Purification-Free and Protection-Free Synthesis of Regioregular Poly(3-hexylthiophene) and Poly(3-(6-hydroxyhexyl)thiophene) Using a Zincate Complex of $^{t}Bu_4ZnLi_2$

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Ⓢ *Supporting Information*

ABSTRACT: The controlled synthesis of head-to-tail regioregular poly(3-hexylthiophene) (P3HT) using a dianion-type zincate complex, $^{t}Bu_4ZnLi_2$, is described. The molecular weights of P3HTs could be increased up to 30 kDa by increasing the feed ratio of the monomer to Ni catalyst while maintaining a low polydispersity (PDI < 1.2) and a high regioregularity (>97%, when M_n > 10 kDa). Surprisingly, this new system can be used in as-received THF as well as in THF containing protic impurities, such as isopropanol, methanol, and even 1000 ppm water. In addition, the direct synthesis of poly[3-(6-hydroxyhexyl)thiophene] (P3HHT) could be performed without protection based on the developed system.
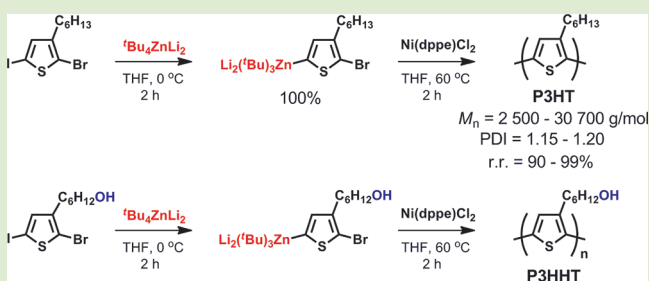
There has been growing attention paid to poly(3-alkylthiophene)s (PATs) in the field of polymer electronic devices, such as organic field-effect transistors[1] and organic photovoltaic cells,[2] because PATs are the best class of balanced high-performance materials used as *p*-type semiconductors in terms of solubility, chemical stability, charge mobility, and commercial availability. The synthetic method for regioregular PATs, first discovered by McCullough et al.,[3,4] followed by Rieke,[5] affords the formation of defect-free head-to-tail PATs, based on nickel-catalyzed cross-coupling reactions using Grignard thiophene monomers or Rieke zinc, respectively. The development of the Grignard metathesis (GRIM) polymerization system starting from 2,5-dihalo-substituted thiophene monomers then allowed the media to be at room or reflux temperature, which was preferable for the low-cost and large scale synthesis of PATs.[6,7]

A further breakthrough with the GRIM polymerization system was undoubtedly the discovery of the "living" nature of the system to afford PATs, as independently reported by McCullough et al.[8] and Yokozawa et al.[9] Practically, the polycondensation of the Grignard thiophene monomer, 2-bromo-5-chloromagnesio-3-hexylthiophene, with 1,3-bis(diphenylphosphino)propanenickel dichloride (Ni(dppp)Cl₂) as a catalyst proceeded via a chain-growth polymerization mechanism to yield PATs with controlled molecular weights (MWs) and low PDIs. This chain-growth polymerization is based on the specific reactivity of an intermediate Ni species, which is transferred only to the elongated polymer propagating end without diffusion after the cross-coupling reactions, as described by Yokozawa.[9] McCullough proposed another mechanism of the intermediate associated pair of Ni(0) species and Br/Br

terminated PATs.[8] However, thorough purification steps of the monomers and solvents are often necessary for the GRIM polymerization system, because highly reactive and moisture-sensitive Grignard agents are employed. In addition, many functional groups such as hydroxy, aldehyde, ketone, ester, amide, and so on, cannot generally be tolerated in the presence of the Grignard agents.

Uchiyama et al. reported the impressive results of the anionic polymerization of *N*-isopropylacrylamide in aqueous media using a newly designed bulky zincate complex of $^{t}Bu_4ZnLi_2$ with little basicity as a highly selective anionic initiator.[10] They also reported the protection-free halogen-metal exchange reaction of 4-iodobenzyl alcohol with $^{t}Bu_4ZnLi_2$.[11] By further reacting the generated zincate complex with allyl bromide, the 4-allylbenzyl alcohol was quantitatively obtained. In addition, the zincate complex reacted with iodobenzene, catalyzed by tetrakis(triphenylphosphine)palladium, to afford 4-hydroxymethyl biphenyl.[11]

Herein, we report the first demonstration of the catalyst-transfer polycondensation for the synthesis of high-MW regioregular P3HT using the dianion-type zincate complex, dilithium tetra(*tert*-butyl) zincate ($^{t}Bu_4ZnLi_2$). This new system can be used in the purification-free polymerization media of tetrahydrofuran (THF), in the presence of an alcohol or even water as a protic impurity. Furthermore, P3HHT could directly

be obtained without protection by applying the developed system.

We first investigated the halogen-metal exchange reaction of 2-bromo-3-hexyl-5-iodothiophene (**1**) with an equivalent molar amount of $^tBu_4ZnLi_2$ in THF at 0 °C. After quenching the reaction with HCl solution or allyl bromide, 2-bromo-3-hexylthiophene or 5-allyl-2-bromo-3-hexylthiophene, respectively, was quantitatively obtained, which indicated that the halogen-metal exchange reaction quantitatively and selectively took place at 5-position to afford a zincate complex of the thiophene monomer, dilithium tris(*tert*-butyl)-(2-bromo-3-hexyl-5-thienyl) zincate (**2**; Scheme 1 and Figure S1,

Scheme 1. Halogen-Metal Exchange Reactions and Catalyst-Transfer Polycondensation for Synthesis of Regioregular P3HT Using $^tBu_4ZnLi_2$
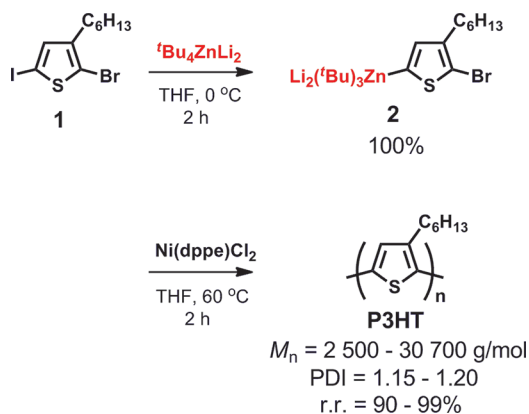
Supporting Information). Based on these results, the catalyst-transfer polycondensation of **2** was performed using a Ni catalyst in THF, as depicted in Scheme 1. These results are summarized in Table 1.

Table 1. Characterization Results of P3HT Obtained by Catalyst-Transfer Polycondensation of 2 Using $^tBu_4ZnLi_2$ in THF[a]

run	additive[b]	yield[c]	$[1]_0/[Ni]_0$	M_n[d] (kDa)	PDI[d]	r.r.[e]
1		90	15	2.50	1.20	90
2		88	30	5.40	1.18	94
3		90	60	10.2	1.15	97
4		85	120	21.7	1.15	98
5		80	180	30.7	1.19	99
6[f]		75	60	11.5	1.17	97
7	^iPrOH	60	60	10.9	1.15	97
8	MeOH	52	60	11.9	1.19	97
9	H_2O	50	60	16.8	1.72	97

[a]The polymerization was carried out using Ni(dppe)Cl$_2$ at 60 °C for 2 h. [b]Additives ([additive]$_0$/[1]$_0$ = 1.0) were placed before the halogen−metal exchange reaction. [c]The yields of P3HT were determined by gravimetry after precipitation. [d]M_n and PDI were determined by SEC using polystyrene standards without soxhlet extraction. [e]The regioregularity (r.r.) was determined by comparing the peak intensities of thienyl methylene protons in ^{1}H NMR spectra after soxhlet extraction with methanol, acetone, and chloroform. [f]Undistilled THF (dehydrated, stabilizer-free, Wako Pure Chemical Industries Ltd., 99.5%) was used.

At first, the polymerization of **2** was performed using 1,3-bis(diphenylphosphino)ethanenickel dichloride (Ni(dppe)Cl$_2$)

as the catalyst in THF, which was freshly distilled from sodium benzophenone, at 25 °C. However, the monomer conversion was low (<5%) even after a sufficient polymerization time (24 h), probably due to the sluggish transmetalation reaction between the polymer−Ni−Br and the incoming bulky monomer **2** at 25 °C. On the other hand, the conversion was significantly increased (>80%) by raising the polymerization temperature to 60 °C. Furthermore, the polymerization proceeded in a controlled manner to afford P3HTs with the predicted M_n values (2.50−30.7 kDa) and low PDIs (<1.2) in high yields (runs 1−5). It should be noted that these values were determined by SEC using the samples obtained just after quenching the polymerization solution, so that the products had not yet been isolated with residual oligomers by precipitation. Figure 1A shows that the SEC peaks shift to a
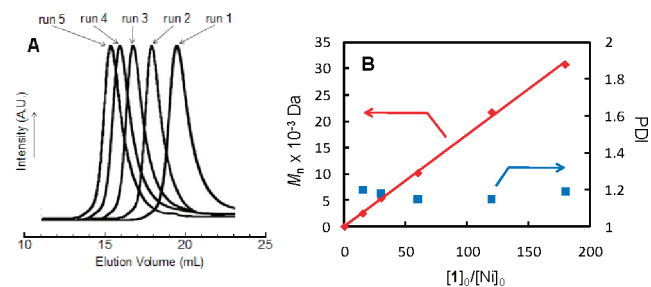

Figure 1. (A) SEC UV curve traces of P3HTs (runs 1−5). (B) Plots of M_n and PDI values of P3HTs (runs 1−5) determined by SEC using polystyrene standards (eluent: CHCl$_3$, 40 °C) as a function of the feed ratio of **1** to the Ni catalyst.

higher MW region while maintaining their sharp and unimodal shapes by increasing the feed ratio of **1** to the Ni catalyst ($[1]_0/[Ni]_0$). The proportional relationship between the M_n values of P3HT and $[1]_0/[Ni]_0$ with low PDIs is clearly seen in Figure 1B. The regioregularity (r.r.) of high-MW P3HT (>10 kDa) was greater than 97%, as determined by ^{1}H NMR (Figure S2 and S3 for the representative samples (runs 3 and 5), Supporting Information). In the expanded ^{1}H NMR spectrum (Figure S2(B)), two small triplets appear at 2.50 and 2.58 ppm, assignable to the methylene protons on the first carbon substituent (**h′** and **h**, respectively) on the P3HT end units with similar intensity.[8b] This indicates that H/Br terminated P3HT is dominantly formed.

To further corroborate the "living" nature of this system, a postpolymerization of **2** was demonstrated. After the complete consumption of **2** in the polymerization using Ni(dppe)Cl$_2$, as monitored by SEC (M_n = 9.8 kDa, PDI = 1.15), another portion of **2** was added to perform a chain-extension. The SEC peak shifted to a higher molecular weight region while keeping a relatively sharp MW distribution (M_n = 25.0 kDa, PDI = 1.29; Scheme S1 and Figure S5, Supporting Information). Also, there was no shoulder for the first block.

As already mentioned, $^tBu_4ZnLi_2$ has little basicity due to its bulkiness. Therefore, some electrophiles including even protic impurities may possibly be inert toward the related zincate complex of **2**. We intended to apply the developed polymerization system to purification-free media, such as undistilled THF or THF artificially contaminated with protic impurities. This realization requires satisfying two criteria as follows: (1) the halogen−metal exchange reaction of **1** with $^tBu_4ZnLi_2$ must selectively occur without terminating $^tBu_4ZnLi_2$ with impurities, and (2) the generated **2** must be tolerable to the impurities

during the polymerization. In practice, the halogen exchange reaction of **1** with $^tBu_4ZnLi_2$ followed by the polymerization of **2** with $Ni(dppe)Cl_2$ was carried out in undistilled THF as received (dehydrated, stabilizer-free, Wako Pure Chemical Industries Ltd., 99.5%; run 6). As a result, P3HT with a controlled MW and low PDI could be obtained. Surprisingly, similar experiments in THF containing a protic impurity of ^iPrOH or MeOH ($[ROH]_0/[\mathbf{1}]_0 = 1.0$, $[ROH]_0/[Ni(dppe)Cl_2]_0 = 60$) were also successful (runs 7 and 8). In addition, high-MW P3HT could be obtained in 50% yield in THF containing 1000 ppm water ($[H_2O]_0/[\mathbf{1}]_0 = 1.0$, $[H_2O]_0/[Ni(dppe)Cl_2]_0 = 60$), although the PDI increased to 1.72, probably due to the competitive termination reactions with water during the polymerization (run 9).

By exploiting the stability of $^tBu_4ZnLi_2$ and its derived zincate complex, the protection-free synthesis of P3HHT, which possesses hydroxyhexyl side chains, was further performed. The halogen–metal exchange reaction of 2-bromo-3-(6-hydroxyhexyl)-5-iodothiophene (**3**) was conducted in THF at 0 °C for 10 min to obtain the zincate complex monomer (**4**), followed by the catalyst-transfer polycondensation of **4** at 60 °C in the presence of $Ni(dppe)Cl_2$ ($[\mathbf{3}]_0/[Ni(dppe)Cl_2]_0 = 60$). As a result, P3HHT was successfully obtained in 89% yield (Scheme 2).

Scheme 2. Catalyst-Transfer Polycondensation for Protection-Free Synthesis of Regioregular P3HHT Using $^tBu_4ZnLi_2$
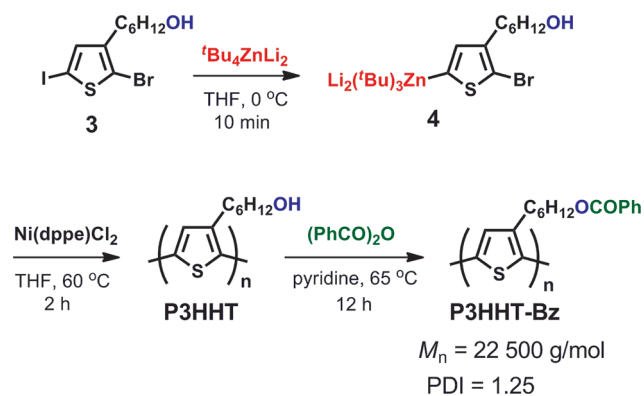
The polymerization homogeneously proceeded and P3HHT in the solution did not precipitate even after cooling to room temperature; however, after the workup by the precipitation of P3HHT in water, it became insoluble in THF and $CHCl_3$, probably due to the strong interaction between polymers via hydrogen bonding formation of the hydroxy groups. It was only soluble in N,N-dimethylformamide (DMF) and dimethyl sufoxide (DMSO) at elevated temperature. FT-IR spectrum of P3HHT (Figure S6(A), Supporting Information) showed a characteristic absorption peak assignable to the OH groups at 3386 cm^{-1}. Because SEC and NMR characterizations of P3HHT were very difficult due to its poor solubility, the benzoylated P3HHT (P3HHT-Bz, Scheme 2) was instead characterized based on a the similar reported procedure.[12]

P3HHT-Bz showed an excellent solubility in the common solvents of THF, chloroform, and toluene at room temperature. The absorption peak for the OH groups disappeared in the FT-IR spectrum of P3HHT-Bz (Figure S6(B), Supporting Information), while a characteristic absorption peak corresponding to the C=O stretching was newly observed at 1720 cm^{-1}.

The M_n and PDI values of P3HHT-Bz were determined to be 22.5 kDa and 1.25, respectively, by SEC (Figure S7, Supporting Information), based on a calibration using polystyrene standards. Taking the gained mass by benzoylation into consideration, the M_n value of the original P3HHT was calculated to be 14.2 kDa. From the ^1H NMR spectra of P3HHT-Bz (Figure S8, Supporting Information), all signals could be assigned to the expected structure, in which a singlet corresponding to one proton at the 4-position of the thiophene ring was observed at 6.95 ppm, together with the characteristic signals (7.30–7.60 ppm, 7.98 ppm) assigned for the five protons on the aromatic rings with a reasonable intensity ratio (1:5.09). These results indicated a nearly quantitative benzoylation yield. The symmetrical signal at 6.95 ppm with almost no side signals is also indicative of the very high regioregularity of P3HHT.

In conclusion, the selective halogen-metal exchange reaction of **1** with $^tBu_4ZnLi_2$ and catalyst-transfer polycondensation of **2** with $Ni(dppe)Cl_2$ have been first demonstrated for the synthesis of high-MW regioregular P3HT in high yields. This polymerization system was also applicable to the purification-free polymerization media of THF even in the presence of 1000 ppm water. Finally, we could directly synthesize P3HHT from the monomer precursor **3** without protection based on the developed system. Because the OH functional groups of P3HHT can further be converted into other functional groups, a wide variety of new polythiophene derivatives should be easily accessible.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Experimental, synthetic schemes, ^1H NMR spectra of the products obtained by halogen−metal exchange reactions and P3HT, and SEC curves of P3HTs obtained by postpolymerization of **2**. SEC curve and ^1H NMR spectrum of P3HHT-Bz. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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