Preparation and Properties of a Novel Polythiophene, Poly[(3-hexyliminomethyl)thiophene] with a High Regioregularity

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ABSTRACT: Poly[(3-hexyliminomethyl)thiophene]s (P3HITs) were synthesized from the polymerizations of 2,5-dibromo-(hexyliminomethyl)thiophene and 5-bromo-2-iodo-3-(hexyliminomethyl)thiophene by Grignard metathesis method. The corresponding P3HITs with low regioregularity (70%) and high regioregularity (95%) were obtained, respectively. UV–vis and photoluminescence spectra of P3HIT were dependent on the regioregularity and solvent polarity. By hydrolysis of the imino groups in the side chains under acidic conditions, P3HIT was successfully converted into the polythiophene (P3TCHO) having aldehyde groups. This transformation was also performed facilely by exposing the P3HIT film to HCl gas to give the polythiophene having aldehyde moiety. The reverse way from aldehyde to imine was also successfully demonstrated by treating the film with triethylamine vapor. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1190–1194, 2011

KEYWORDS: conjugated polymers; functionalization of polymers; polythiophene; UV-vis spectroscopy

INTRODUCTION Polythiophenes (PTs) have been studied intensively as functional polymers for organic optoelectronic devices such as organic thin film transistors,[1] light-emitting diodes,[2] and polymer solar cells.[3] Poly(3-hexylthiophene) (P3HT) has been used for the fabrication of those devices due to its thermal stability, processibility based on its high solubility in organic solvents, and high charge mobility. Currently, further improvement of properties for such optoelectronic devices has been attempted by side chain modifications and control of regioregularity of PTs.[4]

PTs having imino groups in the side chains have attracted interests as new candidate materials for photovoltaic and electroluminescent devices. Sharma et al. have fabricated photovoltaic devices with poly(phenyl azo methane thiophene) prepared by the oxidative polymerization of the corresponding thiophene monomer using ferric chloride.[5] However, its molecular structure and molecular weight have not been clarified fully. Brembilla et al. prepared conducting polymer films by electrochemical polymerizations of various thiophene monomers.[6] However, the corresponding conducting polymer was not formed with that method probably due to rigid Schiff base. Somanathan et al. have reported the preparation of PTs functionalized with benzothiazole groups linked by —CH=N— and their application to electroluminescent devices.[7]

Poly(3-thiophenecarboxaldehyde) (P3TCHO) is one of simple structural PT derivatives. However, to the best of our knowledge, the preparation of P3TCHO as a homopolymer has not been reported so far, probably due to a poor solubility of a resulting polymer in organic solvents. Copolymers involving P3TCHO and soluble long alkyl substituted-thiophene unit have been reported.[8]

We here report synthesis of a new PT derivative, poly[(3-hexyliminomethyl)thiophene] (P3HIT) by Grignard metathesis (GRIM) method, which is frequently used for synthesizing P3HT.[9] By using an appropriately designed dihalothiophene monomer, a highly regioregular P3HIT was successfully synthesized. Another highlight of this report is the utilization of the obtained P3HIT as a precursor for a regioregular P3TCHO. By treating a P3HIT film under acidic conditions, hydrolysis of the imino pendants into aldehyde pendants was achieved, to give a film of P3TCHO successfully.

EXPERIMENTAL

Materials

THF was dried over sodium/benzophenone ketyl and distilled just before use. Chloroform was distilled over CaH_2. DMF, methanol, and dichloromethane were used as received. 3-Thiphenecarboxaldehyde, isopropyl magnesium chloride (2 M solution in THF; Aldrich chemical), iodobenzene diacetate (TCI chemical), iodine, *n*-hexyl amine, $NiCl_2$(dppp), and NBS (Wako chemical) were used without further purification. 5-Bromo-3-thiophenecarboxaldehyde (**2**) and 2,5-dibromo-3-

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Additional Supporting Information may be found in the online version of this article. Correspondence to: T. Endo (E-mail: tendo@mol-eng.fuk.kindai.ac.jp)

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thiophenecarboxaldehyde (**3**) were prepared according to the literature.[10]

Instruments

^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 NMR spectroscopy using tetramethylsilane as an internal standard in chloroform-*d* ($CDCl_3$). IR spectrum was recorded from Thermo fishier Scientific NICOLET iS10. UV–vis spectroscopy was measured on JASCO V570 spectrometer. Photoluminescne spectra were obtained on Hitachi F-2500 fluorescence spectrophotometer. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography with TOSOH HLC-8120GPC in THF with a calibration curve of polystyrene standards. P3HIT film was prepared on a glass substrate with a spin coater (700 rpm for 10 s and then 3000 rpm for 60 s) using 10 mg/mL solution.

Preparation of 5-bromo-2-iodo-3-thiophenecarboxaldehyde (4)

To a solution of **4** (0.88 g, 4.61 mmol) in CH_2Cl_2 (10 mL) was added iodine (0.59 g, 2.31 mmol) and of $PhI(OAc)_2$ (0.81 g, 2.51 mmol) at 0 °C. After the solution was stirred for 3 h at room temperature 10 wt % $Na_2S_2O_3$ aqueous solution (20 mL) was added to the reaction mixture. After the mixture was stirred for 5 min, the crude product was extracted with ethyl ether (50 mL × 3). After the ethereal layer was dried over $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using hexane/$CHCl_3$ (1:1) as an eluent to afford 1.1 g (76%) of **4** as a pale yellow solid.

Mp. 98.5–99.0 °C; ^{1}H NMR ($CDCl_3$): δ(ppm) 7.29 (s, thiophene proton, 1H), 9.56 (s, —CHO, 1H); ^{13}C NMR ($CDCl_3$): δ(ppm) 87.87, 117.91, 129.39, 142.32, 185.62.

2,5-Dibromo-3-(hexyliminomethyl)thiophene (5)

To a solution of **2** (2.00 g, 7.42 mmol) in of MeOH (50 mL) was added of *n*-hexylamine (0.75 g, 7.42 mmol) at room temperature. After the solution was refluxed for 20 min, the solvent was removed under reduced pressure to give 2.5 g (96%) of **5** as colorless oil [The purity checked by gas chromatography (GC) was 99%].

^{1}H NMR ($CDCl_3$): δ(ppm) 0.89 (t, J = 6.8 Hz, —CH_3, 3H), 1.29–1.36 (m, —CH_2—,6H), 1.62–1.68 (m, —CH_2—, 2H), 3.57 (dt, J = 7.0 and 1.2 Hz, =NCH_2—, 2H), 7.41 (s, thiophene proton, 1H), 8.15 (t, J = 1.2 Hz, —CH=N—, 1H); ^{13}C NMR ($CDCl_3$): δ(ppm) 14.06, 22.59, 26.97, 30.78, 31.16, 61.83, 112.08, 115.10, 129.13, 152.84, 163.24.

5-Bromo-2-iodo-3-(hexyliminomethyl)thiophene (6)

Compound **6** was prepared by the same procedure as synthesis of compound **5** using **4** and *n*-hexylamine in 96% yield as a white solid (The purity checked by GC was 99%).

Mp. 39.5–40.5 °C. ^{1}H NMR ($CDCl_3$): δ(ppm) 0.90 (t, J = 7.0 Hz, —CH_3, 3H), 1.29–1.37 (m, —CH_2—,6H), 1.62–1.68 (m, —CH_2—, 2H), 3.59 (dt, J = 7.0 and 1.2 Hz, =NCH_2—, 2H), 7.34 (s, thiophene proton, 1H), 7.98 (t, J = 1.2 Hz, —CH=N—, 1H); ^{13}C NMR ($CDCl_3$): δ(ppm) 14.08, 22.60, 26.98, 30.80, 31.62, 61.71, 79.67, 116.51, 129.62, 142.55, 155.31.

Preparation of LR-P3HIT

To a solution of **5** (0.71 g, 2.00 mmol) in THF (20 mL) was added 2.0 M THF solution of ^{i}ProMgCl (1.0 mL, 2.0 mmol) at 0 °C. After the solution was stirred for 30 min at 0 °C, $NiCl_2$(dppp) (5.4 mg, 0.010 mmol, 0.5 mol % to **5**) was added. After refluxed for 20 h, the solution was poured into MeOH (200 mL). The precipitate was collected by filtration. The obtained crude polymer was purified by column chromatography (silica gel treated by Et_3N) using THF as an eluent to give 0.23 g (60%) of LR-P3HIT as a purple solid.

Preparation of HR-P3HIT

HR-P3HIT was prepared by the same procedure for the preparation of LR-P3HIT using **6** (0.80 g, 2.00 mmol) in 64% yield as a purple solid.

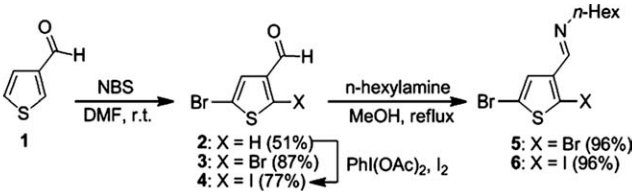
^{1}H NMR ($CDCl_3$): δ(ppm) 0.90 (t, J = 7.0 Hz, —CH_3, 3H), 1.33–1.41 (m, —CH_2—, 6H), 1.70–1.75 (m, —CH_2—, 2H), 3.67 (t, J = 6.6 Hz, =NCH_2—, 2H), 7.73 (s, thiophene proton, 1H), 8.61 (s, —CH=N—, 1H); ^{13}C NMR ($CDCl_3$): δ(ppm) 14.11, 22.65, 27.10, 30.96, 31.69, 62.18, 127.96, 132.53, 137.00, 138.62, 153.93.

RESULTS AND DISCUSSION

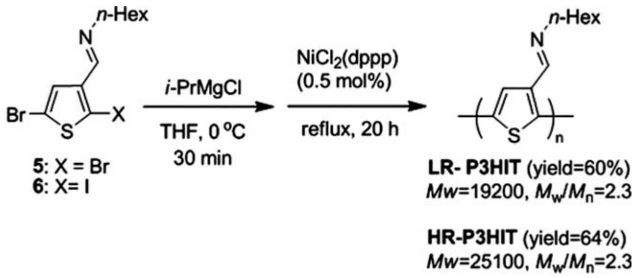
Preparation of P3HITs

The synthetic route to dihalothiophene monomers **5** and **6** is shown in Scheme 1. Bromination of 3-thiophenecarboxaldehyde (**1**) with 1 equiv of NBS afforded 5-bromo-3-thiophenecarboxaldehyde (**2**) in 51% yield. The reaction of **1** with excess amount of NBS gave 2,5-dibromo-3-thiophenecarboxaldehyde (**3**) in 87% yield. 5-Bromo-2-iodo-3-thiophenecarboxaldehyde (**4**) was readily prepared by iodination of **2** using iodobenzene diacetate and iodine. The aldehyde groups of **3** and **4** were converted into the corresponding imino group by treatment with *n*-hexylamine to afford **5** (96% yield) and **6** (96% yield), respectively.

Before the investigation on the GRIM polymerizations of **5** and **6**, their reaction behaviors with isopropyl magnesium chloride (IPMC) were investigated (Scheme 2). Compound **5** was treated with an equimolar amount of IPMC for 30 min at 0 °C. A small portion of the mixture taken by a syringe was treated with water to protonate anionic species. The resulting mixture was analyzed by GC (see Fig. S1 in the Supporting Information) and ^{1}H NMR (see Fig. S2 in the Supporting Information). It was found that the corresponding monobromothiophenes A′ and B′ were formed in a molar ratio of 7:3 as the consequence of the formation of the Grignard reagents A and B in 7:3. There was no indication of an unfavorable consumption of the imine moiety by its reaction with IPMC. The predominant formation of A would reflect the regioselective metalation assisted by the Lewis basic imino moiety. Highly selective metalation was achieved by treatment of **6** with IPMC. The selective reduction of the iodo atom at 2-position permitted the exclusive formation of A, which was confirmed by observation of the selective



SCHEME 1 Synthesis of monomers **5** and **6**.



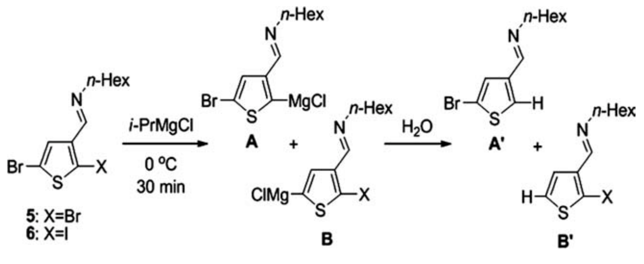
SCHEME 3 Preparation of P3HITs.

formation of the hydrolyzed product A′ by GC and ^{1}H NMR (see Figs. S1 and S2 in the Supporting Information).

The GRIM polymerization of **5** was performed in the presence of NiCl$_2$(dppp) as a catalyst (Scheme 3). Under the same conditions described above, **5** was converted to a regioisomeic mixture of the corresponding Grignard reagents, to which the nickel catalyst was added. After the solution was refluxed for 20 h, the resulting polymer was separated as methanol-insoluble fractions and was purified by column chromatography packed with triethylamine-treated silica gel to remove metal catalyst. The GRIM polymerization of **6** and the purification of the resulting polymer were also conducted under the same conditions. The polymers obtained from **5** and **6** afforded a low regioregular P3HIT (LR-P3HIT; $M_w = 19{,}200$, $M_w/M_n = 2.3$) and a high regioregular P3HIT (HR-P3HIT; $M_w = 25{,}100$, $M_w/M_n = 2.3$), respectively (Scheme 3). The polydispersities of resulting P3HITs were higher those reported for P3HT prepared by GRIM method ($M_w/M_n = 1.1$–1.5).[9,11] In general, the lower polydispersity of P3HT can be achieved by quenching the polymerization with HCl solution, which prevents the formation of P3HT-P3HT by the disproportionation of the P3HT-Ni(II)-Br complex. However, this method cannot be used in our system, because the imine group can be decomposed easily.

The IR spectra of the resulting polymers showed a strong absorption at 1627 cm^{-1}, which was attributable to C=N stretching. In the ^{1}H and ^{13}C NMR spectra, the signals corresponding to proton and carbon of imino groups were observed at 8.6 and 154 ppm, respectively. These spectroscopic results supported that LR- and HR-P3HIT have imino groups in the side chain, which survived the polymerization and purification processes.

The regioregularity of the resulting polymers was evaluated by ^{1}H NMR spectroscopy, which was used for distinguishing head-to-tail (HT) and head-to-head diads of poly(3-alkylthiophene).[11] The ^{1}H NMR spectrum of HR-P3HIT showed sharp signals to indicate its high HT-diad selectivity, whereas that of LR-P3HIT shows signals having shoulders to clarify the deteriorated regularity by the formation of HH diad (Fig. 1). The HT contents of LR- and HR-P3HIT estimated by using the signals of —CH$_b$=N— were 70 and 95%, respectively.



SCHEME 2 Reactions of 5 and 6 with *i*-PrMgCl.

Optical Properties of P3HITs

Optical properties of P3HITs in THF and chloroform solutions were investigated by UV–vis spectroscopy. In general, UV–vis spectra of π-conjugated polymers depend on solvent, where those measured in poor solvents exhibit red shifts from those measured in good solvents due to their aggregation.[12] UV–vis spectra of P3HITs also exhibited a strongly dependence on solvent. However, in contrast to the generality, the spectra of P3HIT measured in a poor solvent (THF) exhibited "blue shift" from those measured in chloroform. The absorption maxima of LR-P3HIT in THF and chloroform appeared at 410 and 423 nm, respectively, whereas those of HR-P3HIT in THF and chloroform appeared at 393 and 425 nm, respectively (see Fig. S3 in the Supporting Information). This finding can be attributable to a polymer folding and formation of an intramolecular aggregate in THF due to a rigid imine substituent in the side chain.[12b] The introduction of an electron withdrawing imino group to PT was expected to cause a red shift of absorption maximum. However, the absorption maximum of P3HIT appeared at a shorter wavelength compared with that of P3HT (ca. 550 nm). This fact implied that the introduction of the rigid imino group at the 3-position was unfavorable for maintaining the planarity of polymer backbone, which is essential for elongation of π-conjugated system.

Besides the spectroscopic analyses in solution state, those in film state were investigated. Spin-casted P3HIT films were

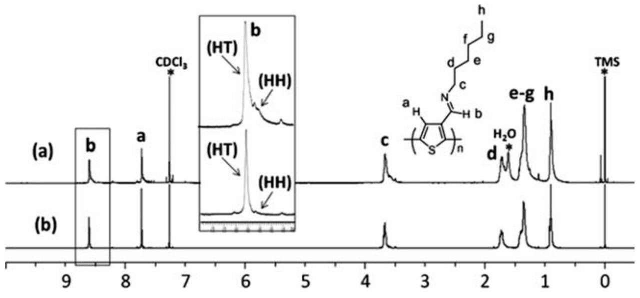


FIGURE 1 ^{1}H NMR spectra of LR- (a) and HR-P3HIT (b) in CDCl$_3$.

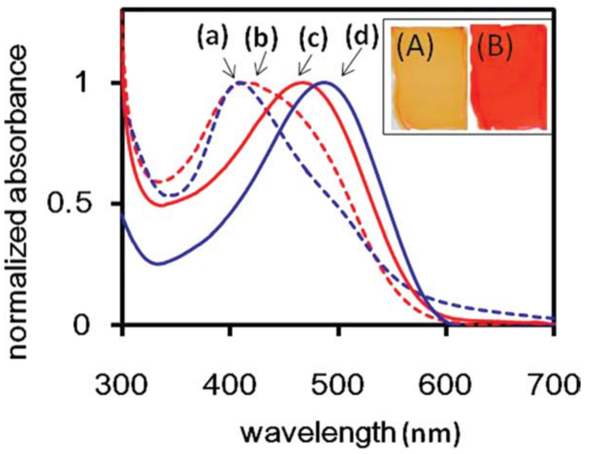


FIGURE 2 UV–vis spectra of LR-P3HIT films from THF (b) and chloroform (c) and HR-P3HIT films from THF (a) and chloroform (d). Insert shows the photographs of spin-casted HR-P3HIT films from THF (A) and chloroform solutions (B).

prepared from the THF and chloroform solutions, and their UV–vis spectra were investigated. Absorption maxima of the films of LR-P3HIT prepared from the THF and chloroform solutions appeared at 416 and 467, respectively (Fig. 2). On the other hand, those of HR-P3HIT films prepared from the THF and chloroform solutions appeared at 408 and 487 nm, respectively (Fig. 2). These wavelengths were longer than those observed in the solutions. Interestingly, UV–vis spectra of P3HIT films exhibited a strong dependence on the solvent used for casting. The drastic red shifts of absorption maxima of P3HIT films from chloroform are attributed to the intermolecular aggregation of polymer chains.[12b] On the other hand, the twist and intramolecularly aggregated structures of the polymers in THF solution may be retained even in the film; absorption maximum of the film was slightly shifted when compared with that in THF solution. The spectrum pattern of P3HIT films prepared from chloroform solution significantly depended on the regioregularity. The HR-P3HIT film exhibited an absorption maximum at longer wavelength by 20 nm than that of the LR-P3HIT film. However, the films prepared from THF solution showed a different result; absorption maximum of HR-P3HIT was blue-shifted by 8 nm compared with LR-P3HIT film. Despite the fact that HR-P3HIT has higher regioregularity than LR-P3HIT, UV–vis spectra of both HR-P3HIT in THF and HR-P3HIT film prepared from THF solution exhibited λ_{max}s at shorter wavelength than those of LR-P3HIT (Table 1). This phenomenon is not currently explainable clearly. As described above, both HR- and LR-P3HITs in THF seems to have twist and intramolecularly aggregated structure due to imino groups. We assume that LR-P3HIT containing more tail-to-tail parts, which may give relatively planar skeleton in THF due to weak repulsion by imino groups, afforded more red shift of absorption maxima than those of HR-P3HIT.

TABLE 1 Optical Properties of P3HITs

	UV–Vis λ_{max} (nm)				PL λ_{max} (nm)			
	Solution[a]		Film[b]		Solution[a]		Film[b]	
	THF	$CHCl_3$	THF	$CHCl_3$	THF	$CHCl_3$	THF	$CHCl_3$
LR-P3HIT	410	423	416	467	555	558	599	608
HR-P3HIT	393	425	408	487	559	558	606	618

[a] Conc. = 1.0×10^{-5} M.

[b] Spin casted using THF and chloroform solutions.

Photofluorescence (PL) spectra of P3HITs were measured in solution and film states (Table 1). LR-P3HIT in THF and chloroform exhibited PL λ_{max}s at 555 and 558 nm, respectively. HR-P3HIT in THF and chloroform showed those at 559 and 558 nm, respectively (see Fig. S4 in the Supporting Information). It was found that PL spectra of polymers are not affected significantly by polymer regioregularity and solvent polarity in the solution state. On the other hand, PL spectra of HR- and LR-P3HITs prepared from THF and chloroform solution were clearly dependant on the regioregularity and solvent polarity. HR- and LR-P3HIT films prepared from chloroform solution showed PL λ_{max}s at 618 and 608 nm, respectively, which are red shifted compared with those films from THF solution (606 and 599 nm for HR- and LR-P3HIT, respectively; Fig. 3).

Preparation and Optical Properties of P3TCHO

Preparation of P3TCHO from P3HIT by hydrolysis of the imino group was conducted. P3HIT solution in THF was added into 1 M HCl aqueous solution, and the solution was stirred for 30 min at 70 °C. The resulting precipitates were collected by filtration and washed with water and methanol to give P3TCHO as a black solid in 84% yield. Resulting P3TCHO was insoluble in THF, chloroform, DMF, DMSO, and so forth. IR spectrum of P3TCHO shows strong and broad C=O stretching band at 1673 cm^{-1} (see Fig. S4 in the Supporting Information). Although the complete disappearance of C=N stretching band was not clear due to the overlap by broad C=O band, a very weak intensity of aliphatic band at 2850–2940 cm^{-1} indicated disappearance of the imino moieties.

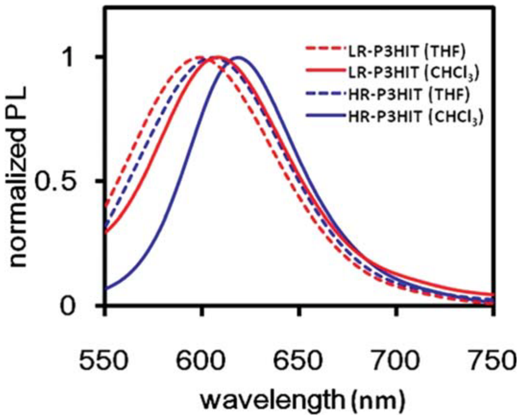


FIGURE 3 PL spectra of LR- and HR-P3HIT films from THF and chloroform solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

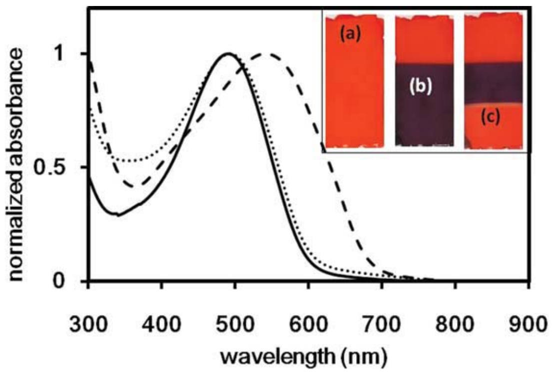
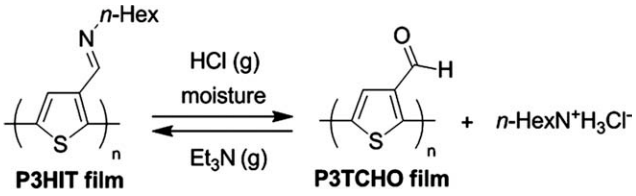


FIGURE 4 UV–vis spectra and a photo (insert) of an as-prepared P3HIT film [solid line, (a)], a film [dashed line, (b)] obtained after exposed to HCl vapor and a film [dotted line, (c)] after Et_3N teatment of HCl-exposed film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

We also succeeded in the facile preparation of a P3TCHO film from the P3HIT film by treatment with HCl gas in the presence of moisture (Scheme 4). The film of HR-P3HIT prepared from its chloroform solution by spin-coating was used. As shown in Figure 3, the film was red with the UV–vis absorption maximum at 487 nm. A part of the film (two-thirds from the bottom) was exposed to HCl gas vaporized from concentrated hydrochloric acid for 30 s. As a result, the color of the film changed from red to deep violet very quickly, with the significant shift of the absorption maximum to 550 nm. This change was in good accordance with the hydrolysis of the imino moiety into aldehyde, which was confirmed by ATR-IR analysis of the film (see Fig. S5 in the Supporting Information); the intensity of the IR absorption due to the imino group at 1627 cm^{-1} was decreased, whereas the absorption due to the aldehyde moiety at 1673 cm^{-1} appeared clearly. Another interesting feature of this system was its reversibility. When a half of the violet area was treated with triethylamine vapor, the red color of the HR-P3HIT film was recovered. At the same time, the UV–vis and IR spectra also confirmed the recovery of P3HIT having imino pendants. Hexylamine hydrochloride, which was formed by the hydrolysis of the imino group and remained in the film, would be the source of hexylamine for the recovery of the imino group.

CONCLUSIONS

P3HIT was synthesized by GRIM method. By the polymerizations of the 2,5-dibromothiophene-type monomer **5** and the 5-bromo-2-iodothiophene-type monomr **6**, the corresponding P3HITs with low regioregularity and high regioregularity were obtained, respectively. By hydrolysis of the imino groups in the side chains under acidic conditions, P3HIT was successfully converted into the correspoding PT (P3TCHO) having aldehyde groups. This transformation was also performed facilely by exposing the P3HIT film to HCl gas to give the PT having aldehyde moiety. The reverse way from aldehyde to imine was also successfully demonstrated.



SCHEME 4 Reversible preparation of P3HIT and P3TCHO films.

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