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Aggregation of Polythiophene Homopolymer and Block Copolymer in Solution Utilizing the Characteristics of Pyridine at the Side Chain

Koji Takagi,* Eiki Kawagita, Ryo Kouchi, and Junpei Kawai

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Additional Supporting Information may be found in the online version of this article.
ABSTRACT:
Poly[3-(5’-hexylpyridine-2’-yl)thiophene] (P3PT) ($M_n = 13900$, H-T content = 90%) was prepared by the regioselective Grignard metathesis reaction and the subsequent Kumada coupling polymerization. Likewise, poly(3-hexylthiophene)-b-poly[3-(5’-hexylpyridine-2’-yl)thiophene] (P3HT-b-P3PT) ($M_n = 17300$) was synthesized in the one-pot and successive monomer addition protocol, in which the segment ratio was calculated to be 56 (P3HT) / 44 (P3PT) base on the $^1$H-NMR spectrum. The absorption and emission spectra of homopolymer P3PT(H), obtained by the protonation of the pyridine nitrogen, in THF/cyclohexane shifted to the longer wavelength as compared with those collected in THF, suggesting the aggregation in poor solvent. The aggregation of P3PT induced by the addition of Sc(OTf)$_3$ could be controlled by the molar ratio of pyridine and scandium complex. The protonated block copolymer P3HT-b-P3PT(H) was also subjected to the aggregate formation. The absorption maximum in THF/CH$_3$OH showed a bathochromic shift and the fluorescence emission was almost quenched. From the $^1$H-NMR spectra and DLS measurements, P3HT-b-P3PT(H) forms nano meter scale aggregates particularly with the insolubility and stacking of non-ionic P3HT in alcohol as the driving force.

KEYWORDS: aggregation / conjugated polymers / diblock copolymers / polythiophene / UV-vis spectroscopy
INTRODUCTION

Conjugated polymers play a pivotal role in the flexible electronic devices, including bulk heterojunction solar cells,\(^1\) field-effect transistors,\(^2\) and light-emitting diodes,\(^3\) due to the good solubility in organic solvents and the easy film-forming property with printing processes. In the case of applying conjugated polymers to these devices, not only the chemical structure of materials but also the precise control of morphology on the nano meter scale is very important to attain the best device performance. Since the conjugated polymers generally have a rigid rod main chain, the post-treatment of as-cast films would be a reliable technique to obtain the well-ordered arrangement of polymer chains. For example, in the bulk heterojunction solar cells composed of regioregular poly(3-hexylthiophene) and phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM) serving as the electron-donor and electron-acceptor, respectively, the thermal\(^4\) and solvent\(^5\) annealing of the blend film can produce the ideal bulk heterojunction morphology and eventually improve the photovoltaic efficiency.

On the other hand, the research interest about block copolymers has been increasing in both academia and industry owing to the intrinsic character to form self-assembled nanostructures driven by the phase separation of two immiscible chains.\(^6\) Block copolymers consisting of the rigid rod conjugated polythiophenes in one segment and the coiled poly(alkyl methacrylate),\(^7,8\) poly(2-vinylpyridine),\(^9\) and poly(ethylene glycol)\(^10\) in another segment were synthesized utilizing the atom transfer radical polymerization or the Huisgen 1,3-dipolar cycloaddition. The self-assembly of these block copolymers in solution and solid states were investigated to obtain the fiber-like micelle, vesicle, sheet, and ribbon structure induced by the \(\pi-\pi\) stacking interaction of the crystalline polythiophene segment. Meanwhile, more complex and diverse nanostructures with a potentially useful application for the electronic devices can be obtained by combining two rigid rod segments, namely, rod-rod diblock copolymers. The precision syntheses of regioregular poly(3-alkylthiophene)s\(^11-15\) employing the Grignard metathesis reaction followed by the nickel-catalyzed Kumada coupling polymerization allow us to access various block copolymers in the one-pot and successive monomer addition protocol. All conjugated block copolymers comprising the crystalline poly(3-hexylthiophene) segment and the amorphous poly(3-
or poly[3-(2-ethylhexyl)thiophene] segment exhibited the microphase-separated nanostructure after the thermal annealing. Furthermore, polar functional groups were introduced to the side chain of one polythiophene segment to ensure and stabilize the microphase separation. In 2007, the research group of Tu and Scherf firstly synthesized amphiphilic poly[9,9-di(n-octyl)fluorene]-b-poly[3-(6-diethylphosphonatoethyl)thiophene] and showed the formation of vesicular aggregate in dilute solution. Recently, it has been demonstrated that all conjugated block copolymer comprising poly(3-hexylthiophene) and poly[3-(2,5,8,11-tetraoxadodecane)thiophene] permits the selective assembly of carboxylic acid-functionalized fullerene derivative or cadmium ion in the hydrophilic domain to obtain the sophisticated nanostructure suitable for the photovoltaic devices. On the other hand, all conjugated polyelectrolyte-based block copolymers carrying cationic ammonium and pyridinium functionalities were reported to self-organize into the vesicle and lamella structure in solution, in which the aggregation behavior was influenced by the solvent polarity. Since the solubility of ionic conjugated polymers in organic solvents is rather different from the non-ionic one, the unique and programmable self-assembly of block copolymers in solution can be expected by the judicious selection of solvent quality and concentration. Conjugated polyelectrolytes with the cationic polythiophene in both homopolymer and block copolymer were also used as the interfacial layer between the active layer and the metal cathode to improve the power conversion efficiency.

In the present study, we have prepared poly[3-(5’-hexylpyridine-2’-yl)thiophene] homopolymer and a rod-rod block copolymer, poly(3-hexylthiophene)-b-poly[3-(5’-hexylpyridine-2’-yl)thiophene], by the Kumada coupling polymerization of Grignard monomers. The aggregation of protonated homopolymer was examined in solution utilizing the basicity and coordination ability of the pyridine functional group at the polythiophene side chain. With these results in our hand, we next performed, after protonating the pyridine nitrogen, the self-assembly of block copolymer in selective solvent. The spectroscopic studies based on the $^1$H-NMR, UV-vis, and fluorescence data along with the DLS measurement suggested that block copolymer forms aggregate with a size of several hundreds nanometers by virtue of the insolubility and stacking of non-ionic P3HT in alcohol.
EXPERIMENTAL

Materials

Monomer synthesis and polymerization were performed under dry nitrogen atmosphere. Organic reagents were purchased from commercial suppliers and used without purification. Isopropylmagnesium chloride solution (i-PrMgCl, 2.0 M in tetrahydrofuran (THF)) was purchased from Sigma-Aldrich (St. Louis, MO, USA). 1,3-Bis(diphenylphosphinopropane)nickel(II) dichloride (Ni(dppp)Cl$_2$) and scandium triflate (Sc(OTf)$_3$) were purchased from TCI (Tokyo, Japan). The synthesis and characterization of poly[3-(5’-hexylpyridine-2’-yl)thiophene] (P3PT) was described previously.$^{24}$

Instrumentations

$^1$H nuclear magnetic resonance ($^1$H NMR) spectra were measured on Bruker (Billerica, MA, USA) AVANCE 200 and 500 FT-NMR spectrometers in CDCl$_3$, CD$_3$OD, and THF-d$_8$. Gel permeation chromatographic (GPC) analyses were carried out on a Shodex (Tokyo, Japan) GPC-104 system using tandem LF□□□□ columns (THF as an eluent, flow rate = 1.0 mL/min, 40 °C) equipped with an ultraviolet (UV) detector (Shimadzu SPP-20A). Number-averaged molecular weight ($M_n$) and molecular weight distribution ($M_w/M_n$) were determined on the basis of a calibration curve made from standard polystyrene samples. UV-vis and fluorescence spectra were measured on Shimadzu UV-1650 spectrophotometer and RF-5300 spectrofluorometer, respectively, in a 10 mm quartz cell. Dynamic light scattering (DLS) measurements were performed on a Malvern (Worcestershire, UK) Zetasizer Nano ZS in a 12 mm quartz cell (PCS1115) under the concentration of 0.01 wt%.

Synthesis of Block copolymer (P3HT-b-P3PT)

To a THF solution (4 mL) of 2,5-dibromo-3-hexylthiophene (3HT) (342 mg, 1.05 mmol) in flask A was added i-PrMgCl solution (0.50 mL, 1.05 mmol) at 0 °C, and the mixture was stirred at room temperature for 30 min. After 17.5 mM THF suspension of Ni(dppp)Cl$_2$ (3.0 mL, 5.0 mol%) was added in one shot, the polymerization was carried out at room temperature for 5 min. On the other hand, in flask B, i-
PrMgCl solution (0.13 mL, 0.27 mmol) was added to a THF solution (1.5 mL) of 2,5-dibromo-3-(5’-hexylpyridine-2’-yl)thiophene (3PT) (109 mg, 0.27 mmol) at 0 °C, and the mixture was stirred at room temperature for 30 min. After the content in flask B was added to the flask A, the mixture was heated to reflux for 4 hr. The polymerization was quenched with 5 M HCl, and the solution was neutralized with saturated aq. NaHCO₃. An aqueous layer was extracted with CHCl₃ and the combined organic phase was dried over MgSO₄. The solution was concentrated to pour in ethanol/hexane (1/4 in volume ratio) to obtain red solid (34 mg, 11% yield). \( M_n = 17300, \frac{M_w}{M_n} = 1.27 \). ¹H NMR (δ, CDCl₃) 8.54 (s, 1H), 7.54–7.38 (3H), 7.07 (1.3H), 2.91–2.65 (4.6H), 1.69–1.37 (18.4H), 0.98–0.93 (6.9H).

RESULTS AND DISCUSSION

Synthesis

The Grignard metathesis reaction of 3PT with \( i \)-PrMgCl (1 equiv.) was carried out at room temperature. The reaction occurred at the 2-position in the 86% selectivity to give 5-bromo-2-chloromagnesio-3-(5’-hexylpyridine-2’-yl)thiophene. Subsequently, the Kumada coupling polymerization was carried out using Ni(dppp)Cl₂ (3 mol%) for 2 hr to obtain a homopolymer (P3PT) having the number-averaged molecular weight of 13900.²⁴,²⁵ Although 5-bromo-2-chloromagnesio-3-(5’-hexylpyridine-2’-yl)thiophene has the bulky substituent at the ortho position relative to the chloromagnesio group and is regarded as the reverse monomer, the polymerization smoothly proceeded at the refluxing temperature probably due to the chelation effect of the pyridine nitrogen.²⁶–²⁸ The relatively high head-to-tail content (ca. 90%) was confirmed by the ¹H-NMR spectrum (Figure S1) while the GPC chart and MALDI-TOF mass spectrum (Figure S6) indicated the diffusion of the nickel catalyst from the propagating end. On the other hand, it was reported that 2-bromo-5-chloromagnesio-3-hexylthiophene can be polymerized in the catalyst transfer mechanism and the propagating nickel catalyst re-initiates the polymerization of the second monomer.²⁹–³¹ Accordingly, for the synthesis of a block copolymer (P3HT-b-P3PT), 2-bromo-5-chloromagnesio-3-hexylthiophene and 5-bromo-2-chloromagnesio-3-(5’-hexylpyridine-2’-yl)thiophene were polymerized at the first and second stage, respectively (Scheme 1). As shown in...
Figure 1, the block efficiency was good to obtain P3HT-\textit{b}-P3PT having the number averaged molecular weight of 17300. The molecular weight distribution (1.27) was relatively narrow. In the $^1$H-NMR spectrum (Figure S2), the thiophene proton signal in the P3HT segment and the pyridine proton signal in the P3PT segment were independently observed at 6.98 ppm and 8.48 ppm, respectively. Based on the integral ratio of these signals, the segment ratio was calculated to be 56 (P3HT) / 44 (P3PT). The methylene proton signals adjacent to the aromatic ring were also detected in the different position at 2.63 ppm and 2.81 ppm, and the calculated segment ratio therefrom agreed well with the above value.

(Insert here Scheme 1 and Figure 1)

**Aggregation of homopolymer**

The CHCl$_3$ solution of P3PT was treated with 1 M HCl in the separating funnel. The organic phase was dried over MgSO$_4$, evaporated, and dried in vacuo to obtain P3PT(H) as red solid. In the $^1$H-NMR spectrum of P3PT(H) (Figure S3), the aromatic proton signals and methylene proton signals adjacent to the pyridine ring were shifted to the down field region suggesting that the protonation of the pyridine nitrogen decreased the electron density of the polythiophene. The solubility of polymers in organic solvents is summarized in Table 1. The native P3PT was soluble in CHCl$_3$, THF, and toluene while the protonated P3PT(H) was soluble in CHCl$_3$ and CH$_3$OH. The UV-vis absorption and fluorescence emission spectra of P3PT and P3PT(H) were recorded in CHCl$_3$, a good solvent for both polymers (Figure 2a). The absorption peak A at 271 nm observed for P3PT can be ascribed to the repeating unit being capable of the donor-acceptor interaction between thiophene and pyridine. On the other hand, the absorption peak B at 438 nm would be stemmed from the $\pi$-conjugation along the polymer main chain. Upon the protonation of the pyridine nitrogen, the peak A observed for P3PT(H) was shifted to the longer wavelength (290 nm) owing to the enhanced donor-acceptor interaction$^{32-35}$ and, conversely, the peak B was shifted to the shorter wavelength (416 nm) due to the increased steric hindrance between the repeating units. The fluorescence peak maxima (563 nm) were about the same for P3PT and P3PT(H).
Subsequently, the UV-vis absorption and fluorescence emission spectra of P3PT(H) were measured in THF and THF/cyclohexane\textsuperscript{36} (1/9 in volume ratio) (Figure 2b). P3PT(H) is visually soluble in THF at $10^{-5}$ M, but the absorption maximum was red shifted to 428 nm as compared with that in CHCl$_3$. The fluorescence peak maximum (563 nm) was still identical to that in CHCl$_3$. In sharp contrast, both the absorption and emission spectra were considerably shifted to the longer wavelength in THF/cyclohexane (UV-vis: 483 nm and fluorescence: 626 nm). The solution color was changed from yellow (in THF) to purple (in THF/cyclohexane) (Figure S10). It should be noted that non-protonated P3PT showed the comparable UV-vis absorption and fluorescence emission spectra irrespective of the solvent character (Figure S7). Therefore the protonation of the pyridine nitrogen of P3PT influenced not only the electronic state but also the polymer solubility to induce the aggregation in poor solvent, which prompt us to investigate the self-assembly of the block copolymer in the next section.

(Insert here Table 1 and Figure 2)

The THF solution of P3PT was titrated with Sc(OTf)$_3$ between 0 mol% and 300 mol% relative to the pyridine unit. From 0 to 100 mol%, the absorbance at 438 nm was decreased and the UV-vis spectra were gradually changed with the isosbestic point at 392 nm and 452 nm (Figure 3a). The fluorescence peak centered at 563 nm was shifted to the longer wavelength (574 nm) and the intensity became one-tenth of the original one by the addition of 100 mol% Sc(OTf)$_3$ (Figure 3c). The UV-vis spectra were further changed upon the addition of more than 100 mol% Sc(OTf)$_3$ with the isosbestic point at 430 nm (Figure 3b) and the fluorescence emission was recovered to the 50% intensity of the original one (Figure 3d). Sc(OTf)$_3$ has been utilizing in many organic reactions due to its strong Lewis acidity, tolerance for aqueous condition, and large coordination number which can vary between 3 and 7.\textsuperscript{37,38} In the present case, below 100 mol% Sc(OTf)$_3$, P3PT can aggregate by the multidentate coordination of the pyridine nitrogen to the scandium center. Above 100 mol% Sc(OTf)$_3$, on the other hand, the aggregated polymer chains are disentangled because of the excessive amount of Sc(OTf)$_3$. 
Aggregation of block copolymer

Initially, the UV-vis absorption and fluorescence emission spectra of P3HT-b-P3PT were measured in THF (Figure S8). The absorption maxima at 270 nm and 434 nm were similar to those of P3PT (Figure S7), whereas the intensity of the longer wavelength absorption was obviously large reflecting the presence of the P3HT segment. Next, the self-assembly of P3HT-b-P3PT(H), obtained by the protonation of the pyridine nitrogen using 1 M HCl, was investigated in THF and THF/cyclohexane (1/9 in volume ratio) following to the aggregation behavior of P3PT(H) (vide supra). The tailing to the longer wavelength was observed in the UV-vis spectrum collected in THF/cyclohexane, but the absorption and emission maxima showed ignorable shifts as compared with the spectra in THF (Figure S9). Both segments of P3HT-b-P3PT(H) have a poor solubility in cyclohexane (Table 1) that might inhibit the effective aggregation of neither P3HT nor P3PT(H). We then used methanol instead of cyclohexane because methanol is a good solvent for the P3PT(H) segment and a poor solvent for the P3HT segment. As indicated in Figure 4, the UV-vis absorption spectrum of P3HT-b-P3PT(H) was shifted to the longer wavelength and the peak maximum was observed at 454 nm in THF/CH$_3$OH (1/9 in volume ratio). The fluorescence emission was almost quenched. The dramatic decrease of the fluorescence emission can be explained by the energy transfer from P3PT(H) to P3HT and the concentration fluorescence quenching. In order to clarify the self-assembled structure of block copolymer in solution, the $^1$H-NMR spectroscopy and DLS measurement were also carried out. When the $^1$H-NMR spectrum was measured in THF-d$_8$/CD$_3$OD, the thiophene proton signal derived from the P3HT segment at ca. 6.9 ppm was considerably small (Figure S4). Meanwhile, the proton signals of both segments having the theoretical integral ratio were clearly observed in the $^1$H NMR spectrum collected in CDCl$_3$ indicating the dissolution of both segments (Figure S5). From the DLS measurements of P3HT-b-P3PT(H), the increase of the hydrodynamic radius (R$_h$) in THF/CH$_3$OH (205
nm) as compared with $R_h$ in THF (9 nm) was observed (Figure 5). Accordingly, It is considered that P3HT-$b$-P3PT(H) can self-assemble to form nano meter scale aggregates with the insolubility and stacking of non-ionic P3HT in alcohol as the driving force. The details about the self-assembled structure of block copolymer in solution will be disclosed and reported in future.

(Insert here Figures 4 and 5)

CONCLUSIONS
The aggregation of polythiophene homopolymer carrying the pyridine functional group at the side chain was investigated in solution utilizing the solubility of conjugated polyelectrolyte and the coordination chemistry between pyridine and scandium complex. The block copolymer comprised poly(3-hexylthiophene) and poly[3-(5'-hexylpyridine-2'-yl)thiophene] was successfully obtained by the consecutive Kumada coupling polymerization of two Grignard monomers. The absorption and emission spectra of the protonated block copolymer showed bathochromic shift and fluorescence quenching, respectively, in selective solvent. From the $^1$H-NMR spectra and DLS measurements, the block copolymer likely self-assembles into nano meter scale aggregates driven by the insolubility and stacking of poly(3-hexylthiophene) segment.

ACKNOWLEDGEMENTS
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REFERENCES AND NOTES


(16) Ohshimizu, K.; Ueda, M. Macromolecules **2008**, 41, 5289.


(36) The addition of THF was required for the complete dissolution of PolyPT(H) in cyclohexane.


Figure Legends

Figure 1. GPC chromatograms of P3HT (dotted line) and P3HT-b-P3PT (solid line) (Eluent: THF, Detector: UV).

Figure 2. (a) UV-vis absorption and fluorescence emission spectra of P3PT (dotted line) and P3PT(H) (solid line) in CHCl₃. (b) UV-vis absorption and fluorescence emission spectra of P3PT(H) in THF (dotted line) and THF/cyclohexane (solid line).

Figure 3. UV-vis absorption (a and b) and fluorescence emission (c and d) spectra of P3PT with Sc(OTf)₃ in 0, 10, 30, 50, 80, and 100 mol% (a and c) and 100, 120, 150, 200, and 300 mol% (b and d).

Figure 4. UV-vis absorption and fluorescence emission spectra of P3HT-b-P3PT(H) in THF (dotted line) and THF/methanol (solid line).

Figure 5. DLS profiles of P3HT-b-P3PT(H) in THF and THF/methanol.

Scheme 1. Synthesis of P3HT-b-P3PT.
Figure 1. GPC chromatograms of P3HT (dotted line) and P3HT-b-P3PT (solid line) (Eluent: THF, Detector: UV).

134x88mm (300 x 300 DPI)
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134x88mm (300 x 300 DPI)
Figure 2. (a) UV-vis absorption and fluorescence emission spectra of P3PT (dotted line) and P3PT(H) (solid line) in CHCl3. (b) UV-vis absorption and fluorescence emission spectra of P3PT(H) in THF (dotted line) and THF/cyclohexane (solid line).

134x88mm (300 x 300 DPI)
Figure 3. UV-vis absorption (a and b) and fluorescence emission (c and d) spectra of P3PT with Sc(OTf)3 in 0, 10, 30, 50, 80, and 100 mol% (a and c) and 100, 120, 150, 200, and 300 mol% (b and d).

134x88mm (300 x 300 DPI)
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134x88mm (300 x 300 DPI)
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Scheme 1. Synthesis of P3HT-b-P3PT.
71x40mm (300 x 300 DPI)
Table 1. Solubility of polymers in organic solvents.\textsuperscript{a}

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\textsuperscript{a} Symbols: (+); soluble, (+/–); partly soluble, and (–); insoluble
GRAPHICAL ABSTRACT

Aggregation of Polythiophene Homopolymer and Block Copolymer in Solution Utilizing the Characteristics of Pyridine at the Side Chain

Koji Takagi, Eiki Kawagita, Ryo Kouchi, and Junpei Kawai

The synthesis and aggregation of polythiophene homopolymer and block copolymer bearing pyridine at the side chain were investigated in solution. A block copolymer was found to form nano meter scale aggregates in selective solvent, which was characterized by UV-vis, fluorescence, NMR, and DLS measurements.
Supplementary Materials Available for

Aggregation of Polythiophene Homopolymer and Block Copolymer in Solution Utilizing the Characteristics of Pyridine at the Side Chain

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1. $^1$H-NMR spectra of materials

Figure S1. $^1$H-NMR spectrum of P3PT in CD$_2$Cl$_2$

Figure S2. $^1$H-NMR spectrum of P3HT-\textit{b}-P3PT in CDCl$_3$

Figure S3. $^1$H-NMR spectrum of P3PT(H) in CDCl$_3$
Figure S4. $^1$H-NMR spectrum of **P3HT-b-P3PT(H)** in THF-$d_8$/CD$_3$OD (1/9)

Figure S5. $^1$H-NMR spectrum of **P3HT-b-P3PT(H)** in CDCl$_3$
2. MALDI-TOF mass spectrum

Figure S6. MALDI-TOF mass spectrum of P3PT (Reason for multiply distributed peaks was discussed in reference 24)
3. UV-vis and fluorescence spectra

Figure S7. UV-vis and fluorescence spectra of P3PT in THF (dotted line) and THF/cyclohexane (solid line)

Figure S8. UV-vis and fluorescence spectra of P3HT-b-P3PT in THF
Figure S9. UV-vis and fluorescence spectra of P3HT-b-P3PT(H) in THF (dotted line) and THF/cyclohexane (solid line).
4. Photograph of polymer solution

![Polymer Solution Image]

Figure S10. From left to right: \( \text{P3PT} \) in THF, \( \text{P3PT} \) in THF/cyclohexane, \( \text{P3PT(H)} \) in THF, and \( \text{P3PT(H)} \) in THF/ cyclohexane