

# Thermally Induced Self-Doping of $\pi$ -Conjugated Polymers Bearing a Pendant Neopentyl Sulfonate Group

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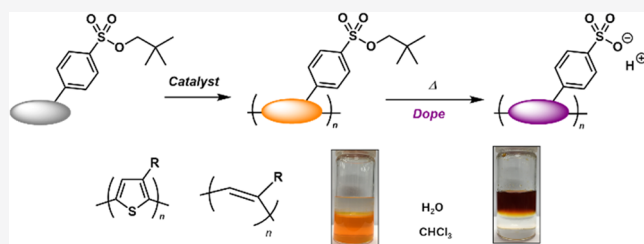


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**ABSTRACT:** A regioregular head-to-tail (HT)-type polythiophene was synthesized by the deprotonative nickel-catalyzed cross-coupling polymerization of 2-chlorothiophene bearing a neopentyl benzenesulfonate group at the 3-position. The obtained HT-regioregular polymer was found to dissolve in chloroform or THF, while it became soluble in water upon heating at 185 °C for 10 min by the liberation of the protected neopentyl group. The thin film of the polymer showed a remarkable improvement in conductivity of ca.  $10^3$  times before/after heating, suggesting the thermally induced intramolecular doping of polythiophene by the formed sulfonic acid at the side chain. The related doping was also observed in a poly(phenylacetylene) derivative, which was synthesized by rhodium-catalyzed polymerization. Copolymerization of such thiophene- and acetylene-bearing neopentyl sulfonate with 3-alkylthiophene and phenylacetylene, respectively, produced the corresponding statistical copolymers, demonstrating the formal self-doping of poly(3-alkylthiophene) and poly(phenylacetylene).



## INTRODUCTION

Polymers of extended  $\pi$ -conjugation have been attracting a lot of attention in material science as organic electronic materials showing a wide range of conductivities covering insulative, semiconductive, and metallic materials.<sup>1–5</sup> Although most such conjugated polymers are, in general, much less conductive by themselves, the external addition of a dopant remarkably changes their characteristics to make them conductive or semiconductive. Doping of electron-enriched conjugated polymers (p-type) has been performed by the addition of one (radical) or two (cation) electron acceptors to form polarons/bipolarons on the polymer main chain. For example, the conductivity of an undoped head-to-tail-type regioregular polythiophene (HT-P3HT) is ca.  $10^{-5}$ – $10^{-7}$  S  $\text{cm}^{-1}$ ; however, addition of iodine as a dopant improves its conductivity to  $10^2$  S  $\text{cm}^{-1}$ .<sup>6</sup> Self-doping bearing a dopant moiety in the skeleton of the conjugated polymer has also been a major concern that decreases the amount of addition of excess dopants and thus causes the possible deterioration of the durability to oxidation or humidity. Introduction of a sulfonic acid moiety into the side chain of polythiophenes has been performed and several polymers thus designed have been shown to demonstrate improved conductivity.<sup>7–12</sup> On the other hand, development of a practical method for the preparation of  $\pi$ -conjugated polymers with well-defined structures is an attractive issue in polymer synthesis, organic synthesis, and organometallic chemistry, in which organometallic species as well as transition-metal complexes as polymerization catalysts are powerful tools.<sup>6,13–15</sup> However, such a methodology generally

causes synthetic difficulties in forming potentially self-doping conjugated polymers because of the use of a carbanion species for polymerization, which is in conflict with the acidic doping functionality. Indeed, self-doping polythiophenes bearing such functionality at the side chain could have only been synthesized by oxidative polymerization with stoichiometric or usually much excess  $\text{FeCl}_3$  as an oxidant, leading to the corresponding polymer with uncontrolled regioregularity.<sup>7–12,16–25</sup> In contrast, cross-coupling polymerization to give regioregular polythiophene with the GRIM method employing metalated thiophene and transition-metal catalyst would not be tolerable for the doping functionality at the side chain. Accordingly, the introduction of HT-regioregularity into self-doping polythiophenes is therefore a significant challenge in materials science<sup>13–15</sup> (Figure 1). We considered the synthesis of a water-soluble HT-regioregular poly-3-substituted thiophene, which possesses benzenesulfonic acid at the side chain, employing the deprotonative polymerization of 2-halo-3-substituted thiophene as a monomer precursor<sup>26–33</sup> since we have already shown the synthesis of several side-chain-functionalized polythiophenes to date.<sup>34,35</sup> The acidic moiety should be protected during the polymerization by employing an organometallic monomer and/or a transition-metal

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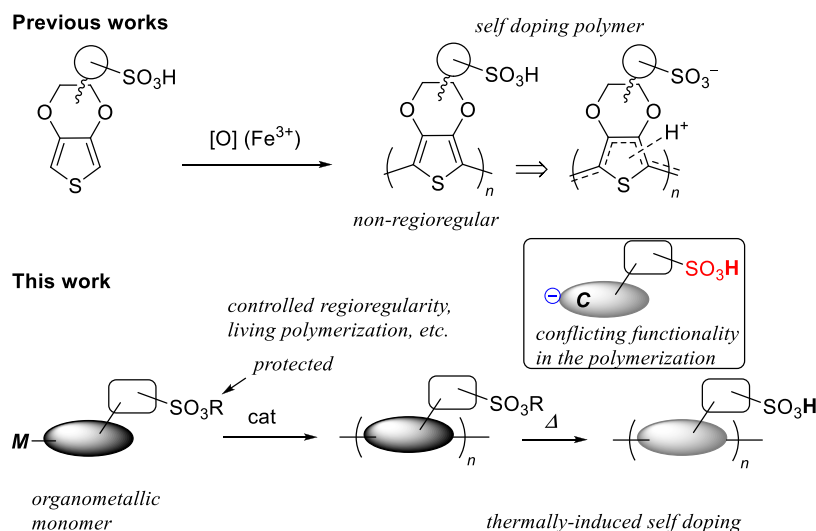


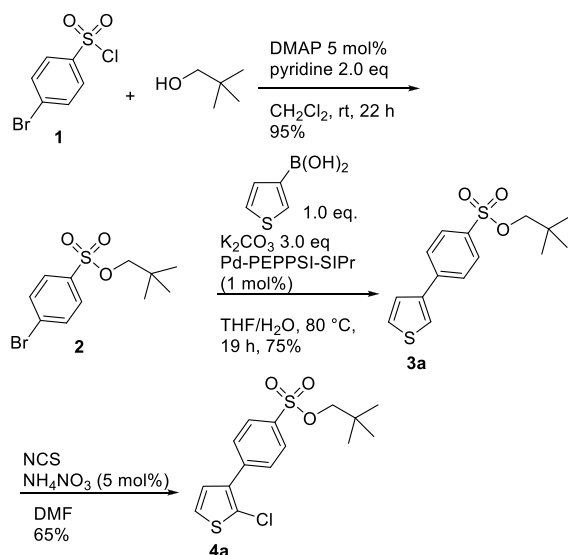
Figure 1. Self-doping vs thermally induced self-doping.

catalyst.<sup>36</sup> The protected functionality can be removed after the formation of the polymer thin film, wherein the protective group may be preferably removed without using any additional chemicals. Accordingly, we focused on the use of neopentyl sulfonate, which was shown to be removed by thermal treatment, leading to the corresponding sulfonic acid.<sup>37</sup> Herein, we describe that the self-doping of  $\pi$ -conjugated polymers is induced by heating the thin film, whose improved conductivity is ca.  $10^3$ – $10^6$  times higher.

## RESULTS AND DISCUSSION

**Preparation and Characterization of Polythiophene Bearing a Sulfonate Group at the Side Chain.** We first studied the introduction of such a side chain into the thiophene ring. The synthesis of the monomer was carried out as represented in Scheme 1. The reaction of 4-bromobenzenesulfonyl chloride (**1**) with neopentyl alcohol afforded sulfonate **2**, whose synthetic efficiency was remarkably improved by the addition of the catalyst *N,N*-dimethylamino-

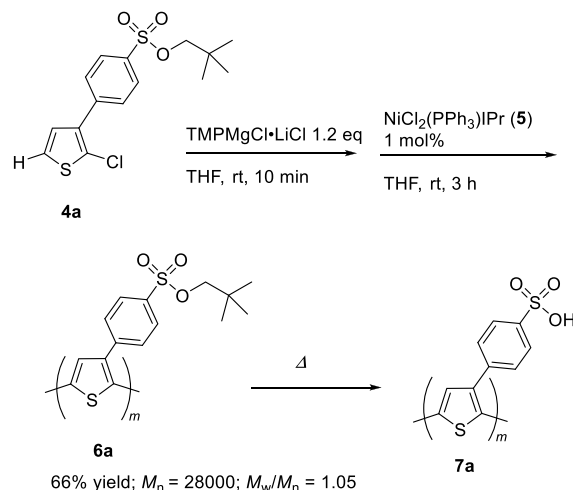
Scheme 1. Preparation of Thiophene Monomer **4a** Bearing Benzenesulfonate Group at the 3-Position



pyridine (DMAP) (95%).<sup>38</sup> Cross-coupling with thiophene-3-boronic acid<sup>39–42</sup> catalyzed by Pd-PEPPSI-SIPr<sup>43</sup> gave **3a** in 75% yield and subsequent chlorination with NCS gave monomer **4a** in 65% yield.

Polymerization of the thus-obtained chlorothiophenes **4a** was carried out by the reaction with a bulky magnesium amide TMPMgCl-LiCl (2,2,6,6-tetramethylpiperidine-1-yl chloromagnesium: Knochel–Hauser base)<sup>44</sup> to undergo deprotonative metallation.<sup>26–35</sup> Then, nickel catalyst **5** was added to the thus-formed thiophene–magnesium species. Smooth polymerization took place at room temperature, as shown in Scheme 2,

Scheme 2. Nickel-Catalyzed Polymerization of **4a** through the Deprotonation with the Knochel–Hauser Base

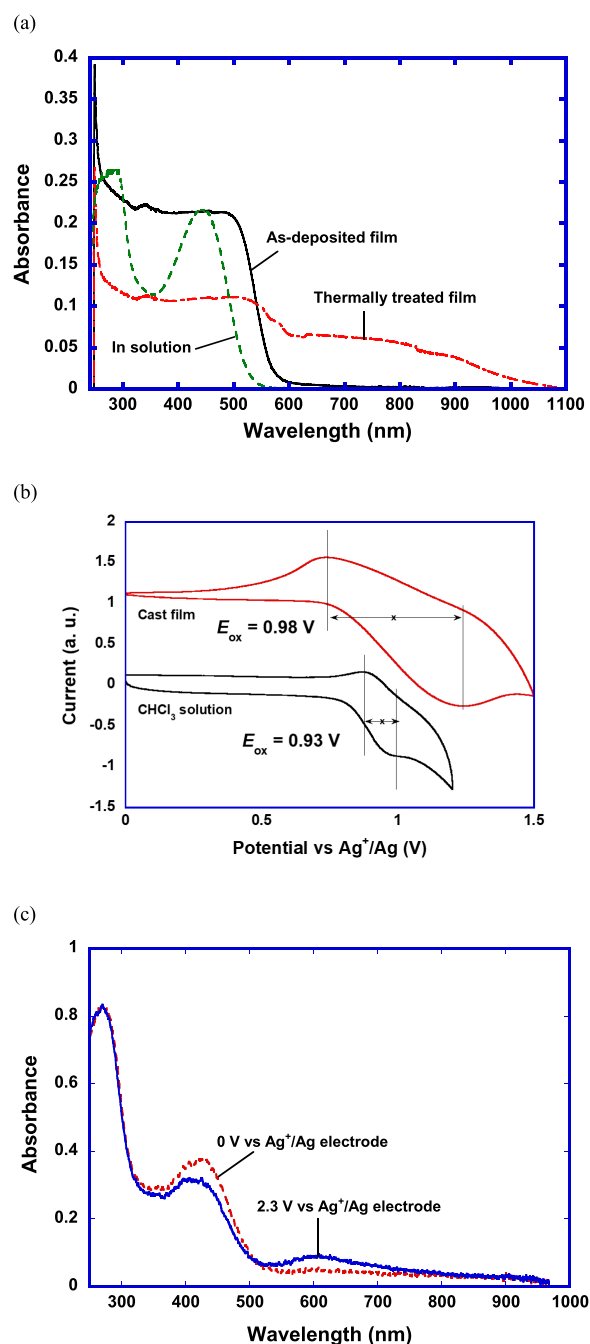


to afford the corresponding polythiophene **6a** in 66% yield as a deep orange solid. Measurement of the obtained polymer revealed a molecular weight of ca. 28 000, which reasonably corresponded to the monomer/catalyst feed ratio, and the molecular weight distribution was also found to be narrow ( $M_w/M_n = 1.05$ ). The NMR spectra of **6a** suggested that the obtained polymer has a highly regioregular head-to-tail (HT) orientation. Polymer **6a** was found to be soluble in several organic solvents such as chloroform and THF.

Thermogravimetric analysis of **6a** revealed that a remarkable mass loss took place at 185 °C, whose amount was consistent with the thermolysis of neopentyl ester to sulfonic acid. Indeed, heating of the solid polymer **6a** at 180 °C showed an immediate color change to dark purple and leading to **7a**. It was also remarkable that addition of **7a** to neutral water resulted in dissolution, while it was found to be completely insoluble in chloroform, despite a highly regioregular HT-type poly(3-substituted thiophene) of extended  $\pi$ -conjugation.

Figure 2 shows a comparison of the properties of the obtained polythiophenes before/after thermolysis of the thin-film cast on a quartz substrate. The UV-vis spectrum of sulfonate **6a** was found to show  $\lambda_{\text{max}}$  value at 440 nm in a chloroform solution (ca.  $10^{-5}$  M), which was comparable with that of (poly(3-hexylthiophen-2,5-diyl): P3HT) ( $\lambda_{\text{max}} = 442$  nm).<sup>6</sup> Measurement of the UV-vis spectrum of the cast film of **6a** revealed the red shift of the absorption edge from 530 to 580 nm, as well as the  $\lambda_{\text{max}}$  value from 440 to 510 nm. Treatment of the thus-formed cast film at 180 °C for 10 min resulted in a remarkable color change. The UV-vis spectrum of the film of **6a** after heating indicated absorption at the range of a near-infrared region (Figure 2a). Measurement of the cyclic voltammetry of a chloroform solution of **6a** indicated a reversible wave at 0.93 V vs  $\text{Ag}^+/\text{Ag}$  standard electrode owing to one-electron oxidation (Figure 2b) and the UV-vis spectrum of **6a** in the oxidation state exhibited absorption at ca. 600 nm (Figure 2c). Accordingly, the color change of the cast film of **6a** caused by thermolysis leading to **7a** could be attributed to the formation of cation radical species stabilized by the formed sulfonic anions. Similar oxidation was also observed in the cast film of **6a** to indicate the oxidation wave at 0.98 V vs  $\text{Ag}^+/\text{Ag}$  standard electrode accompanied by the change in the color of the film to dark brown, although such a color change of the film was irreversible. It is worth noting that the change in the doping state was induced by the heating of the polymer film.

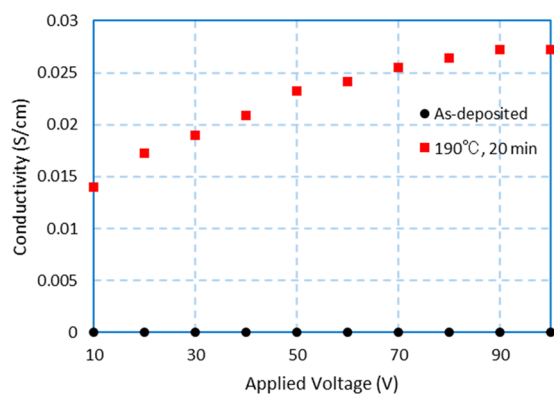
These results, based on the characterization of polymer **6a** in the thin-film state before/after heating, suggest that the thermally induced self-doping of the polythiophene main chain occurred due to the impact of sulfonic acid on the polythiophene side chain. The film thus transformed to **7a** indeed dissolved in water, suggesting the formation of the sulfonic acid moiety. The doped thin film improved the conductivity when the thus-formed polymer **6a** was cast on an electrode. The polymer **6a** was cast to form the thin film of 200 nm thickness, and the measurement of the current at a certain applied voltage showed that the current level was  $1 \times 10^{-7}$  to  $1 \times 10^{-5}$  A and thus the calculated conductivities were ca.  $10^{-5}$  S  $\text{cm}^{-1}$ . A remarkable increase in the current values was observed after the thin film on the electrode was heated at 190 °C for 20 min, as shown in Figure 3, to result in the conductivity of  $1 \times 10^{-2}$  S  $\text{cm}^{-1}$ .<sup>45,46</sup> The results suggested that the conductivity of the polythiophene thin film was improved by ca.  $10^3$  times upon heating. Although several self-doping polythiophenes bearing sulfonic acid moiety have also been developed to date,<sup>7–12</sup> formation of such polymers with a transition-metal-catalyzed polymerization leading to completely regiocontrolled polymers cannot be performed due to the inconsistency of the organometallic thiophene monomer from **4a** and the acidic side chain bearing  $\text{SO}_3\text{H}$ . It should also be pointed out that such an improved conductivity was observed only upon the thermal treatment of the thin film without external additive



**Figure 2.** (a) UV-vis absorption spectrum of the chloroform solution of **6a** (green dotted), cast film of **6a** (black), and cast film of **6a** after heating at 180 °C for 10 min (red) (considered to form **7a** in the film). (b) Cyclic voltammogram of the chloroform solution of **6a** (black) (1 mM/0.1 M  $\text{Bu}_4\text{NPF}_6/\text{CHCl}_3$ , scan rate  $0.01 \text{ V s}^{-1}$ ) and the cast film (red) (0.1 M  $\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$ , scan rate  $0.1 \text{ V s}^{-1}$ ). (c) UV-vis spectrum of **6a** in chloroform upon electro-oxidation (0.1 M  $\text{Bu}_4\text{NPF}_6$ ) (red dotted: 0 V; blue: 2.3 V).

chemicals due to the liberation of the protected neopentyl group.

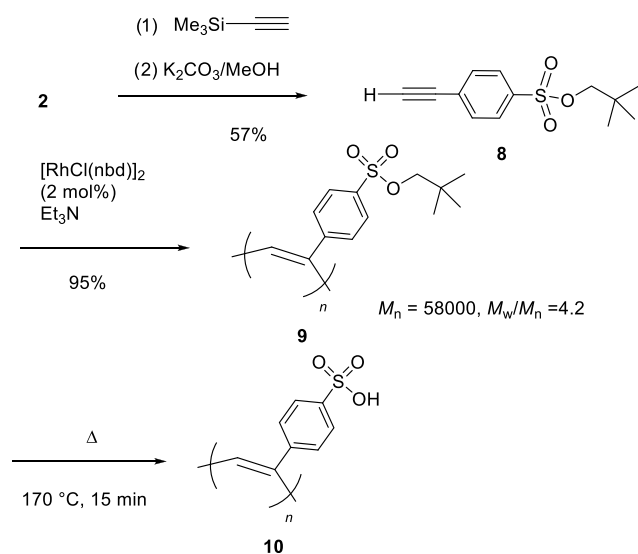
**Synthesis and Characterization of a Polyacetylene Derivative.** It was also found that such a thermally induced self-doping behavior was observed in a different type of conjugate polymer. Polyacetylenes have also been recognized as a kind of p-type semiconductive material in which doping occurs by the addition of acid, iodine, etc.<sup>47</sup> Preparation of



**Figure 3.** Electronic properties on current–voltage characteristics of the as-deposited and thermally treated cast film of polythiophene **6a** (as deposited: black) and after heating at 190 °C for 20 min, leading to **7a** (red).

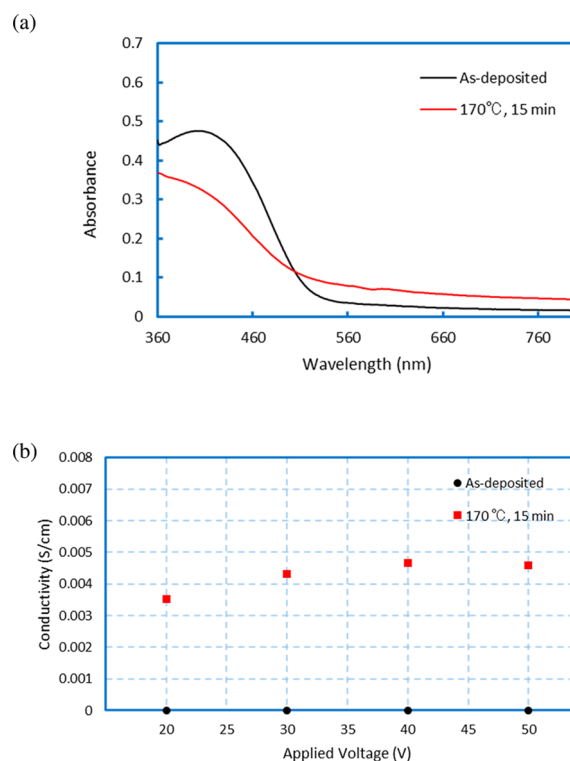
polyacetylenes can be performed by polymerization of alkynes, and treatment of a terminal alkyne by rhodium catalyst is shown to lead to smooth formation of Z-polyalkynes.<sup>48,49</sup> Arylalkyne bearing a neopentyl sulfonate substituent was synthesized as illustrated in Scheme 3. The Sonogashira

### Scheme 3. Preparation and Polymerization of Arylalkyne 8 Bearing a Benzenesulfonate Substituent in the Aromatic Ring



coupling<sup>50</sup> of bromobenzenesulfonate **2** with trimethylsilylacetylene followed by the removal of the silyl group afforded the monomer **8**. Subsequent polymerization of **8** was carried out in the presence of rhodium(I) catalyst  $[\text{RhCl}(\text{nbd})_2]$  (2 mol %) to afford the corresponding Z-polyacetylene **9** in 95% yield.<sup>48</sup>

The obtained polyacetylene **9** was also subjected to the formation of the cast thin film. Measurement of UV–vis spectrum of **9** showed the characteristic absorption at 400 nm, as shown in Figure 4a, suggesting the formation of the conjugated polyene. Thermal treatment of **9** at 170 °C for 15 min leading to **10** showed the absorption at the NIR region, as observed for the regioregular polythiophene **7**. Figure 4b shows the change in conductivity before/after the thermal treatment of the film and thus suggests the formation of cation radicals in the polymer main chain. The film of polyene **9**



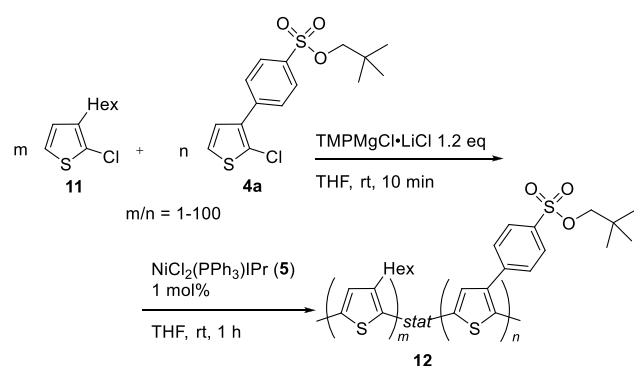
**Figure 4.** (a) Absorption spectrum of the thin film of polyacetylene **9** and (b) electronic properties on the current–voltage characteristics of the as-deposited and thermally treated cast film of polyacetylene **9** (as-deposited: black) and after heating at 170 °C for 15 min leading to **10** (red).

showed little current at the applied voltages in the range 20–50 V. The conductivity after the treatment of the film at 170 °C for 15 min was observed to be improved to ca. 0.003–0.005  $\text{S cm}^{-1}$  (20–50 V). The results suggest that the improved conductivity is at least ca.  $10^6$  times higher after the thermal treatment.

### Synthesis and Characterization of Copolymers of Polyacetylene Derivative and Polythiophene Bearing a Sulfonate Group at the Side Chain.

Such a thermally induced self-doping protocol is also found to be applicable to regioregular poly(3-hexylthiophene) HT-(P3HT), which is shown to be widely available for a broad range of electronic materials.<sup>1–5</sup> P3HT bearing an alkyl group in the side chain can only be doped by an external additive and is thus incapable of self-doping. However, incorporation of a partial thiophene unit bearing a functional group enables thermally induced doping by copolymerization. As shown in Scheme 4, the prepared monomer **4a** was employed for statistical copolymerization with 2-chloro-3-hexylthiophene (**11**) with a nickel(II) catalyst.<sup>26–33</sup> Copolymerization of **4a** and **11** was carried out using 1–20 mol % of **4a**. A mixture of **4a** and **11** was treated with 1.2 equiv of  $\text{TMPMgCl}\cdot\text{LiCl}$  at room temperature for 10 min, followed by the addition of nickel catalyst **5** (1.0 mol %) to initiate copolymerization. Table 1 summarizes the result. Use of different ratios of **4a**:**11** (1/100, 1/50, 1/20, 1/10, 1/5) was found to result in polymerization to afford poly(3-hexylthiophene) containing statistical amounts of comonomer **4a**. The <sup>1</sup>H NMR spectrum revealed reasonable amount of **4a** toward **11** was incorporated in the copolymer **12**, and the obtained polymers showed  $M_n = 20\,000\text{--}30\,000$  ( $M_w/M_n = 1.10\text{--}1.44$ ). Analysis of the organic filtrate by <sup>1</sup>H NMR

### Scheme 4. Statistical Copolymerization of Sulfonate-Containing Thiophene 4a and 2-Chloro-3-hexylthiophene (11)



**Table 1. Copolymerization of Sulfonate Group-Containing Chlorothiophene 4a and 2-Chloro-3-hexylthiophene (11) with the Nickel(II) Catalyst 5<sup>a</sup>**

11 (mmol)	11/4a	%conv of 11 <sup>b</sup>	%conv of 4a <sup>b</sup>	$M_n^c$	$M_w/M_n^c$	$m/n^d$
2.5	100	95	>99	$3.0 \times 10^4$	1.44	100
1.3	50	95	>99	$2.9 \times 10^4$	1.18	45
0.5	20	99	89	$2.6 \times 10^4$	1.11	16
0.5	10	99	95	$2.5 \times 10^4$	1.59	10
0.5	5	89	92	$3.1 \times 10^4$	1.17	3.7

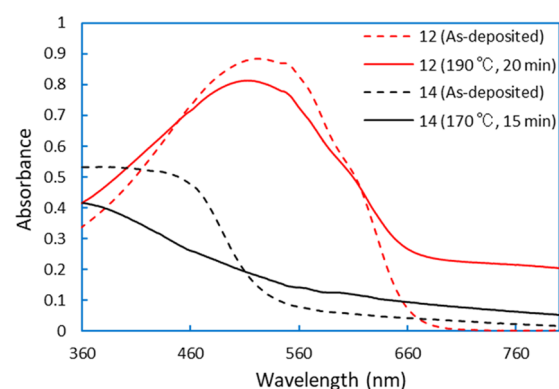
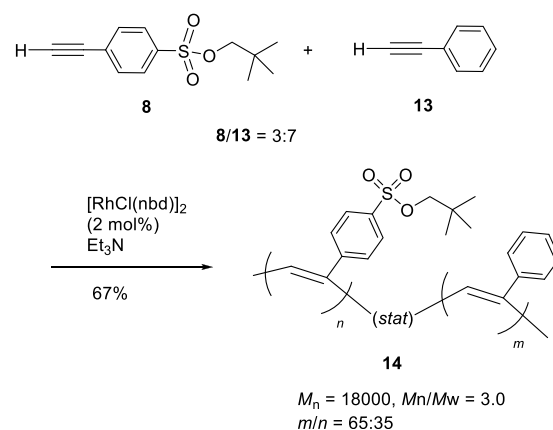
<sup>a</sup>The reaction was carried out with 2-chloro-3-hexylthiophene (11), chlorothiophene bearing benzenesulfonate group 4a with TMPMgCl·LiCl (1.2 equiv) in THF, followed by the addition of NiCl<sub>2</sub>(PPh<sub>3</sub>)IPr (5, 1.0 mol %) at room temperature for 1 h. <sup>b</sup>Consumption of monomer was estimated by the measurement of <sup>1</sup>H NMR of the filtrate after precipitation of the obtained polymer 12. <sup>c</sup>The molecular weight ( $M_n$ ) and the molecular weight distribution ( $M_w/M_n$ ) were measured by SEC analysis. <sup>d</sup>Contents of the monomer unit derived from 4a and 11 were estimated by the <sup>1</sup>H NMR analysis of the polymer.

to detect the remaining monomers showed that both were almost equally consumed, suggesting little preferential incorporation of sulfonate comonomer 4a to the P3HT chain and vice versa.

The related statistical copolymer was also found to be prepared by the copolymerization of the terminal arylacetylene 8 and phenylacetylene (13), which was also performed by the catalysis of rhodium(I) complex in a similar manner to the case of homopolymerization of 8. The reaction of 8 and 13 in 3:7, respectively, afforded the copolymer 14 in 67% yield. Measurement of the <sup>1</sup>H NMR spectrum of 14 revealed the presence of ca. 35% of benzenesulfonate moiety derived from 8, and  $M_n$  and  $M_w/M_n$  values of the copolymer 13 were revealed to be 18 000 and 3.0, respectively (Scheme 5).

The obtained copolymers were then subjected to measurements of optoelectronic properties as a thin film on quartz or the ITO electrode.<sup>51</sup> As shown in Figure 5, the value of  $\lambda_{\max}$  the as-deposited film of 12 ( $m = 3.7$ ;  $n = 1$ ) was 520 nm, while the film was transparent at the NIR region (>700 nm). When heated at 190 °C for 20 min, the film of 12 showed absorbance at 700–1000 nm, suggesting that P3HT was formally doped by the generation of sulfonic acid in the polythiophene side chain. The conductivity of the copolymer also exhibited a drastic change, as summarized in Table 2. The as-deposited thin film of 12 ( $m = 3.7$ ;  $n = 1$ ) showed an improved conductivity from

### Scheme 5. Statistical Copolymerization of Arylalkyne 8 and Phenylacetylene 12



**Figure 5.** Absorption spectra of the as-deposited (black)/thermally treated (red) cast film of 12 ( $m = 3.7$ ;  $n = 1$ ) and those of 14 ( $m = 65$ ;  $n = 35$ ).<sup>52</sup>

$1.2 \times 10^{-5}$  to  $4.1 \times 10^{-2}$  S cm<sup>-1</sup> (at 50 V) after thermal treatment at 190 °C for 20 min, which is ca.  $10^3$  times higher than that obtained by thermally induced self-doping.<sup>52</sup> The related properties of the statistical polyacetylene copolymer 14 are also shown in Figure 5 and Table 2 to observe absorption at the NIR region and the improved conductivity. It was also shown that self-doping of the polymer main chain of polyacetylene was induced by heating, and the improved conductivity before/after thermal treatment was found to be ca.  $10^6$  times higher. Since both homopolymers poly(3-alkylthiophene) and poly(arylalkyne) are incapable of self-doping, the results show formal doping of such polymers. Worthy of note is a remarkable improvement of the conductivity of the polymer thin-film ca.  $10^3$ – $10^6$  times whereas each conductivity is dependent on the conditions of thin-film fabrication.

## EXPERIMENTAL SECTION

**Materials and Methods.** All of the reactions were carried out under a nitrogen atmosphere. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz) spectra were measured on a JEOL ECZ400 NMR spectrometer with a CDCl<sub>3</sub> solution unless noted. The chemical shifts were expressed in ppm with CHCl<sub>3</sub> (7.26 ppm for <sup>1</sup>H) or CDCl<sub>3</sub> (77.16 ppm for <sup>13</sup>C) as internal standards. The IR spectra were recorded on a Bruker Alpha with an ATR attachment (Ge). High-resolution mass spectra (HRMS) were measured by a JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. For thin-layer chromatography (TLC) analyses through-

**Table 2. Thermally Induced Change in Conductivities of Thin Films Obtained by Copolymerization of 11 and 4a (Polythiophene) and 8 and 13 (Polyene)<sup>a</sup>**

copolymer	comonomer		ratio <sup>b</sup>	M <sub>n</sub> <sup>c</sup>	conductivity (S cm <sup>-1</sup> ) <sup>d</sup>	
					as-deposited	after heating
12	11	4a	3.7:1.0	31 000	1.2 × 10 <sup>-5</sup>	4.1 × 10 <sup>-2</sup>
14	8	13	1.0:1.9	18 000	3.6 × 10 <sup>-9</sup>	1.6 × 10 <sup>-3</sup>

<sup>a</sup>The measurement of conductivity was carried out with the cast thin film of copolymers 12 and 14. <sup>b</sup>The incorporated ratio of 11/4a or 8/13 estimated by <sup>1</sup>H NMR measurement. <sup>c</sup>The molecular weights (M<sub>n</sub>) were measured by SEC analysis. <sup>d</sup>The conductivity was calculated based on the current at 100 V (for 12) and 50 V (for 14), respectively.

out this work, Merck precoated TLC plates (silica gel 60 F<sub>254</sub>) were used. Purification by HPLC with a preparative SEC column (JAI-GEL-1H and JAI-GEL-2H) was performed by JAI LC-9201. SEC analyses were carried out with a standard HPLC system equipped with a UV detector at 40 °C using CHCl<sub>3</sub> as eluent with Shodex KF-402HQ and KF-404HQ. Molecular weights and molecular weight distributions were estimated based on the calibration curve obtained by 6 standard polystyrenes. UV–vis–NIR absorption spectra of the polymer films were measured with a Shimadzu UV-3150 UV–vis spectrophotometer. Cyclic voltammetry was conducted by ALS 600B. The conductivity of polymer films was measured with a digital electrometer ADCMT8340A. Concerning the solvent for the nickel and palladium-catalyzed reactions THF (anhydrous grade) was purchased from Kanto Chemical Co. Ltd. and passed through alumina and copper column (Nikko Hansen & Co. Ltd.) or distilled from sodium dispersion in a mineral oil/benzophenone ketyl<sup>53</sup> prior to use. The Knochel–Hauser base (TMPMgCl·LiCl)<sup>44</sup> was purchased from Sigma-Aldrich Co. Ltd. as a 1 M THF solution. NiCl<sub>2</sub>(IPr)·PPh<sub>3</sub><sup>54,55</sup> and [RhCl(nbd)]<sub>2</sub><sup>48</sup> were purchased from TCI Co. Ltd. Other chemicals were purchased and used without further purification.

**(2,2-Dimethylpropan-1-yl)4-bromobenzenesulfonate (2).**<sup>56</sup> To a mixture of 4-bromobenzene-1-sulfonyl chloride (4.09 g, 16.0 mmol) and neopentyl alcohol (1.69 g, 19.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (24 mL), pyridine (2.6 mL, 32.2 mmol) and *N,N*-dimethyl-4-aminopyridine (DMAP) (0.0972 g, 0.796 mmol) were added. The reaction mixture was stirred at room temperature for 21 h and diluted with Et<sub>2</sub>O. The organic layer was washed with 1 M aqueous HCl, water, dried over anhydrous sodium sulfate, and concentrated in vacuo to afford 4.68 g of 2 in 95% yield as a light brown solid, which was directly employed for the following reaction. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (d, *J* = 9.2 Hz, 2H), 7.70 (d, *J* = 9.2 Hz, 2H), 3.69 (s, 2H), 0.91 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 135.2, 132.7, 129.5, 129.0, 80.1, 31.8, 26.1.

**(2,2-Dimethylpropan-1-yl)4-(thiophen-3-yl)benzenesulfonate (3).** To a degassed mixture of 3-thiopheneboronic acid (1.95 g, 15.2 mmol), K<sub>2</sub>CO<sub>3</sub> (6.32 g, 45.7 mmol), (2,2-dimethylpropan-1-yl) 4-bromobenzenesulfonate (2, 4.68 g, 15.2 mmol), and Pd-PEPPSI-SIPr (0.105 g, 0.154 mmol), THF (3.8 mL) and water (7.5 mL) were added. The mixture was vigorously stirred at 80 °C for 19 h and then concentrated in vacuo and passed through a Celite pad. The solvent was removed under reduced pressure, and the residue was purified by recrystallization with CH<sub>2</sub>Cl<sub>2</sub> and hexanes to give 1.13 g of 3 as a colorless solid in 75% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.61 (dd, *J* = 1.4, 2.7 Hz, 1H), 7.49–7.42 (m, 2H), 3.70 (s, 2H), 0.91 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 140.8, 140.1, 133.9, 128.5, 127.2, 126.8, 126.0, 122.8, 79.7, 31.6, 26.0. IR (ATR) 2967, 1596, 1420, 1357, 1194, 1178, 1103, 1016, 955, 938, 870, 851, 840, 819, 783, 759, 729, 722, 640, 628 cm<sup>-1</sup>. HRMS (DART–ESI<sup>+</sup>) calcd for C<sub>15</sub>H<sub>19</sub>O<sub>2</sub>S<sub>2</sub>: 311.0776; found *m/z* 311.0781.

**(2,2-Dimethylpropan-1-yl)4-(2-chlorothiophene-3-yl)benzenesulfonate (4a).** To a solution of (2,2-dimethylpropan-1-yl)4-(thiophen-3-yl)benzenesulfonate (3, 2.8 g, 9.1 mmol) and NH<sub>4</sub>NO<sub>3</sub> (36 mg, 0.45 mmol) in DMF (11 mL), *N*-chlorosuccinimide (NCS) (1.3 g, 9.9 mmol) was added and the mixture was stirred at 60 °C for 13 h. The reaction mixture was washed with aqueous Na<sub>2</sub>SO<sub>3</sub> and NH<sub>4</sub>Cl. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the

combined organic phase was dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left a crude solid, which was purified by column chromatography on a silica gel using CH<sub>2</sub>Cl<sub>2</sub>/hexanes (1/1, v/v) and recrystallization with CH<sub>2</sub>Cl<sub>2</sub> and hexanes to give 2.04 g of 4a as a colorless solid in 75% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 5.7 Hz, 1H), 7.09 (d, *J* = 5.7 Hz, 1H), 3.74 (s, 2H), 0.93 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 139.5, 136.2, 134.8, 129.1, 128.1 × 2, 126.8, 123.7, 79.9, 31.8, 26.1. IR (ATR) 2961, 1598, 1478, 1403, 1353, 1194, 1177, 1100, 1025, 952, 937, 879, 846, 824, 757, 741, 727, 721, 671, 641 cm<sup>-1</sup>. HRMS (DART–ESI<sup>+</sup>) calcd for C<sub>15</sub>H<sub>18</sub><sup>35</sup>ClO<sub>2</sub>S<sub>2</sub>: 345.0386; found *m/z* 345.0394.

**Poly(3-(4-(2,2-dimethylpropylsulfonyl)benzen-1-yl)thiophene-2,5-diyl) (6a).** To a 20 mL Schlenk tube equipped with a magnetic stirring bar, 4a (172 mg, 0.5 mmol), THF (5.0 mL), and 1.0 M THF solution of TMPMgCl·LiCl (0.6 mL, 0.6 mmol) were added at room temperature. After stirring at room temperature for 10 min, NiCl<sub>2</sub>(PPh<sub>3</sub>)IPr (5, 4.4 mg, 5.6 μmol) was added to initiate polymerization. The color of the solution turned to dark orange. After stirring at room temperature for 3 h, the reaction mixture was poured into a mixture of hydrochloric acid (1.0 M, 2 mL) and methanol (10 mL) to form a precipitate, which was filtered off to leave an orange solid. After washing with methanol and hexanes repeatedly, the solid was dried under reduced pressure to afford 101 mg of 6a (66%). The molecular weight (M<sub>n</sub>) and the molecular weight distribution (M<sub>w</sub>/M<sub>n</sub>) were estimated by SEC analysis. M<sub>n</sub> = 28 000, M<sub>w</sub>/M<sub>n</sub> = 1.05. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 6.93 (s, 1H), 3.70 (s, 2H), 0.88 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 140.6, 137.9, 135.6, 134.2, 132.7, 130.2, 130.0, 128.4, 80.1, 31.8, 26.1. IR (ATR) 2961, 1598, 1478, 1402, 1361, 1179, 1103, 963, 937, 826, 756, 725, 651, 606 cm<sup>-1</sup>.

**Poly(3-(4-(benzenesulfonic acid)-1-yl)thiophen-2,5-diyl) (7a).** Polythiophene 6a bearing benzenesulfonate substituent (30 mg) was taken in a Schlenk tube, which was heated by a heating gun for a few minutes, to observe the color change from purple to dark purple solid, which resulted to be dissolved in water. Measurement of the <sup>1</sup>H NMR spectrum in D<sub>2</sub>O showed broad signals, suggesting low mobility of the organic moiety in an aqueous medium, while the disappearance of the neopentyl group was confirmed. The TG-DTA profile also supported the conversion of neopentyl sulfonate into the corresponding sulfonic acid by indicating the mass loss of equivalent to C<sub>5</sub>H<sub>10</sub> at 185 °C.

**4-(2,2-Dimethylpropylsulfonyl)-phenyl)ethyne (8).** To a 50 mL Schlenk tube equipped with a magnetic stirring bar, (2,2-dimethylpropyl)4-bromobenzenesulfonate (2, 1.53 g, 5.0 mmol), THF (15 mL), trimethylsilylacetylene (1.06 mL, 7.5 mmol), copper(I) iodide (101 mg, 0.53 mmol), bis(triphenylphosphine)palladium(II) (175 mg, 0.25 mmol), and triethylamine (7.0 mL, 50 mmol) were added at room temperature for 21 h. Water (20 mL) was added to the mixture to quench the reaction. The organic layer was extracted with Et<sub>2</sub>O, a water of NH<sub>4</sub>Cl, brine, and water. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by column chromatography on silica gel with hexane/CH<sub>2</sub>Cl<sub>2</sub> (1/1, v/v) as the eluent to afford 1.40 g of (2,2-dimethylpropyl)4-[2-(trimethylsilyl)ethynyl]benzenesulfonate. Then, to a solution of (2,2-dimethylpropyl)4-[2-(trimethylsilyl)ethynyl]benzenesulfonate (1.28 g, 3.8 mmol) in MeOH/CH<sub>2</sub>Cl<sub>2</sub>

(1/1, v/v, 11.4 mL),  $K_2CO_3$  (1.06 g, 7.6 mmol) was added and stirred at room temperature for 21 h. Water (20 mL) was added to the mixture to quench the reaction. The organic layer was extracted with  $Et_2O$ , brine, and water. The combined organic extracts were dried over  $Na_2SO_4$  and concentrated in vacuo. The residue was purified by column chromatography on a silica gel with hexane/ $Et_2O$  (1/8, v/v) as the eluent to afford 653 mg of **8** as a colorless solid in 57% yield (over 2 steps).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.86 (d,  $J$  = 8.7 Hz, 2H), 7.65 (d,  $J$  = 8.2 Hz, 2H), 3.69 (s, 2H), 3.29 (s, 1H), 0.90 (s, 9H).  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  135.8, 132.7, 127.8  $\times$  2, 81.7, 81.5, 79.9, 31.6, 25.9.

**Poly(4-(2-(2-dimethylpropylsulfonyl)phenyl)-ethen)-1,2-diyl (9)**. To a 20 mL Schlenk tube equipped with a magnetic stirring bar,  $[RhCl(nbd)]_2$  (2.6 mg, 5.6  $\mu$ mol), **8** (76 mg, 0.30 mmol),  $Et_3N$  (8.4  $\mu$ L, 60  $\mu$ mol), and THF (2 mL) were added at room temperature. The mixture was further stirred at room temperature for 90 min. The reaction mixture was poured into a large amount of MeOH (50 mL), centrifugally separated, and dried under vacuum to afford 72 mg of **9** as an orange solid in 95% yield. The molecular weight ( $M_n$ ) and the molecular weight distribution ( $M_w/M_n$ ) were estimated by SEC analysis.  $M_n$  = 58 000,  $M_w$  = 240 000, and  $M_w/M_n$  = 4.2.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.58 (d,  $J$  = 8.2 Hz, 2H), 6.87 (d,  $J$  = 8.2 Hz, 2H), 5.60 (s, 1H), 3.70 (s, 2H), 0.93 (s, 10H).  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  146.2, 139.8, 135.7, 132.1, 128.0  $\times$  2, 80.4, 31.9, 26.1. IR (ATR) 2962, 1593, 1479, 1402, 1357, 1262, 1176, 1099, 1016, 959, 936, 827, 757  $cm^{-1}$ .

**Typical Procedure for the Copolymerization of (2,2-Dimethylpropan-1-yl)4-(2-chlorothiophen-3-yl)benzenesulfonate (4a) and 2-Chloro-3-hexylthiophene (12)**. To a 50 mL Schlenk tube equipped with a magnetic stirring bar, **4a** (8.6 mg, 0.025 mmol), 2-chloro-3-hexylthiophene (**11**, 506 mg, 2.5 mmol), THF (25 mL), and 1.0 M THF solution of  $TMPMgCl \cdot LiCl$  (3.0 mL, 3.0 mmol) were added at room temperature. After stirring for 10 min,  $NiCl_2(PPh_3)IPr$  (19.3 mg, 0.025 mmol) was then added to initiate polymerization. The color of the solution turned to dark orange. After further stirring at room temperature for 1 h, the reaction mixture was poured into a mixture of hydrochloric acid (1.0 M, 2 mL) and methanol (10 mL) to form a precipitate, which was filtered off to leave a dark orange solid. After washing with methanol and hexanes repeatedly, the solid was dried under reduced pressure to afford 0.38 g of poly[(3-(4-(2,2-dimethylpropylsulfonyl)benzen)-1-yl)thiophene-2,5-diyl]-*stat*-(3-hexylthiophen-2,5-diyl)] (**12**) (90%). The molecular weight ( $M_n$ ) and the molecular weight distribution ( $M_w/M_n$ ) were estimated by SEC analysis.  $M_n$  = 30 000 and  $M_w/M_n$  = 1.44.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.93 (br,  $J$  = 7.6 Hz, 0.020H), 7.66 (br,  $J$  = 7.6 Hz, 0.020H), 7.14–6.72 (m, 1.01H), 3.73 (br, 0.020H), 2.98–2.50 (m, 2.0H), 1.91–1.14 (m, 8.0H), 0.91 (br, 3.09H).  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  140.0, 133.8, 130.6, 128.7, 31.9, 30.7, 29.6, 29.4, 22.8, 14.3. IR (ATR) 3054, 2955, 2925, 2856, 1509, 1456, 1377, 1188, 1179, 820, 723, 672, 664  $cm^{-1}$ . Other copolymers were synthesized in a similar manner to afford the corresponding statistical copolymers as summarized in Tables S1 and 1: copolymer **12** with **11** (1.3 mmol) and **4a** (**11/4a** = 50). Yield 0.21 g (96%);  $M_n$  = 28 500,  $M_w/M_n$  = 1.18 ( $m/n$  = 45). Copolymer **12** with **11** (0.5 mmol) and **4a** (**11/4a** = 20): Yield 58 mg (64%);  $M_n$  = 26 000;  $M_w/M_n$  = 1.11, ( $m/n$  = 16). Copolymer **12** with **11** (0.5 mmol) and **4a** (**11/4a** = 10): Yield 81 mg (84%);  $M_n$  = 25 000;  $M_w/M_n$  = 1.59, ( $m/n$  = 10). Copolymer **12** with **11** (0.5 mmol) and **4a** (**11/4a** = 5): Yield 81 mg (84%);  $M_n$  = 31 000;  $M_w/M_n$  = 1.17, ( $m/n$  = 3.7).

**Copolymerization of 8 and 1-Phenylethyne (14)**. To a 20 mL Schlenk tube equipped with a magnetic stirring bar, **8** (23 mg, 90  $\mu$ mol), 1-phenylacetylene (**13**, 23  $\mu$ L, 0.21 mmol), THF (2 mL),  $Et_3N$  (8.4  $\mu$ L, 60  $\mu$ mol), and  $[RhCl(nbd)]_2$  (31 mg, 6.7  $\mu$ mol) were added at room temperature. After stirring at room temperature for 60 min, the reaction mixture was poured into a large amount of MeOH (50 mL), centrifugally separated, and dried under vacuum to afford 30 mg of **14** as an orange solid in 67% yield. The molecular weight ( $M_n$ ) and the molecular weight distribution ( $M_w/M_n$ ) were estimated by SEC analysis.  $M_n$  = 18 000,  $M_w$  = 54 000, and  $M_w/M_n$  = 3.0.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.60 (s, 2H), 7.22–6.25 (br, 12H), 5.84 (s,

2H), 3.65 (s, 2H), 0.90 (s, 16H). Measurement of  $^{13}C\{^1H\}$  NMR spectrum (100 MHz,  $CDCl_3$ ) of **14** in  $CDCl_3$  only showed broad signals:  $\delta$  127.9, 127.7, 31.9, 26.1, 1.2. IR (ATR) 2962, 1594, 1481, 1358, 1261, 1177, 1097, 1018, 963, 801, 757  $cm^{-1}$ .

## CONCLUSIONS

In summary, we described the preparations of HT-regioregular polythiophene and polyacetylene-bearing benzenesulfonic acid moiety in the side chain by nickel- or rhodium-catalyzed polymerization, followed by thermolysis of thin films to convert neopentylsulfonate to the corresponding sulfonic acid. Protected polymers showed high solubility in organic solvents, while the deprotected ones showed solubilities in the water despite involving extended  $\pi$ -conjugation. The formation of the thin film of polymers was followed by the thermolysis-induced self-doping of polythiophene and remarkably improved conductivity by ca.  $10^3$ – $10^6$  times. Such behavior of thermally induced self-doping was also applied to copolymers of HT-P3HT and poly(phenylacetylene) by statistical copolymerization with the 3-arenesulfonate-substituted ones, which also achieved improved conductivity. It should be pointed out that the self-doping is successful only by thermal treatment without any additions of external chemicals. Such behaviors serve as formal self-doping of polymer thin films that bear side-chain functionalities incapable of doping. The obtained thin film would be potentially available for a wide range of electronic materials.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.9b02554>.

Detailed spectroscopic and analytical data (PDF)

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## Notes

The authors declare no competing financial interest.

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