

Synthesis and Properties of Poly(ferrocenylsilane)s Containing Si-Vinylene Units in the Main Chain

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Abstract

Poly(ferrocenylsilane)s containing Si-vinylene unit in the main chain have been synthesized by Mizoroki-Heck reaction of 1,1'-bis(dimethylvinylsilyl)ferrocene (MVFS) and dibromo aryl compounds using palladium diacetate as a catalyst. The alternating copolymers with relatively low molecular weight were obtained in good yields. Cyclic voltammetry of the copolymers in CH₂Cl₂ solutions showed redox potential derived from the ferrocene units in the copolymers. The voltammograms the copolymers indicated that almost no difference in numbers of electron transfer compared with MVFS. By contrast, diffusion coefficients of the ferrocene units in the copolymers were smaller than that of MVFS. The copolymers showed reversible electrochromism from yellow to blue-green due to the redox of ferrocene units in the main chain by 3V of application.

Keywords: poly(ferrocenylsilane), vinylene unit, Mizoroki-Heck reaction, copolymerization

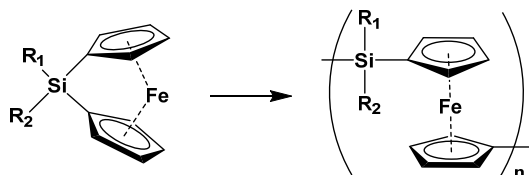
1. Introduction

Metallocene containing polymers have been developed because of their high potentials such as redox, magnetic, photo-physical, and catalytic properties (for example Abd-El-Aziz, Agatemor, & Etkin, 2014). Poly(ferrocene) is one of the most synthesized and studied metallocene containing polymers due to their characteristic features derived from the ferrocene units in the polymer. The main chain type poly(ferrocene)s have been synthesized by ring opening polymerization, condensation polymerization, coupling reaction, and so on (for examples Bellas & Rehahn, 2007; Miles, Ward, & Foucher, 2009; Miles, Ward, & Foucher, 2010; Wang, Huo, Ding, & Tan, 2008; Huo, Wang, Yu, Deng, Zhou, & Yang, 2007; Cazacu, Munteanu, Racles, Vlad, & Marcu, 2006; Caracu, Vlad, Marcu, Racles, Airinei, & Munteanu, 2006; Southard & Curti, 2001). Poly(ferrocenylsilane)s have been widely synthesized by ring opening polymerization of Si bridged ferrocene compounds, as shown in Scheme 1 (for example Bellas & Rehahn, 2007). Modification of substituted groups, R₁ and R₂ in Scheme 1, of the Si bridge of ferrocene compounds or resulting polymers, and copolymerization are usable to develop the highly functionalized poly(ferrocenylsilane)s (for examples Zechel, Hultsch, Rulkens, Balaishis, Pudelski, Lough, & Manners, 1996; Nanjo, Cyr, Liu, Sargent, & Manners, 2008; Qian, Lu, Cambridge, Guerin, Manners, & Winnik, 2012; Sui, Hempenius, & Vancso, 2012; Wang, Wang, Wang, Chen, Yu, Wang, & Wang, 2006; Gilroy, Rupar, Whittell, Chabanne, Terrill, Winnik, Manners, & Richardson, 2011; Roerdink, van Zanten, Hempenius, Zhou, Feijen, & Vancso, 2007; Ren, Shaushan, Liu, & Tong, 2007; Bunz, Maker, & Porz, 2011).

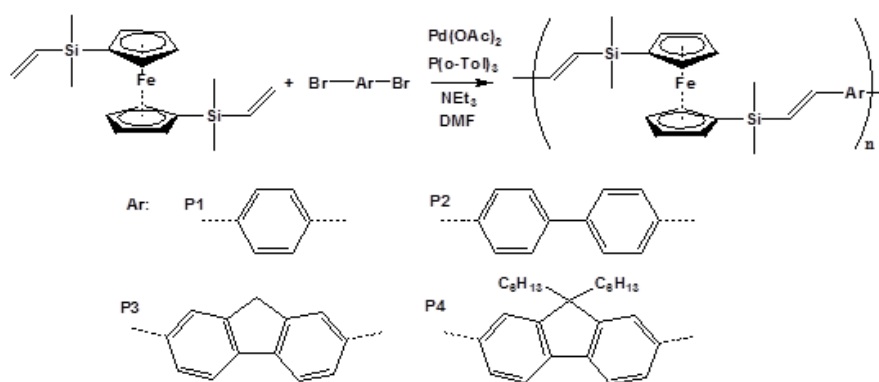
Incorporation of the ferrocene units in the main chain of π -conjugated polymers has been investigated by metathesis polymerization, Pd catalyzed coupling polymerization, and click reaction (Bueretea & Tilley, 1997; Heo, Park, & Lee, 2005; Weyhardt & Plenio, 2008; Masson, Lugh, & Manners, 2008; Lang, Voll, Inglis, Dingenouts, Goldmann, Barner, & Barner-Kowollik, 2011; Choi, Lee, Joo, Lee, Lee, & Chae, 2007; Yamamoto, Morikita, Maruyama, Kubota, & Katada, 1997; He, Gadt, Jones, Scholes, Manners, & Winnik, 2009). Sheridan et al. synthesized poly(ferrocenylsilane)s having conjugation units in the main chain using hydrosilylation reaction of 1,1'-bis(dimethylsilyl)ferrocene and diethynylbenzenes (Jain, Lalancette, & Sheridan, 2004). The resulting copolymers have ferrocene, silyl, and phenylene-vinylene units in the polymer backbone.

We developed fluorene- and carbazole-based alternating copolymers containing Si-vinylene units in the main chain (Naga, Tagaya, Noda, Imai, & Tomoda, 2008; Naga, Ohkura, Tagaya, & Tomoda, 2011). These copolymers were synthesized by alternating copolymerization of dibromofluorene or dibromocarbazole with Si containing divinyl or diallyl compounds using Mizoroki-Heck reaction with a Pd catalyst. Incorporation of Si and unsaturated vinylene units

in the main chain of the conjugated polymers was effective to improve solubility of the polymers in organic solvents. Furthermore, the copolymerization is usable to control the photophysical properties of the conjugated polymers. We came to an idea to synthesize poly(ferrocenylsilane)s containing Si-vinylene units in the main chain using the alternating copolymerization. This paper reports the alternating copolymerization of 1,1-bis(dimethylvinylsilyl)ferrocene (MVSF) with aromatic dibromo compounds (ArBr_2) using Mizoroki-Heck reaction with a Pd catalyst, as shown in Scheme 2, and the photophysical and electro chemical properties of the resulting copolymers.



Scheme 1. Synthesis of poly(ferrocenylsilane) by ring-opening polymerization of bridged ferrocene.



Scheme 2. Synthesis of poly(ferrocenylsilane)s containing Si-vinylene unit in the main chain by Mizoroki-Heck reaction of bis(dimethylvinylsilyl)ferrocene (MVFS) and dibromo aryl compounds.

2. Method

2.1 Materials

Ferrocene (Tokyo Chemical Industry Co., Ltd.), *n*-butyllithium (1.63 M *n*-hexane solution, Kanto Chemical Co. Ltd.), *N,N,N',N'*-tetramethylethylenediamine (TMEDA, Kanto Chemical Co. Ltd.), and chlorodimethylvinylsilane (AZmax.co) were commercially obtained, and used without further purification. *n*-Hexane was dried over calcium hydride under refluxing for 6 h and distilled before use under nitrogen atmosphere. Palladium(II) acetate ($\text{Pd}(\text{OAc})_2$) (Sigma-Aldrich Co. LLC.), tri-*o*-tolylphosphine ($\text{P}(\text{o-Tol})_3$) (Kanto Chemical Co. Ltd.), triethylamine (NEt_3) (Kanto Chemical Co. Ltd.), and *N,N*-dimethylformamide (DMF) (dehydrated grade, Kanto Chemical Co. Ltd.), were commercially obtained and used as received. *p*-Dibromobenzene (Bz, Kanto Chemical Co. Ltd.), 4,4'-dibromobiphenyl (BPh, Sigma-Aldrich Co. LLC.), 2,7-dibromofluorene (Flu, Wako Pure Chemical Industries, Ltd.), and 9,9'-dihexyl-2,7-dibromofluorene (HFlu, Sigma-Aldrich Co. LLC.) were commercially obtained and used without further purification.

Indium tin oxide (ITO) coated glass slide (surface resistivity: 8-12 Ω/sq) was purchased from Sigma-Aldrich Co. LLC. Chloroform and CH_2Cl_2 (spectroscopy grade) were commercially obtained from Dojindo Molecular Technologies, Inc. Tetrabutylammonium hexafluorophosphate was commercially obtained from Tokyo Chemical Industry Co., Ltd., and used as received.

2.2 Synthesis of 1,1-bis(dimethylvinylsilyl)Ferrocene (MVSF)

MVSF was synthesized according to the previous report (Majchrzak, Marciniec, Kubicki, & Pawelczyk, 2005). A *n*-hexane solution of *n*-butyllithium (40.0 mmol, 1.63 M, 24.5 mL) was added dropwise to a hexane (80 mL) solution of TMEDA (40.8 mmol) and ferrocene (19.9 mmol) at room temperature under nitrogen atmosphere, and the reaction system was stirred for 20 h. The reaction system was cooled to -78°C , and chlorodimethylvinylsilane (41.8 mmol) was added dropwise to the reaction solution, and stirred for 25 min. The reaction system was gradually warmed to room temperature, and stirred for 8 h. The solvent was evaporated, and the products was purified by silica gel column using

n-hexane as an eluent.

2.3 Synthesis of Poly(ferrocenylsilane)s Containing Si-vinylene Unit in the Main Chain

The copolymerization was carried out in a 100 mL glass reactor equipped with a magnetic stirrer. Equivalent molar of MVSF (1.25 mmol) and a ArBr_2 (1.25 mmol) were added to the reactor under nitrogen atmosphere. $\text{P}(o\text{-Tol})_3$ (0.25 mmol), NEt_3 (3.13 mmol), and a DMF solution (4.0 mL) of $\text{Pd}(\text{OAc})_2$ (0.05 mmol) were introduced to the reactor. The copolymerization was conducted at 100°C for 24 h. The reaction was terminated by adding a small amount of methanol. The polymer was precipitated in a large excess of methanol and recovered by decantation. The copolymer obtained was dissolved in chloroform and re-precipitated in methanol. The precipitate was collected by decantation and dried in vacuo at 60°C for 6 h.

2.4 Analytical Procedures

^1H NMR spectra of the copolymers were recorded at room temperature on a JEOL-JNM-LA300 spectrometer in pulse Fourier transform mode. The sample solution was made in CDCl_3 as a solvent and the resonance of CDCl_3 (7.24 ppm) was used as an internal reference. Molecular weight and molecular weight distribution of the copolymers were measured at 40°C by means of gel-permeation chromatography, SHIMADZU Prominence GPC System, using chloroform as a solvent, and calibrated with standard polystyrene samples. UV-vis absorption spectroscopy of the copolymers was conducted with SHIMADZU UV-1200 in a chloroform or CH_2Cl_2 solution. Photoluminescence (PL) spectroscopy was investigated with a SHIMADZU RF-1500 in a chloroform solution of the copolymer. Cyclic voltammetry was conducted with Electrochemical Measurement System HZ-5000 (Hokuto Denko) using $\text{Ag}|\text{AgCl}$ reference electrode, glassy carbon working electrode, and Pt counter electrode at a scan rate of 0.1 V/s. Voltage for electrochromism observation was applied by GP 025-5 (Takasago Ltd.) ranged from 0 to 3.0 V at a scan rate of 10 mV/s.

3. Results and Discussion

3.1 Synthesis and Structure of Poly(ferrocenylsilane)s

Copolymerizations of MVSF with ArBr_2 compounds have been investigated with $\text{Pd}(\text{OAc})_2$ in DMF at 100°C. The results are summarized in Table 1. Although the molecular weights of the copolymers were relatively low, the corresponding copolymers were obtained in good yield.

Table 1. Synthesis of alternating copolymers of MVFS with ArBr_2 , and their structure and optical properties

Sample	ArBr_2	Yield [wt%]	M_n [g/mol]	M_w/M_n	Absorption ^a [nm]	Emission ^{a,b} [nm]
P1	Bz	46	2000	1.9	275	381, 416
P2	BPh	37	2100	2.0	275	386, 418
P3	Flu	53	2900	3.1	275	385, 420
P4	HFlu	75	3000	6.0	275	380, 420
MVSF					275	379, 418
Ferrocene					275	381, 416

^a Evaluated in CHCl_3 (10^{-8} mol/L of ferrocene unit). ^b Emission was exited at λ_{max} of absorption.

Structure of the copolymers was studied by ^1H NMR spectroscopy. Figure 1 shows ^1H NMR spectrum of P1 prepared by the copolymerization of MVFS and Bz. The signals derived from methyl, cyclopentadienyl, vinylene, and phenyl groups are observed at 0.3-0.4, 4.1-4.4, 6.6-6.9, and 7.4 ppm, respectively. The peaks assignments of the ^1H NMR spectra of the obtained copolymers are listed below. P1 (ppm) : 0.3-0.4 (d, 12H), 4.1-4.4 (m, 8H), 6.6-6.9 (m, 4H), 7.4 (s, 6H); P2 (ppm) : 0.3-0.4 (d, 12H), 3.9 (s, 2H), 4.2-4.4 (m, 8H), 6.6-6.9 (m, 4H), 7.6 (m, 8H); P3 (ppm) : 0.3-0.4 (d, 12H), 4.1-4.4 (m, 8H), 6.6-6.9 (m, 4H), 7.4-7.7 (m, 6H); P4 (ppm) : 0.3-0.4 (m, 18H), 0.6-1.1 (m, 20H), 4.1-4.4 (m, 8H), 6.6-6.9 (m, 4H), 7.4-7.7 (m, 6H). These chemical shift assignments and quantitative analyses of the peaks intensity cleared that the copolymerizations yielded the corresponding copolymers.

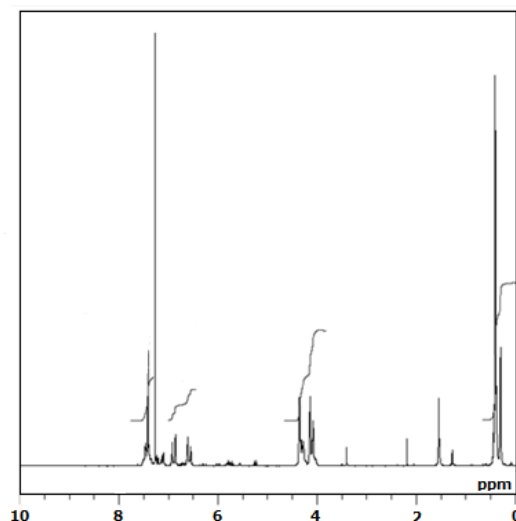


Figure 1. ^1H NMR spectrum of P1.

3.2 Optical Properties

UV-vis and PL spectra of the copolymers were acquired in chloroform. Figure 2 shows absorption and emission spectra of P1. The wavelengths UV-vis and PL spectra of the copolymers are summarized in Table 1. All the copolymers showed an absorption peak at 275 nm, and emission peaks at around 380 and 420 nm. These wavelengths were almost same those of MVSF or ferrocene. The absorption and emission of the copolymers are derived from ferrocene units, and their wavelengths are independent of structure of the aryl units.

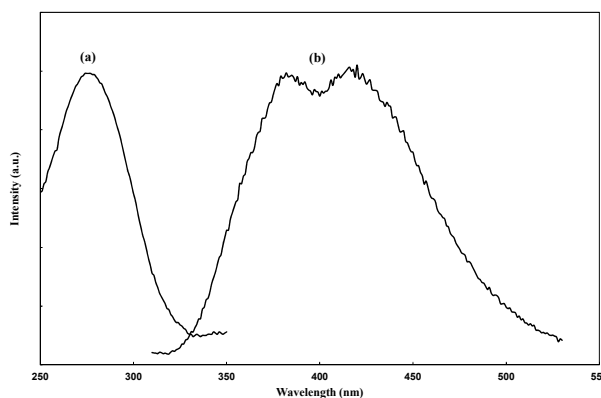


Figure 2. UV-vis (a) and PL (b) spectra of P1 in CHCl_3 solution, 10^{-8} mol/L of ferrocene unit, emission was excited at λ_{max} of absorption of 275 nm.

3.3 Electrochemical Properties

Wang et al. reported effect of molecular structure of poly(ferrocenylsilane)s on electrochemical behavior (Wang, Wang, Wang, Chen, & Chen, 2006; Wang, Wang, Wang, & Chen, 2007). Electrochemical properties of the present copolymers in CH_2Cl_2 solution containing 0.1 M of tetrabutylammonium hexafluorophosphate were investigated with cyclic voltammetry. The results are summarized in Figure 3, and Table 2. The copolymers showed redox potential, derived from ferrocene units in the main chain. All the copolymers and MVFS, which have dimethylsilylene-vinylene units, showed higher $E_{1/2}$ values than that of ferrocene, indicating shift of the voltammograms to anode due to the electron withdrawing of the ferrocene units by the vinylene units. ΔE values of the copolymers (0.08 -0.11 V) were almost same with those of the MVFS. The results indicate almost no difference in numbers of electron transfer between the copolymers and MVFS. By contrast, I_{pa} and I_{pc} of the copolymers were smaller than those of MVFS. Small diffusion coefficient of the ferrocene units in the copolymers, which was caused by large molecular weight, should decrease the I_{pa} and I_{pc} values of the copolymers.

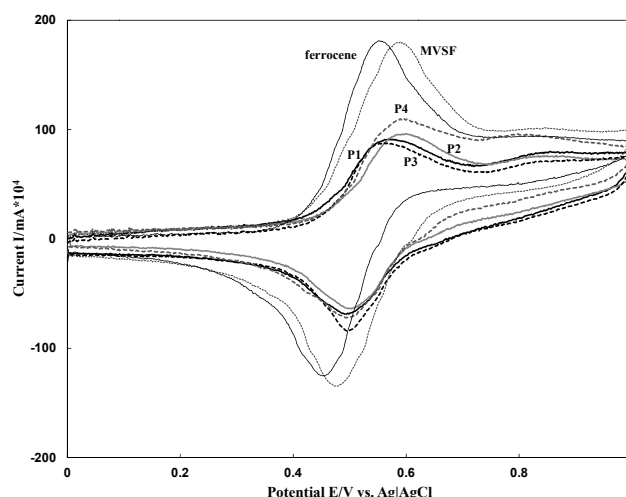


Figure 3. Cyclic voltammograms of alternating copolymers of MVFS with ArBr_2 , P1: black bold line, P2: black dot line, P3: gray bold line, P4: gray dot line, MVFS: thin dot line, and ferrocene: thin line, in CH_2Cl_2 containing 0.5 mM of ferrocene unit and 0.1 M of tetrabutylammonium hexafluorophosphate, at a scan rate of 0.1 V/s.

Table 2. Electrochemical properties of MVFS/ ArBr_2 alternating copolymers ^a

Sample	E_{pa} [V]	I_{pa} [mA*10 ⁴]	E_{pc} [V]	I_{pc} [mA*10 ⁴]	$E_{1/2}$ [V]	ΔE [V]
P1	0.57	91.1	0.49	-68.7	0.53	0.08
P2	0.60	96.2	0.50	-63.8	0.55	0.10
P3	0.57	87.7	0.49	-84.2	0.53	0.08
P4	0.60	110.1	0.49	-72.2	0.55	0.11
Ferrocene	0.55	181.2	0.46	-125.3	0.50	0.10
MVFS	0.59	180.1	0.48	-134.7	0.53	0.11

^a Determined by cyclic voltammetry of CH_2Cl_2 solution of the copolymers containing 0.5 mM of ferrocene unit and 0.1 M electrolyte (tetrabutylammonium hexafluorophosphate) at scan rate of 0.1 V/s. E_{pa} = peak anodic potential; I_{pa} = peak anodic current, E_{pc} = peak cathodic potential; I_{pc} = peak cathodic current; $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$, ΔE = difference between E_{pa} and E_{pc} .

3.4 Electrochromism

Electrochromism of the polymer in CH_2Cl_2 solution was investigated in an ITO cell shown in Figure 4. UV-vis spectra of the P2 solution containing tetrabutylammonium hexafluorophosphate in the ITO cell without or with applied voltage are shown in Figure 5. The application of 3.0 V increased intensity of the absorption ranged from 200-450 nm. Figure 6 shows photos of the ITO cell containing the P2 solution. The change of UV-vis spectrum induced electrochromism of the polymer solution from yellow to blue-green derived from oxidation of ferrocene units in the polymer chain. The electrochromism was reversible for several times of electronic cycles. The copolymers of P1, P2, and P4 showed similar electrochromism behavior.

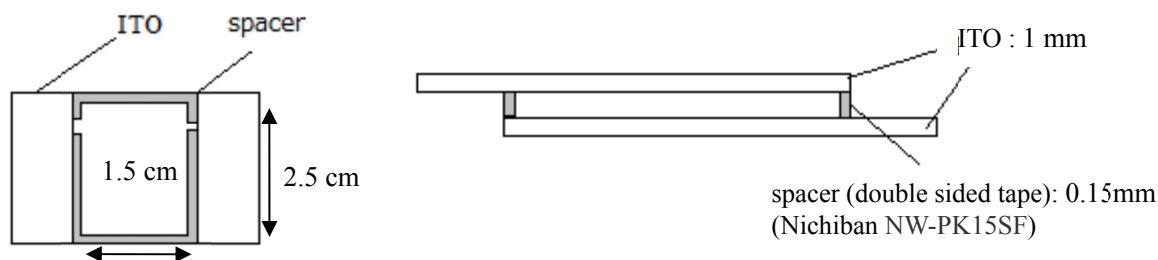


Figure 4. Sandwich-type ITO electrode cell.

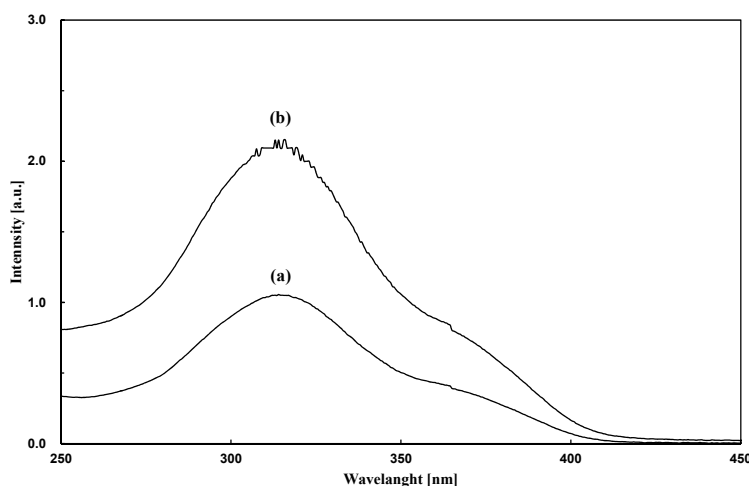


Figure 5. UV-vis spectra of CH_2Cl_2 solution of P2, (a) without voltage, (b) with 3.0 V containing 1.0 M of ferrocene unit and 0.2 M of tetrabutylammonium hexafluorophosphate.

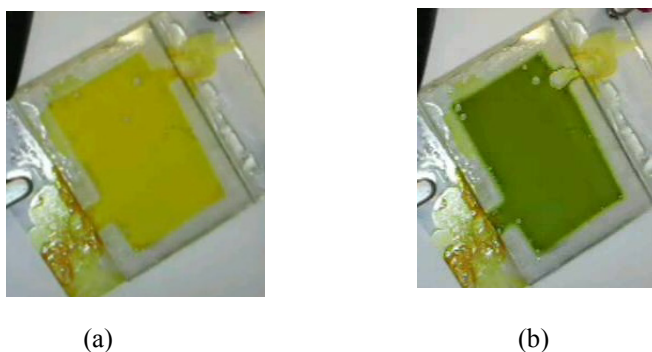


Figure 6. Photos of CH_2Cl_2 solution of P2 in ITO cell, (a) without voltage, (b) with 3.0 V, containing 1.0 M of ferrocene unit and 0.2 M of tetrabutylammonium hexafluorophosphate.

4. Conclusions

Poly(ferrocenylsilane)s containing Si-vinylene unit in the main chain were obtained with Mizoroki-Heck reaction of bis(dimethylvinylsilyl)ferrocene and dibromo aryl compounds using $\text{Pd}(\text{OAc})_2$ catalyst. The copolymers showed good solubility in CHCl_3 and CH_2Cl_2 . The CHCl_3 solutions of the copolymers showed absorption and photo luminescence derived from the ferrocene units in the copolymers. The absorption and luminescence wavelengths were almost independent of the molecular structure of the aryl compounds. The cyclic voltammograms of the alternating copolymers indicated the electron withdrawing of the ferrocene units by the vinylene units, and small diffusion coefficient of the ferrocene units in the copolymers caused by low mobility derived from large molecular weight. The copolymers also showed reversible electrochromism due to the redox of the ferrocene units in the main chain.

Although, the present copolymerization should be one of the useful methods to design and synthesize the poly(ferrocenylsilane)s containing conjugation, the molecular weights of the copolymers were too low to form the films. Furthermore, the optical properties of the copolymers were independent with the structure of Ar units. The ferrocene units are dominant of the optical properties of the copolymers. As the next step, we are trying to synthesize the high molecular weight poly(ferrocenylsilane)s containing long conjugation, which can control the optical properties of the resulting copolymers, and the results will be reported elsewhere.

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