used for palladium-catalyzed direct arylation. Cs_2CO_3 was selected as the base after a review of literature reports on direct arylation chemistry.[5] Reactions were performed in a gastight Schlenk tube in order to achieve reaction temperatures higher than the boiling point of THF.

Scheme 1



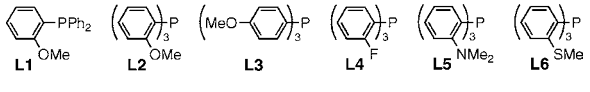
At the beginning of our investigations, $Pd(OAc)_2$, which is recognized as the most common catalyst precursor for direct arylation, was employed as a palladium source. We soon discovered, however, that this catalytic system was not stable enough for polymerization. Although the reaction formed P3HT with relatively high molecular weight ($M_n \approx 10\,000$) in the presence of an appropriate ligand (see below), the reaction was not reproducible and frequently provided low molecular weight products ($M_n < 3000$) along with deposition of palladium black. The catalyst decomposition took place even at 80 °C. Therefore, we next tested Herrmann's catalyst (**2**) as a palladium source. Complex **2**, which is derived from $Pd(OAc)_2$ and $P(o\text{-tolyl})_3$ under heated conditions, has been proven to be a good catalyst precursor with high thermal stability.[7]

Table 1 lists the representative results. All of the reactions except for entry 10 were carried out at 120 °C. The catalytic performance

Table 1. Effect of Supporting Ligand (L) on Polycondensation of **1** Using **2** as the Catalyst Precursor[a]

		HT-P3HT			
entry	L[b]	M_n[c]	M_w/M_n[c]	% HT[d]	yield (%)
1	$P(t\text{-Bu})_3$	1000	1.78	63	63
2	PCy_3	900	1.76	64	58
3	PPh_3	6200	2.53	77	53
4	**L1**	9900	2.16	89	99
5	**L2**	30300	2.42	93	99
6	**L3**	2400	2.04	68	99
7	$P(o\text{-tolyl})_3$	800	1.81	65	85
8	**L4**	1400	1.21	69	3
9	**L5**	24000	1.98	96	98
10[e]	**L5**	30600	1.60	98	99
11	**L6**	1000	1.33	72	47

[a] Reactions were run at 120 °C for 48 h in THF (1 mL) using **1** (1 mmol), **2** (2 mol %), L (4 mol %), and Cs_2CO_3 (1 mmol), unless otherwise noted. [b] The structures of **L1**−**L6** are shown below. [c] Estimated by GPC calibration based on polystyrene standards. [d] Estimated by ^1H NMR spectroscopy. [e] The reaction was run at 125 °C for 24 h in THF (1 mL) using **1** (2 mmol), **2** (1 mol %), **L5** (2 mol %), and Cs_2CO_3 (2 mmol).



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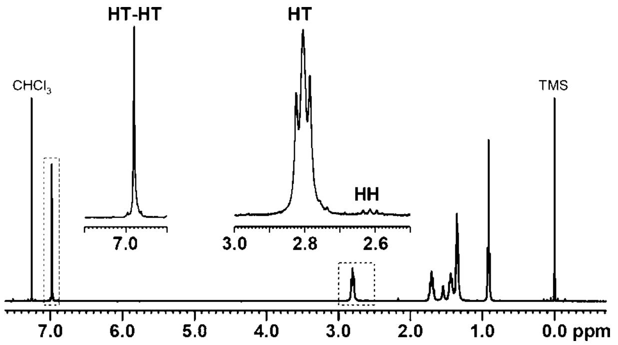


Figure 1. ^{1}H NMR spectrum of HT-P3HT with 98% regioregularity (400 MHz, CDCl$_3$, 20 °C).

was markedly dependent on the supporting ligand. Alkylphosphines such as P(*t*-Bu)$_3$ and PCy$_3$ were totally ineffective and caused rapid decomposition of the palladium catalyst (entries 1 and 2). The catalytic system using PPh$_3$ was fairly stable, and P3HT with moderate molecular weight was obtained (entry 3). The catalytic activity was remarkably improved by introduction of MeO substituents at the ortho positions of the phenyl groups (entries 4 and 5). Tris(*o*-anisyl)phosphine (**L2**) was particularly effective, affording HT-P3HT with M_n = 30 300 and 93% regioregularity (entry 5). Since **L3** with *p*-MeO groups and P(*o*-tolyl)$_3$ and **L4** having simple ortho substituents with donor (Me) and acceptor (F) properties, respectively, were ineffective (entries 6−8), it is likely that the coordinating ability of the *o*-MeO groups rather than steric or electronic effects contributes to the high ligand performance of **L2**. Actually, **L5** bearing *o*-Me$_2$N groups with higher coordinating ability led to further improvement in the regioregularity (96%, entry 9), while **L6** with *o*-MeS groups was ineffective (entry 11).

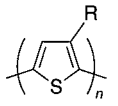
The polycondensation reaction using **2** and **L5** as catalyst precursors was affected to a considerable extent by reaction temperature, substrate concentration, and catalyst loading. The catalytic system exhibited reactivity above 110 °C, but catalyst decomposition was observed at 130 °C. Higher concentrations of substrate **1** provided higher molecular weights but eventually caused polymer deposition from the reaction solution. Lower catalyst loading tended to increase the molecular weight of the polymer but reduced the reaction rate. Taking the balance of these factors into consideration, we established the optimized reaction conditions given in entry 10 in Table 1. Heating a mixture of **1** (2 mmol), **2** (1 mol %), **L5** (2 mol %), and Cs$_2$CO$_3$ (2 mmol) in THF (1 mL) at 125 °C for 24 h led to the formation of HT-P3HT with M_n = 30 600 (M_w/M_n = 1.60) and 98% regioregularity.

Figure 1 shows the ^{1}H NMR spectrum of the resulting polymer. The regioregularity was estimated from peak integration of the α-methylene signals of the 3-hexyl groups at δ 2.81 (HT) and 2.61 (HH).[3c] In the aromatic region, a sharp singlet arising from the 4-position of the 3-hexylthiophene unit in the HT−HT linkage was observed at δ 6.98. On the other hand, signals assignable to other regioisomers [δ 7.00 (TT−HT), 7.03 (HT−HH), and 7.05 (TT−HH)] were negligible. Hence, the formation of highly regioregular HT-P3HT was evidenced.

An interesting feature emerging from the data in Table 1 is that the head-to-tail regioregularity improved with increasing molecular weight. In fact, P3HT (M_n = 1100) isolated from the reaction solution of entry 5 at an early stage (1 h) clearly showed lower regioregularity (74%) than the final product (93%). MALDI-TOF mass spectrometry analysis of this product revealed contamination with considerable amounts of the polymers with Br/Br and H/H termini (∼14 and 13%, respectively), in addition to the main product with expected H/Br termini. These observations suggest that the homocoupling reactions between C−H and C−H bonds and C−Br and C−Br bonds are operative to a considerable extent at the initial stage, while the cross-coupling reaction between C−Br and C−H bonds dominates the polycondensation at the later stage.

Although the reaction using **L5** showed a similar tendency, the regioregularity (85%) of the initial product after 1 h was higher than that observed for **L2** (74%). Thus, it has been found that **L5** more effectively restrains the homocoupling reactions at the early stage, thereby leading to the higher regioregularity of the final product. The higher ligand performance of **L5** should be caused by its better bidentate coordinating ability relative to **L2**. The fact that the polymerization did not proceed with diphosphine ligands such as dppe and dppp suggests that **L5** may serve as a part-time bidentate ligand that can cope with the various coordination numbers and oxidation states of palladium intermediates.

In conclusion, we have succeeded in developing a highly efficient catalyst for dehydrohalogenative polycondensation of 2-bromo-3-hexylthiophene (**1**) to afford HT-P3HT with high molecular weight and high regioregularity. The key to the high catalytic performance is the use of Herrmann's catalyst (**2**) and ligand **L5** with *o*-Me$_2$N substituents as catalyst precursors. This catalytic system is also effective for other 2-bromo-3-alkylthiophenes, as illustrated below. Details about the substrate scope and catalytic mechanism will be reported in due course.



R = 7-oxaoctyl (98% yield) — M_n = 14600, M_w/M_n = 2.04, H-T regioregularity = 98%

R = 2,5-dioxahexyl (98% yield) — M_n = 11200, M_w/M_n = 2.60, H-T regioregularity > 98%

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Supporting Information Available: Experimental procedures and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Roncali, J. *Chem. Rev.* **1997**, *97*, 173. (b) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93. (c) Arias, A. C.; MacKenzie, J. D.; McCulloch, I.; Rivnay, J.; Salleo, A. *Chem. Rev.* **2010**, *110*, 3. (d) Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281. (e) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897. (f) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*, 5868.

(2) (a) 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. (b) Woo, C. H.; Thompson, B. C.; Kim, B. J.; Toney, M. F.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2008**, *130*, 16324.

(3) (a) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70. (b) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087. (c) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233. (d) Yamamoto, T.; Koizumi, T. *Polymer* **2007**, *48*, 5449.

(4) (a) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169. (b) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526. (c) Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202. (d) Yokozawa, T.; Yokoyama, A. *Chem. Rev.* **2009**, *109*, 5595.

(5) (a) Satoh, T.; Miura, M. *Chem. Lett.* **2007**, *36*, 200. (b) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (c) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792. (d) Bellina, F.; Rossi, R. *Tetrahedron* **2009**, *65*, 10269.

(6) (a) Sévignon, M.; Papillon, J.; Schulz, E.; Lemaire, M. *Tetrahedron Lett.* **1999**, *40*, 5873. (b) Hassan, J.; Schulz, E.; Gozzi, C.; Lemaire, M. *J. Mol. Catal. A: Chem.* **2003**, *195*, 125.

(7) Herrmann, W. A.; Brossmer, C.; Reisinger, C.-P.; Riermeier, T. H.; Öfele, K.; Beller, M. *Chem.*−*Eur. J.* **1997**, *3*, 1357.

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