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## Synthesis and Properties of Regioregular Poly(3-substituted thiophene) Bearing Disiloxane Moiety in the Substituent. Remarkably High Solubility in Hexane

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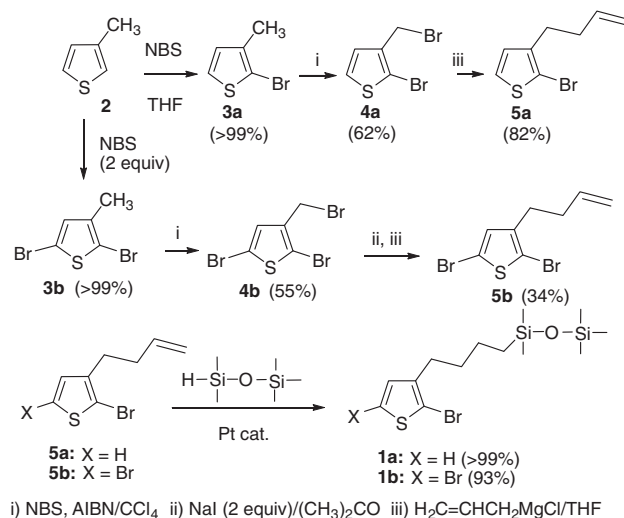
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Regioregular poly(3-substituted thiophene) derivative bearing pentamethyldisiloxane moiety at the 3-substituent is prepared by nickel-catalyzed polymerization reactions with dehydrobrominative or debrominative generation of the organometallic monomer. The monomer precursors 2-bromo-3-(4-pentamethyldisiloxybutan-1-yl)thiophene (**1a**) and 2,5-dibromo-3-(4-pentamethyldisiloxybutan-1-yl)thiophene (**1b**) are prepared from 3-methylthiophene with 4–5 steps in overall good yields. Treatment of **1a** with  $\text{TMPMgCl}\cdot\text{LiCl}$  at room temperature for 3 h forms an organometallic monomer and following the addition of a nickel catalyst affords the corresponding polythiophene bearing a disiloxane moiety in the side chain. The reaction of **1b** with Grignard reagent leads to the similar monomer and addition of a catalytic amount of  $[\text{NiCl}_2(\text{dppf})]$  also affords polythiophene in highly regioregular manners. The obtained polythiophene is found to be dissolved in a hydrocarbon such as hexane.

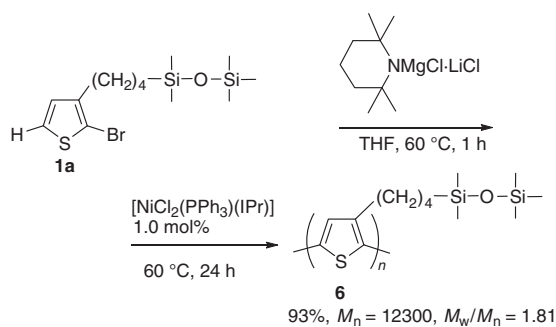
Synthesis of regioregular poly(3-substituted thiophene)s attracts much attention because of their wide-ranging utilities as materials.<sup>1</sup> It is, therefore, important to develop a new class of high-performance polythiophene derivatives. In particular, considerable attention has been paid to develop flexible and highly processible materials. Siloxane bearing SiOSi linkage with a longer bond distance and a strong bond energy generating flexible but chemically and thermally stable compounds<sup>2</sup> is a promising structure that may fulfill the above requirements. It is thus intriguing to introduce siloxane moieties into the substituent because it is well known that the polymeric materials bearing a siloxane group generally improve solubility in organic solvents, particularly in hydrocarbons; moreover, such compounds exhibit excellent thermal stability that induces easy fabrication of functionalized polymeric thin films.<sup>3</sup> However, there are few examples for the preparation of regioregular poly(3-substituted thiophene) bearing a siloxane moiety in the substituent. Only limited reports of nonregioregular polythiophene that is synthesized by oxidative polymerization with  $\text{Fe}^{\text{III}}$  reagents have been shown with a siloxane-containing 3-substituted thiophene as a monomer species.<sup>4</sup> On the other hand, regioregular polythiophenes are shown to be synthesized with 2-halo- or 2,5-dihalothiophene derivatives as a monomer precursor, which is in situ transformed into the corresponding organometallic thiophene by deprotonation with a metallic amide<sup>5</sup> or dehalogenative metalation with the Grignard metathesis (GRIM) via halogen–metal exchange.<sup>6–8</sup> Nevertheless, a few studies have been reported on the synthesis of halogenated thiophenes

bearing a siloxane group,<sup>4</sup> probably due to the synthetic difficulties in the halogenation of the thiophene ring when a siloxane group exists in the substituent. Herein, we report the preparation of regioregular poly(3-substituted thiophene) bearing a pentamethyldisiloxy group by dehydrogenative or GRIM polymerization with a nickel catalyst, whose success is based on an effective synthetic pathway for the monomer precursor.

Synthesis of the monomer precursor bromothiophenes **1a** and **1b** was achieved, as represented in Scheme 1. Both compounds were prepared starting from ubiquitous 3-methylthiophene (**2**) via halogenation of the thiophene ring and following radical bromination to afford 3-(bromomethyl)halothiophenes **4a** and **4b**. Treatment of **2** with an equimolar amount of *N*-bromosuccinimide (NBS) leads to 2-bromo-3-methylthiophene (**3a**), while the reaction with 2 equivalents of NBS furnished 2,5-dibromo-3-methylthiophene (**3b**). These thiophenes are subjected to radical bromination with NBS in the presence of AIBN in  $\text{CCl}_4$ , leading to **4a** and **4b** in 62% and 55% yields, respectively. The reaction of **4a** with allylmagnesium chloride afforded 2-bromo-3-(3-buten-1-yl)thiophene (**5a**), whereas the similar reaction of **4b** afforded a side product also allylated at the 5-position along with the desired **5b**. Transformation into **5b** with an improved yield was achieved by the use of the iodomethyl derivative, which was formed by the treatment of **4b** with  $\text{NaI}$  in acetone, to afford **5b**. Introduction of



**Scheme 1.** Preparation of thiophene monomers **1a** and **1b** bearing a pentamethyldisiloxane moiety.



**Scheme 2.** Nickel-catalyzed dehydrobrominative polymerization of **1a** with Knochel–Hauser base.

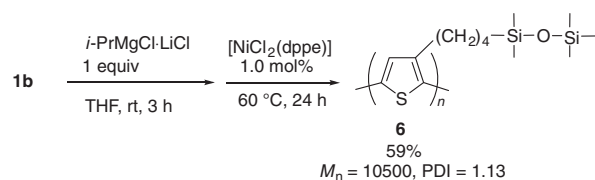
pentamethyldisiloxy group into the obtained **5a** and **5b** was carried out with pentamethyldisiloxane by hydrosilylation with a platinum catalyst leading to **1a** and **1b** in >99% and 93% yields, respectively.

The key for successful preparation of brominated thiophene derivatives bearing a pentamethyldisiloxane moiety is the use of 3-halomethylated thiophene, which allowed treatment of the allyl Grignard reagent to afford 3-(3-buten-1-yl)halothiophenes; otherwise, halogenation of the thiophene ring with NBS would be unsuccessful for the thiophene derivatives bearing a carbon–carbon double bond. Furthermore, the disiloxane moiety would not be tolerable toward metalation–bromination with a strong base and following treatment of  $\text{Br}^+$ . In contrast, the synthetic pathway shown in Scheme 1 proceeded to afford halothiophenes in reasonable overall yields, thus providing practical synthesis leading to the corresponding polythiophene.

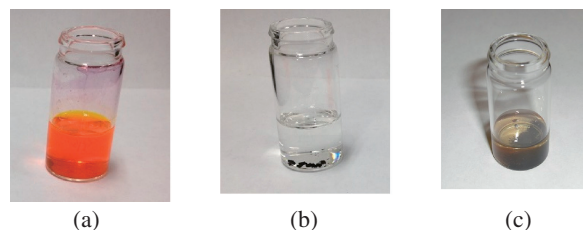
The obtained monomer precursor **1a** was then subjected to polymerization by deprotonation with the Knochel–Hauser base<sup>9</sup> (60 °C, 1 h), following cross-coupling polycondensation with a nickel(II) catalyst.<sup>5</sup> Use of the reaction condition that was available for the synthesis of regioregular poly(3-hexylthiophene) was found to be successful in affording the corresponding polythiophene bearing a disiloxane moiety. When 1.0 mol % of  $[\text{NiCl}_2(\text{PPh}_3)(\text{IPr})]$  was employed for the polymerization, polymer **6** was obtained in 93% yield to exhibit  $M_n$  of 12300 ( $M_w/M_n = 1.81$ ), as shown in Scheme 2. The HT-regioregularity of **6** was estimated to be >98% by the measurement of  $^1\text{H}$  NMR (see Supporting Information). It is remarkable that the color of the reaction mixture remains clear reddish-orange throughout the polymerization. This sharply contrasts with the preparation of regioregular poly(3-hexylthiophene) (HT-P3HT), whose reaction mixture gradually turns to heterogeneous dark purple suspension with the progress of polymerization.<sup>5–8</sup>

We next examined GRIM polymerization<sup>8</sup> of 2,5-dibromothiophene derivative bearing siloxane **1b**. Treatment of **1b** with an equimolar amount of  $i\text{-PrMgCl}\cdot\text{LiCl}$  to form the corresponding thienyl Grignard reagent and addition of nickel(II) catalyst  $[\text{NiCl}_2(\text{dppe})]$  (1.0 mol %) induced the polymerization leading to **6** (Scheme 3). The obtained polymer showed  $M_n$  of 10500 ( $M_w/M_n = 1.13$ ) and the regioregularity was also found to be excellent (>99:1).

It should be pointed out that the obtained polythiophene bearing a pentamethyldisiloxane moiety **6** was found to be soluble in hexanes. When polythiophene **6**, whose  $M_n$  and PDI were 12300 and 1.81, respectively, was dissolved in hexane



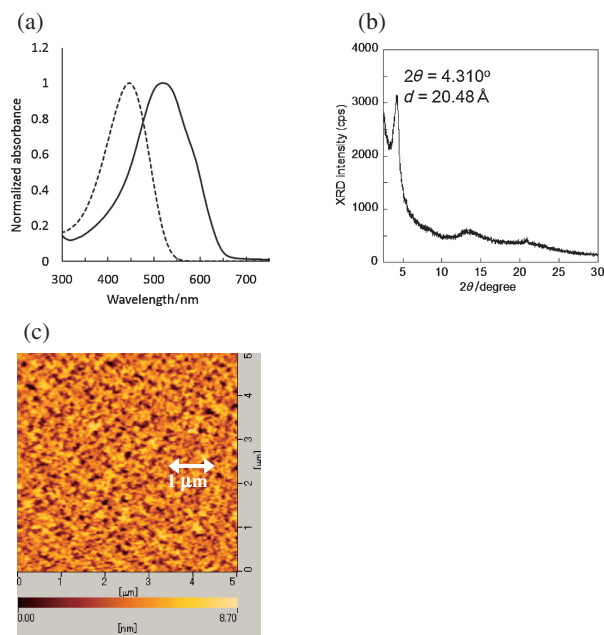
**Scheme 3.** Nickel-catalyzed debrominative GRIM polymerization of **1b**.



**Figure 1.** Attempted dissolution of 1 mg of polythiophene derivatives in 1 mL of hexane. (a) Polythiophene **6** bearing siloxane moiety,  $M_n = 12300$ , PDI = 1.81; (b) poly(3-hexylthiophene),  $M_n = 12500$ , PDI = 1.35; (c) poly(3-dodecylthiophene),  $M_n = 12200$ , PDI = 1.72.

(1 mg mL<sup>-1</sup>) at room temperature, a clear deep orange solution was immediately formed, as shown in Figure 1a, while other regioregular polythiophene poly(3-hexylthiophene) ( $M_n = 12500$ , PDI = 1.35) was shown to be hardly soluble under similar conditions, as observed in Figure 1b. Although polythiophene bearing a longer alkyl chain poly(3-dodecylthiophene) ( $M_n = 12200$ , PDI = 1.72) slightly improved the solubility (Figure 1c), it was found to be much inferior to that of **6**.

The obtained polymer was used to measure spectroscopic and physical properties. Polythiophene **6** was dissolved in hexane and spin coated. The corresponding thin film of 53-nm thickness was obtained after annealing at 110 °C for 10 min. Measurement of UV–vis absorption spectrum exhibited the  $\lambda_{\text{max}}$  value of 519 nm in the film. Comparison of the spectra in a hexane solution ( $\lambda_{\text{max}} = 446$  nm) and in the film state reveals that the latter has a red-shifted absorption, as shown in Figure 2a, indicating strong interchain interactions among the thiophene chains in the film. The XRD analysis of polythiophene **6** was then performed to observe a peak at  $2\theta = 4.310^\circ$ , suggesting edge-on orientation and a layer distance of  $d = 20.48$  Å. Comparing with HT-P3HT ( $2\theta = 5.325^\circ$ ,  $d = 16.60$  Å), the layer distance of **6** was found to be slightly longer because of the steric bulkiness of the siloxane moiety (Figure 2b). The HOMO level of the thin-film of **6** bearing siloxane moiety is estimated to be  $-4.96$  eV by photoelectron yield spectroscopy, which was found to be slightly lower than that of P3HT ( $-4.74$  eV). This is because of better  $\pi$  stacking and improved interchain coupling in the HT-P3HT film that enhances the donor character. This tendency is in accordance with the literature that shorter side chains in regioregular poly(3-substituted thiophene) enhances the donor character.<sup>10</sup> The observation of the AFM image of the thin film of **6** is performed as shown in Figure 2c, indicating a flat film within the region  $5\ \mu\text{m} \times 5\ \mu\text{m}$ , in which the root mean square (RMS) roughness of the film was 1.45 nm. Further studies on the use of the thin film of polythiophene **6**



**Figure 2.** (a) UV-vis spectrum of thin film (solid line), as a hexane solution (dot line); (b) XRD profile; (c) AFM image ( $5\ \mu\text{m} \times 5\ \mu\text{m}$ ) of **6** (film).

bearing a siloxane moiety in the side chain as electronic devices such as thin-film photovoltaic cells and organic thin-film transistors are under way and will be described in due course.

In conclusion, we have shown the synthesis of regioregular poly(3-substituted thiophene) bearing a siloxane moiety in the substituent. Synthesis of the monomer precursors **1a** and **1b** was successfully achieved in 5–6 steps with reasonable yields. Polymerization was revealed to proceed via deprotonative or GRIM metalation, and following nickel-catalyzed catalyst-transfer polymerization, it afforded polythiophene **6**. The obtained polythiophene was found to be dissolved in hexane, while the related alkylthiophenes were hardly soluble. Fabrication of the thin film of **6** was also achieved by spin coating to reveal the HOMO level of  $-4.96\ \text{eV}$  by photoelectron yield spectroscopy and edge-on orientation with a layer distance of  $20.48\ \text{Å}$ . Utilizing the high solubility of **6** in hydrocarbons, the polymer would allow the environmentally friendly formation of electronic devices as well as improving the solvent choice in the preparation of multilayered thin-film materials.<sup>11</sup>

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