Thermally Induced Self-Doping of π-Conjugated Polymers Bearing a Pendant Neopentyl Sulfonate Group

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Thermally-induced self-doping of π-conjugated polymers bearing a pendant neopentyl sulfonate group

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polythiophene, self doping, benzenesulfonate, water-soluble, polyacetylene

ABSTRACT Regioregular Head-to-tail (HT)-type polythiophene was synthesized by deprotonative nickel-catalyzed cross-coupling polymerization of 2-chlorothiophene bearing neopentyl benzenesulfonate group at the 3-position. The obtained HT-regioregular polymer was found dissolved in chloroform or THF, while it turned to water soluble upon heating the polymer at 185 °C for 10 min by the liberation of the protected neopentyl group. The thin-film of the polymer showed remarkable improvement of the conductivity ca. 10^3 times before/after heating suggesting thermally-induced intramolecular doping 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 produced the corresponding statistical copolymers, respectively, demonstrating the formal self-doping of poly(3-alkylthiophene) and poly(phenylacetylene).

Introduction

Polymers of extended π-conjugation attract much attention in material science as organic electronic materials showing a wide range of conductivities covering insulative, semiconductive, and metallic materials.[1-5] Although the most of such conjugated polymers are, in general, much less conductive by themselves, external addition of a dopant remarkably changes the characteristics as 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 polarones/bipolarons on the polymer main chain. For example, the conductivity of undoped head-to-tail-type regioregular polythiophenes (HT-P3HT) shows ca. $10^{-5}-10^{-7}$ $\mathrm{S{\cdot}cm^{-1}}$, while the addition of iodine as a dopant improves its conductivity to 10^2 $\mathrm{S{\cdot}cm^{-1}}$.[6] Self-doping bearing a dopant moiety in the skeleton of the conjugated polymer has also been a major concern decreasing the amount of the addition of excess dopants and thus caused deterioration of durability to oxidation or humidities can also be diminished. Introduction of a sulfonic acid moiety into the side chain of polythiophenes has been performed and several polymers thus designed have been shown to establish the improved conductivity by the effect of doping.[7-12] On the other hand, development of a practical method for the preparation of π-conjugated polymers with well-defined structure is an attractive issue in polymer synthesis, organic synthesis, and organometallic synthesis, in which use of an organometallic species as well as a transition metal complex for the polymerization catalyst has been powerful tools, accordingly.[6,13-15] However, such methodology generally causes synthetic difficulties in forming potentially self-doping conjugated polymers because of the use of a carbanion species for the polymerization, which 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 $FeCl_3$ leading to the corresponding polymer of uncontrolled regioregularity.[7-12,16-25] By contrast, cross-coupling polymerization to give the regioregular polythiophene with the GRIM method employing metalated thiophene and transition metal catalyst would not be tolerable toward the doping functionality at the side chain. Accordingly, the introduction of HT-regioregularity into self-doping polythiophenes is thereby a significant challenge in materials science.[13-15] (Fig 1) We considered synthesis of a water-soluble HT-regioregular poly-3-substituted thiophene, which posseses benzenesulfonic acid at the side chain employing deprotonative polymerization of 2-halo-3-substituted thiophene as a monomer precursor is employed[26-33] since we have, indeed, shown that synthesis of several side-chain functionalized polythiophenes have been prepared to date.[34,35] The acidic moiety should be protected during the polymerization employing an organometallic monomer and/or a transition metal catalyst.[36] The protected functionality can be removed after the formation of the polymer thin-film, wherein, the protective group may preferably removed without using any additional chemicals. Accrodingly, we focused on the use of neopentyl sulfonate, which was shown to be removed by thermal treatment leading to the corresponding sulfonic acid.[37] Herein, we describe that self-doping of π-conjugated polymers is induced by heating of the thin-film, whose improved conductivity is ca. $10^3 - 10^6$ times higher.

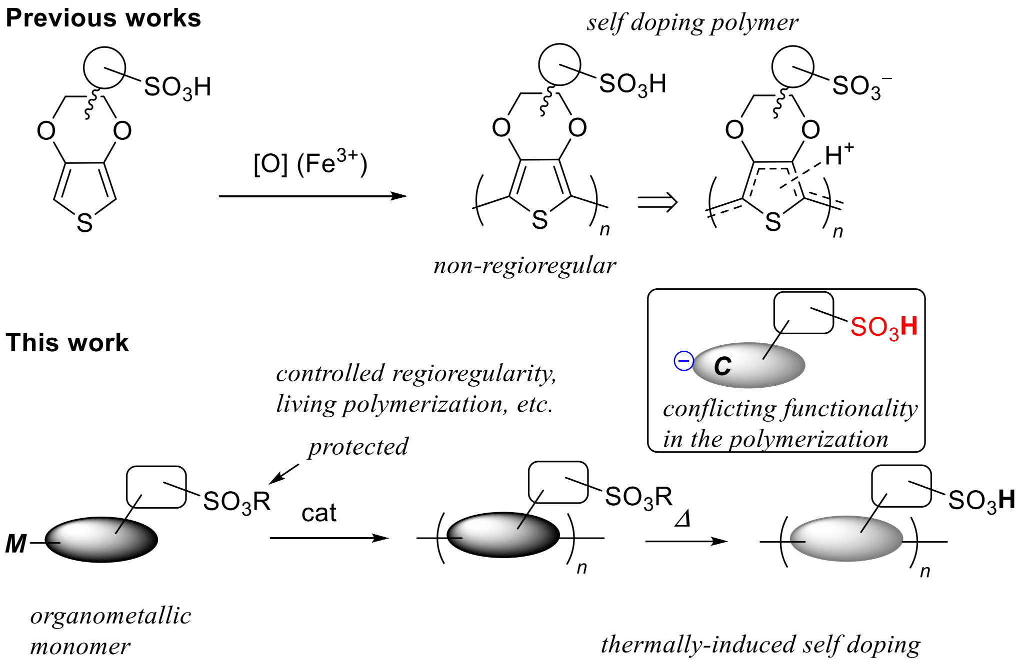


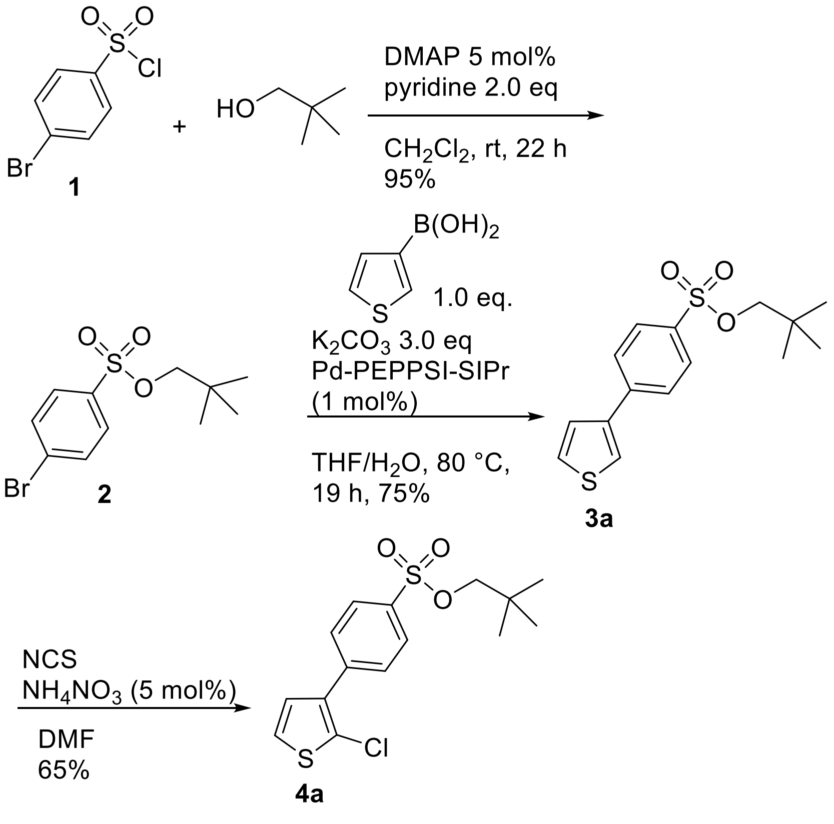
Fig. 1 Self-doping vs. thermally-induced self-doping

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. Synthesis 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 catalytic *N*, *N*-dimethylaminopyridine (DMAP) (95%).[38] Cross coupling with thiophene-3-boronic acid[39-42] catalyzed by Pd-PEPPSI-SIPr[43] gave **3a** in 75% yield and following chlorination with NCS gave monomer **4a** in 65% yield.

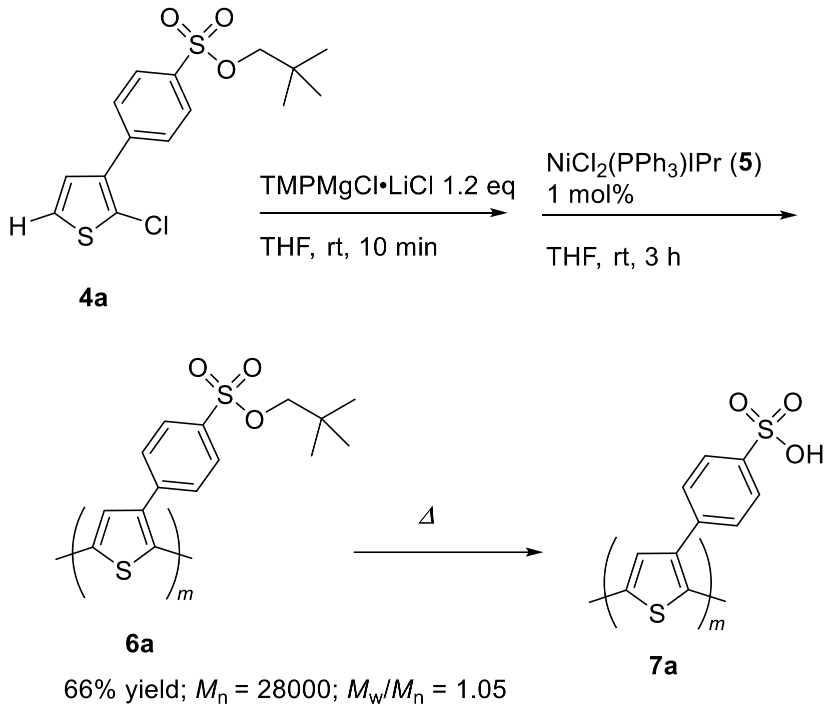
Scheme 1 Preparation of thiophene monomer **4a** bearing benzenesulfonate group at the 3-position



Polymerization of the thus obtained chlorothiophenes **4a** was carried out by the reaction with a bulky magnesium amide TMPMgCl·LiCl (2,2,6,6-teteramethylpiperidine-1-yl chloromagnesium: Knochel−Hauser base)[44] to undergo deprotonative metallation.[26-35] The addition of nickel catalyst

5 to the thus formed thiophene−magnesium species followed. Smooth polymerization took place at room temperature as shown in Scheme 2 to afford the corresponding polythiophene **6a** in 66% yield as deep orange solid as shown in Scheme 2. Measurement of the obtained polymer was revealed to show molecular weight of ca. 28000, 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). ^{1}H NMR spectrum of **6a** showed that the obtained polymer is highly regioregular head-to-tail (HT) orientation (>99:1). Polymer **6a** was found to be soluble in several organic solvents such as chloroform and THF.

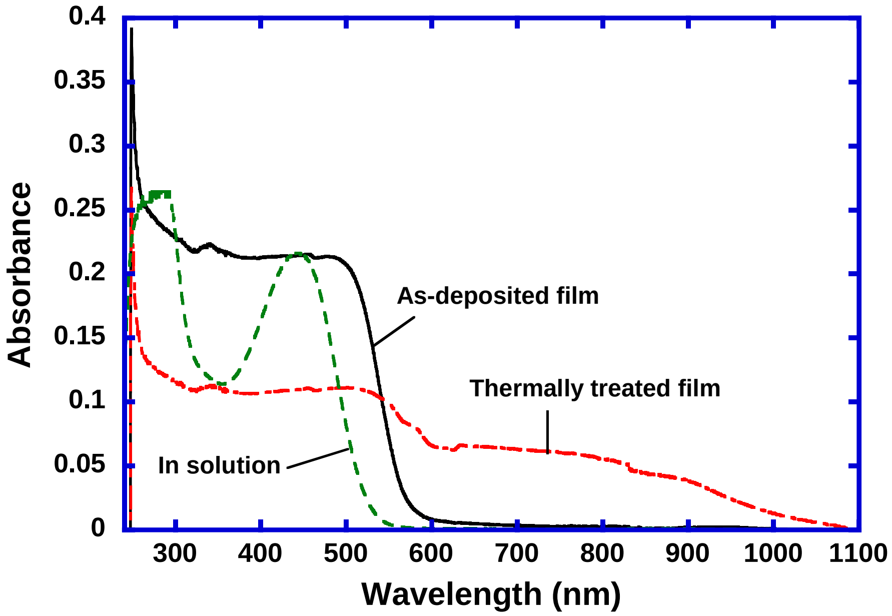
Scheme 2 Nickel-catalyzed polymerization of **4a** by deprotonation with Knochel-Hauser base



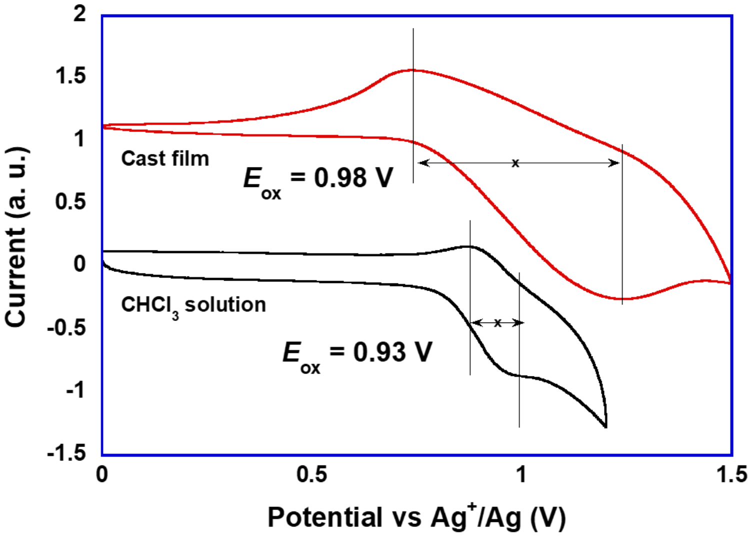
Thermogravimetric analysis of **6a** revealed that a remarkable mass loss took place at 185 °C, which amount was consistent with the thermolysis of the neopentyl ester leading to sulfonic acid. Indeed, heating of the solid polymer **6a** at 180 °C showed the immediate color change to durk purple leading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

Fig. 2 shows compared properties of the obtained polythiophenes before/after thermolysis of the thin-film casted on a quartz substrate. UV-vis spectrum of sulfonate **6a** was found to show λ_{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) (λ_{max} = 442 nm).[6] Measurement of the UV-vis spectrum of the cast film of **6a** revealed to show the red shift of the absorption edge from 530 nm to 580 nm as well as that of the λ_{max} value from 440 nm to 510 nm. Treatment of the thus formed cast film at 180 °C for 10 min resulted to observe remarkable color change. The UV-vis spectrum of the film of **6a** after heating indicated to show absorption at the range of a near infrared region. (Fig. 2a) Measurement of cyclic voltammetry of a chloroform solution of **6a** indicated to show reversible wave at 0.93 V vs. Ag^+/Ag standard electrode induced by one-electron oxidation (Fig. 2b) and the UV-vis spectrum of **6a** at the oxidation state exhibited absorption at ca. 600 nm (Fig. 2c). Accordingly, the color change of the cast film of **6a** caused by thermolysis leading to **7a** would be attributed to the formation of cation radical species stabilized by formed sulfonic anions. The similar oxidation was also observed in the cast film of **6a** to indicate oxidation wave at 0.98 V vs. Ag^+/Ag standard electrode accompanied by the color of the film to dark brown whereas such a color change of the film was irreversible. It is worthy of note that the change to the doping state was induced by heating of the polymer film. The result markedly contrasts with the case of PEDOT, which only shows spontaneous dope as received.

(a)



(b)



(c)

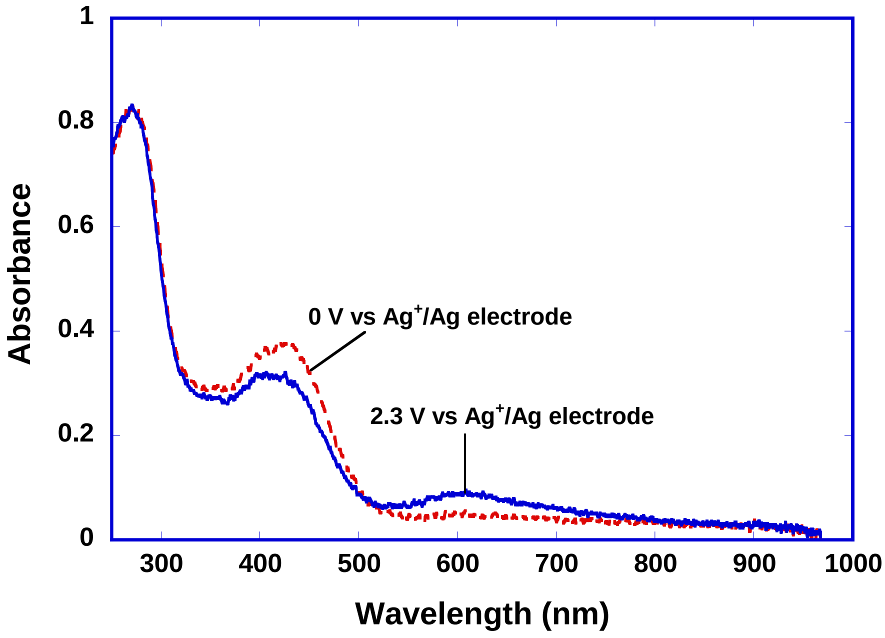


Fig. 2 (a) UV-vis absorption spectrum of chloroform solution of **6a** (green dotted), cast film of **6a** (black), and the cast film of **6a** after heating at 180 °C for 10 min (red) (considered to form **7a** in the film). (b) Cyclic voltammogram of a chloroform solution of **6a** (black) (1 mM/0.1 M $Bu_4NPF_6/CHCl_3$, scan rate 0.01 Vs^{-1}) and the cast film (red) (0.1 M Bu_4NClO_4/CH_3CN, scan rate 0.1 Vs^{-1}); (c) UV-vis spectrum of **6a** in chloroform upon electrooxidation (0.1 M Bu_4NPF_6) (red dotted: 0 V; blue: 2.3 V)

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 by the effect of sulfonic acid at the polythiophene side chain. The film thus transformed to **7a** indeed dissolved in water suggesting formation of the sulfonic acid moiety. The doped thin-film would improve the conductivity, accordingly, when the thus formed polymer **6a** is cast on an electrode. The polymer **6a** was casted to form the thin-film of 200 nm thickness and the measurement of a current value at a certain applied voltage showed the current level of 1 x 10^{-7} to 1 x 10^{-5} A and thus calculated conductivities as ca. 10^{-5} S/cm. Remarkable increase of the current values was observed after the thin-film on the electrode was heated at 190 °C for 20 min as shown in Fig. 3 to result in 1 x 10^{-2} S/cm. The results suggested that the conductivity of the polythiophene thin-film was ca. 10^{3} times improved by heating. Although several self-doping polythiophenes bearing sulfonic acid moiety have also been developed to date,[7-12] formation of such polymers with a transition-metal-catalyzed polymerization leading to completely regiocontrolled polymers cannot be performed caused by inconsistency of the organometallic thiophene monomer from **4a** and acidic side chain bearing SO_3H. It should also be pointed out that such improved conductivity was observed only by thermal treatment of the thin-film without external additive chemicals by the liberation of the protected neopentyl group.

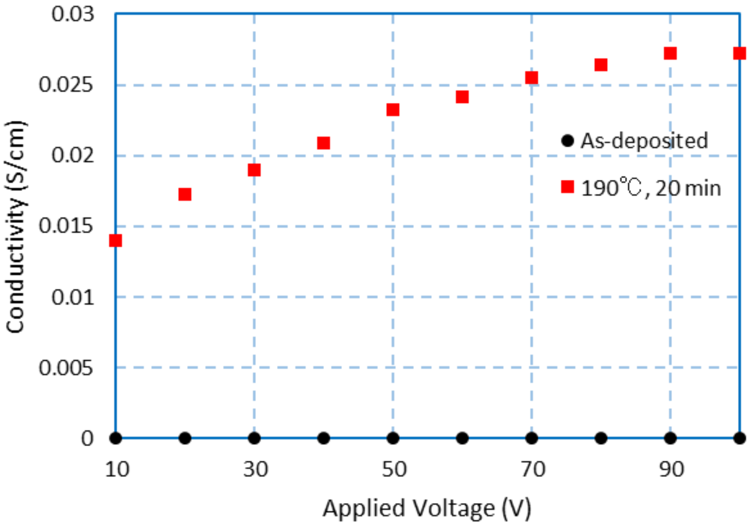
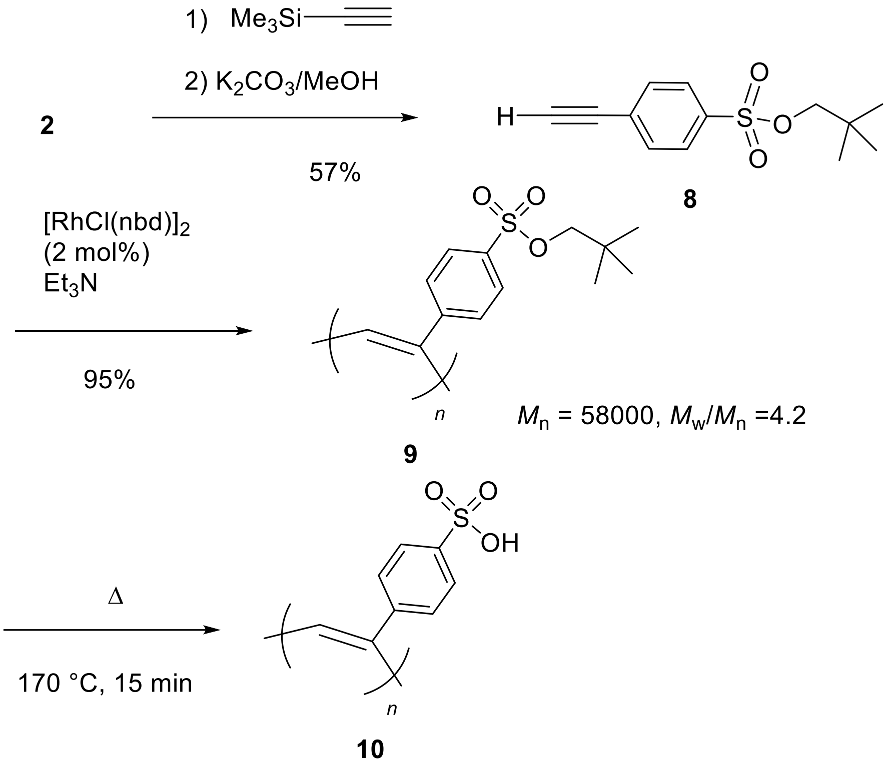


Fig. 3 Electronic properties on current-voltage characteristics of as-deposited and thermally treated cast film of polythiophene **6a** (as deposited: black) and after heated at 190 °C for 20 min leading to **7a** (red)

Synthesis and characterization of a polyacetylene derivative

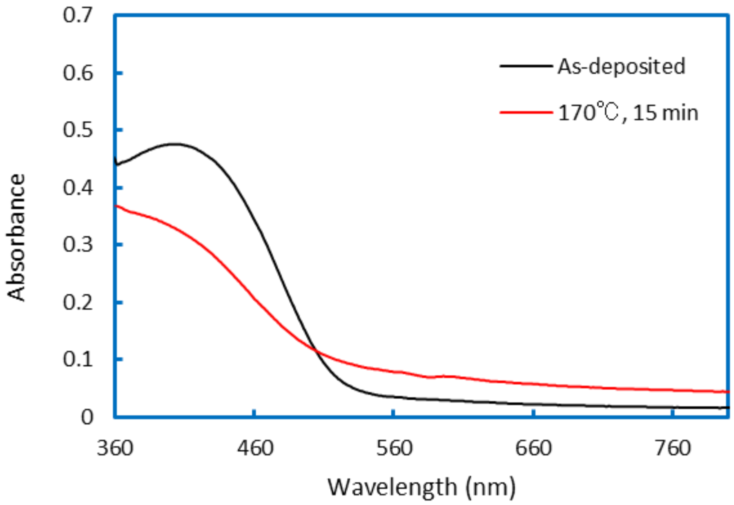
It was also found that such a thermally-induced self-doping behavior was observed in a different-type of conjugate polymer. Polyacetylenes have also been recognized as a kind of p-type semiconductive material thus doping occurs by the addition of acid, iodine, etc.[45] Preparation of polyacetylenes can be performed by polymerization of alkynes and treatment of a terminal alkyne by a rhodium catalyst is shown to lead to *Z*-polyalkynes smoothly.[46,47] Arylalkyne bearing the neopentyl sulfonate substituent was synthesized as illustrated in Scheme 3. The Sonogashira coupling[48] of bromobenzenesulfonate **2** with trimethylsilylacetylene followed by removal of the silyl group afforded the monomer **8**. Following polymerization of **8** was carried out in the presence of rhodium(I) catalyst $[RhCl(nbd)]_2$ (2 mol%) afforded the corresponding *Z*-polyacetylene **9** in 95% yield.[48]

Scheme 3. Preparation and polymerization of arylalkyne **8** bearing a benzenesulfonate substituent at the aromatic ring.



The obtained polyacetylene **9** was also subjected to the formation of the cast thin-film. Measurement of UV-vis spectrum of **9** showed characteristic absorption at 400 nm as shown in Fig. 4 (a) suggesting the formation of conjugated polyene. Thermal treatment of **9** at 170 °C for 15 min leading to **10** showed the absorption at the nir region as observed in that of regioregular polythiophene **7**. Fig. 4 (b) shows the change of conductivity before/after thermal treatment of the film and thus suggested the formation of cation radicals in the polymer main chain. The film of polyene **9** showed little current at the applied voltages ranging 20−100 V. The improved conductivity was observed after treatment of the film at 170 °C for 15 min to indicate conductivities of ca. 0.003−0.005 S/cm^{-1} (20−50 V). The results suggests that the improved conductivity is at least ca. 10^6 times higher after thermal treatment.

(a)



(b)

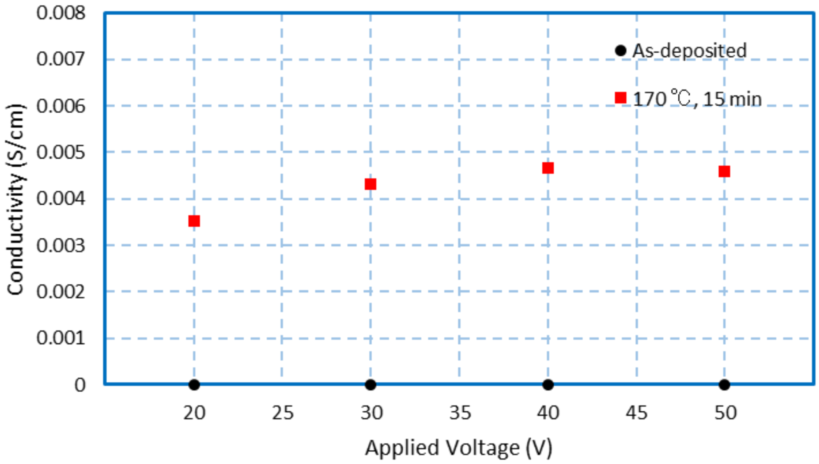


Fig. 4 (a) Absorption spectrum of the thin-film of polyacetylene **9** and (b) electronic properties on current-voltage characteristics of as-deposited and thermally treated cast film of polyacetylene **9** (as deposited: black) and after heated at 170 °C for 15 min leading to **10** (red)

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.[1-5] P3HT bearing an alkyl group at the side chain can only be doped by an external additive and thus incapable of self-doping by itself. However, incorporation of a partial thiophene unit bearing a functional group that 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.[26-33] 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 TMPMgCl·LiCl at room temperature for 10 min followed by addition of nickel catalyst **5** (1.0 mol %) to initiate copolymerization. Table 1 summarizes the result. Use of the different ratio of **4a** : **11** (1/100, 1/50, 1/20, 1/10, 1/5) was found to undergo polymerization to afford poly(3-hexylthiophene) containing the statistic amount of comonomer **4a**, respectively. Measurement of ^{1}H NMR spectrum revealed to involve a reasonable amount of **4a** toward **11** and the obtained polymers showed M_n = 20000-30000 (M_w/M_n = 1.10-1.44). Analysis of the organic filtrate by ^{1}H NMR to detect the remaining monomers showed that both were almost equally consumed suggesting little preferential incorporation of sulfonate comonomer **4a** to the P3HT chain, otherwise, vice versa.

Scheme 4. Statistical copolymerization of sulfonate-containing thiophene **4a** and 2-chloro-3-hexylthiophene (**11**)

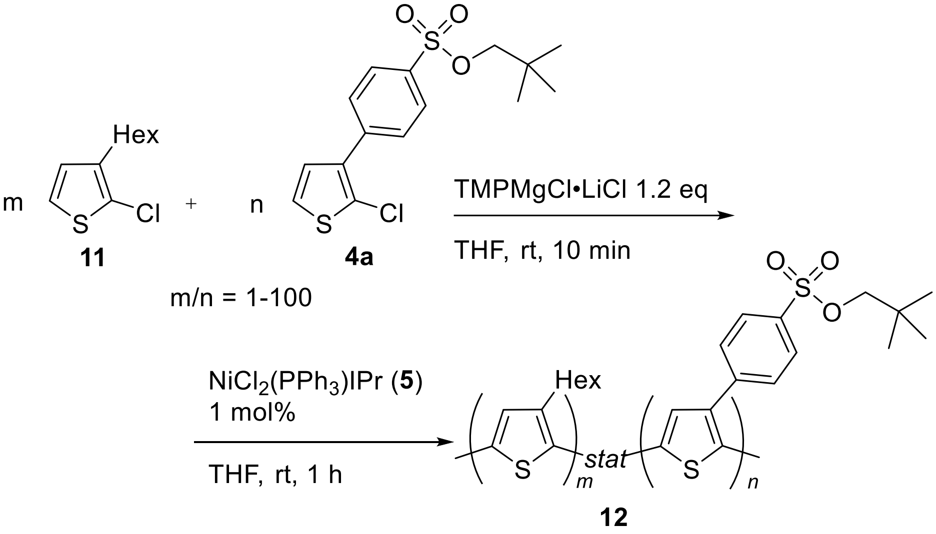


Table 1. Copolymerization of sulfonate group-containing chlorothiophene **4a** and 2-chloro-3-hexylthiophene (**11**) with nickel(II) catalyst **5**[a]

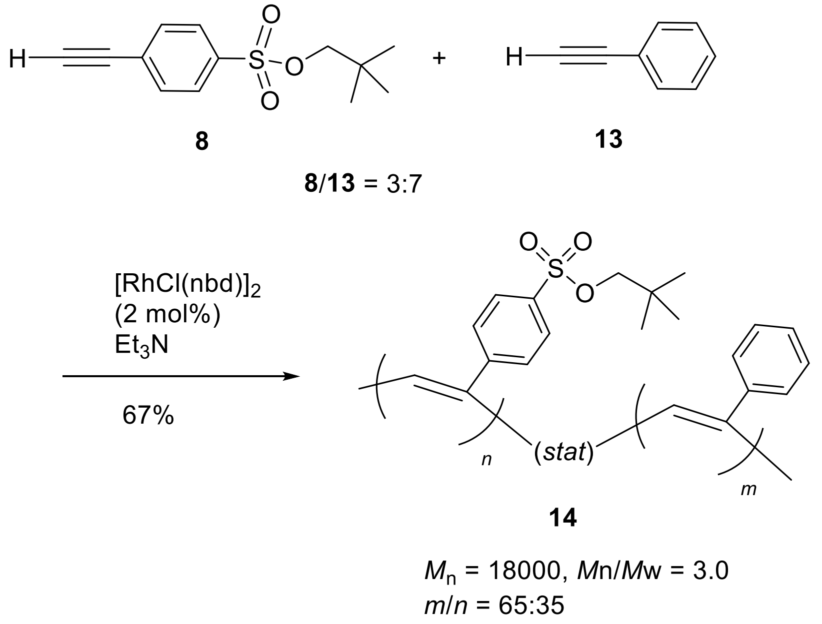
11 (mmol)	**11**/**4a**	%conv of **11**[b]	%conv of **4a**[b]	M_n[c]	M_w/M_n[c]	m/n[d]
2.5	100	95	>99	3.0 x 10^4	1.44	100
1.3	50	95	>99	2.9 x 10^4	1.18	45
0.5	20	99	89	2.6 x 10^4	1.11	16
0.5	10	99	95	2.5 x 10^4	1.59	10
0.5	5	89	92	3.1 x 10^4	1.17	3.7

[a] 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 addition of $NiCl_2(PPh_3)IPr$ (**5**, 1.0 mol %) at room temperature for 1 h. [b] Consumption of monomer was estimated by measurement of ^1H NMR of the filtrate after precipitation of the obtained polymer **12**. [c] The molecular weight (M_n) and the molecular weight distribution (M_w/M_n) were measured by SEC analysis. [d] Contents of monomer unit derived from **4a** and **11** were estimated by ^1H NMR analysis of the polymer.

The related statistical copolymer was also found to be prepared by 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 with

3:7 of **8** and **13**, respectively, afforded the copolymer **14** in 67% yield. Measurement of ^{1}H NMR spectrum of **14** revealed to contain ca. 35% of benzenesulfonate moiety derived from **8** and the M_n and $M_\mathrm{w}/M_\mathrm{n}$ values of copolymer **13** were revealed to be 18000 and 3.0, respectively. (Scheme 5)

Scheme 5. Statistical copolymerization of arylalkyne **8** and phenylacetylene (**12**)



The obtained copolymers were then subjected to measurements of optoelectronic properties as a thin-film on a quartz or the ITO electrode.[49] As shown in Fig 5, the film of **12** ($m = 3.7$; $n = 1$) as deposited showed λ_max of 520 nm while transparent at higher than ca. 700 nm (NIR region). When the film **12** was heated at 190 °C for 20 min, it was found to show 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 drastic change as summarized in Teble 2. The thin-film of **12** ($m = 3.7$; $n = 1$) as deposited indicating conductivity of 1.2 x 10^{-5}

S/cm improved to 4.1 x 10^{-2} S/cm (at 50 V) by thermal treatment at 190 °C for 20 min suggesting ca. 10^3 times higher conductivity by thermally-induced self-doping.[50] The related properties of statistical polyacetylene copolymer **14** are also shown in Fig. 4(a) and 4(b) 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 poly(3-alkylthiophene) and poly(arylalkyne) are incapable of self-doping by themselves, the results show formal doping of such polymers, accordingly. Worthy of note is remarkable improvement of the conductivity of the polymer thin-film ca. 10^3−10^6 times whereas each conductivity is dependent of the conditions of thin-film fabrication.

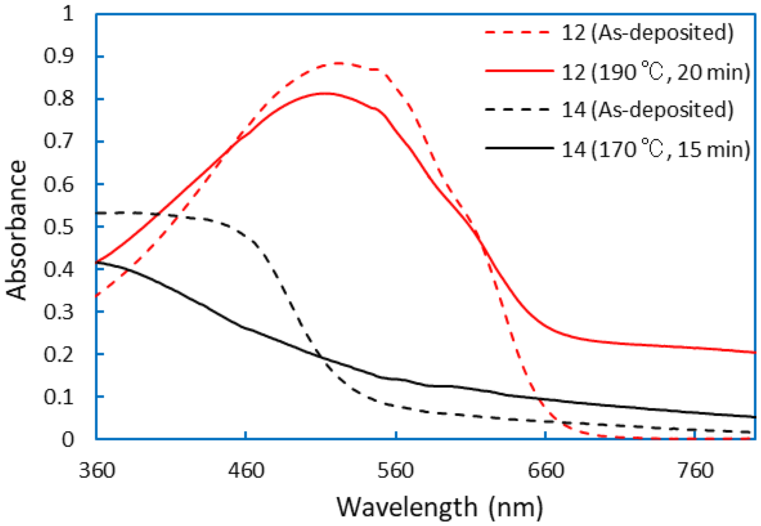


Fig. 5 Absorption spectra of as-deposited (black)/thermally treated (red) cast film of **12** (m = 3.7; n = 1) and those of **14** (m=65; n=35) [50]

Table 2. Thermally-induced change of conductivities of the thin films obtained by copolymerization of **11** and **4a** (polythiophene) and **8** and **13** (polyene) [a]

copolymer	comonomer		ratio[b]	M_n[c]	conductivity (S/cm)[d]	
					as-deposited	after heating
12	**11**	**4a**	3.7:1.0	31000	1.2x10^{-5}	3.4x10^{-2}
14	**8**	**13**	1.9:1.0	18000	3.6x10^{-9}	1.6x10^{-3}

[a] The measurement of conductivity was carried out with the cast thin film of copolymers **12** and **14**. [b] The incorporated ratio of **11**/**4a** or **8**/**13** estimated by the ^{1}H NMR measurement. [c] The molecular weights (M_n) were measured by SEC analysis. [d] The conductivity was calculated based on the current at 50 V.

Experimental section

Materials and methods

All the reactions were carried out under nitrogen atmosphere. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra were measured on JEOL ECZ400 as a $CDCl_3$ solution unless noted. The chemical shifts were expressed in ppm with $CHCl_3$ (7.26 ppm for ^{1}H) or $CDCl_3$ (77.16 ppm for ^{13}C) as internal standards. IR spectra were recorded on Bruker Alpha with an ATR attachment (Ge). High resolution mass spectra (HRMS) were measured by JEOL JMS-T100LP AccuTOF LC-

Plus (ESI) with a JEOL MS-5414DART attachment. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F_{254}) were used. Purification by HPLC with 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 $CHCl_3$ as an eluent with Shodex KF-402HQ and KF-404HQ. Molecular weights and molecular weight distributions were estimated on the basis of the calibration curve obtained by 6 standard polystyrenes. UV-vis absorption spectra of the polymer films were measured with Shimadzu UV-3150. Cyclic voltammetry was conducted by ALS 600B. Conductivity of polymer films were measured with a digital electrometer ADCMT8340A. Concerning the solvent of 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[51] prior to use. Knochel-Hauser base (TMPMgCl·LiCl)[44] was purchased from Sigma-Aldrich Co. Ltd. as a 1 M THF solution. $NiCl_2(IPr)PPh_3$[53] and $[RhCl(nbd)]_2$[46] were purchased from TCI Co. Ltd. Other chemicals were purchased and used without further purification.

(2,2-Dimethylpropan-1-yl)4-bromobenzenesulfonate (2):[54] 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_2Cl_2 (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_2O. 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. ^{1}H NMR (400 MHz, $CDCl_3$) 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). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 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_2CO_3 (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. The mixture was 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_2Cl_2 and hexanes to give 1.13 g of **2** in 75% as a colorless solid. ^1H NMR (400 MHz, $CDCl_3$) 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). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 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^{-1}. HRMS (DART−ESI^+) calcd for $C_{15}H_{19}O_2S_2$: 311.0776; found *m/z* 311.0781.

(2,2-Dimethylpropan-1-yl)4-(2-chlorothiophene-3-yl)benzensulfonate (4a): To a solution of (2,2-dimethylpropan-1-yl)-4-(thiophen-3-yl)benzenesulfonate (**3**, 2.8 g, 9.1 mmol) and NH_4NO_3 (36 mg, 0.45 mmol) in DMF (11 mL) was added *N*-chlorosuccinimide (NCS) (1.3 g, 9.9 mmol) and stirring was continued at 60 °C for 13 h. The reaction mixture was washed with aqueous Na_2SO_3 and NH_4Cl. The aqueous layer was extracted with CH_2Cl_2 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 silica gel using CH_2Cl_2 /hexanes (1/1, v/v) and recrystallization with CH_2Cl_2 and hexanes to give 2.04 g of **4a** in 75% as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) 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). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.5, 136.2, 134.8, 129.1, 128.1x2, 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^{-1}. HRMS (DART−ESI$^+$) calcd for $C_{15}H_{18}{}^{35}ClO_3S_2$: 345.0386; found *m/z* 345.0394.

Poly(3-(4-(2,2-dimethylpropylsulfonylbenzen)-1-yl)thiophene-2,5-diyl) (6a): To 20 mL Schlenk tube equipped with a magnetic stirring bar were added **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) at room temperature. After stirring at room temperature for 10 min, $NiCl_2(PPh_3)IPr$ (**5**, 4.4 mg, 5.6 μmol) was then added to initiate polymerization. The color of the solution was 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_n) and the molecular weight distribution (M_w/M_n) was estimated by SEC analysis. M_n = 28000, M_w/M_n = 1.05. ^{1}H NMR (400 MHz, $CDCl_3$) 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). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 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^{-1}.

Poly(3-(4-(benzenesulfonic acid)-1-yl)thiophen-2,5-diyl) (7a): Polythiophene bearing benzenesulfonate substituent (30 mg) was taken in a Schlenk tube, which was heated by a heating gun for a few minutes, to observe color change from purple to dark purple solid, which resulted to be dissolved in water. Measurement of ^{1}H NMR spectrum in D_2O showed broad signals suggesting low mobility of organic moiety in an aqueous medium while dissappearence of neopentyl group was confirmed. TG-DTA profile also supported the conversion to neopentyl sulfonate into the corresponding sulfonic acid by indicating the mass loss of equivalent to C_5H_{10} at 185 °C.

(4-(2,2-dimethylpropylsulfonyl)-phenyl)ethyne (8):

To 50 mL Schlenk tub equipped with a magnetic stirring bar were added (2,2-dimethylpropyl)4-bromobenzenesulfonate (**2**, 1.53 g, 5.0 mmol), THF(15 mL), trimetylsilylacetylene(1.06 mL, 7.5 mmol), copper(I) iodide (101 mg, 0.53 mmol), bis(triphenylphosphine)palladium(II) (175 mg, 0.25 mmol) and trietylamine(7.0 mL, 50 mmol) at room tempreture for 21 h . Water(20 mL) was added to the mixture to quench the reaction. The organic layer was extracted with Et_2O, a water of NH_4Cl, 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 silica gel with hexanes/CH_2Cl_2 (1/1, v/v) as the eluent to afford 1.40 g of (2,2-dimethylpropyl)4-[2-(trismethylsilyl)ethynyl]benzenesulfonate. Then to a solution of (2,2-dimetylpropyl)4-[2-(trismethylsilyl)ethynyl]benzenesulfonate (1.28 g, 3.8 mmol) in MeOH/CH_2Cl_2 (1/1, v/v, 11.4 mL) was added K_2CO_3 (1.06 g, 7.6 mmol) and stirring was continued 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 silica gel with hexanes/Et_2O (1/8, v/v) as the eluent to afford 653 mg of **8** in 57% yield (over 2 steps) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 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{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.8, 132.7, 127.8x2, 81.7, 81.5, 79.9, 31.6, 25.9.

Poly((4-(2,2-dimethylpropylsulfonyl)phenyl)-ethen)-1,2-diyl) (9):

To 20 mL Schlenk tube equipped with a magnetic stirring bar were added $[RhCl(nbd)]_2$ (2.6 mg, 5.6 μmol) , **8** (76 mg, 0.30 mmol), Et_3N (8.4 μL, 60 μmol) and THF (2 mL) 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), centrifugal separated and dried under vacuum to afford 72 mg of **9** in 95% as orange solid. The molecular weight (M_n) and the molecular weight distribution (M_w/M_n) was estimated by SEC analysis. $M_n = 58000$, $M_w = 240000$, $M_w/M_n = 4.2$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 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{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.2, 139.8, 135.7, 132.1, 128.0x2, 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 copolymerization of (2,2-dimethylpropan-1-yl) 4-(2-chlorothiophen-3-yl)benzenesulfonate (4a) and 2-chloro-3-hexylthiophene (12): To 50 mL Schlenk tube equipped with a magnetic stirring bar were added **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·LiCl (3.0 mL, 3.0 mmol) was 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 was turned to dark orange. After 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-dimethylpropapylsulfonylbenzen)-1-yl)thiophene-2,5-diyl)-stat-(3-hexylthiopen-2,5-diyl)] (**12**) (90%). The molecular weight (M_n) and the molecular weight distribution (M_w/M_n) was estimated by SEC analysis. $M_n = 30000$, $M_w/M_n = 1.44$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$) δ 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 Table s1 Table 1 of the text): Copolymer **12** with **11** (1.3 mmol) and **4a** (**11**/**4a** = 50). Yield 0.21 g (96%); $M_n = 28500$, $M_w/M_n = 1.18$ ($m/n = 45$). Copolymer **12** with **11** (0.5 mmol) and **4a** (**11**/**4a** = 20): Yield 58 mg (64%); $M_n = 26000$; $M_w/M_n = 1.11$, ($m/n = 16$). Copolymer **12** with **11** (0.5 mmol) and **4a** (**11**/**4a** = 10): Yield 81 mg (84%); $M_n = 25000$; $M_w/M_n = 1.59$, ($m/n = 10$). Copolymer **12** with **11** (0.5 mmol) and **4a** (**11**/**4a** = 5): Yield 81 mg (84%); $M_n = 31000$; $M_w/M_n = 1.17$, ($m/n = 3.7$).

Copolymerization of 8 and 1-phenylethyne (14):

To 20 mL Schlenk tube equipped with a magnetic stirring bar were added **8** (23 mg, 90 μmol) , 1-phenylacetylene (**13**, 23 μL, 0.21 mmol), THF (2 mL), Et_3N(8.4 μL, 60 μmol) and $[RhCl(nbd)]_2$ (31 mg, 6.7 μmol) at room temperature. After stirring at room temperature for 60 min. The reaction mixture was poured into a large amount of MeOH (50 ml), centrifugal separated and dried under vacuum to afford 30 mg of **14** in 67% as an orange solid. The molecular weight (M_n) and the molecular weight distribution (M_w/M_n) was estimated by SEC analysis. M_n = 18000, M_w = 54000, M_w/M_n = 3.0. ^{1}H NMR (400 MHz, $CDCl_3$) δ 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: δ 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 that preparations of HT-regioregular polythiophene and polyacetylene bearing benzenesulfonic acid moiety in the side chain, which was obtained by nickel or rhodium-catalyzed polymerization and following thermolysis of thin-films to the convert neopentylsulfonate to the corresponding sulfonic acid. Protected polymers showed high solubility in organic solvents while the deprotected ones showed solubilities in water despite involving extended π-conjugation. Formation of the thin-film of polymers followed by thermolysis induced self-doping of polythiophene and remarkably improved conductivity to ca. 10^3 to 10^6 times higher. 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 serves as formal self-doping of polymer thin-films that bear side-chain functionalities incapable of doping. The obtained thin-film would be potentially available to a wide range of electronic materials.

Supporting Information. The following files are available free of charge.

Detailed spectroscopic and analytical data (PDF)

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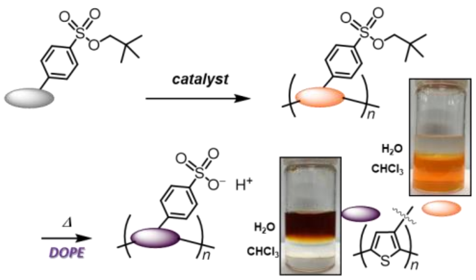
catalyst
n
H₂O
CHCl₃
Δ
DOPE
H⁺
n
H₂O
CHCl₃
S
n