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Synthesis and properties of polythiophene bearing an alkylsulfonic acid ester at the side chain

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Introduction of an alkylsulfonic acid moiety into the side chain of polythiophene was carried out. Synthesis of 2,5-dihalothiophene bearing an alkylsulfonate group at the 3-position was performed. The reaction of 2-chloro-5-iodothiophene with a Grignard reagent to form organometallic monomer of the corresponding thiophene followed by nickel(II)-catalyzed cross-coupling polymerization lead to head-to-tail-type regioregular polythiophene. The ester group at the side chain was converted into alkali metal sulfonate by treatment with NaI or metal hydroxides (Li, Na, K). The obtained metal salts were successfully transformed to sulfonic acid by the treatment with ion exchange resin. The electric conductivity of the regioregular polythiophene bearing sulfonic acid was remarkably improved ca. 10^2 times from the corresponding metal salts. (10^6 times higher than sulfonate ester)

Introduction

Polythiophenes have attracted much attention as advanced materials showing a variety of optoelectronic performances such as electronic conductivity, semi-conductivity, application to solar cells, etc.[1–3] In particular, poly-3-substituted alkyl thiophenes (P3RT) which regioregularity is controlled as a head-to-tail (HT) manner are shown to exhibit superior performances as materials[4] and synthetic methodology to prepare such regioregularity efficiently has been extensively developed to date.[5–9] We have also been engaged in the development of effective and practical synthesis of regioregular polythiophene by a deprotonative metalation with 2-halo-3-substituted thiophene and thus metalated thiophene has been employed for the nickel-catalyzed cross-coupling polymerization.[10–13] In addition to the study on the preparative synthetic methodology, design of the side-chain structure of polythiophene (side-chain functionalization) is also a significant issue for the development of advanced materials. We have shown that the modification of the side chain suggests an additional functionality of polythiophene.[14] (Chart 1) We have reported, for example, that the introduction of an oligosiloxane moiety remarkably improved the solubility of polythiophene (**A**) in a hydrocarbon solvent.[15–17] We have recently revealed that polythiophene bearing benzene sulfonic acid 2,2-dimethylpropyl ester is successfully synthesized by nickel-catalyzed cross-coupling polymerization and the thin film of thus obtained polymer expresses thermally-induced self-doping by leading to polymer (**B**) only by heating without use of any additional additives.[18–20] Although the self-doping brought about the electric conductivity of polythiophene, its performance was lower than that of existing HT-P3RT probably because of the steric bulkiness of the benzene ring[21,22] Accordingly, we considered that further design of the side-chain structure of benzene sulfonate at the polythiophene and envisaged to switch benzene sulfonate to alkyl sulfonate shown as **C**, which would suggest less steric bulkiness. Herein, we wish to report that regioregular HT-type polythiophene bearing alkylsulfonate at the side chain is successfully synthesized by the GRIM (Grignard metathesis)-type polymerization.[23] The obtained polythiophene is shown to be transformed into metal sulfonate, which is further transformed into the corresponding sulfonic acid by the treatment with ion exchange resin. The thin film of the obtained polythiophene is also subjected to measurement of properties as materials.

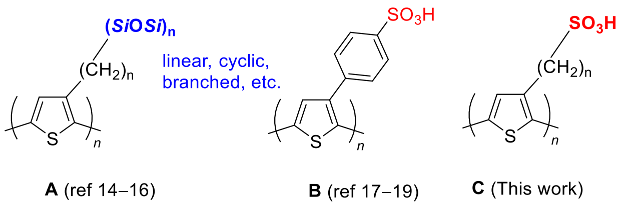

Chart 1. Polythiophene derivatives bearing a functional group at the side chain

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Results and discussion

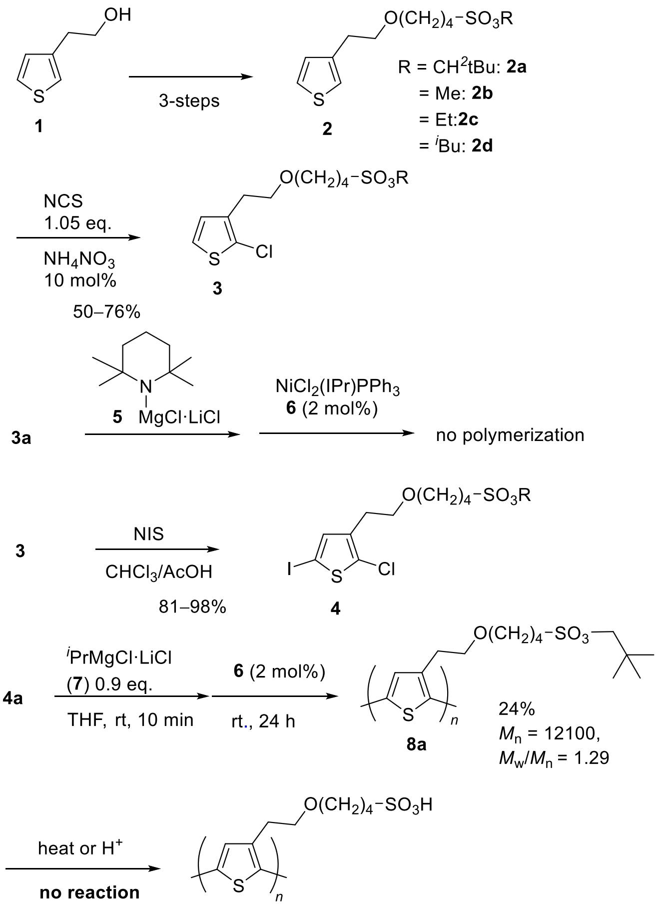
Preparation of the thiophene monomer was carried out as outlined in Scheme 1 from thiophene-3-ethanol (**1**) in three steps by following literature procedures[18,24] leading to thiophene bearing 2,2-dimethylpropyl alkylsulfonate side chain at the 3-position **2a**. Other sulfonate derivatives **2b**–**2d** were also synthesized in a similar manner. The obtained thiophene was then subjected to chlorination at the 2-position with N-chlorosuccinimide (NCS) to give **3a**–**3d** in 50–76% yield.

We first attempted the polymerization of **3a** by the deprotonative metalation with magnesium amide TMPMgCl·LiCl (**5**) (TMP: 2,2,6,6-tetramethylpiperidin-1-yl).[25] However, following addition of 2 mol% of nickel catalyst $NiCl_2(PPh_3)(IPr)$ (**6**: IPr = 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene)[26,27] hardly induced polymerization only to afford unidentified oligomers.

Then, we envisaged the further halogenation of **3** at the 5-position with N-iodosuccinimide (NIS). Dihalothiophenes **4a**–**4d** were obtained in good yields (81–98%). (details: See Supporting Information) We examined the reaction of chloro(iodo)thiophene **4a** with Grignard reagent ^{i}PrMgCl・LiCl[6] (**7**) at room temperature for 10 min followed by the addition of nickel catalyst **6** (2 mol%) initiated the polymerization.[28] Polythiophene **8a** was obtained in 24% yield after stirring at room temperature for 24 h with average molecular weight M_n = 12100 and the molecular weight distribution M_w/M_n = 1.29.[6]

Since polythiophene bearing alkylsulfonate at the side chain was in hand, transformation of sulfonate **8a** was examined in a manner to our previous report[18] with benzenesulfonate **B** by heating or acidic treatment. However, no desired reaction was found to take place at all. (Scheme 1) Thermogravimetric analysis of **8a** showed the mass loss of 52% at >200 °C suggesting that elimination of SO_3R group took place (See Supporting Information).

Next, we examined the use of other sulfonic acid esters. Chloro(iodo)thiophenes **4b**–**4d** were subjected to the polymerization by the reaction with a Grignard reagent followed by the addition of nickel(II) catalyst **6**. Table 1 summarizes the results of the polymerization. Dihalothiophene **4b** bearing methyl sulfonate was first attempted by the reaction with EtMgCl at room temperature for 10 min under similar conditions to that of **4a**. The addition of nickel catalyst **6** (2 mol%) and continuous stirring at room temperature for further 24 h resulted in the formation of water-soluble light orange material accompanied by the formation of polymer soluble in THF after the reaction was quenched with hydrochloric acid. The result suggested that partial hydrolysis of sulfonic acid methyl ester took place under basic conditions during the polymerization leading to the corresponding sulfonate salt of magnesium. Halogen–metal exchange reaction of ethyl sulfonate **4c** was then examined with EtMgCl. Following addition of nickel catalyst **6** (2 mol%) and stirring at room temperature for 24 h afforded polythiophene **8c** in 59% yield. The reaction with isobutyl ester **4d** also proceeded under similar conditions to afford **8d** in 53% yield. The molecular weight of polythiophene **8c** and **8d** was measured by SEC analysis to reveal M_n = 9100 and 7800 (M_w/M_n = 1.28 and 1.45), respectively, which were found to be smaller than those of the theoretical value (M =14500 and 15900, respectively) based on the ratio of monomer feed/catalyst loading. Polymerization at higher temperature (60 °C) was also examined with **4c**, however, it was found that little polymer **8c** was obtained. When the reaction of **8c** was quenched with hydrochloric acid, the obtained product was dissolved in water. On the other hand, lowering the polymerization temperature to 0 °C improved the yield of **8c** and **8d** in 86% and 71% yields, respectively, with M_n = 7500–8400 (M_w/M_n = 1.28). However, the reaction of methyl ester **4b** at 0 ° C did not improve the result. The reaction of **4c** at further lower temperature (–20 °C) resulted in no reaction. When the polymerization of **4d** was terminated at further shorter reaction period, polymer **8d** was obtained in a comparable yield (53%) with similar molecular weight and the molecular weight distribution.

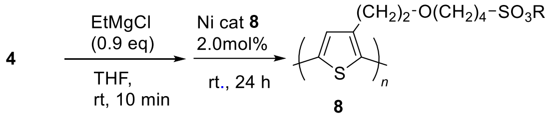


Scheme 1. Preparation of halothiophene derivatives and polymerization of the obtained halothiophenes

On the based of the above studies, we consider that the reaction of chloro(iodo)thiophene bearing alkylbenzene sulfonate at the side chain **4** proceeds in a manner to that of the related alkylthiophene such as 2,5-dihalo-3-alkylthiophene, which are shown to take place in a catalyst-transfer manner.[28] The reaction of poly(alkylthiophene) therefore shows linear relationship with the ratio of monomer feed and the catalyst loading and thus, the obtained polymer indicates narrow molecular weight distribution, which is the typical characteristics for living polymerization.[4,5] Although the reaction of **4** would proceed similarly in a catalyst-transfer manner considering the structural similarity of the thiophene ring, the obtained polymer **8** involves problems in an insufficient chemical yield and the difference of M_n from the theoretical molecular weight particularly in the reaction at an elevated temperature and the use of sterically less bulky R group at the sulfonate moiety (**4b**). We consider that the reaction proceeds partly in a catalyst-transfer manner to undergo living-like polymerization albeit not perfect. However, problematic side reaction at the sulfonate ester with an organomagnesium species competes with the desired polymerization. The subsequent formation magnesium sulfate would lower the solubility of polythiophene to result in the termination of the nickel-catalyzed propagation. Considering that the polymerization reaction of **4c** and **4d** at 0 °C afforded the corresponding polymer **8c** and **8d** in a reasonable yield with high molecular weight, the obtained polymers can be available for further transformation reactions directed to studies on polymer properties as electronic materials.

Concerning the regioregularity of **8** cross-coupling polymerization of halothiophenes bearing alkyl side chain proceeds in a regiocontrolled manner regardless of chain growth or step growth mechanism. The polymerization of chloro(iodo)thiophene **4** would also proceed in a regioregular manner albeit insufficient catalyst-transfer polymerization whereas quantitative analysis of the regioregularity by ^{1}H NMR is difficult by the overlapping of other signals.

Table 1. Polymerization of chloro(iodo)thiophene with nickel(II) catalyst

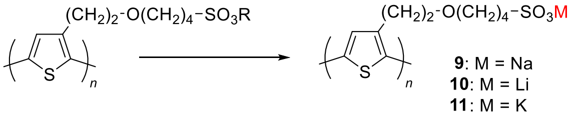


monomer	R	temp (°C)	time (h)	yield (%)	M_n	M_w/M_n
4b	Me	rt	24	–	–	–
	Me	0	24			
4c	Et	rt	24	59	9100	1.28
4c	Et	60	24	–	–	–
4c	Et	0	24	86	7500	1.28
4c	Et	–20	24	–	–	–
4d	^{i}Bu	rt	24	46	7800	1.45
4d	^{i}Bu	rt	3	53	8100	1.22
4d	^{i}Bu	0	24	71	8400	1.28

[a] The reaction was carried out as shown the equation shown above with 0.1 mmol of chloro(iodo)thiophene **10** in 1.0 mL of THF under an argon atmosphere. [b] Isolated yield. [c] The number average molecular weight (M_n) and the weight average molecular weight (M_w) were measured by SEC analysis based on 8 polystyrene standards.

We next studied the transformation of the obtained polymers **8** bearing sulfonic acid esters. Neither acidic nor thermal hydrolysis to sulfonic acid took place similar to the case of 2,2-dimethylpropyl ester **8a**. However, polythiophene **8** was found to be transformed into the sodium salt of sulfonic acid **9** by the reaction with sodium iodide. When **8c** was treated with NaI in DMSO, precipitation formed after stirring at 80 °C for 6 h suggesting that the removal of the ester group occurred. (87% yield) The reaction of isobutyl ester **8d** also proceeded in a similar manner to afford **9** in 56% yield, while the use of 2,2-dimethylpropyl ester **8a** resulted in no reaction under similar conditions. We next examined the transformation into the related lithium and potassium salts **10** and **11**, respectively, in a similar manner. However, the related reaction with LiI or KI did not proceed with recovery of the starting material. The reactions leading to the alkaline metal salt **10** and **11** were found to occur when the reaction was carried out with LiOH or KOH. The reaction with lithium hydroxide in ethanol at 78 °C afforded lithium salt **10** in 85% yield and the formation of the corresponding potassium salt **11** proceeded with KOH under similar conditions (95% yield). The use of NaOH to give sodium salt **9** was also successful in a similar manner (96% yield). The reaction of isobutyl ester **8d** with LiOH afforded lithium salt **10** in 75%. These results are summarized in Table 2.

Table 2. Transformation of sulfonate esters into the metal salts[a]



11	R	reagent	solv	conditions temp, time	product	yield (%)
8c	Et	NaI	DMSO	80 °C, 6 h	**9**	87
8d	^{i}Bu	NaI	DMSO	80 °C, 6 h	**9**	56
8a	$CH_2{}^tBu$	NaI	DMSO	80 °C, 6 h		0
8c	Et	LiBr	DMSO	80 °C, 6 h		0
8c	Et	LiI	DMSO	80 °C, 6 h		0
8c	Et	LiOH	EtOH	78 °C, 6 h	**10**	85
8c	Et	NaOH	EtOH	78 °C, 6 h	**9**	96
8c	Et	KOH	EtOH	78 °C, 6 h	**11**	95
8d	^{i}Bu	LiOH	EtOH	78 °C, 6 h	**10**	75

[a] The reaction was carried out with 0.1 mmol of polymer **8** with 0.15 mmol of alkali metal halide (alkoxide) in 1.0 mL of DMSO. [b] Isolated yield.

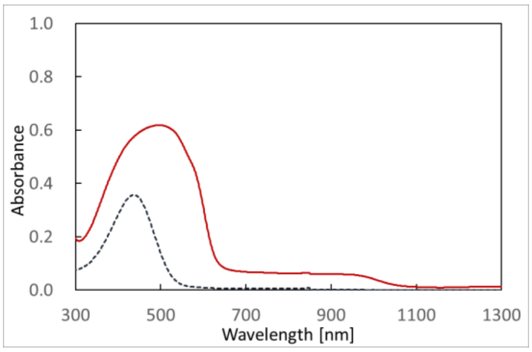
The obtained sodium salt **9** was found to be soluble in water, while hardly dissolved in any of organic solvents such as chloroform, THF, and DMSO. Although **9** was soluble in methanol, the solubility in ethanol was found to be significantly lower. The results markedly contrast with excellent solubilities of polythiophene sulfonate esters **8** in a variety of organic solvents. The related lithium and potassium salts **10** and **11**, respectively, were also subjected to the solubility test to reveal similar behaviors with sodium salt **9**.

Figure 1a shows the UV–vis–NIR spectra of polythiophene bearing sulfonate **8** and sodium salt **9** in a solution. The sulfonate ester **8c** (M_n = 7500) showed λ_{max} = 437 nm and the aqueous solution of **9** indicated λ_{max} = 498 nm. A remarkable red-shift of ca. 61 nm was observed by the transformation of the ester to the corresponding sulfonic acid metal salt. Figure 1b compares absorption spectra of polythiophene of lithium salt **10** and potassium salt **11**. The results suggest little difference depending on the metal species.

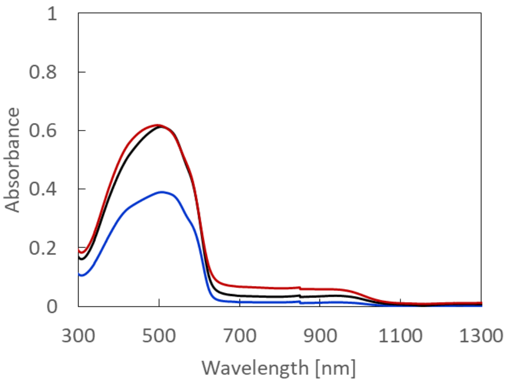
We next carried out the transformation of lithium salt **10** to sulfonic acid **12** by the treatment of the metal salt with ion-exchange resin. Amberlite IR120B H was added to an aqueous solution of **10** (lithium salt) and subjected to the measurement of absorption spectrum. It was revealed to find increased absorbance at the NIR region as shown in Figure 1(c). As the increment of the treatment period, stronger absorption at >700 nm was observed. After treatment of the solution for 2 h, the strongest absorption at the NIR region was found in **12**.

These results on the measurements of UV-vis-nir spectra suggest that planarity of polythiophene main chain is improved after the transformation of sulfonate ester **8** to the metal salts of sulfonic acid (**9**, **10**, **11**) by the observation of the red-shift of λ_{max}. However, a less remarkable absorption was found in the nir region in **9**. The result suggests that little doping of the polythiophene main chain takes place in the transformation to a metal salt partly because of the relief of steric congestion through the removal of the alkyl moiety of sulfonate. Doping of the polythiophene main chain can be found after the ion exchange leading to sulfonic acid, which facilitates the formation of the quinoid structure of polythiophene as observed in the characteristic absorption at 1500–1600 cm^{-1} (Figure 1d).[29,30]

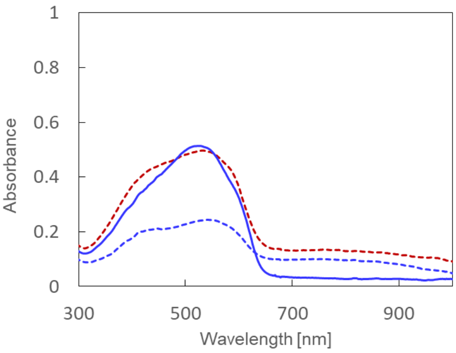
(a)



(b)



(c)



(d)

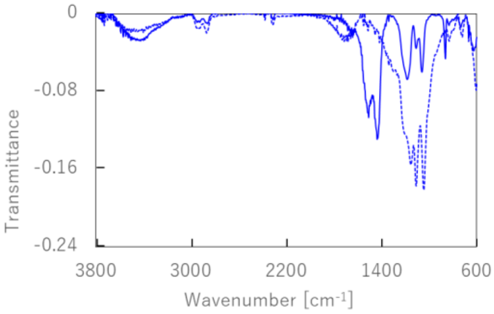


Fig 1. Spectroscopic characterization of polythiophene bearing sulfonic acid ester **8** and the corresponding metal salt **9**–**11**. (a) UV–vis–NIR absorption spectra of **8** in chloroform (ca. 1.0 x 10^{-2} M, dotted black) and aqueous solution of **9** (ca. 1.0 x 10^{-2} M, red) (b) UV–vis–NIR absorption spectra of **9** (red), **10** (blue), and **11** (black) in an aqueous solution (ca. 1.0 x 10^{-2} M) (c) UV–vis–NIR absorption spectra of **10** (blue) and, **12** as an aqueous solution (ca. 1.0 x 10^{-2} M) after treatment of ion exchange resin for 5 min (dotted blue) and 2 h (dotted red) (d) IR (ATR) spectrum of **10** (blue) and **12** (dotted blue) Preparation of 2,5-dihalothiophene bearing alkyl sulfonate group at the side chain **9**

The measurements of electric conductivity of the polymer thin film of polythiophene bearing sulfonate group at the side chain were performed on a glass substrate. Table 3 summarizes the results. Polythiophene bearing alkyl sulfonate **8c** showed rather low conductivity (>10^8 Scm^{-1}) suggesting mostly insulative. After treatment with NaI leading to the corresponding sodium salt **9**, remarkable improvement of the conductivity was not observed (2.21 x 10^{-4} Scm^{-1}) and little difference was observed also in lithium and potassium salts (**10** and **11**, respectively). These results showed that the removal of the sulfonic acid ester moiety to the corresponding alkaline metal salt (Li, Na, K) improved the conductivity of the polymer slightly higher. However, remarkable improvement of the conductivity was achieved by the transformation into the corresponding sulfonic acid. Further higher conductivities was observed in polythiophene **12** (SO_3H). Indeed, the conductivity of **12** indicated 5.03–6.69 x 10^{-2} Scm^{-1}. The result supports the self-doping by the formation of sulfonic acid, which protonated the thiophene ring and thus formed delocalized cation further extended π-conjugation. The electric conductivity of polythiophene bearing alkyl sulfonic acid at the side chain was found to show a higher conductivity than that with benzenesulfonic acid moiety **B**. When the measurement of the conductivity of **12'** was carried out under similar conditions, **B** (M_n = 27500, M_w/M_n =1.23) indicated 1.58 x 10^{-3} Scm^{-1}. The result showed that the conductivity was improved by switching the side chain structure from aromatic to a certain number of alkylene side chain. The electric conductivity of **12** was also compared with that of related non-regioregular polythiophene **12'**, which was synthesized by oxidative polymerization employing Fe^{3+} as an oxidant. The measurement of the conductivity of **12'** under similar conditions showed 5.14 x 10^{-4} Scm^{-1}, which was remarkably lower than that of regioregular **12**. These results suggest that polythiophene formed by nickel-catalyzed cross coupling affording the regioregular polymer gives superior extended π-conjugation to the related non-regioregular one as well as polymerization catalyzed by nickel brings about higher degree of polymerization than that by oxidative polymerization mediated by Fe^{3+}.

Table 3. Electric conductivity of polythiophenes **8**, **9**–**12**, **B**, and **12'**[a]

polythiophene	end group	resistance R (Ω)	thickness d (μm)	conductivity, (Scm^{-1})
8c	SO_3Et	>10^8	–	–
9	SO_3Na	1.81 x 10^7	2.5	2.21 x 10^{-4}
10	SO_3Li	3.50 x 10^7	2.0	2.50 x 10^{-4}
11	SO_3K	2.79 x 10^7	2.8	1.28 x 10^{-4}
12[b]	SO_3H	3.31 x 10^5	0.6	5.03 x 10^{-2}
12[c]	SO_3H	1.15 x 10^5	1.3	6.69 x 10^{-2}
B	$C_6H_4SO_3H$	1.57 x 10^6	0.5	1.27 x 10^{-2}
12'[c]	SO_3H	1.68 x 10^5	16.6	5.14 x 10^{-4}

[a] Measurement was performed with a polymer film cast on a glass plate by four-point probe method. [b] After the treatment of the polymer solution with ion exchange resin for 5 min, [c] After the treatment of the polymer solution with ion exchange resin for 2 h.

Conclusions

In conclusion, we have shown the synthesis of head-to-tail-type regioregular polythiophene bearing alkylsulfonic acid derivatives at the side chain. Polythiophenes bearing a related side chain have only been synthesized by oxidation polymerization protocol. Preparation of the regioregular polythiophene was achieved by the GRIM-type cross coupling polymerization for the first time. It was also shown that the polymer bearing sulfonate of Group 1 metals **9**–**11** was synthesized through the transformation of the sulfonate ester **8** and that such metal salts were transformed into the corresponding sulfonic acid by the treatment of the metal salt with ion exchange resin. Measurements of electric conductivities revealed that a slight improvement of the conductivity was observed after the transformation to sulfonic acid metal salts. Additional transformation to sulfonic acid **12** showed further higher conductivity, which was much higher than that of an existing non-regioregular one **12'** that was synthesized by oxidative polymerization[21,31,32] as well as previously reported benzene sulfonic acid derivative **B**[18] under similar conditions. The obtained metal salts would be potentially ion conductive and therefore allows dual ionic and electric conductivities by switching the structure of polymer side chain. The findings would lead to a new class of functionality design.

Author Contributions

A. M. conceived the ideas and designed the project. A. K., S. Y., Y. S., and K. O. performed synthetic experimental studies. A. K., M. Y., and M. F. performed measurements of electronic studies. A. K. and M. H. performed spectroscopic measurements. A. M. wrote the manuscript with contributions from all authors.

Conflicts of interest

There are no conflicts to declare.

Data availability

Detailed reaction scheme for the preparation of thiophene monomer **4**, experimental procedures, additional thermal and spectroscopic analyses, copies of NMR spectra, and references can be found in ESI.

Acknowledgements

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