Synthesis and Characterization of Poly(arylene-ethynylene)s with Ferrocene Unit by Reaction of 1,1'-Bis(ethynyldimethylsilyl)ferrocene and Aromatic Dihalides

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New poly(arylene-ethynylene)s with silicon-containing ferrocene moiety in the polymer main chain were synthesized *via* the C-C bond forming reactions of 1,1′-bis(ethynyldimethylsilyl)ferrocene and various aromatic dihalides in high yields. The aromatic dihalides include 1,4-dibromobenzene, 4,4′-dibromobiphenyl, 9,10-dibromoanthracene, 2,5-dibromopyridine, 2,5-dibromothiophene, and 2,6-diiodo-4-nitroaniline. The polymer structures and properties were characterized by such instrumental methods as NMR (^{1}H-, ^{13}C-, and ^{29}Si-), IR, UV-visible spectroscopies and TGA/DSC. The spectral data indicated that the present polymers have the regular alternating structure of 1,1′-bis(ethynyldimethylsilyl)ferrocenylene and arylene units. The resulting polymers were completely soluble in such organic solvents as methylene chloride, chloroform, benzene, chlorobenzene, and THF. The thermal behaviors of the resulting polymers were examined.

Key Words: Aromatic dihalides, 1,1′-Bis(ethynyldimethylsilyl)ferrocene, Coupling reaction, Poly(arylene-ethynylene), Palladium catalyst

Introduction

One of the most useful properties of terminal acetylenes is their ability to couple under very mild conditions to form conjugated polyacetylenes.[1,2] The reactions included the Glaser oxidative coupling, the Chodkiewicz-Cadiot coupling of an acetylene with a 1-haloacetylene, and the Grignard reagent coupling. The Glaser and Chodkiewicz-Cadiot systems are the most important and they complement each other. Intense interest is naturally occurring polyacetylenes had spurred research on coupling reactions.[3,4] The oxidative coupling had been modified so that α,ω-diynes can be coupled and cyclized to macrocyclic polyacetylenes.[5] This coupling reaction has been applied for the preparation of linear polymers.[6]

Conjugated organic materials have attracted much attention because of their good ability to form thin films, good mechanical properties, excellent electro-optical properties, etc.[7-15] The class of conjugated polymers which has found the most attention in the past is undoubtedly the poly(*p*-phenylenevinylene)s (PPVs). Since the groups of Tang and Friend first demonstrated high-efficiency light-emitting diodes (LEDs) consisting of organic fluorescent dyes and π-conjugated polymers as an emitting materials,[16-18] dramatic improvements have been accomplished in the area of LEDs, flat-panel displays (FPDs), organic thin film transistors, active semiconductors, nonlinear optical devices, etc.[8,12,19]

The structurally closest relative to PPV, the poly(phenylene-ethynylene)s (PPEs) with internal acetylenic units in the polymer main chain have attracted much less attention in the polymer community, despite their interesting properties.[20-22] However, poly(arylene-ethynylene)s (PAEs) have been promising as molecular rods, shape-persistent molecular architectures, rigid rod-like polymers-building blocks for photonic devices, molecular recognition, and the construction of carbon networks, molecular wires in bridging nanogaps.[22]

The palladium-catalyzed coupling of terminal acetylenes to aromatic bromides or iodides in basic amines have been well known since 1975.[23-25] It is called the Heck-Cassar-Sonogashira-Hagihara reaction, which has been frequently used as one of various C-C coupling reactions in organic synthetic chemistry. Linear polymers of alternating ethynylene and arylene units were synthesized by a cross-coupling reaction utilizing the same catalyst.[22] Various organic polymers bearing silanylene and ethynylene units in the conjugated polymer backbone have been reported.[26-30] The organosilicon units with aromatic or flexible aliphatic group improved their processibility and limited the π-conjugation length, resulting in blue light-emitting diodes.[31,32] In our previous work, we reported the synthesis of new PAEs with 2,5-bis(ethynylene-dimethylsilylene)thienylene unit *via* the reaction of 2,5-bis (ethynyldimethylsilyl)thiophene and aromatic dihalides.[33] And we also prepared poly(dipropargylfluorene) *via* the oxidative coupling reaction of dipropargylfluorene in the presence of $(PPh_3)_2PdCl_2/CuI$.[34]

Here, we report the synthesis of new PAEs containing ferrocene unit by the reaction of 1,1′-bis(ethynyldimethylsilyl)ferrocene and various aromatic dihalides and the characterization of the resulting polymers.

Experimental Section

Materials. Ferrocene (Aldrich Chemicals, 98%), $(PPh_3)_2$-$PdCl_2$ (Aldrich Chemicals, 98%), Chlorodimethylsilane (Aldrich Chemicals, 98%), $PdCl_2$ (Aldrich Chemicals, 99%), and copper(I) iodide (Aldrich Chemicals, >99%) were used as received. *n*-Butyllithium (Aldrich Chemicals, 2.5 M in hexanes) and ethynylmagnesium bromide (Aldrich Chemicals, 0.5 M in tetrahydrofuran) were used as received. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) and aromatic dihalides were purchased from Aldrich Chemicals and uesd as received. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

General procedure. ^{1}H, ^{13}C, and ^{29}Si NMR were recorded on a Bruker Avance 400 and Varian 500 spectrometers in $CDCl_3$ at KBSI and the chemical shifts were reported in ppm units with tetramethylsilane (TMS) as an internal standard. Mass spectra were obtained by Shimadzu model QP-1000A spectrometer. Infrared spectra were obtained with Mattson Galaxy 7020A FT-IR spectrometer using a KBr pellet, and frequencies are given in reciprocal centimeters. GC analyses were performed on a Hewlett-Packard 5890 FID on a HP-1 capillary column (5% cross-linked methylphenylsilicone, 25m). UV-visible spectra were taken in THF on a Shimadzu UV -2100 PC spectrometer. Molecular weights were determined by a gel permeation chromatography (Waters 254) equipped with μ-Styragel columns using CH_2Cl_2 as an eluent. Monodisperse polystyrene standard samples were used for molecular weight calibration. Thermal properties of polymer were performed with SSC 5200H TG/DTA 320 and 5200H DSC 220 under a nitrogen atmosphere at a heating rate of 10 °C/min.

Synthesis of 1,1′-bis(dimethylsilyl)ferrocene. A 500 mL three-neck flask equipped with a magnetic bar, reflux condenser, and dropping funnel was charged with 12 mL (80 mmol) of TMEDA in 10 mL of anhydrous hexane. 50 mL (80 mmol) of *n*-BuLi (1.6 M in hexanes) was placed in the dropping funnel and slowly added dropwise to the vigorously stirred solution under nitrogen atmosphere at room temperature. 5 g (27 mmol) of ferrocene in 200 mL of anhydrous hexane was slowly added to the solution at room temperature. The orange-colored lithiated ferrocene was started to precipitate into the bottom. After stirring for additional 7 hrs at room temperature, 9 mL (81 mmol) of chlorodimethylsilane in 10 mL of anhydrous hexane was added dropwise to the reaction solution maintained at –78 °C (dry-ice/acetone bath). After addition was completed, the reaction mixture was stirred for additional 12 hrs at room temperature followed by filtration of the salts, then the organic layer was treated with water and the organic layer was dried over anhydrous magnesium sulfate. The volatile solvent was evaporated to give 1,1′-bis(dimethylsilyl)ferrocene as a red oil. The residue was purified by column chromatography on a silica gel column using with hexane eluent (5 g, 16.5 mmol, 61%). The physical properties are identical with those reported in the literature.[35] MS (m/z, rel. intensity): 302 (M^+, 100).

Synthesis of 1,1′-bis(chlorodimethylsilyl)ferrocene. In 500 mL two-neck flask equipped with a magnetic bar, rubber septum, and reflux condenser was placed a mixture of 5.0 g (16.5 mmol) of 1,1′-bis(dimethylsilyl)ferrocene and 5.8 g (32.7 mmol) of $PdCl_2$ in 200 mL dry CCl_4. The reaction mixture was heated to reflux for 12 hrs. The reaction progress was checked on a gas chromatograph. Filtration on celite and concentration under vacuum afforded 5.2 g (14.0 mmol, 85%) of the target compound. The physical properties are identical with those reported in the literature.[36] MS (m/z, rel. intensity): 370 (M^+,100) 372 (M+2, 74), 374 (M+4, 15).

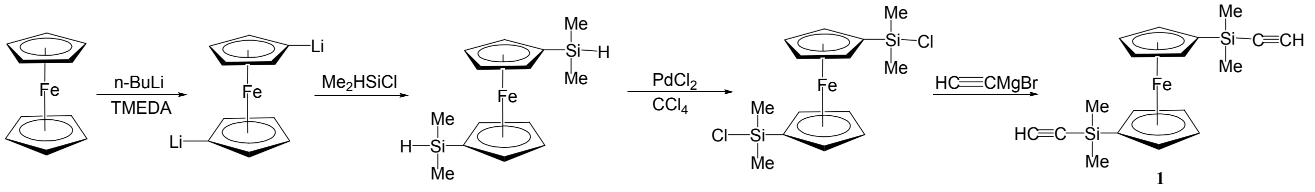
Synthesis of 1,1′-bis(ethynyldimethylsilyl)ferrocene (**1**). A 250 mL three-neck flask equipped with a magnetic bar, dropping funnel, and reflux condenser was charged with 90.0 mL (45.0 mmol) of 0.5 M ethynylmagnesium bromide in THF. A solution of 5.2 g (14.0 mmol) of 1,1′-bis(chlorodimethylsilyl) ferrocene in 10 mL THF was added dropwise to the solution at 0 °C. After the addition was finished, the reaction mixture was stirred for 12 hrs at 45 °C followed by filtration of the salts. The organic layer was treated with water and dried over anhydrous magnesium sulfate. The volatile solvent was evaporated and the residue was purified by column chromatograpy using alumina with hexane as eluent (3.2 g, 9.1 mmol, 65%). Compound **1**: IR (KBr, cm^{-1}): 2038 (C≡C), 3281 (≡C-H). MS (m/z, rel. intensity): 350 (M^+, 100) 335 (37). ^{1}H NMR ($CDCl_3$) : δ 0.43 (s, 12H, $SiCH_3$), 2.51 (s, 2H, C≡CH), 4.22 (s, 4H, Fc), 4.44 (s, 4H, Fc). ^{13}C NMR ($CDCl_3$) : δ -0.26 ($SiCH_3$), 68.00 (Fc), 72.39 (Fc), 73.54 (Fc), 89.10 (Si*C*≡C), 93.65 (C≡*C*H). Anal.calcd. for $C_{18}H_{22}FeSi_2$**:** C, 61.70; H, 6.33. Found: C, 61.44; H, 6.52.

Polymerization procedures. All polymerization procedures were carried out under dry nitrogen atmosphere because the active species are sensitive to moisture or oxygen. A typical polymerization procedure is as follows.

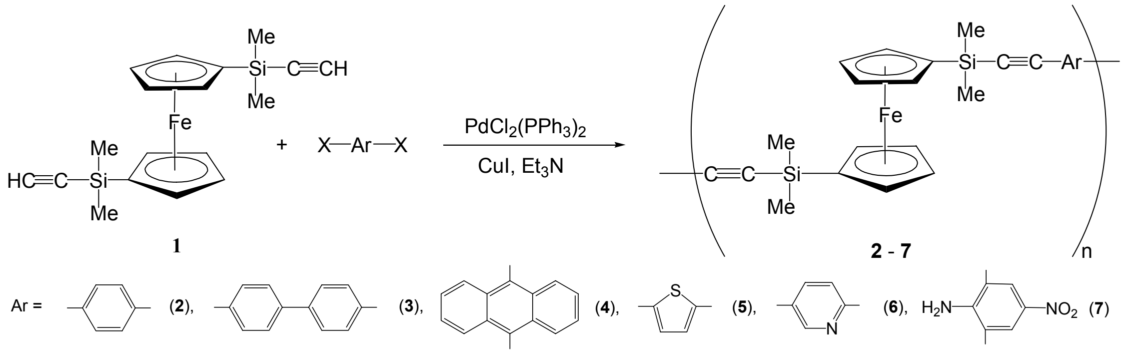
Polymerization of 1,1′-bis(ethynyldimethylsilyl)ferrocene and 1,4-dibromobenzene. In a magnetic-stirred 30 mL flask, 1,1-bis(ethynyldimethylsilyl) ferrocene (0.35 g, 1.0 mmol), 1,4-dibromobenzene (0.24 g, 1.0 mmol), $(PPh_3)_2PdCl_2$ (2 mg, 2.8×10^{-3} mmol), CuI (8.6 mg, 4.5×10^{-2} mmol), and 12 mL of triethylamine were added in that order given. Then the polymerization was carried out at 90 °C oil bath for 24 hrs under nitrogen atmosphere. After a given time of polymerization, the reaction mixture was filtered, and concentrated by using rotary evaporator. After adding 10 mL of THF, the polymer solution was precipitated into an large excess of pentane, filtered from the solution, and then dried under vacuum at 40 °C for 24 hrs. The product was purified with repeated precipitation of the THF solution of polymer into a large excess of pentane. On completion of the work-up, 0.3 g (71% yield, brown solid) of poly{[1,4-phenylene][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]}(**2**) was isolated. Compound **2**: M_w = 13700 (M_w/M_n = 1.60). IR (KBr, cm^{-1}): 2140 (C≡C). UV: λ_{max} (THF) 298 nm. ^{1}H NMR ($CDCl_3$): δ 0.45 (s, 12H, $SiCH_3$), 4.24 (s, 4H, Fc), 4.46 (s, 4H, Fc), 7.44 (s, 4H, phenylene protons). ^{13}C NMR ($CDCl_3$): δ -0.09 ($SiCH_3$), 68.57, 72.27, 73.60 (Fc carbons), 95.58 (Si*C*≡C), 105.01 (C≡*C*-Ar), 123.28, 131.81 (phenylene carbons). ^{29}Si NMR ($CDCl_3$): δ -19.95. DSC: 63 °C (endothermic), 224 °C (exothermic).

The other poly(arylene-ethynylene)s having different aromatic units were prepared according to the same procedure described above.

Poly{[4,4′-biphenylene][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]}(3): yield 80% (brown solid). M_w = 7100 (M_w/M_n = 2.01). IR (KBr, cm^{-1}): 2154 (C≡C). UV: λ_{max} (THF) 302 nm. ^{1}H NMR ($CDCl_3$): δ 0.49 (s, 12H, $SiCH_3$), 4.30 (s, 4H, Fc), 4.51(s, 4H, Fc), 7.52-7.60 (m, 8H, biphenylene protons). ^{13}C NMR ($CDCl_3$): δ -0.01 ($SiCH_3$), 68.70, 72.30, 73.64(Fc carbons), 94.39 (Si*C*≡C), 105.30 (C≡*C*-Ar), 122.43, 126.79, 132.46, 140.22 (biphenylene carbons). ^{29}Si NMR ($CDCl_3$): δ -20.85. DSC: 74 °C (endothermic), 245 °C (exothermic).



Scheme 1



Scheme 2

Poly{[9,10-anthrylene][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]}(4): yield 86% (brick red solid). M_w = 11500 (M_w/M_n = 2.77). IR (KBr, cm^{-1}): 2131 (C≡C). UV: λ_{max} (THF) 270, 398, 419, 444 nm. ^{1}H NMR ($CDCl_3$): δ 0.65 (s, 12H, $SiCH_3$), 4.43 (s, 4H, Fc), 4.60 (s, 4H, Fc), 7.59-7.63 (m, 4H, anthrylene protons), 8.53-8.69 (m, 4H, anthrylene protons). ^{13}C NMR ($CDCl_3$): δ 0.33 ($SiCH_3$), 68.68, 72.36, 73.63 (Fc carbons), 102.23 (Si*C*≡C), 107.18 (C≡*C*-Ar), 126.96, 128.22, 132.34, 133.31 (anthrylene carbons). ^{29}Si NMR ($CDCl_3$): δ -20.44. DSC: 79 °C (endothermic), 275 °C (exothermic).

Poly{[2,5-thienylene)][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]}(5): yield 70% (dark brown solid). M_w = 8600 (M_w/M_n = 2.43). IR (KBr, cm^{-1}): 2147 (C≡C). UV: λ_{max} (THF) 315, 330 nm. ^{1}H NMR ($CDCl_3$): δ 0.45 (s, 12H, $SiCH_3$), 4.23 (s, 4H, Fc), 4.46 (s, 4H, Fc), 7.09 (s, 2H, thienylene protons). ^{13}C NMR ($CDCl_3$): δ -0.21 ($SiCH_3$), 68.21, 72.37, 73.63 (Fc carbons), 97.38 (Si*C*≡C), 99.28 (C≡*C*-Ar), 124.69, 132.38 (thienylene carbons). ^{29}Si NMR ($CDCl_3$): δ -20.27. DSC: 62 °C (endothermic), 179 °C (exothermic).

Poly{[2,5-pyridylene][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]}(6): yield 45% (dark brown solid). M_w = 6900 (M_w/M_n = 1.78). IR (KBr, cm^{-1}): 2162 (C≡C). UV: λ_{max} (THF) 300 nm. ^{1}H NMR ($CDCl_3$): δ 0.48 (br. s, 12H, $SiCH_3$), 4.25 (s, 4H, Fc), 4.46 (s, 4H, Fc), 7.44, 7.73 (m, 2H, pyridylene protons), 8.67 (s, 1H, pyridylene proton). ^{13}C NMR ($CDCl_3$): δ -0.38, -0.27 ($SiCH_3$), 68.21, 72.37, 73.63 (Fc carbons), 96.26, 99.53(Si*C*≡C), 101.66, 103.87 (C≡*C*-Ar), 119.51, 126.54, 126.61 (pyridylene carbons), 138.76, 138.85 (pyridylene carbons), 141.82, 152.71 (pyridylene carbons). ^{29}Si NMR ($CDCl_3$): δ -19.53, -20.81. DSC: 61 °C (endothermic), 249 °C (exothermic).

Poly{[2,6-(4-nitroanilylene)][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]}(7): yield 62% (brick red solid). M_w = 7000 (M_w/M_n = 2.87). IR (KBr, cm^{-1}): 2147 (C≡C). UV: λ_{max} (THF) 362 nm. ^{1}H NMR ($CDCl_3$): δ 0.49 (s, 12H, $SiCH_3$), 4.22 (s, 4H, Fc), 4.43 (s, 4H, Fc), 5.53 (s, 2H, NH_2), 8.15 (s, 2H, phenylene protons). ^{13}C NMR ($CDCl_3$): δ -0.22 ($SiCH_3$), 67.97, 72.23, 73.45 (Fc carbons), 99.05 (Si*C*≡C), 101.92 (C≡*C*-Ar), 106.74, 128.39, 137.52, 153.93 (phenylene carbons). ^{29}Si NMR ($CDCl_3$): δ -20.19. DSC: 67 °C (endothermic), 242 °C (exothermic).

Results and Discussion

Ferrocene-containing ethynylsilyl compound, 1,1′-bis (ethynyldimethylsilyl)ferrocene, was prepared according to the Scheme 1. 1,1′-Bis(dimethylsilyl)ferrocene was prepared by the reaction of dilithioferrocene and chlorodimethylsilane at low temperature. The oily orange product was obtained in 61% yield. The intermediate, 1,1′-bis(chlorodimethylsilyl)-ferrocene, was prepared by the reaction of 1,1′-bis(dimethylsilyl)ferrocene and $PdCl_2$ in CCl_4 solvent. The oily red product was obtained in 85% yield. The diethynyl ferrocene monomer, 1,1′-bis(ethynyldimethylsilyl)ferrocene, was prepared *via* the reaction of 1,1′-bis(chlorodimethylsilyl)ferrocene and ethynylmagnesium bromide in 65% yield.

The polymers containing ethynylene units in the polymer main chain were synthesized by the Heck coupling reaction of bis(ethynylenedimethylsilyl) ferrocene and aromatic dihalides as shown in Scheme 2. The aromatic dihalides include 1,4-dibromobenzene, 4,4′-dibromobiphenyl, 9,10-dibromoanthracene, 2,5-dibromothiophene, 2,5-dibromopyridine, and 2,6-diiodo-4-nitroaniline.

The properties of resulting poly[(arylene)(1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]s are summarized in Table 1. A mixture of 1 equivalent of 1,1′-bis(ethynyldimethylsilyl)ferrocene and 1,4-dibromobenzene in the presence of $(PPh_3)_2PdCl_2$-CuI catalyst system in triethylamine was heated up to 90 °C. The polymerization was carried out for 24 hrs. The reaction was monitored by the disappearance of C≡C bond stretching absorption in the IR spectrum of 1,1′-bis(ethynyldimethylsilyl)ferrocene at 2038 cm^{-1}. The

Table 1. Properties of Poly[(arylene)(1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]s

Polymer	NMR (ppm)				IR ν(C≡C) (cm^{-1})	UV λ_{max}, nm	M_w (M_w/M_n)	
	^{13}C^{a}		^{1}H	^{29}Si				
	C_α	C_β	SiMe					
2	95.58	105.01	0.45	-19.95	2140	298	13700	(1.60)
3	94.39	105.30	0.49	-20.85	2154	302	7100	(2.01)
4	102.23	107.18	0.65	-20.44	2131	270, 398, 419, 444	11500	(2.77)
5	97.38	99.28	0.45	-20.27	2147	315, 330	8600	(2.43)
6	96.26, 99.53	101.66, 103.87	0.48	-19.53, -20.81	2162	300	6900	(1.78)
7	99.05	101.92	0.49	-20.19	2147	362	7000	(2.87)

[a] Si-C_α≡C_β-Ar

brown polymeric product was obtained in 71% yield. The polymer yields for the present coupling reaction by using such aromatic dihalides as 4,4′-dibromodiphenyl, 9,10-dibromoanthracene, and 2,5-dibromothiophene, were 80%, 86%, and 70%, respectively. However, in the cases of aromatic dihalides such as 2,5-dibromopyridine and 2,6-diiodo-4-nitroaniline, the polymer yields were found to be relatively low (45% and 62%, respectively). The reason for the low polymer yields was deduced to be due to the catalytic poisoning effect of the heteroatom of aromatic rings. The weight-average molecular weight (M_w) of the resulting polymers were in the range of 7000-13700, whereas the polydispersities were in the range of 1.60-2.87. The polymer showing the highest molecular weight was obtained when 1,4-dibromobenzene was used as aromatic dihalide. These polymers were completely soluble in such common organic solvents as methylene chloride, chloroform, benzene, chlorobenzene, THF, etc. The chemical structures of resulting polymers were characterized by NMR (^{1}H, ^{13}C and ^{29}Si), infrared, and UV-visible spectroscopies.

Figure 1 shows the ^{1}H NMR spectrum of poly{[1,4- phenylene][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]} (**2**) in $CDCl_3$. The aromatic proton peaks of phenylene and ferrocene moieties are shown in 7.44, 4.24, and 4.46 ppm, respectively. The methyl proton peak of dimethylsilylene moiety is observed at 0.45 ppm as singlet. As shown in Table 1, the chemical shifts of methyl proton peaks for the dimethylsilylene groups of these polymers were in the range of 0.45-0.65 ppm, depending on the structures of aromatic dihalides used. The acetylenic proton peak of 1,1′-bis(ethynyldimethylsilyl)ferrocene (**1**) at 2.51 ppm was not seen in the ^{1}H NMR spectrum of the polymers.

Figure 2 shows the ^{13}C NMR spectrum of **2** in $CDCl_3$. The aromatic carbon peaks of polymer chain were observed at 123.28 and 131.81 ppm (phenylene carbons) and 68.57, 72.27, and 73.60 ppm (ferrocenylene carbons), respectively. The methyl carbon peaks of dimethylsilylene groups is seen at -0.09 ppm. As shown in Table 1, the carbon peaks for both the ethynylene carbons, C_α and C_β, of the polymer **2** are at 95.58 and 105.01 ppm, and these values are more deshielded relative to those for the monomer, 1,1′-bis(ethynyldimethylsilyl) ferrocene (**1**). The signal for the C_α (102.23 ppm) of ethynylene unit of poly{[9,10-anthrylene][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]} (**4**) appears farther downfield with respect to those for the other polymers, because there may be some electron delocalization in this polymer.[37] In the ^{13}C and ^{29}Si NMR spectra of poly{[2,5-pyridylene][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]} (**6**), multiful resonances at 96.26, 99.53 ppms (Si*C*≡C) and 101.66, 103.87 ppms (C≡*C*-Ar) and two resonances at -20.81 and -19.53 ppms for silicon peaks of dimethylsilylene moiety observed may be caused by each ethynylpyridine linkage being in either the 2- or 5-position of pyridine in the polymer backbone. The ^{29}Si NMR spctrum data of these polymers is also given in Table 1. These results suggest that the polymers have the regular alternating structure of arylene and bis(ethynylenedimethylsilylene)ferrocenylene unit. It was reported that the multiple resonances for ethynylene carbons of the 2,5-pyridylene polymers containing a tetraphenylsilole[37], diphenylsilylene unit[38b] and disilanylene

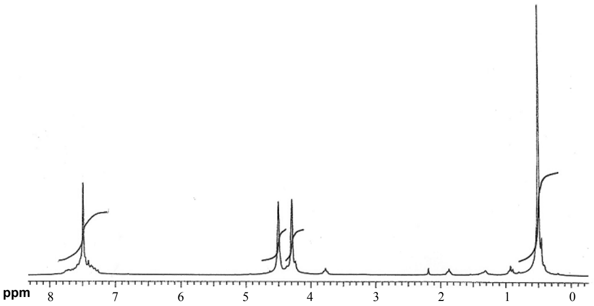


Figure 1. ^{1}H NMR spectrum of poly{[1,4-phenylene][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]} (**2**) in $CDCl_3$.

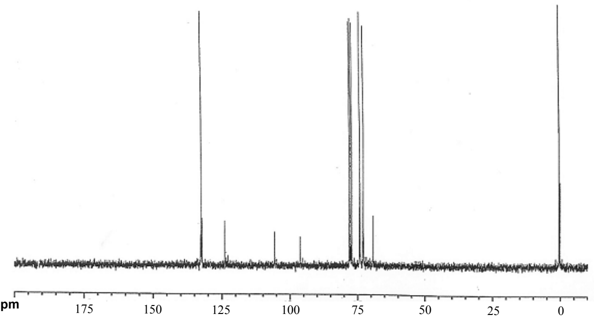


Figure 2. ^{13}C NMR spectrum of poly{[1,4-phenylene][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]} (**2**) in $CDCl_3$.

unit.[38c] The IR spectra of poly[arylene-bis(ethynylenedimethylsilylene)ferrocenylene] (**2-7**) in KBr pellet did not show any terminal acetylenic ≡C-H bond stretching frequencies around 3280 cm^{-1}. Instead, the C≡C bond stretching frequencies of internal ethynylene units were observed between at 2131 and 2162 cm^{-1} in Table 1. The C≡C bond stretching absorption of the polymer **4** containing anthrylene occurs at the lowest wave number 2131 cm^{-1} as Corriu has observed in the case of the polymer containing tetraphenylsilole[37] or diphenylsilylene[38a] in the backbone. This is probably due to some degree of conjugation between anthrylene and ethynylene units for **4**. The aliphatic and aromatic C-H stretching peaks of the polymers were observed in the range of 2955-2965 cm^{-1} and 3075-3092 cm^{-1}, respectively. The Si-CH_3 group of the polymers was recognized by a strong and sharp band at about 1250 cm^{-1} together with one strong band at about 812 cm^{-1}. The UV absorption bands of the present polymers **2**-**7** are summarized in Table 1.

Thermal properties of polymers were studied by thermogravimetric analyses and differential scanning calorimetry. TGA thermograms were obtained under nitrogen atmosphere at a heating rate of 10 °C/min up to 900 °C. As shown in Figure 3, the TGA thermogram of poly[phenylene-bis(ethynylenedimethylsilylene)ferrocenylene] (**2**) showed the first weight loss in the temperature range of 200-300 °C (7.82 % weight loss after 485 °C). And it showed second weight loss over the wide temperature range of 485-900 °C. This polymer showed high char yield (73.65%) after exposing to high temperature (900 °C). The high content of residual weight even after 900 °C may be deduced to be due to the formation of carbons containing ceramics, such as β-SiC matrices under inert atmosphere. The IR spctrum of ash obtained by the carbonization of this polymer at 900 °C shows a strong absorption at 1089 cm^{-1} of $\upsilon_{Si\text{-}O}$ with a weak shoulder around 1200 cm^{-1} due to $\upsilon_{Si\text{-}C}$ as Kunai had observed in the IR spectrum of the organosilicon polymers with diethynylanthracene unit in the polymer main chain.[39]

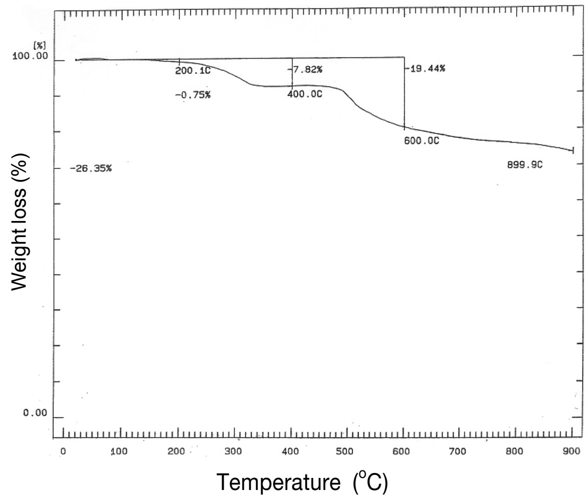


Figure 3. TGA thermogram of poly{[1,4-phenylene][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]} (**2**) measured under nitrogen atmosphere at a heating rate of 10 °C/min.

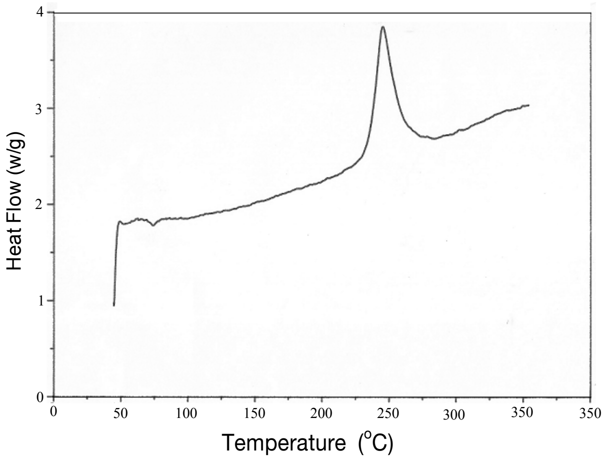


Figure 4. DSC thermogram of poly{[4,4′-biphenylene][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]} (**3**) measured under nitrogen atmosphere at a heating rate of 10 °C/min.

Figure 4 shows the DSC thermogram of poly{[4,4′-biphenylene][1,1′-bis(ethynylenedimethylsilylene)ferrocenylene]} (**3**). This polymer shows small endothermic peak at 75 °C, which may be due to the glass-transition of polymer chain. The exothermic reaction started at about 200 °C (the peak temperature: 245 °C). The exothermic peak was originated by the thermal cross-linking of the ethynylene units in the polymer main chain and/or the initial thermal decomposition.[40]

Conclusions

We prepared various alternating copolymers composed of 1,1′-bis(dimethylsilylethynylene)ferrocenylene and arylene units by using the Heck coupling reaction. The polymer structure was characterized by various instrumental methods to have the regular alternating structure of 1,1′-bis(dimethylsilylethynylene)ferrocenylene and arylene units. The polymers were generally soluble in halogenated hydrocarbons and various aromatic solvents. The thermal behavior of polymers was examined by thermogravimetric analyses and differential scanning calorimetry. These polymers were found to be thermally stable up to 200 °C. The high char yields of these polymers after heating up to 900 °C were concluded to be due to the formation of SiC matrices.

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