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Synthesis of a Rod-rod Diblock Copolymer, Poly(3-hexylthiophene)-block-poly(furfuryl isocyanate), through the Anionic Polymerization with an Oxyanionic Macroinitiator

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Abstract A rod-rod diblock copolymer (diBCP), poly(3-hexylthiophene)-block-poly(furfuryl isocyanate) (P3HT-*b*-PFIC), was synthesized through the anionic polymerization with an oxyanionic macroinitiator of P3HT. The properties of the diBCP (molecular weight, dispersity, composition, thermal stability, UV-visible absorption, and thin film morphology) were determined by various analytical methods. P3HT-*b*-PFIC was blended with C₆₀ in a toluene solution to prepare a thin film of binary electron donor/acceptor system. Such blending enabled partial conjugation of the two components by the Diels-Alder reaction between furan and C₆₀ at 60 °C for 3 h; the mixture was then spin-cast as a thin film, and annealed at 250 °C for 24 h. Tapping-mode atomic force microscopy (AFM) revealed that P3HT and C₆₀ domains had nanoscale interfaces without a large phase segregation. This result indicated that the microphase separation of C₆₀-functionalized P3HT-*b*-PFIC preserved even at high temperature provided free C₆₀ molecules with channels to diffuse on the sides of P3HT domain, thus preventing the macroscopic crystallization of free C₆₀ through the interfacial stabilization.

Keywords Rod-rod diblock copolymer; Poly(3-hexylthiophene)-block-poly(furfuryl isocyanate); C₆₀; Diels-Alder reaction; Nanoscale interfaces

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INTRODUCTION

The donor/acceptor bulk heterojunction (BHJ) of π -conjugated polymers and fullerene derivatives has been widely utilized for the solution-processed organic photovoltaics (OPVs).^[1–4] Thin film of rod-like poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) blend is the most classic type of BHJ-based active layers because of its good charge mobility, processability, and commercial availability.^[5–7] Since many OPVs using lower-bandgap materials (polymers or small molecules) and state-of-the-art fabrication techniques were developed to achieve higher PCE,^[8–12] the P3HT:PCBM-based OPVs have been the typical standard for comparison.

The interfacial morphology of polymer:fullerene blends largely affects the photovoltaic performance.^[13,14] Efficient exciton dissociation and charge transportation require a large interfacial area with a domain size close to the exciton diffusion length (~10 nm)^[15] and well-ordered nanostructures. Currently, the interpenetrating networks of polymer:fullerene

blends are obtained by applying the kinetic force of spin-casting.^[1–4] However, these bicontinuous phases are thermodynamically unstable as a result of the immiscibility of the two components.^[16] Therefore, a more stabilized interfacial morphology should be made by manipulating processing parameters. Many studies have used a variety of physical fabrication methods, such as solvent selection,^[17–19] employing additives,^[20–23] thermal annealing,^[24–26] and solvent annealing.^[27,28]

The self-assembly of block copolymers (BCPs) through microphase separation has been an effective method for realizing the highly ordered nanoscale morphology of binary phases.^[29] In particular, donor/acceptor BCPs, which are composed of π -conjugated polymer and fullerene-containing polymer, have been an alternative of unstable blending systems. The domain width and type of nanostructure (lamellae, cylinders, or spheres) can be controlled by tuning the molecular weight (MW) and composition ratio of the BCPs.^[30] Many donor/acceptor BCPs composed of P3HT and C₆₀-containing coil polymer have been utilized as active layers with nanoscale interfaces,^[31–33] or as compatibilizers to reduce the interfacial tension between P3HT and PCBM.^[34–36] Several groups have taken advantage of the rod-coil poly(3-hexylthiophene)-block-poly(4-vinylpyridine) for accumulation of PCBM in the coil domain^[37–39] through the non-covalent

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charge-transfer complexation between pyridine and C₆₀.^[40] All π -conjugated polythiophene BCPs containing C₆₀ have also been incorporated in the P3HT:C₆₀ blend to eliminate the efficiency drop attributed to the insulating coil block.^[41]

Although pure C₆₀ is cheap compared to PCBM, it has been hardly used as an electron acceptor due to its high crystallinity that brings in macroscopic segregation.^[42] If the diffusion pathway and crystallinity of C₆₀ are controlled by an adequately designed donor/acceptor material, C₆₀ can indeed replace PCBM. We anticipate that the Diels-Alder reaction^[43,44] is a suitable synthetic strategy for the OPV application, because the cycloaddition between a diene group and the dienophilic C₆₀ is feasible under mild conditions without an external catalyst. Most importantly, monomers containing highly reactive diene substituents, such as furan, are commercially available and polymerizable.^[45,46]

Interestingly, helical polymers have been employed as the counter blocks of polythiophenes.^[47–49] The list includes poly(*n*-hexyl isocyanate) (PHIC), a rod-like polymer with dynamic helical conformation and liquid crystalline properties.^[50–52] Stefan's group has prepared a rod-rod diblock copolymer (diBCP), poly(3-hexylthiophene)-block-poly(*n*-hexyl isocyanate) (P3HT-*b*-PHIC), and utilized it as an additive in the P3HT:PCBM-based OPVs.^[48] The microphase separation of this diBCP has been found to endow the microstructure of P3HT:PCBM blend with paths favorable for charge transport. We envisioned that the development of diBCP containing P3HT and C₆₀-functionalized polyisocyanate is advantageous to afford a highly cost-effective P3HT:C₆₀ active layer with nanoscale interfaces. Living anionic polymerization of isocyanates using a wide variety of initiators allows the preparation of polyisocyanates with side-chain functionalities as well as various molecular architectures.^[53–65] In particular, we have developed the living anionic polymerization of furfuryl isocyanate (FIC) to prepare well-defined poly(furfuryl isocyanate) (PFIC) capable of conjugating with C₆₀.^[57]

For the formation of nanoscale interfaces between P3HT and C₆₀, we herein report the synthesis of a rod-rod diBCP, poly(3-hexylthiophene)-*b*-poly(furfuryl isocyanate) (P3HT-*b*-PFIC). A hydroxyl-end-functionalized P3HT is prepared through the Grignard metathesis (GRIM) polymerization^[66,67] and employed as a macroinitiator in the anionic polymerization of FIC to afford the diBCP. We sequentially applied the Diels-Alder reaction and high-temperature thermal annealing to a P3HT-*b*-PFIC:C₆₀ blend to fabricate a donor/acceptor thin film with nanoscale interfaces.

EXPERIMENTAL

Materials

All reagents were purchased from several commercial suppliers (Sigma-Aldrich, TCI, Alfa Aesar, Fisher Scientific, etc.) and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from a sodium naphthalenide (NaNaph) solution under 1.33×10^{-4} Pa ($= 10^{-6}$ Torr). Furfuryl isocyanate (FIC) was distilled over calcium hydride (CaH₂) under reduced pressure and then

redistilled over CaH₂ under 1.33×10^{-4} Pa. Sodium tetraphenylborate (NaBPh₄) was dried under 1.33×10^{-4} Pa. All pure reagents to be employed in the break-seal method were diluted with THF and distributed in pure glass ampules equipped with break-seals under 1.33×10^{-4} Pa.

Instruments and Analyses

Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded using a JNM-ECX 400 NMR spectrometer (JEOL) in chloroform-*d* (CDCl₃, 99.8% atom D, contains 0.03 vol% tetramethylsilane (TMS)) at 25 °C. Number-average molecular weight (*M_n*) and dispersity (*D*) values of polymers were measured using a size exclusion chromatography-multiangle laser light scattering (SEC-MALLS) instrument equipped with a 515 HPLC pump (Waters), a set of four Styragel columns connected in series (HR 0.5, HR 1, HR 3, and HR 4 with pore sizes of 50, 100, 500, and 1000 Å, respectively, Waters), a miniDAWN TREOS light scattering detector (Wyatt Technology), and an Optilab T-REX refractive index detector (Wyatt Technology). The SEC-MALLS ran in THF: triethylamine (98:2, *V:V*) with an elution rate of 1.0 mL·min^{−1} at 40 °C. The refractive index increment (*dn/dc*) values of polymers were determined from the assumption of 100% mass recovery. Thermal properties were investigated using thermogravimetric analysis (TGA, TA Instrument TGA-Q50) and differential scanning calorimetry (DSC, TA Instrument DSC-Q20) with a heating rate of 10 °C·min^{−1} under an N₂ atmosphere. UV-visible absorption spectra were recorded on a UV-Vis spectrophotometer (K-MAC, Spectra-view-2000). Morphologies of the polymer thin films were investigated by transmission electron microscopy (TEM, Tecnai G2 S-Twin) and tapping-mode atomic force microscopy (AFM, Park Systems XE-100).

Synthesis of P3HT-OH

Hydroxyl-end-functionalized P3HT (P3HT-OH) was synthesized according to a two-step procedure reported in the literature.^[68] In a flame-dried 250 mL two-neck flask, 2,5-dibromo-3-hexylthiophene (5.0 g, 15.4 mmol) was dissolved in THF (100 mL), and the solution was stirred under N₂. A 2.0 mol·L^{−1} solution of isopropylmagnesium chloride in diethyl ether (10 mL, 20 mmol) was then added *via* a syringe, and the mixture was stirred with refluxing for 60 min. The mixture was cooled to room temperature and Ni(dppp)Cl₂ (0.54 g, 0.1 mmol) was added to the mixture to induce polymerization. After polymerization for 1 h, a 1.0 mol·L^{−1} solution of vinylmagnesium chloride in THF (3 mL, 3 mmol) was added to the reaction mixture, and the mixture was stirred for 1 h. The reaction was completely quenched by adding methanol and then it was poured into a large amount of methanol to precipitate the polymer. The filtered polymer was purified by sequential Soxhlet extractions with methanol, hexane, and chloroform. Vinyl-terminated P3HT was isolated by precipitation in a large amount of methanol, filtration, and drying under vacuum.

Vinyl-terminated P3HT. Yield: 1.30 g (50%). *M_n* = 5.0 kDa, *D* = 1.50. ¹H-NMR (CDCl₃ with 0.03 vol% TMS, 400 MHz, δ , ppm): 6.98 (s, mH, Th), 6.61 (m, 2H, $-\text{CH}_2=\text{CH}_2$), 5.66, 5.19 (m, 2H, $-\text{CH}_2=\text{CH}_2$), 2.80 (t, *J* =

7.6 Hz, 2 mH, ThCH_2-), 1.69 (m, 2 mH, $\text{ThCH}_2\text{CH}_2-$), 1.48–1.24 (m, 6 mH, $-(\text{CH}_2)_3\text{CH}_3$), 0.91 (t, $J = 6.8$ Hz, 3 mH, $-\text{CH}_3$).

In a flame-dried 250 mL two-neck flask, vinyl-terminated P3HT (0.75 g, 0.15 mmol) was dissolved in THF (50 mL), and the solution was stirred under N_2 . A $0.5 \text{ mol}\cdot\text{L}^{-1}$ solution of 9-borabicyclo[3.3.1]nonane in THF (1.5 mL, 0.75 mmol) was added to the solution *via* a syringe, and the mixture was stirred at 40°C for 24 h. After stirring, a $6.0 \text{ mol}\cdot\text{L}^{-1}$ aqueous solution of NaOH (0.5 mL, 3.0 mmol) was added to the reaction mixture, followed by stirring for 15 min. After cooled to room temperature, the mixture was added with a 33 wt% aqueous solution of H_2O_2 (0.5 mL) and stirred at 40°C for 24 h. After the mixture was cooled to room temperature again, P3HT-OH was isolated by precipitation in a large amount of methanol:water, filtration, and drying under vacuum. The product was dried under 1.33×10^{-4} Pa, appropriately diluted with THF, and stored in pure glass ampules equipped with break-seals under 1.33×10^{-4} Pa.

P3HT-OH. Yield: 0.720 g (96%). $M_n = 5.0$ kDa, $\bar{D} = 1.50$. $^1\text{H-NMR}$ (CDCl_3 with 0.03 vol% TMS, 400 MHz, δ , ppm): 6.98 (s, mH, Th), 3.50 (t, $J = 8.0$ Hz, 2H, $-\text{CH}_2\text{OH}$), 2.80 (t, $J = 7.6$ Hz, 2 mH, ThCH_2-), 1.69 (m, 2 mH, $\text{ThCH}_2\text{CH}_2-$), 1.48–1.24 (m, 6 mH, $-(\text{CH}_2)_3\text{CH}_3$), 0.91 (t, $J = 6.8$ Hz, 3 mH, $-\text{CH}_3$).

Synthesis of P3HT-*b*-PFIC

Anionic polymerization was performed by using a break-seal technique under 1.33×10^{-4} Pa. The reactor was prewashed with a NaNaph solution in THF prior to the polymerization. A typical polymerization proceeded as follows. A NaNaph solution (2.6 mg, 0.017 mmol) in THF (5.2 mL) was transferred into a reaction flask. A solution of P3HT-OH (85 mg, 0.017 mmol) in THF (25.3 mL) was slowly added to the NaNaph solution at room temperature, and the solution was kept for 30 min to let P3HT-OH convert into the P3HT macroinitiator, P3HT-ONa. A solution of NaBPh₄ (74 mg, 0.215 mmol) in THF (5.1 mL) was then added to the macroinitiator solution and the solution was cooled to -98°C . Polymerization was performed by mixing a solution of FIC (169 mg, 1.37 mmol) in THF (6.1 mL) with the macroinitiator solution for 20 min. The reaction was terminated by adding a solution of HCl:methanol in THF. P3HT-*b*-PFIC was isolated by precipitation in a large amount of methanol, filtration, and drying under vacuum.

P3HT-*b*-PFIC. Yield: 0.253 g (~100%). $M_n = 12$ kDa, $\bar{D} = 1.55$. $^1\text{H-NMR}$ (CDCl_3 with 0.03 vol% TMS, 400 MHz, δ , ppm): 7.22 (s, nH, $-\text{OCH}-$), 6.98 (s, mH, Th), 6.20 (s, nH, $-\text{OCH}=\text{CH}-$), 6.04 (s, nH, $-\text{OC}=\text{CH}-$), 4.80 (br, 2nH, $-\text{NCH}_2-$), 3.82 (m, 2H, $-\text{CH}_2\text{O}-$), 2.80 (t, $J = 7.6$ Hz, 2 mH, ThCH_2), 1.69 (m, 2 mH, $\text{ThCH}_2\text{CH}_2-$), 1.48–1.24 (m, 6 mH, $-(\text{CH}_2)_3\text{CH}_3$), 0.91 (3 mH, $-\text{CH}_3$).

Sample Preparation for TEM and AFM Analyses

A TEM sample of a P3HT-*b*-PFIC thin film was prepared by drop-casting from a polymer solution (1 mg/mL in toluene) on a copper grid and drying under reduced pressure at room temperature for 24 h. The PFIC phase was selectively stained

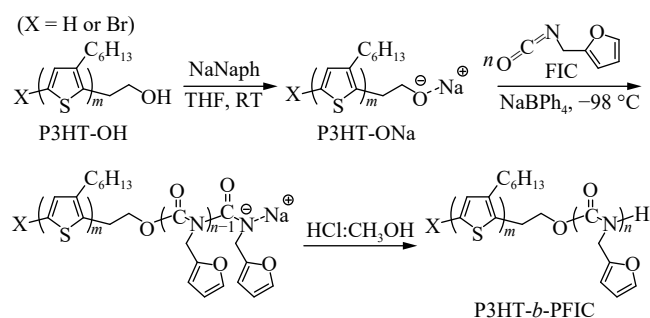
with iodine vapor for 8 h.

The thin film sample for AFM study was prepared as follows. A $1 \text{ mg}\cdot\text{mL}^{-1}$ solution of P3HT-*b*-PFIC:C₆₀ blend (1:1, *W:W*) in toluene was stirred at 60°C for 3 h to induce the Diels-Alder reaction between furan group and C₆₀. The resulting blend was spin-cast on a silicon wafer substrate at $1000 \text{ r}\cdot\text{min}^{-1}$, and the film obtained was thermally annealed at 250°C for 24 h for the self-assembly of the blend.

RESULTS AND DISCUSSION

Synthesis of P3HT-*b*-PFIC

The initiation using an end-functionalized homopolymer is frequently used to obtain BCPs when two types of incompatible polymerization methods are required. As proposed by McCullough and Yokozawa, the catalyst-transferred GRIM polymerization for the synthesis of P3HT mimics the chain-growth mechanism,^[66,67] which allows for the preparation of end-functionalized P3HTs.^[69,70] On the other hand, polyisocyanates can be synthesized by anionic polymerization using a wide range of nucleophilic initiators.^[55,58,59,64,65] We attempted to synthesize P3HT-*b*-PFIC using an oxyanionic macroinitiator of P3HT (Scheme 1).



Scheme 1 Synthesis of P3HT-*b*-PFIC

As a precursor of the macroinitiator, P3HT-OH ($M_n = 5.0$ kDa, $\bar{D} = 1.50$) was prepared according to a previously established method.^[68] Although the obtained P3HT-OH is known to include either a hydrogen or a bromo group at the chain end, the adverse effect on the anionic polymerization of FIC was expected to be negligible because of high tolerance of oxyanion to these groups. The stoichiometric reaction of P3HT-OH with NaNaph generated an oxyanionic macroinitiator, P3HT-ONa. The block copolymerization was performed by the anionic polymerization of FIC initiated by P3HT-ONa in THF at -98°C . If necessary, NaBPh₄ was added into the macroinitiator solution prior to polymerization.

When the anionic polymerization of FIC initiated by P3HT-ONa was performed in the absence of NaBPh₄, no BCP was obtained. The SEC curve of the isolated polymer was exactly the same as that of P3HT-OH. $^1\text{H-NMR}$ analysis confirmed that the isolated polymer was the P3HT homopolymer and all FIC monomers were included in the methanol-soluble residues. When the macroinitiator solution was once again cooled to -98°C , a color change of the solution from red to dark brown was observed, indicating the aggregation of macroinitiator chains. In fact, most previous reports

on the polymerization with vinyl monomers using anionic macroinitiators of P3HT in THF at $-78\text{ }^{\circ}\text{C}$ have shown the incomplete initiation due to partially aggregated macroinitiator chains.^[71,72] In our case, the temperature of $-98\text{ }^{\circ}\text{C}$ appeared to preclude the initiation of P3HT-ONa.

To prevent the aggregation of macroinitiators at $-98\text{ }^{\circ}\text{C}$, adding NaBPh_4 was considered. The highly dissociating ion salt has been used in the anionic polymerization of *n*-hexyl isocyanate.^[54,56,62–65] NaBPh_4 induces the equilibrium shift of free ions to ion pairs, which results in relatively fast initiation.^[64,65] In addition, NaBPh_4 sometimes breaks the self-associated structure of the initiator, which increases the initiation efficiency.^[65]

The anionic polymerization was performed in the presence of NaBPh_4 ($[\text{NaBPh}_4]_0/[\text{P3HT-ONa}]_0 = 12.6$). The results revealed that NaBPh_4 effectively prevented the self-association of macroinitiators in THF at $-98\text{ }^{\circ}\text{C}$. Consequently, the conversion of FIC reached nearly 100% within 20 min and no remaining monomers and trimers were observed in the $^1\text{H-NMR}$ spectrum of methanol-soluble residues. The fraction of P3HT in P3HT-*b*-PFIC (f_{P3HT}) was determined to be 34 wt%. The M_n value of P3HT-*b*-PFIC (12 kDa) determined by SEC-MALLS was in moderate agreement with the theoretical M_n value ($M_{n,\text{theo}} = 15\text{ kDa}$). P3HT-*b*-PFIC also maintained its dispersity ($\bar{D} = 1.55$) close to the original dispersity of P3HT-OH.

The conversion of P3HT-OH to P3HT-*b*-PFIC was confirmed by $^1\text{H-NMR}$ spectroscopy (Fig. 1). In the $^1\text{H-NMR}$ spectra of P3HT-OH and P3HT-*b*-PFIC, a proton resonance corresponding to the methylene group beside the hydroxyl group of P3HT-OH shifted from 3.50 ppm to 3.82 ppm after block copolymerization. This downfield shift is characteristic of deshielding of the methylene protons, which is attributed to the carbamate interlinkage generated by the initiation of P3HT-ONa. The composition of P3HT-*b*-PFIC was also determined from the integral ratio between two proton reson-

ances corresponding to the α -methylene groups of the repeating units.

The change in MW after block copolymerization was verified in the SEC-dRI traces (Fig. 2). The SEC-dRI traces of P3HT-OH and P3HT-*b*-PFIC showed a shift to a higher MW region, indicating the chain extension through the oxyanionic initiation of P3HT-ONa. The distribution shape was nearly maintained after block copolymerization. However, a minor trace at the low MW region was observed, because a small amount of macroinitiators remained unreacted. However, we considered the fraction was not serious for the self-assembly of BCP.

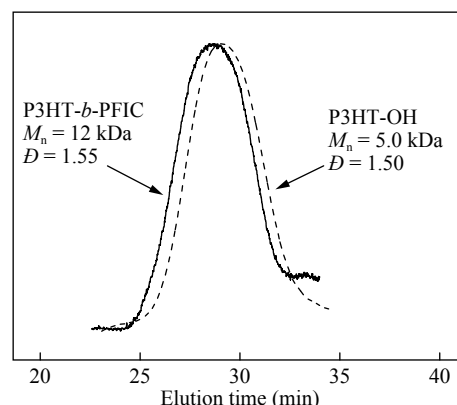


Fig. 2 SEC-dRI traces of P3HT-OH ($M_n = 5.0\text{ kDa}$, $\bar{D} = 1.50$) and P3HT-*b*-PFIC ($M_n = 12\text{ kDa}$, $\bar{D} = 1.55$, $f_{\text{P3HT}} = 34\text{ wt\%}$) in THF

Thermal, Optical, and Morphological Properties of P3HT-*b*-PFIC

Thermogravimetric analysis at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under N_2 atmosphere was implemented to identify the thermal stability and composition ratio of P3HT-*b*-PFIC (Fig. 3a). The decomposition temperature corresponding to the initial 5 wt% loss ($T_{d,5\text{wt\%}}$) for the PFIC homopolymer was $215\text{ }^{\circ}\text{C}$ and a drastic weight loss continued up to $330\text{ }^{\circ}\text{C}$. It is known that the thermal decomposition of polyisocyanates begins at relatively low temperatures and mainly produces cyclotrimers as a result of intramolecular backbiting from the chain end due to the thermodynamic instability of amide backbone.^[73,74] On the other hand, P3HT-OH exhibited higher thermal stability with a $T_{d,5\text{wt\%}}$ of $422\text{ }^{\circ}\text{C}$ and a weight loss continuing up to $525\text{ }^{\circ}\text{C}$. The TGA thermodiagram of P3HT-*b*-PFIC showed a two-stage weight loss, indicating different decomposition features of the two blocks. The PFIC block was first degraded in the range of $210\text{--}345\text{ }^{\circ}\text{C}$, and the decomposition of P3HT block subsequently proceeded at temperatures above $440\text{ }^{\circ}\text{C}$. DSC analysis was also implemented on the second heating cycle at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under N_2 atmosphere (Fig. 3b). The DSC thermogram of P3HT-*b*-PFIC showed one glass transition temperature ($T_g = 104\text{ }^{\circ}\text{C}$) that originated from the T_g of P3HT.^[4] The T_g of the PFIC block was not observed due to its rigid main chain.

The UV-visible absorption spectra of P3HT-OH and P3HT-*b*-PFIC thin films showed π - π^* transitions of P3HT segments in the solid state before and after block copolymer-

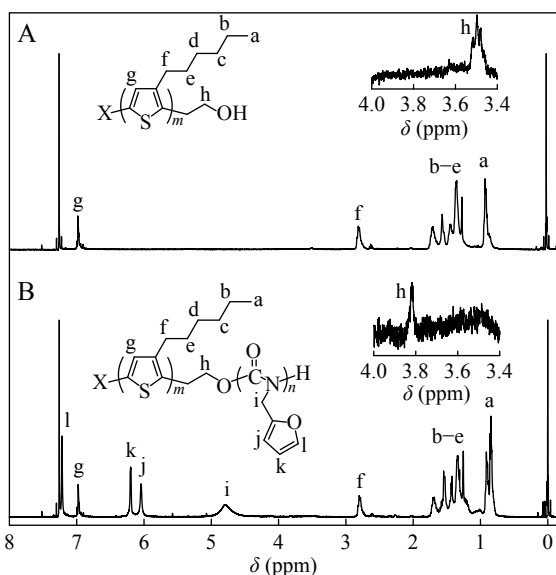


Fig. 1 $^1\text{H-NMR}$ spectra of (A) P3HT-OH ($M_n = 5.0\text{ kDa}$, $\bar{D} = 1.50$) and (B) P3HT-*b*-PFIC ($M_n = 12\text{ kDa}$, $\bar{D} = 1.55$, $f_{\text{P3HT}} = 34\text{ wt\%}$) in CDCl_3

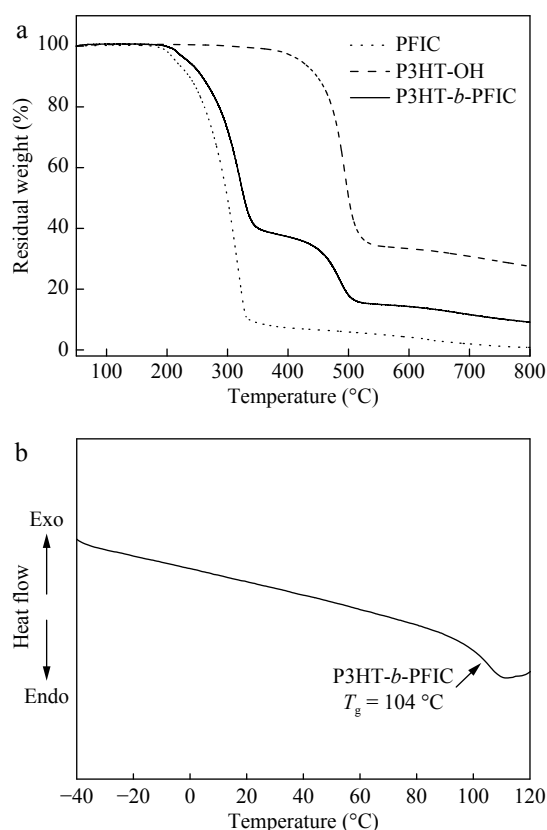


Fig. 3 (a) TGA thermograms of PFIC, P3HT-OH, and P3HT-*b*-PFIC and (b) DSC thermogram of P3HT-*b*-PFIC on the second heating cycle at a heating rate of 10 °C·min⁻¹ under N₂

ization (Fig. 4). The absorption spectrum of P3HT-*b*-PFIC was similar to that of P3HT-OH, and the absorption edges of both polymers were fixed at 660 nm, indicating that the conjugation length of P3HT block was not affected by the PFIC block. The weak absorption shoulders observed at 615 nm in both P3HT-OH and P3HT-*b*-PFIC indicate that the interchain interaction of P3HT was still preserved after block copolymerization.^[41] The wavelengths of the absorption maxima of P3HT-OH and P3HT-*b*-PFIC were determined to be 503 and 494 nm, respectively. A slight blue-shift of the absorption spectrum for P3HT-*b*-PFIC might result from the change of

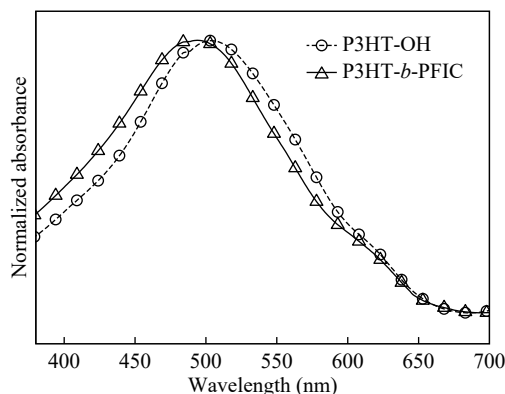


Fig. 4 Normalized UV-visible absorption spectra of P3HT-OH and P3HT-*b*-PFIC thin films

the π - π stacking distance of P3HT due to helical conformation of PFIC.

TEM analysis of the P3HT-*b*-PFIC thin film was conducted to identify its morphology and domain scale (Fig. 5). The sample prepared by drop-casting from a 1 mg·mL⁻¹ toluene solution on a copper grid was dried under vacuum and stained with iodine vapor to increase the contrast between the two phases. In the TEM micrograph, the bright and dark regions correspond to the P3HT and PFIC domains, respectively. The diBCP self-assembled into microphase-separated nanostructures with a periodicity (*D*) of 12.5 nm, which differ from the nanofibrillar structures typically observed in the thin films of P3HT homopolymer.^[4] The nanostructure of the diBCP is attributed to the interchain interaction of PFIC, which is strong enough to achieve a balance with the π - π interchain interaction of P3HT.

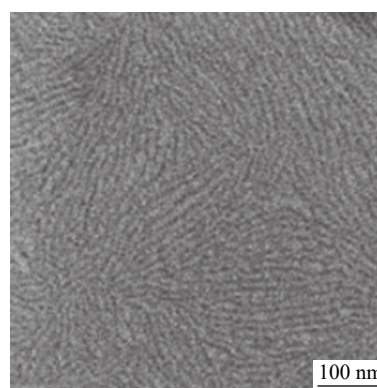


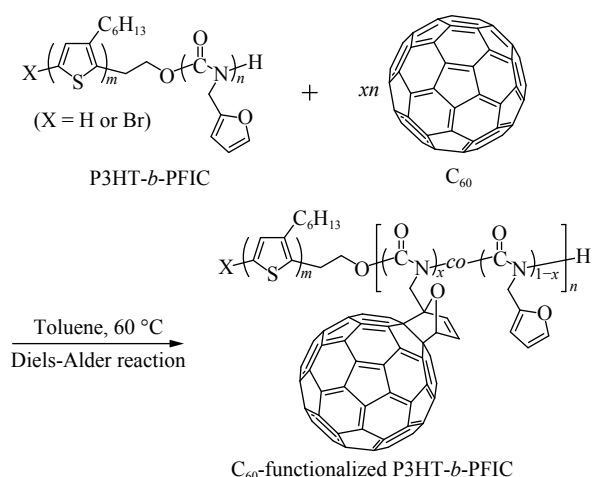
Fig. 5 TEM micrograph of P3HT-*b*-PFIC thin film stained with iodine vapor

Effect of Diels-Alder Reaction and Thermal Annealing on the Thin Film Morphology of P3HT-*b*-PFIC:C₆₀ Blend

To obtain the morphology with nanoscale donor/acceptor interfaces using P3HT-*b*-PFIC, we utilized the Diels-Alder reaction and post thermal annealing. The partial functionalization of diBCP by C₆₀ through Diels-Alder reaction was expected to reduce the interfacial tension between diBCP and C₆₀ in the blend thin film. It was also expected that sufficient thermal annealing at high temperature allows the remaining unreacted C₆₀ molecules to diffuse and fill into the PFIC domain. A major concern was the large phase segregation caused by independent crystallization of P3HT and C₆₀ under thermal treatment.^[42]

The Diels-Alder reaction was attempted in a 1 mg·mL⁻¹ solution of P3HT-*b*-PFIC:C₆₀ blend (1:1, *W:W*) in toluene at 60 °C with stirring (Scheme 2). After 6 h, a brown precipitate appeared on the surface of the magnetic stirrer. This precipitate was not rinsed from the stirrer with toluene. When diBCP and C₆₀ were left separately in the toluene solutions with stirring at the same temperature, no precipitate was observed on the stirrer. The insoluble precipitate generated from the P3HT-*b*-PFIC:C₆₀ blend was assumed to be cross-link products. To avoid crosslinking, the blend solution was stirred at 60 °C for only 3 h.

The C₆₀-functionalized P3HT-*b*-PFIC:free C₆₀ blend was



Scheme 2 Diels-Alder reaction between P3HT-*b*-PFIC and C₆₀

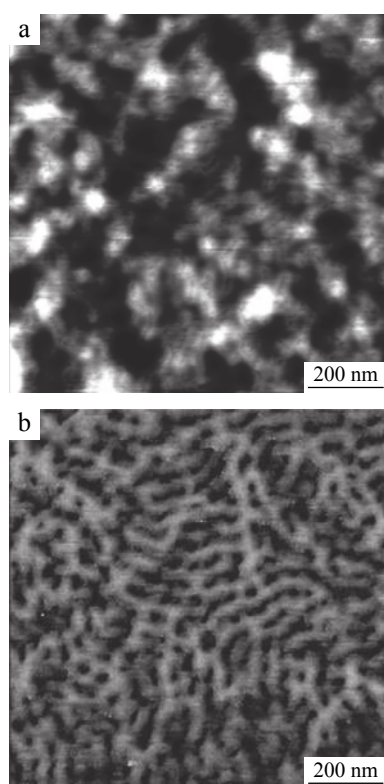


Fig. 6 AFM (a) height and (b) phase micrographs of C₆₀-functionalized P3HT-*b*-PFIC:C₆₀ (1:1, *W:W*) blend thin film after thermal annealing at 250 °C for 24 h

spin-cast on a silicon wafer substrate and annealed at 250 °C for 24 h for the self-assembly. The morphology of the resulting film was confirmed by tapping-mode AFM (Fig. 6). The thin film exhibited the disordered arrangement of C₆₀ domain (dark region) with a domain width of 15 nm and a pitch of 30 nm. Noticeably, the macroscopic phase segregation between P3HT and C₆₀ did not occur during long-term thermal treatment.

Thermal annealing at 250 °C was considered to provide a sufficient driving force for the self-assembly of C₆₀-functionalized P3HT-*b*-PFIC and free C₆₀. During this process, the

C₆₀-functionalized PFIC domain would be the channel for the diffusion of free C₆₀ molecules due to their intermolecular attraction between each other. If the free C₆₀ molecules were completely located at the C₆₀-functionalized PFIC domain, the scale of the crystalline domain formed by slow cooling would be confined into the domain width of C₆₀-functionalized PFIC. This would be attributed to the strong microphase separation of C₆₀-functionalized P3HT-*b*-PFIC preserved even at 250 °C and the resultant interfacial stabilization of P3HT and C₆₀ phases.

Thermal annealing at 250 °C may cause the reverse of Diels-Alder reaction. Even though this process is basically not safe for the C₆₀-functionalized P3HT-*b*-PFIC, the C₆₀ molecules left from the PFIC block would still be captured in their original places maintaining the nanoscale domain width, as the macroscopic crystallization of C₆₀ would be hindered by the neighboring P3HT domain. Another possible effect of this temperature is the partial removal of the PFIC block through thermal decomposition. We believe that this effect would be rather useful to generate the channels for diffusion of free C₆₀.

CONCLUSIONS

We synthesized a rod-rod diBCP, P3HT-*b*-PFIC. The anionic polymerization of FIC using an oxyanionic macroinitiator of P3HT in the presence of NaBPh₄ was found to be feasible for the block copolymerization even at extremely low temperature. The Diels-Alder reaction of P3HT-*b*-PFIC:C₆₀ blend generated partially C₆₀-functionalized P3HT-*b*-PFIC as a donor/acceptor diBCP. High-temperature thermal annealing was applied in the fabrication of thin film comprising C₆₀-functionalized P3HT-*b*-PFIC:free C₆₀ blend for the self-assembly of the two components. This process allowed the C₆₀-functionalized P3HT-*b*-PFIC to play two major roles in providing the channels for diffusion of free C₆₀ and stabilizing the interfaces between P3HT and C₆₀ phases. Our study proposes a new strategy for the formation of a nanoscale donor/acceptor interfacial morphology. This technique also capitalizes on the availability of cost-effective C₆₀ replacing PCBM. The elaborate molecular design (MW and composition) and in-depth morphological characterization will prove a direct correlation between the self-assembly mechanism and its contribution to cell performance in OPVs.

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