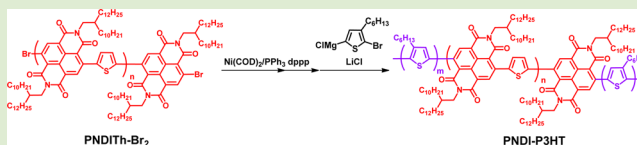


Synthesis of All-Conjugated Donor–Acceptor–Donor ABA-Type Triblock Copolymers via Kumada Catalyst-Transfer Polycondensation

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Supporting Information

ABSTRACT: A novel initiator, *N,N'*-bis(2-decyltetradecyl)-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide) (NDI-Br₂), was found effective in the Kumada catalyst-transfer polycondensation (KCTP) for the synthesis of regioregular poly(3-hexylthiophene) (P3HT). In addition, a two-step method of synthesizing all-conjugated triblock copolymers comprised of both *n*-type and *p*-type blocks was proposed. With a 10:9 feed molar ratio of NDI-Br₂ to 2,5-bis(trimethylstannyl)thiophene, an *n*-type macroinitiator (PNDITh-Br₂) was prepared via the Stille coupling reaction. Two outer P3HT blocks were then emanated via KCTP initiated by PNDITh-Br₂ to produce all-conjugated ABA-type triblock copolymers. The size exclusion chromatography (SEC) curves of all the triblock copolymers showed narrow distribution, with the lowest polydispersity index (PDI) of 1.15. Moreover, the molecular weight of the block copolymer was found to be independent of the amount of Ni catalyst, while it can be tailored by the feed molar ratio of the thiophene monomer to PNDITh-Br₂. The transmission electron microscopy (TEM) images and grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns of the block copolymer thin film revealed a well-defined lamellar structure and two distinguished crystalline domains, where the P3HT layer was in the range of 10–20 nm and presented an edge-on rich alignment.



π -Conjugated polymer-based bulk heterojunction (BHJ) photovoltaic devices have received considerable attention both in academia and in industry due to their exceptional potential for achieving lightweight, flexible, and low-cost solar cells.^{1–3} Among them, poly(3-hexylthiophene) (P3HT) is one of the most studied polymers because of their high mobility, stability, and relatively efficient light absorption in the visible range of the solar spectrum.^{4,5} The breakthrough in this area was made by the discovery of chain-growth polycondensation of regioregular P3HT with well-defined molecular weight and low polydispersity (PDI) by McCullough et al.^{6,7} and Yokozawa et al.,^{8,9} independently. Block copolymers are well-known for the template system for the creation of periodic morphologies on a nanoscale. Indeed, various block copolymers containing P3HT segments have been reported so far, such as P3HT-*b*-polystyrene (PS),¹⁰ P3HT-*b*-poly(methyl acrylate),¹⁰ P3HT-*b*-poly(2-vinylpyridine),¹¹ and PS-*b*-P3HT-*b*-PS.¹²

Moreover, the sequential monomer addition technique in quasi-living Grignard metathesis (GRIM) polymerization, also known as Kumada catalyst-transfer polycondensation (KCTP),^{13–15} gives birth to a variety of all-conjugated block copolymers based on thiophene backbones including P3HT-*b*-poly(dodecylthiophene),⁷ P3HT-*b*-poly(3-(2-(2-methoxyethoxy)ethoxy)methylthiophene),¹⁶ P3HT-*b*-poly(3-phenoxy methylthiophene),¹⁷ P3HT-*b*-poly(3-(2-ethylhexyl)thiophene),¹⁸ P3HT-*b*-poly(3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methylthiophene),¹⁹ poly(3-butylthiophene)-*b*-poly(3-octylthiophene) (P3BT-*b*-P3OT),²⁰ and P3BT-*b*-

P3HT.²¹ Meanwhile, all-conjugated block copolymers comprising different backbones were also prepared via the sequential polymerization of different monomers, such as poly(2,5-dihexyloxyphenylene) and poly(*N*-hexylpyrrole),²² poly(dioctylfluorene) (PF)-*b*-poly(2,5-dihexyloxyphenylene),²³ PF-*b*-P3HT,²³ and poly(3-hexylselenophene)-*b*-P3HT.²⁴

Recently, externally initiated KCTP has also been developed to be a powerful strategy to synthesize regioregular P3HT with well-defined α -end groups such as ethynylene, azide, and carboxylic acid.²⁵ Interestingly, by using hexaphenylbenzene and V-shaped and Y-shaped core compounds as initiators, 6-arm²⁶ and 2- and 3-arm²⁷ all-conjugated P3HT were prepared. Nevertheless, only a few reports concern all-conjugated block copolymers comprising both *n*-type and *p*-type blocks due to the synthetic challenges.^{28–31} The reported strategies involve either end-capping of Br- α -end-functional P3HT with *n*-type polymers or copolymerization between Br- α -end-functional P3HT and *n*-type monomers. The former end-capping process may be in need of an excess amount of Br- α -end-functional P3HT to guarantee the efficient coupling reaction, while the latter copolymerization method might result in the contamination with byproducts such as homo-P3HT generated by dimerization of Br- α -end-functional P3HT and even *n*-type homopolymer unreacted with Br- α -end-functional P3HT.

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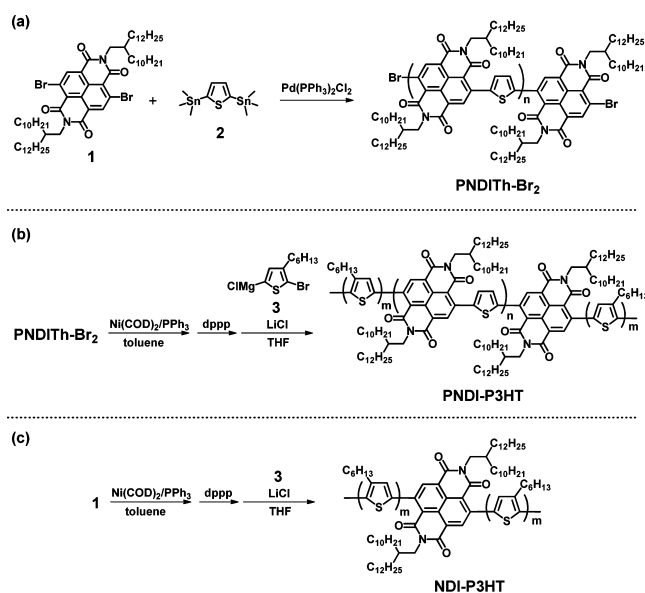
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Hence, the reported all-conjugated donor–acceptor block copolymers generally possess broad molecular weight distributions (>1.2).^{28–31}

In this work, we proposed a more facile and reliable method to synthesize all-conjugated triblock copolymers comprised of both *n*-type and *p*-type blocks via KCTP as shown in Schemes 1a and 1b. An *n*-type macroinitiator, poly(*N,N'*-bis(2-

Scheme 1. Synthetic Routes for PNDITH-Br₂ (a), All-Conjugated ABA-Type Triblock Copolymer via KCTP (b), and Model Reaction of KCTP Initiated with NDI-Br₂ (c)



decyltetradecyl)-1,4,5,8-naphthalene diimide-*co*-thiophene) (PNDITH-Br₂), was first prepared by the Stille coupling reaction.^{32,33} Then, P3HT blocks were emanated from both α,ω -ends of PNDITH-Br₂ via KCTP to produce an all-conjugated ABA-type block copolymer containing both donor and acceptor blocks. This opposite process to the reported method^{28–31} has never been reported. The significance of the developed process is the facility in tailoring the weight ratio of P3HT to PNDITH simply by varying the feed molar ratio of thiophene monomers to PNDITH-Br₂, derived from the quasi-living nature of KCTP. In addition, narrowly distributed all-conjugated block copolymers would be produced. Both aspects are crucial in considering the fact that the weight ratio between *p*-type and *n*-type and the PDI of the active polymers play an important role in the morphological properties, which should affect their organic photovoltaic (OPV) device performances.

Before carrying out the synthesis of all-conjugated triblock copolymers, a model polymerization of the thiophene monomer, 2-bromo-5-chloromagnesio-3-hexylthiophene (3), was performed via KCTP initiated by NDI-Br₂, a widely studied *n*-type monomer (1 in Scheme 1a), to confirm if it can effectively initiate the polymerization of 3. As described in Scheme 1c, 1 equiv of Ni(COD)₂ and 4 equiv of PPh₃ were added into 0.5 equiv of NDI-Br₂ (1 equiv of Br active site) in toluene, and the mixture was stirred for 24 h.^{27,34} Then, 2 equiv of 1,3-diphenylphosphinopropane (dppp) was added and allowed to stand for 2 h for the ligand exchange. Subsequently, 3, which was prepared in situ by the Grignard exchange reaction of 2,5-dibromo-3-hexylthiophene and isopropylmagnesium chloride in THF, was added into the initiator solution containing the NDI-Br₂/Ni complex. All the reactions were carried out at room temperature without any isolation process. The yield and molecular weight of the product are presented in Table 1.

The ¹H NMR spectrum of the NDI-Br₂ initiated P3HT product (NDI-P3HT) shown in Figure S1 (Supporting Information) indicates that the P3HT chain was successfully initiated from NDI-Br₂, as the signals of protons from P3HT (*d* and *e*) can be clearly identified. In the meantime, the signal corresponding to the aromatic protons on the NDI unit (*a*) was shifted upfield from 8.99 ppm in NDI-Br₂ to 8.79 ppm in NDI-P3HT. By comparing the integral peak areas of *a* from NDI and *d* from P3HT, the number average molecular weight (*M_n*) of NDI-P3HT was calculated to be 4.5 kDa, which was lower than that (6.6 kDa) determined by size exclusion chromatography (SEC), probably due to the overestimation for SEC (Table 1). The MALDI-TOF spectrum of the product was presented in Figure S2 (Supporting Information). As can be seen, there are two major series of P3HTs: Br/H (homo-P3HT with Br and H chain ends) and NDI/H₂ (P3HT with a NDI core and two H chain ends). The result indicates that NDI-Br₂ can initiate the polymerization of P3HT, although the initiation efficiency is not high. Nevertheless, the application of the Ni(COD)₂/PPh₃ catalyst system shows a comparable initiation efficiency to that of other complicated initiators such as methyl 4-bromobenzoate, 4-bromoanisole, and 4-bromo-chlorobenzene,³⁵ which encourages us to synthesize all-conjugated triblock copolymers by adopting this process.

Taking the above results into consideration, an *n*-type conjugated polymer, PNDITH-Br₂, was prepared via the Stille coupling reaction^{32,33} simply by controlling the feed molar ratio to be 10:9 for the monomers 1:2 (Scheme 1a). Thus, with 10% excess of 1, Br- α,ω -end-functional PNDITH could be prepared. The ¹H NMR spectrum of PNDITH-Br₂ presented in Figure 1A shows all the signals from thiophene units (*b*) and NDI units (*a*, *c*, *d*, and *e*). Moreover, the resonance signals of the aromatic

Table 1. Characterization Results of NDI-P3HT, PNDITH-Br₂, and PNDI-P3HT

entry	Ni ^a	Mon ^a	<i>M_n</i> ^b	PDI ^b	<i>M_n</i> ^c	weight ratio ^c	yield
	(equiv)	(equiv)	(kDa)		(kDa)	P3HT:PNDI	
NDI-P3HT	1.0	10	6.6	1.39	4.5		61
PNDITH-Br ₂			16.8	2.46	10.1		84
PNDI-P3HT1 ^d	1.3	65	26.4	1.15	22.5	1.2:1	83
PNDI-P3HT2 ^d	2.6	65	27.0	1.20	24.8	1.4:1	93
PNDI-P3HT3 ^d	2.6	130	33.7	1.29	40.5	3.0:1	90

^aAmount of Ni(COD)₂ or monomer 3 referring to Br active site in NDI-Br₂ or PNDITH-Br₂. ^bDetermined by SEC using THF as eluent at 40 °C. ^cCalculated from ¹H NMR. ^dThe number after each sample means different batches by varying the amount of catalyst or monomers.

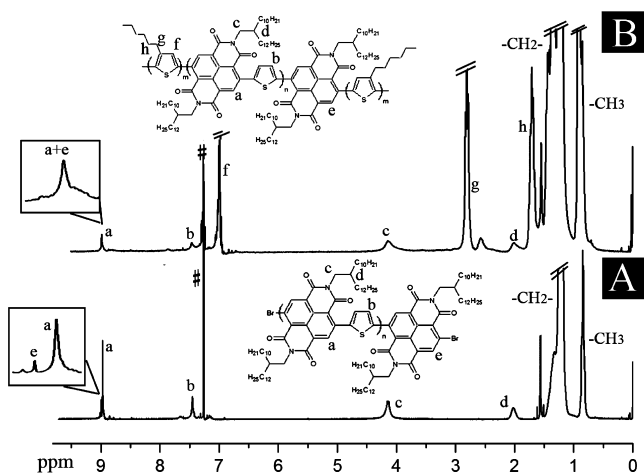


Figure 1. ^1H NMR spectra of (A) PNDITH- Br_2 and (B) PNDI-P3HT triblock copolymers.

protons on NDI units were split into two distinguished signals, as indicated by *a* and *e*, which correspond to the protons in the inner chain and the protons at the chain end, respectively. Thus, the M_n value of PNDITH- Br_2 could be calculated by comparing the integral area of peaks located at 8.99 ppm (*e*) and 8.97 ppm (*a*) (Figure 1A and Figure S3, Supporting Information). As summarized in Table 1, the M_n values of PNDITH- Br_2 were 10.1 and 16.8 kDa, as determined by ^1H NMR and SEC, respectively. The value determined by SEC was higher than that by ^1H NMR, which is consistent with the reported results on the conjugated polymer with rigid rod-like structure. The aggregation in THF may also result in an apparent large M_n value of these polymers by SEC (Figure S4, Supporting Information).^{32,33,36,37}

An ABA-type all-conjugated triblock copolymer was prepared via the same process as described in the model reaction (Scheme 1b). The only difference was the use of PNDITH- Br_2 as the macroinitiator instead of NDI- Br_2 . The composition of the product is illustrated in Table 1 as named PNDI-P3HT1. The ^1H NMR spectrum of the product is shown in Figure 1B.

As can be seen in Figure 1B, all the signals from PNDITH (*a–e*) and P3HT (*f* and *g*) could be identified, indicating that the block copolymer has been successfully synthesized. Furthermore, the two signals of aromatic protons on NDI units of PNDITH in the main chain and at the ends (*a* and *e* in Figure 1A) broadened and merged into a single peak in the product (*a + e* in Figure 1B), which demonstrated that the P3HT blocks were generated from the PNDITH chain ends so that the chemical environment of *a* and *e* became similar. By comparing the integral area of *f* from P3HT and *c* from PNDITH, the weight ratio of P3HT as well as M_n of the product can be determined. As shown in Table 1, the M_n of PNDI-P3HT1 determined by SEC was 26.4 kDa. The increase in M_n (from 16.8 to 26.4 kDa) and decrease of PDI from 2.46 of PNDITH- Br_2 to 1.15 of the product indicate that P3HT was successfully initiated by PNDITH- Br_2 . The significant decrease of PDI of the block copolymers was supposed to be the result of living nature of the KCTP process and a comprehensive decreasing of aggregation of the PNDITH block due to the introduction of P3HT segments. A more accurate M_n value of PNDI-P3HT1 was determined by ^1H NMR (22.5 kDa).

The SEC trace of PNDI-P3HT1 presented in Figure 2 shows a sharp and unimodal peak. It should be noted that the all-

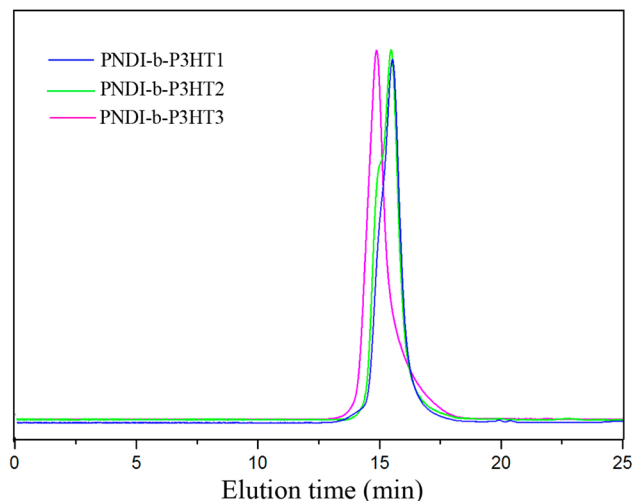


Figure 2. SEC curves of PNDI-P3HT block copolymers.

conjugated triblock copolymer prepared by the proposed initiation method possesses low polydispersity, regardless of using a broadly distributed *n*-type precursor which was obtained by the general polycondensation approach. According to the reported methods via opposite processes,^{28–31} P3HT with low PDI was first prepared, and then block copolymers were prepared by Stille, Suzuki, or Yamamoto coupling reactions, which resulted in the products with large PDIs of the products (in most cases PDI > 1.2).

It should be mentioned that PNDITH- Br_2 was transformed into the macroinitiator by adding Ni catalyst to oxidatively insert the Ni species to the C–Br chain end.^{25–27} Therefore, an excess amount of Ni catalyst toward Br end groups would be favorable for complete insertion. However, since the triblock copolymer was synthesized in a one-pot process (shown in Scheme 1) without any purification process, the excess amount of Ni catalyst might result in some side reactions. To deny this hypothesis, PNDI-P3HT2 was prepared via the same process as PNDI-P3HT1, in which the only difference was the use of a large excess amount of Ni catalyst (2.6 equiv) toward Br end groups. The ^1H NMR spectrum of PNDI-P3HT2 shown in Figure S5 (Supporting Information) is the same as that in Figure 1B, which indicates that the second block of P3HT has been successfully generated. Moreover, the disappearing of the peak *e* (Figure 1A) from the chain end of NDI suggests that the P3HT blocks were connected to the PNDITH blocks. Interestingly, the M_n of PNDI-P3HT2 determined by SEC is 27.0 kDa (Table 1), almost the same value as that of PNDI-P3HT1. The SEC trace of PNDI-P3HT2 (Figure 2) also shows a sharp and unimodal shape, and it is almost overlapped with that of PNDI-P3HT1, though a side peak appeared which possibly resulted from the quenching process.^{24–27,34} The M_n values of PNDI-P3HT2 and PNDI-P3HT1 determined by ^1H NMR (Table 1) are also nearly equal. These results demonstrate that the amount of Ni catalyst in use does not affect the molecular weight of the products unless the molar ratio of 3/PNDI-P3HT is changed.

This conclusion was further confirmed by another model reaction in which only the mixture of Ni(COD)₂ and PPh₃ was applied as initiator without any Br-functional compound (Scheme S1, Supporting Information). The ^1H NMR spectrum of the product presented in Figure S6 (Supporting Information) indicates that the product was P3HT. However,

the yield of P3HT was very low (ca. 10%). In addition, the SEC result (Figure S7, Supporting Information) indicates that extremely high M_n of P3HT was produced ($M_n = 72.9$ kDa, PDI = 1.78) even though the theoretical M_n of P3HT is 2.5 kDa (15 equiv of **3** to 1 equiv of Ni catalyst was used in this model reaction). The reason for the low yield and extremely high M_n and PDI of the product is not clear at the present time. However, according to the results reported by Luscombe et al.,³⁸ the excess Ni(COD)₂ might be transferred to Ni(dppp)₂, which has been noted to be unreactive.³⁹ Similarly, the results in this work demonstrate that the excess amount of Ni catalyst does not efficiently initiate the polymerization of homo-P3HT in the preparation of PNDI-P3HT₂; otherwise, the SEC curve of PNDI-P3HT₂ would not show such a sharp peak.

The molecular weight of these triblock copolymers synthesized via KCTP would be controlled simply by varying the amount of **3** to the Br-functional compound.^{20,21,25–27} In practice, the triblock copolymer, PNDI-P3HT₃, was prepared by increasing the amount of **3** from 65 equiv (PNDI-P3HT₁) to 130 equiv toward PNDIth-Br₂. The ¹H NMR spectrum of the product shown in Figure S8 (Supporting Information) indicates the successful preparation of the triblock copolymer. Interestingly, the SEC trace of the product illustrated in Figure 2 shows a unimodal sharp peak and an obvious decrease in elution time as compared to PNDI-P3HT₁ and **2**, which indicates that the M_n of PNDI-P3HT₃ is narrowly distributed (PDI = 1.29 in Table 1) and higher than that of PNDI-P3HT₁ and **2**. This result shows that the molecular weight of the triblock copolymers as well as the composition of P3HT can be tailored.

As a primitive study, the morphologies and crystalline properties of the block copolymer were investigated by TEM and grazing-incidence wide-angle X-ray scattering (GIWAXS). As shown in Figure 3A, P3HT domains are phase separated

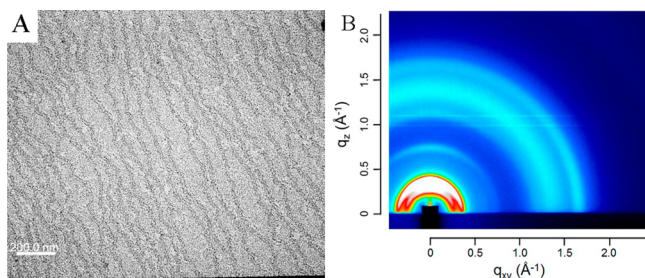


Figure 3. TEM (A) and 2D GIWAXS (B) images of thin film based on PNDI-P3HT₁.

from PNDI domains and form lamellar structure (dark region) in the range of 10–20 nm. This lamellar structure is stable even annealed at 150 °C for 1 h (see Figure S9, Supporting Information). The physical mixture of P3HT and PNDIth also shows a lamellar morphology; however, after annealing at 150 °C for 1 h, the lamellar structure was destroyed with forming large grains (Figure S9, Supporting Information). This result supports that the P3HT segments are chemically connected to the PNDI inner block. Regarding the GIWAXS result presented in Figure 3B and Figure S10 (Supporting Information), the strong P3HT (*h*00) diffractions at 16.8, 8.2, and 5.4 Å were observed in out-of-plane direction in addition to the diffraction of PNDI (100) at 23.0 Å. In the in-plane direction profile, there were two distinct P3HT (100) and PNDI (100) diffractions at 16.8 and 23.0 Å, respectively. The P3HT (010) diffraction was

also observed at 3.8 Å. The result indicates that there were two distinguished crystalline domains corresponding to PNDI and P3HT segments, in which P3HT aligns in the edge-on rich structure and PNDI isotropically dispersed. The crystal structure was further confirmed by DSC as shown in Figure S11 (Supporting Information), where two melting peaks can be identified at 173 and 219 °C, corresponding to the T_m s of P3HT and PNDI segments, respectively.

In summary, NDI-Br₂ was found to be an effective initiator for the externally initiated KCTP of P3HT, and a facile method was developed for synthesizing all-conjugated triblock copolymers comprising both *n*-type and *p*-type blocks. In the first step, a Br- α,ω -ends-functional *n*-type conjugated polymer was prepared via the Stille coupling reaction. A *p*-type block, P3HT, was then emanated via KCTP by using the *n*-type polymer with Br- α,ω -ends-functionality as the macroinitiator. The yields of the products were high, and the PDIs of all the samples were lower than 1.3, suggesting a good controlling feature of this method. Moreover, an excess amount of Ni catalyst can be used regardless of the one-pot process of addition of Ni species, ligand exchange to dppp, and polymerization of **3**. In addition, the molecular weights of the triblock copolymers or the content of P3HT can be controlled simply by varying the feed molar ratio of the thiophene monomer to the *n*-type precursors. The TEM and GIWAXS results indicated that P3HT and PNDI segments were phase separated, forming well-defined lamellar morphology and respective crystalline domains.

■ ASSOCIATED CONTENT

📄 Supporting Information

The detailed information of materials, characterizations, and synthesis. ¹H NMR spectra of PNDI-P3HT_{2/3} and PNDIth-Br₂. SEC traces of the products and morphology characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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