Poly(3-alkylthiophene) Films as Solvent-Processable Photoelectrocatalysts for Efficient Oxygen Reduction to Hydrogen Peroxide

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Poly(3-alkylthiophene) films play a central role in various organic devices due to their solvent processability and their remarkable electrical and optical properties. The (photo)electrocatalytic abilities of unsubstituted and solvent-insoluble polythiophenes in the reduction of O$_2$ to H$_2$O$_2$ in a basic aqueous electrolyte have recently emerged as an advanced function. Herein, the electrocatalytic and photoelectrocatalytic abilities of solvent-processable poly(3-alkylthiophene) films at pH 12 are demonstrated, as well as their characteristics are re-examined from the viewpoints of the polymer structure, electrochemistry, photochemistry, and film nanostructure. A comparison of the above characteristics reveals the requirements for effective (photo)electrocatalytic O$_2$ reduction to H$_2$O$_2$ production. In addition, the addition of an organic salt to the polymer solution changes the formed film characteristics. The thin film of the regioregular poly(3-hexylthiophene-2,5-diyl) containing a small amount of tetramethylammonium bis(trifluoromethanesulfonyl) imide is easily formed by a solvent-based process and features lower crystallinity, a porous film nanostructure, and high conductivity. This polymer acts as a robust photoelectrocatalyst for the reduction of O$_2$ to H$_2$O$_2$ with a conversion rate of 3.9 $\times$ 10$^3$ mg (H$_2$O$_2$) $\text{photocat}^{-1}$ h$^{-1}$ or $\approx$ 0.040 mg (H$_2$O$_2$) cm$^{-2}$ h$^{-1}$ and a high Coulombic efficiency of $>$ 95% at 0.1 V bias from the theoretical potential.

1. Introduction

Poly(3-alkylthiophene) films, such as poly(3-hexylthiophene-2,5-diyl) (P3HT) films, exhibit excellent electrical and optical properties, such as high charge mobilities and visible light-absorption.$^{[1]}$ In addition, due to their high solubilities, they can easily form thin films and hence have been used in a wide range of organic devices, such as solar cells,$^{[2]}$ transistors,$^{[3]}$ and sensors.$^{[1c]}$ Basic and theoretical studies into their film morphology, crystallinity, and molecular structure have been conducted with the aim of developing efficient charge transport materials.$^{[4]}$

Recently, solvent-unprocessable and unsubstituted polythiophenes have been demonstrated to act as photoelectrocatalysts for the reduction of O$_2$ to H$_2$O$_2$ with a high efficiency ($>$ 95%), a high selectivity ($\approx$ 100%), and an extremely high durability in basic aqueous electrolytes (pH 12–13), due to their unique catalytic cycles.$^{[5]}$ They also act as electrocatalysts in the dark,$^{[6]}$ and the light absorption enables their photocatalytic abilities without changing their catalytic cycles.$^{[1c]}$ A polythiophene derivative, whose highest occupied molecular orbital (HOMO) level was properly tuned by introducing a benzene ring into the polythiophene structure, acted as a visible light-driven photocatalyst for the production of H$_2$O$_2$ in combination with a common electrocatalyst for oxygen evolution.$^{[1c,7]}$

H$_2$O$_2$ is a common and green oxidant used in pulp bleaching, water purification, sterilization, and in the manufacture of key chemicals and recently attracted attention as a next-generation fuel to replace hydrogen.$^{[5d,8]}$ However, H$_2$O$_2$ is commonly manufactured by the anthraquinone method, which incurs a heavy environmental load, in addition to high manufacturing and transportation costs.$^{[5d,8]}$ Moreover, due to the use of anthraquinone as a catalyst, this method presents numerous other disadvantages, including the use of harmful and toxic solvents (e.g., benzene), the use of high-pressure hydrogen gas ($\geq$ 5 atm), and the use of precious metals (e.g., palladium catalysts) in the hydrogenation process. The use of high-pressure hydrogen gas limits the H$_2$O$_2$ production sites to locations where hydrogen gas can be easily obtained, such as areas close to refineries. Moreover, to support its wide range of applications, the produced H$_2$O$_2$ must be transported as a highly concentrated aqueous solution (35–70 wt%) containing a stabilizer. It should be noted that concentrated H$_2$O$_2$ solution ($\geq$ 5 wt%) is often treated as a harmful substance, and a low-concentration H$_2$O$_2$ solution (i.e., 0.1–5 wt%) is commonly used for most of the applications. For a future sustainable society, an environmentally friendly H$_2$O$_2$ production method is required. In this context, the...
electrochemical or photochemical reduction of $O_2$ to produce $H_2O_2$ on polythiophene has been reported to provide a low-concentration aqueous $H_2O_2$ solution.\textsuperscript{[5d]} As the required reactants are only $O_2$ and water, in situ $H_2O_2$ production can be applied in any locations, which may lead to a breakthrough in $H_2O_2$ production. However, for the practical application, it is desirable that the catalyst itself is commercially available and facilely solvent processable.

Herein, we focus on solvent-processable poly(3-alkylthiophene) films, which can be formed on a wide area uniformly, coated on various substrates, and whose thickness can be adjusted easily. The characteristics of poly(3-alkylthiophenes) with different regioregularities and alkyl chain lengths are re-examined by unified methods from the viewpoint of the polymer structure, electrochemistry, photochemistry, and film nanostructure. Their (photo)electrocatalytic abilities for the reduction of $O_2$ to produce $H_2O_2$ are demonstrated. We clarify the correlation between their physical properties and catalytic abilities and introduce a facile strategy to improve their catalytic abilities, for efficient $H_2O_2$ production.

2. Results and Discussion

2.1. Characterization of Poly(3-alkylthiophene) Films

The characteristics of poly(3-alkylthiophenes) with different regioregularities and alkyl chain lengths (i.e., rr-P3BT, rr-P3HT, rra-P3HT, and rr-P3OT) were re-examined from the viewpoints of the polymer structure, electrochemistry, photochemistry, and the film nanostructure. Although there are numerous reports for each poly(3-alkylthiophene),\textsuperscript{[4c]} the use of different measurement methods resulted in significant variations in the characteristics. For example, the HOMO level of rr-P3HT has been reported to range from $-4.6$ to $-5.2$ eV.\textsuperscript{[9]} Therefore, this study aimed to make a legitimate comparison of the physical characteristics of such materials using the unified method, first of all. The regioregularity, molecular weight, band structure, and conductivity are shown in Table 1.

The X-ray diffraction (XRD) patterns showed crystalline signals for thin films of rr-P3BT, rr-P3HT, and rr-P3OT; no peak observed for the rra-P3HT thin film indicated its amorphous characteristic (Figure S1, Supporting Information). From the surface scanning electron microscope (SEM) images (Figure S2a, S2b, and S2d, Supporting Information) of rr-P3BT, rr-P3HT, and rr-P3OT, it was observed that rr-P3BT (Figure S2a, Supporting Information) exhibited surface roughness and cracks, whereas the longer alkyl chains associated with rr-P3HT and rr-P3OT resulted in fewer cracks and a reduced roughness. In the case of rra-P3HT (Figure S2c, Supporting Information), similar cracks, for rr-P3BT (Figure S2a, Supporting Information), were observed, whereas the roughness was reduced (Figure S2b, Supporting Information).

From the photoelectron spectroscopy in air (Figure S3, Supporting Information) and the UV–vis spectra (Figure S4, Supporting Information) obtained for poly(3-alkylthiophene)s, their HOMO level, bandgap, and lowest unoccupied molecular orbital (LUMO) level were estimated (Table 1). Although the HOMO levels of rr-P3BT, rr-P3HT, and rr-P3OT were similar (i.e., $\approx -4.68$ eV), the HOMO level of rra-P3HT was slightly deeper, at $-4.73$ eV. In terms of the bandgap, rr-P3BT, rr-P3HT, and rr-P3OT presented

| Table 1. Characterization of poly(3-alkylthiophene)s. |
|-----------------------------------------------|
| Regioregularity\textsuperscript{a} [%] | $M_a$ ($\times 10^4$)\textsuperscript{b} | $M_w/M_n$\textsuperscript{c} | HOMO\textsuperscript{d} [eV] | Bandgap\textsuperscript{d} [eV] | LUMO [eV] | Conductivity\textsuperscript{e} ($\times 10^{-4}$ S cm$^{-1}$) |
|-----------------------------------------------|
| rr-P3BT | 95 | 2.66 | 2.52 | $-4.68$ | 1.9 | $-2.74$ | 1.9 |
| rr-P3HT | 97 | 2.63 | 2.11 | $-4.69$ | 1.86 | $-2.83$ | 2.2 |
| rra-P3HT | 59 | 2.22 | 2.11 | $-4.73$ | 2.25 | $-2.48$ | 3.1 |
| rr-P3OT | 97 | 3.45 | 1.39 | $-4.69$ | 1.94 | $-2.75$ | 1.5 |

\textsuperscript{a}Determined from the NMR spectra (dichloromethane-$d_2$) of the poly(3-alkylthiophene)s. (Figure S8, Supporting Information); \textsuperscript{b}Determined by GPC (N,N-dimethylformamide (DMF)). The weight-average molecular weights and dispersities of the polymers were calculated based on linear polystyrene standards; \textsuperscript{c}Estimated by photoelectron spectroscopic in air (Figure S3, Supporting Information); \textsuperscript{d}Estimated from the UV–vis spectra (Figure S4, Supporting Information); \textsuperscript{e}The four types of poly(3-alkylthiophene) film with similar thicknesses ($\leq 50$ nm) showed comparable conductivity values in the order of $10^{-4}$ S cm$^{-1}$. |
similar values of $\approx 1.9$ eV with some fluctuation, whereas rra-P3HT exhibited a higher value of 2.25 eV. This difference can be visually observed in the film colors of rr-P3HT and rra-P3HT (Figure S4 inset, Supporting Information). In the context of the absorbance, rr-P3HT exhibited the strongest absorbance, whereas rra-P3HT exhibited a weak absorbance that was approximately two-thirds that of rr-P3HT. This was presumably ascribed to the dense and semi-crystalline structure (the $\pi \cdots \pi$ overlap) of rr-P3HT (Figure S1, Supporting Information), and amorphous (unpacked) structure of rra-P3HT (Figure S1, Supporting Information).

Based on these results, it was considered that a comparison of the catalytic abilities of these poly(3-alkylthiophene) films, which have been shown to possess slightly different physical properties, would reveal the requirements for the efficient reduction of $\text{O}_2$ to $\text{H}_2\text{O}_2$.

### 2.2. Photo- and Electrochemical Properties of Poly(3-alkylthiophene) Films

As a typical example, the electrochemical properties of rr-P3HT (thickness $50 \pm 10$ nm on a glassy carbon substrate) in a basic aqueous electrolyte (pH 12) in the dark were investigated (Figure 1a). rr-P3HT showed almost no reduction current under an argon atmosphere, although a reduction current was observed in air (see the current density at $-0.4$ V vs Ag/AgCl in Figure 1a).

Quantification of the amount of $\text{H}_2\text{O}_2$ produced after long-term chronoamperometric measurements at $-0.4$ V also confirmed that $\text{H}_2\text{O}_2$ production was successful with a high Coulombic efficiency of 96%. It was demonstrated that this reduction current under air can be ascribed to the reduction of $\text{O}_2$ to produce $\text{H}_2\text{O}_2$, and that the solvent-processable rr-P3HT acts as an $\text{O}_2$ reduction electrocatalyst with a low overpotential. Strictly speaking, at a higher pH than the $\text{pK}_a$ of $\text{H}_2\text{O}_2$ (11.6), $\text{O}_2$ reduction follows Equation (1) to form $\text{HO}_2^-$ with the theoretical potential ($E^\circ$).

$$\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightleftharpoons \text{HO}_2^- + \text{OH}^-$$

$$E^\circ = +0.358\text{V versus standard hydrogen electrode (SHE)}$$  \hspace{1cm} (1)

By following the previous article,$^{[10c]}$ the equilibrium potential ($E_{eq}$) for the reaction conditions is calculated to be $+0.79$ V versus reversible hydrogen electrode (RHE) ($-0.12$ V vs Ag/AgCl) with $[\text{HO}_2^-] = 0.001$ m, $[\text{OH}^-] = 0.01$ m, and $\text{O}_2$ 160 torr. $\text{HO}_2^-$ is regarded as a $\text{H}_2\text{O}_2$ equivalent and instantaneously reacts with an acid to form $\text{H}_2\text{O}_2$.

Similarly, rr-P3BT, rra-P3HT, and rr-P3OT (thickness $50 \pm 10$ nm) also demonstrated an electrocatalytic ability at pH 12 in the dark (Figure 1b). Among these species, rra-P3HT acted as an exceptionally active electrocatalyst with small overpotential (see the blue line in Figure 1b). Considering that rr-P3BT,

![Figure 1.](image-url)
rr-P3HT, and rr-P3OT had almost the same overpotential \( \approx 0.15 \) V, these relatively large overpotentials were presumably ascribed to a highly stacked structure (see the XRD pattern in Figure S1, Supporting Information), which inhibited the catalytic cycle \(^{[5]}\) (the attachment of \( \text{O}_2 \) to the thiophene structure or the detachment of \( \text{O}_2\text{H}^- \)) and enhanced these required activation energies. rra-P3HT also showed the steeper slope of the current trace (see in Figure 1b), which was ascribed to favorable reactant diffusion conditions or exposure of more catalytic sites due to its amorphous and porous film structure (see the XRD pattern in Figure S1, Supporting Information, and the SEM images in Figure S2c and S2g, Supporting Information) and low reaction resistance due to its high conductivity (see Table 1).

Under light irradiation, rr-P3BT, rr-P3HT, rra-P3HT, and rr-P3OT demonstrated photoelectrocatalytic abilities (Figure 1c, positive shift of onset potential and increase in reduction current) \((\text{Figure 2})\). It was found that rr-P3HT showed a high photovoltage (Figure 1d) corresponding to its deep HOMO level, but other three types of poly(3-alkylthiophene) showed a low photovoltage (Figure 1c,d), not corresponding to their HOMO levels, which indicates that the semicrystalline structure (brought by the alkyne chains) inhibits or limits the photovoltage. This should be ascribed to an interface barrier between crystalline and amorphous regions for excitons in the poly(3-alkylthiophene) film with high regioregularity, which corresponded to \( \approx 0.3 \) eV as an energy gap in the previous literature \(^{[11]}\) and was consistent with the difference of open-circuit potentials between rra-P3HT and rr-P3HT (see Figure 1d). While rra-P3HT is mainly composed of the amorphous region, the others are composed of both crystalline and amorphous regions \(^{[11]}\) (see Figure S1, Supporting Information), and the excitons photoinduced in rr-P3HT have to be transported between crystalline and amorphous regions in most cases, which presumably limits its photochemical properties.

However, rr-P3HT presented a low reduction current at more positive potentials than \( \text{E}_{\text{eq}} \). This was attributed to its reduced level of light absorption (see Figure S4, Supporting Information) and the shallower LUMO level, that might prevent transfer of an electron to the reactant (Figure 2). At more negative potentials than \( \text{E}_{\text{eq}} \), a high reduction current was observed, as in the case of the electrocatalyst in the dark. On the other hand, the small differences found in the catalytic activities among these three types of poly(3-alkylthiophene) films with high regioregularity were presumably due to the strength of light absorption (as indicated in Figure S4, Supporting Information). In the chronoamperometrical measurement at \(-0.2\) V (relatively close to \( \text{E}_{\text{eq}} \)), rr-P3HT showed a stable reduction current of \(-20\) \( \mu \text{A cm}^{-2} \), which was the highest value \((\text{Figure 3a})\). In contrast, the current of rr-P3HT decreased with time due to delamination, which was presumably caused by the weak adhesiveness to the substrate (rra-P3HT film was completely peeled off after 30 min of measurement.)

Subsequent optimization of the film thickness of the rr-P3HT thin film showed that the reduction current reached its highest value at 50 nm (Figure 3b). This is supported by considering the diffusion length of excitons.\(^{[12]}\) Furthermore, considering that the film thickness does not dramatically affect the reduction current, the reduction current, in this case, can be limited by the interface itself.

Based on the earlier results and the physical characteristics of the poly(3-alkylthiophene)s described in Section 3.1, the requirements for a highly efficient \( \text{O}_2 \) reduction reaction to produce \( \text{H}_2\text{O}_2 \) in the dark and under light irradiation could be deduced. More specifically, in the dark, favorable reactant diffusion conditions or exposure of more catalytic sites (i.e., amorphous and porous structure) are necessary to ensure an appropriate number of reaction sites, and a high conductivity is required for efficient charge transfer; low crystallinity (amorphous) is preferred to

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**Figure 2.** Energy diagrams for rr-P3HT and rra-P3HT.

**Figure 3.** Photoelectrochemical properties. a) Chronoamperometric measurements of rr-P3BT (black trace), rr-P3HT (red trace), rra-P3HT (blue trace), and rr-P3OT (green trace) at \(-0.2\) V versus Ag/AgCl and pH 12. b) Chronoamperometric measurements of the rr-P3HT films of 10 nm (black trace), 25 nm (blue trace), 50 nm (red trace), and 75 nm (green trace) thickness at \(-0.2\) V versus Ag/AgCl and pH 12.
activate the catalytic ability. Under light irradiation, superior absorbance properties are necessary to enhance the effect of light energy, the film thickness must correspond to the diffusion length of the excitons, and low crystallinity (amorphous) is preferred to remove an interface barrier between crystalline and amorphous regions in the polymer for efficient exciton transport.

2.3. Improvement of the (Photo)electrocatalytic Activity by the Addition of Organic Salts

To improve the efficiency of H2O2 production, the influence of organic salt addition to the rr-P3HT solution was examined. The addition of organic salt is relatively facile as many types of organic salts based on different cations and anions are commercially available, and they can be simply mixed with the polymer solution. In addition, the addition of organic salt is expected to produce polymer films with different physical properties (e.g., electrical conductivity) depending on the type and amount of organic salt. For this study, LiTFSI, TEAPF6, TBAPF6, and TBATFSI were selected as the organic salts to form a homogeneous rr-P3HT film, due to their high commercially availability and high solubility in the polymer solution (organic solvents).

The additive salt concentration was fixed at 10 mol% of the rr-P3HT monomer unit, four types of rr-P3HT film containing an organic salt with similar film thicknesses (≈60 nm) and chronoamperometric measurements were conducted at −0.2 V (Figure 4a). As indicated, rr-P3HT containing 10 mol% TEAPF6, TBAPF6, or TBATFSI exhibited a higher reduction current (e.g., −28 μA cm−2 for rr-P3HT containing 10 mol% TBATFSI) than in the absence of an organic salt (i.e., −20 μA cm−2), whereas the use of LiTFSI gave a lower current (i.e., −16 μA cm−2). The low current associated with LiTFSI was presumably ascribed to formation of polymer grain boundary, which serves as resistance component by the dissolution of salt, and ascribed to the reaction inhabitation from the heat of dissolution. In contrast, TEAPF6, TBAPF6, and TBATFSI are insoluble in water, the higher reduction current was achieved in the case of TBATFSI (see Figure 4a). The salt concentration was optimized to 10 mol% (Figure 4b). From a comparison of the linear sweep voltammograms of the rr-P3HT thin films prepared in the presence and absence of TBATFSI (Figure 5), it was apparent that there was a remarkable difference in catalytic ability in the dark. Overall, these results indicated that the overpotential was small in the presence of TBATFSI, and an enhancement in the slope of the reduction current was also observed.

The physical properties of the rr-P3HT thin film containing 10 mol% TBATFSI were evaluated (Figure 6 and S5, Supporting Information), and it was possible to describe the improvement in the catalytic ability based on the discussion in Section 2.2. The small overpotential is presumably ascribed to lower crystallinity by adding TBATFSI (see Figure S5c, Supporting Information). TBATFSI should dilute rr-P3HT concentration in the film (see Figure S5a, Supporting Information) and prevent the stacking and aggregation of rr-P3HT. The enhancement in the slope of the reduction current by adding salt is supported by the favorable diffusion condition or due to low crystallinity (see Figure S5c, Supporting Information) and a porous film structure similar to that of Emmental cheese (see Figure 6b) and the higher conductivity of 4.3 × 10−4 S cm−1. It is also noteworthy that the addition of organic salt can change...
the crystallinity, the film morphology, and the conductivity. Also, the more amorphous structure may expose more catalytic sites (thiophene groups) to the water interphase, suggesting that the addition of the salt facilitates a better interface. Indeed, under light irradiation, the superior reduction current at potentials below −0.1 V was observed, which could be ascribed to the improved electrocatalytic ability, resulting from the addition of an organic salt. However, the onset potential (photovoltage) did not change. It should be noted that the lower crystallinity affects the electrocatalytic ability, but does not significantly affect the photocatalytic ability, especially onset potential (photovoltage). This can be ascribed to the existence of the interface barrier between crystalline and amorphous regions even after reducing the crystallinity.

Very recently, the 3D-structured and hydrophilized rr-P3HT film was reported for the photochemical oxygen reduction to produce H₂O₂ at low pH.[13] However, the photocurrent remained <50 μA cm⁻² even supplying pure oxygen, and the plasma-treated film was degraded or delaminated from the substrate after 10 h.

In this study, long-term measurement over several hours at 0.080 V bias from Eeq under light irradiation (Figure S6, Supporting Information) gave a H₂O₂ production rate of 3.9 × 10⁻⁴ mg (H₂O₂) μgphotocat⁻¹ h⁻¹ or ≈0.040 mg (H₂O₂) cm⁻² h⁻¹, in addition to a high Coulombic efficiency of 95%, with no degradation (Figure S7, Supporting Information).

3. Conclusion

We clarified the electrocatalytic and photoelectrocatalytic abilities of solvent-processable poly(3-alkylthiophene)s in the reduction of O₂ to H₂O₂ in a basic aqueous electrolyte solution. Our results indicated that a catalyst film can be easily produced using a commercially available polymer through a solvent-processable route. A comparison of the catalytic abilities of the prepared poly(3-alkylthiophene) films, which had slightly different physical properties, revealed some requirements to achieve an efficient catalytic O₂ reduction to H₂O₂ production. More specifically, in the dark, favorable reactant diffusion conditions, a high conductivity, and low crystallinity are required, whereas under light irradiation, superior light absorbance properties, an appropriate film thickness related to the diffusion length of the excitons, and amorphous property to remove the interface barrier between crystalline and amorphous regions are necessary. It was also found that the addition of an organic salt to the rr-P3HT solution alters the formed film properties, such as porous surface, high conductivity, and low crystallinity, thereby enhancing the performance of the electrocatalyst to give a stable and high H₂O₂ production rate of 3.9 × 10⁻³ mg (H₂O₂) μgphotocat⁻¹ h⁻¹ (at 0.080 V bias from Eeq). The addition of organic salt, which changes their crystallinity, film morphology, and conductivity, is extremely facile and practical, not only in the context of this study into π-conjugated polymers for catalytic applications, but also for investigations into π-conjugated polymers for other organic devices. This strategy will therefore be expected to accelerate research aimed at improving the characteristics of π-conjugated polymers.

4. Experimental Section

Materials: Regioregular poly(3-hexylthiophene-2,5-diyl) (rr-P3HT; Production code: P2513) and tetrabutylammonium hexafluorophosphate (TBAPF₆; Production code: T1279) were purchased from Tokyo Chemical Industry. Chlorobenzene (Production code: 284513-100ML), regioregular poly(3-butylthiophene-2,5-diyl) (rr-P3BT; Production code: 495336-1G), regiorandom poly(3-hexylthiophene-2,5-diyl) (rra-P3HT; Production code: 510823-1G), regioregular poly(3-octylthiophene-2,5-diyl) (rr-P3OT; Production code: 682799-250MG), tetraethylammonium hexafluorophosphate (TEAPF₆; Production code: 434116-25G), and tetrabutylammonium bis(trifluoromethanesulfonyl)imide (TBATFSI; Production code: 86838-5G) were purchased from Sigma-Aldrich. Bis(trifluoromethane)sulfonylimide lithium salt (LITFSI; Production code: 24290-35) was obtained from Kanto Chemical Co. Standard H₂O₂ solutions were purchased from Millipore.

Material Characterization: For the legitimate evaluation of the catalytic effect of an organic material, it should always be confirmed that no residual metal is present that could affect the catalytic activity.[14] Hence, by inductively coupled plasma mass spectrometric measurements, it was confirmed that the poly(3-alkylthiophene)s, which were used in this work, contained low levels of precious metals with catalytic ability (i.e., platinum, gold, and mercury[15]) below the detection limit (0.3 ppm). It was also confirmed that the electrochemical behaviors discussed in Sections 2.2 and 2.3 were completely different from those of such conventional metal catalysts. We prepared commercially available poly(3-alkylthiophene)s with almost the same number average molar mass (Mₙ) as much as possible. Gel permeation chromatography (GPC) confirmed Mₙ of about 2 × 10⁴ – 4 × 10⁵ (Table 1). Even considering the degree of dispersion, they possessed the same order of the molecular weight (10⁴). The regioregularity of each poly(3-alkylthiophene) was determined by ¹H NMR spectroscopy from the integral ratios of the signals originating from two types of proton in the alkyl chain at ≈2.5–3.0 ppm (Table 1 and Figure S8, Supporting Information, as a representative example). The ¹H NMR signal at...
2.8 ppm was assigned to the head-to-tail polymeric structure, whereas that at 2.6 ppm was assigned to the head-to-head structure. Based on the obtained results, rr-P3BT, rr-P3HT, and rr-P3OT were found to possess a high regioregularity of >95%, whereas rra-P3HT had a low regioregularity of 59%.

Substrates: Each substrate was sonicated in chlorobenzene for 15 min and then rinsed with chlorobenzene prior to the film formation. Glassy carbon, fluorine-doped tin oxide (FTO)-coated glass, and indium tin oxide (ITO)-coated glass were purchased from Alfa Aesar (Production code: 38023-GH), Nippon Sheet Glass (Production code: FTN 1.6), and Matsunami Glass Ind., Ltd. (Production code: S9226), respectively.

Film Formation in the Absence of an Organic Salt: A chlorobenzene solution of poly(3-alkylthiophene) (20 mg mL\(^{-1}\)) was prepared and spin coated onto a glassy carbon (GC) substrate (after ozone cleaning) or a glass substrate (after cleaning with 2-propanol) at 4000 rpm for 20 s. Subsequently, the substrate was heated and dried on a hot plate at 85 °C for 15 min and then stored in nitrogen atmosphere. Thin films with different thicknesses were prepared by changing the solution concentration. The film thickness measurement had an error of ±10 nm.

Film Formation in the Presence of an Organic Salt: A chlorobenzene solution of poly(3-alkylthiophene) and the desired organic salt (mol%) was prepared and spin coated onto a GC substrate (after ozone cleaning) or a glass substrate (after cleaning with 2-propanol) at 4000 rpm for 20 s. Subsequently, the substrate was heated and dried on a hot plate at 85 °C for 15 min and then stored in nitrogen atmosphere. The film thickness measurement had an error of ±10 nm.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
K.O. and K.K. contributed to experiment planning, experiment execution, data analysis, and manuscript preparation. B.W.-J. contributed to experiment planning, data analysis, and manuscript preparation. H.N. contributed to manuscript preparation. All authors have given approval to the final version of the manuscript.

Data Availability Statement
Research data are not shared.

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