ORIGINAL ARTICLE

Protection-free one-pot synthesis of alcohol end-functionalized poly(3-hexylthiophene)

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Abstract

Alcohol end-functionalized poly(3-hexylthiophene) (P3HT-OH) is a high-value material used for the generation of conjugated P3HT-coil block copolymers via controlled polymerization methods. Previously, P3HT-OH was prepared by Kumada catalyst-transfer polycondensation, which required effort-intensive postpolymerization modifications and additional protecting group techniques. Herein, we report the direct one-pot synthesis of P3HT-OH by Suzuki-Miyaura catalyst-transfer polycondensation. Mild reaction conditions with good functional group tolerance allowed the preparation of well-defined P3HT-OH without protective groups or postmodification processes. Notably, the [Pd]/[alcohol initiator] ratio should be ≤1 to obtain well-defined P3HT-OH because at this ratio the oxidation of the alcohol group is suppressed, which reduces end-group fidelity. Moreover, the polymerization should be quenched before full conversion of the monomer to prevent disproportionation into P3HT dimers. The high end-group fidelity of P3HT-OH was confirmed by block copolymerization with polystyrene through atom-transfer radical polymerization. Our protocol provides facile access to P3HT-OH, which is useful for small-molecule functionalization and block copolymer synthesis.

Introduction

Poly(3-hexylthiophene) (P3HT) is a conjugated polymer with high hole mobility and applied to organic and perovskite solar cells and organic thin-film transistors [1–4]. A wide range of studies have been reported for fine-tuning the optoelectronic and physical properties of P3HT through molecular engineering of its microstructure, i.e., the regioregularity, side chains, end groups, composition, and architectures. In particular, the introduction of a versatile synthetic handle to the P3HT end-group is important for the preparation of functional P3HT and its block copolymers. Hence, P3HT with reactive end groups such as alkynes and pentafluorobenzene has been developed,

especially for click coupling reactions [5–7]. In addition, alcohol end-functionalized P3HT plays a central role in the synthesis of conjugated rod-coil block copolymers in conjunction with controlled polymerization reactions, including ring-opening, atom-transfer radicals, reversible addition-fragmentation chain-transfer, and cationic polymerizations, and a wide range of functional conjugated materials have been obtained with high precision [8–12].

The development of living polymerization methods has paved the way to the production of well-defined end-functional polymers [13–16]. In particular, catalyst-transfer polycondensation (CTP) is a controlled chain-growth polymerization method used to produce conjugated polymers with controlled molecular weight, low dispersity, and well-defined end groups [17]. In a seminal work, Kumada CTP (KCTP) revolutionized the controlled synthesis of conjugated polymers, including P3HT [18]. Given the power of this method, a wide range of well-defined end-functional P3HTs have been prepared with precisely controlled molecular weights and narrow dispersity [12]. In particular, the well-established protocol for the synthesis of P3HT-OH via KCTP involves the preparation of allyl end-functional P3HT and its postmodification by hydroboration-oxidation (Scheme 1a). However, this protocol requires multistep postmodifications that can reduce the end-group
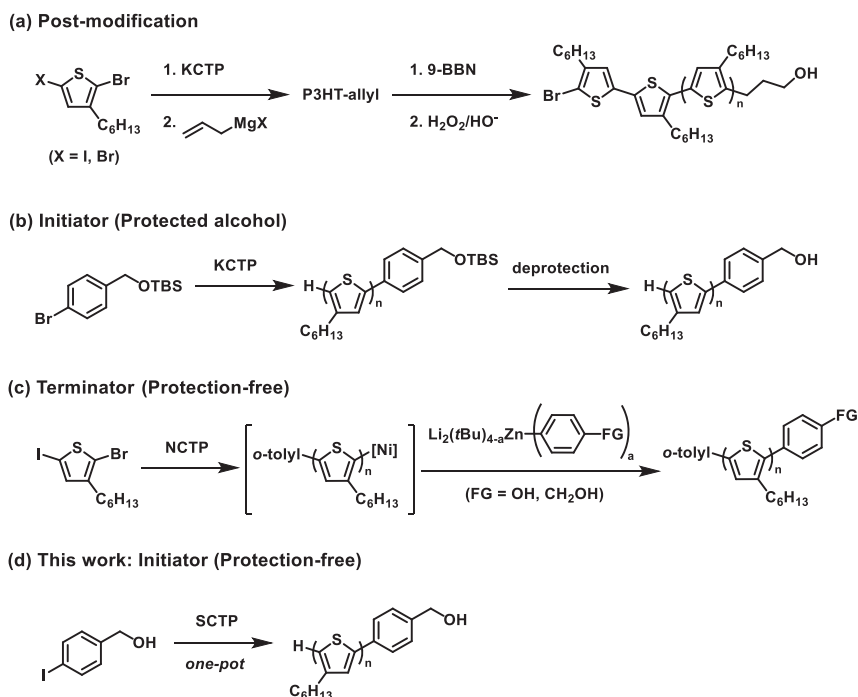

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Scheme 1 Preparation of P3HT-OH by (**a**) KCTP and postmodifications, (**b**) KCTP with a protected functional initiator, (**c**) NCTP with an alcohol-functionalized terminator, and (**d**) SCTP with an alcohol-functionalized initiator

(a) Post-modification

(b) Initiator (Protected alcohol)

(c) Terminator (Protection-free)
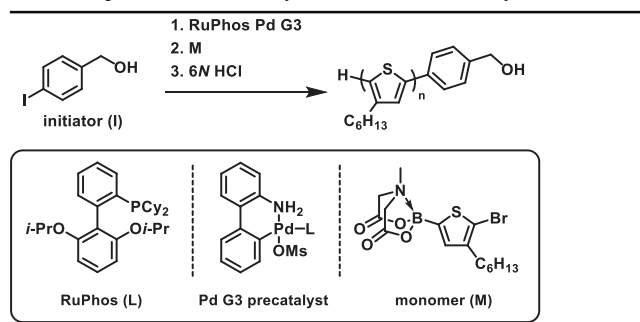
(d) This work: Initiator (Protection-free)

fidelity of P3HT, as well as involves time-consuming purification steps. Another method involves the use of functional initiators for KCTP, which might ensure high end-group fidelity of P3HT (Scheme 1b) [19]. However, because of the use of the Grignard reagent in KCTPs, the alcohol end-group should be protected during polymerization, eventually necessitating additional deprotection and purification steps (Scheme 1b). To address this issue, Negishi CTP (NCTP) with an alcohol-functional zincate complex used as a terminator has been developed and can directly produce alcohol end-functional P3HT without the need for a protection technique (Scheme 1c) [20, 21]. Nevertheless, this method requires an excessive number of terminators to guarantee high chain-end fidelity [21].

To improve accessibility to P3HT-OH and its block copolymers, a new direct synthetic pathway for P3HT-OH needs to be developed. The Suzuki-Miyaura reaction features high coupling efficiency and good functional group tolerance for polar functionalities [22]. Moreover, recent advances in Suzuki-Miyaura CTP (SCTP) have paved the way for the synthesis of P3HT with excellent control and high productivity [23, 24]. Thus, the introduction of an alcohol-functional initiator to this SCTP can allow the preparation of well-defined P3HT-OH without compromising polymerization control (Scheme 1d). Additionally, the process occurs in one pot even without a protecting group or the use of an excessive amount of terminators, which is beneficial to the improved synthetic accessibility of P3HT-OH (Scheme 1d).

Herein, we report the one-pot synthesis of P3HT-OH from an unprotected alcohol initiator via SCTP. The effects of the catalyst amount and reaction time were systematically investigated to obtain high-quality P3HT-OH. Under optimized reaction conditions, the preparation of low to high molecular weight P3HT-OH was attempted. Finally, the utility of P3HT-OH for block copolymerization was shown by the preparation of P3HT-*block*-polystyrene.

Results and discussion

Since the Suzuki-Miyaura reaction has high functional group tolerance, we attempted SCTP using 4-iodobenzyl alcohol without a protecting group. The RuPhos Pd G3 precatalyst was used to efficiently generate RuPhos Pd(0), enabling facile external initiation with 4-iodobenzyl alcohol to produce Ar-Pd(RuPhos)-I [23, 25]. Additionally, extra RuPhos ligand was added during polymerization to stabilize the active Pd chain-end and promote the catalyst-transfer reaction [25, 26]. A *N*-methyliminodiacetic acid (MIDA)-protected monomer (M) was chosen to minimize side reactions such as protodeboronation and boronate homo-coupling [26]. Initially, polymerization was carried out using 4.0 equivalent of the RuPhos Pd G3 precatalyst relative to that of the alcohol initiator to ensure complete consumption of the initiator (Table 1, entry 1). Size-exclusion chromatography (SEC) analysis of the final product confirmed the formation of a polymer with an M_n of 2.0 kDa and $Đ$ of 1.31 (Table 1, entry 1). A closer

Table 1 Optimization of the synthesis of P3HT-OH by SCTP

(a)

Entry	[Pd]/[I]	[M]/[I]	time (h)	M_n (kDa)[a]	$Đ^a$	yield (%)[b]	[OH]:[CHO][c]
1	4.0	25	24	2.0	1.31	55	62:38
2	1.5	25	24	2.5	1.20	67	74:26
3	1.0	25	24	5.2	1.09	84	97:3
4	0.7	25	24	6.1	1.18	92	97:3
5	1.0	25	72	7.7	1.31	99	97:3
6	1.0	25	120	8.3	1.35	99	97:3
7	1.0	15	15	3.3	1.10	95	96:4
8	1.0	75	36	16.5	1.05	80	95:5

[a]Determined using tetrahydrofuran SEC calibrated using PS standards
[b]Isolated yield
[c]Determined by ^{1}H NMR analysis

(b)

Fig. 1 Structural analysis of P3HT-OH. (**a**) ^{1}H NMR spectra addressing the end groups of P3HT depending on the [Pd]/[I] ratio. (**b**) MALDI-TOF mass spectrum of P3HT-OH in Table 1, entry 3

investigation of the end-group of the final polymer by ^{1}H NMR revealed two major end-group signals at 4.72 and 9.99 ppm corresponding to the methylene group of benzyl alcohol and aldehyde end groups, respectively (Fig. 1a). The formation of aldehyde was probably due to the Pd-mediated oxidation of benzyl alcohol, which significantly reduced the alcohol end-group fidelity to 62% (Table 1, entry 1). To address this issue, we systematically lowered the [Pd]/[I] ratio to suppress oxidation and simultaneously improve polymerization control. As the [Pd]/[I] ratio was decreased from 4.0 to 1.5 and then to 1.0, the end-group selectivity of alcohol over aldehyde gradually increased from 62% to 74% and then to 97% (Table 1, entries 1−3 and Fig. 1a). Moreover, the polymerization control was greatly improved, affording P3HT-OH with an M_n of 5.2 kDa and Đ of 1.09 (Table 1, entry 3). Since there was a minimal amount of free Pd(0) catalyst at a [Pd]/[I] ratio of 1.0, the homocoupling of monomers producing Br-aryl-Pd (II)-Br might also have been suppressed, thus enhancing both polymerization control and end-group fidelity [26]. No further improvement was observed when a [Pd]/[I] ratio of 0.7 was adopted (Table 1, entry 4). Therefore, in terms of atom economy and polymerization control, the optimal [Pd]/[I] ratio was set to 1.0. Additionally, matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass analysis of the product in entry 3 revealed a major series of signals corresponding to the mass of the benzyl
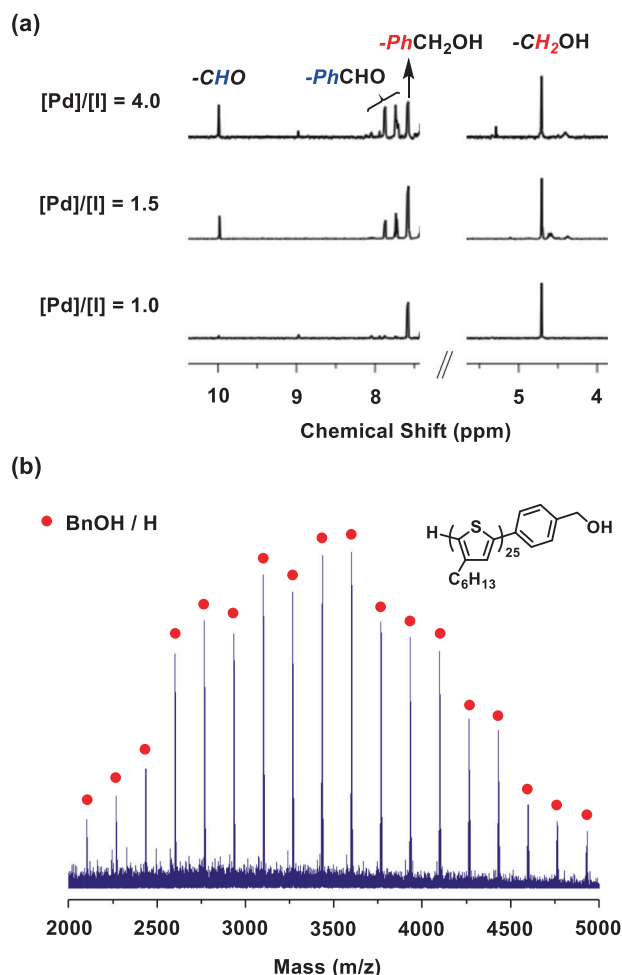
alcohol/H end-group, further corroborating the formation of the well-defined P3HT-OH (Fig. 1b, Fig. S2).

After determining the optimal [Pd]/[I] ratio, we investigated the effect of reaction time on the polymerization control and fidelity of the alcohol end-group. Initially, we prepared three independent batches of P3HT-OH with different reaction times (Table 1, entries 3, 5, and 6). Within 24 h, the polymerization was well controlled (Đ = 1.09) with high alcohol end-group fidelity (97%) (Table 1, entry 3). However, when the reaction was prolonged from 24 h to 72 h and then to 120 h, the SEC trace broadened, and the intensity of the higher molecular weight shoulder signal gradually increased (Fig. S1). This phenomenon can probably be attributed to disproportionation of the active Pd end-group, causing P3HT dimer formation [27, 28]. Nevertheless, the prolonged reaction did not affect the high alcohol end-group fidelity (Table 1, entries 3, 5, and 6). With this observation, we carried out kinetic monitoring of the reaction to determine the relationship between monomer conversion and the formation of the shoulder signal in the SEC
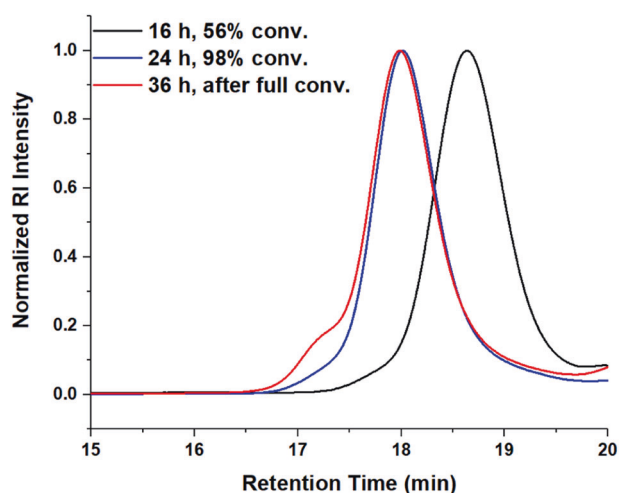
Fig. 2 Monitoring of SEC traces depending on the reaction time and monomer conversion when $[M]/[I] = 25$

trace. Interestingly, a unimodal SEC trace was observed until 98% conversion of the monomer, suggesting that disproportionation might occur when the monomer is completely consumed (Fig. 2). Considering these data, we identified the following two conditions to obtain high-purity P3HT-OH: (1) the [Pd]/[I] ratio must be ≤1.0, and (2) the polymerization should be quenched before complete consumption of the monomer.

The distinct advantage of controlled polymerization over conventional step-growth polymerization is its ability to control molecular weight with high precision. Thus, using optimal conditions, we next examined the control of the molecular weight of P3HT-OH while maintaining high alcohol end-group fidelity. Notably, as the targeted degree of polymerization increased, the ratio of [RuPhos]/[RuPhos Pd] increased from 1.5 to 10 to effectively stabilize the active Pd chain-end, thereby achieving well-controlled polymerization [25, 26]. Upon varying the $[\mathbf{M}]/[\mathbf{I}]$ ratio from 15 to 75, the SEC traces of the final polymer gradually shifted to the higher molecular weight region up to 16.5 kDa, with overall excellent control ($Đ \leq 1.10$) and high yield (80−95%) (Fig. 3). Moreover, ^{1}H NMR analysis of the product revealed excellent alcohol end-group selectivity over aldehydes (≥95%) for low to high molecular weight P3HT (Table 1, entries 3, 7, and 8; Fig. S3).

P3HT-containing block copolymers show unique self-assembly behavior and can therefore form various nanostructures that are useful for applications in solar cells, thin-film transistors, batteries, and sensors [29–35]. In particular, block copolymers from P3HT and functional coil-type polymers can enhance the processability, optoelectronic properties, and self-assembly behavior of the P3HT homopolymer [36, 37]. Thus, as a showcase example, we carried out the straightforward synthesis of P3HT-*block*-PS from P3HT-OH (Fig. 4). P3HT-OH with $M_n = 5.0$ kDa and $Đ = 1.07$ was prepared by the one-pot method described
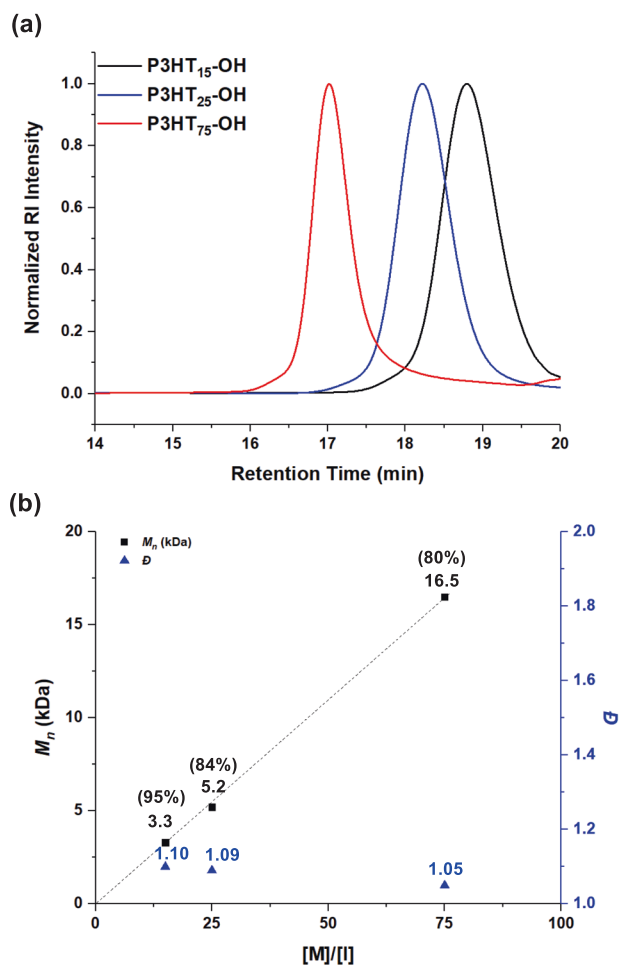

Fig. 3 Controlled synthesis of P3HT-OH with low to high molecular weights. (**a**) SEC traces and (**b**) M_n, $Đ$, and the isolated yield of P3HT-OH depending on the $[M]/[I]$ ratio from 15 to 75

herein and was readily converted to an atom-transfer radical polymerization (ATRP) macroinitiator with high efficiency (Fig. 4 and S3). Subsequently, the ATRP of styrene using a P3HT-Br macroinitiator was performed to produce the desired block copolymers (Fig. 4). ^{1}H NMR showed the characteristic signals corresponding to P3HT and PS blocks, and the SEC analysis revealed a complete shift of the SEC trace of P3HT to the higher molecular weight region while maintaining its unimodal trace shape ($M_n = 9.3$ kDa and $Đ = 1.12$), indicating the formation of a well-defined block copolymer (Fig. 4 and S3). This successful block copolymerization confirmed the high end-group fidelity of P3HT-OH, demonstrating the effectiveness of the one-pot SCTP protocol for synthesizing P3HT-OH.

Conclusions

In summary, alcohol end-functionalized P3HT was successfully prepared by one-pot SCTP without protection techniques.
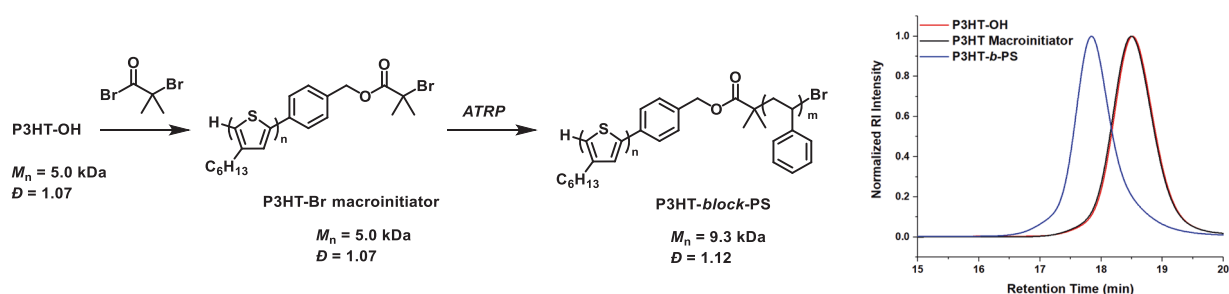
Fig. 4 Synthesis of P3HT-*block*-PS using P3HT-OH. Synthetic scheme (left) and the SEC traces (right)

A systematic investigation revealed that high chain-end fidelity of P3HT can be achieved only when the [Pd]/[I] ratio is ≤1 because at this ratio alcohol oxidation is suppressed. In addition, the polymerization should be quenched before full conversion of the monomer to minimize the dimerization of P3HT chains. Under optimized reaction conditions, low to high molecular weight P3HT-OH can be prepared with high precision and productivity. Moreover, the high end-group fidelity and utility of P3HT-OH were highlighted by the synthesis of P3HT-*block*-PS.

Experimental section

Materials

Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Tetrahydrofuran (THF) was purified by passing through the activated alumina column. Radical inhibitors were removed from styrene before use by running styrene through a basic aluminum oxide plug. All solvents and styrene were degassed by argon bubbling for 10 min before polymerization.

General analytical information

^{1}H NMR spectra were recorded with a JEOL Resonance ECZ600R (600 MHz) spectrometer. Chemical shifts are reported in delta (δ) units on the basis of parts per million (ppm) downfield from TMS. Size-exclusion chromatography (SEC) was performed at 35 °C using Shodex LF-804 columns eluted with tetrahydrofuran in a Waters 1515 pump, a Waters 2414 refractive index detector, and a Waters 2489 UV detector. Number average molecular weights (M_n) and weight average molecular weights (M_w) were calculated relative to linear polystyrene standards. Dispersity (Đ) values are reported as the quotient of M_w/M_n. MALDI-TOF mass analysis was performed with an Ultraflex III TOF/TOF spectrometer (Bruker Daltonics) using dithranol as the matrix.

Preparation of 5-bromo-4-*n*-hexylthien-2-yl-MIDA-boronate (M)

Monomers (**M**) were prepared according to a previously described procedure [25].

Preparation of P3HT-OH via SCTP

To a round-bottom flask equipped with a magnetic stir bar, the RuPhos Pd G3 precatalyst (0.033 g, 0.040 mmol), 4-iodobenzyl alcohol (0.0094 g, 0.040 mmol), RuPhos (0.028 g, 0.060 mmol), and K_3PO_4 (1.3 g, 6.0 mmol) were added. The flask was evacuated and backfilled with argon three times. Then, THF (10 mL) and H_2O (3.6 mL) degassed with argon were added to the flask. The mixture was heated and stirred at 50 °C for 1 h to prepare the externally initiated catalyst. **M** (1 mmol) in degassed THF (85 mL) was then added to the flask, and the mixture was stirred at 45 °C for 24 h before quenching with 6 N HCl (25 mL). The crude reaction mixture was diluted with $CHCl_3$ and washed with brine. The organic layer was concentrated under reduced pressure and purified by precipitation into MeOH. The precipitate was collected by filtration, washed with MeOH, and dried under vacuum to afford P3HT-OH as a violet solid. The molecular weight ($M_n = 5.2$ kg/mol) and dispersity (Đ = 1.09) of the polymer were obtained by SEC, with elution by THF (using a polystyrene standard). The reaction conditions with various [M]/[I] ratios are summarized below.

[M]/[I]	initiator (mmol)	cat. (mmol)	M (mmol)	RuPhos (mmol)	K3PO4 (mmol)	THF (mL)	H2O (mL)	yield (%)
15	0.067	0.067	1.0	0.1	6	10 + 85	3.6	95
25	0.04	0.04	1.0	0.06	6	10 + 85	3.6	84
75	0.0053	0.0053	0.4	0.053	2.4	4 + 34	1.4	80

Preparation of P3HT-Br macroinitiator

P3HT-Br macroinitiator was prepared according to a previously described procedure [25]. P3HT-OH (0.12 g, 0.028 mmol), anhydrous THF (2 mL), triethylamine (0.14 mL,

1.0 mmol), and 2-bromoisobutyryl bromide (0.069 mL, 0.56 mmol) were added to a 20-mL vial equipped with a magnetic stir bar. The mixture was degassed by purging with argon for 10 min and then heated overnight at 50 °C. The crude reaction mixture was diluted in chloroform and washed with brine three times. The organic layer was concentrated and precipitated into MeOH to afford P3HT-Br as a violet solid (yield = 80%). The molecular weight (M_n = 5.0 kg/mol) and dispersity ($Đ$ = 1.07) of the polymer were obtained by SEC, with elution by THF (using a polystyrene standard).

Preparation of P3HT-*block*-PS

P3HT-*block*-PS was prepared according to a previously described procedure [25]. P3HT-Br macroinitiator (0.078 g, 0.018 mmol), CuBr (0.0025 g, 0.018 mmol), and PMDETA (0.0037 mL, 0.018 mmol) were added to a 4-mL vial equipped with a magnetic stir bar. The vial was evacuated and backfilled with argon three times. Toluene (0.6 mL) and styrene (0.6 mL) degassed by purging with argon for 10 min in a separate vial were added to the vial containing the mixture. Subsequently, the vial was sealed with Teflon tape and Parafilm and stirred at 90 °C for 4 h. The crude reaction mixture was diluted with CHCl₃ and washed with brine. The organic layer was concentrated under reduced pressure and purified by precipitation into MeOH. The precipitate was collected by filtration, washed with MeOH, and dried under vacuum. The molecular weight (M_n = 9.3 kg/mol) and dispersity ($Đ$ = 1.12) of the polymer were obtained by SEC, with elution by THF (using a polystyrene standard).

Compliance with ethical standards

Competing interests The authors declare no competing interests.

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References

1. Yang CD, Lee JK, Heeger AJ, Wudl F. Well-defined donor–acceptor rod–coil diblock copolymers based on P3HT containing C₆₀: the morphology and role as a surfactant in bulk-heterojunction solar cells. J Mater Chem. 2009;19:5416–23.

2. Segalman RA, McCulloch B, Kirmayer S, Urban JJ. Block copolymers for organic optoelectronics. Macromolecules. 2009; 42:9205–16.

3. Malliaras GG, Herrema JK, Wildeman J, Wieringa RH, Gill RE, Lampoura SS, et al. Tuning of the photo- and electroluminescence in multi-block copolymers of poly[(silanylene)thiophene]s via exciton confinement. Adv Mater 1993;5:721–23.

4. Boudouris BW, Frisbie CD, Hillmyer MA. Nanoporous poly(3-alkylthiophene) thin films generated from block copolymer templates. Macromolecules. 2008;41:67–75.

5. Li Z, Ono RJ, Wu Z-Q, Bielawski CW. Synthesis and self-assembly of poly(3-hexylthiophene)-block-poly(acrylic acid). Chem Commun 2011;47:197–9.

6. Boufflet P, Casey A, Xia Y, Stavrinou PN, Heeney M. Pentafluorobenzene end-group as a versatile handle for para fluoro "click" functionalization of polythiophenes. Chem Sci 2017;8:2215–25.

7. Kim J-S, Kim Y, Kim H-J, Kim HJ, Yang H, Jung YS, et al. Regioregularity-driven morphological transition of poly(3-hexylthiophene)-based block copolymers. Macromolecules. 2017; 50:1902–8.

8. Nguyen TH, Nguyen LT, Nguyen VQ, Pan LNT, Zhang G, Yokozawa T, et al. Synthesis of poly(3-hexylthiophene) based rod–coil conjugated block copolymers via photoinduced metal-free atom transfer radical polymerization. Polym Chem 2018; 9:2484–93.

9. Ho V, Boudouris BW, McCulloch BL, Shuttle CG, Burkhardt M, Chabinyc ML, et al. Poly(3-alkylthiophene) diblock copolymers with ordered microstructures and continuous semiconducting pathways. J Am Chem Soc 2011;133:9270–3.

10. Iovu MC, Craley R, Jeffries M, Krankowski AB, Zhang R, Kowalewski T, et al. Conducting regioregular polythiophene block copolymer nanofibrils synthesized by reversible addition fragmentation chain transfer polymerization (RAFT) and nitroxide mediated polymerization (NMP). Macromolecules 2007;40:4733–5.

11. Lee JU, Jung JW, Emrick T, Russell TP, Jo WH. Synthesis of C60-end capped P3HT and its application for high performance of P3HT/PCBM bulk heterojunction solar cells. J Mater Chem 2010;20:3287–94.

12. Handa NV, Serrano AV, Robb MJ, Hawker CJ. Exploring the synthesis and impact of end-functional poly(3-hexylthiophene). J Polym Sci Part A: Polym Chem 2015;53:831–841.

13. Ouchi M, Terashima T, Sawamoto M. Transition metal-catalyzed living radical polymerization: toward perfection in catalysis and precision polymer synthesis. Chem Rev 2009;109:4963–5050.

14. Matyjaszewski K, Xia J. Atom transfer radical polymerization. Chem Rev 2001;101:2921–90.

15. Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, et al. Living free-radical polymerization by reversible addition-fragmentation chain transfer: the RAFT process. Macromolecules. 1998;31:5559–62.

16. Aoshima S, Kanaoka S. A renaissance in living cationic polymerization. Chem Rev 2009;109:5245–87.

17. Yokozawa T, Ohta Y. Transformation of step-growth polymerization into living chain-growth polymerization. Chem Rev 2016;116:1950–68.

18. Yokoyama A, Miyakoshi R, Yokozawa T. Chain-growth polymerization for poly(3-hexylthiophene) with a defined molecular weight and a low polydispersity. Macromolecules. 2004;37: 1169–71.

19. Smeets A, Bergh KV, Winter JD, Gerbaux P, Verbiest T, Koeckelberghs G. Incorporation of different end groups in conjugated polymers using functional nickel initiators. Macromolecules. 2009;20:7638–41.

20. Higashihara T, Goto E, Ueda M. Purification-free and protection-free synthesis of regioregular poly(3-hexylthiophene) and poly(3-(6-hydroxyhexyl)thiophene) using a zincate complex of ᵗBu₄ZnLi₂. ACS Macro Lett. 2012;1:167–70.

21. Inagaki S, Yamamoto T, Higashihara T. Direct synthesis of chain-end-functionalized poly(3-hexylthiophene) without protecting

groups using a zincate complex. Macromol Rapid Commun. 2020; 41:200148.

22. Miyaura N, Suzuki A. A new stereospecific cross-coupling by the palladium-catalyzed reaction of 1-alkenylboranes with 1-alkenyl or 1-alkynyl halides. Tetrahedron Lett. 1979;20:3437–40.

23. Seo K-B, Lee I-H, Lee J, Choi I, Choi T-L. A rational design of highly controlled Suzuki−Miyaura catalysttransfer polycondensation for precision synthesis of polythiophenes and their block copolymers: marriage of palladacycle precatalysts with MIDA-boronates. J Am Chem Soc 2018;140:4335–43.

24. Kobayashi S, Fujiwara K, Jiang D-H, Yamamoto T, Tajima K, Yamamoto Y, et al. Suzuki–Miyaura catalyst-transfer polycondensation of triolborate-type fluorene monomer: toward rapid access to polyfluorenecontaining block and graft copolymers from various macroinitiators. Polym Chem 2020;11:6832–39.

25. Choi H-N, Yang H-S, Chae J-H, Choi T-L, Lee I-H. Synthesis of conjugated rod-coil block copolymers by RuPhos Pd-catalyzed Suzuki-Miyaura catalyst-transfer polycondensation: initiation from coil-type polymers. Macromolecules. 2020;53:5497–503.

26. Lee JH, Park H, Hwang S-H, Lee I-H, Choi T-L. RuPhos Pd precatalyst and MIDA boronate as an effective combination for the precision synthesis of poly(3-hexylthiophene): systematic investigation of the effects of boronates, halides, and ligands. Macromolecules. 2020;53:3306–14.

27. Rudenko AE, Thompson BC. Optimization of direct arylation polymerization (DArP) through the identification and control of defects in polymer structure. J Polym Sci Part A: Polym Chem 2015;53:135–47.

28. Bautista MV, Varni AJ, Ayuso-Carrillo J, Tsai C-H, Noonan KJT. Chain-growth polymerization of benzotriazole using Suzuki–Miyaura cross-coupling and dialkylbiarylphosphine palladium catalysts. ACS Macro Lett. 2020;9:1357–62.

29. Jiang D-H, Ree BJ, Isono T, Xia X-C, Hsu L-C, Kobayashi S, et al. Facile one-pot synthesis of rod-coil bio-block copolymers and uncovering their role in forming the efficient stretchable touch-responsive light emitting diodes. Chem Eng J. 2021;418:129421–9.

30. Javier AE, Patel SN, Hallinan DT, Srinivasan V, Balsara NP. Simultaneous electronic and ionic conduction in a block copolymer: application in lithium battery electrodes. Angew Chem Int Ed 2011;50:9848–51.

31. Hu J, Zhang G, Geng Y, Liu S. Micellar nanoparticles of coil–rod–coil triblock copolymers for highly sensitive and ratiometric fluorescent detection of fluoride ions. Macromolecules. 2011;44:8207–14.

32. de Cuendias A, Hiorns RC, Cloutet E, Vignau L, Cramail H. Conjugated rod–coil block copolymers and optoelectronic applications. Polym Int 2010;59:1452–76.

33. Lee YJ, Kim SH, Yang H, Jang M, Hwang SS, Lee HS, et al. Vertical conducting nanodomains self-assembled from poly(3-hexyl thiophene)-based diblock copolymer thin films. J Phys Chem C 2011;115:4428–34.

34. Sary N, Richard F, Brochon C, Leclerc N, Lévêque P, Audinot J-N, et al. A new supramolecular route for using rod-coil block copolymers in photovoltaic applications. Adv Mater 2010;22:763–68.

35. Wang J-T, Takshima S, Wu H-C, Shin CC, Isono T, Kakuchi T, et al. Stretchable conjugated rod–coil poly(3-hexylthiophene)-block-poly(butyl acrylate) thin films for field effect transistor applications. Macromolecules. 2017;50:1442–52.

36. Olsen BD, Segalman RA. Self-assembly of rod-coil block copolymers. Mater Sci Eng R 2008;62:37–66.

37. Li J-H, Li Y, Xu J-T, Luscombe CK. Self-assembled amphiphilic block copolymers/CdTe nanocrystals for efficient aqueous-processed hybrid solar cells. ACS Appl Mater Interfaces 2017; 9:17942–48.