Studies on the Properties of Poly(3-alkylthiophene) Copolymerized by a Small Amount of Thiophene Derivative Bearing a Cyclic Siloxane Moiety at the Side Chain

Kubota, Chihiro ; Kashimoto, Masaki ; Yamashita, Ryutaro ; Okano, Kentaro ; Horie, Masaki ; Funahashi, Masahiro ; Matsumoto, Takuya ;…

(Citation)
Bulletin of the Chemical Society of Japan,95(6):882-888

(Issue Date)
2022-06

(Resource Type)
journal article

(Version)
Accepted Manuscript

(URL)
https://hdl.handle.net/20.500.14094/90009572

Studies on the properties of poly(3-alkylthiophene) copolymerized by a small amount of thiophene derivative bearing a cyclic siloxane moiety at the side chain

Chihiro Kubota,[1] Masaki Kashimoto,[1] Ryutaro Yamashita,[1] Kentaro Okano,[1] Masaki Horie,[2] Masahiro Funahashi,[3] Takuya Matsumoto,[1] Takashi Nishino,*[1] and Atsunori Mori*[1,4]

[1] Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan

[2] Department of Chemical Engineering, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Road, Hsinchu 30013, Taiwan

[3] Department of Advanced Materials Science, Kagawa University, 2217-20 Hayashi-cho, Takamatsu, Kagawa 761-0396, Japan

[4] Research Center for Membrane and Film Technology, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan

E-mail: amori@kobe-u.ac.jp, tnishino@kobe-u.ac.jp

Atsunori Mori
Atsunori Mori received Ph. D. from Nagoya University in 1987 under the supervision of Professor Hisashi Yamamoto. After postdoctoral work at University of California Berkeley with Professor K. Peter C. Vollhardt. He started his academic career at The University of Tokyo in 1988. After he was engaged in researches at JAIST (1993-1995), Tokyo Institute of Technology (1995-2005), he has been a Professor of Kobe University since 2005. His research interest covers synthetic organic chemistry, polymer synthesis, and materials science.

Takashi Nishino
Takashi Nishino received Ph. D. from Kobe University in 1991 under the supervision of Professor Katsuhiko Nakamae. He started his academic career at Kobe University in 1985, then postdoctoral work at Eindhoven University of Technology with Professor P. J. Lemstra. He has been a Professor of Kobe University since 2004. His research interest covers structure vs. properties relationship of polymers and composites.

Abstract

Thiophene–thiophene copolymers composed of 3-alkylthiophene and a small amount of thiophene bearing cyclic siloxane are synthesized by random copolymerizatin of 2-chloro-3-dodecylthiophene and 2-chlorothiophene bearing cyclic tetrasiloxane as a substituent. Deprotonative metalation of chlorothiophenes with a bulky magnesium amide followed by the addition of nickel catalyst undergoes polymerization to afford statistical copolymer based on the feed ratio. The copolymer bearing a small amount of (1–10%) cyclic siloxane is subjected to the formation of thin film. The treatment of the obtained thin film with an acid vapor results in the formation of the film insoluble in any of solvent through the formal networking of poly(3-dodecylthiophene) by the effect of a small amount of cyclic siloxane moiety. The measurement of electric properties reveals to exhibit improved conductivities to 10^6 times higher before and after the acid treatment.

o

Keywords: poly(3-alkylthiophene), statistical copolymer, cyclic siloxane.

1. Introduction

The synthesis of organic electronic materials based on conjugated polymers is major of our concern in the field of materials science.[1–3] Highly regioregular polythiophenes bearing an alkyl substituent at the side chain attracts much attention as organic materials with high performance and are the subject of extensive research. [2,4–10] We have found that nickel-catalyzed polythiophene synthesis using deprotonative metalation is useful for the synthesis of polythiophenes. [11–13] Polythiophenes bearing an alkyl substituent, which are, in general, moderately soluble in organic solvents allowed the formation of thin film on a substrate, and thus indicated remarkable electronic conductivity.[2,4–9] However, the alkyl substituent in the polythiophene is inert to transformation reactions. Introduction of a functional group into poly(alkylthiophene)s directed to reveal additional functionality through a transformation reaction has been considered incapable because of difficulties in a chemical reaction at the alkyl side chain itself.

We have been engaged in researches to synthesize and design polythiophene derivatives with a variety of functional groups at the side chain and showed that several polymers thus modified indicated potential characteristics as materials. [14–18] Recently, we have reported that polythiophene, which has a cyclic siloxane structure on the side chain of the thiophene ring, is well soluble in hydrocarbon solvents such as hexane, and when the resulting polythiophene thin film is treated with acid vapor, a network structure is formed by ring opening of the cyclic siloxane. [19] The obtained thin films changed to insoluble in any organic solvents by ring-opening of the cyclic siloxane moiety, and at the same time was induced acid doping to the main chain of polythiophene, which dramatically improved the conductivity before and after acid treatment. However, a low electronic conductivity compared with simple poly(alkylthiophene) has been a major drawback in the functionalized polythiophenes caused by the limited extension of π-conjugation because of its bulkiness of the side-chain structure. It is therefore intriguing to achieve formal modification of poly(3-alkylthiophene) that allows, for example, the formation of a network by cross linking.

In the course of our ongoing research, we became interested in the copolymerization of thiophene monomers with cyclic siloxane structures and alkyl-substituted thiophenes at the 3-position. If we could introduce only a small amount of cyclic siloxane moiety into the backbone of poly(3-alkylthiophene), we expected that a new performance could be introduced into the formal alkylated polythiophene, which originally cannot form a network. The network structure of cross-linked siloxanes is known to exhibit rubber elasticity due to the flexibility of the Si–O–Si framework. [20–25] If this property is utilized, it will be possible to introduce molding processability into the conductive but rigid structure of polythiophene, and new physical properties can be expected. [26,27] We report herein the copolymerization of thiophene with an alkyl group substituted at the 3-position and that of a small amount of cyclic siloxane structure to afford a statistical copolymer of the two. The resulting thin film of copolymers induces ring opening of cyclic siloxane at the side chain by acidic treatment and the copolymer changes to be insoluble in any of organic solvents through the formation of cross linking despite by the effect of only a small amount of the cyclic siloxane moiety. At the same time, doping of the polythiophene main chain occurs under the acidic condition resulting in improved electrical conductivity of the copolymer.

2. Experimental

General. Manipulations for polythiophene synthesis were carried out in a glove box or with the standard Schlenk technique under an inert gas atmosphere (nitrogen or argon). Measurements of ^{1}H (400 MHz) and ^{13}C{^{1}H} (100 MHz) NMR spectra were performed with JEOL ECZ 400 as a $CDCl_3$ solution. The chemical shift was expressed in ppm using $CHCl_3$ = 7.26 (for ^{1}H) and $CDCl_3$ = 77.2 (for ^{13}C{^{1}H}) as internal standards). High resolution mass spectra (HRMS) were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. IR spectra were recorded on Bruker Alpha with an ATR attachment (Ge). 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-405LHQ. Molecular weights and molecular weight distributions were estimated on the basis of the calibration curve obtained by 6 standard polystyrenes. UV–vis–nir spectra (as a thin film) were measured with Shimadzu UV-3101PC. XRD analysis was carried out with Rigaku SmartLab with the power of 40 kV, 30 mA, and the wavelength of 1.5418 Å (CuKα). The incidence angle α of the X-ray beam was 0.20°. The XRD measurements were performed with the out-of-plane geometry. Conductivity of polymer films were measured with a digital electrometer ADCMT8340A. Differential scanning calorimetry (DSC) profiles were recorded on a Rigaku DSC8230 with a scan rate of 10 °C/min under dried nitrogen.

Materials. THF employed as a solvent for polythiophene synthesis was purchased from Kanto Chemicals Co. Ltd. as an anhydrous grade and passed through alumina and copper columns (Nikko Hansen & Co. Ltd.) prior to use or alternatively distilled from sodium dispersion/benzophenone[28] prior to use. TMPMgCl·LiCl (2,2,6,6-tetramethylpiperidine-1-yl chloromagnesium lithium chloride salt: **3**, Knochel−Hauser base) was purchased from Sigma-Aldrich Co. Ltd. as a 1 M THF solution and stored in a glove box. Nickel catalyst $NiCl_2(IPr)PPh_3$ (IPr: 1,3-bis(2,6-diisopropylphenyl)imidazolin-1-yl, **4**) was purchased from TCI Co. Ltd. and employed as a catalyst for the polymerization as received. Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex was purchased from Sigma-Aldrich Co. Ltd. as a xylene solution (~2%Pt) and directly used as received. Preparation of 2-chloro-3-dodecylthiophene (**1**) by the chlorination of 3-dodecylthiophene with *N*-chlorosuccinimide and following polymerization of **1** to afford poly(3-dodecylthiophen-2,5-diyl) (**11**) were performed in a manner as we reported previously. [29] Chlorothiophene **2a** bearing a cyclic siloxane moiety was prepared from commercially available 3-bromo-2-chlorothiophene. Polythiophene bearing cyclic siloxane with C4 alkylene unit **6b** was prepared in a manner as described previously.[19]

Synthesis of 3-allyl-2-chlorothiophene (5)[30]: To a solution of 3-bromo-2-chlorothiophene (0.53 mL, 5.0 mmol) in THF (0.75 mL) and hexane (7.5 mL) was added ethylmagnesium chloride (5.0 mL, 1.0 M THF solution) at 25 °C. After further addition of THF (0.75 mL) and hexane (2.5 mL) stirring of the resulting mixture was continued at 25 °C for 14 h, addition of allyl bromide (1.2 mL, 10 mmol) followed. Further stirring was continued at 25 °C for 1 h and the mixture was poured into hydrochloric acid and diethyl ether. The aqueous phase was extracted twice with diethyl ether and the combined organic layer was dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left a crude oil, which was purified by column chromatography on silica gel using hexanes as an eluent. The fraction containing the product was concentrated under reduced pressure carefully to afford **5** containing a small amount of hexanes and 3-bromo-2-chlorothiophene, which was directly used for the following reaction.

Synthesis of 3-(3-(1,3,3,5,5,7,7-heptamethyltetrasiloxan-1-yl)-propan-1-yl)-2-chlorothiophene (2a): To a crude mixture of **5** (0.32 g, 2.0 mmol) and hexanes and 1,3,3,5,5,7,7-heptamethyl-tetrasiloxane (**7**, 0.65 mL, 2.2 mmol) was added platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (~2%Pt) as a solution of xylenes. The mixture was heated at 60 °C for 15 h to initiate the reaction. After the reaction was confirmed to complete by ^{1}H NMR analysis by taking aliquot of the mixture, the reaction mixture was subjected to column chromatography on silica gel and thereafter further purified by preparative SEC to afford **2a** (0.62 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (d, J = 6.0 Hz, 1H), 6.79 (d, J = 6.0 Hz, 1H), 2.59 (t, J = 7.8 Hz, 2H), 1.65 (quint, J = 7.8 Hz, 2H), 0.54–0.61 (m, 2H), 0.08–0.09 (brs, 15H), 0.07–0.08 (brs, 6H) ; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.1, 128.1, 124.8, 122.1, 31.3, 23.3, 17.0, 0.95x2, 0.92x5, –0.58; IR (ATR): 2963, 2938, 2864, 1557, 1412, 1260, 1220, 1064, 805, 698, 636 cm^{-1}. HRMS (DART−ESI$^+$) *m*/*z*: calcd for $C_{14}H_{30}{}^{37}ClO_4SSi_4$, 443.0601; found, 443.0611.

Preparation of poly(3-(1,2,2,5,5,7,7-heptamethyltetrasiloxan-1-yl)propan-1-yl)thiophen-2,5-diyl) (6a): Synthesis of **6a** was performed in a similar manner as reported previously with **2a** (136 mg, 0.31 mmol) to afford 77 mg of **6a** (61%).[19] SEC analysis using chloroform as an eluent showed M_n = 29000; M_w/M_n = 1.42. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.97 (s, 1H), 2.71–2.91 (br, 2H), 1.65–1.85 (br, 2H) 0.59–0.63 (m, 2H), 0.09 (br, 3H), 0.08 (br, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ): 139.7, 133.8, 130.9, 128.8, 32.9, 31.0, 24.3, 17.4, 1.12x2, 0.96x4, 0.91, –0.5; IR (ATR): 2962, 2931, 2866, 1564, 1446, 1411, 1260, 1066, 804, 696 cm^{-1}.

General procedure for the copolymerization of 2-chloro-3-dodecylthiophene (1) and 2-chlorothiophene bearing a cyclic siloxane at the alkyl side chain (2a): To a 20 mL Schlenk tube equipped with a magnetic stirring bar were dissolved chlorothiophenes **1** and **2a** in 5.6 mL of THF. To the resulting solution TMPMgCl·LiCl (**3**, 0.68 mL, 0.68 mmol) was added dropwise and stirring was continued for 1 h. $NiCl_2(IPr)PPh_3$ (**4**, 4.0 mg, 0.0051 mmol) was added to the mixture and initiation of the polymerization was confirmed by the color change of the solution to bright orange. After stirring at room temperature for 1 h, 0.68 mL of 1.0 M hydrochloric acid and 10 mL of methanol were added to form dark purple precipitates, which was filtered off. The residue was washed with methanol and acetone repeatedly to afford the statistical copolymer poly[(3-(4-(1,3,3,5,5,7,7-heptamethyltetrasiloxan-1-yl)propen-1-yl)thiophene-2,5-diyl)-*stat*-(3-dodecylthiophene-2,5-diyl)] (**8**). The molecular weight was measured by SEC analysis and the incorporated ratio of **1**:**2a** was estimated by ^1H NMR analysis based on the signals of methylene protons adjacent to the thiophene rings.

Copolymer 8 with 1 (160 mg, 0.56 mmol) and 2a (2.7 mg, 0.006 mmol): Yield 140 mg (80%). $M_n = 46000$, $M_w/M_n = 1.21$ ($m : n = 1 : 0.01$). ^1H NMR (400 MHz, $CDCl_3$): δ 6.98 (s, 1H), 2.70–2.90 (m, 2H), 1.62–1.78 (br, 2H), 1.10–1.48 (m, 18H), 0.87 (t, $J = 6.8$ Hz, 3H), 0.67–0.74 (m, 0.02H), 0.07 (s, 3H), 0.00 (s, 18H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.0, 133.8, 130.6, 128.7, 32.1, 30.7, 29.9 x3, 29.8x3, 29.7, 29.6, 29.5, 22.9, 14.3. IR (ATR) 2957, 2922, 2852, 1466, 1261, 1092, 1022, 802, 721, 658 cm^{-1}.

Copolymer 9 with 1 (0.33 mmol) and 2a (1/2a = 20): Yield 90 mg (58%); $M_n = 41000$, $M_w/M_n = 1.30$ ($m : n = 1 : 0.04$). ^1H NMR (400 MHz, $CDCl_3$): δ 6.98 (s, 1H), 2.71–2.89 (br, 2H), 2.50–2.65 (br, 0.07H), 1.62–1.90 (br, 2H), 1.01–1.49 (m, 18H), 0.87 (br, 3H), 0.64–0.73 (m, 0.08H), 0.09 (s, 3H), 0.00 (s, 18H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.0, 133.8, 130.6, 128.7, 32.0, 30.7, 29.9 x3, 29.8x3, 29.7, 29.6, 29.5, 22.8, 14.2, 0.9 x7. IR (ATR) 2919, 2906, 2851, 1556, 1459, 1148, 1133, 855, 721, 668 cm^{-1}.

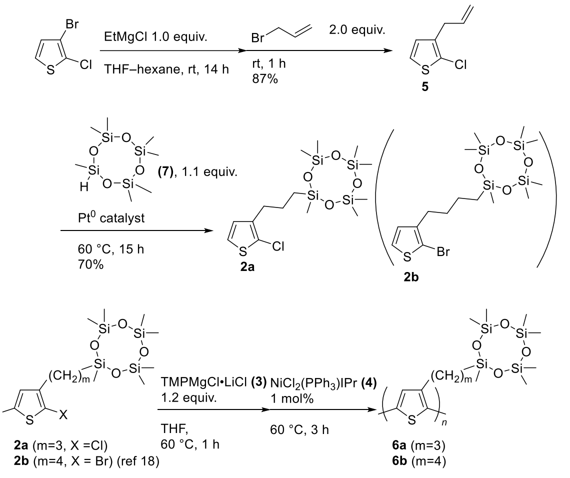
Copolymer 10 with 1 (0.29 mmol) and 2a (1/2a = 10): Yield 59 mg (69%); M_n =42000; $M_w/M_n = 1.26$, ($m : n = 1 : 0.10$). ^1H NMR (400 MHz, $CDCl_3$): δ 6.98 (s, 1H), 2.69–2.91 (br, 2H), 2.50–2.65 (br, 0.06H), 1.61–1.82 (br, 2H), 1.05–1.485 (m, 18H), 0.87 (t, 3H), 0.63–0.74 (m, 0.21H), 0.09 (s, 3H), 0.00 (s, 18H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 139.9, 133.7, 130.5, 128.7, 32.3, 30.7, 29.8 x3, 29.7x3, 29.6, 29.5, 22.8, 14.2, 0.9 x7. IR (ATR) 2958, 2922, 2867, 1466, 1259, 1081, 1070, 810, 722, 667 cm^{-1}.

Formation of thin films: Formation of thin films was carried out with a chloroform solution of copolymer **8**–**10** (10 mg/mL) by dropcast on a quartz substrate for measurements of UV–vis spectra and on a silicon wafer for XRD analyses. Acid treatment of the thin film was performed under a vapor of methanesulfonic acid at 80 °C for 30 min. The thin film for the measurement of the conductivity was formed on an ITO electrode by dropcast with a solution of copolymer **8**–**10** (2.2 mg/mL) to afford the corresponding thin film with the thickness of 200 nm and gap width of 200–800 μm. The film of copolymer for dynamic mechanical analysis (DMA) was formed by melt press at 190 °C at 5 MPa followed by ca. 100 times of pressurize and degassing cycles.

3. Results and Discussion

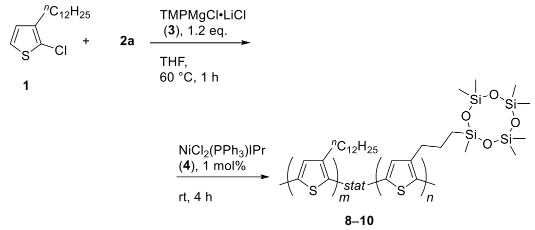
Preparation of Copolymers

Preparation of thiophene **2a** bearing cyclic siloxane at the side chain was prepared as summarized in Scheme 1. The reaction of 3-bromo-2-chlorothiophene with a Grignard reagent induced halogen-metal exchange selectively at the bromine atom at the 3-position in a mixed solvent system of THF/hexane followed by addition of allyl bromide afforded the 3-allylated thiophene **5**. [30] Hydrosilylation of **5** with cyclic siloxane 1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane (**7**) in the presence of a platinum catalyst lead to the formation of the monomer precursor **2a** in 70% yield. Our previous preparation of the related thiophene derivative **2b** bearing a longer C4 carbon chain has been carried out employing 2-chloro-3-methylthiophene as a starting material. The preparation protocol required radical halogenation of the methyl group prior to afford the hydrosilylation precursor. The radical reaction caused over-halogenation at the methyl group, which revealed difficulties in the purification and thus lowering the overall yield of the monomer precursor **2b**. [19] By contrast, the synthetic pathway to **2a** involving allylation to the thiophene ring is straightforward and the overall yield of **2a** was shown to be superior. Polymerization of **2a** was preliminarily examined employing the similar method involving deprotonative metalation with magnesium amide **3** followed by nickel-catalyzed cross-coupling polymerization with **4** as a catalyst. [19] The reaction similarly proceeded to the case for **2b** to afford polymer **6a** in excellent yield and with reasonable molecular weight distribution (PDI = 1.42). The obtained polymer resulted in forming of networking also by the treatment with an acid vapor and the accompanying improved conductivity (5.1×10^{-2} Scm^{-1}), which was comparable with that of **6b** (6.7×10^{-2} Scm^{-1}), was observed by doping with acid.



Scheme 1. Preparation and polymerization of chlorothiophene monomer **2a**

Copolymerization of 2-chloro-3-dodecylthiophene (**1**) and chlorothiophene bearing a cyclic siloxane moiety at the side chain **2a** was carried out by the deprotonation of a mixture of **1** and **2a** (**1**/**2a** = 100:1) with magnesium amide TMPMgCl·LiCl[31] (**3**) followed by nickel-catalyzed cross-coupling polymerization (Scheme 2). The reaction of TMPMgCl·LiCl with a mixture of comonomers **1** and **2** at 60 °C for 1 h formed the mixture of organometallic monomers. Addition of nickel catalyst $NiCl_2(IPr)PPh_3$ (**4**, 1 mol%) [32–35] to the mixture initiated polymerization to afford copolymer **8**. The ratio of each monomer contents incorporated was estimated by the measurement of ^{1}H NMR referring the methylene signals adjacent to the thiophene ring at the 3-positions of **1** and **2a**, respectively. The ratio based on the NMR measurement showed reasonable agreement with the feed ratio of comonomers **1** and **2a** as summarized in Table 1. The result suggested that statistical copolymerization indeed took place.



Scheme 2. Statistical copolymerization of **1** and **2a** (1%–10%)

Table 1. Copolymerization of 2-chloro-3-dodecylthiophene (**1**) and chlorothiophene bearing cyclic siloxane at the side chain **2a**[a]

Polymer	Feed Ratio	Yield	m:n^b	$M_n{}^c$ $M_w/M_n{}^c$
11[d]	1/10	52%	1:0	23500 1.26
8	1/0.01	80%	1:0.01	46000 1.21
9	1/0.05	58%	1:0.04	41000 1.30
10	1/0.10	69%	1:0.10	42000 1.42
6a[e]	0/1	61%	0:1	26000 1.42

[a] Unless otherwise noted, polymerization was carried out with 2-chloro-3-dodecylthiophene (**1**) (0.3 mmol) and chlorothiophene bearing cyclic siloxane (1–10 mol%); Deprotonation was carried out with **3** (0.36 mmol) at 60 °C for 1 h in THF. Polymerization was performed with 1 mol% of nickel catalyst **4** at room temperature for 4 h; [b] The incorporated ratio was measured by ^{1}H NMR analysis. [c] M_n and M_w/M_n were measured by SEC (Size Exclusion Chromatography) [d] Polymerization was carried out in a manner as described in ref 18. [e] Synthesis of **6a** was performed as shown in Scheme 1.

Characterization of Copolymer Thin Films

The polymer **8**–**10** was then subjected to the film formation by drop cast/spin coating with a solution of the copolymer dissolved in chloroform. The film was alternatively afforded by melt press. The obtained film was treated with an acid vapor at 80 °C for 0.5 h. The film after treatment with acid was found to be insoluble to any of organic solvents and water whereas copolymers before acidic treatment was easily dissolved in organic solvents such as chloroform, THF, toluene, etc. The finding shows that cross-linking took place induced by the acid-mediated ring-opening to form network of the siloxane moiety. Measurement of UV-vis spectra of copolymers **8**–**10** as thin films revealed to show absorption at ca. 520 nm and were transparent at higher than 700 nm. The polymer film showed decrease of the absorbance at ca. 520 nm after the film was treated by an acid vapor to form networking and appearance of the absorption at >700 nm, which is characteristic in the doped state of the polythiophene main chain by the formation of a partial quinoid structure in the thiophene–thiophene single bonds (Figure 1). [36]

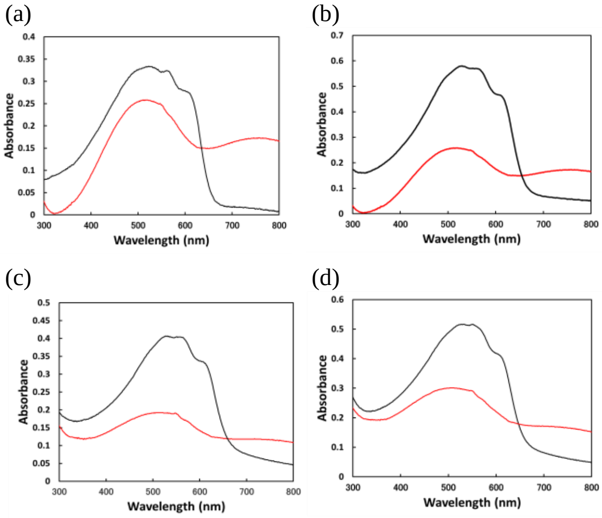
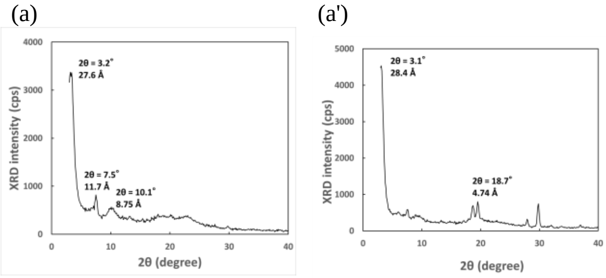


Figure 1. UV-vis spectra (thin film) of thiophene copolymers **8a**–**c** (a)–(c), respectively, and poly(3-dodecylthiophene) **10** (d) before (black) and after (red) acid treatment

Results on the measurement of XRD analysis of the obtained polythiophenes are shown in Figure 2. The out-of-plane profile of **8**–**10** showed characteristic peaks of 2θ = 3.1° (100 reflection) suggesting layer structure derived from the side chain of polythiophene corresponds to 28.5 Å. This value reasonably resembled to that of authentic (27 Å). [36,37] The result suggests that incorporation of a partial cyclic siloxane moiety do not significantly influence the crystal structure of poly-3-alkylthiophene. It was also found that weak peaks at 2θ = 6.6–6.8° and 9.9–10.1° that corresponded to 200 and 300 reflections, respectively, were apparent. These results suggested that the film shows highly ordered crystalline structures and consists of the edge-on structure toward the glass substrate [38] despite that the poly(3-dodecylthiophene) (**11**) contains 1–4% of the thiophene moiety contains cyclic siloxane structure. On the other hand, the XRD profiles of the thin film after acid treatment showed the strong peak at 2θ = ca. 17–18°, in **9** and **10** (contents of **2a** = 4% and 10%, respectively), which are characteristic as the layer distance of ca. 5 Å and have not been observed before acid treatment whereas such a peak has not been found in copolymer **8** (contents of **2a** moiety = 1%). Such a similar peak was also revealed in the homopolymer of poly(3-dodecylthiophene) (**11**). These results suggest that the thin film of polythiophenes **8**–**10** changed the structure to face-on after the acid treatment. Since the preference of face-on orientation has been shown in higher molecular weight polythiophenes,[38] increase of the molecular weight by networking through the ring opening of cyclic siloxane would induce the change of the orientation.



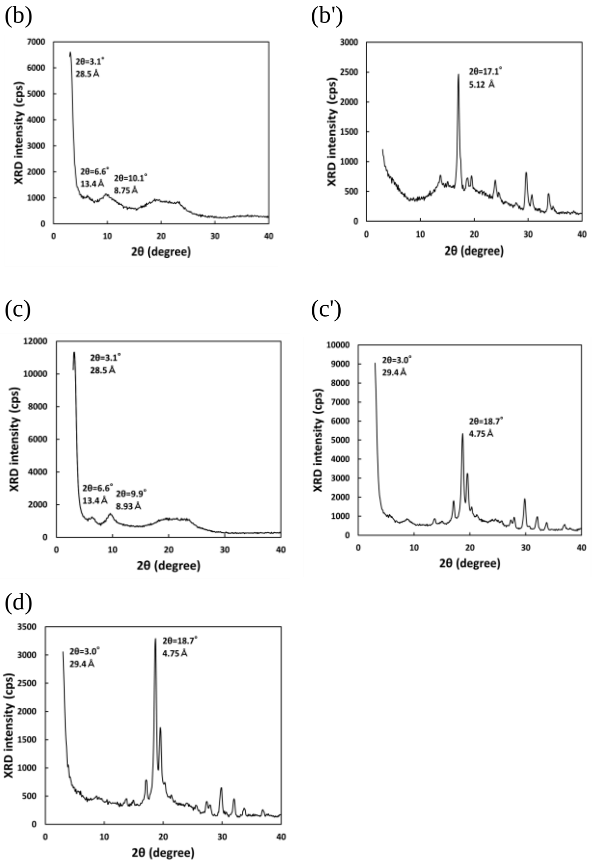


Figure 2. XRD profiles of statistical copolymer consisted of 3-dodecylthiophene and 3-substituted thiophene bearing cyclic siloxane before and after acid treatment. **8** (a) and (a'); **9** (b) and (b)'; **10** (c) and (c'), respectively, and poly(3-dodecylthiophene) homopolymer (**11**) after acid treatment (d)

DMA (dynamic mechanical analyses) measurements of the polythiophene thin films were preliminary examined for the evaluation of mechanical properites.[40,41] Table 3 summarizes the changes in the glass transition temperature of the copolymers **8**–**10** before and after the acid treatment. A slight increase in the glass transition temperature was observed for copolymers with 1–10 mol% cyclic siloxane moieties, and these values were found to be still below room temperature suggesting a rubber-like elasticity of the copolymers at an ambient condition.[27] The change in the T_g value of **10** with 10% siloxane moieties was found to be smaller compared to the differences in the T_g values of **8** and **9** with 1% and 4% cyclic siloxane moieties. This result suggests that the ring opening of the cyclic siloxane moiety is ristricted due to the high siloxane content, and the subsequent networking is insufficient.

Table 2. Glass transition temperature of polythiophene copolymer **8**–**10** before/after the acid treatment [a]

	T_g before acid treatment [°C]	T_g after acid treatmen [°C]	ΔT_g, [°C][b]
8	–2.9	0.1	3.0
9	–1.9	1.1	3.0
10	–2.0	–0.9	1.1

[a] The glass transition temperature T_g was estimated by the measurement of DMA with a melt pressed film of the thiophene copolymer before and after acid treatment as described in the experimental section. [b] The difference of T_g between before and after the acid treatment.

The thin film of the statistical copolymer derived from 2-chloro-3-dodecylthiophene (**1**) and cyclic-siloxane containing thiophene **2a** was fabricated also on the ITO electrode as shown in Table 2. [17,18] Measurement of conductivity was carried out at the applied voltage of 0–100 V before and after the treatment with an acid vapor. As summarized in Table 3, remarkable improvement of the conductivity after the acid treatment was observed in copolymers as well as poly(3-dodecylthiophene) homopolymer (m = 0) (**11**). These results suggest that doping of polythiophene main chain took place. From the absorption spectra of the doped thin films, the concentration of the doped states should be deduced to be around 30 %, considering the reported absorption spectra of polythiophene thin films synthesized by the electrochemical method.[42] The obtained copolymers of different contents of siloxane moiety (1–10%) exhibited conductivities of 10^{-1} to 10^{0} Scm^{-1} whereas it was found to slightly decrease the conductivity at an increased contents of the siloxane moiety because of the steric effect of siloxane toward the decrease of the extended π-conjugation of polythiophene main chain. These results indicate that statistical copolymers **8**–**10** containing a thiophene moiety bearing siloxane at the side chain do not affect the characteristics of poly(3-alkylthiophene)[37,39] concerning the electronic property despite that a small amount of siloxane moiety introduced acid-promoted networking of polythiophene, which has been hardly achieved in the poly-alkylthiophene homopolymer itself.

Table 3. Measurement of electric conductivities of the thin film of statistical polythiophene copolymers composed of 3-dodecylthiophene and 3-substituted thiophene bearing cyclic siloxane moiety[a]

Copolymer	Contents of **2a**	Conductivity[b]/ Scm^{-1}	
8	1/0.01	4.8 x 10^{-6}	1.6 x 10^{0}
9	1/0.05	6.6 x 10^{-6}	5.7 x 10^{-1}
10	1/0.10	6.1 x 10^{-7}	2.3 x 10^{-1}
11	0	1.9 x 10^{-6}	3.9 x 10^{0} [c,d]
6a	1.0		5.1 x 10^{-2}

[a] Unless noted, measurement of conductivity was performed by an apparatus shown in the Supporting Information and the conductivities were calculated from the current at the applied voltage of 30 V on ITO electrodes with 200 nm thickness of polythiophene film. Acid treatment was performed with trifluoromethanesulfonic acid vapor at 80 °C for 30 min; [b]Left: before acid treatment; Right: after acid treatment. [c]Formation of network gel was not observed after acid treatment; [d]Applied voltage was 6 V.

4. Conclusion

We have shown that random copolymerization of 3-alkylthiophene and as little as 1–10% of thiophene units bearing a cyclic siloxane moieties results in the formation of the corresponding statistical copolymers **8**–**10**. These polymers were shown to form networking by acid treatment with trifluoromethanesulfonic acid vapor, which promoted ring opening of the cyclic siloxane moiety. The formation of such a network makes the polymer film insoluble in both organic and aqueous solvents. This behavior has not been achieved with poly(3-alkylthiophene) itself. Doping of polythiophene main chain was also found to occur by the acid treatment and the thus doped copolymer induced the extended π-conjugation. In such doped copolymers, increased conductivity of ca. 10^{5-6} times resulted. The obtained copolymers involve the potential of additional elastic properties due to the formation of siloxane linkage interchain of the polymers. Further studies on mechanical properties are now in progress and will be described in due course.

Acknowledgement

This work was supported by JSPS Kakenhi B (JP19182273) by MEXT and Hyogo Science and Technology Association.

References

1. P. M. Beaujuge, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2011**, *133*, 20009.
2. A. C. Grimsdale, K. Leok Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* **2009**, *109*, 897.
3. T. Yamamoto, *Bull. Chem. Soc. Jpn.* **2010**, *83*, 431.
4. H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw, *Nature* **1999**, *401*, 685.
5. H. Sirringhaus, N. Tessler, R. H. Friend, *Science* **1998**, *280*, 1741.
6. Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C.-S. Ha, M. Ree, *Nat. Mater.* **2006**, *5*, 197.
7. I. Osaka, R. D. McCullough, *Acc. Chem. Res.* **2008**, *41*, 1202.
8. T. A. Chen, R. D. Rieke, *J. Am. Chem. Soc.* **1992**, *114*, 10087.
9. H. A. Bronstein, C. K. Luscombe, *J. Am. Chem. Soc.* **2009**, *131*, 12894.
10. T. Yokozawa, A. Yokoyama, *Chem. Rev.* **2009**, *109*, 5595.
11. Y. Shibuya, A. Mori, *Chem. Eur. J.* **2020**, *26*, 6976.
12. A. Mori, *Bull. Chem. Soc. Jpn.* **2020**, *93*, 1200.
13. A. Mori, *J. Synth. Org. Chem. Jpn.* **2011**, *69*, 1202.
14. K. Fujita, Y. Sumino, K. Ide, S. Tamba, K. Shono, J. Shen, T. Nishino, A. Mori, T. Yasuda, *Macromolecules* **2016**, *49*, 1259.
15. K. Murakami, S. Tanaka, A. Mori, *Polym. Chem.* **2015**, *6*, 6573.
16. A. Mori, C. Kubota, K. Fujita, M. Hayashi, T. Ogura, T. Suzuki, K. Okano, M. Funahashi and M. Horie, *Macromolecules*, **2020**, *53*, 1171.
17. A. Mori, K. Fujita, C. Kubota, T. Suzuki, K. Okano, T. Matsumoto, T. Nishino, M. Horie, *Beilstein J. Org. Chem.* **2020**, *16*, 317.
18. T. Ogura, C. Kubota, T. Suzuki, K. Okano, N. Tanaka, T. Matsumoto, T. Nishino, A. Mori, T. Okita, M. Funahashi, *Chem. Lett.* **2019**, *48*, 611.
19. A. Mori, C. Kubota, D. Morita, K. Fujita, S. Yamamoto, T. Suzuki, K. Okano, M. Funahashi, M. Horie, *Heterocycles* **2021**, *103*, 249.
20. M. Funahashi, A. Sonoda, *Org. Electron.* **2012**, *13*, 1633.
21. M. Funahashi, A. Sonoda, *J. Mater. Chem.* **2012**, *22*, 25190.
22. M. Funahashi, A. Sonoda, *Phys. Chem. Chem. Phys.* **2014**, *16*, 7754.
23. M. Funahashi, A. Sonoda, *Dalt. Trans.* **2013**, *42*, 15987.
24. K. Takenami, S. Uemura, M. Funahashi, *RSC Adv.* **2016**, *6*, 5474.
25. S. Miyane, H.-F. Wen, W.-C. Chen, T. Higashihara, *J. Polym. Sci. Part A Polym. Chem.* **2018**, *56*, 1787.
26. J. Shen, M. Kashimoto, T. Matsumoto, A. Mori, T. Nishino, *Polym. J.* **2020**, *52*, 1273.
27. J. Shen, K. Fujita, T. Matsumoto, C. Hongo, M. Misaki, K. Ishida, A. Mori, T. Nishino, *Macromol. Chem. Phys.* **2017**, *218*, 1700197.
28. R. Inoue, M. Yamaguchi, Y. Murakami, K. Okano, A. Mori, *ACS Omega* **2018**, *3*, 12703.
29. S. Tamba, K. Shono, A. Sugie, A. Mori, *J. Am. Chem. Soc.* **2011**, *133*, 9700.
30. X. Wu, T. A. Chen, L. Zhu, R. D. Rieke, *Tetrahedron Lett.* **1994**, *35*, 3673.
31. A. Krasovskiy, V. Krasovskaya, P. Knochel, *Angew. Chem. Int. Ed.* **2006**, *45*, 2958.
32. S. Tamba, S. Tanaka, Y. Okubo, H. Meguro, S. Okamoto, A. Mori, *Chem. Lett.* **2011**, *40*, 398.
33. W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.
34. S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612.
35. K. Matsubara, K. Ueno, Y. Shibata, *Organometallics* **2006**, *25*, 3422.
36. A. O. Patil, Y. Ikenoue, F. Wudl, A. J. Heeger, *J. Am. Chem. Soc.* **1987**, *109*, 1858.
37. K. C. Park, K. Levon, *Macromolecules* **1997**, *30*, 3175.
38. T. Matsumoto, K. Nishi, S. Tamba, M. Kotera, C. Hongo, A. Mori, T. Nishino, *Polymer* **2017**, *119*, 76.
39. S. L. Liu, T. S. Chung, *Polymer* **2000**, *41*, 2781.
40. I. M. Ward, J. Sweeney, *Mechanical Properties of Solid Polymers*, 3rd ed. , John Wiley & Sons, Ltd, Chichester, UK, **2012**.
41. K. P. Menard, N. R. Menard, *Dynamic Mechanical Analysis*, 3rd ed. , CRC Press, Boca Raton, U. S. A., **2020**.
42. K. Kaneto, S. Hayashi, S. Ura, K. Yoshino, *J. Phys. Soc. Japan* **1985**, *54*, 1146.

Graphical Abstract

<Title>
Studies on the properties of poly(3-alkylthiophene) copolymerized by a small amount of thiophene derivative bearing a cyclic siloxane moiety at the side chain

<Authors' names>
Chihiro Kubota, Masaki Kashimoto, Ryutaro Yamashita, Kentaro Okano, Masaki Horie, Masahiro Funahashi, Takuya Matsumoto, Takashi Nishino, and Atsunori Mori

<Summary>
Thiophene–thiophene copolymers composed of 3-alkylthiophene and cyclic siloxane pendant thiophene are synthesized. Statistical copolymer based on the feed ratio (1–10%) of cyclic siloxane is obtained. Acidic treatment of the film results in the formation of the film insoluble in any of solvent. The improved electronic conductivity before/after the acid treatment is observed.
<Diagram>

A small diagram or other informative illustration that shows the most striking feature of the paper in pictorial form.

This size should be 4.8 × 4.8 cm or 10.0 × 3.0 cm.