

## INVITED ARTICLE

# Synthesis of block copolymers consisting of poly(3-hexylthiophene) and polystyrene segments through ionic interaction and their self-assembly behavior

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A series of well-defined aniline-chain-end-functionalized regioregular poly(3-hexylthiophene)s (P3HT-NH<sub>2</sub>) have been successfully synthesized on the basis of Grignard metathesis polymerization. The molecular weights of P3HT-NH<sub>2</sub> could be varied from 1960 to 28 000 g mol<sup>-1</sup>, with low polydispersity indices in the range of 1.06–1.29, as determined by gel permeation chromatography. The selectivity of monofunctionalization reactions and the high degrees of amine functionality (85–92%) were confirmed by Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy. Block copolymers through ionic interaction were successfully synthesized by simply blending P3HT-NH<sub>2</sub> with carboxy chain-end-functionalized polystyrene, which was prepared on the basis of living anionic polymerization. The thermal and optical properties of block copolymers were investigated by differential scanning calorimetry, Thermogravimetric analysis and UV-vis spectroscopy. The self-assembly behavior of the polymer was investigated by atomic force microscopy and grazing incidence X-ray scattering.

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**Keywords:** amine; carboxy; chain-end-functionalized polymer; ionic interaction; poly(3-hexylthiophene); polystyrene

## INTRODUCTION

Block copolymers consisting of stiff-rod and flexible-coil segments, referred to as ‘rod-coil block copolymers’, have been of great interest because of their specific properties, unexpected behavior and hierarchical nanostructures by self-assembly, as reported in several papers.<sup>1–6</sup> In particular, rod-coil block copolymers, based on  $\pi$ -conjugated rods such as poly(3-hexylthiophene) and poly(phenylene vinylene), have received much attention because of their prompt application to a wide variety of optoelectric devices.

Since Iovu *et al.*<sup>7</sup> discovered the quasi-living Grignard metathesis polymerization system for regioregular poly(3-hexylthiophene) (P3HT), followed by the improvement by Miyakoshi *et al.*,<sup>8</sup> various block copolymers containing P3HT segments with relatively low polydispersity indices (PDIs) have been synthesized. Among them are some successful examples of AB-type rod-coil diblock copolymers, for instance, P3HT-*b*-poly(methyl acrylate),<sup>9</sup> P3HT-*b*-polystyrene

(PS),<sup>10</sup> P3HT-*b*-polyisoprene,<sup>10</sup> poly(alkylthiophene)-*b*-polylactide<sup>11</sup> and P3HT-*b*-poly(2-vinylpyridine) (P2VP).<sup>12</sup> Recently, our group reported new ABA-type coil-rod-coil triblock copolymers of PS-*b*-P3HT-*b*-PS<sup>13</sup> and PMMA-*b*-P3HT-*b*-PMMA.<sup>14</sup> In addition, attractive block copolymers comprised of donor-acceptor segments have emerged, in which rod and coil segments correspond to P3HT and fullerene-substituted PS<sup>15</sup> or PMMA,<sup>16</sup> respectively. New block copolymers bearing P3HT and poly(meth)acrylate substituted with perylene bisimide have also been developed.<sup>17,18</sup>

Nano-ordered microphase separation has been found in a rod-coil block copolymer film, similar to a conventional coil-coil block copolymer, induced by spontaneous self-assembly of each immiscible segment in which domains rich in one block are separated from domains rich in the other so as to minimize contact energy. Indeed, Iovu *et al.* observed the nanofibril structures of P3HT-*b*-PS,<sup>10</sup> P3HT-*b*-polyisoprene<sup>10</sup> and P3HT-*b*-poly(methyl acrylate)<sup>19</sup> by atomic force

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microscope (AFM). Similar morphologies were also observed from PS-*b*-P3HT-*b*-PS and PMMA-*b*-P3HT-*b*-PMMA triblock copolymers.<sup>13,14</sup> Recently, Dai *et al.*<sup>12</sup> reported clear sphere, cylinder and lamellar structures of a P3HT-*b*-P2VP film, depending on composition.

Although these studies using covalently bonded block copolymers are currently very competitive, a blend system of well-defined chain-end-functionalized polymers to achieve similar nanostructures has scarcely been focused on yet. The advantages of using such a blend system are as follows: (1) more facile synthetic approaches are available for chain-end-functionalized polymers than for block copolymers, thus being preferred for industry; (2) the combination of block segments is versatile without the component limitations seen in covalently bonded block copolymers; (3) there is a possibility of creating nano-porous films by removing one of the segments with a selective solvent after cleaving the ionic bonds under acidic or alkaline conditions.

Tessié *et al.*<sup>20,21</sup> investigated the ionic interaction between amino-chain-end-functionalized PS and carboxy-chain-end-functionalized polybutadiene. The ionic interactions of the polymer termini resulted in the formation of a multiblock copolymer, which was confirmed by infrared spectroscopy and differential scanning calorimetry (DSC) measurements. Russell *et al.*<sup>22</sup> reported that a microphase-separated structure was promoted by coulombic interaction between chain-end groups in similar systems. Iwasaki *et al.*<sup>23</sup> demonstrated a direct visualization of nano-ordered morphologies by transmission electron microscopy and scanning electron micrography, derived from blends of  $\alpha,\omega$ -diamino-functionalized PS and  $\alpha,\omega$ -dicarboxy-functionalized poly(ethylene oxide). Pispas *et al.*<sup>24</sup> reported the synthesis of star-branched polymers through an ionic interaction between chain-end-functionalized PS with three dimethylamino groups and chain-end-functionalized polyisoprene with a sulfonic acid group.

In the course of these studies, only conventional polymers were used and the above-mentioned  $\pi$ -conjugated polymers have not ever been used. Recently, Hirao *et al.*<sup>25,26</sup> reported the synthesis of block and star-branched copolymers consisting of  $\pi$ -conjugated polyacetylene segments through ionic interaction. They used blends between chain-end- or in-chain-functionalized PSs with carboxy groups and chain-end- or in-chain-functionalized poly(phenyl vinyl sulfone)s with dimethylamino groups, which were transformed into polyacetylenes by a thermal treatment eliminating sulfenic acids. However, the insolubility of the resulting material seems to be problematic for practical device application.

In this study, we demonstrate the first example of soluble P3HT-based block copolymers through ionic interaction, (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH), prepared by blending aniline-chain-end-functionalized P3HT (P3HT-NH<sub>2</sub>) and carboxy-chain-end-functionalized PS (PS-COOH). As both polymers possess predictable molecular weights ( $M_{WS}$ ) and low PDIs, well-defined self-organizing nano-structures could be expected from their blend films.

## EXPERIMENTAL PROCEDURE

### Materials

All chemicals (>98%) were purchased from Sigma-Aldrich Japan K. K. (Tokyo, Japan) and used as received unless otherwise stated. Tetrahydrofuran (THF) was refluxed over sodium benzophenone for 12 h and then distilled. 2-Bromo-3-hexyl-5-iodobenzene<sup>27</sup> and PS-COOH<sup>28</sup> were prepared according to the previous paper.

### Synthesis of regioregular P3HT-NH<sub>2</sub>

The representative synthetic procedure is described as follows. In a three-neck 30 ml flask, lithium chloride (0.211 g, 4.97 mmol) was placed and dried at

150 °C for 30 min. After cooling to room temperature and purging with dry nitrogen, freshly distilled 2-bromo-3-hexyl-5-iodobenzene (0.538 g, 1.44 mmol) was charged and pumped up for 15 min. After purging again with dry nitrogen, dry THF (15 ml) was added and cooled to 0 °C for 30 min with stirring. A THF solution of isopropylmagnesium chloride (<sup>i</sup>PrMgCl, 2 M  $\times$  0.790 ml = 1.58 mmol) was then added and kept at 0 °C for an additional 30 min to prepare the monomer, 2-bromo-5-chloromagnesio-3-hexylthiophene. In a separate three-neck 10 ml flask, diphenylphosphinopropanenickel(II) dichloride (Ni(dppp)Cl<sub>2</sub>, 43 mg, 0.0793 mmol) was charged and pumped up for 15 min with stirring and purged with dry nitrogen. Dry THF (5 ml) was then added to prepare the suspension solution of Ni(dppp)Cl<sub>2</sub>. This solution was added to the monomer solution immediately with vigorous stirring adjusted to 700 r.p.m. at room temperature. After polymerization for 10 min, a THF solution of 3-[bis(trimethylsilyl)amino]phenylmagnesium chloride (3, 1 M  $\times$  1.5 ml = 1.5 mmol) was added and stirred for 10 min, followed by quenching with 5N-HCl (2 ml). The mixture solution was poured into water/methanol (3/7, v/v, 200 ml) to precipitate the polymer. Soxhlet extraction was performed using methanol, acetone and chloroform. A chloroform solution of the polymer was then washed with Na<sub>2</sub>CO<sub>3</sub> aqueous three times and poured again into water/methanol (3/7, v/v, 200 ml) to precipitate the polymer. It was finally freeze-dried using benzene solution to afford regioregular P3HT-NH<sub>2</sub>. Monomer conversion: 96%; isolation yield: 182 mg, 76%;  $M_n$ : 3 700; PDI: 1.29; regioregularity: 95%; aniline functionality: 90%.

### Synthesis of (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH)

In a typical experiment, an equimolar of P3HT-NH<sub>2</sub> ( $M_n$ : 5520, PDI: 1.13, 2.37 mg,  $4.29 \times 10^{-4}$  mmol) and PS-COOH ( $M_n$ : 17800, PDI: 1.04, 7.63 mg,  $4.29 \times 10^{-4}$  mmol) was dissolved in toluene (5 ml) and slowly evaporated. For an AFM study, the (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) thin film was treated by thermal annealing at 120 °C for 24 h or by solvent annealing in a closed chamber exposed with toluene steam at room temperature for 3 h.

### Measurements

Molecular weights and PDIs were measured by gel permeation chromatography (GPC) on a Jasco GULLIVER 1500 (Jasco Corporation, Tokyo, Japan) equipped with a pump, an absorbance detector (ultraviolet,  $\lambda=254$  nm) and three PS gel columns by means of a conventional calibration curve using polystyrene standards. Chloroform was used as a carrier solvent at a flow rate of 1.0 ml min<sup>-1</sup> at room temperature. <sup>1</sup>H NMR was recorded on a Bruker DPX (300 MHz) (Bruker Biospin K. K., Kanagawa, Japan) in chloroform-*d* calibrated to tetramethylsilane as an internal standard ( $\delta$ H 0.00). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Shimadzu AXMA-CFR mass spectrometer (Shimadzu Corporation, Kyoto, Japan). The spectrometer was equipped with a nitrogen laser (337 nm) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV by linear-positive ion mode. A sample polymer solution of 10  $\mu$ l in THF (5 mg ml<sup>-1</sup>) and 100  $\mu$ l of the matrix 2,2':5'2''-terthiophene (Aldrich) solution in THF (75 mg ml<sup>-1</sup>) were mixed well. An aliquot of 1  $\mu$ l of the final solution was deposited onto a sample target plate and dried in air at room temperature. Mass values were calibrated by the three-point method with insulin plus H<sup>+</sup> at  $m/z$  5734.62, insulin- $\beta$  plus H<sup>+</sup> at  $m/z$  3497.96 and  $\alpha$ -cyanohydroxycinnamic acid dimmer plus H<sup>+</sup> at  $m/z$  379.35. Fourier transform-infrared spectra were measured by a Horiba FT-120 Fourier transform spectrophotometer (Horiba Ltd., Kyoto, Japan). DSC was performed with a Seiko EXSTAR 6000 DSC 6200 (Seiko Instruments Inc., Chiba, Japan). Samples were heated at 20 °C min<sup>-1</sup> under nitrogen and second thermograms were recorded. Calibrations were performed using indium as a standard. Thermogravimetric analysis (TGA) was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer (Seiko Instruments Inc.) at a heating rate of 10 °C min<sup>-1</sup>. UV-vis absorption spectra of a polymer solution in chloroform and a thin film were recorded on a Jasco FP-750 spectrometer over a wavelength range of 250–800 nm. AFM phase images were taken with a SIT-NT SPA 400 operating in tapping mode. Grazing incidence X-ray scattering (GIXS) experiments were carried out at 4C1 and 4C2 beamlines at the Pohang Accelerator Laboratory (PAL, Pohang University of Science and Technology, Pohang, Republic of Korea).<sup>29–33</sup> Samples were measured on a homemade  $z$ -axis goniometer

under vacuum condition, using a synchrotron X-ray radiation source of  $\lambda=0.138$  nm. Two-dimensional GIXS images were measured at a sample-to-detector distance of 126.6 mm using a two-dimensional charge-coupled device camera (Roper Scientific, Trenton, NJ, USA). The incidence angle  $\alpha_i$  of the X-ray beam was set at  $0.16^\circ$ .  $\alpha_i$ , as well as scattering angles in measurements, was corrected by using the positions of the reflected X-ray beam from silicon substrate and a precalibrated Silver Behenate as a standard sample. GIXS measurements were carried out at  $25^\circ\text{C}$ . Each measurement was determined for 120 s.

## RESULTS AND DISCUSSION

### Synthesis of regioregular P3HT-NH<sub>2</sub>

Iovu *et al.*<sup>7</sup> reported a quasi-living Grignard metathesis polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene initiated with Ni(dppp)Cl<sub>2</sub>, starting from 2,5-dibromo-3-hexylthiophene, which was treated with *tert*-butylmagnesium chloride by means of the Grignard exchange reaction. As a result, the obtained P3HTs possess low PDIs in the range of 1.1–1.4. A subsequent end-functionalization reaction has also been developed by them, in which the quasi-living P3HT was reacted *in situ* with an excess of Grignard agents.<sup>34,35</sup> Indeed, a wide variety of functional groups have been introduced at P3HT chain end(s), including vinyl, allyl, alkyne, alkyl, aryl, phenol (pyrane protected), formyl (acetal protected) and aniline (dimethylsilyl protected). They pointed out that  $\omega$ -end monosubstitution or  $\alpha,\omega$ -ends disubstitution depends on the nature of Grignard reagents. If vinyl-, allyl- and alkyne-containing Grignard reagents are used, monosubstitution takes place, whereas others result in disubstitution. The complexation between Grignard reagents and an Ni catalyst might be related to this selectivity. Interestingly, Grignard reagents consisting of a dimethylsilyl-protected aniline group brought about monosubstitution.

We were interested in P3HT-NH<sub>2</sub> for a blend system with PS-COOH; therefore, an end-functionalization reaction using 3-[bis(trimethylsilyl)amino]phenylmagnesium chloride (**3**) was carried out under modified conditions. First, 2-bromo-3-hexyl-5-iodothiophene (**1**) and <sup>i</sup>PrMgCl were used instead of 2,5-dibromo-3-hexylthiophene and *tert*-butylmagnesium chloride to further enhance the quantitative and selective Grignard exchange reaction at the 5-position and

lower PDIs (PDI=1.1–1.2) without any shoulder from a GPC trace, as described by Yokozawa *et al.*<sup>8</sup> Second, our group used lithium chloride in the reaction system aiming at a dissociation of Grignard reagents and an increase in their reactivity in THF.<sup>36</sup> The synthetic routes are depicted in Scheme 1.

The monomer, 2-bromo-5-chloromagnesio-3-hexylthiophene (**2**), was prepared by the stoichiometric Grignard exchange reaction of **1** with <sup>i</sup>PrMgCl at  $0^\circ\text{C}$  for 30 min in the presence of lithium chloride in THF. The initiator, Ni(dppp)Cl<sub>2</sub>, was then added and polymerization was carried out at room temperature for 10 min, followed by an *in situ* reaction with **3** for 10 min, which was always used at least 20 times in excess to the chain-end. Quenching the system with 5N-HCl aqueous deprotected the dimethylsilyl groups to generate an HCl salt of P3HT-NH<sub>2</sub>. After neutralization with NaHCO<sub>3</sub> aqueous, an aniline-chain-end could be regenerated. The obtained P3HT was characterized by GPC, NMR and MALDI-TOF mass spectroscopy.

Results are summarized in Table 1. As the target  $M_w$  increased by increasing the feed ratio (monomer)/(initiator), the observed  $M_w$  increased proportionally (Figure 1). PDIs were low in the range of 1.06–1.29. The GPC curves of all samples are shown in Figure 2, indicating sharp, monomodal and symmetrical peaks. The <sup>1</sup>H NMR

Table 1 Synthesis of regioregular P3HT-NH<sub>2</sub>

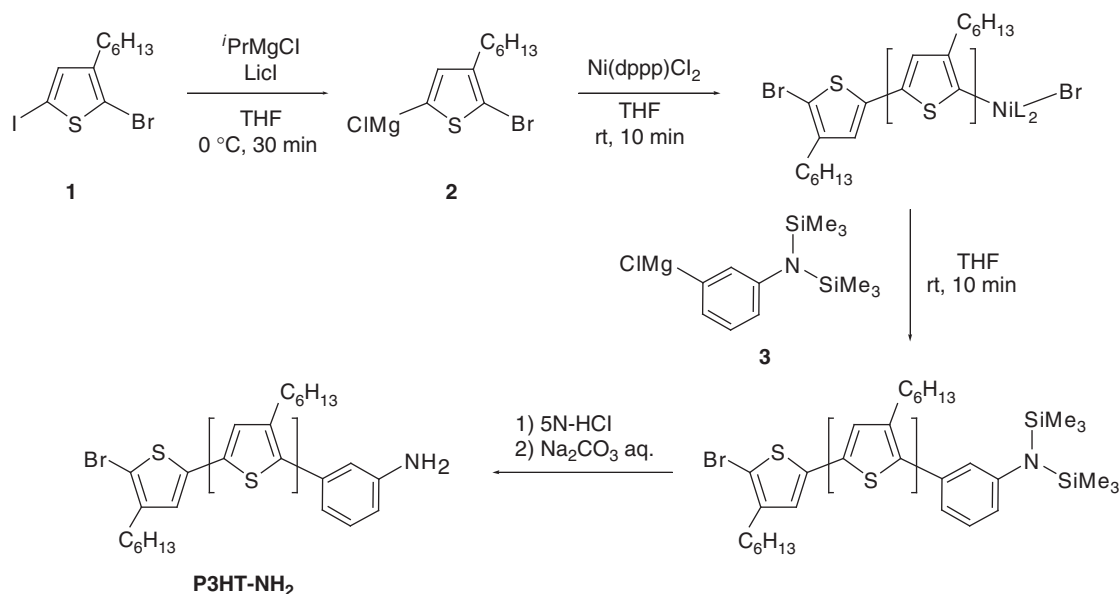
Run	[M]/[I]	$M_n$ (g mol <sup>-1</sup> )		Polydispersity indices <sup>a</sup>	Conversion (%) <sup>b</sup>	Functionality (%) <sup>c</sup>
		calcd <sup>d</sup>	GPC <sup>a</sup>			
1	12	2000	1960	1.12	—	—
2	18	3000	3700	1.29	96	90
3	30	5000	5520	1.13	—	—
4	30	5000	6800	1.21	85	88
5	54	9000	11 100	1.09	99	92
6	72	12 000	15 200	1.06	80	88
7	150	25 000	28 000	1.19	84	85

<sup>a</sup>Determined by GPC using polystyrene standards.

<sup>b</sup>Monomer conversion determined by GPC.

<sup>c</sup>Aniline-chain-end-functionality determined by MALDI-TOF mass spectroscopy.

<sup>d</sup>Calculated from feed ratio of monomer and initiator.



Scheme 1 Synthetic routes for regioregular P3HT-NH<sub>2</sub>.

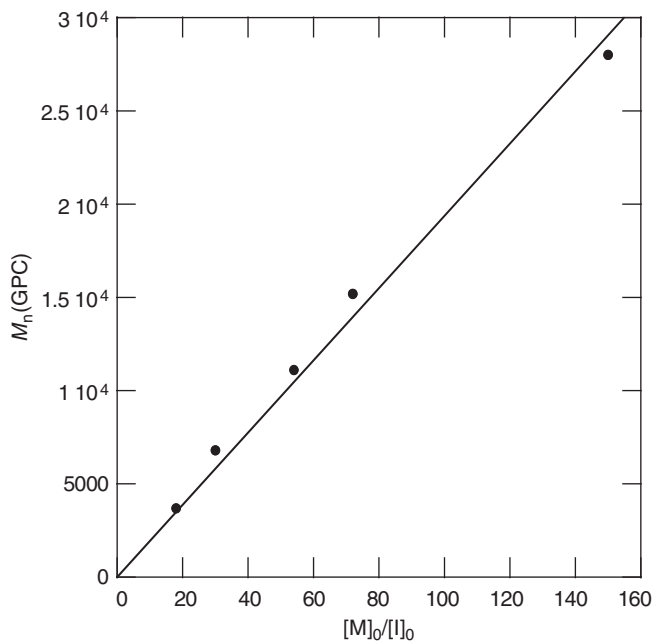


Figure 1 Dependence of  $[M]_0/[I]_0$  on  $M_n$  values.

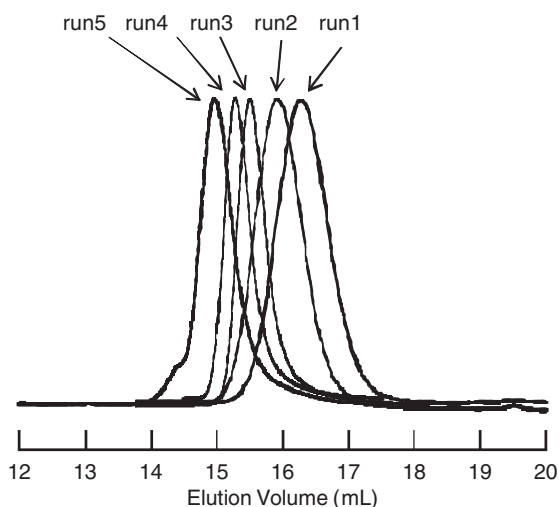


Figure 2 GPC ultraviolet curves of regioregular P3HT-NH<sub>2</sub> samples.

spectra of the P3HT-NH<sub>2</sub> series show a characteristic resonance assignable to NH<sub>2</sub> protons at the end group with a reasonable intensity (Figure 3 (run 1)). The head-to-tail regioregularities were determined from <sup>1</sup>H NMR to be more than 95% in all runs by comparing the signal intensities of the methylene protons next to thiophene rings corresponding to the head-to-tail structure and others. The MALDI-TOF mass spectrum of P3HT is shown in Figure 4 (run 3). The major series of signals with intervals corresponding to the monomer unit was found, assigning the  $\alpha$ - and  $\omega$ -ends to bromo and aniline groups, respectively. No disubstituted products with aniline groups were found at all. For instance, the 13-mer of P3HT bearing bromo and aniline groups was observed at  $m/z=2332.25$ , which was very close to the theoretical value ( $m/z=2333.66=79.9$  (Br)+166.28 (monomer unit) $\times$ 13 (degree of polymerization)+92.12 (aniline)). A very minor series was also found, which was attributed to unfunctionalized P3HT having bromo and proton end groups. End functionalities were calculated by comparing the signal intensities of both series<sup>34</sup>

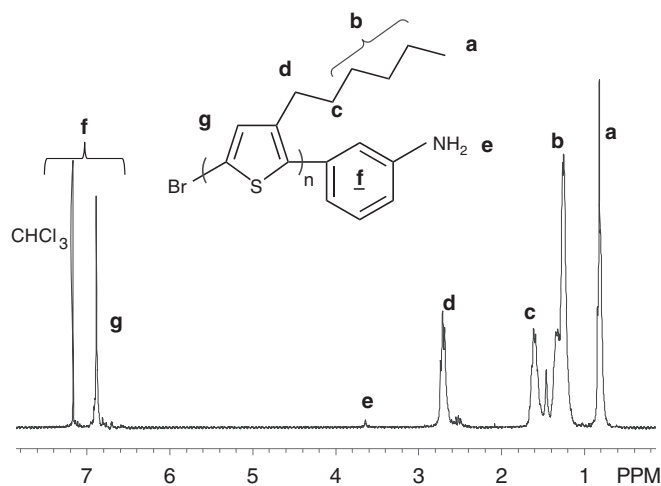


Figure 3 <sup>1</sup>H NMR spectrum of regioregular P3HT-NH<sub>2</sub> (run 1).

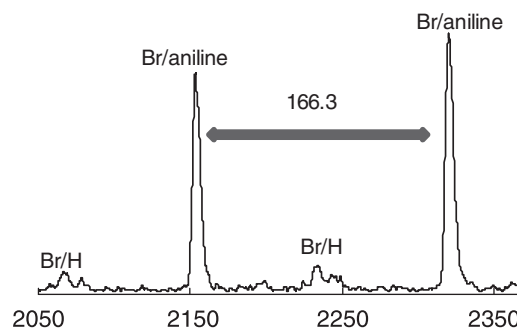


Figure 4 MALDI-TOF mass spectrum of regioregular P3HT-NH<sub>2</sub> (run 3).

and they ranged from 85 to 92%. Thus, an efficient monosubstitution reaction was revealed to yield the expected well-defined regioregular P3HT-NH<sub>2</sub> without difficulty.

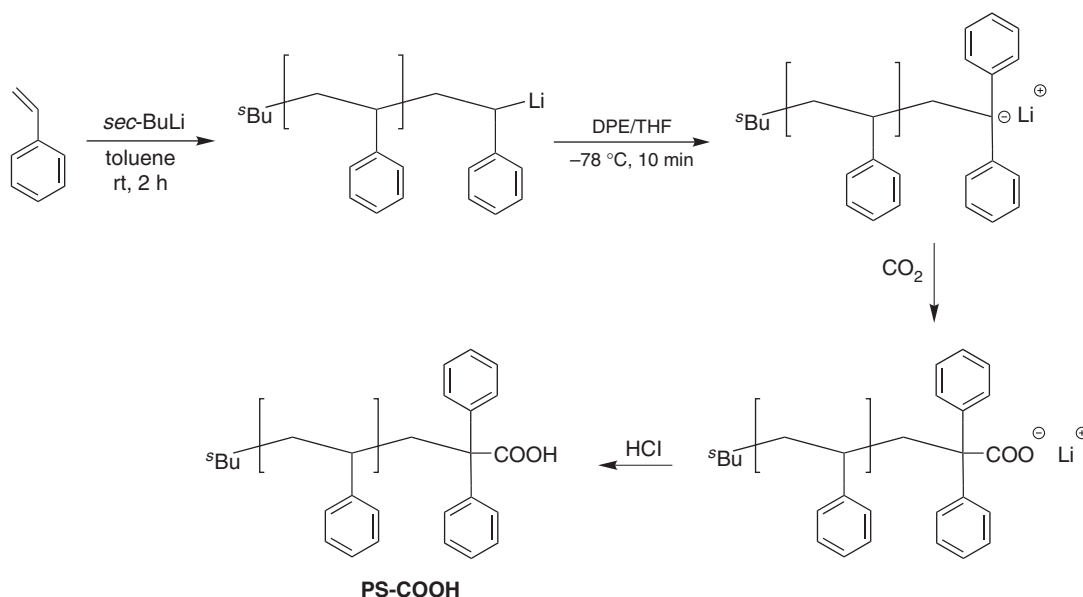
#### Synthesis of (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH)

The precursor, PS-COOH, could be successfully synthesized on the basis of living anionic polymerization according to a previous paper.<sup>28</sup> Styrene was polymerized with *sec*-BuLi as the initiator in toluene at room temperature for 2 h and THF (toluene/THF=1/1, *v/v*) was added at  $-78$  °C. Polystyryllithium was then end-capped with 1,1-diphenylethylene at  $-78$  °C for 30 min and quenched with dry ice. The lithium salt of PS-COOH was neutralized with a 5N-HCl aqueous solution (see Scheme 2). The results are summarized in Table 2 and GPC curves (run 8 and 10) showed extremely narrow distributions, as shown in Figure 5. The nearly 100% carboxy functionality was confirmed by TLC. The carboxy end groups were also corroborated by Fourier transform-infrared showing a carbonyl stretching absorbance at  $1700.91$   $\text{cm}^{-1}$ .

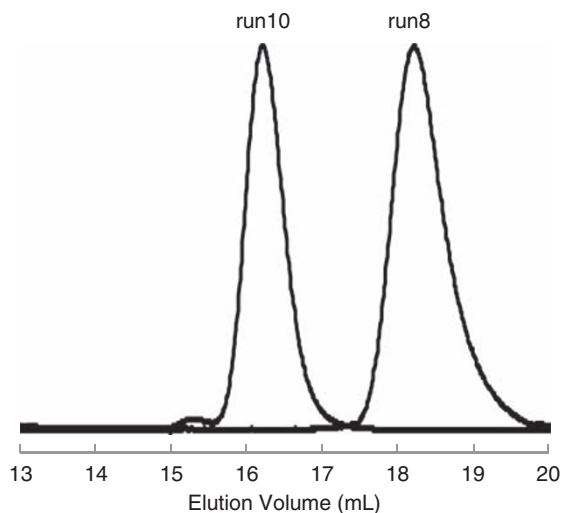
The target block copolymer, (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH), was prepared by blending equimolars of P3HT-NH<sub>2</sub> ( $M_n=5520$ , run 3) and PS-COOH ( $M_n=17800$ , run 10) in hydrocarbon solvents such as toluene and *o*-dichlorobenzene, rather than in polar solvents, so that an ionic interaction was enforced (Scheme 2). A self-standing film was easily obtained by slowly evaporating it from this blend solution.

#### Thermal and optical properties of (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH)

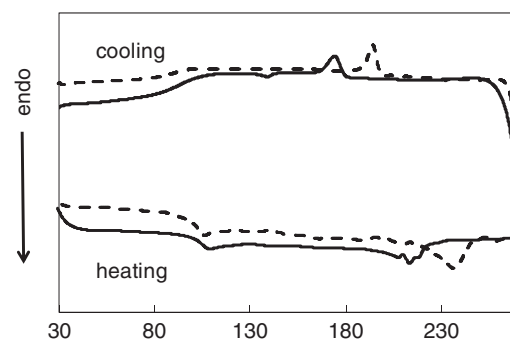
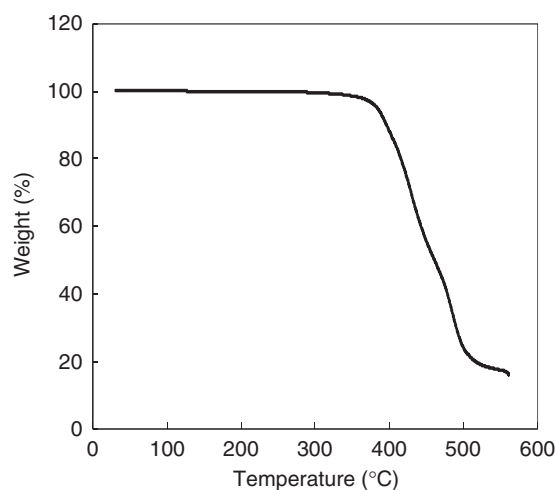
The thermal property of (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) ( $M_n=5520+17800$ ) was investigated by DSC and compared with a blend (P3HT/

**Scheme 2** Synthetic routes for PS-COOH and (P3HT-NH<sub>2</sub>)-b-(PS-COOH).**Table 2** Synthesis of PS-COOH<sup>a</sup>

Run	$M_n(\text{g mol}^{-1})^b$	Polydispersity indices <sup>b</sup>	functionality (%) <sup>c</sup>
8	2950	1.09	100
9	7700	1.04	100
10	17800	1.04	100

<sup>a</sup>Yields of all polymers were 100%.<sup>b</sup>Determined by GPC using polystyrene standards.<sup>c</sup>Determined by TLC.**Figure 5** GPC ultraviolet curves of PS-COOH samples.

PS-COOH) of unfunctionalized P3HT and PS-COOH having similar  $M_w$  and composition. P3HT/PS-COOH showed two distinct transition temperatures on heating,  $T_g$  at 100 °C and  $T_m$  at 235 °C, corresponding to PS- and P3HT-aggregated domains, respectively (Figure 6, dashed line). (P3HT-NH<sub>2</sub>)-b-(PS-COOH) also showed two transition temperatures ( $T_g$  at 104 °C and  $T_m$  at 211 °C) for both domains on heating, indicating a phase separation, but the intervals of

**Figure 6** Differential scanning calorimetry thermogram of P3HT/PS-COOH (dashed line) and (P3HT-NH<sub>2</sub>)-b-(PS-COOH) (solid line).**Figure 7** TG curve of (P3HT-NH<sub>2</sub>)-b-(PS-COOH).

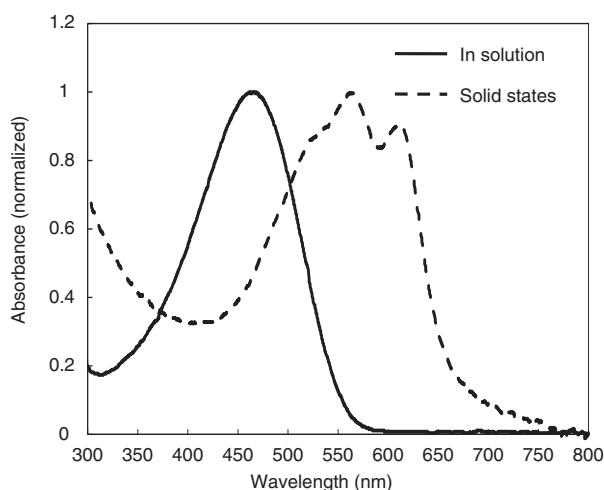
both temperatures became somewhat closer compared with those of P3HT/PS-COOH (Figure 6, solid line). This observation may be derived from a phase-separated structure of (P3HT-NH<sub>2</sub>)-b-(PS-COOH), which is smaller than that of P3HT/PS-COOH because of

the ionic interaction. A similar trend was also observed in a cooling scan. Figure 7 shows the TG curve of (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH). A two-stage weight loss behavior was observed from 350 to 420 °C and above 420 °C. The first one was because of the degradation of PS segments, whereas the second one was attributed to the decomposition of P3HT segments.

The optical properties of the polymer were studied by UV-vis spectroscopy. The solution-state UV-vis spectrum of (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) in chloroform showed maximum absorptions ( $\lambda_{\text{max}}$ ) at 465 nm (see Figure 8). In the film state,  $\lambda_{\text{max}}$  was bathochromically shifted to 562 nm compared with that in the solution state. The film showed a shoulder at around 612 nm, related to vibronic absorption as seen in a pristine P3HT film, indicating a high degree of ordering in polymer films, even though amorphous PS was mostly incorporated. These thermal and optical properties did not change much by changing the block ratio.

#### AFM images of (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) thin film

To gain an insight into morphology, a thin film of (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) (P3HT: 24 wt%) was prepared by drop casting from a toluene solution onto a mica substrate. The surface morphology of the film was observed by AFM. As a reference, an AFM image was also taken from P3HT/PS-COOH, which was thermally annealed at 120 °C

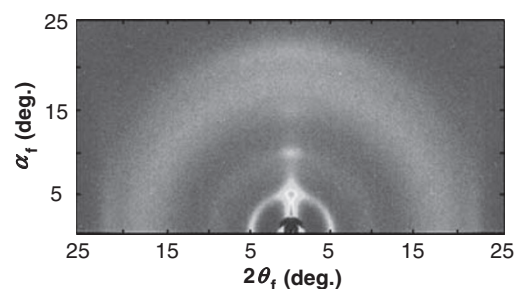


**Figure 8** Ultraviolet-vis spectra of (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) in solution and solid states.

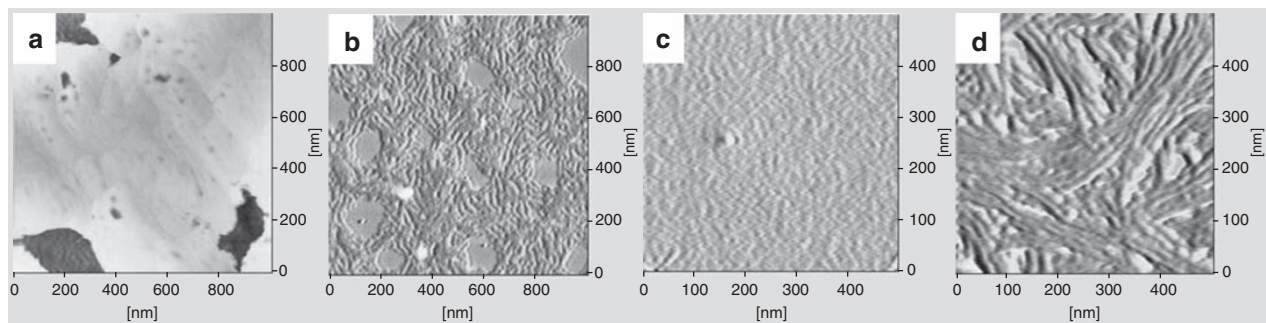
for 24 h and showed macrophase separation without any nano-ordered morphology (Figure 9a). In contrast, nanofibril structures of the (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) thin film treated by thermal annealing at 120 °C for 24 h were observed, wherein the bright and dark areas represent the P3HT and PS domains, respectively (Figure 9b). The difference between the surface morphologies of (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) and P3HT/PS-COOH was consistent with the result from the DSC profile (Figure 6). In Figure 9b, largely aggregated domains are partially observed, probably because of the cleavage of a weak ionic interaction between aromatic amine and carboxylic acid at high annealing temperatures. On the other hand, the (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) thin film after solvent annealing with toluene at room temperature showed continuous nanofibril structures having 12–15 nm widths without any aggregates (Figure 9c). In this case, the ionic interaction of (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) in the film state could be maintained during the mild annealing process. Another similar block copolymer sample having the increased P3HT content (P3HT: 33 wt%) was prepared and investigated by AFM as shown in Figure 9d. The clearer nanofibril structures emerged in large areas probably because of the more stable stacking between higher  $M_w$  P3HT segments.

#### GIXS analysis of (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) thin film

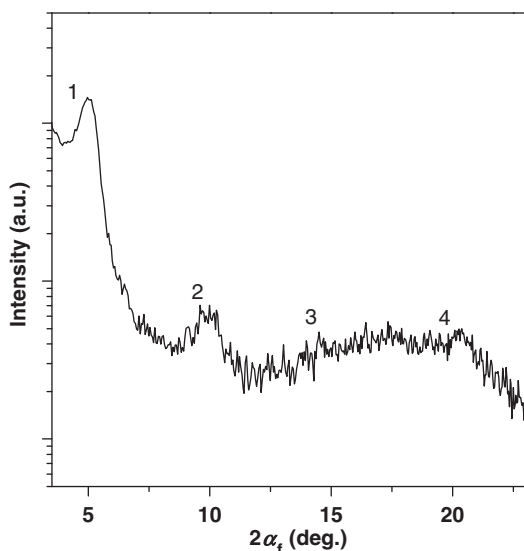
Figure 10 shows a representative two-dimensional GIXS pattern of (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) (P3HT: 24 wt%) thin films at room temperature, from which an out-of-plane scattering profile has been extracted along the  $\alpha_f$  direction at  $2\theta_f = 0^\circ$  and shown in Figure 11. As can be seen in Figures 10 and 11, several scattering spots appear along the  $\alpha_f$  direction at  $2\theta_f = 0^\circ$ . These spots are positioned in the order of a low-to-high scattering angle, with relative scattering angles from the



**Figure 10** Two-dimensional GIWAXS pattern measured at  $\alpha_f = 0.16$  for the (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) thin film.



**Figure 9** Tapping-mode atomic force microscopy phase images of (a) blend film of unfunctionalized P3HT and PS-COOH thermally annealed at 120 °C for 24 h; (b) (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) film (P3HT: 24 wt%) thermally annealed at 120 °C for 24 h; and (c) (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) film (P3HT: 24 wt%) treated by solvent annealing with toluene at room temperature for 3 h. (d) (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) film (P3HT: 33 wt%) treated by solvent annealing with toluene at room temperature for 3 h.



**Figure 11** Out-of-plane GIWAXS profile extracted along the  $q_z$  direction at  $2\theta_f=0^\circ$  from the two-dimensional image measured for the (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) thin film.

specular reflection position of 1, 2, 3 and 4 (Figure 11), indicating that spot 1 is the first-order scattering peak and the other spots are higher-order peaks. The appearance of these spots indicates that a multilayer structure is formed in the thin film and that multilayers are stacked along a direction normal to the film plane. From the scattering spots, it is determined that the  $d$ -spacing value is 1.56 nm, which corresponds to the individual layer thickness. This  $d$ -spacing value is in good agreement with the molecular layer thickness of the P3HT block, the 3-hexyl side groups of which are fully extended in a plane.<sup>37</sup> Thus, the observed multilayer structure consists of P3HT blocks. Furthermore, the observation of the molecularly multilayered P3HT block phase suggests that in the film, the P3HT block was phase separated from the PS block. In addition, a broad amorphous halo appears over the  $2\alpha_f$  scattering angle range of 12–23°. This amorphous halo might originate mainly from the amorphous PS block phase. From the peak maximum of the amorphous halo,  $d$ -spacing was estimated to be 0.45 nm.

## CONCLUSION

A well-defined P3HT-NH<sub>2</sub> series could be successfully synthesized on the basis of Grignard metathesis polymerization. The  $M_w$ s and PDIs of the resulting P3HT-NH<sub>2</sub> varied from 1960 to 28 000 g mol<sup>-1</sup> and from 1.06 to 1.29, respectively, as determined by GPC. The efficient and selective  $\omega$ -end-functionalization of P3HT-NH<sub>2</sub> (functionality=85–92%) was confirmed by MALDI-TOF mass spectroscopy. We were also successful in synthesizing novel block copolymers through ionic interaction, (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH), simply by blending P3HT-NH<sub>2</sub> and PS-COOH, which was prepared on the basis of living anionic polymerization. Thermal and optical properties of block copolymers were investigated by DSC, TGA and UV-vis spectroscopy. AFM images of the block copolymer film indicated the self-assembly of nanofibril structures with 12–15 nm widths. GIXS analysis indicated the in-plane orientation and interlayer  $d$ -spacing of P3HT segments in the (P3HT-NH<sub>2</sub>)-*b*-(PS-COOH) thin film. We are now investigating the creation of a new bulk-heterojunction solar cell device by exploiting the ideal nanostructure derived from the newly developed block copolymer formation.

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- 1 Jenekhe, S. A. & Chen, X. L. Self-assembly of ordered microporous materials from rod-coil block copolymers. *Science* **283**, 372–375 (1999).
- 2 Klok, H. A. & Lecommandoux, S. Supramolecular materials via block copolymer self-assembly. *Adv. Mater.* **13**, 1217–1229 (2001).
- 3 Lee, M., Cho, B.-K. & Zin, W.-C. Supramolecular structures from rod-coil block copolymers. *Chem. Rev.* **101**, 3869–3892 (2001).
- 4 Lee, M. & Yoo, Y.-S. Supramolecular organization of block oligomers based on rod-shaped mesogen into liquid crystalline assembly. *J. Mater. Chem.* **12**, 2161–2168 (2002).
- 5 Lim, Y.-B., Moon, K.-S. & Lee, M. Rod-coil block molecules: their aqueous self-assembly and biomaterials applications. *J. Mater. Chem.* **18**, 2909–2918 (2008).
- 6 Hiorns, R. C. & Holder, S. J. The synthesis of organometallic rod-coil block copolymers from polysilanes. *Polym. Int.* **58**, 323–329 (2009).
- 7 Iovu, M. C., Sheina, E. E., Gil, R. R. & McCullough, R. D. Experimental evidence for the quasi-‘living’ nature of the grignard metathesis method for the synthesis of regioregular poly(3-alkylthiophenes). *Macromolecules* **38**, 8649–8656 (2005).
- 8 Miyakoshi, R., Yokoyama, A. & Yokozawa, T. Catalyst-transfer polycondensation mechanism of Ni-catalyzed chain-growth polymerization leading to well-defined poly(3-hexylthiophene). *J. Am. Chem. Soc.* **127**, 17542–17547 (2005).
- 9 Iovu, M. C., Jeffries-EL, M., Sheina, E. E., Cooper, J. R. & McCullough, R. D. Regioregular Poly(3-alkylthiophene) conducting block copolymers. *Polymer* **46**, 8582–8586 (2005).
- 10 Iovu, M. C., Craley, C. R., Jeffries-EL, M., Krankowski, A. B., Zhang, R., Kowalewski, T. & McCullough, R. D. Conducting regioregular polythiophene block copolymer nanofibrils synthesized by reversible addition fragmentation chain transfer polymerization (RAFT) and nitroxide mediated polymerization (NMP). *Macromolecules* **40**, 4733–4735 (2007).
- 11 Boudouris, B. W., Frisbie, C. D. & Hillmyer, M. A. Nanoporous Poly(3-alkylthiophene) thin films generated from block copolymer templates. *Macromolecules* **41**, 67–75 (2008).
- 12 Dai, C.-A., Yen, W.-C., Lee, Y.-H., Ho, C.-C. & Su, W.-F. Facile synthesis of well-defined block copolymers containing regioregular poly(3-hexylthiophene) via anionic macroinitiation method and their self-assembly behavior. *J. Am. Chem. Soc.* **129**, 11036–11038 (2007).
- 13 Higashihara, T., Ohshimizu, K., Hirao, A. & Ueda, M. Facile synthesis of ABA triblock copolymer containing regioregular Poly(3-hexylthiophene) and polystyrene segments via linking reaction of poly(styryl)lithium. *Macromolecules* **41**, 9505–9507 (2008).
- 14 Higashihara, T. & Ueda, M. Synthesis and characterization of a novel coil-rod-coil triblock copolymers comprised of regioregular poly(3-hexylthiophene) and poly(methyl methacrylate) segments. *React. Funct. Polym.* **69**, 457–462 (2009).
- 15 Richard, F., Brochon, C., Leclerc, N., Eckhardt, D., Heiser, T. & Hadziioannou, G. Design of a linear poly(3-hexylthiophene)/fullerene-based donor-acceptor rod-coil block copolymer. *Macromol. Rapid Commun.* **29**, 885–891 (2008).
- 16 Lee, J. U., Cirpan, A., Emrick, T., Russell, T. P. & Jo, W. H. Synthesis and photophysical property of well-defined donor-acceptor diblock copolymer based on regioregular poly(3-hexylthiophene) and fullerene. *J. Mater. Chem.* **19**, 1483–1489 (2009).
- 17 Sommer, M., Lang, A. S. & Thelakkat, M. Crystalline-crystalline donor-acceptor block copolymers. *Angew. Chem., Int. Ed.* **47**, 7901–7904 (2008).
- 18 Zhang, Q., Cirpan, A., Russell, T. P. & Emrick, T. Donor-acceptor poly(thiophene-block-perylene diimide) copolymers: synthesis and solar cell fabrication. *Macromolecules* **42**, 1079–1082 (2009).
- 19 Sauvé, G. & McCullough, R. D. High field-effect mobilities for diblock copolymers of poly(3-hexylthiophene) and poly(methyl acrylate). *Adv. Mater.* **19**, 1822–1825 (2007).
- 20 Horrión, J., Jérôme, R. & Teyssié, P. Halato-telechelic Polymers. 12. Block Copolymerization of Polystyrene and Polybutadiene via Ionic Interactions. *J. Polym. Sci., Part C: Polym. Lett.* **24**, 69–76 (1986).
- 21 Horrión, J., Jérôme, R. & Teyssié, P. Halato-telechelic polymers. XV. ionic cross-interactions of immiscible telechelic polymers: a reversible pathway to block copolymer-type materials. *J. Polym. Sci., Part A: Polym. Chem.* **28**, 153–171 (1990).
- 22 Russell, T. P., Jérôme, R., Charlier, P. & Foucart, M. The microstructure of block copolymers formed via ionic interactions. *Macromolecules* **21**, 1709–1717 (1988).
- 23 Iwasaki, K., Hirao, A. & Nakahama, S. Morphology of Blends of  $\alpha,\omega$ -Diaminopolystyrene with  $\alpha,\omega$ -Dicarboxypoly(ethylene oxide). *Macromolecules* **26**, 2126–2131 (1993).
- 24 Pispas, S., Floudas, G., Pakula, T., Lieser, G., Sakellariou, S. & Hadjichristidis, N. Miktoarm block copolymer formation via ionic interactions. *Macromolecules* **36**, 759–763 (2003).
- 25 Hirao, A., Karasawa, Y., Higashihara, T., Zhao, Y. & Sugiyama, K. Synthesis of block copolymers and star-branched polymers consisting of conducting polyacetylene segments via ionic interaction to form ionic bonds. *Design. Monom. Polym.* **7**, 647–660 (2004).

- 26 Sugiyama, K., Karasawa, Y., Higashihara, T., Zhao, Y. & Hirao, A. Synthesis of block copolymers and asymmetric star-branched polymers comprised of polyacetylene and polystyrene segments via ionic bond formation. *Monatsh. Fuer Chem.* **137**, 869–880 (2006).
- 27 Yokoyama, A., Miyakoshi, R. & Yokozawa, T. Chain-growth polymerization for poly(3-hexylthiophene) with a defined molecular weight and a low polydispersity. *Macromolecules* **37**, 1169–1171 (2004).
- 28 Quirk, R. P. & Yin, J. Carbonation of polymeric organolithium compounds: effects of chain end structure. *J. Polym. Sci., Part A: Polym. Chem.* **30**, 2349–2355 (1992).
- 29 Lee, B., Park, Y.-H., Hwang, Y.-T., Oh, W., Yoon, J. & Ree, M. Ultralow-k nanoporous organosilicate dielectric films imprinted with dendritic spheres. *Nature Mater.* **4**, 147–150 (2005).
- 30 Lee, B., Oh, W., Hwang, Y., Park, Y.-H., Yoon, J., Jin, K. S., Heo, K., Kim, J., Kim, K.-W. & Ree, M. Imprinting well-controlled nanopores in organosilicate dielectric films: triethoxysilyl-modified six-armed poly( $\epsilon$ -caprolactone) and its chemical hybridization with an organosilicate precursor. *Adv. Mater.* **17**, 696–701 (2005).
- 31 Yoon, J., Kim, K.-W., Kim, J., Heo, K., Jin, K. S., Jin, S., Shin, T. J., Lee, B., Rho, Y., Ahn, B. & Ree, M. Small-angle X-ray scattering station 4C2 BL of Pohang Accelerator Laboratory for advance in Korean polymer science. *Macromol. Res.* **16**, 575–585 (2008).
- 32 Kim, G., Park, S., Jung, J., Heo, K., Yoon, J., Kim, H., Kim, I. J., Kim, J. R., Lee, J. I. & Ree, M. Novel brush polymers with phosphorylcholine bristle ends: synthesis, structure, properties, and biocompatibility. *Adv. Funct. Mater.* **19**, 1631–1644 (2009).
- 33 Yoon, J., Jin, S., Ahn, B., Rho, Y., Hirai, T., Maeda, R., Hayakawa, T., Kim, J., Kim, K.-W. & Ree, M. Phase transitions in thin films of a diblock copolymer composed of a linear polymer block and a brush polymer block with mesogenic oligothiophenyl bristles. *Macromolecules* **41**, 8778–8784 (2008).
- 34 Jeffries-El, M., Sauve, G. & McCullough, R. D. *In-situ* end-group functionalization of regioregular poly(3-alkylthiophene) using the Grignard metathesis polymerization method. *Adv. Mater.* **16**, 1017–1019 (2004).
- 35 Jeffries-El, M., Sauve, G. & McCullough, R. D. Facile synthesis of end-functionalized regioregular poly(3-alkylthiophene)s via modified Grignard metathesis reaction. *Macromolecules* **38**, 10346–10352 (2005).
- 36 Krasovskiy, A. & Knochel, P. A LiCl-mediated Br/Mg exchange reaction for the preparation of functionalized Aryl- and heteroaryl magnesium compounds from organic bromides. *Angew. Chem., Int. Ed.* **43**, 3333–3336 (2004).
- 37 Chen, T.-A., Wu, X. & Rieke, R. D. Regiocontrolled synthesis of poly(3-alkylthiophenes) mediated by Rieke zinc: their characterization and solid-state properties. *J. Am. Chem. Soc.* **117**, 233–244 (1995).