Controlled Synthesis of Poly[(3-alkythio)thiophene]s and Their Application to Organic Field-Effect Transistors

Po-Shen Lin,† Yamato Shoji,† Shakil N. Afraj,† Mitsuru Ueda, Ching-Hsuan Lin, Shin Inagaki, Taiki Endo, Shih-Huang Tung, Ming-Chou Chen,* Cheng-Liang Liu,* and Tomoya Higashihara*

ABSTRACT: Regioregular polythiophenes have been widely used in organic electronic applications due to their solution processability with chemical modification through side chain engineering, as well as their microstructural organization and good hole transport properties. Here, we introduce alkylthio side chains, (poly[(3-alkythio)thiophene]; P3ATTs), with strong noncovalent sulfur molecular interactions, to main chain thiienyl backbones. These P3ATTs were compared with alkyl-substituted polythiophene (poly(3-alkylthiophene); P3AT) variants such that the effects of straight (hexyl and decyl) and branched (2-ethylhexyl) side chains (with and without S atoms) on their thin-film morphologies and crystalline states could be investigated. P3ATTs with linear alkylthio side chains (P3HTT, hexylthio; P3DTT, decylthio) did not attain the expected higher organic field-effect transistor (OFET) mobilities with respect to P3HT (hexyl) and P3DT (decdyl) mainly due to their lower regioregularity (76−78%), although P3ATTs exhibit an enhanced tendency for aggregation and compact molecular packing, as indicated by the red-shifting of the absorption spectra and the shortening of the π−π stacking distance, respectively. Moreover, the loss of regioregularity issue can be solved by introducing more soluble 2-ethylhexylthio branched side chains to form poly[3-(2-ethylhexylthio)thiophene] (P3EHTT), which provides enhanced crystallinity and efficient charge mobility (increased by up to a factor of 3) with respect to the poly(2-ethylhexylthiophene) (P3EHT) without S atoms in the side moieties. This study demonstrates that the presence of side chain alkylthio structural motifs with nonbonded interactions in polythiophene semiconductors has a beneficial impact on the molecular conformation, morphologies, structural packing, and charge transport in OFET devices.

KEYWORDS: polythiophene, organic field-effect transistor, noncovalent interaction, alkylthio side chain, molecular aggregation
mark p-type semiconducting polymers due to their excellent balance of crystallinity and solubility. The discovery of the chain-growth mechanism in the Ni-catalyst-transfer polycondensation (also called Grignard metathesis (GRIM) polymerization) system has made it possible to supply well-defined \( \text{P}3\text{ATT} \) with predicted \( M_n \) low \( D_M \) and high \( R.R. \) up to 99%.\(^{39-42} \) Regardless of the tremendous effort expended on such controlled polymerization, \( \text{P}3\text{ATT} \) exhibits only moderate performance; for example, an OFET mobility of \( \sim 10^{-4} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\)\(^{14-15} \) and a power conversion efficiency (PCE) of around 4–5% were obtained in bulk-heterojunction (BHJ)-type PSCs based on the \( \text{P}3\text{AT}:[6,6]-\text{phenyl} \ C_{60}, \) butyric acid methyl ester (PCBM) blend system.\(^{43} \)

The use of alkylthio side chain substituents in poly-(thiophene)s, namely, poly[(3-alkylthio)thiophene] (\( \text{P}3\text{ATT} \)), is of great interest because of the dual potential applicability of strong S···S chalcogen–chalcogen and S···π intra/intermolecular interactions and controlled polymerization. Rieke and co-workers synthesized regioregular head-to-tail \( \text{P}3\text{ATT} \) (R.R. \( \sim 90\)%) with moderate \( M_n \) values of \( \sim 6k \) through the Ni-catalyzed polymerization of 3-alkylthio-2-bromo-5-(bromomocino)thiophenes via the regioselective oxidative addition of Rike zinc (\( Zn^* \)) to 3-alkylthio-2,5-dibromothiophenes.\(^{45} \) Koeckelberghs and co-workers introduced the design of the 2-regioselective dehydration at the 5-position of the thiophene dibromothiophenes.\(^{45} \) Koeckelberghs and co-workers improved the \( M_n \) value of \( \text{P}3\text{ATT} \) up to 9.6k (regioregular) and 17.5k (regio-irregular) by introducing the 3,7-dimethylol branched side chain using the "modified McCullough method" and GRIM polymerization, respectively.\(^{46} \) There seems to be a trade-off between the \( M_n \) and R.R. of \( \text{P}3\text{ATT} \), as higher R.R. generally corresponds to lower solubility, probably due to an increased number of coplanar π-conjugated structures. Thus, it prevents the propagation reaction by unwanted precipitation of \( \text{P}3\text{ATT} \) during polymerization, resulting in limited \( M_n \) values.\(^{47} \) Swager et al. synthesized \( \text{P}3\text{ATT} \) with very high \( M_n \) (54.6k) with a high R.R. of 96% via dehydrobrominative polymerization employing 3-alkylthio-2-bromothiophene as a monomer and Knochel’s base\(^{48} \) for regioselective dehydration at the 5-position of the thiophene ring.\(^{48} \) This success may arise from the design of the 2-butylolcy group as a bulky side chain. These \( \text{P}3\text{ATT}s \) were utilized as precursors for poly[3-(alkylsulfone)thiophene], exhibiting a large Faraday effect with Verdet constants up to \( 7.67 \pm 0.78 \times 10^4 \) deg T\(^{-1}\) cm\(^{-1}\). Regardless of the considerable previous effort toward the controlled synthesis of \( \text{P}3\text{ATT}s \), unfortunately, no information regarding the mobilities of \( \text{P}3\text{ATT} \) has been reported except for an octamer of head-to-head/tail-to-tail alkylthiophiene exhibiting a hole mobility of \( \sim 10^{-5} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\).\(^{49} \) Note that Li and co-workers reported PSCs fabricated with \( \text{P}3\text{ATT} \) as a donor and PCBM as an acceptor (1:1, w/w) showing a relatively low PCE of 0.34%;\(^{50} \) however, there is a lack of reports regarding the OFET mobility of \( \text{P}3\text{ATT} \). Overall, in these \( \text{P}3\text{ATT} \) molecular frameworks, the fine modulation of S···S and S···π interactions along the polythiophene backbone influences the interchain organization, film morphology, and electronic properties.

Herein, we describe the synthesis of well-defined \( \text{P}3\text{ATT} \) polymers via GRIM polymerization or dehydrohalogenative polymerization using Knochel’s base\(^{47} \) to elucidate their OFET characteristics in comparison with those of regioregular poly[3-(3-alkylthiophene] (\( \text{P}3\text{AT} \)) prepared using dehydrohalogenative polymerization. To enhance the solubility of the \( \text{P}3\text{ATT}s \), three different side chains (\( R = –\text{SC}_6\text{H}_{13}, –\text{SC}_{18}\text{H}_{37}, \) and \( –\text{SC}_6\text{H}_7(\text{br}) \)) were installed and assessed to determine the criteria for the trade-off between the R.R. and \( M_n \) values. Therefore, the modification of the side chains in polythiophenes was systematically studied, including the variation of the side chain from hexyl to longer or branched chains, as well as the replacement of the bridging carbon with a sulfur atom, to boost the interchain packing, thin-film morphology, and charge transport properties. To the best of our knowledge, the OFET characteristics of \( \text{P}3\text{ATT} \)s have not yet been clarified.

### Experimental Section

**Materials.** All reagents and solvents were commercial products purchased from Sigma-Aldrich, TCI, and Wako Pure Chemical Industries, Ltd., and used without further purification. Tetrahydrofurran (THF, 99.5%, Kanto Chemical Co., Inc.) was refluxed over sodium benzophenone under nitrogen for 2 h and then distilled immediately before use.

**Measurements.** \(^1\)H nuclear magnetic resonance (\(^1\)H NMR) spectra for polymer characterization and determination of R.R. were recorded on a JEOL JNM-ECX400 (400 MHz) in deuterated chloroform-d\(_4 \) \( (\text{CDCl}_3) \) at 25 °C, calibrated to chloroform as a standard (\( \delta_1 \) 7.24), or on a JEOL JNM-ECX600 (600 MHz) in deuterated 1,1,2,2-tetrachloroethane-d\(_2 \) \( (\text{CDCl}_3) \) at 100 °C, calibrated to 1,1,2,2-tetrachloroethane as a standard (\( \delta_1 \) 6.00). The number average and weight average molecular weights (\( M_n \) and \( M_w \)) and molar-mass dispersity (\( D_M \)) were measured via size exclusion chromatography (SEC) using a JASCO GULLIVER HPLC system equipped with a pump (JASCO PU-1580), a column oven (JASCO CO-2065Plus), a UV detector (\( \lambda = \) 254 nm, JASCO UV-1575), and an RI detector (RI-1580). The column set was as follows: a guard column (Shodex KF-G) and two consecutive columns (Shodex KF-804L and Shodex KF-805L) eluted with THF at 40 °C at a flow rate of 1.0 mL min\(^{-1}\). Polystyrene standards were used for the calibration.

Thermal analysis was performed on an SII EXSTAR 6000 system, thermogravimetry (TG) was performed with a TG/DTA 6300 thermal analyzer at a heating rate of 10 °C min\(^{-1}\), and differential scanning calorimetry (DSC) was performed using a DSC 6200 thermal analyzer connected to a cooling system at a heating/cooling rate of 10 °C min\(^{-1}\). UV–vis absorption spectra were recorded on a JASCO V-670 UV–vis spectrophotometer. Polarized optical microscopy (POM) images were obtained using a Leica 2700 M microscope equipped with a Nikon digital camera. Photoelectron spectroscopy in air (PESA) measurements were recorded using a Riken Keiki AC-2 PESA spectrometer. Atomic force microscopy (AFM) measurements were carried out in the tapping mode on an SPA-400 under ambient conditions. Grazing incidence X-ray diffraction (GIXRD) measurements were performed at the National Synchrotron Radiation Research Center (NSRRC) of Taiwan on the beamline 13AI/17A2/23A1.

**General Synthetic Procedure for Poly[3-(hexylthio)-thiophene] (\( \text{P}3\text{HTT} \)).** In a 100 mL round-bottom flask purged with \( N_2 \), 2,5-dibromo-3-(hexylthio)thiophene (\( \sim 0.6 \) g, \( \sim 1.7 \) mmol) was dissolved in dehydrated THF or dehydrated 1,4-dioxane (60 mL). To this solution was added a THF solution of 1,3-bis(diphenylphosphino)propanenickel(II) dichloride (Ni(dppe)Cl\(_2\)) was added, which was prepared just before use by mixing bis(triphenylphosphine)nickel(II) dichloride (Ni(dppe)Cl\(_2\)) and 2 equiv of 1,3-bis(diphenylphosphino)propane (dppe) in dehydrated THF (4 mL) in a 20 mL round-bottom flask purged with \( N_2 \). The mixture was allowed to stand at the set temperature (room temperature, 40 °C, 60 °C, or 100 °C) for 3 h to undergo polymerization. After quenching the polymerization with 5 M aq HCl (1 mL), the solution was poured into methanol/water (300–100 mL) in a 500 mL beaker to precipitate the polymer. After filtration, the collected polymer was purified by Soxhlet extraction with methanol, acetone, and hexane and recovered with chloroform. The chloroform

ACS Applied Materials & Interfaces

Research Article

www.acsami.org

ACS Appl. Mater. Interfaces 2021, 13, 31898–31909

31899

https://doi.org/10.1021/acsami.1c04404
solution was passed through a short silica gel column to remove residual metal contaminants and condensed using a rotary evaporator followed by freeze-drying from its absolute benzene solution to afford the purified polymer (**P3HTT**) as a purple-colored powder.

**P3HTT (8k).** Grignard exchange reaction/polymerization: in THF at room temperature. Yield: 0.081 g, 25%. **Mn** (target) = 30,000, **Mn** (SEC) = 13,200, **Dn** = 1.47. R.R. = 78%. **H NMR** (600 MHz, C$_2$D$_2$Cl$_4$, ppm): 7.34 (s, TH-4(H-T)), 7.30–7.05 (m, TH-4(H-H/T-T)), 2.97 (m, –SCH$_2$–), 1.73 (m, –SCH$_2$CH$_2$–), 1.48 (m, –SCH$_2$CH$_2$CH$_2$–), 1.32 (m, –CH$_2$CH$_2$CH$_2$–/CH$_2$CH$_3$), 0.92 (m, –CH$_3$).

**P3HTT (10k).** Grignard reaction/polymerization: in THF at 60 °C. Yield: 0.114 g, 36%. **Mn** (target) = 20,000, **Mn** (SEC) = 17,700, **Dn** = 1.29. R.R. = 78%. **H NMR** (600 MHz, C$_2$D$_2$Cl$_4$, ppm): 7.30–7.10 (m, TH-4(H-H/T-T)), 2.97 (m, –SCH$_2$–), 1.73 (m, –SCH$_2$CH$_2$–), 1.47 (m, –SCH$_2$CH$_2$CH$_2$–), 1.35–1.10 (m, other –CH$_2$–), 0.89 (m, –CH$_3$).

**P3DTT (18k).** Yield: 0.187 g, 68%. **Mn** (target) = 20,000, **Mn** (SEC) = 17,700, **Dn** = 1.29. R.R. = 78%. **H NMR** (600 MHz, C$_2$D$_2$Cl$_4$, ppm): 7.43 (s, TH-4(H-T)), 7.30–7.10 (m, TH-4(H-H/T-T)), 2.96 (m, –SCH$_2$–), 1.72 (m, –SCH$_2$CH$_2$–), 1.45 (m, –SCH$_2$CH$_2$CH$_2$–), 1.35–1.10 (m, other –CH$_2$–), 0.89 (m, –CH$_3$).

**General Synthetic Procedure for Poly[3-(2-ethylhexylthiopheno)] (P3EHT).** In a 100 mL round-bottom flask purged with N$_2$, 3-(alkylthio/alkyl)-2-bromothiophene was dissolved in dehydrated THF (50 mL). To this solution was added a THF/toluene solution of Ni(dppe)Cl$_2$ and 2 equiv of a stoichiometric amount of 2,2,6-tetramethylpiperdinylmagnesium chloride (2.97 g, 1.34 L, 1 M) at 0 °C. The Mg/H exchange reaction was performed at 0 °C for 30 min. A Ni(dppe)Cl$_2$ solution was then added to the mixture, which was prepared just before by mixing Ni(PPh$_3$)$_2$Cl$_2$ and 2 equiv of a stoichiometric amount of 2,2,6-tetramethylpiperdinylmagnesium chloride (2.97 g, 1.34 L, 1 M) at 0 °C. The Mg/H exchange reaction was performed at 0 °C for 30 min. A Ni(dppe)Cl$_2$ solution was then added to the mixture, which was prepared just before by mixing Ni(PPh$_3$)$_2$Cl$_2$ and 2 equiv of a stoichiometric amount of 2,2,6-tetramethylpiperdinylmagnesium chloride (2.97 g, 1.34 L, 1 M) at 0 °C.

**P3EHTT (27k).** Polymerization: at 60 °C for 6 h. Purple-colored powder. Yield: 0.177 g, 54%. **Mn** (target) = 30,000, **Mn** (SEC) = 26,200, **Dn** = 1.40. R.R. = 99%. **H NMR** (400 MHz, CDCl$_3$, δ ppm): 7.13 (s, TH-4(H-T)), 7.30–7.10 (m, TH-4(H-H/T-T)), 0.95 (m, S–CH$_3$), 2.97 (m, –CH$_2$CH$_2$CH$_2$–/CH$_2$CH$_3$), 1.34 (m, –CH$_2$CH$_2$CH$_2$–/CH$_2$CH$_3$), 0.92 (m, –CH$_3$).

**P3HT (26k).** Polymerization: at room temperature for 2 h. Purple-colored powder. Yield: 0.164 g, 55%. **Mn** (target) = 25,000, **Mn** (SEC) = 26,200, **Dn** = 1.20. R.R. = 99%. **H NMR** (400 MHz, CDCl$_3$, δ ppm): 6.98 (s, TH-4(H-T)), 2.79 (m, TH$_2$CH$_2$–), 1.69 (m, –CH$_3$), 1.50–1.20 (m, other –CH$_2$–), 0.90 (m, –CH$_3$).

**P3DT (26k).** Polymerization: at room temperature for 2 h. Red-colored powder. Yield: 0.164 g, 55%. **Mn** (target) = 25,000, **Mn** (SEC) = 26,200, **Dn** = 1.10. R.R. = 99%. **H NMR** (400 MHz, CDCl$_3$, δ ppm): 6.98 (s, TH-4(H-T)), 2.79 (m, TH$_2$CH$_2$–), 1.69 (m, –CH$_3$), 1.50–1.20 (m, other –CH$_2$–), 0.86 (m, –CH$_3$).

**P3EHT (23k).** Polymerization: at room temperature for 3 h. Red-colored powder. Yield: 0.176 g, 50%. **Mn** (target) = 25,000, **Mn** (SEC) = 22,800, **Dn** = 1.20. R.R. = 99%. **H NMR** (400 MHz, CDCl$_3$, δ ppm): 6.92 (s, TH-4(H-T)), 2.71 (m, TH$_2$CH$_2$–), 1.69 (m, –CH$_3$), 1.40–1.10 (m, other –CH$_2$–), 0.88 (m, –CH$_3$).

**OFET Fabrication and Characterization.** The OFETs with solution-sheared films of **P3ATTs** and **P3ATs** were fabricated to evaluate the intrinsic p-type mobility, and the method for semi-conducting polymer thin-film processing was similar to that reported previously. Highly doped Si substrates with thermally grown 300-nm-thick SiO$_2$ were sonicated successively in acetone, 2-propanol, and deionized water and then passivated using a 0.1% solution of octadecyltrichlorosilane (ODTS) in toluene at room temperature for 90 min. The polymer semiconductor solution was dissolved in a mixed solvent of chlorobenzene/chloroform (3:97 v/v) at a concentration of 10 mg mL$^{-1}$ heated at 55 °C for 30 min and deposited via the solution-shearing method with a fast shear rate at 1–3 mm s$^{-1}$ and a deposition temperature of 25 °C followed by annealing at 55 °C overnight under vacuum to remove the bulk solvent from the sample. Finally, a 60-nm-thick gold electrode was deposited via evaporation through a shadow mask at a base pressure of $<10^{-6}$ Torr. The final device architecture from bottom to top for these bottom-gate top-contact (BGTC) OFETs was Si/OTDS-treated SiO$_2$/polymer semiconductor/Al. All the OFET character-
The characteristics were measured using a Keithley 4200 semiconductor parametric analyzer inside a nitrogen-purged glove box to guarantee reproducibility. The mobility ($\mu$) of the OFET devices was obtained by fitting the following equation to the saturation region of the transfer characteristic curves: $I_d = (W/2L)C \mu (V_G - V_TH)^2$, where $W$ is the channel width (1500 $\mu$m), $L$ is the channel length (20 $\mu$m), $C$ is the gate dielectric layer capacitance per unit area (11 nF cm$^{-2}$), $V_G$ is the gate voltage, $V_TH$ is the threshold voltage, and $I_d$ is the drain current.

**RESULTS AND DISCUSSION**

Three regioregular P3ATTs were synthesized by adopting GRIM polymerization and Ni-catalyzed polycondensation using Knochel's base from monomers such as 3a–3c (see Supporting Information for the synthetic procedure) with different alkylthio chain lengths ($R = -SC_6H_{13}, -SC_10H_{21},$ and $-SC_{12}H_{25}$) and denoted P3HTT, P3DTT, and P3EHTT, respectively, via the modification of a previously reported procedure. The synthetic routes are depicted in Scheme 1a,b, and the polymerization results are summarized in Table 1. The R.R. values of the resulting P3HTT were calculated from the signal intensity ratio corresponding to the 4-$H$ thiophene proton at 7.4–7.5 ppm (head-to-tail) and 7.1–7.3 ppm (others) in the 600 MHz $^1$H NMR spectra measured in deuterated 1,1,2,2-tetachloroethane-$d_2$ (C$_2$D$_2$Cl$_4$) at 100 °C, and found to be in the range of 68–84% depending on the polymerization temperature (see Figure 1a for the representative $^1$H NMR spectrum of P3HTT (15k), Figures S2–S6 for other samples, and Figure S7 for the SEC UV traces for all the P3HTT samples). The relatively low R.R. values are probably due to there being less chemoselectivity in the Mg-Br exchange reaction between 2,5-dibromo-(3-hexylthio)thiophene and isopropylmagnesium chloride-lithium chloride ($^{2}$PrMgCl-LiCl) in tetrahydrofuran (THF), where a 43–58% and 57–58% Mg-Br exchange occurs at the 2- and 5-positions, respectively. It was found that the increase in polymerization temperature (see Figure 1a for the representative $^1$H NMR spectrum of P3HTT (15k), Figures S2–S6 for other samples, and Figure S7 for the SEC UV traces for all the P3HTT samples) and the polymerization results are summarized in Table 1. The R.R. values of the resulting P3HTT were calculated from the signal intensity ratio corresponding to the 4-$H$ thiophene proton at 7.4–7.5 ppm (head-to-tail) and 7.1–7.3 ppm (others) in the 600 MHz $^1$H NMR spectra measured in deuterated 1,1,2,2-tetachloroethane-$d_2$ (C$_2$D$_2$Cl$_4$) at 100 °C, and found to be in the range of 68–84% depending on the polymerization temperature (see Figure 1a for the representative $^1$H NMR spectrum of P3HTT (15k), Figures S2–S6 for other samples, and Figure S7 for the SEC UV traces for all the P3HTT samples). The relatively low R.R. values are probably due to there being less chemoselectivity in the Mg-Br exchange reaction between 2,5-dibromo-(3-hexylthio)thiophene and isopropylmagnesium chloride-lithium chloride ($^{2}$PrMgCl-LiCl) in tetrahydrofuran (THF), where a 43–58% and 57–58% Mg-Br exchange occurs at the 2- and 5-positions, respectively. It was found that the increase in polymerization temperature improves the $M_n$ of the obtained P3HTTs, but with the concomitant lowering of R.R. and increasing $D_M$, which indicates low polymerization controllability. In particular, the obvious trade-off between the R.R. and $M_n$ values (see Figure 2) implies that a higher R.R. prevents further propagation of the reaction at the end of GRIM polymerization, thus limiting the $M_n$ of the resulting polymers. In fact, insoluble materials emerged in the polymerization apparatus in all cases at the end of polymerization, probably because of the high intermolecular interaction of P3HTT. Similar results and trade-offs could also be confirmed in the case of P3DTT by extending the linear side chains to decylthio groups (Scheme 1, Table 1, Figure 2, and Figures S8–S11). Nevertheless, we succeeded in obtaining soluble P3HTT (15k) and P3DTT (18k) samples with relatively high $M_n$ and moderate R.R. > 76% for OFET fabrication.

To improve the solubility of P3ATTs, a typical 2-ethylhexyl branched side chain group was introduced into the new thiophene monomer, 2-dibromo-(3-(2-ethylhexylthio))thiophene. Furthermore, Ni-catalyzed polycondensation was employed using Knochel's base for the completely regioselective H/MgCl exchange at the S-position of the monomer. Consequently, regioregular P3EHTT could be synthesized with a high R.R. of 99% while maintaining a high $M_n$ of 26,500 and good solubility due to the branched side chain (Table 1 and Figure S12). While the use of Knochel’s base in the synthesis of P3HTT and P3DTT facilitated the selective H/MgCl exchange reactions at the S-position of the monomer, insoluble oligomeric materials were obtained via precipitation before the polymerization reactions were completed, possibly because of the very high crystallinity of the resulting linear-side-chain-based polymers with high R.R. and therefore coplanar main chains. The $^1$H NMR spectrum of P3EHTT (27k) is presented in Figure 1b, showing the sharp singlet signal at 7.43 ppm and doublet signals at 2.97 ppm assignable to one proton at the 4-position of the thiophene ring and two protons of the methylene protons next to the thioether unit, respectively, confirming the quite high regularity of P3EHTT (27k). These samples break the trade-off between $M_n$ and R.R. as mentioned above (Figure 2). Thus, both the polymerization method and the side chain architecture are important for the practical synthesis of high-molecular-weight regioregular P3ATTs. For comparison, high-molecular-weight
regioregular P3HT, P3DT, and P3EHT polymers were synthesized from monomers such as 5a–5c (see Supporting Information for the synthetic procedure) via a similar Ni-catalyzed polycoupling using Knochel’s base, as depicted in Scheme 1b (see Figures S13–S15 for 1H NMR spectra and Figure S16 for SEC traces). The high thermal stability of all the studied samples for device fabrication was confirmed by TGA, with 5 wt % loss temperature (T_d,5%) values in the range of 317–345 °C for P3ATTs, although they are lower than those of P3ATs (T_d,5% = 427–445 °C), probably due to the existence of heteroatom-based thiophene-S-alkyl linkages in P3ATTs (Figure S17 and Table S1). There were no transition peaks in the DSC thermograms of the P3ATTs (Figure S18 and Table S1).

Three P3ATT polymers, P3HTT (15k), P3DTT (18k), and P3EHTT (27k), were used for the described experiments to characterize the thin-film properties. The P3AT and P3ATT solutions resulted in a color change in the solution from bright orange to dark purple (Figure 3a), which is indicative of different types of polymer aggregation. The assembly behavior of the polythiophenes, depending on the side chains, was probed using UV-vis spectroscopy. Figure 3b,c presents the optical absorption spectra of the P3ATT and P3AT solutions and the corresponding films, respectively. The optical properties of the synthesized polymers are summarized in Table 2. The P3ATs dissolve well in the solutions to form isolated chains, resulting in a single low-absorption band at 440–450 nm. All P3ATT solutions exhibited broad absorption in the range of 400–650 nm, with two distinct high- and low-energy bands. The measured absorption maxima (λ_{max} (soln)) of P3HTT, P3DTT, and P3EHTT were 515, 516, and 559 nm, respectively, with a vibronic shoulder at 609, 617, and 610 nm, respectively, indicative of a strong intermolecular interaction between P3ATT backbones that can induce prominent molecular aggregation in the solution. The similarity of the absorption spectra for P3HTT and P3DTT shows that changing the length of the alkylthio group from hexyl to decyl has a weak effect on the optical properties of the polymer. Besides, the temperature-dependent absorption of P3ATT in the solution was also performed to investigate the aggregation behavior, as shown in Figure S19. All three P3ATTs yield the blue-shifted absorption band and decreased absorption and decreased absorption intensity when increasing the temperature from 20 to 70 °C. These achieve the aggregation behavior attributed to the strong noncovalent molecular interaction. In addition, the fact that there were almost no longer changes in the absorption spectra when the temperature reaches 70 °C indicates the disaggregation in the single molecular P3ATT state. The absorption of P3EHTT at 70 °C was red-shifted by ~16 nm when compared with P3HTT and P3DTT, implying that its backbone is more coplanar. The UV–vis spectra of all solution-sheared thin films show similar red-shifted absorption spectra and more noticeable vibronic shoulders at higher wavelengths, which reveal structural ordering in the solid state (Figure 3c). All the P3ATT thin films with alkylthio side chains feature red-shifted structured absorption and a more distinctive low energy 0–0 transition with respect to the alkylated-P3ATs. The absorption spectra of the P3HTT and P3DTT thin films show distinct absorption maxima (λ_{max} (film)) at 568 and 571 nm and a shoulder at 618 and 621 nm, which are assigned to the 0–1 and 0–0 vibronic transitions, respectively. The similarity of the solid-state absorption spectra also suggests that increasing the length of the alkylthio group from hexyl to decyl has a weak effect on the molecular aggregation. However, the branched side chain derivative P3EHTT has a maximum at 614 nm, accompanied by a less intense 0–1 peak at 561 nm, indicating that the absorption caused by the interchain transition is dominated by the intrachain (backbone) transition. The formation of vibrational fine structures in the P3ATTs was mainly due to the enhanced molecular S···S and S···π interactions, which increased the extent of coupling between and across the π-conjugated chromophore segments, giving rise to intermolecular packing and related structured absorption. A similar trend was noted for the bandgap determined from the absorption onset, with values from 1.87 to 2.18 eV, thus further suggesting that alkylthio side chain manipulation strongly impacts the aggregation tendency of the polymers. Owing to the high rigidity and strong intermolecular interaction, the interchain electronic coupling between P3EHTT chains cannot be disrupted even though bulky branched alkylthio side chains are attached. In contrast,

Table 1. The Results of Grignard Exchange Reaction and Synthesis of P3HTT, P3DTT, and P3EHTT.

<table>
<thead>
<tr>
<th>polymer</th>
<th>Mg/Br exchange a (%)</th>
<th>temp (°C)</th>
<th>M_0 (target)</th>
<th>M_0 (SEC)</th>
<th>D_0 (SEC)</th>
<th>R.R. (9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HTT (8k)</td>
<td>43:57</td>
<td>rt</td>
<td>30,000</td>
<td>8300</td>
<td>1.33</td>
<td>84</td>
</tr>
<tr>
<td>P3HTT (10k)</td>
<td>45:55</td>
<td>60</td>
<td>10,000</td>
<td>10,400</td>
<td>1.40</td>
<td>74</td>
</tr>
<tr>
<td>P3HTT (13k)</td>
<td>53:47</td>
<td>40</td>
<td>30,000</td>
<td>13,200</td>
<td>1.47</td>
<td>78</td>
</tr>
<tr>
<td>P3HTT (14k)</td>
<td>52:48</td>
<td>60</td>
<td>15,000</td>
<td>14,000</td>
<td>1.47</td>
<td>77</td>
</tr>
<tr>
<td>P3HTT (15k)</td>
<td>52:48</td>
<td>60</td>
<td>50,000</td>
<td>15,000</td>
<td>1.50</td>
<td>76</td>
</tr>
<tr>
<td>P3HTT (20k)</td>
<td>58:42</td>
<td>100</td>
<td>50,000</td>
<td>20,200</td>
<td>1.73</td>
<td>68</td>
</tr>
<tr>
<td>P3DTT (10k)</td>
<td>41:59</td>
<td>rt</td>
<td>20,000</td>
<td>10,100</td>
<td>1.25</td>
<td>86</td>
</tr>
<tr>
<td>P3DTT (12k)</td>
<td>48:52</td>
<td>60</td>
<td>15,000</td>
<td>12,400</td>
<td>1.25</td>
<td>77</td>
</tr>
<tr>
<td>P3DTT (18k)</td>
<td>55:45</td>
<td>60</td>
<td>20,000</td>
<td>17,700</td>
<td>1.29</td>
<td>78</td>
</tr>
<tr>
<td>P3EHTT (27k)</td>
<td>0:100</td>
<td>rt</td>
<td>30,000</td>
<td>26,500</td>
<td>1.40</td>
<td>99</td>
</tr>
<tr>
<td>P3HT (26k)</td>
<td>0:100</td>
<td>rt</td>
<td>25,000</td>
<td>26,200</td>
<td>1.20</td>
<td>99</td>
</tr>
<tr>
<td>P3DT (26k)</td>
<td>0:100</td>
<td>rt</td>
<td>25,000</td>
<td>26,000</td>
<td>1.10</td>
<td>99</td>
</tr>
<tr>
<td>P3EHT (23k)</td>
<td>0:100</td>
<td>rt</td>
<td>25,000</td>
<td>22,800</td>
<td>1.2100</td>
<td>99</td>
</tr>
</tbody>
</table>

“The Grignard exchange reaction of 2,5-dibromo-(3-hexylthio)thiophene with an equivalent of PrMgCl-LiCl were carried out in THF under a N2 atmosphere. x and y indicate the ratio of 3-alkylthio-5-bromothiophene (Grignard exchange at the 2-position) and 3-alkylthio-2-bromothiophene (Grignard exchange at the S-position) in the products after quenching with HCl aq as determined by 1H NMR. aCarried out in THF under a N2 atmosphere. bPolymerization temperature. cCalculated as follows: M_0 (target) = molecular weight of monomer repeating unit [N + [monomer]_0/([Ni catalyst])_0. d Determined by SEC using a calibration with polystyrene standards. e Determined by 1H NMR (600 MHz) in CDCl3 at 100 °C. fThe polymerization was carried out in 1,4-dioxane. gThe Ni-catalyzed polycoupling was employed using Knochel’s base. hThe regioselective dehydration at the S-position of the monomer in the Mg/H exchange reaction.”
P3EHT showed the most blue-shifted absorption peaks, mainly due to the presence of steric distortion in the conjugated backbones hindered by the branched alkyl side chain. Thus, the most apparent difference in the \( \lambda_{\text{max}} \) for P3EHTT and the corresponding P3EHT can be observed in the absorption spectra of polythiophenes with branched side chains. Here, we can conclude that the incorporation of alkylthio side chains enhances molecular interactions and strengthens the tendency to aggregate between the conjugated backbones.

The molecular ordering and conjugation length along the polythiophene chains were quantitatively analyzed by intensity ratio of the 0–0 and 0–1 transitional peaks (\( A_{0-0}/A_{0-1} \)). We see that the \( A_{0-0}/A_{0-1} \) values of the P3ATT films are

---

**Figure 1.** \(^1\)H NMR spectra of (a) P3HTT (15k) and (b) P3EHTT (27k).

**Figure 2.** Plots of R.R. vs \( M_n \) of P3HTT, P3DTT, and P3EHTT.
Figure S21. The HOMO energies of LUMO was estimated. All the energy levels are provided with respect to those of P3AT data are summarized in Table 2. By combining the data from PESA with the optical bandgap of the UV photoelectron spectroscopy in air (PESA; Figure S20), and the interactions, which promotes increased and favorable intermolecular interactions.

The HOMO of all P3ATTs and P3ATs was measured via photoelectron spectroscopy in air (PESA; Figure S20), and the data are summarized in Table 2. By combining the data from PESA with the optical bandgap of the UV–vis spectrum, the LUMO was estimated. All the energy levels are provided in Figure S21. The HOMO energies of P3ATTs move downward with respect to those of P3ATs, which agree well with previously reported trends.\textsuperscript{53,55}

The surface morphology of the polymer thin films was monitored via POM and AFM. Uniform solution-sheared morphologies can be found in the optical microscope images. The POM images were taken when the films were rotated 0° and 45° to the analyzing polarizer, as shown in Figure 4. It is evident from Figure S22 that there is no change in color and contrast in the POM images of the P3DT, P3EHT, P3HTT, and P3DTT films for any rotation angle. However, bright birefringence textures under cross polarizers were observed when both the P3HT and P3EHTT films were rotated to the crossed polarization axes. This change in optical brightness between crossed polarizers indicates that the resultant films were highly oriented.\textsuperscript{53} The high regioregularity (more extended chains) of P3HT and P3EHTT allows the chains to be well aligned under shearing, and the resultant orientation can be maintained during the solvent evaporation process due to their high molecular weights (longer chain relaxation times).\textsuperscript{56} AFM height images of the P3ATT and P3AT solution-sheared thin films are shown in Figure 4 to examine the nanoscale morphologies. The observation of a randomly entangled nanofibrillar network in the P3HT, P3DT, and P3EHT films implies the existence of polymer crystallites.\textsuperscript{57} In addition, it is evident that nanofibrils are distributed in-plane due to the π–π stacking of polymer chains during the shearing process. Notably, all the AFM images of the P3ATT films revealed more densely packed nanofibrils, demonstrating enhanced aggregation through the introduction of alkylthio side chains. In particular, shear coating of the P3EHT film results in macroscopic nano brils, which is also consistent with the results observed in the POM and absorption spectra. In addition, the increased surface roughness of P3HT and P3EHTT (2.51 and 2.06 nm, respectively) as compared with deposited films from other samples (0.73–1.50 nm) may be

<table>
<thead>
<tr>
<th>polymer</th>
<th>$\lambda_{\text{vis}}$ (nm)</th>
<th>$\lambda_{\text{HOMO}}$ (nm)</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>449</td>
<td>559</td>
<td>1.94</td>
<td>−4.74</td>
</tr>
<tr>
<td>P3DT</td>
<td>450</td>
<td>565</td>
<td>1.93</td>
<td>−4.79</td>
</tr>
<tr>
<td>P3EHT</td>
<td>441</td>
<td>494</td>
<td>2.18</td>
<td>−5.10</td>
</tr>
<tr>
<td>P3HTT</td>
<td>515</td>
<td>568</td>
<td>1.90</td>
<td>−4.94</td>
</tr>
<tr>
<td>P3DTT</td>
<td>516</td>
<td>571</td>
<td>1.90</td>
<td>−4.98</td>
</tr>
<tr>
<td>P3EHTT</td>
<td>559</td>
<td>614</td>
<td>1.12</td>
<td>−4.90</td>
</tr>
</tbody>
</table>

Table 2. The Optical Properties and HOMO/LUMO Energies of P3ATTs and P3ATs.
attributed to the increased quantity of nanofibril aggregates caused by the increased crystallinity.\textsuperscript{58,59}

Grazing incidence X-ray diffraction (GIXRD) analysis was performed on the solution-sheared films to provide insight into the detailed microstructure and crystallinity of the thin films. Figure 5 and Figure S24b show the two-dimensional GIXRD patterns of P3ATs and P3ATTs with the incident X-rays parallel and perpendicular to the shearing direction.

Figure 5. Two-dimensional GIXRD patterns of (a) P3HT, (b) P3DT, (c) P3EHT, (d) P3HTT, (e) P3DTT, and (f) P3EHTT recorded for the incident X-ray oriented parallel to the shearing direction.

Figure 6. (a) Out-of-plane ($q_z$) and (b) in-plane ($q_{xy}$) one-dimensional scattering profile derived from two-dimensional scattering images of solution-sheared P3TT and P3ATT thin films.

Table 3. Crystallographic Parameters and OFET Performance of P3ATs and P3ATTs.

<table>
<thead>
<tr>
<th>polymer</th>
<th>crystallographic parameters</th>
<th>OFET parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d_{100}$ (Å)</td>
<td>$d_{010}$ (Å)</td>
</tr>
<tr>
<td>P3HT</td>
<td>16.97</td>
<td>3.88</td>
</tr>
<tr>
<td>P3DT</td>
<td>24.15</td>
<td>3.88</td>
</tr>
<tr>
<td>P3EHT</td>
<td>15.31</td>
<td>/</td>
</tr>
<tr>
<td>P3HTT</td>
<td>18.51</td>
<td>3.76</td>
</tr>
<tr>
<td>P3DTT</td>
<td>25.14</td>
<td>3.78</td>
</tr>
<tr>
<td>P3EHTT</td>
<td>17.05</td>
<td>3.77</td>
</tr>
</tbody>
</table>
correspond to P3HT with respect to π-stacking distance of 3.77 Å, while that of the P3EHTT shows an out-of-plane (010) peak at around 1.67 Å⁻¹, corresponding to a π−π stacking distance of 3.77 Å, while P3EHT has no trace of this peak in both qₓ and qᵧ directions. The reduced π−π distance with the introduction of the alkylthio side chain may potentially shorten the pathway for carrier migration in P3EHTT molecules as compared with the random orientation associated with the amorphous microstructure of P3EHT (as indicated by the less discernible crystalline peak intensities).

To correlate the aforementioned thin-film morphologies with the charge transport properties of solution-sheeted P3ATT and P3AT thin films, BGTC OFETs were fabricated with standard dimensions and measured inside a nitrogen atmosphere. The output and transfer plots of the p-type P3ATT and P3AT OFETs are depicted in Figure 7 and Figure S23, and the calculated OFET figures of merit, including the field-effect mobility (μ), threshold voltage (Vₜh), and ON/OFF ratio (I.ON/I.OFF), are shown in Figure 7c and Table 3. The P3HTT- and P3DTT-based OFETs are expected to exhibit moderately high maximum mobilities (μ.max) of 2.14 × 10⁻¹ and 7.41 × 10⁻² cm² V⁻¹ s⁻¹, respectively, with average mobilities (μ.avg) of (1.69 ± 0.19) × 10⁻² and (6.66 ± 0.51) × 10⁻² cm² V⁻¹ s⁻¹, respectively. However, the P3EHTT-based OFETs exhibited electrical mobilities degraded by 2–3 orders of magnitude, which are clearly due to the disruption of conjugation introduced by the branched alkyl side chain in the twisted thiophene backbone. The mobility in alkylthio-substituted P3ATT OFETs follows trends similar to those exhibited by P3AT OFETs in the following order: P3HTT > P3DTT > P3EHTT. Thus, μ.max(μ.avg) falls from 1.48 × 10⁻³ ((1.01 ± 0.18) × 10⁻²) cm² V⁻¹ s⁻¹ for P3HTT to 7.68 × 10⁻⁴ ((5.89 ± 0.96) × 10⁻³) cm² V⁻¹ s⁻¹ for P3DTT and 1.47 × 10⁻³ ((7.98 ± 3.41) × 10⁻³) cm² V⁻¹ s⁻¹ for P3EHTT. Both the mobilities of P3HTT and P3DTT with smaller alkyl side chain lengths (−C₆H₁₃ or −SC₆H₁₃) were enhanced compared to those of the P3DT and P3DTT counterparts with longer side chains (−C₆H₁₇ or −SC₆H₁₇). Thus, the longer insulating linear side chains of P3DT and P3DTT may not be beneficial for charge transport, although they have a packing motif similar to that of P3HTT and P3HTT. A comparison of the P3ATT and P3AT series reveals that the mobility in P3HTT and P3DTT still lags behind that in P3HT and P3DT, even though strong molecular interactions can be observed based on absorption spectra and AFM morphologies, and a decreased π−π stacking distance can be obtained. The main reason for the mobility reduction of the P3HTT and P3DTT samples is the regiorandomness due to their limited solubility, which decreases the crystallinity and π-conjugated backbone alignment. Although the mobility of the P3HTT OFETs is not as high as expected, it should be noted that regiorandom P3HT with a similar regioregularity of ~77% showed a peak charge mobility of ~10⁻⁷ cm² V⁻¹ s⁻¹, which is 100 times lower than that of the P3HTT OFETs studied here. With the aid of a
branched side chain to overcome the solubility issue, the comparable high regioregularity of P3EHTT and P3EHT results in the former having a 3 times higher mobility than the latter. It can be seen that the introduction of an alkylthio side chain helps in the formation of S⋯S and S⋯π interactions and enhances the charge transport properties in the polythiophene films. The $L_{ON}/L_{OFF}$ increases in the range of 10² to 10⁶, depending on the electric field-induced ON state $L_{ON}$ of the devices. The large negative $V_{th}$ of the P3HTT and P3DTT OFETs probably arises from the presence of defects caused by the regiorandomness. This study provides a guideline for the molecular design of side chain engineering, and alkylthio-substituted polythiophene has a positive effect on device performance.

**CONCLUSIONS**

In summary, we have shown that noncovalent S⋯S and S⋯π molecular interactions are caused by the functionalization of the alkylthio side chain in semiconducting regioregular polythiophenes. The effects of additional sulfur atoms attached to alkyl chains of different lengths and branching on the aggregation behavior, molecular packing, nanoscale morphologies, and their solid-state electronic behaviors were systemically investigated. A series of P3ATs and P3ATTs were synthesized by considering the lengths of the alkyl/alkylthio spacer consisting of P3HT, P3DT, and P3HTT/P3DTT and bulky branched moieties consisting of P3EHTT. Comparison of the P3ATTs with the P3AT variants demonstrates that the alkylthio-substituted side chain has a pronounced effect on the aggregation/self-assembly behavior and frontier energy levels. The corresponding charge transport properties can also be connected to the thin-film morphologies and crystalline microstructures investigated by POM/AFM images and GIXRD, respectively. The use of P3HT and P3HTT results in a significantly increased charge mobility in OFET devices compared to P3DT and P3DTT with the longer side chain spacer and P3EHT and P3EHTT with bulky branched chains. The enhanced aggregation and decreased π⋯π stacking distance in P3HTT and P3DTT do not lead to any increase in the thin-film crystalline order and mobility compared to alkylated P3HT and P3DT, mainly because of their regiorandomness. Only the obtained regioregular P3EHTT has a higher mobility than the low-crystallinity P3EHTT counterpart, as P3EHTT exhibits the face-on stacking mode. Our study highlights that the incorporation of noncovalent S⋯S and S⋯π interactions to control the conformation of regioregular polythiophenes is a useful way to optimize the solid-state structural organization and effective charge carrier transport in a range of electronic devices.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c04404. Materials and measurements, synthesis of monomers and polymers, 1H NMR charts, SEC traces, TGA/DSC thermograms, molecular frontier orbital energies, PESA measurements, OM/POM images, output plot, and GIXRD patterns (PDF).

**AUTHOR INFORMATION**

**Corresponding Authors**

Ming-Chou Chen — Department of Chemistry and Research Center of New Generation Light Driven Photovoltaic Modules, National Central University, Taoyuan 32001, Taiwan; orcid.org/0000-0001-9033-0131; Email: mcchen@ncu.edu.tw.

Cheng-Liang Liu — Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan; orcid.org/0000-0002-8778-5386; Email: liucl@ntu.edu.tw.

Tomoya Higashihara — Department of Organic Materials Science, Graduate School of Organic Materials Science, Yamagata University, Yonezawa, Yamagata 992-8510, Japan; orcid.org/0000-0003-2115-1281; Email: thigashihara@yz.yamagata-u.ac.jp.

**Authors**

Po-Shen Lin — Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan.

Yamato Shoji — Department of Organic Materials Science, Graduate School of Organic Materials Science, Yamagata University, Yonezawa, Yamagata 992-8510, Japan.

Shakil N. Afraj — Department of Chemistry and Research Center of New Generation Light Driven Photovoltaic Modules, National Central University, Taoyuan 32001, Taiwan.

Mitsuru Ueda — Department of Organic Materials Science, Graduate School of Organic Materials Science, Yamagata University, Yonezawa, Yamagata 992-8510, Japan.

Ching-Hsuan Lin — Department of Chemistry and Research Center of New Generation Light Driven Photovoltaic Modules, National Central University, Taoyuan 32001, Taiwan.

Shin Inagaki — Department of Organic Materials Science, Graduate School of Organic Materials Science, Yamagata University, Yonezawa, Yamagata 992-8510, Japan.

Taiki Endo — Department of Organic Materials Science, Graduate School of Organic Materials Science, Yamagata University, Yonezawa, Yamagata 992-8510, Japan.

Shih-Huang Tung — Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan; orcid.org/0000-0002-6787-4955.

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.1c04404.

**Author Contributions**
P.-S.L., Y.S., and S.N.A. contributed equally to this work.

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

M.-C.C. thanks the funding provided by MOST (109-3111-8-008-001) and the NCU-DSM Research Center. C.-L.L. gratefully acknowledges the funding from the Young Scholar Fellowship Program (Columbus Program) by the Ministry of Science and Technology (MOST) in Taiwan under Grant MOST 110-2636-E-002-021. T.H. thanks the Japan Society for the Promotion of Science (JSPS: KAKENHI 19K22211) and Tokuyama Science Foundation for the financial support. The authors thank Beamline B13A1/B17A1/B23A1 from the
Organic Field-effect Transistors.

phene-based Polymers and Its Impact on Charge Carrier Mobility

M.; Bristow, H.; Moser, M.; Salleo, A.; Anthopoulos, T. D.;

(Grant 108-2926-I-002-002-MY4) sponsored by the Ministry for English editing by National Taiwan University under the National Synchrotron Radiation Research Center (NSRRC) of Taiwan for providing beam time. This article was subsidized for English editing by National Taiwan University under the Excellence Improvement Program for Doctoral Students.

REFERENCES


