

FOCUS REVIEW

Controlled synthesis of low-polydisperse regioregular poly(3-hexylthiophene) and related materials by zincate-complex metathesis polymerization

Tomoya Higashihara^{1,2} and Eisuke Goto¹

The recent progress in the development of zincate-complex metathesis polymerization (ZCMP) is reviewed. The Zn–I exchange reaction between 2-bromo-3-hexyl-5-iodothiophene and dilithium tetra-*t*-butyl zincate ($t\text{Bu}_4\text{ZnLi}_2$) and subsequent polymerization initiated with a Ni catalyst afforded poly(3-hexylthiophene)s (P3HTs) with predictable molecular weights and low polydispersity indices (PDIs). The direct synthesis of poly(3-(6-hydroxyhexyl)thiophene) was successfully demonstrated without protection of the hydroxyl group. The ligands of the Ni catalyst were further tuned for the preparation of extremely low-polydisperse P3HTs with high reproducibility. Then, the bulkiness and/or the electron-donating effect of the ligands were found to be very important for accessing a living system for ZCMP. Consequently, the modified ZCMP system with the Ni(dcpe)Cl₂ catalyst accomplished the preparation of well-defined P3HTs (M_n up to 33 000 g mol⁻¹) with extremely low PDIs (1.03–1.11). In addition, an all-conjugated block copolythiophene, P3HT-*b*-poly(3-octadecylthiophene)(P3ODT), was synthesized for the first time through the sequential monomer addition approach with ZCMP.

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INTRODUCTION

Poly(3-alkylthiophene)s (P3ATs), in which the alkyl side chains are substituted at the 3-position of poly(thiophene-2,5-diyl), have received much attention in the field of electronic devices, including organic field-effect transistors^{1–6} and organic photovoltaic cells,^{7–11} because P3ATs are among the best type of balanced high-performance materials used as *p*-type semiconductors in terms of solubility, chemical stability, charge mobility and commercial availability.

Along the main chain of P3ATs, there are three different dyad regiostructures: head-to-tail, head-to-head and tail-to-tail structures. Although P3ATs are supposed to have perfect head-to-tail structures, in practice, depending on the synthetic approach, they also contain minor defects of head-to-head and tail-to-tail structures. Regioregularity, defined as the ratio of head-to-tail structures to the total number of regiostructures, is a very important parameter in P3ATs because even small differences in regioregularity may significantly influence the thermal and optoelectronic properties of the P3ATs.

Control of the molecular weight (MW) is just as important as control of the regioregularity because the MW directly affects the conjugation length along the main chain. In addition, the diffusion coefficient, chain entanglement and film properties depend on the MW. In the synthesis of P3ATs by conventional polycondensation,

adjustment of the polymerization time and purification of monomers are the methods typically used to control the MW. However, recent advances in a quasi-living chain-growth polymerization system for the synthesis of P3ATs more readily facilitates control of the MW through the feed ratio of the monomer to initiator, as mentioned below.

The synthesis of low-polydisperse P3ATs is also interesting and challenging, especially when applied to a morphological study of block copolymers containing P3AT segments, because the order and clarity of the nanostructures from self-assembly/microphase separation generally depend on the polydispersity index (PDI) of the P3ATs and the combination of blocks. At this point, quasi-living polymerization systems are the only way to control the PDI below 1.2 for high-MW P3ATs (> 10 K).

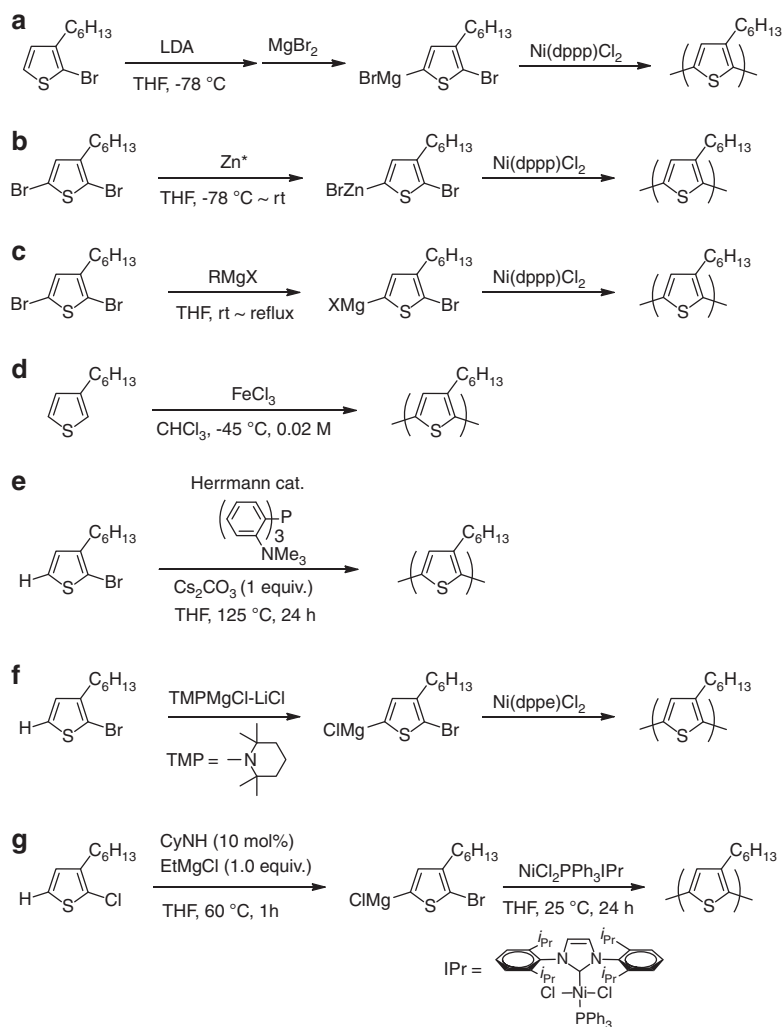
The synthetic methods for regioregular poly(3-hexylthiophene) (P3HT) afford the formation of head-to-tail P3HT with >98% regioregularity through nickel-catalyzed cross-coupling reactions using Grignard reagents or Rieke zinc, as independently discovered by McCullough *et al.*^{12,13} and Rieke and co-workers,¹⁴ respectively (Scheme 1a and b). The development of the Grignard metathesis (GRIM) polymerization system 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

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Scheme 1 Conventional synthesis of regioregular P3HT using (a) LDA/MgBr₂ and Ni(dppp)Cl₂; (b) Rieke-zinc and Ni(dppp)Cl₂; (c) RMgX and Ni(dppp)Cl₂; (d) FeCl₃; (e) Herrmann cat. and Cs₂CO₃; (f) TMPMgCl-LiCl and Ni(dppe)Cl₂; and (g) CyNH/EtMgCl and NiCl₂PPh₃IPr.

synthesis of P3HT (Scheme 1c).^{15,16} Alternatively, the more simple and straightforward dehydrogenative polycondensation afforded P3HT with 92% regioregularity by carefully controlling the monomer concentration and the polymerization temperature (Scheme 1d).¹⁷ Quite recently, the dehydrogenative polycondensation of 2-bromo-3-hexylthiophene (Scheme 1e¹⁸ and Scheme 1f¹⁹) or 2-chloro-3-hexylthiophene (Scheme 1g)²⁰ was reported to synthesize P3HT with >98% regioregularity and further progress in this area is definitely expected in the near future.

In addition, a further breakthrough with the chain-growth GRIM polymerization system was undoubtedly the discovery of the 'living' nature of the system that affords P3ATs, as independently reported by Yokozawa and coworkers^{21,22} and McCullough and coworkers.^{23,24} The mechanism proposed by Yokozawa²² is as follows (see Scheme 2): two equivalents of the thiophene monomer, 2-bromo-5-chloromagnesium-3-hexylthiophene (**1**), are coupled through the addition of the catalytic Ni(dppp)Cl₂ (dppp = 1,3-diphenylphosphinopropane) to afford the tail-to-tail dimer. The Ni species then transfers to the next C-Br bond by walking through the π conjugation without diffusion of the Ni(0) species to afford the dimer (**2**). Then, **2** acts as the virtual initiator to start the polymerization of **1** by transmetalation.

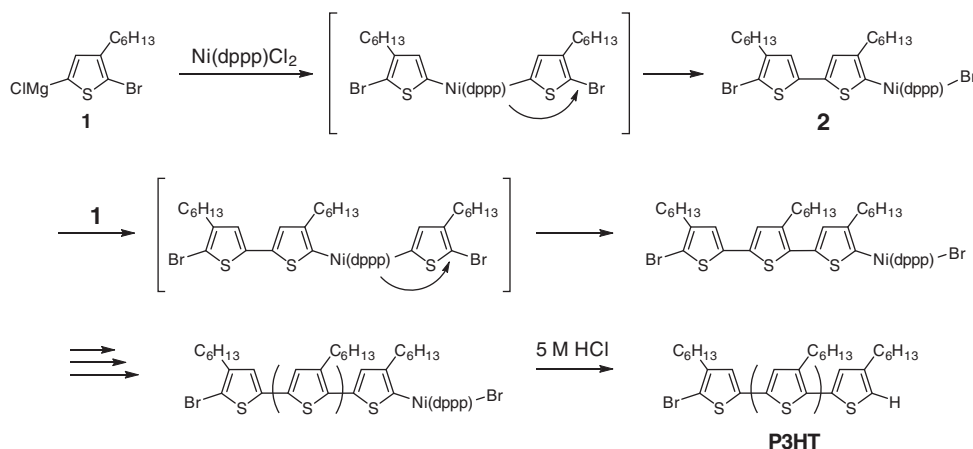
The polymerization proceeds in the chain-growth manner without diffusion of the Ni(0) species, and only the cross-coupling reaction takes place between the activated polymer chain end and the incoming monomer **1**. This system is referred to as 'catalyst-transfer polycondensation'. When the initiation rate is faster than or similar to the propagation rate, the MW and low PDI <1.2 of the resulting P3HT can be controlled through the feed ratio of **1** to Ni(dppp)Cl₂. McCullough *et al.* proposed alternatively that the associated pairing between the generating polymer and the Ni(0) species prevents the diffusion of the Ni(0) species into the polymerization media to achieve the chain-growth mechanism.²⁴

In this focus review, recent progress in the controlled synthesis of low-polydisperse regioregular P3ATs by a newly developed living zincate-complex metathesis polymerization (ZCMP) system is described. In addition, this review reports the first synthesis of well-defined block copolymers containing P3HT segments by ZCMP.

EXPERIMENTAL PROCEDURE

Materials

Tetrahydrofuran (THF, dehydrated, stabilizer free, 99.5%, Wako Pure Chemical Industries, Osaka, Japan) was dried over sodium benzophenone and was



Scheme 2 Proposed mechanism for the synthesis of regioregular P3HT by catalyst-transfer polycondensation.

Table 1 Characterization results for P3HT obtained from catalyst-transfer polycondensation of **3** with ^tBu₄ZnLi₂ in THF^a

Run	Additive ^b	Yield ^c	[I] 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	ⁱ PrOH	60	60	10.9	1.15	97
8	MeOH	52	60	11.9	1.19	97
9	H ₂ O	50	60	16.8	1.72	97

Abbreviations: PDI, polydispersity index; r.r., regioregularity; THF, tetrahydrofuran.

^aThe polymerization was carried out using Ni(dppe)Cl₂ at 60 °C for 2 h.

^bAdditives ([Additive]₀/[**3**]₀ = 1.0) were placed before the halogen-metal exchange reaction.

^cThe yields of P3HT were determined by gravimetry after precipitation.

^dM_n and PDI were determined by SEC using polystyrene standards without soxhlet extraction.

^eThe r.r. was determined by comparing the peak intensities of thieryl methylene protons in ¹H NMR spectra after soxhlet extraction with methanol, acetone and chloroform.

^fUndistilled THF (dehydrated, stabilizer free, Wako Pure Chemical Industries, 99.5%) was used.

distilled before use under nitrogen. Dilithium tetra(*tert*-butyl) zincate (^tBu₄ZnLi₂, 0.430 M in THF solution) was kindly donated by Tosoh Finechem (Yamaguchi, Japan). All other reagents were purchased from Sigma-Aldrich Japan K.K., Tokyo, Japan or Tokyo Chemical Industry Co., Ltd., Tokyo, Japan and were used as received.

Measurements

Size-exclusion chromatography (SEC) was measured on a JASCOGULLIVER 1500 (JASCO, Tokyo, Japan) equipped with a pump, an absorbance detector (UV, λ = 254 nm) and three polystyrene gel columns with a conventional calibration curve based on polystyrene standards. THF (40 °C) was used as the carrier solvent at a flow rate of 1.0 ml min⁻¹ after calibration with the standard polystyrenes. ¹H NMR spectra were recorded on a JEOL JNM-ECX400 spectrometer (JEOL, Tokyo, Japan) at 25 or 40 °C. Deuterated chloroform was used as the solvent. The chemical shifts are reported in p.p.m. (parts per million) with an internal reference of either tetramethylsilane or residual solvent signals. The coupling constants (J) are given in Hz. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet) or m (multiplet). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Shimadzu AXMA-CFR mass spectrometer (Shimadzu Corp., Kyoto, Japan). The spectrometer was equipped with a nitrogen laser (337 nm) and with pulsed ion extraction. The measurement was performed at an accelerating potential of 20 kV in the linear positive-ion mode.

Dithranol was used as the matrix. The mass values were calibrated by the three-point method with insulin plus H⁺ at m/z 5734.62, insulin-β plus H⁺ at m/z 3497.96 and α-cyanohydroxycinnamic acid dimer plus H⁺ at m/z 379.35.

General procedure for the synthesis of P3HT by ZCMP

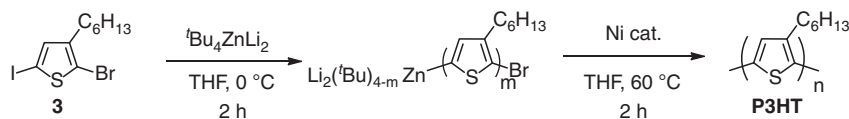
The ZCMP was performed in THF at 60 °C under a nitrogen atmosphere with various Ni catalysts in the prescribed [2-bromo-3-(nonyl)thiophene(**3**)]₀/[Ni catalyst]₀ ratio. In a typical experiment, **3** (0.206 g, 0.552 mmol) was placed in a 20-ml two-necked flask purged with a nitrogen atmosphere. After the dissolution of **3** in THF (15 ml), a THF solution of ^tBu₄ZnLi₂ (0.430 M × 0.336 ml = 0.144 mmol) was added and the mixture was stirred at room temperature for 20 min to afford a solution of the monomer in THF. Finally, an aliquot (5 ml) of Ni(dcpe)Cl₂ (0.00920 mmol) solution, which was prepared in another batch by mixing Ni(PPh₃)₂Cl₂ (6.02 mg, 0.00920 mmol) and dcpe (19.4 mg, 0.0459 mmol) in THF (5 ml), was added to start the polymerization. The polymerization was carried out at 60 °C for 1 h, followed by quenching with a 5 M HCl solution (2 ml). The quenched solution was extracted with CHCl₃, washed with water and analyzed by SEC directly before precipitation (M_n (SEC) = 12 000, PDI = 1.03). The solution was poured into a large excess of methanol/H₂O (200/100 ml) to precipitate the polymer. After filtration and drying under vacuum, the crude P3HT was obtained (0.0733 g, 80%, regioregularity = 98%). ¹H NMR (CDCl₃): δ 0.92 (t, J = 7.2 Hz, 3H), 1.36 (m, 4H), 1.44 (m, 2H), 1.71 (m, 2H), 2.80 (t, J = 7.6 Hz, 2H), 6.98 p.p.m. (s, 1H). ¹³C NMR (CDCl₃): δ 14.5, 23.0, 29.6, 29.8, 30.9, 32.1, 129.0, 130.8, 134.0, 140.2.

Synthesis of poly(3-(6-hydroxyhexyl)thiophene)

2-Bromo-3-(6-hydroxyhexyl)-5-iodothiophene, **4** (0.382 g, 0.982 mmol), was placed in a 50-ml two-necked flask purged with argon atmosphere. After dissolving **4** in THF (50 ml), a THF solution of ^tBu₄ZnLi₂ (0.535 M × 1.84 ml = 0.984 mmol) was added and stirred at 0 °C for 10 min. Finally, Ni(dppe)Cl₂ (8.67 mg, 0.0164 mmol) was added to start the polymerization. The polymerization was carried out at 60 °C for 2 h, followed by quenching with a 5 M HCl solution (2 ml). The solution was poured into a large excess of MeOH/H₂O (20/180 ml) to precipitate the polymer. After filtration and drying under vacuum at 60 °C for 24 h, poly(3-(6-hydroxyhexyl)thiophene) (P3HHT) was obtained (0.160 g, 89%). Fourier transform infrared spectroscopy ν (cm⁻¹): 737 (C-H bending), 1107 (C-O stretching), 1361, 1398, 1454, 2935 (C-H stretching), 3386 (O-H stretching).

Synthesis of P3HT-*b*-P3ODT by ZCMP

3 (0.110 g, 0.300 mmol) was placed in a 50-ml two-necked flask purged with argon atmosphere. After dissolving **3** in THF (35 ml), a THF solution of ^tBu₄ZnLi₂ (0.430 M × 0.167 ml = 0.0718 mmol) was added and stirred at room temperature for 20 min. Ni(dcpe)Cl₂ (0.0118 mmol) solution, which was



Scheme 3 Controlled synthesis of regioregular P3HT by $t\text{Bu}_4\text{ZnLi}_2$.

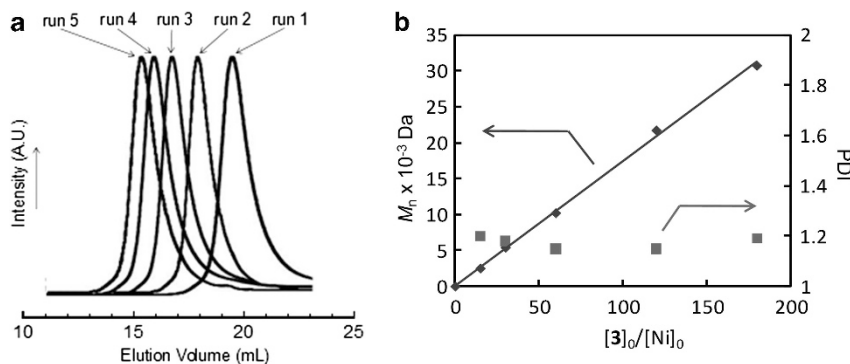


Figure 1 (a) SEC UV curves for P3HTs (run 1–5). (b) Plots of M_n and PDI values for P3HTs (run 1–5) determined by SEC with polystyrene standards (eluent: CHCl_3 , 40 °C) as a function of the feed ratio of **3** to $\text{Ni}(\text{dppf})\text{Cl}_2$.

prepared in another batch by mixing of $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ (7.74 mg, 0.0118 mmol) and *dcpe* (10.0 mg, 0.0237 mmol) in THF (5 ml), was then added to start the polymerization. The polymerization was carried out at 60 °C for 30 min. After sampling an aliquot of the solution and quenching with a 5 N HCl solution, a THF solution of 2-bromo-5-iodo-3-octadecylthiophene was added to the rest solution, which was prepared in another batch as described below. The solution was further stirred at 60 °C for additional 2 h, followed by quenching with a 5 M HCl solution (2 ml). The quenched solution was extracted with CHCl_3 , washed with water and analyzed by SEC directly before precipitation (M_n (SEC) = 15 000, PDI = 1.05). It was poured into a large excess of methanol/ H_2O (200/100 ml) to precipitate the polymer. After filtration and drying under vacuum, the crude P3HT-*b*-P3ODT was obtained (0.0986 g, 57%, regioregularity = 98%). ^1H NMR (CDCl_3): δ 0.87 (t, J = 6.8 Hz, 3H (P3HT)), 0.92 (t, J = 6.8 Hz, 3H (P3ODT)), 1.19–1.49 (m, 20H (P3HT and P3ODT)), 1.71 (m, 4H (P3HT and P3ODT)), 2.81 (t, J = 7.2 Hz, 4H (P3HT and P3ODT)), 6.98 p.p.m. (s, 2H (P3HT and P3ODT)). ^{13}C NMR (CDCl_3): δ 14.5, 23.0, 29.6, 29.7, 29.8, 29.9, 30.0, 30.1, 30.9, 32.1, 32.3, 129.0, 130.9, 134.1, 140.3.

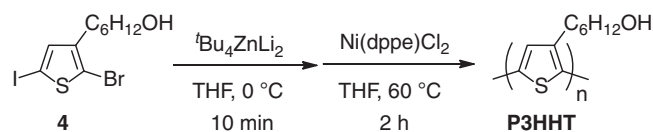
Preparation of a THF solution of the second monomer: 2-bromo-5-iodo-3-octadecylthiophene, **17** (0.202 g, 0.372 mmol), was placed in a 10-ml two-necked flask purged with argon atmosphere. After dissolving **17** in THF (10 ml), a THF solution of $t\text{Bu}_4\text{ZnLi}_2$ (0.430 M × 0.210 ml = 0.0903 mmol) was added and stirred at room temperature for 20 min.

RESULTS AND DISCUSSION

Controlled synthesis of regioregular P3HT using zincate complex

The GRIM polymerization system is a promising method in the sense of controlling the MWs, PDIs and regioregularity of P3ATs capable under the relatively gentle condition at room temperature to reflux in THF. On the other hand, thorough purification steps of the monomers and solvents as well as inert gas atmospheres 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, 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, dilithium tetra-*t*-butyl zincate ($t\text{Bu}_4\text{ZnLi}_2$), with little basicity as a highly selective anionic initiator.²⁵



Scheme 4 Protection-free synthesis of regioregular P3HHT by $t\text{Bu}_4\text{ZnLi}_2$.

They also reported the protection-free halogen–metal exchange reaction of 4-iodobenzyl alcohol with $t\text{Bu}_4\text{ZnLi}_2$.²⁶

Inspired by his research, the catalyst-transfer polycondensation for the synthesis of high-MW regioregular P3HT using $t\text{Bu}_4\text{ZnLi}_2$ has been demonstrated.²⁷ At first, the polymerization of zincate-complex thiophene monomer, which was prepared by Zn–I exchange reactions between **3** and $t\text{Bu}_4\text{ZnLi}_2$, was performed using [1,2-bis(diphenylphosphino)ethane]nickel dichloride ($\text{Ni}(\text{dppf})\text{Cl}_2$) 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 at 25 °C. On the other hand, the conversion was significantly increased (>80%) by raising the polymerization temperature to 60 °C (Scheme 3, Table 1). 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 (run 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 higher MW region while maintaining their sharp and unimodal shapes by increasing the feed ratio $[\text{3}]_0/[\text{Ni}(\text{dppf})\text{Cl}_2]_0$. The proportional relationship between the M_n values of P3HT and $[\text{3}]_0/[\text{Ni}(\text{dppf})\text{Cl}_2]_0$ with low PDIs is clearly seen in Figure 1b. The regioregularity of high-MW P3HT (>10 kDa) was greater than 97%, as determined by ^1H NMR.

As already mentioned, $t\text{Bu}_4\text{ZnLi}_2$ has little basicity due to its bulkiness. Therefore, some electrophilic functions including even protic impurities may possibly be inert toward the related zincate

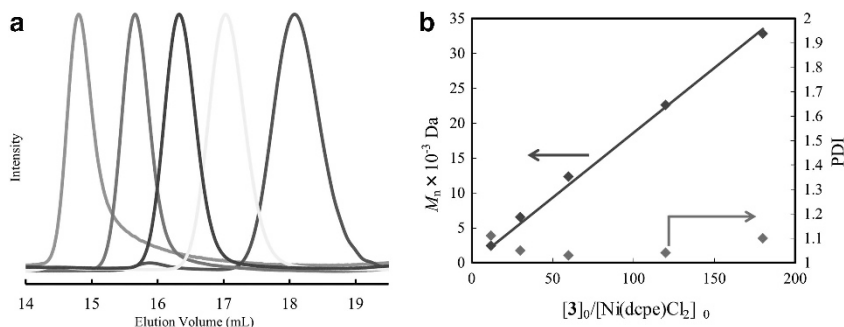


Figure 2 (a) SEC UV curves for P3HTs from Ni(dcpe)Cl₂. (b) Plots of M_n and PDI values of P3HTs determined by SEC with polystyrene standards (eluent: CHCl₃, 40 °C) as a function of the feed ratio of **3** to Ni(dcpe)Cl₂.

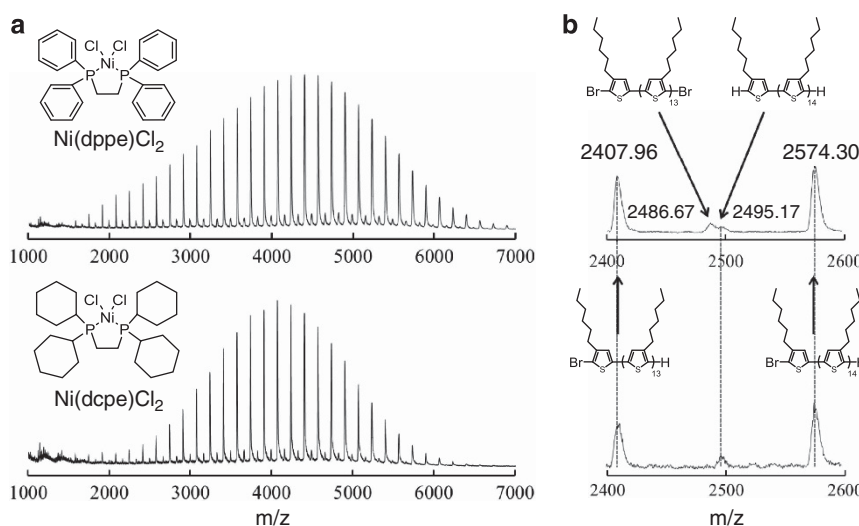


Figure 3 (a) MALDI-TOF mass spectra of P3HTs catalyzed by Ni(dcpe)Cl₂ and Ni(dppe)Cl₂ and (b) magnified spectra in the range of 2400–2600 m/z.

complex of the monomer. We intended to apply the developed polymerization system to purification-free media, such as undistilled THF or THF artificially contaminated with protic impurities. This requires satisfying two criteria as follows: (a) the halogen–metal exchange reaction of **3** with ^tBu₄ZnLi₂ must selectively occur without terminating ^tBu₄ZnLi₂ with impurities, and (b) the generated monomer must be tolerable to the impurities during the polymerization. In practice, the halogen exchange reaction of **3** with ^tBu₄ZnLi₂ followed by the polymerization with Ni(dppe)Cl₂ was carried out in undistilled THF as received (dehydrated, stabilizer free, Wako Pure Chemical Industries, 99.5%) (run 6). As a result, P3HT with a controlled MW and low PDI could be obtained. Surprisingly, similar experiments in THF with artificially added protic impurity of ^tPrOH or MeOH ([ROH]₀/[**3**]₀ = 1.0, [ROH]₀/[Ni(dppe)Cl₂]₀ = 60) were also successful (runs 7 and 8). In addition, high-MW P3HT could be obtained in 50% yield in THF containing 1000 p.p.m. water ([H₂O]₀/[**3**]₀ = 1.0, [H₂O]₀/[Ni(dppe)Cl₂]₀ = 60), although the PDI increased to 1.72, probably due to the competitive termination reactions with water during the polymerization (run 9).

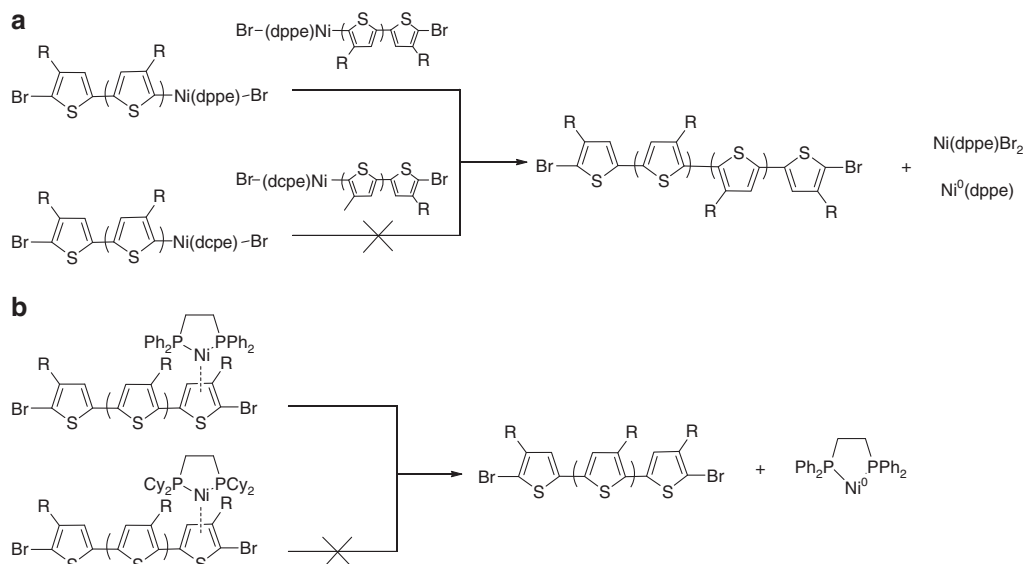
Protection-free synthesis of poly(3-(6-hydroxy)hexylthiophene) using zincate complex

As mentioned in the preceding section, GRIM polymerization methodology faces the serious limitation because many functional groups cannot generally be tolerated in the presence of the Grignard

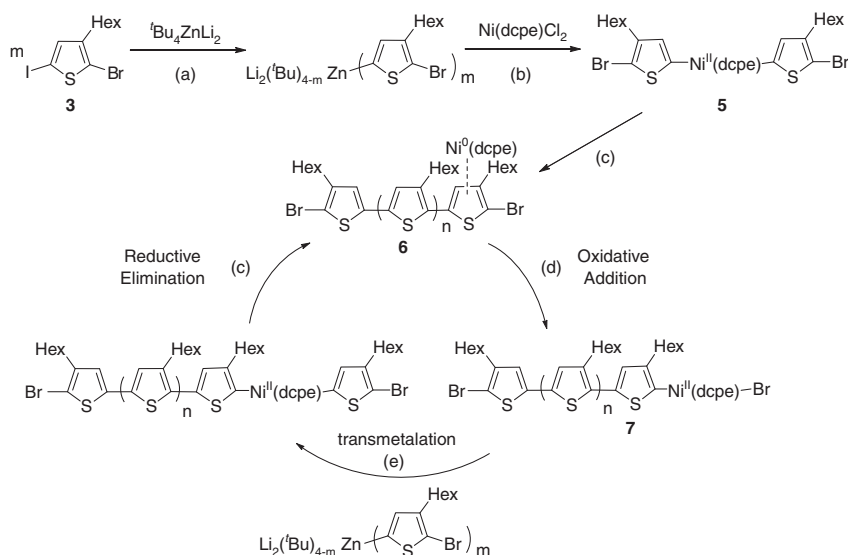
agents. By exploiting the stability and chemoselectivity of the zincate complex, the protection-free synthesis of poly(3-(6-hydroxyhexyl)thiophene) (P3HHT), which possesses hydroxyhexyl side chains, was performed. The halogen–metal exchange reaction of **4** was conducted in THF at 0 °C for 10 min to obtain the zincate-complex monomer, followed by the catalyst-transfer polycondensation at 60 °C in the presence of Ni(dppe)Cl₂ ([**4**]₀/[Ni(dppe)Cl₂]₀ = 60). As a result, P3HHT was successfully obtained in 89% yield (Scheme 4). This is the first successful example of protection-free synthesis of P3HHT using zincate complex.

Tuning ligands for controlled synthesis of low-polydisperse regioregular P3HT

Quite recently, the ligands of Ni catalyst were reinvestigated in detail to accomplish the living nature of ZCMP, resulting in the quite low PDI (< 1.1) in the controlled synthesis of regioregular P3HT as well as the successful post-polymerization and block copolymerization with high reproducibility. It is known that the ligand scaffold of the Ni catalyst has a substantial influence on the polycondensation of π -conjugated monomers.^{28–39} In 2009 and 2010, McNeil's group reported that the ligand structure on the Ni catalyst has a strong influence on the rate-limiting step in the GRIM polymerization.^{28,29} They then investigated the polymerization of 4-bromo-2,5-bis(hexyloxy)phenylmagnesium chloride using commercially available bis(dialkylphosphino)ethane ligands with varying steric properties.³⁰



Scheme 5 Generation mechanisms for Br/Br-terminated P3HT by (a) a recombination reaction and (b) diffusion of the Ni⁰ species during polymerization.



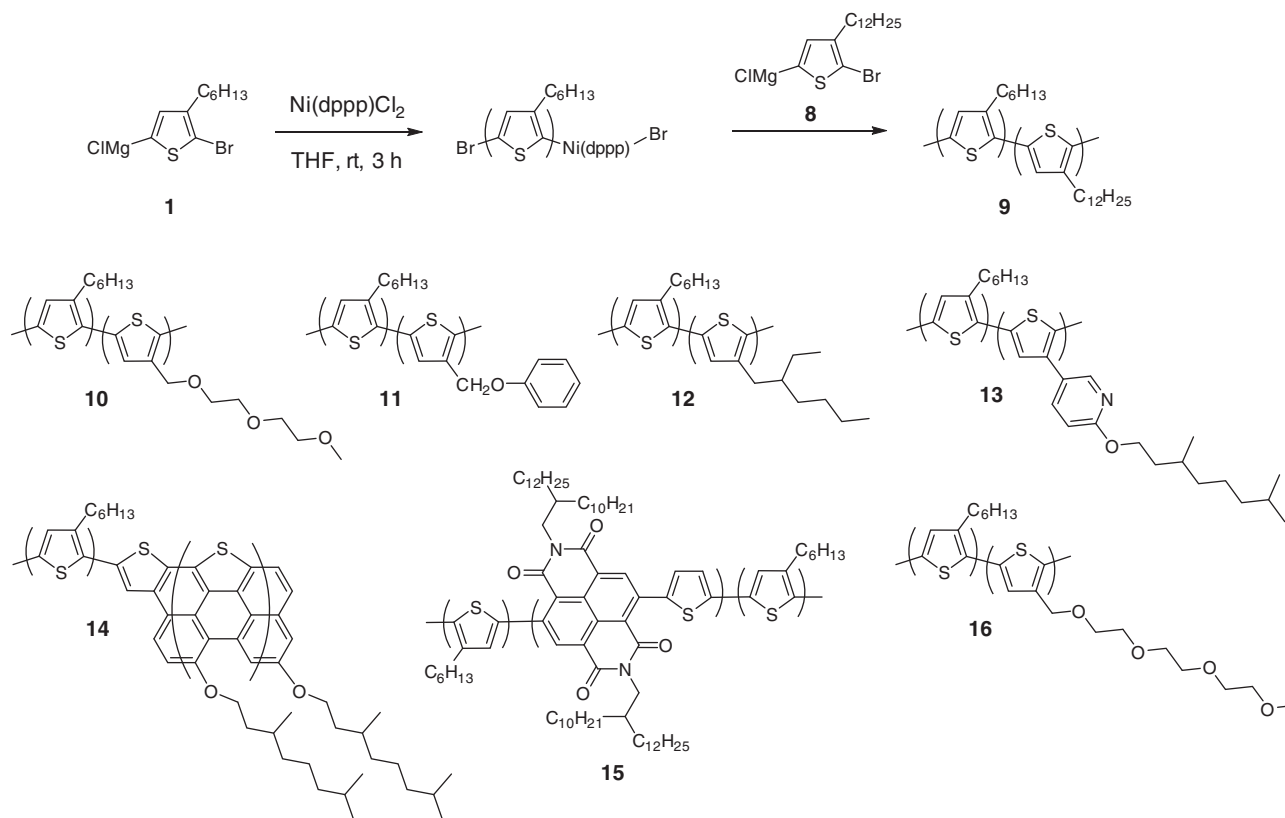
Scheme 6 Possible mechanism for zincate-complex metathesis polymerization (ZCMP)

They concluded that altering the ligand-based steric properties had a significant impact on the MW and PDI values of the resulting polymers. To establish a living system in the case of ZCMP for the synthesis of the regioregular P3HT, the details of the Ni ligand effects were investigated.

First, the Zn–I exchange reaction between **3** and $t\text{Bu}_4\text{ZnLi}_2$ was successfully conducted in THF at room temperature for 20 min to afford the monomer (see Scheme 3). The polymerization was then performed at 60 °C for 1 h, initiated by various Ni catalysts with several phosphorous ligands. The best result was obtained using [1,2-bis(dicyclohexylphosphino)ethane]nickel dichloride ($\text{Ni}(\text{dcpe})\text{Cl}_2$), affording regioregular P3HT with controlled MW and extremely low PDI (< 1.1). Dcpe with the relatively greater cone angle and electron-donating ability than dppe produces a highly controlled MW and lower PDI, probably due to the increase in the stability of generating polymer chain end (P3HT–Ni^{II}(dcpe)–Br) (no recombination) and/or

stronger Ni⁰(dcpe)– π interaction to reduce the diffusion of Ni⁰(dcpe) to the polymerization media (no chain transfer and termination) as discussed later. Figure 2a shows the SEC curve traces of the unfractionated crude P3HT samples before precipitation with varied feed ratio of **3** to $\text{Ni}(\text{dcpe})\text{Cl}_2$. The top peak shifted to the higher MW region ($M_n = 2400\text{--}33\,000$) when the feed ratio $[\text{3}]_0/[\text{Ni}(\text{dcpe})\text{Cl}_2]_0$ is increased, and still maintaining a unimodal and sharp form. Figure 2b shows the dependence of the feed ratio $[\text{3}]_0/[\text{Ni}(\text{dcpe})\text{Cl}_2]_0$ on the M_n and PDI values. The M_n values linearly increase with the increasing $[\text{3}]_0/[\text{Ni}(\text{dcpe})\text{Cl}_2]_0$ while maintaining very low PDIs (< 1.1), which supports the living nature of ZCMP catalyzed by $\text{Ni}(\text{dcpe})\text{Cl}_2$.

The regioregularity of the P3HTs calculated from the ¹H NMR spectra was 96–99% ($M_n > 6.5$ kDa) on comparing the α -methylene protons at the 3-position of the thiophene ring at the chain end and within the chain, which appear in the range of 2.5–2.9 p.p.m.²⁴ These



Scheme 7 Synthesis of block copolythiophenes by GRIM polymerization.

observed values are consistent with the theoretical ones, having only one defect of a tail-to-tail structure at the initiating fragment or within chain into consideration, as can also be seen in the GRIM polymerization.²⁴ Excellent performance for organic electronic devices should be expected using such a high P3HT regioregularity.

Plausible mechanism for ZCMP

For further investigation of the mechanism for ZCMP, MALDI-TOF mass spectroscopy of the resulting P3HTs is an efficient tool. Figure 3a shows the MALDI-TOF mass spectra of P3HTs initiated by Ni(dppe)Cl₂ and Ni(dcpe)Cl₂, targeting the M_n of 5000. There is a clear difference between these two spectra particularly in polydispersity, that is, P3HT obtained using Ni(dcpe)Cl₂ displays a narrower MW distribution than that using Ni(dppe)Cl₂. In addition, the magnified MALDI-TOF mass spectra in the range of 2400–2600 m/z of the same P3HT samples (Figure 3b) show the difference in the structure of the terminal units.

In the case of P3HT obtained using Ni(dcpe)Cl₂, there are major peaks from the H/Br-terminated P3HT and very minor peaks from the H/H-terminated P3HT. The former is obtained by living ZCMP quenched with HCl and the latter is presumably generated by a Zn–Br exchange reaction of the H/Br-terminated P3HT with the eliminated zincate complex, ^tBu₃ZnLi₂Cl or ^tBu₃ZnLi₂Br, followed by protonation with HCl. It should be noted that the existence of the minor H/H-terminated P3HT did not practically interfere with producing the narrowly distributed P3HT. In contrast, using Ni(dppe)Cl₂, there are extra peaks assignable to the Br/Br-terminated P3HT besides the H/Br- and H/H-terminated P3HTs, which suggests that a termination and/or chain-transfer reaction takes place to some extent because the Br/Br-terminated P3HT is generated by the undesired recombination

between the polymers and/or diffusion of the Ni⁰(dppe) from the associated pair during the polymerization as shown in Scheme 5.

As mentioned in the previous section, the ZCMP results were strongly influenced by steric hindrance based on the cone and bite angle factors. As dcpe has a higher larger cone angle than dppe, the reactivity of the Ni species inserted at the chain end of P3HT-Ni^{II}(dcpe)-Br may decrease its reactivity to prevent the undesired recombination reaction between P3HT-Ni^{II}(dcpe)-Br. On the other hand, the electron-donating ability of the phosphorous ligands should also be considered (Scheme 5b). Several researchers reported that during the GRIM polymerization, the electron-donating ability of the phosphorous ligands enhances the π -Ni interaction between the thiophene ring and Ni catalyst, which results in a controlled M_n and low PDI by reducing the diffusion of the Ni⁰ catalyst from the polymerization media to minimize the termination and/or chain-transfer reaction.^{31–39} A similar explanation can be adopted for ZCMP, namely, the best ligand of dcpe possesses a higher electron-donating ability than dppe. It can be speculated that the intermediate Ni⁰(dcpe) species associates with Br-(polymer)-Br via a stronger π -Ni interaction than the Ni⁰(dppe) species to suppress the termination and/or chain-transfer reaction and thus to realize the living ZCMP (Scheme 5b).

Taking all the results into consideration, the possible mechanism of ZCMP catalyzed by Ni(dcpe)Cl₂ is similar to that of GRIM polymerization as follows (Scheme 6): (a) the Zn–I exchange reaction between **3** and ^tBu₄ZnLi₂ to afford the zincate complex monomer, (b) transmetalation between the monomer and Ni(dcpe)Cl₂ to afford a dimer (**5**), (c) reductive elimination of Ni⁰(dcpe) from the dimer to afford the intermediate associate pair, Br-(dimer)-Br + Ni⁰(dcpe) (**6**), (d) selective transfer of the Ni⁰(dcpe) to the terminal C–Br bond,

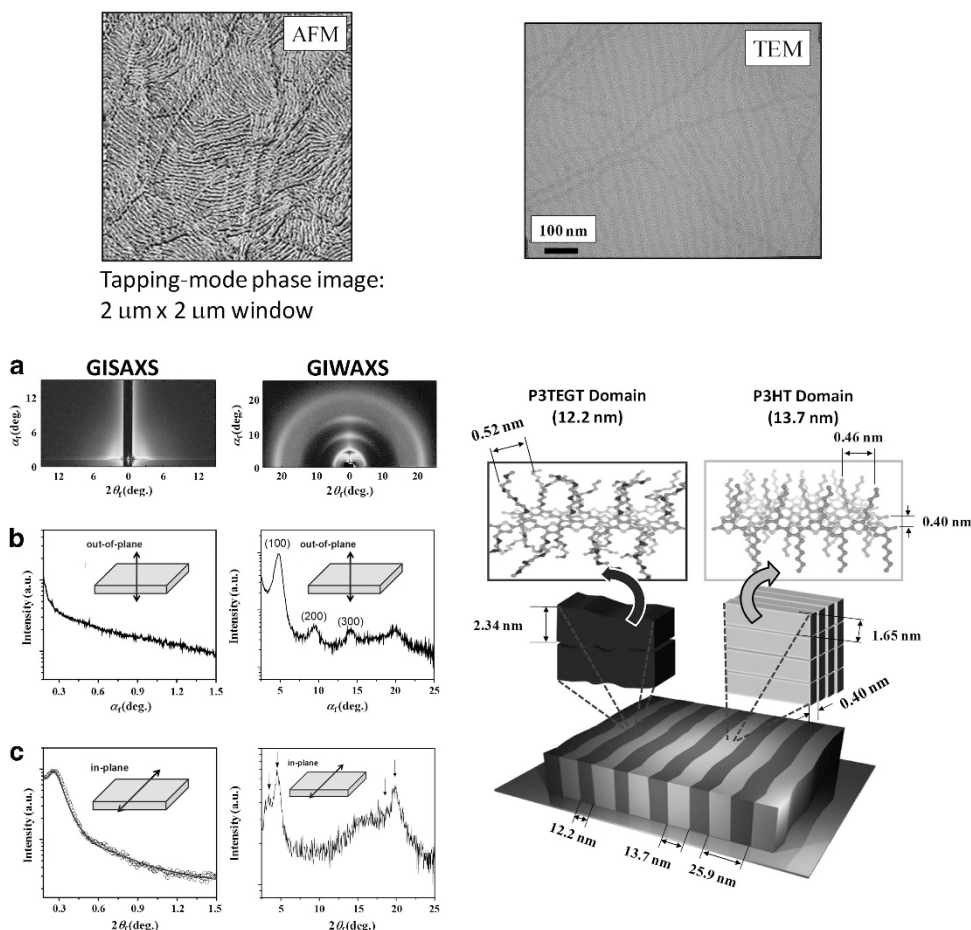
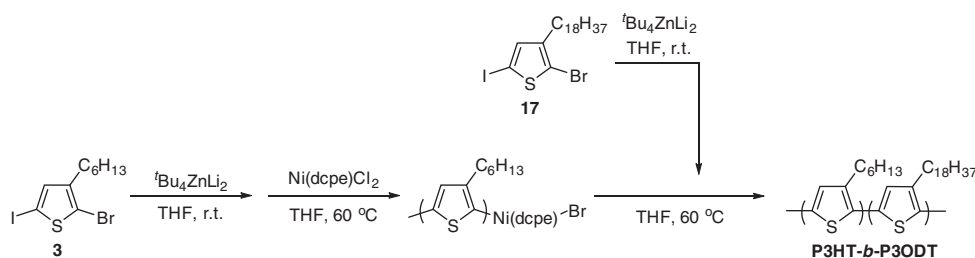


Figure 4 Hierarchical morphology of P3HT-*b*-P3TEGT (**16**). (a) 2D-GISAXS and 2D-GIWAXS patterns of P3HT-*b*-P3TEGT films, (b) out-of-plane scattering profiles extracted from the scattering patterns in (a), and (c) in-plane scattering profiles extracted from the scattering patterns in (a).



Scheme 8 Synthesis of block copolythiophenes by ZCMP.

producing Br-(dimer)-Ni^{II}(dcppe)-Br (**7**), (e) transmetalation of **7** with the incoming monomer and (f) propagation of the polymer chain by repeating (c)–(e). As reaction (e) takes place only at the polymer chain end, the low-polydisperse and head-to-tail regioregular P3HT with one defect at the initiating fragment or within chain can be obtained in a chain-growth manner, as evidenced by the SEC, NMR and MALDI-TOF mass spectroscopy results.

Synthesis of block copolythiophenes

On the basis of the quasi-living GRIM polymerization method, an array of block copolythiophenes has been synthesized by the simple sequential monomer addition technique. McCullough and coworkers first reported the sequential polymerization of 2-bromo-5-chloromagnesio-3-dodecylthiophene (**8**) just after the completion of the first

block obtained by the polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene (**1**) to afford P3HT-*block*-poly(3-dodecylthiophene) (**9**) (Scheme 7).²⁴ Yokozawa *et al.*⁴⁰ reported the synthesis of amphiphilic P3HT-*block*-poly(3-(2-(2-methoxyethoxy)ethoxy)thiophene) (**10**) based on a similar approach. Ueda and Tajima groups independently synthesized crystalline–amorphous block copolythiophenes, that is, P3HT-*block*-poly(3-phenoxyethylthiophene) (**11**)⁴¹ and P3HT-*block*-poly(3-(2-ethylhexyl)thiophene) (**12**),⁴² respectively. Higashihara and coworkers reported the synthesis of P3HT-*block*-poly(3-(4-(3,7-dimethyloctyloxy)-3-pyridyl)thiophene) (**13**),⁴³ a soluble block copolymer having P3HT and a graphene-like nanoribbon (**14**),⁴⁴ and all-conjugated donor-acceptor-donor block copolymer, P3HT-*b*-poly(naphthalene diimide-*alt*-(*bi*)thiophene)-*b*-P3HT (**15**).⁴⁵ They also found that the thin film of P3HT-*block*-

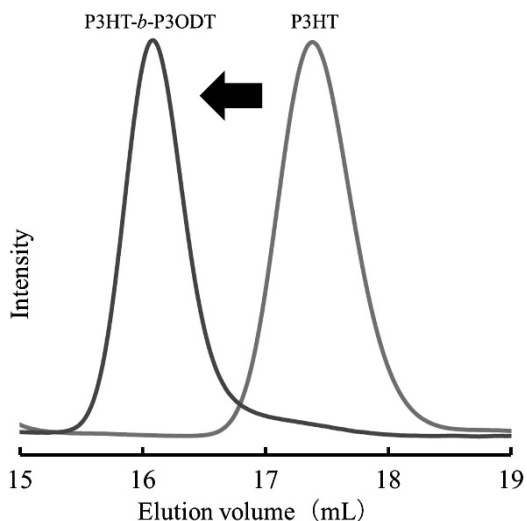


Figure 5 SEC curve traces of P3HT (first block) and P3HT-*b*-P3ODT.

poly(3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene)(P3TEGT) (16), having an amphiphilic structure, displayed a periodic perpendicular lamellar morphology at the nano level, as observed by atomic force microscopy and transmission electron microscopy (Figure 4).⁴⁶ These results suggested that a microphase separation took place between hydrophobic P3HT and hydrophilic P3TEGT domains. A further detailed investigation has been done by Ree and coworkers by glazing incidence X-ray diffraction experiments.⁴⁶ As a result, the thin-film block copolymer 16 consists of a hierarchical morphology of perpendicularly aligned lamellae with a *d*-spacing of 25.9 nm, in which the crystalline P3HT domains form an edge-on structure on the substrate excluded by amorphous P3TEGT domains, as is also shown in Figure 4. This perpendicularly oriented morphology is very important in polymer-based solar cell applications because of the high speed of charge transport before recombination of the separated charges occurs.

As mentioned above, GRIM polymerization is a promising method for the synthesis of block copolythiophenes. To extend the utility of ZCMP as well, P3HT-*b*-poly(3-octadecylthiophene) (P3HT-*b*-P3ODT, $M_n = 14\,000$, PDI = 1.07, P3HT/P3ODT = 42/58 by wt.) was synthesized by the sequential ZCMP of different monomers of 3 and 17 (Scheme 8). The SEC traces of the products before and after the addition of the second monomer are shown in Figure 5. Only one sharp peak is seen for P3HT-*b*-P3ODT without a shoulder for the residual first block. As calculated from the ¹H NMR spectrum, the molar ratio of the two monomers in the block copolymer agreed well with the molar ratio of the feed. This result is the first example of the synthesis of the block copolythiophene by ZCMP.

CONCLUSIONS

In this focus review, the development of ZCMP and its application to the protection-free direct synthesis of P3HHT and to block copolythiophene were described. In addition, suitable ligands for the Ni catalyst were reinvestigated in detail for the preparation of P3HT based on ZCMP. During the course of the study on ligand effects, the bulkiness and/or electron-donating effect of the ligands were found to be key factors in the control of the ZCMP system. The developed system is accessible for well-defined P3HTs with predictable MWs and extremely low PDIs of <1.1 for the best catalyst of Ni(dcp)Cl₂. Unimodally distributed P3HHT could be obtained directly by ZCMP

without protecting the OH functionality. Finally, ZCMP achieved the synthesis of narrowly distributed (PDI = 1.07) block copolythiophene P3HT-*b*-P3ODT for the first time. Although the GRIM polymerization system has already been established for the synthesis of well-controlled P3HT-related polymers, the new polymerization system using zincate complexes with lower basicity than that of Grignard reagents should open a new window for the development of various thiophene-based conjugated polymers with functional groups. The application of ZCMP to electron-deficient monomers for the synthesis of *n*-type semiconducting polymers is now under investigation.

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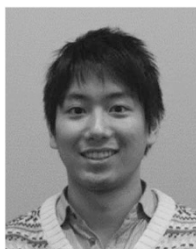
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