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THERMALLY-INDUCED DOPING OF THE REGIOREGULAR POLYTHIOPHENE BEARING ALKYLENE SPACERED BENZENE-SULFONATE GROUP AT THE SIDE CHAIN

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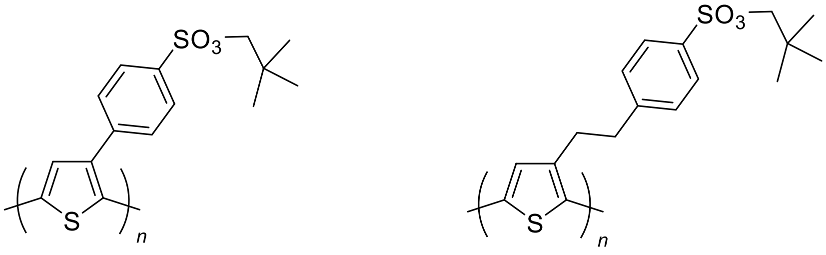
‡This paper is dedicated to Professor Yasuyuki Kita on celebration of his 77th birthday.

Abstract – Regioregular polythiophene bearing a benzenesulfonate group, which involved an alkylene spacer between thiophene and benzene ring, was synthesized. The obtained polythiophene was shown to improve its conductivity by heating the polymer thin film through the transformation of the ester group into the corresponding sulfonic acid.

INTRODUCTION

The regioregular head-to-tail (HT)-type polythiophenes bearing a substituent at the 3-position are of much interest in materials science. HT-poly(3-alkylthiophene)s have been employed as electronic materials such as electrodes, p-type semiconductors, photovoltaic cells, etc.[1] The development of the efficient synthetic protocol of such polymers has been our major concern.[2] We have been engaged in the development of the practical synthesis of conjugated polymers representative as regioregular polythiophenes.[3] Introduction of a functional group into the side chain of polythiophene also attracts much attention and a variety of functionalities have been incorporated to polythiophenes.[4] We have recently shown that a thiophene monomer bearing benzenesulfonate at the 3-position of thiophene is prepared and allows cross-coupling polymerization leading to the HT-regioregular polythiophene, which is successfully transformed into the corresponding sulfonic acid by thermolysis that also induced water-soluble characteristics. The obtained product showed improved conductivity of polythiophene through the doping of the thiophene main chain by the sulfonic acid.[5] Our further interest has been turned to the development of a new class of such thermally-induced self-doping polythiophenes whose electronic and steric characteristics are similar to those of poly(3-alkylthiophene)s. The direct connection of thiophene and benzene rings may cause steric congestion as well as the conjugated structure in **1**. The introduction of a non-conjugate alkylene spacer would cause a sterically less hindered side chain and thus forms stronger π-π interaction in the polythiophene main chain and such structural change would influence characteristics of the polymer in the thin-film state. Herein, we describe synthesis and characterization of poly(3-substituted thiophene) bearing the alkylene-spacered benzenesulfonic group **2**.

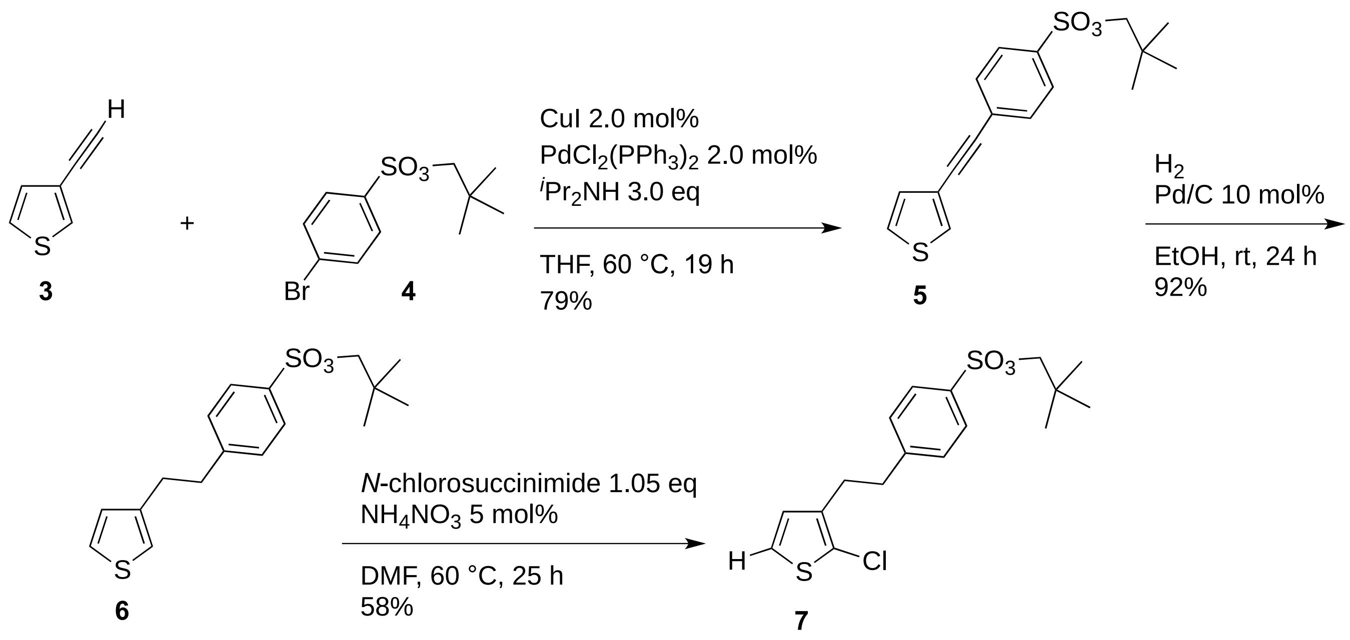


1 **2**

Chart 1. Polythiophene bearing a benzenesulfonate substituent with/without alkylene spacer

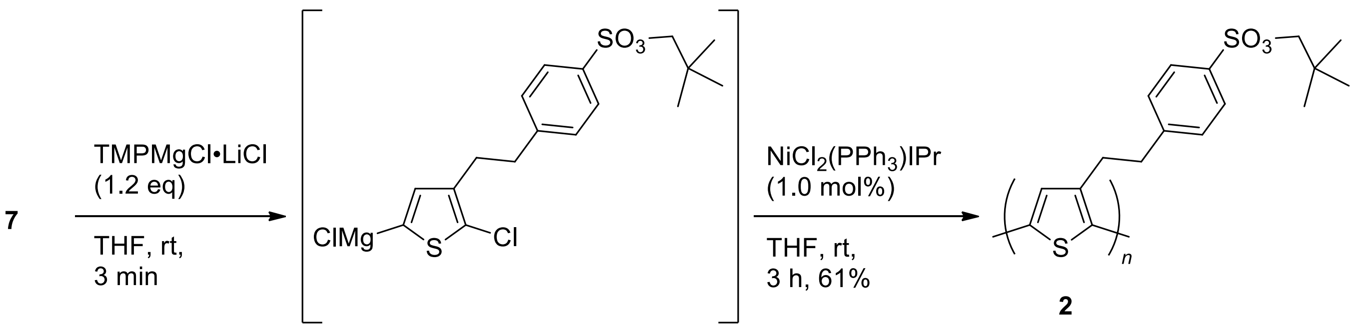
RESULTS AND DISCUSSION

Preparation of 3-ethynylthiophene (**3**) with 3-bromothiophene and (trimethylsilyl)ethyne followed by desilylation was performed by the literature method with slight modification.[6] Sonogashira-Hagihara coupling[7] of neopentyl (4-bromobenzene)sulfonate (**4**)[5] with **3** catalyzed by palladium/copper system afforded the disubstituted alkyne **5** in 79% yield. Hydrogenation of **5** in the presence of 10 mol% Pd/C obtained the alkylene spacered thiophene bearing benzenesulfonate **6** in 92% yield. The introduction of chlorine atom at the 2-position of thiophene was carried out with *N*-chlorosuccinimide to give the monomer precursor **7** (58%) (Scheme 1).



Scheme 1. Preparation of 2-chloro-3-substituted thiophene bearing benzenesulfonate moiety with an alkylene spacer

Polymerization of **7** was carried out under the standard conditions for that of chlorothiophenes as we have reported.[3] The reaction was found to proceed smoothly at room temperature for 3 h in the presence of 1.0 mol% nickel(II) catalyst bearing N-heterocyclic carbene ligand IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)[8] to afford the corresponding polymer **2** in 61% yield as shown in Scheme 2. Measurement of ^{1}H NMR suggested that the head-to-tail regioregularity of polythiophene **2** was ca. 93:7.[9] The obtained polymer showed M_n = 36000 (M_w/M_n = 1.93) and the result of the UV−vis absorption spectrum of the chloroform solution indicated the λ_{max} value of 438 nm, which shows little difference from the conjugated derivative **1** (440 nm) as well as P3HT (442 nm).[5]



Scheme 2. Polymerization of chlorothiophene **7** with nickel(II) catalyst $NiCl_2(PPh_3)IPr$

The obtained polythiophene **2** bearing benzenesulfonate at the side chain with an alkylene spacer was then subjected to the formation of the thin film on a substrate. The cast film of polythiophene revealed to show λ_{max} of 530 nm, which shows the shift to longer wavelength to ca. 90 nm from the solution state. Comparing that λ_{max} of polythiophene bearing no alkylene spacer **1** (510 nm),[5] the λ_{max} of **2** was shifted to 20 nm. The result suggests stronger π−π stacking in the film state because of the effect of the insertion of the alkylene spacer. Thermal treatment of the thin film at 190 °C for 15 min and the measurement of the UV−vis spectrum indicated absorption at the NIR region (>700 nm) as shown in Figure 1(a) suggesting doping of the thiophene main chain as observed in the case of **1**. The results indicated that the thermally-induced doping of polythiophene **2** also occurred by the formation of the corresponding sulfonic acid through the liberation of the neopentyl group by the thermolysis. Figure 1(b) shows the cyclic voltammetry profile of the thin film of polythiophene **2**. A reversible oxidation wave was observed at 0.90 V vs Ag/AgCl standard electrode owing to one-electron oxidation accompanied by the remarkable color change of the film from orange to dark purple. Measurement of the conductivity was carried out on the thin film of polythiophene **2**. The result is summarized in Figure 2. The polythiophene thin film **2** before/after the thermal treatment also showed the improved conductivity ca. 10^{5} times higher, while that of non-spacered polythiophene only improved the conductivity value ca. 10.[3] These results also support the stronger π−π interaction as suggested by the λ_{max} of the thin film shown in Figure 1(a).

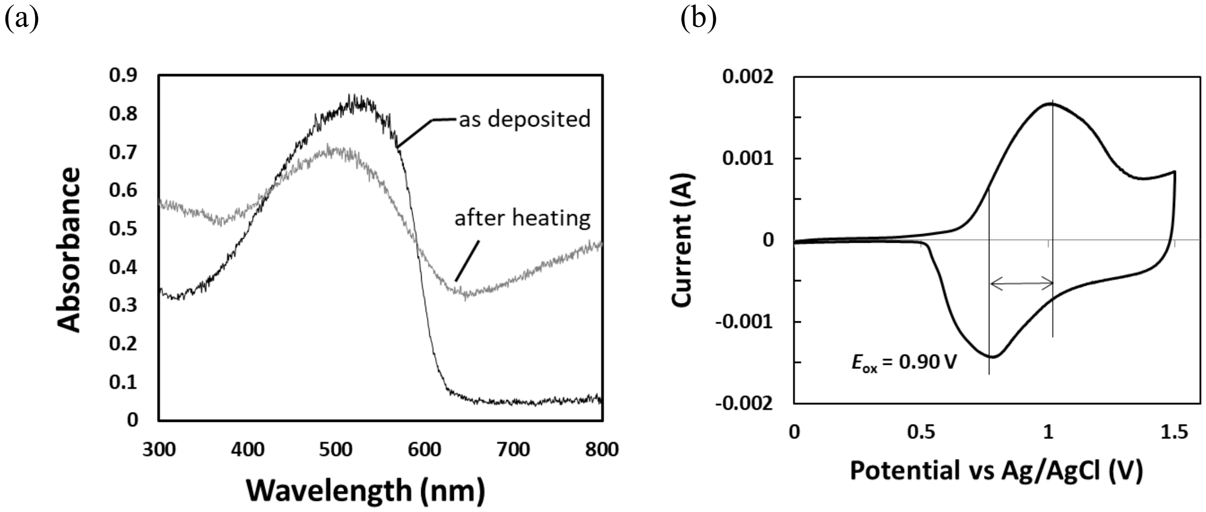


Figure 1. (a) UV−vis spectra of the thin-film of polythiophene **2** before/after the thermal treatment (b) Cyclic voltammogram of the thin-film of polythiophene **2**

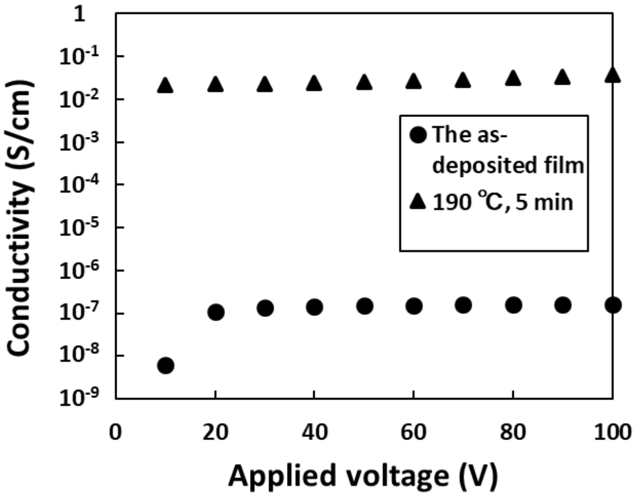


Figure 2. Conductivity of the thin-film of polythiophene **2** before/after the thermal treatment

In short, we have prepared a new class of polythiophene derivative bearing a benzenesulfonic acid at the side chain of the thiophene ring with a certain number of alkylene chains, which was prepared by the heating of the corresponding neopentyl sulfonate thus showing thermally-induced self doping without external additives. The thus doped polythiophene film showed improved conductivity, which would potentially be applied to the formation of polymer semiconductive materials.

EXPERIMENTAL

General. All of the reactions were carried out under a nitrogen atmosphere. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra were measured on a JEOL ECZ400 NMR spectrometer. 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. The IR spectra were recorded on a Bruker Alpha with an ATR attachment (Ge). High-resolution mass spectra (HRMS) were measured by a JEOL JMST100LP 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 a preparative SEC column (JAIGEL-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 eluent with Shodex KF402HQ and KF-404HQ. Molecular weights and molecular weight distributions were estimated based on the calibration curve obtained by 6 standard polystyrenes. The thickness of the thin films was measured by Bruker DEKTAK 6. UV−vis−NIR absorption spectra of the polymer films were measured with the BAS SEC-2000 UV/VIS spectrometer with SEC-2000 DH. Measurement of cyclic voltammetry was performed at 0.1 Vs^{-1} in the ALS2325 electrochemical analyzer with a three-electrode cell, Ag/AgCl as reference electrode, platinum wire as counter electrode and platinum plate as he working electrode in nitrogen-purged anhydrous 0.10 M MeCN solution of tetrabutylammonium hexafluorophosphate at room temperature. 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[10] prior to use. The Knochel−Hauser base (TMPMgCl·LiCl)[11] was purchased from Sigma-Aldrich Co. Ltd. as a 1 M THF solution. $NiCl_2(IPr)PPh_3$[8] was purchased from TCI Co. Ltd. Preparation of 3-ethynylthiophene (**3**)[6] and neopentyl (4-bromobenzene)sulfonate (**4**)[5] were carried out following the literature procedure. Other chemicals were purchased and used without further purification.

2,2-Dimethylpropan-1-yl 4-(2-(thiophen-3-yl)ethynyl-benzene)sulfonate (5): To 100 mL Schlenk tube equipped with a magnetic stirring bar were added 3-ethynylthiophene[6d] (**3**, 1.08 g 10.0 mmol), neopentyl (4-bromobenzene)sulfonate (**4**, 2.10 g, 6.8 mmol) copper(I) iodide (25 mg, 0.13 mmol), bis(triphenylphosphine)palladium(II) chloride (98 mg, 0.14 mmol) and diisopropylamine (2.9 mL, 20.4 mmol). Stirring was continued at 60 °C for 19 h under nitrogen atmosphere. After cooling to room temperature, the mixture was diluted with Et_2O and poured into water to result in phase separation. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated in vacuo. The obtained crude material was purified by column chromatography on silica gel with hexanes/CH_2Cl_2 (1/1, v/v) as an eluent to afford 1.82 g of **5** in 79% yield as a colorless solid. ^1H NMR ($CDCl_3$): δ 7.87 (d, 2H, *J* = 8.2 Hz), δ 7.66 (d, 2H, *J* = 8.2 Hz), δ 7.60 (dd, 1H, *J* = 3.2, 1.4 Hz), δ 7.34 (dd, 1H, *J* = 5.0, 3.2 Hz), δ 7.21 (dd, 1H, *J* = 5.0, 1.4 Hz), δ 3.69 (s, 2H), δ 0.91 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.1, 132.1, 130.1, 129.9, 129.2, 128.0, 126.0, 121.4, 88.8, 87.4, 80.0, 31.8, 26.1; mp 110−111 °C. IR (ATR) 3085, 2970, 2961, 2170, 2154, 1356, 1188, 1174, 1093, 956, 852, 836, 784, 676 cm^{-1}. HRMS (DART-ESI$^+$) calcd for $C_{17}H_{19}O_3S_2$: 335.0776; found *m/z* 335.0787.

2,2-Dimethylpropan-1-yl 4-(2-(thiophen-3-yl)ethyl-benzene)sulfonate (6): To a solution of **5** (2.3 g, 7.0 mmol) in EtOH (70 mL) was added palladium (10%) on carbon (745 mg, 0.70 mmol). The resulting mixture was stirred at 60 °C for 6 h under hydrogen atmosphere. The reaction mixture was filtered through a celite pad. The filtrate was concentrated under reduced pressure to give the crude material, which was purified by silica gel column chromatography (hexane/AcOMe = 10:1) to provide **6** as a colorless solid (2.2 g, 6.4 mmol, 92%). ^1H NMR ($CDCl_3$): δ 7.80 (d, 2H, *J* = 8.2 Hz), 7.32 (d, 2H, *J* = 8.2 Hz), 7.26−7.23 (m, 1H), 6.92−6.86 (m, 2H), 3.66 (s, 2H), 3.06−2.94 (m, 4H), 0.89 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 148.2, 141.0, 133.7, 129.4, 128.1, 125.8, 120.9, 79.7, 37.0, 31.8, 31.7, 26.1; mp 67−69 °C; IR

(ATR) 2962, 2956, 2944, 2907, 1357, 1189, 1176, 1098, 966, 937, 852, 783, 665 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{17}H_{22}O_3S_2$: 338.1010; found *m/z* 338.1001.

2,2-Dimethylpropan-1-yl[4-(2-(2-chlorothiophen-3-yl)ethynyl]benzenesulfonate (7): To a solution of **6** (0.17 g, 0.50 mmol) and NH_4NO_3 (2.0 mg, 0.025 mmol) in DMF (0.50 mL) was added *N*-chlorosuccinimide (0.071 g, 0.53 mmol) and stirring was continued at 60 °C for 25 h. The reaction mixture was washed with an aqueous solution of $Na_2S_2O_3$ and NH_4Cl. The aqueous layer was extracted with Et_2O 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 (hexane/AcOMe = 10:1) to provide **7** as a colorless oil (0.11 g, 0.29 mmol, 58%). ^{1}H NMR ($CDCl_3$): δ 7.79 (d, 2H, *J* = 8.2 Hz), δ 7.29 (d, 2H, *J* = 8.2 Hz), δ 7.02 (d, 1H, *J* = 5.5 Hz), δ 6.70 (d, 1H, *J* = 5.5 Hz), δ 3.64 (s, 2H), δ 3.01−2.88 (m, 4H), δ 0.89 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.6, 137.0, 133.7, 129.4, 128.1, 127.8, 125.6, 122.7, 79.7, 35.9, 31.8, 29.4, 26.1. IR (ATR) 2978, 2950, 2908, 1353, 1173, 967, 816, 678, 639 cm^{-1}. HRMS (DART - ESI$^+$) calcd for $C_{17}H_{22}{}^{35}ClO_3S_2$: 373.0699; found *m/z* 373.0696.

Poly(3-(2-(4-(2,2-dimethylpropylsulfonylbenzen)-1-yl)ethyl)thiophene-2,5-diyl) (2): To solution of **7** (112 mg, 0.30 mmol) in THF (2.6 mL) under a nitrogen atmosphere was added a 1.0 M THF solution of TMPMgCl·LiCl (0.36 mL, 0.36 mmol) at room temperature. After stirring for 3 min, $NiCl_2(PPh_3)IPr$ (2.4 mg, 3.0 μmol) was added to the resulting mixture, which was further stirred at room temperature for 3 h. Hydrochloric acid (0.1 M, 1 mL) and MeOH were added to the mixture to quench the reaction and the formed precipitate was filtered off and the residue was washed with MeOH repeatedly to leave dark purple solid, which was dried under reduced pressure to afford 613 mg of polymer **2** in 61% yield as a dark red solid. Molecular weight and the molecular weight distribution were estimated by SEC analysis to show $M_n = 36000$, $M_w/M_n = 1.93$. ^{1}H NMR ($CDCl_3$) δ 7.92 (d, 2H, *J* = 8.0 Hz), δ 7.37 (d, 2H, *J* = 8.0 Hz), δ 6.79 (s, 1H), δ 3.67 (s, 2H), δ 3.22−2.97 (m, 4H), δ 0.88 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.7 138.1 134.0 133.6 131.6 129.7 129.0 128.2 79.8 36.7 31.8 30.7 26.1. IR (ATR) 2970, 2803, 1355, 1172, 1096, 966, 830, 757, 651 cm^{-1}.

Formation of the thin film of 2: Polythiophene **2** (2.2 mg) was dissolved in 1 mL of $CHCl_3$ and the solution was cast on a quartz plate and exposed in a vapor of $CHCl_3$. The formed film was dried 80 °C for 1 h to show 137 nm of its thickness and subjected to the measurement of conductivity as deposited. The measurement of the conductivity of the thermolyzed film was performed after the treatment of the film on a hot plate at 190 °C for 5 min.

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