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ORIGINAL ARTICLE

Catalytic oxidative polymerization of thiophene derivatives

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The oxidative polymerization of thiophene derivatives was carried out using palladium (II) acetate as a catalyst in combination with copper (II) acetate and trifluoroacetic acid under an oxygen atmosphere. The poly(3-hexylthiophene) (P3HT) obtained through palladium-catalyzed polymerization exhibited a richer head-to-head content than authentic P3HT prepared using a conventional oxidant, and the maximum absorption and luminescence wavelengths of the P3HT were blue-shifted to 338 and 534 nm in the ultraviolet and photoluminesce spectra, respectively. The palladium-catalyzed oxidative polymerization process was applied to 3,4-disubstituted thiophene monomers. 3,4-Ethylenedioxythiophene in aqueous media was also polymerized using poly(styrenesulfonic acid). The oxidative polymerization mechanism in the palladium system is discussed.

INTRODUCTION

Aromatic polymers with long π-conjugated structures have applications in organic electronic devices such as organic light-emitting diodes, thin film transistors, and polymer solar cells because of their excellent carrier transport properties. In particular, regioregular poly(3-hexylthiophene) (P3HT) exhibits a high hole mobility, with maximal values on the order of $0.1 \, cm^2 \, V^{-1} \, s^{-1}$,[1] although it is much lower when P3HT exists in an amorphous state.[2] A number of π-conjugated polymers with various chemical structures have been synthesized, and the preparation techniques can be roughly classified into two categories. One group of techniques exploits a transition metal catalyst to construct an aryl–aryl bond from an aryl halide and a metalated aryl compound.[3–5] These metal-catalyzed coupling polymerizations require appropriate monomer preparations, for example, boronic ester derivatives are the necessary monomer units in the Suzuki coupling polymerization method. As the coupling position can be properly controlled by the positions of the leaving groups, the desired polymers can be produced with high regioregularity. The other group of techniques builds the polymer backbone using oxidative coupling between aryl compounds.[6] Because C–H bonds can be directly converted to C–C bonds, polymerization proceeds atom-economically. However, excessive amounts of metal ions such as Fe^{3+} are generally used as oxidants and have to be removed by repeated purification steps for these polymers to serve in electronic devices.

Oxidative polymerization via catalytic processes represents a more atom-economical, cleaner way to prepare a polymer backbone through C–C bond formations. One of the most common examples of catalytic oxidative polymerization, although it is C–O bond formation rather than C–C bond formation, is the polymerization of 2,6-dimethylphenol using CuCl/pyridine as a catalyst to produce poly(2,6-dimethyl-1,4-phenylene ether), a widely used engineering plastic.[7] This catalytic system utilizes oxygen as an oxidant and therefore produces only H_2O as a by-product. Some researchers have developed catalytic systems that use oxygen as an oxidant to synthesize polythiophene derivatives.[8–11] Haba *et al.* demonstrated that vanadyl acetylacetonate $(VO(acac)_2)$ catalyzed the polymerization of 3-(4-octylphenyl)thiophene in the presence of trifluoromethanesulfonic acid under an oxygen atmosphere, although an excess amount of trifluoroacetic anhydride is required to remove water, which poisons the vanadyl catalyst.[8] The resulting polythiophene exhibited a high regioregularity of ∼94%. Recently, Lee *et al.* reported that thiophene in aqueous media can be effectively polymerized using iron (III) chloride $(FeCl_3)$ as a catalyst and hydrogen peroxide as an oxidant.[10] Polythiophene nanoparticles with a narrow size distribution can be quantitatively obtained under ambient atmospheric conditions.

Carbon-carbon bond formation using palladium as the catalyst has attracted considerable attention in organic synthesis research, especially for the preparation of aryl–aryl compounds. In comparison with C–C coupling reactions employing preactivated reagents such as halogenated aryl compounds, the preparation of biaryl compounds via C–H activation proceeds through a facile and versatile synthesis process. However, few studies have been reported because of the difficulty of this synthesis.[12–16] The palladium catalyst system has been extensively investigated in the context of C–H activation. For

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example, Stuart *et al.* demonstrated that the reaction of *N*-acetylindole with aromatics at the 3-position proceeded predominantly using palladium(II) trifluoroacetate and copper(II) acetate in the presence of pivalic acid.[14] In this article, we demonstrate the polymerization of thiophene derivatives utilizing the palladium catalytic system under an oxygen atmosphere. The structural characteristics and physical properties of the resulting polythiophenes were also investigated.

EXPERIMENTAL PROCEDURES

Measurements
^{1}H and ^{13}C NMR spectra were obtained using a JEOL ALPHA500 instrument (JEOL Ltd., Tokyo, Japan) at 500 and 125 MHz, respectively. Deuterated chloroform was used as a solvent, and tetramethylsilane was used as an internal standard. Number- and weight-average molecular weights (M_n and M_w) were determined using gel permeation chromatography analysis with a JASCO RI-2031 detector eluted with chloroform at a flow rate of 1.0 ml min^{-1} and calibrated on standard polystyrene samples. Ultraviolet (UV)–vis and photoluminescent (PL) analyses were conducted using a JASCO V-570 spectrophotometer and a JASCO FP-6500 spectrofluoromer (JASCO Corporation, Tokyo, Japan), respectively. Differential scanning calorimetry (DSC) analyses were performed using a Rigaku DSC-8230 (Rigaku Corporation, Tokyo, Japan) under a nitrogen atmosphere at heating and cooling rates of 10 °C min^{-1}.

Materials
3,4-Dihexylthiophene was prepared from 3,4-dibromothiophene and *n*-hexyl magnesium bromide in the presence of dichloro[1,3-bis(diphenylphosphino)-propane]nickel(II).[17] 3,4-Dihexyloxythiophene and 3,4-dimethoxythiophene were prepared using a four-step process from diethyl thiodiglycolate and diethyl oxalate as reported in the literature.[18,19] Regioregular P3HT was prepared from 2-bromo-3-hexylthiophene using nickel as a catalyst according to the reported procedure.[20] The number-average molecular weight, polydispersity index, and regioregularity of the regioregular P3HT were 10 000, 1.31 and 98.6%, respectively. Other chemicals and solvents were used as received.

Polymerization of thiophene derivatives using the palladium catalyst system
The stated amounts of palladium(II) acetate, copper(II) acetate, and additive (base or acid) were added to a solution of monomer (5 mmol) in chloroform (5 ml) under an oxygen atmosphere. The mixture was vigorously stirred for 24 h at the stated temperatures. After the mixture had cooled to room temperature, the solution was concentrated using a rotary evaporator and poured into methanol. The precipitate was collected by filtration, washed using methanol, and dried to yield a black solid.

Synthesis of poly(3-hexylthiophene) using FeCl$_3$ (control experiment)
FeCl$_3$ (11 mmol) was added to a solution of monomer (5 mmol) in chloroform (5 ml) under an oxygen atmosphere. The mixture was vigorously stirred for 24 h at room temperature. After the mixture had cooled to room temperature, the solution was poured into methanol. The solid was extracted with chloroform using a Soxhlet apparatus, and the extract was concentrated and reprecipitated in methanol. The precipitate was collected by filtration, washed using methanol, and dried to yield a black solid.

### Dispersion polymerization of 3,4-ethylenedioxythiophene in water
3,4-Ethylenedioxythiophene (0.71 g, 5 mmol), poly(styrene sulfonic acid) (aq.) (10 g, 18 wt% in water), and water (10 ml) were added to a flask, and the mixture was dispersed using a homogenizer. Palladium(II) acetate (0.05 or 0.005 mmol) and copper(II) chloride (0.05 or 0.005 mmol) were added to the dispersion, and the mixture was stirred using a mechanical stirrer (300 r.p.m.) at 50 °C for 24 h. The dispersion was cooled to room temperature, filtered to remove a small amount of large particles, and diluted in water (50 ml) to a concentration of 1 wt%. The resulting dispersion was used without further purification.

RESULTS AND DISCUSSION

Synthesis of Poly(3-hexylthiophene) (P3HT)
In a preliminary experiment, the polymerization of 3-hexylthiophene using the palladium catalyst system with an excess of various additives was investigated (Scheme 1 and Table 1). Palladium(II) acetate and copper(II) acetate were used as the coupling and re-oxidizing agents, respectively. All of the experiments were conducted under an oxygen atmosphere to aim for oxidation of copper(I) and copper(II) mediated by oxygen, which is observed in the polymerization of 2,6-dimethylphenol. As shown in Runs 1 and 2, no coupling reaction occurred without an additive or with a base such as pyridine. However, acidic additives assisted the coupling reaction. The yields and molecular weights of the obtained polymers varied according to the acidity of the additives. When acetic acid was used as an additive, only the dimer and a small amount of a methanol-insoluble oligomer were detected. However, stronger acids such as trifluoroacetic acid or methanesulfonic acid facilitated the coupling reaction and produced the polymer after precipitation in methanol. Trifluoroacetic acid produced the polymer with the highest weight-average molecular weight (M_w), 6 300. Therefore, we investigated the polymerization conditions using palladium(II) acetate, copper(II) acetate, and trifluoroacetic acid in further detail.

The effects of the catalyst concentration, temperature, and amount of trifluoroacetic acid on the polymerization of 3-hexylthiophene are summarized in Table 2. Decreasing the amount of catalysts or withholding the copper (II) acetate entirely decreased the yield and molecular weight, and no reaction occurred without palladium(II) acetate. Using other copper salts such as copper (II) chloride provided similar results as using copper (II) acetate. The reaction temperature also influences the polymerization process. When the reaction temperature was set to 50 °C, the polymer with the highest molecular weight was obtained, and the yield was also improved. Decreasing the temperature to 25 °C reduced both the molecular weight and the yield. Finally, the ratio of trifluoroacetic acid to monomer was varied to study the role of the acidic additive. When the ratio of trifluoroacetic acid to monomer was 1, the molecular weight and the yield of the polymer decreased. Furthermore, no polymer was
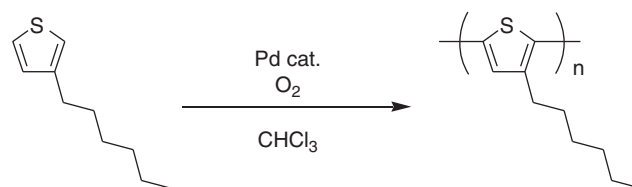
Scheme 1 Oxidative polymerization of 3-hexylthiophene.

Table 1 Effect of additives on oxidative polymerization

Run	Additive[a]	Yield (%)	M_w[b] (kDa)	M_w/M_n[b]
1	none	0	—	—
2	pyridine	0	—	—
3	CH$_3$COOH	trace	—	—
4	CF$_3$COOH	20	6.3	1.59
5	CH$_3$SO$_3$H	70	3.9	1.73
6	CF$_3$SO$_3$H	trace	2.2	9.21

[a]Polymerization was carried out using monomer of 5 mmol, catalysts of 10 mol%, and additive of 4 equiv. to monomer in chloroform at 70 °C under O$_2$ atmosphere.
[b]Determined by gel permeation chromatography eluted with chloroform using polystyrene standards.

Table 2 Oxidative polymerization using palladium catalyst at various conditions

Run	Catalysis (mol%)[a]	Additive[b]	Temp. (°C)	Yield (%)	M_w[c] (kDa)	M_w/M_n[c]
1	Pd(OAc)$_2$ (10)	4 equiv.	70	12	1.5	3.05
2	Cu(OAc)$_2$ (10)	4 equiv.	70	0	—	—
3	Pd(OAc)$_2$ (1),Cu(OAc)$_2$ (1)	4 equiv.	70	17	3.9	1.91
4	Pd(OAc)$_2$ (10), Cu(OAc)$_2$ (10)	4 equiv.	25	25	3.9	1.67
5	Pd(OAc)$_2$ (10), Cu(OAc)$_2$ (10)	4 equiv.	50	39	7.0	1.75
6	Pd(OAc)$_2$ (10), Cu(OAc)$_2$ (10)	1 equiv.	50	25	1.9	2.06
7	Pd(OAc)$_2$ (10), Cu(OAc)$_2$ (10)	5 mol%	50	0	—	—

[a]Polymerization was carried out using monomer of 5 mmol, catalysts, and CF$_3$COOH in chloroform of 5 ml under O$_2$ atmosphere.
[b]The amount of CF$_3$COOH against monomer.
[c]Determined by gel permeation chromatography eluted with chloroform using polystyrene standards.

Table 3 Effect of atmosphere on oxidative polymerization

Run	Atmosphere[a]	Yield (%)	M_w[b] (kDa)	M_w/M_n[b]
1	O$_2$	39	7.0	1.75
2	Air	24	7.0	3.50
3	N$_2$	28	3.1	3.04

[a]Polymerization was carried out using monomer of 5 mmol, catalysts of 10 mol%, and CF$_3$COOH of 4 equiv. to monomer in chloroform of 5 ml at 50 °C.
[b]Determined by gel permeation chromatography eluted with chloroform using polystyrene standards.

Figure 1 ^{1}H NMR spectra of (**a**) authentic P3HT and (**b**) P3HT obtained under our conditions, and (**c**, **d**) ^{13}C NMR spectra of the obtained P3HT.

obtained using a catalytic amount of trifluoroacetic acid (5 mol%). These findings demonstrate that an excess amount of an acidic additive is required to enable the polymerization mechanism when using the palladium catalyst system.

Finally, the polymerization under optimized conditions (Run 5 in Table 2) was conducted under various atmospheres to demonstrate the role of oxygen as an oxidant. Table 3 summarizes the results of polymerization under oxygen, air, and nitrogen. Although the polymer is still obtained when air or nitrogen were used, both the yield and the molecular weight of the polymer obtained under oxygen exceeded those obtained under the other atmospheres. This result indicates that oxygen presumably acts as a re-oxidizing agent in the palladium catalytic cycle.
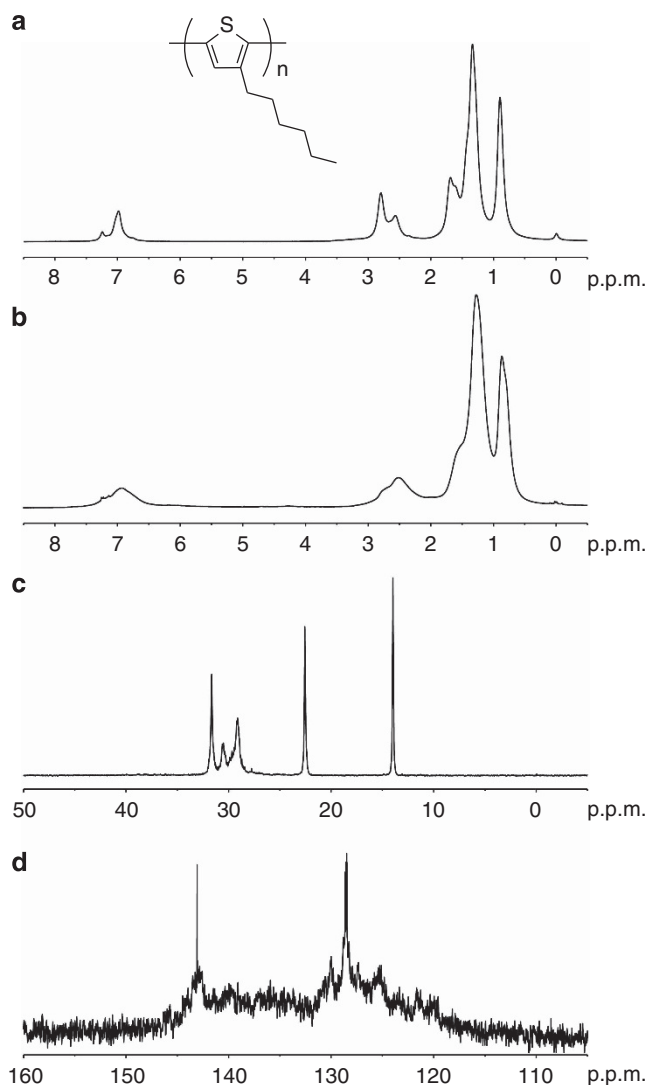
Polymer characterization

The structure of the P3HT obtained using the palladium catalyst system was confirmed through ^{1}H and ^{13}C NMR spectra. Authentic P3HT was prepared as a control sample via oxidative polymerization using FeCl$_3$. The regioregularity of P3HT can be estimated from the ^{1}H NMR spectrum by comparing the integral ratio of the signals at 2.6 and 2.8 p.p.m., which are assigned to the α protons of the hexyl group in head-to-head and head-to-tail configurations, respectively. Generally, the regioregularity of the P3HT obtained by oxidative polymerization will be random without employing any elaborate procedures. Therefore, the two signals indicate rich head-to-head content when compared with regioregular P3HT, as demonstrated in Figure 1a. The polymer derived from the palladium coupling exhibited more head-to-head content than the authentic polymer obtained using FeCl$_3$, and all of the signals were broadened (Figure 1b). Furthermore, two sharp signals at 143.14 and 128.46 p.p.m., in addition to broadened signals, are observed in the aromatic region of the ^{13}C NMR spectrum of the polymer (Figure 1d). These two sharp signals are assumed to arise from carbons at the 2- and 3-position of the thiophene ring with head-to-head linkage, as reported in the literature.[21] However, the broadened signals imply that undesired linkages, such as a reaction at the 4-position, probably also occurred to some degree. Therefore, only the signals assignable to the linkage at the 2-positions of the two thiophene rings are emphasized because of the ambiguity of the coupling position of tail-to-tail linkages. Undesired branching structures may also be formed, which could explain the low molecular weights and low yields of the polymers.

Optical properties

UV–vis absorption and PL measurements of the P3HTs prepared using the two different procedures were conducted in chloroform solution (Figure 2). For comparison, regioregular P3HT (head-to-tail content is 98.6%) prepared using nickel-catalyzed polymerization was also measured. The maximum absorption wavelength (λ_{max}) of the P3HT prepared by palladium catalyst is 338 nm, which is blue-shifted compared with the λ_{max} of 424 nm for the authentic polymer

prepared using FeCl₃. In addition, tailing of the absorption band of P3HT prepared using the palladium catalyst can be observed over the 500-nm region, whereas the authentic P3HT exhibits a cutoff wavelength around 550 nm. Moreover, the UV spectrum of the thin film prepared from the polymer produced using palladium coupling nearly coincides with that of the solution (not described in the figure). In the PL spectrum, the maximum luminescent wavelength is also blue-shifted to 534 nm, and the spectrum is broadened. These results indicate that an increase in the ratio of head-to-head linkage and possible grafting due to undesired couplings made the structure of the resulting P3HT nonplanar and bulky, and hence, π-π stacking between the polymer chains was hampered to produce a blueshift in the UV and PL spectra. The regioregular P3HT shows the most red-shifted UV–vis and PL spectra, with λ_{max} values at 453 and 570 nm, respectively. This result also indicates a high head-to-head content in the P3HT prepared using the palladium catalyst. The regioregular P3HT produced the sharpest PL spectra among the three P3HTs due to the nearly uniform head-to-tail structure. Broadening in both the UV–vis and PL spectra of the P3HT prepared using the palladium catalyst indicates that various structures, including head-to-head linkage and branching, are present in the polymer.

Polymerization of 3,4-disubstituted monomers

To remove the complexity of coupling positions during the polymerization of 3-hexylthiophene, a series of 3,4-disubstituted
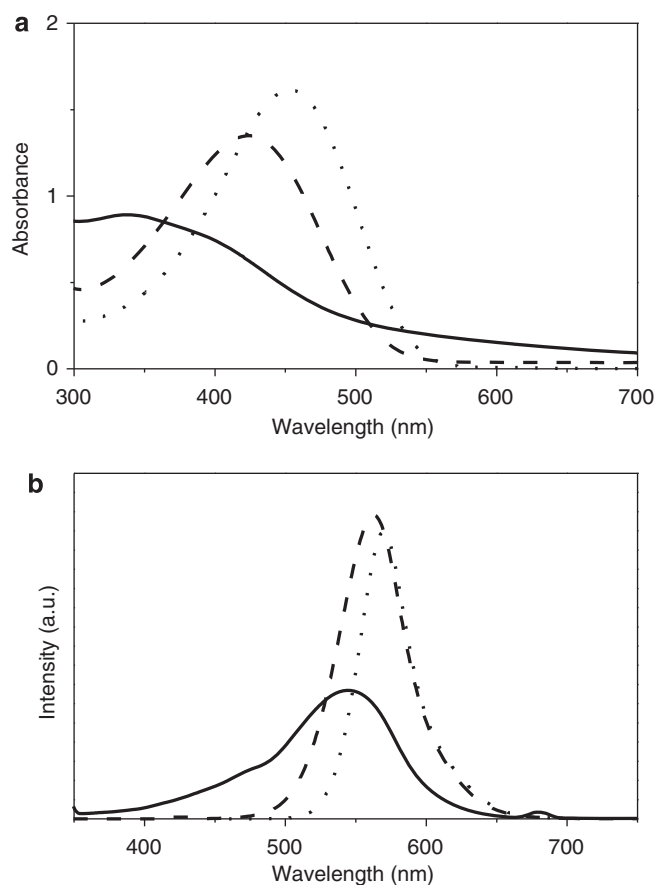

Figure 2 (a) UV and (b) PL spectra of P3HTs. The solid, the broken, and the dotted lines present the spectra of P3HTs prepared using the palladium catalyst system, FeCl₃, and nickel catalyst, respectively.

thiophenes, namely 3,4-dihexylthiophene (**1**), 3,4-dihexyloxythiophene (**2**), 3,4-dimethoxythiophene (**3**), and 3,4-ethylenedioxythiophene (**4**), were polymerized using the palladium catalytic system (Scheme 2). All of these monomers couple with each other at only the 2- and 5-positions, and thus, undesired branching at the β-position of the thiophene ring can be suppressed. Polymerizations were performed under the optimized conditions for P3HT, which are the conditions of Run 5 in Table 2, and the results are summarized in Table 4. The polymerization of **1** using 10 mol% of catalysts produces a low yield (29%) of a polymer with M_w of 1 800. When the amount of catalyst was reduced to 5 mol%, no polymer insoluble in methanol was obtained. Dialkyloxy-substituted thiophene derivatives **2** and **3**, which possess lower oxidation potentials because they possess more electron-donating groups, underwent palladium-catalyzed polymerization with 5 mol% of catalysts. Although the M_ws of the polymers were relatively low (up to 1 900), the yields increased by more than 50% compared with those of the alkyl-substituted thiophenes. Increasing the amount of catalyst did not improve the molecular weight or yield. Notably, we cannot achieve high molecular weights in the polymerization of **2** and **3** even when using FeCl₃ ($M_w = 5\,000$ for **2**, 2 600 for **3**). Finally, poly(3,4-ethylenedioxythiophene) (PEDOT), a well-known conductive polymer, was prepared from **4** using the palladium catalyst system. Unfortunately, measurement of the molecular weight failed because PEDOT is insoluble in any solvent. PEDOT was obtained when the oxidative polymerization was conducted using 5 mol% of catalysts. Reducing the amount of catalyst to 0.1 mol% produced a PEDOT yield greater than 90%. The structures of the series of PEDOT polymers prepared using the palladium catalyst system were confirmed by comparing the infrared spectra with that of authentic PEDOT obtained by oxidative polymerization using FeCl₃, and there were no significant differences between our experimental and authentic polymers. From these results, oxidative polymerization using the palladium catalyst system is assumed to be significantly dependent on the oxidation potential of the monomers. Because **4** exhibits a low oxidation potential, which becomes lower as it turns to oligothiophene,[22] polymerization proceeded rapidly with significant yield.

Dispersion polymerization of PEDOT in water

Because PEDOT is widely used as a conducting polymer in the form of a dispersion doped with poly(styrene sulfonic acid) (PSS) in water,[22,23] the dispersion polymerization of **4** in water was performed using the palladium catalytic system. PSS was used as an additive
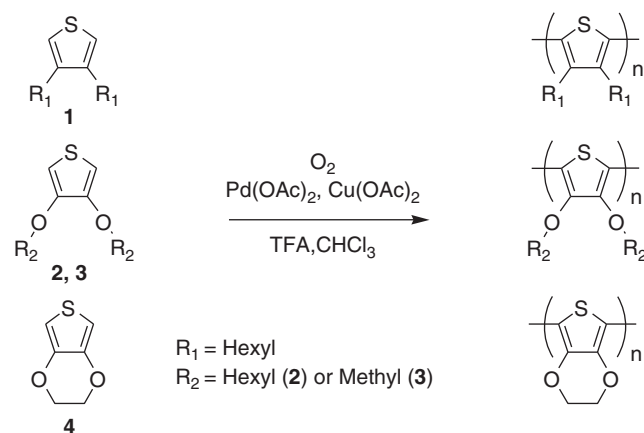
Scheme 2 Oxidative polymerization of 3,4-disubstituted thiophenes.

instead of trifluoroacetic acid, which also acts to stabilize the dispersion. The dispersion of **4** and PSS in water was mechanically stirred in the presence of palladium(II) acetate and copper(II) acetate under ambient atmosphere. The dispersion polymerization was performed with catalyst contents of 1 or 0.1 mol%. Each of the resulting dispersions became a deep blue color after polymerization. The dispersion could be stably preserved for 6 months without any precipitation. The formation of a PEDOT/PSS dispersion was verified using the infrared spectra of the thin films, and the spectrum of the dispersion prepared using the palladium catalyst system was nearly the same as that of a commercially available PEDOT/PSS dispersion (Clevios, Heraeus Holding GmbH, Hanau, Germany), even when the catalyst content of 0.1 mol% was used. The transparencies of the thin films (50 nm) prepared from the two dispersions prepared using catalyst contents of 1 and 0.1 mol% were examined and are presented in Figure 3b. A broad absorption band above 600 nm was observed and was assigned to the absorption band of oxidized PEDOT. Both films exhibited high transparencies greater than 95% in the visible light region.

Mechanism for polymerization

A plausible mechanism for the palladium-catalyzed oxidative polymerization of 3-hexylthiophene is treated in the reference concerning the C–C coupling reaction[14] and is presented in Scheme 3. Because the system contains no reductant such as phosphine ligands, which are generally exploited in palladium cross-coupling reactions, the substitution of a proton with palladium without a valent change may be the initial step. Under this hypothesis, the cycle would involve either an electrophilic aromatic palladation or a concerted

palladation–deprotonation pathway. Because the head-to-head content is relatively high in the P3HT produced using palladium coupling, the polymerization proceeds via the electrophilic metallation process, as a cationic intermediate would be stabilized by the hexyl group. After the reductive elimination of palladium produces a C–C bonding between thiophene rings, zero-valent palladium undergoes re-oxidation to doubly valent palladium with the aid of copper

Table 4 Polymerizations of 3,4-disubstituted thiophenes using palladium catalyst system

Run	Monomer[a]	Cat. (mol%)	Yield (%)	M_w[b] (kDa)	M_w/M_n[b]
1	**1**	5	0	—	—
2	**1**	10	29	1.8	1.88
3	**2**	5	57	1.6	2.51
4	**3**	5	76	1.9	2.06
5	**4**	5	>99	—[c]	—[c]
6	**4**	1	>99	—[c]	—[c]
7	**4**	0.1	90	—[c]	—[c]

[a]Polymerization was carried out using 5 mmol of monomer, catalysts and 4 equiv. of CF_3COOH in 5 ml of chloroform at 50 °C under O_2 atmosphere.
[b]Determined by gel permeation chromatography eluted with chloroform using polystyrene standards.
[c]Insoluble in chloroform.
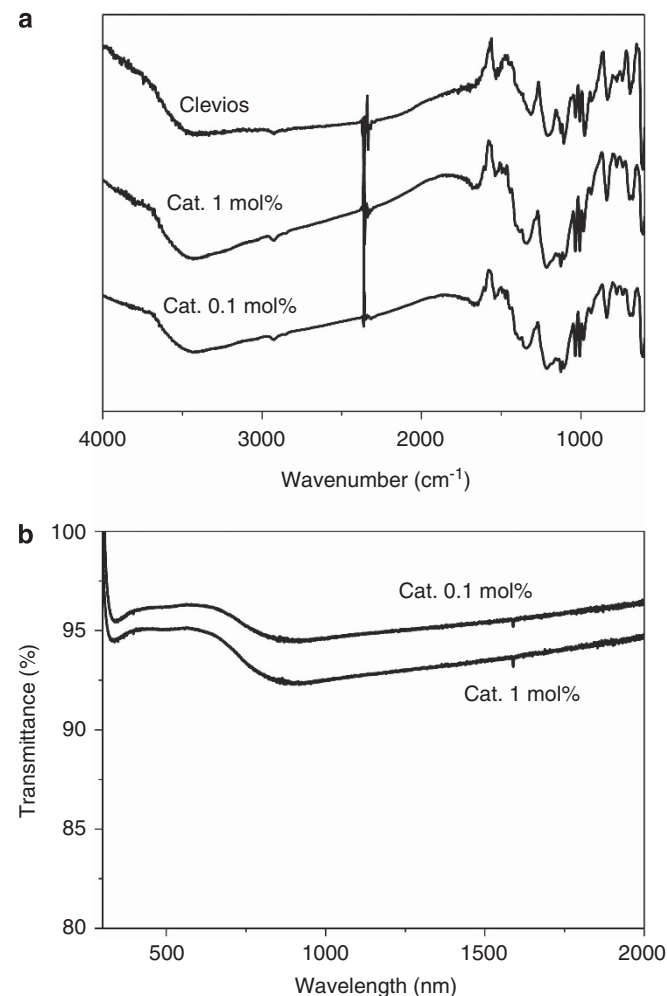
Figure 3 (**a**) Infrared spectra and (**b**) transmittances of the PEDOT/PSS dispersion films prepared using the palladium catalyst system.
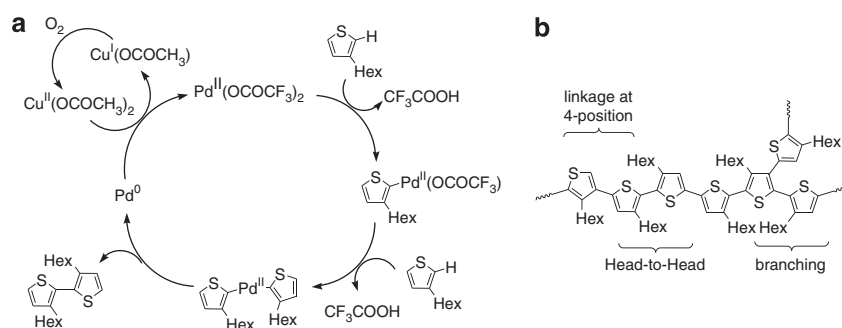
Scheme 3 (**a**) A plausible mechanism for oxidative polymerization using the palladium catalyst system and (**b**) possible structures of the obtained poly(3-hexylthiophene).

(II) acetate. We suppose that the oxygen-mediated redox cycle of the copper co-catalyst acts as a re-oxidant for the palladium catalyst, although the details of this process are not yet fully understood. The acidity of the additive is a critical factor in the catalytic cycle as the additive presumably facilitates the re-oxidation of the palladium species. A strong acid probably coordinates with palladium more than copper in the re-oxidation process. In addition, the acid also affects the oxidation potential of the thiophene monomers, because an excess amount of acid is required to achieve polymerization.

CONCLUSION

We described a novel catalytic system using palladium (II) acetate to achieve the oxidative polymerization of thiophene derivatives. In the investigation of the oxidative polymerization of 3-hexylthiophene, it was found that stronger acids such as trifluoroacetic acid or methanesulfonic acid activate the catalytic system of palladium (II) acetate and copper (II) acetate under an oxygen atmosphere. The polymerization conditions were optimized using trifluoroacetic acid as an additive, and the optimized conditions produced P3HT with the highest observed weight-average molecular weight of 7 000. The structure of the obtained P3HT was examined using ^{1}H and ^{13}C NMR spectra. The head-to-head content of the obtained P3HT was higher than that of the authentic P3HT control sample prepared by conventional oxidative polymerization. The UV and PL spectra also revealed that a rich head-to-head structure was obtained using the palladium catalytic system, which is indicated by blueshifts in the maximum absorption and luminescence wavelengths. To remove the additional complexity of regioselectivity, 3,4-disubstituted thiophene derivatives also underwent the catalytic oxidative polymerization process. The molecular weights of poly(3,4-disubstituted thiophene) were relatively low compared with those of P3HT. In addition, the reactivity in the palladium-catalyzed oxidative polymerization process was improved when thiophene derivatives with lower oxidation potentials were used. All of the results were considered to propose a hypothetical mechanism for the palladium catalytic cycle to explain the observed polymerization behaviors. Further investigation of the underlying mechanism will be required to further develop the palladium-catalyzed oxidative polymerization process as an effective technique for polythiophene synthesis.

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