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Synthesis of poly{[bis(diethynylphenyl)silylene]phenylene}s with highly heat-resistant properties and an application to conducting materials

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Abstract

Poly{[bis(3,5-diethynylphenyl)silylene]-*p*-phenylene} was prepared by the reaction of poly[(diethoxysilylene)-*p*-phenylene] with 3,5-bis(trimethylsilylethynyl)phenyllithium, followed by desilylation of the resulting substitution product. The present polymer exhibited extremely high heat-resistance and their thermogravimetric analysis (TGA) in a nitrogen atmosphere showed the temperature of 5% weight loss (Td_5) of 791 °C. Total weight loss at 1000 °C in TGA was determined to be 6% based on the initial weight. Treatment of a polymer film on a quartz plate at 1200 °C in vacuo led to the formation of a conducting thin film with a thickness of 74 nm and a conductivity of 9 S/cm.
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Keywords: Silicon-polymer; Heat-resistant materials; Conducting materials

1. Introduction

There has been much attention in organosilicon polymers composed of an alternating arrangement of an organosilicon unit and π-electron system, since they may be used as functionality materials [1], such as, for example, organic semiconductors [2] and hole-transporting materials [3]. In addition, an interest has been focused on these types of the polymers regarding their heat-resistant properties. In particular, polymers having ethynylene units in the π-electron system have been extensively studied [4]. An example includes the synthesis of poly[(hydrosilylene)ethynylene(phenylene)ethynylene]s with excellent heat- and frame-resistant properties, reported by Itoh et al. [5]. Thermogravimetric analysis (TGA) of the polymers in an argon atmosphere reveals only 3–12% weight loss at 1000 °C based on the initial weight and it has been proposed that the high heat-resistant properties of these polymers owe to the cross-linking

reactions concerning the Si–H and C≡C triple bonds. In contrast, diorganosilylene–diethenylenephenylene alternating polymers exhibit much less thermal stability in nitrogen (Td_5 (5% weight loss temperature) = 409–504 °C and total weight loss at 1000 °C = 22–37% of the initial weight) [6].

We recently studied thermal properties of variously substituted poly[(silylene)phenylene]s and found that introduction of unsaturated groups on the silicon atom led to high thermal stability of the polymers, despite that these polymers have no ethynylene linkage in the backbone [7–9]. Of these, poly{[bis(ethynylphenyl)silylene]phenylenes} (**1** in Chart 1) exhibited remarkably high heat-resistant properties in a nitrogen atmosphere. In the TGA analysis in nitrogen, $Td_5 = 651–711$ °C and total weight loss at 1000 °C = 8–10% of the initial weight were noted, depending on the substitution modes of phenylene units in the side groups and the backbone. Monitoring the thermal reactions by differential thermal analysis (DTA) and IR spectrometry indicated that cross-linking reactions of the terminal acetylene units around 210 °C would be responsible for the high

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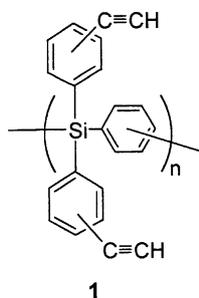*E-mail address:* akunai@hiroshima-u.ac.jp (A. Kunai).

Chart 1.

Table 1
Synthesis and properties of polymers **1** [9], **2a,b**, and **3a,b**

Polymer	Yield (%)	M_w $(M_w/M_n)^a$	TGA in N_2^b	
			Td_5 (°C)^c	Weight loss (%)^d
2a	77	15 700 (1.6)	613	11
3a	74	19 000 (1.5)	791	6
2b	95	20 500 (1.5)	534	21
3b	79	23 500 (1.3)	415	23
1p^e	84	33 000 (2.2)	655	9
1m^f	56	22 000 (1.8)	651	9

^{a} Determined by GPC, relative to polystyrene standards.
^{b} At a rate of 10 °C/min from 25 to 1000 °C.
^{c} Temperature resulting in 5% weight loss based on the initial weight.
^{d} Total weight loss at 1000 °C.
^{e} Poly[bis(4-ethynylphenyl)silylene-*p*-phenylene].
^{f} Poly[bis(3-ethynylphenyl)silylene-*p*-phenylene].

thermal stability of polymers **1**. In an effort to obtain polymers with even better heat-resistance, we prepared poly{[(3,5-diethynylphenyl)methylsilylene]phenylene} (**2a**) and poly{[bis(3,5-diethynylphenyl)silylene]phenylene} (**3a**) bearing two or four terminal acetylene groups in a silylene-phenylene repeating unit. Conversion of polymer **3a** to a conducting thin solid film is also reported.

2. Results and discussion

We have demonstrated that substitution of an EtO–Si group of poly[(ethoxysilylene)phenylene]s with organolithium reagents provides a convenient route to prepare variously substituted poly[(silylene)phenylene]s [8]. When poly[ethoxymethylsilylene- and (diethoxysilylene)phenylene] were treated with 3,5-bis(trimethylsilylethynyl)phenyllithium, the corresponding 3,5-bis(trimethylsilylethynyl)phenyl-substituted polymers (**2b** and **3b**) were obtained as shown in Scheme 1 and Table 1. Further treatment of the resulting polymers **2b** and **3b** with methanol in the presence of a catalytic amount of K_2CO_3 gave desilylated polymers **2a** and **3a**, respectively. These reactions proceeded smoothly. Molecular weights of the polymers were in good agreement with those calculated on the basis of the molecular weights of the starting polymers, indi-

cating that neither significant cleavage of the polymer backbone nor cross-linking reactions were involved in these reactions (Table 1). ^{1}H and ^{13}C NMR spectra of the product polymers also proved that the regular alternating arrangement of silylene and *p*-phenylene units was kept in the polymer backbone, and the diethynylphenyl moiety was introduced quantitatively onto the silylene unit. For example, the ^{13}C NMR spectrum of **3a** (Fig. 1) revealed two sharp resonances due to ethynyl carbons and six resonances due to aromatic carbons, but did not show any other signals, verifying the proposed structure for **3a**. For **2a** and **3a**, no signals due to the residual trimethylsilyl group were observed in the ^{1}H NMR spectra, and a strong IR absorption band appeared at about 3300 cm^{-1}, assignable to the ethynyl C–H bond stretching frequencies (Fig. 2(a)). Polymers **2a,b** and **3a,b** were obtained as colorless solids. They were soluble in aromatic hydrocarbons, halocarbons, and ethers but were insoluble in alcohols and saturated hydrocarbons.

Thermal properties of polymers **2a,b** and **3a,b** were examined by TGA–DTA in nitrogen. Their Td_5 and final
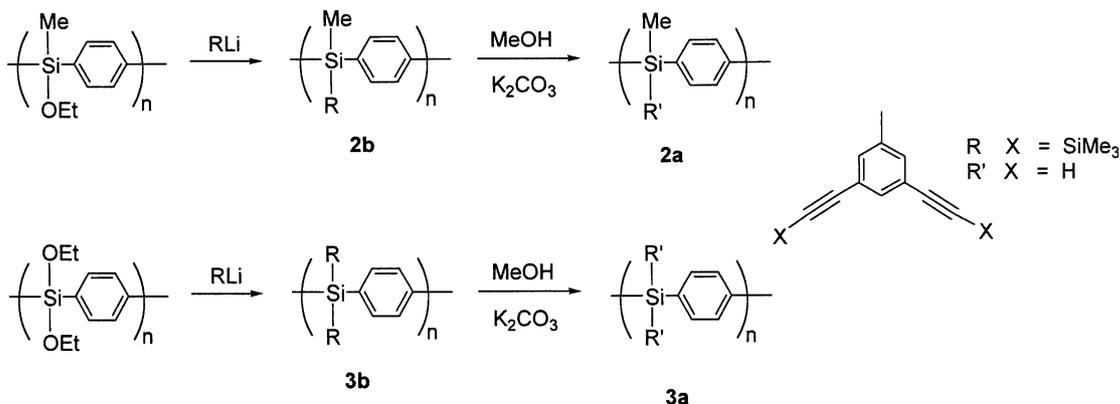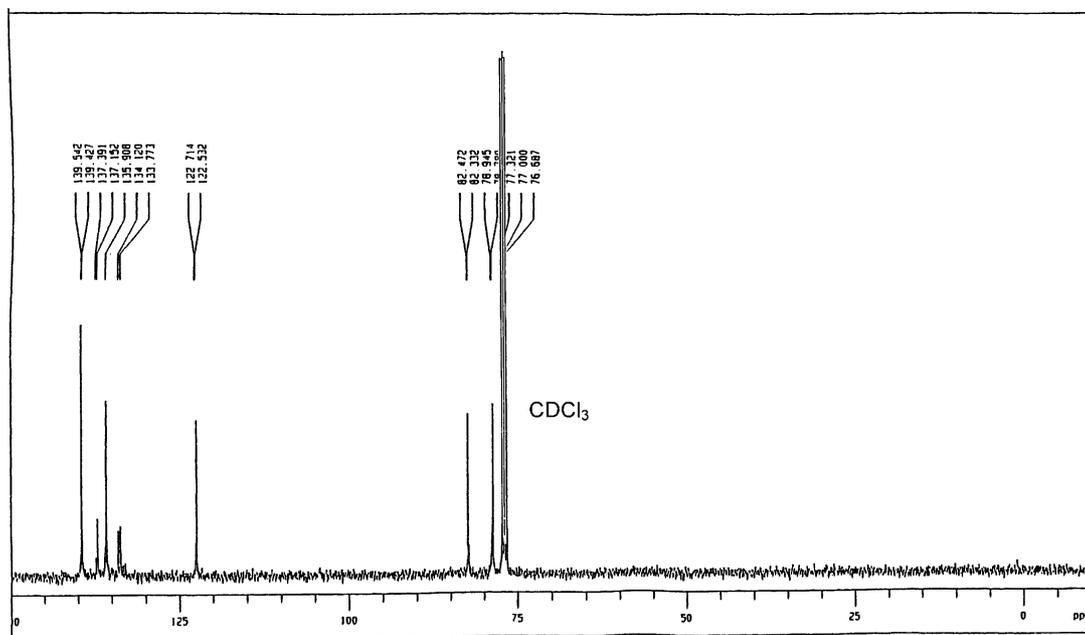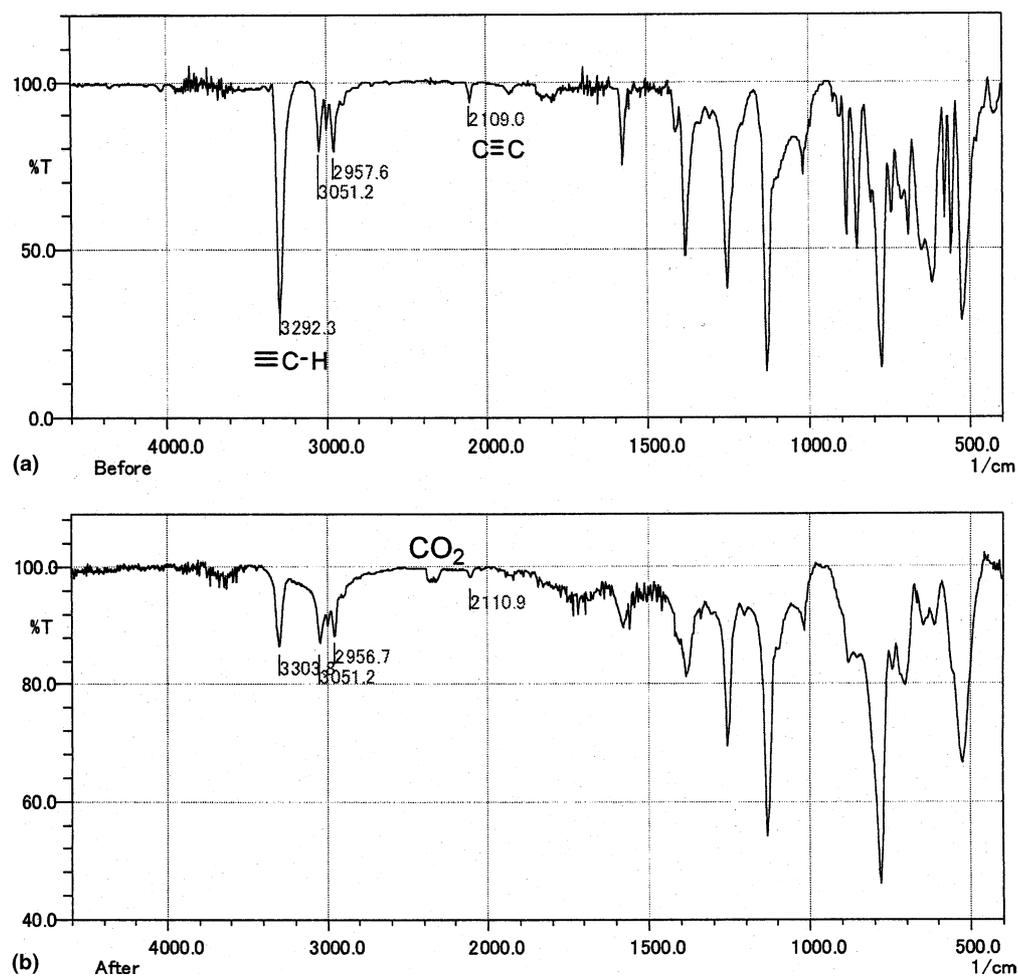

Scheme 1.

Fig. 1. ^{13}C NMR spectrum of polymer **3a**.

Fig. 2. IR spectra of polymer **2a**: (a) before and (b) after heating at 210 °C for 3 min.
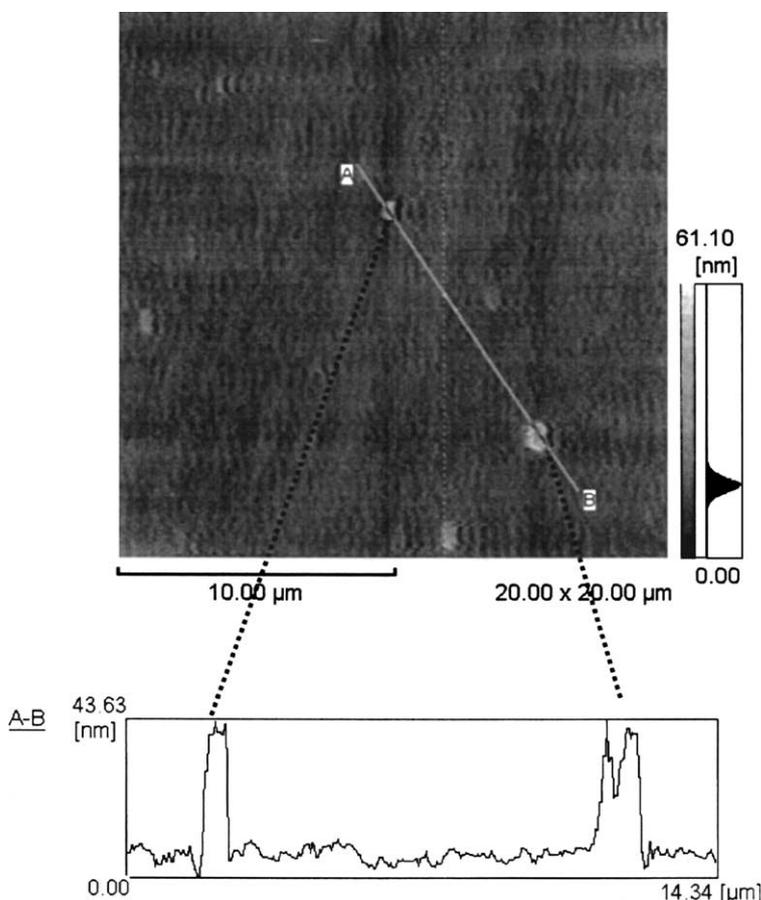
Fig. 3. An AFM profile of a conducting film prepared by heating a spin coated film of **3a** on a quartz plate at 1200 °C.

weight loss at 1000 °C are listed in Table 1. As expected, the materials obtained from the polymers exhibited excellent heat-resistant properties in nitrogen. In particular, polymer **3a** showed higher Td_5 and lower weight loss at 1000 °C (Table 1), than those of polymers **1**. Introduction of two more terminal ethynyl groups in a repeating unit may be the reason for higher heat resistance of polymer **3a**, relative to **1** and **2a**. Lower Td_5 and higher weight loss of **3b** than those of **2b**, are probably due to the larger number of Si–Me bonds in a repeating unit that are relatively unstable as indicated by the smaller bond dissociation energy of Si–Me (318 kJ/mol) than that of Si–Ph (358 kJ/mol) [10]. DTA of polymers **2a** and **3a** revealed a sharp exothermic peak at 200–210 °C, as observed for polymers **1**, while polymers **2b** and **3b** showed only an ambiguous exothermic maximum around 250 °C in the DTA curves. Presumably, cross-linking reactions of polymers **2a** and **3a** concerning terminal ethynyl groups occurred at this temperature, which would be responsible for the high heat resistance of these polymers. In fact, when polymer **2a** was heated at 210 °C in nitrogen for 3 min, the polymer became insoluble, indicating that some cross-linking reactions had occurred. The IR spectrum of **2a** after heating revealed a decrease of the absorption band at around 3300 cm^{-1} due to the ethynyl C–H bond

stretching frequency (Fig. 2(b)), although we have no date to discuss detailed mechanism of the cross-linking.

Interestingly, when a spin-coated film of polymer **3a** on a quartz plate was heated at 1200 °C for 4 h in vacuo, a black conducting film was obtained. The thickness and conductivity of the thermally treated film were 74 nm and 9 S/cm, respectively. Fig. 3 shows an AFM profile of the conducting film. Although it reveals the presence of small gaps, the film surface is almost flat without any large cracks.

In conclusion, we prepared poly{[bis(diethynylphenyl)silylene]phenylene}s as the highly heat-resistant materials, which were soluble in organic solvent and could be spin coated to thin solid films. It was also found that polymer **3a** may be used as a precursor of silicon-containing semiconducting ceramic films.

3. Experimental

3.1. General procedure

All reactions were carried out under an atmosphere of dry nitrogen. Ether and THF were dried over sodium–potassium alloy and distilled just before use.

Methanol and triethylamine were distilled from magnesium methoxide and potassium hydroxide, respectively, and stored over activated molecular sieves until use. Poly[(diethoxysilylene)-*p*-phenylene] and poly[(ethoxymethylsilylene)-*p*-phenylene] were prepared as reported in the literature [8].

3.2. Preparation of bromo-3,5-bis[(trimethylsilyl)ethynyl]benzene

A mixture consisting of 10.0 g (31.8 mmol) of 1,3,5-tribromobenzene, 6.6 g (66.8 mmol) of (trimethylsilyl)acetylene, 21 mg of copper(I) iodide, 52 mg of tetrakis(triphenylphosphine)palladium(0), and 60 ml of triethylamine was stirred at 80 °C for 12 h. The resulting precipitates were filtered and the solvent was evaporated. The residue was chromatographed on a silica gel column eluting with hexane to give 5.0 g (45% yield) of 1-bromo-3,5-bis[(trimethylsilyl)ethynyl]benzene as pale yellow oil: MS m/z 348 (M$^+$). ^{1}H NMR (δ in CDCl$_3$) 0.22 (s, 18H, Me$_3$Si), 7.48 (t, 1H, $J = 1.7$ Hz, H on C4), 7.52 (d 2H, $J = 1.7$ Hz, H on C2 and C6). ^{13}C NMR (δ in CDCl$_3$) −0.23 (Me$_3$Si), 96.6, 102.4 (C≡C), 121.6, 125.0, 133.9, 134.4 (aromatic carbons). IR v(C≡C) 2158 cm^{-1}. Anal. Found: C, 55.02; H, 6.03. Calcd. for C$_{16}$H$_{21}$BrSi$_2$: C, 55.00; H, 6.06%.

3.3. Preparation of polymer 2b

To a solution of 3,5-bis[(trimethylsilyl)ethynyl]phenyllithium prepared from 1.00 g (2.86 mmol) of 1-bromo-3,5-bis[(trimethylsilyl)ethynyl]benzene and one equivalent of tert-butyllithium in 65 ml ether was added drop wise a solution of 0.31 g of poly[(ethoxymethylsilylene)-*p*-phenylene] ($M_w = 13\,700$, $M_n = 8000$) in 24 ml of ether. The mixture was stirred at room temperature for 18 h and then hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvents, the residue was reprecipitated from chloroform-ethanol to give 0.71 g (95% yield) of polymer **2b**: m.p. 219–223 °C. $M_w = 20\,500$ ($M_w/M_n = 1.5$). ^{1}H NMR (δ in CDCl$_3$) 0.19 (br s, 18H, Me$_3$Si), 0.79 (s, 3H, MeSi), 7.45–7.59 (br s, 7H, phenylene). ^{13}C NMR (δ in CDCl$_3$) −3.4 (MeSi), 0.0 (Me$_3$Si), 95.3, 104.5, (C≡C), 123.3, 123.4, 134.7, 136.6, 136.7, 138.1 (aromatic carbons). ^{29}Si NMR (δ in CDCl$_3$) −17.6, −11.0. IR v(C≡C) 2155 cm^{-1}. Anal. Found: C, 69.29; H, 6.79 [11]. Calcd. for (C$_{23}$H$_{28}$Si$_3$)$_n$: C, 71.06; H, 7.26%.

3.4. Preparation of polymer 2a

A mixture of 0.40 g of polymer **2b** ($M_w = 20\,500$, $M_n = 13\,500$), 0.39 g (2.79 mmol) of K$_2$CO$_3$, 19 ml of methanol, and 28 ml of THF was stirred at room temperature for 2 h. After evaporation of THF and an excess of MeOH under reduced pressure, the residue was reprecipitated from chloroform–methanol to give 0.19 g (77% yield) of polymer **2a**: m.p. >300 °C. $M_w = 15\,700$ ($M_w/M_n = 1.6$). ^{1}H NMR (δ in CDCl$_3$) 0.81 (MeSi), 3.02 (br s, 2H, CH), 7.46 (br s, 4H, phenylene), 7.53–7.64 (br m, 3H, ethynyl phenyl protons). ^{13}C NMR (δ in CDCl$_3$) −3.7 (MeSi), 78.2, 82.8, (C≡C), 122.1, 122.4, 134.7, 136.4, 136.9, 138.7 (aromatic carbons). ^{29}Si NMR (δ in CDCl$_3$) −10.9. IR v(C≡C) 2108 cm^{-1}, v(H–C≡) 3294 cm^{-1}. Anal. Found: C, 81.64; H, 5.16 [11]. Calcd. (C$_{17}$H$_{12}$Si)$_n$: C, 83.56; H, 4.95%.

3.5. Preparation of polymer 3b

To a solution of 3,5-bis[(trimethylsilyl)ethynyl]phenyllithium prepared from 0.31 g (0.89 mmol) of 1-bromo-3,5-bis[(trimethylsilyl)ethynyl]benzene and one equivalent of tert-butyllithium in 15 ml ether was added drop wise a solution of 0.060 g of poly[(diethoxysilylene)-*p*-phenylene] ($M_w = 12\,200$, $M_n = 6900$) in 7 ml of ether. The mixture was stirred at room temperature for 12 h and then hydrolyzed with water. Following the work up involving extraction similar to that for the preparation of **2b**, the organic residue was reprecipitated from chloroform-ethanol to give 0.16 g (79% yield) of polymer **3b**: m.p. 211–218 °C. $M_w = 23\,500$ ($M_w/M_n = 1.3$). ^{1}H NMR (δ in CDCl$_3$) 0.15 (br s, 36H, Me$_3$Si), 7.46–7.59 (br s, 10H, phenylene). ^{13}C NMR (δ in CDCl$_3$) −0.13 (Me$_3$Si), 95.6, 104.0, (C≡C), 123.3, 133.6, 134.2, 135.9, 137.1, 138.9 (aromatic carbons). ^{29}Si NMR (δ in CDCl$_3$) −17.7, −14.6. IR v(C≡C) 2155 cm^{-1}. Anal. Found: C, 70.71; H, 7.10. Calcd. for (C$_{38}$H$_{46}$Si$_5$)$_n$: C, 70.96; H, 7.21%.

3.6. Preparation of polymer 3a

Polymer **3a** was obtained from **3b** in 74% yield, by a reaction similar to the preparation of **2a**. m.p. >300 °C. $M_w = 19\,000$ ($M_w/M_n = 1.5$). ^{1}H NMR (δ in CDCl$_3$) 3.02 (br s, 4H, CH), 7.54–7.66 (br s, 10H, phenylene protons). ^{13}C NMR (δ in CDCl$_3$) 78.8, 82.5, (C≡C), 122.5, 133.8, 134.1 135.9, 137.2, 139.5 (aromatic carbons). ^{29}Si NMR (δ inCDCl$_3$) −14.6. IR v(C≡C) 2108 cm^{-1}, v(H–C≡) 3297 cm^{-1}. Anal. Found: C, 85.32; H, 4.19 [11]. Calcd. (C$_{26}$H$_{14}$Si)$_n$: C, 88.10; H, 3.98%.

3.7. Conductivity measurement of a thermally treated film of 3a

A polymer film was prepared by spin coating of the chloroform solutions (3 g/l) on a quartz plate. The quartz plate was heated at 1200 °C in vacuo (<10^{-5} Torr) for 4 h. The thickness of the resulting film was measured by a Stylus Surface Profiler ET-10 (Kosaka

Laboratory Ltd.). The conductivity of thin film was measured in air by the two-probe method at room temperature.

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