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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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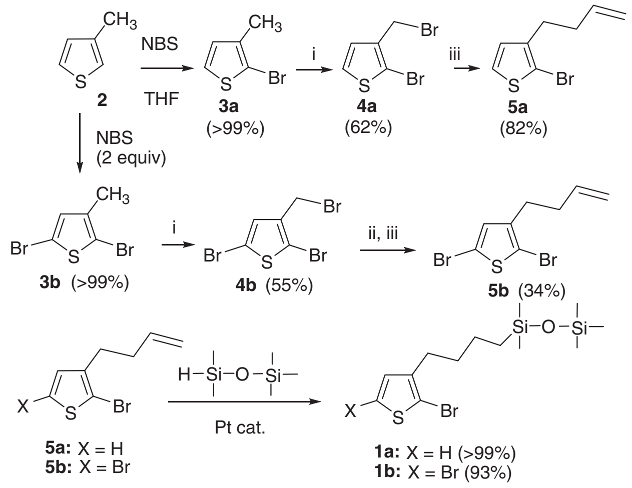
Regioregular poly(3-substituted thiophene) derivative bearing pentamethyldisiloxane moiety at the 3-substituent is prepared by nickel-catalyzed polymerization reactions with dehydrobrominative or debrominative generation of the organometallic monomer. The monomer precursors 2-bromo-3-(4-pentamethyldisiloxybutan-1-yl)thiophene (**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 TMPMgCl•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 [$NiCl_2$(dppe)] also affords polythiophene in highly regioregular manners. The obtained polythiophene is found to be dissolved in a hydrocarbon such as hexane.

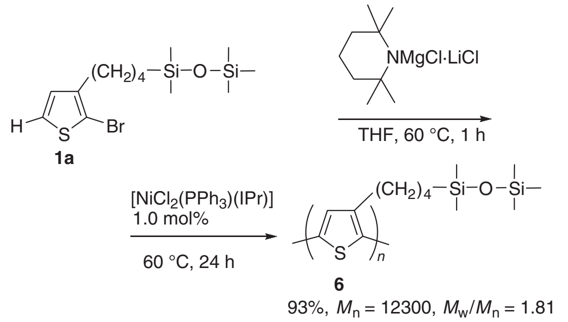
Synthesis of regioregular poly(3-substituted thiophene)s attracts much attention because of their wide-ranging utilities as materials.[1] It is, therefore, important to develop a new class of high-performance polythiophene derivatives. In particular, considerable attention has been paid to develop flexible 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[2] 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.[3] 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 Fe^{III} reagents have been shown with a siloxane-containing 3-substituted thiophene as a monomer species.[4] 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[5] or dehalogenative metalation with the Grignard metathesis (GRIM) via halogen–metal exchange.[6–8] Nevertheless, a few studies have been reported on the synthesis of halogenated thiophenes bearing a siloxane group,[4] 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 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 NaI in acetone, to afford **5b**. Introduction of



i) NBS, AIBN/CCl_4 ii) NaI (2 equiv)/$(CH_3)_2CO$ iii) $H_2C=CHCH_2MgCl$/THF

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



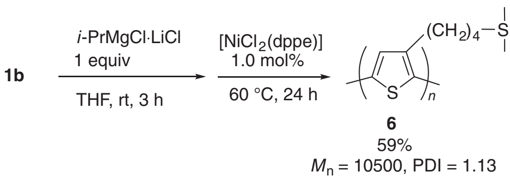
Scheme 2. Nickel-catalyzed dehydrobrominative polymerization of **1a** with Knochel–Hauser base.

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 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[9] (60 °C, 1 h), following cross-coupling polycondensation with a nickel(II) catalyst.[5] 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 [$NiCl_2(PPh_3)$(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 ^1H 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.[5–8]

We next examined GRIM polymerization[8] of 2,5-dibromothiophene derivative bearing siloxane **1b**. Treatment of **1b** with an equimolar amount of *i*-PrMgCl•LiCl to form the corresponding thienyl Grignard reagent and addition of nickel(II) catalyst [$NiCl_2$(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).



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


(a) (b) (c)

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.

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 ($1\,mg\,mL^{-1}$) 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 λ_{max} value of 519 nm in the film. Comparison of the spectra in a hexane solution ($\lambda_{max} = 446\,nm$) 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 $2\theta = 4.310°$, suggesting edge-on orientation and a layer distance of $d = 20.48\,Å$. Comparing with HT-P3HT ($2\theta = 5.325°$, $d = 16.60\,Å$), 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 π 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.[10] 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 μm × 5 μm, 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**

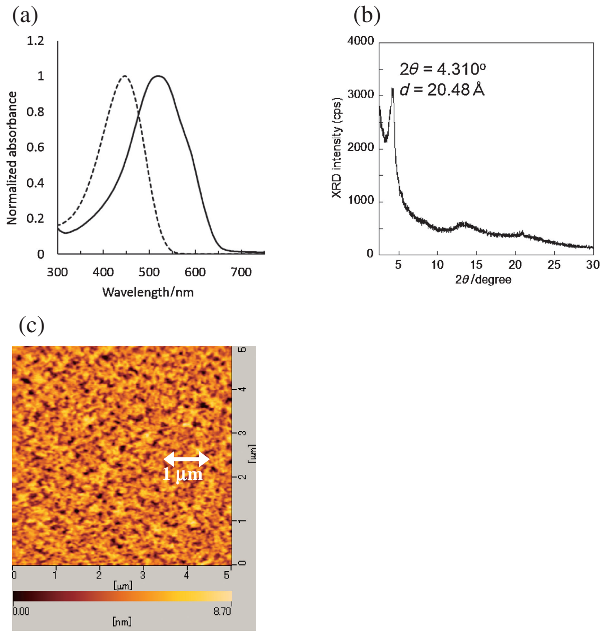


Figure 2. (a) UV–vis spectrum of thin film (solid line), as a hexane solution (dot line); (b) XRD profile; (c) AFM image (5 µm × 5 µm) of **6** (film).

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 eV by photoelectron yield spectroscopy and edge-on orientation with a layer distance of 20.48 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.[11]

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