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Poly(aryleneethynylene) Type Polymers Containing a Ferrocene Unit in the π-Conjugated Main Chain. Preparation, Optical Properties, Redox Behavior, and Mössbauer Spectroscopic Analysis

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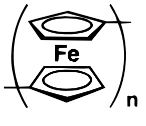
ABSTRACT: Palladium-catalyzed polycondensation between diiodoferrocenes (1,1′-diiodoferrocene and 1,6-diiodo-1′,6′-biferrocene) and diethynyl aromatic compounds HC≡C−Ar−C≡CH (e.g., 2,5-diethynylpyridine and 2,5-diethynyl-3-hexylthiophene) gives poly(aryleneethynylene) (PAE) type polymers containing the ferrocene unit in the π-conjugated main chain. The prepared polymers include $(-\text{Fc}-\text{C}{\equiv}\text{C}-\text{Ph}-\text{C}{\equiv}\text{C}-)_n$, PAE-Fc-1, $(-\text{Fc}-\text{C}{\equiv}\text{C}-\text{Py}-\text{C}{\equiv}\text{C}-)_n$, PAE-Fc-2, and $(-\text{Fc}-\text{C}{\equiv}\text{C}-\text{hexTh}-\text{C}{\equiv}\text{C}-)_n$, PAE-Fc-3 (Fc = 1,1′-ferrocenylene; Ph = *p*-phenylene; Py = pyridine-2,5-diyl; hexTh = 3-hexylthiophene-2,5-diyl). ^{1}H-NMR and IR spectra of the polymers are reasonable for their structures. The PAE type polymer containing the pyridine unit (PAE-Fc-2) is soluble in formic acid, and the polymer containing the hexylthiophene unit (PAE-Fc-3) is soluble in common organic solvents such as CHCl_3, THF, and benzene. UV−visible spectra of the polymers exhibit a main $\pi-\pi^*$ absorption peak at about 330 nm and a d−d absorption peak at about 450 nm. The cyclic voltammogram of the polymers in a $\text{CH}_3\text{CN/CH}_2\text{Cl}_2$ solution shows a reversible Fe(II) $\rightleftarrows$ Fe(III) redox cycle at about 0.25 V *vs* Ag/Ag$^+$, and the redox peaks are broadened compared with those of low-molecular-weight ferrocenes. Exchange of electrons along the main chain is considered to be the origin of the broadening. The polymers themselves are insulating, however, they are converted into semiconducting materials with conductivity of 10^{-7} to 10^{-4} S cm^{-1} by formation of adducts with iodine. Mössbauer spectra of the polymers reveal oxidation of Fe(II) in the ferrocene unit of PAE-Fc-1 to Fe(III), and the ease of the oxidation reflects the electronic properties of the polymer.

Introduction

Extensive studies have been made on ferrocene and its derivatives. They have various interesting electronic and optical properties. For example, they form charge transfer complexes,[1] generate mixed valent states by oxidation,[2] and show nonlinear optical properties.[3] Polymers constituted of the ferrocene units have also attracted attention of chemists, and preparation of poly(ferrocene) (PFc) and its related polymers as well as their conversion into electrically conducting materials by partial oxidation have been reported.[4−6]



Poly(1,1'-ferrocene) PFc

Delocalization of electrons along the PFc main chain and intermolecular exchange of electrons are considered to be the origin of the electrical conductivity. However, characterization of PFc and revealing its chemical and physical properties have been restricted by low solubility of PFc containing the ferrocene (Fc) unit.

On the other hand, Pd-catalyzed polycondensation (eq 1) between dihalo aromatic compounds and diethynyl aromatic compounds provides a useful synthetic tool for π-conjugated poly(aryleneethynylene) (PAE) type polymers.[7] Application of this polycondensation to appropriate monomers containing the Fc unit is expected to give soluble PAE type polymers containing the Fc unit in the π-conjugated main chain, and revealing their optical and electrical properties is considered to be intriguing. Here, we report preparation and properties of such PAE type polymers containing the Fc unit[7f,g] in the π-conjugated main chain.

$$n\text{X}-\text{Ar}-\text{X} + n\text{HC}{\equiv}\text{C}-\text{Ar}'-\text{C}{\equiv}\text{CH} \xrightarrow[\text{NR}_3]{\text{Pd}-\text{Cu}} \underset{\text{PAE}}{(-\text{Ar}-\text{C}{\equiv}\text{C}-\text{Ar}'-\text{C}{\equiv}\text{C}-)_n} \quad (1)$$

Results and Discussion

Preparation. The Pd-catalyzed polycondensation expressed by eq 2 (in cases of PAE-Fc-1, -2, -3, and -4) and by eq 3 (PAE-Fc-4) gives the corresponding PAE type polymers containing the ferrocenylene unit Fc. Table 1 summarizes results of the polymerization.

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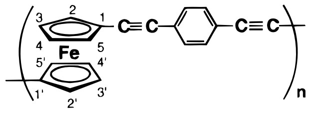
$$\mathrm{I{-}Fc{-}I} + \mathrm{HC{\equiv}C{-}Ar{-}C{\equiv}CH} \xrightarrow[i\text{-}\mathrm{Pr_2NH}]{\text{Pd(0) complex + CuI}} (\mathrm{{-}Fc{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}})_n \quad (2)$$

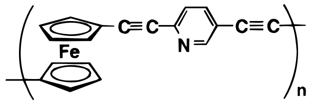
$$\mathrm{I{-}Fc{-}I} + \mathrm{BrMgC{\equiv}C{-}Ar{-}C{\equiv}CMgBr} \xrightarrow[\mathrm{THF}]{\text{Pd(II) complex}} (\mathrm{{-}Fc{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}})_n \quad (3)$$

Use of 1,6-diiodo-1′,6′-biferrocenylene I—Fc—Fc—I, instead of I—Fc—I, also gives the corresponding polymer, PAE-Fc-5, according to eq 3.

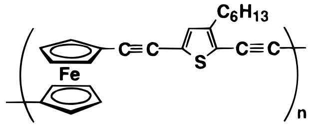
PAE-Fc-1



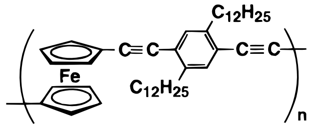
PAE-Fc-2



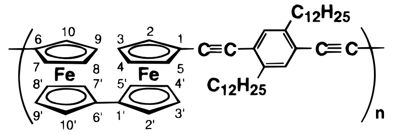
PAE-Fc-3



PAE-Fc-4



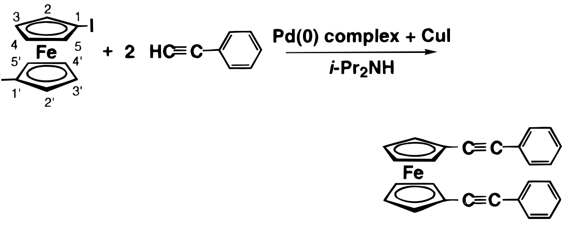
PAE-Fc-5



The Pd-catalyzed polycondensation expressed by eq 1 is based on the Pd-catalyzed coupling reaction between the acetylenic compound and organic halide[8,9]

$$\mathrm{RX} + \mathrm{R'C{\equiv}CH} \xrightarrow[\mathrm{NR''_3}]{\text{Pd(0) complex + CuI}} \mathrm{RC{\equiv}CR'} \quad (4)$$

and we have confirmed that this type of coupling reaction also proceeds well with 1,1′-diiodoferrocene (eq 5).



(5)

di-Etnyl-Fc

For example, 1,1′-bis(phenylethynyl)ferrocene,[10a−c] di-Etnyl-Fc, can be obtained in 90% isolation yield by the reaction. However, 1,1′-dibromoferrocene has low reactivity against the coupling reaction, and gives di-Etnyl-Fc only in low yield. Based on these results, I—Fc—I is used as the monomer in the present polycondensation.

We have also tried synthesis of 1,1′-bis(arylethynyl)-ferrocenes like di-Etnyl-Fc from reactions between 1,1′-diethynylferrocene (HC≡C—Fc—C≡CH) and aryl halide (Ar—X) in order to seek the possibility for carrying out the polycondensation (eq 2) with a reverse type of combination of monomer, 1,1′-diethynylferrocene (HC≡C—Fc—C≡CH) and dihalo aromatic compound (X—Ar—X). However, attempts to synthesize 1,1′-bis-(arylethynyl)ferrocenes by this route have not been successful; 1,1′-diethynylferrocene, which is prepared *in situ* by hydrolysis of $\mathrm{Me_3SiC{\equiv}C{-}Fc{-}C{\equiv}CSiMe_3}$, is unstable and makes cyclized compounds like ferrocenophane.[10d]

PAE-Fc-1 is obtained in 96% yield, and about 25% of this polymer is soluble in organic solvents such as $\mathrm{CHCl_3}$, toluene, and THF. Since IR spectra of the soluble and insoluble polymers are identical, the fraction with relatively low molecular weights is considered to be dissolved in the solvents. PAE-Fc-2 is only partly soluble in usual organic solvents (e.g., about 20 wt % is soluble in $\mathrm{CHCl_3}$); however, it is fully soluble in formic acid, similar to other PAE type polymers with the pyridine unit.[7b,c] Removal of formic acid from the formic acid solutions of PAE-Fc-2 by evaporation gives original PAE-Fc-2 as proved by IR spectroscopy. PAE-Fc-3 is soluble in organic solvents; however, its yield is not high (run 3 in Table 1). 2,5-Diethynyl-3-hexylthiophene (HC≡C—hexTh—C≡CH) has high reactivity[7c] and may give some byproducts under the polymerization conditions. In the preparation of PAE-Fc-4 and -5, THF is well suited to be the polymerization solvent and the polymers are obtained in 100% yield. These polymers have high solubility in organic solvents due to the long alkyl substituent.

IR spectra of these polymers show the ν(C≡C) absorption peak of disubstituted acetylene[7c] at about 2200 $\mathrm{cm^{-1}}$ as well as several absorption peaks characteristic of the ferrocenylene unit. The ν(C—H) stretching absorption peak of terminal acetylene (at about 3250 $\mathrm{cm^{-1}}$) is not observable.

^{1}H-NMR data of the polymers are also reasonable for their structures. For example, Figure 1 exhibits ^{1}H-NMR spectrum of PAE-Fc-4, and peaks at $\delta = 4.2{-}4.6$ ppm are assigned to the Fc protons. The two kinds of Fc protons (protons at 2- and 5-position and those at the 3- and 4-position) give rise to two peaks at δ 4.35 and 4.56 ppm, respectively. Appearance of additional two weak peaks near the two peaks may be attributed to the terminal groups, although the presence of rotamer(s) in view of the angle between the two ethynyl groups attached at the Fc groups may also result in such splitting of the Fc protons. The relative peak area of the Fc protons against those of $\mathrm{CH_2}$ and $\mathrm{CH_3}$ groups in the dodecyl substituent as well as against that of phenylene H's agrees with the structure of PAE-Fc-4. The ^{1}H-NMR absorption pattern of the Fc-H's of PAE-Fc-5 becomes more complicated because of the presence of the —Fc—Fc— unit, which will make the presence of several kinds of rotamers possible.

^{13}C{^{1}H}-NMR data of the polymers are also consistent with the structures shown above. PAE-Fc-4 gives rise to two peaks of ethynylene —C≡C— carbons at δ 85.6 and 91.8 ppm and it has phenylene signals at δ 121.8, 131.3, and 140.7 ppm, respectively (the inset in Figure 1). Its ^{1}H-^{13}C COSY NMR spectrum also agrees with the molecular structure of the polymer.

Light scattering analysis[11] of the $\mathrm{CHCl_3}$ solution of PAE-Fc-2 ($\mathrm{CHCl_3}$-soluble part) and PAE-Fc-3 indicates that they have weight average molecular weights M_w of 2.1×10^4 and 3.4×10^4, respectively. He—Ne laser with $\lambda = 632.8$ nm where the polymer does not show absorption is used for the light scattering analysis. GPC analysis shows PAE-Fc-2 ($\mathrm{CHCl_3}$-soluble part) and PAE-Fc-3 have M_w of 5.7×10^3 and 5.8×10^3, respectively.

Table 1. Preparation of PAE Type Polymers Containing Ferrocene Unit

								λ_{max} (nm)	
run	polymer	method[a]	temp (°C)	time (h)	yield[b] (%)	10^{-4} M_w[c]	ρ_v[d]	$\pi-\pi^*$	d–d
1	PAE-Fc-1	A	75	50	96	0.15[e]	<0.001	325	415 ($CHCl_3$)
2	PAE-Fc-2	A	75	72	75	2.1	0.0065	368	526 (HCOOH)
								332	460 ($CHCl_3$)
3	PAE-Fc-3	A	70	80	43	3.4	0.005	351	420 ($CHCl_3$)
4	PAE-Fc-4	A	60	64	100	0.69[f]		335	442 ($CHCl_3$)
5	PAE-Fc-4	B	65	24	100				
6	PAE-Fc-5	B	65	24	100			313	465 ($CHCl_3$)
7	di-Etnyl-Fc				90			307	451 ($CHCl_3$)

[a] Method A: 1.0 mol of HC≡C—Ar—C≡CH per 1.0 mol of I—Fc—I was added. Catalyst: 0.04 mol $Pd(PPh_3)_4$ and 0.04 mol of CuI per 1.0 mol of the monomer. Method B: 1.0 mol of BrMgC≡C—Ar—C≡CMgBr per 1.0 mol of I—Fc—I or I—Fc—Fc—I was added. Catalyst: 0.03 mol $Pd(OAc)_2$ and 0.03 mol of PPh_3 per 1.0 mol of monomer. [b] Based on carbon recovered (100 × (total weight of carbon in the polymer obtained)/(total weight of carbon in the monomer added)). [c] Weight-average molecular weight determined by the light scattering method (in $CHCl_3$) unless otherwise noted. [d] Degree of depolarization.[11] [e] For the $CHCl_3$-soluble fraction. [f] Determined by GPC.

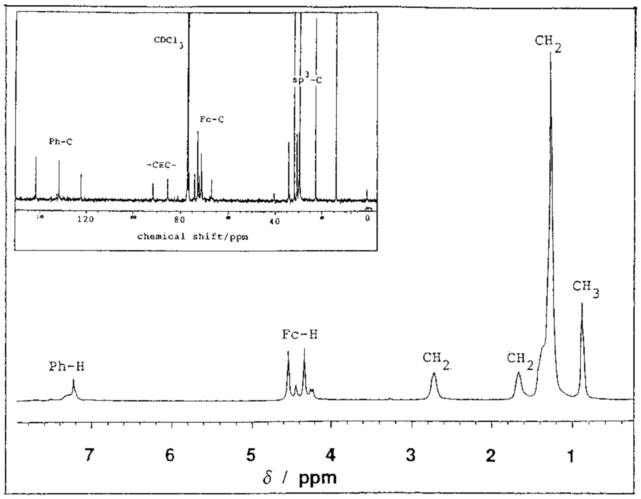


Figure 1. ^1H-NMR spectrum of PAE-Fc-4 in $CDCl_3$ (400 MHz). The inset shows the $^{13}C\{^1H\}$-NMR spectrum of PAE-Fc-4 in $CDCl_3$ (100 MHz).

These data suggest that the light scattering analysis is sensitive to partial aggregation of the polymer in the solution.[11c] The polymers are considered to take essentially a random coil structure in the solution as judged from the negligibly small degree of depolarization ρ_v[11] measured in the light scattering analysis (Table 1). The polymers show a refractive index increment d*n*/d*c* of 0.24 ± 0.03 $cm^3\ g^{-1}$. PAE-Fc-4 gives an η_{sp}/c value of 0.20 dL g^{-1} at $c = 0.055$ g dL^{-1}, and its GPC trace affords a unidispersed peak with M_n and M_w values of 4700 and 6900 (polystyrene standard).

The polymers have high thermal stability, and the TGA analysis reveals that their weight loss starts at bout 400 °C (under N_2) and that they give a residual weight of 40–55% at 900 °C.

UV–Visible Spectra. Figure 2 exhibits UV–visible spectra of PAE-Fc-4 and -5, and UV–visible data for the polymers are given in Table 1. As shown in Figure 2, they show a peak at about 450 nm assignable to a d–d transition in the ferrocene unit;[1–4] ferrocene itself gives the d–d transition peak at 438 nm and di-Etnyl-Fc shows the d–d transition band at 451 nm (Table 1, run 7). In addition to the d–d transition peak, they show a stronger (ϵ = about $1.5 \times 10^4\ M^{-1}\ cm^{-1}$; molarity is based on the repeating unit) absorption peak assigned to a $\pi-\pi^*$ transition at about 330 nm.

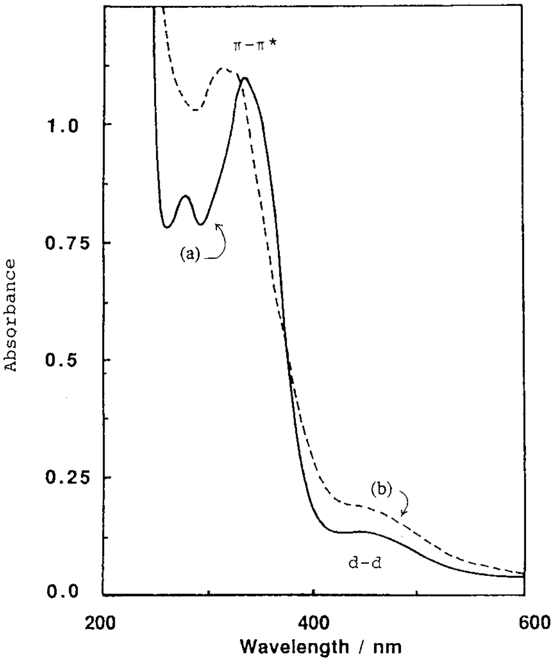


Figure 2. UV–visible spectra of (a) PAE-Fc-4 and (b) PAE-Fc-5 in $CHCl_3$.

The $\pi-\pi^*$ absorption band is shifted by about 20 nm to a longer wavelength from those of the corresponding aromatic monomers (e.g., 2,5-dibromopyridine) and di-Etnyl-Fc (λ_{max} = 307 nm), due to certain expansion of the π-conjugation system along the polymer chain. However, the degree of the bathochromic shift is smaller compared with usual fully π-conjugated PAE type polymers.[7] Cast films of PAE-Fc-1 and PAE-Fc-2 exhibit the $\pi-\pi^*$ absorption band essentially at the same position as for the $CHCl_3$ solutions of the polymers, (λ_{max} = 325 and 332 nm, respectively), suggesting that the polymers do not take a stacked structure[12] in the solid. In the case of the pyridine polymer PAE-Fc-2, the $\pi-\pi^*$ absorption peak is shifted to a longer wavelength (λ_{max} = 368 nm) in HCOOH due to an acid–base interaction, although the interaction seems to be not strong as judged from recovering the original polymer by evaporation of HCOOH (*vide ante*). The polymers are not fluorescent in solutions.

Redox Behavior and Electrical Conductivity. Cyclic Voltammetry. The polymers are electrochemically active, and their redox behaviors have been followed by cyclic voltammetry. As depicted in Figure 3a, the cyclic voltammogram of PAE-Fc-4 in a 1:1 mixture of CH_3CN and CH_2Cl_2 exhibits a Fe(II)–Fe(III) redox couple with oxidation and reduction peaks at 0.33 and 0.20 V *vs* Ag/Ag^+, respectively. The average of the two potentials ((0.33 + 0.20)/2 = 0.27 V) is taken as the $E°$

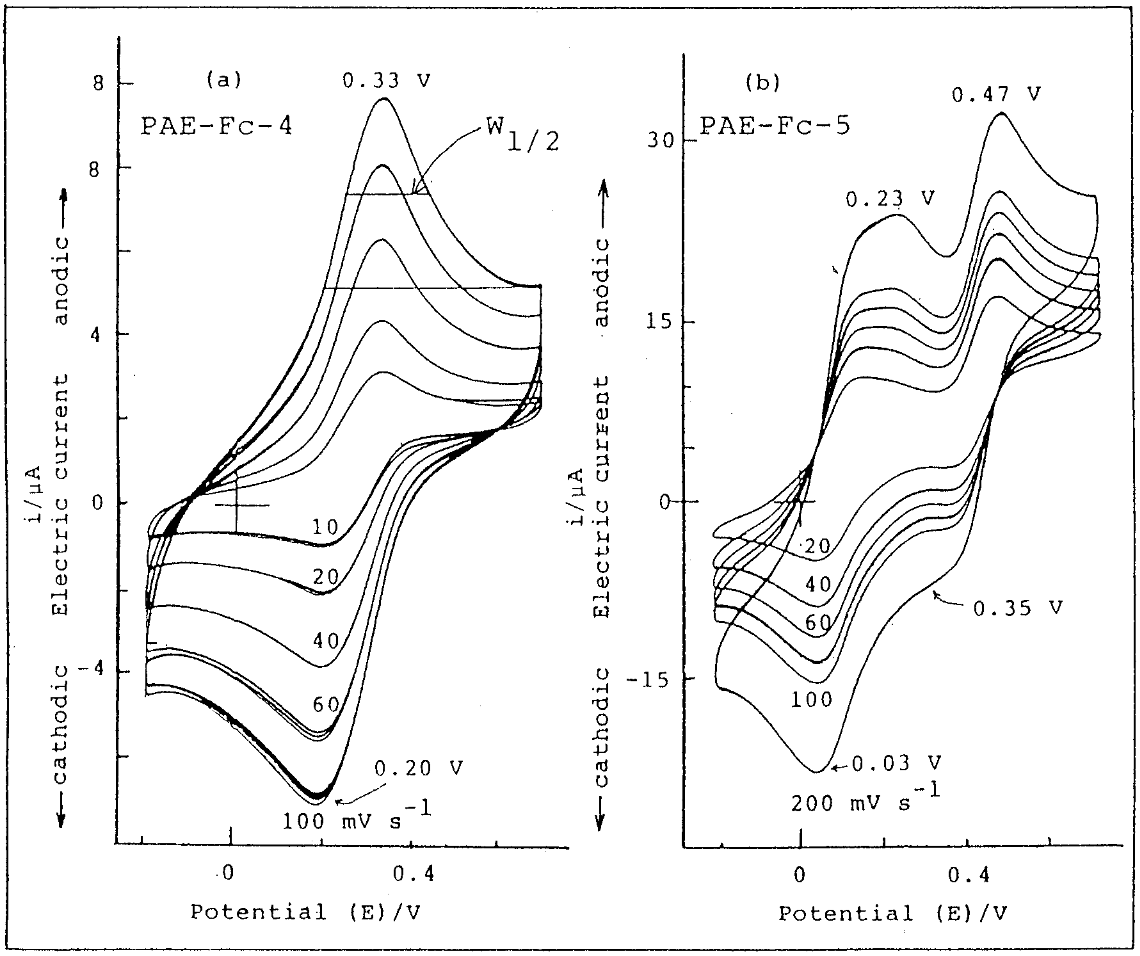


Figure 3. Cyclic voltammograms of (a) PAE-Fc-4 and (b) PAE-Fc-5 in a 1:1 solution of CH_3CN and CH_2Cl_2 containing 0.10 M $[N(n\text{-}C_4H_9)_4]BF_4$ under N_2. The figure attached to each CV curve represents the scanning speed in mV s^{-1}. Potential is given *vs* Ag/Ag$^+$. Working electrode = Pt wire.

Table 2. Redox Potentials of the PAE-Type Polymers Containing a Ferrocene Unit[a]

no.	polymer	E_{pa} (V)	E_{pc} (V)	$E°$ (V)
1	Ferrocene	0.06	−0.03	0.02
2	di-Etnyl-Fc[b]	0.27	0.20	0.23
3	PAE-Fc-1[c]	0.34	0.17	0.25
4	PAE-Fc-2[c]	0.35	0.27	0.31
5	PAE-Fc-3[c]	0.35	0.27	0.31
6	PAE-Fc-4	0.33	0.20	0.27
7	PAE-Fc-5	0.23 0.47	0.03 0.35	0.13 (E_1) } av 0.41 (E_2) } 0.27

[a] Measured in a CH_3CN/CH_2Cl_2 (v/v = 1/1) solution containing ca. 1 × 10^{-3} M of the monomer unit and 0.1 M of $[NEt_4]BF_4$. Sweep rate = 80 mV s^{-1}. At room temperature. All parts of PAE-4 and -5 are soluble in the solvent. However, for PAE-Fc-1, -2, and -3, only the soluble part in the solvent is used. [b] Prepared according to eq 5. [c] For the $CHCl_3$-soluble fraction.

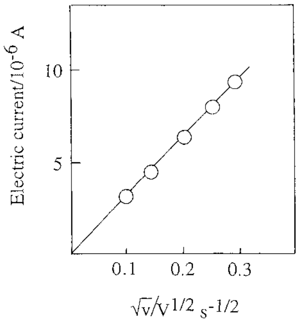


Figure 4. Plot of anodic peak electric current of PAE-Fc-4 (Figure 3a) against $v^{1/2}$ (v = scan rate).

value, and the $E°$ values of the polymers are summarized in Table 2.

PAE-Fc-5 containing the biferrocene unit gives stepwise redox couples at $E_1° = 0.13$ V and $E_2° = 0.41$ V *vs* Ag/Ag$^+$ as shown in Figure 3b, and the average of the $E_1°$ and $E_2°$ values (0.27 V *vs* Ag/Ag$^+$ no. 7 in Table 2) agrees with the $E°$ value of PAE-Fc-4. The two oxidation steps are assigned to the oxidation of the —Fc—Fc— unit of PAE-Fc-5 to an intermediately oxidized [—Fc—Fc—]$^+$ state and to a fully oxidized state [—Fc—Fc—]$^{2+}$, respectively.

As shown in Table 2, the Fe(II)−Fe(III) redox potential of polymers and di-Etnyl-Fc is higher than that of ferrocene,[13] presumably due to the electron-accepting nature of the attached ethynyl groups.[7c] The anodic peak electric current (i) of PAE-Fc-4 (Figure 3a) is proportional to a square root of the scanning rate ($v^{1/2}$ as depicted in Figure 4), indicating that the electric current is controlled by diffusion of the polymer molecule in the solution, as is usually observed with the cyclic voltammogram measured in solution systems. Plot of electric current of the first anodic peak of PAE-Fc-5 at 0.23 V *vs* Ag/Ag$^+$ against $v^{1/2}$ also gives a linear line.

Comparison of the CV chart of PAE-Fc-4 (Figure 3a) with that of ferrocene (curve a in Figure 5) reveals that the CV peak width of PAE-Fc-4 is broadened compared with that of ferrocene. For example, ferrocene gives a half-peak-width $W_{1/2}$ (Figure 5) of 111 mV, whereas PAE-Fc-4 (Figure 3a) gives $W_{1/2}$ of 151 mV. The CV curve of di-Etnyl-Fc (curve b in Figure 5) also shows

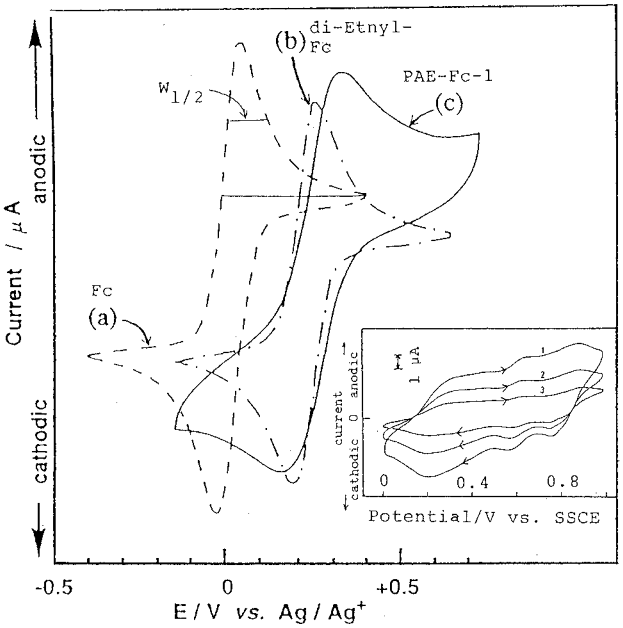


Figure 5. Cyclic voltammograms of (a) ferrocene, (b) di-Etnyl-Fc (eq 5), and (c) PAE-Fc-1 ($CHCl_3$-soluble part) at the same scanning rate of 80 mV s^{-1} in a 1:1 mixture of CH_3CN and CH_2Cl_2 containing 0.10 M of $[NEt_4]BF_4$. Working electrode = Pt wire. The inset shows CV curves of the soluble part (M_n = 900) of PFc (0.98 mM monomer unit) observed in a CH_2Cl_2 solution containing $[NBu_4]BF_4$ (0.2 M) at 380 mV s^{-1} (curve 1), 190 mV s^{-1} (curve 2), and 74 mV s^{-1} (curve 3) (potential is given against SSCE).[5c]

some broadening; however, the degree of broadening is minor. A part of PAE-Fc-1 is soluble in $CHCl_3$ and this $CHCl_3$-soluble part of PAE-Fc-1 also gives rise to a broadened CV curve (curve c in Figure 5). A $CHCl_3$-soluble part of PAE-Fc-2 and soluble PAE-Fc-3 also afford broadened CV peaks.

Such broadening of the CV peak has been reported for a soluble part of PFc[5c] and π-conjugated poly(2,2′-bipyridine-5,5′-diyl) coordinated with Ru,[14a] and the broadening has been ascribed to an exchange of electrons between the metal centers through the main chain. The broadening observed for the present polymers also suggests the presence of similar electron exchange between Fc units; if such electron exchange takes place, the oxidation CV peak will include contribution from various oxidized states such as ··—Fc—C≡C—Ar—C≡C—Fc—C≡C—Ar—C≡C—Fc—··, ··—Fc^+—C≡C—Ar—C≡C—Fc—C≡C—Ar—C≡C—Fc—··, and ··—Fc^+—C≡C—Ar—C≡C—Fc—C≡C—Ar—C≡C—Fc^+—·· to broaden the CV peak. However, the electron exchange is not so fast in view of the Mössbauer time scale, as discussed below. Furthermore, the broadening degree of the CV peak of PAE-Fc-1 and -4 is smaller than that of PFc (the inset in Figure 5),[5c] indicating that the electronic interaction between the Fc units is not so strong as that in PFc because of the presence of the —C≡C—Ar—C≡C— unit between the Fc units.

Mössbauer Spectra. Figure 6 exhibits Mössbauer spectra of PAE-Fc-1 and PAE-Fc-2 in the solid state. As shown in Figure 6 (part a), the Mössbauer spectrum of PAE-Fc-1 shows a doublet characteristic of Fe(II)−ferrocene derivatives.[5b,15] The isomer shift (IS = 0.55 mm s^{-1}) and quadrupole splitting (QS = 2.28 mm s^{-1}) of PAE-Fc-1 is comparable to those of common Fc(II) ferrocene derivatives.

On exposure to a vapor of I_2, PAE-Fc-1 absorbs iodine (200 wt % per polymer), and the Mössbauer spectrum of the iodine adduct of PAE-Fc-1 at 83.9 K shows a new broad peak at IS = 0.62 mm s^{-1} (Figure 6, part b-1). Since Fe(III)−ferrocenium derivatives usually give the Mössbauer peak with a small QS value,[5b,16] the new peak is assigned to the Fe(III)−ferrocenium (Fc^+) species formed by oxidation of PAE-Fc-1 with iodine. The existence mode of iodine in the adduct has not been clarified; however, iodine most probably exists as polyiodine(s) such as I_3^- and I_5^- since similar oxidation of ferrocene derivatives[5b] and π-conjugated poly(arylene)[17] with iodine gives such polyiodine as the counteranion.

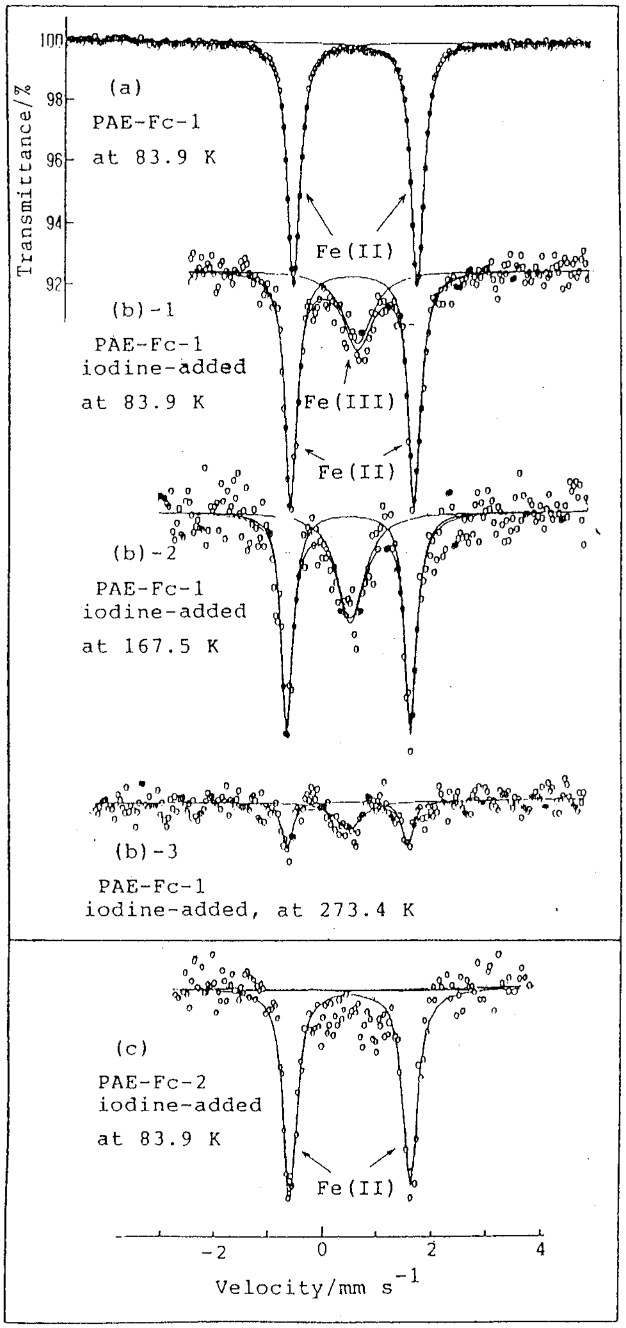


Figure 6. Mössbauer spectra of (a) PAE-Fc-1, (b) the iodine adduct of PAE-Fc-1, and (c) the iodine adduct of PAE-Fc-2, measured at (a) 83.9, (b-1) 83.9, (b-2) 167.5, (b-3) 273.4, and (c) 83.9 K.

When the measurement temperature was raised to 167.5 and 273.4 K (Figure 6, parts b-2 and b-3), both the Fe(II) and Fe(III) peaks are weakened; however, the degree of weakening is larger for the Fe(II) species, suggesting that the Fe(II) species has a lower Debye temperature. However, averaging (or coalescence) of the Fe(II) and Fe(III) signals is not observed at 273.4 K, indicating that rapid exchange of electron between the Fe(II) and Fe(III) species on the Mössbauer time scale (10^{-7} s) does not take place at the temperature; the rapid exchange of electrons between the Fe(II) and Fe(III) species[16,18] has been reported for poly(1,1′-ferrocene) PFc.[5b] Separation of the Fc unit by the $-C{\equiv}C-C_6H_4-C{\equiv}C-$ group in PAE-Fc-1 seems to present such a rapid electron exchange near room temperature (273.4 K, Figure 6, part b-3), although, as described above, the Fc units seem to exchange electrons on the CV time scale (about 1 s).

In contrast to the iodine adduct of PAE-Fc-1, an iodine adduct (iodine content = 170 wt %) of PAE-Fc-2 gives rise to only the Fe(II) signals (IS = 0.53 mm s^{-1}, QS = 2.23 mm s^{-1}) as shown in part c in Figure 6. In the case of the polymer containing the pyridine unit, iodine may form a complex with the pyridine unit through the lone pair electrons of nitrogen,[14a,19] and oxidation of the Fc unit seems to be prevented by the trapping of iodine by a lone pair electron of nitrogen as well as by a lower affinity of the Fc unit in PAE-Fc-2 against iodine due to the π-electron-withdrawing effect of the pyridine unit.[14a]

Unoxidized original PAE-Fc-1, -2, and -3 have a very low electrical-conductivity of about 1.0×10^{-12} S cm^{-1}; however, the iodine adduct of PAE-Fc-1 shows a semiconducting property with an electrical conductivity of 1.3×10^{-4} S cm^{-1}. Iodine adducts PAE-Fc-2 and -3 show electrical conductivities of 1.3×10^{-6} and 6.0×10^{-7} S cm^{-1}, respectively. Na-doped PAE-Fc-2 has an electrical conductivity of 1.2×10^{-5} S cm^{-1}.

Conclusion

A new type of polymer, PAE-Fc's $(-Fc-C{\equiv}C-Ar-C{\equiv}C-)_n$, with the ferrocene unit Fc in the π-conjugated main chain have been prepared by Pd-catalyzed polycondensation. The polymers containing the arylene unit Ar with the long alkyl substituent are soluble in organic solvents. The polymers are redox active and show a higher oxidation potential compared with ferrocene due to the electron-withdrawing ethynylene unit attached to the ferrocene unit. The broadened redox peak in the cyclic voltammogram of the polymer suggests electron exchange between the Fc units. Mössbauer spectrum of the iodine adduct of PAE-Fc-1 containing p-C_6H_4 as the Ar group reveals the partial oxidation of the Fe(II) unit to a $Fe(III)^+$ unit. On the other hand, similar iodine adduct of PAE-Fc-2 containing the pyridine-2,5-diyl group as the Ar group gives rise to only signals of the Fe(II) unit in its Mössbauer spectrum, and the difference observed between the two iodine adducts is explained by the stronger π-accepting ability of the pyridine-2,5-diyl group.

Experimental Section

Materials. 3-Hexyl-2,5-diethynylthiophene,[20] 1,1′-diiodoferrocene,[21] 1,6-diiodo-1′,6′-biferrocene,[21] and $Pd(PPh_3)_4$[22] were synthesized according to the literature. 2,5-Diethynylpyridine was prepared by modifying a reported method.[23] 1,4-Diethynylbenzene and $Pd(OAc)_2$ were used as purchased. Solvents were dried, distilled under N_2, and stored under N_2.

Model Reaction (Eq 5). A mixture of 1,1′-diiodoferrocene (1.15 g, 2.6 mmol), diisopropylamine (40 mL), phenylacetylene (580 mg, 5.7 mmol), CuI (20 mg, 0.10 mmol), and $Pd(PPh_3)_4$ (120 mg, 0.10 mmol) was stirred at 70 °C under N_2. After 5 h, water was added to the reaction mixture. An ether extract was treated with a SiO_2 column (eluent = a 3:1 mixture of hexane and $CHCl_3$) and the crude product was recrystallized twice from a mixture of hexane and $CHCl_3$ to yield reddish brown plates (0.89 g, 90% yield) of di-Etnyl-Fc. NMR and IR data agreed with reported data.[10a−c]

Polymerization. Polymerization was carried out under N_2 by using standard Schlenk techniques. For example, preparation of PAE-Fc-3 (method A expressed by eq 2) and PAE-Fc-4 (method B expressed by eq 3) was carried out as follows.

PAE-Fc-3 by Method A. A dark brown dry diisopropylamine (45 mL) solution containing 2,5-diethynyl-3-hexylthiophene (0.45 g, 2.1 mmol), 1,1′-diiodoferrocene (0.91 g, 2.1 mmol), $Pd(PPh_3)_4$ (0.10 g, 0.09 mmol), and CuI (0.02 g, 0.09 mmol) was stirred at 70 °C for 80 h. GLC analysis indicated that all of the monomers were consumed. Cooling the reaction mixture gave a dark red precipitate and a dark brown solution. Diisopropylamine was removed by evaporation, and the residue was washed with methanol repeatedly. The remaining solid was extracted with chloroform. After removal of chloroform by evaporation, the residue was dried under vacuum to obtain 393 mg (43.2%) of a dark red powder of PAE-Fc-3. PAE-Fc-1, -2, and -4 were prepared analogously.

PAE-Fc-4 by Method B. A solution of ethylmagnesium bromide (670 μL (0.96 M THF solution), 0.64 mmol) was added to THF (5 mL) solution containing a mixture of 1,4-diethynyl-2,5-didodecylbenzene (0.15 g, 0.32 mmol). After being stirred for 1.5 h at room temperature, the mixture was added to a mixture of 1,1′-diiodoferrocene (0.14 g, 0.32 mmol), $Pd(OAc)_2$ (0.03 g, 0.01 mmol), and PPh_3 (0.03 g, 0.01 mmol) placed in a 100 mL Schlenk tube. The dark red reaction mixture was allowed to react under reflux for 2 h. Diluted HCl (aq) was poured into the dark red mixture, and the product was extracted with chloroform. Chloroform was removed by evaporation, and the residue was washed with methanol repeatedly at −20 °C. The remaining solid was dried under vacuum to obtain 206 mg (100%) of a dark red oil of PAE-Fc-4. PAE-Fc-5 was prepared analogously.

^1H-NMR (400 MHz, $CDCl_3$, TMS, ppm) data for the polymers are given below. PAE-Fc-1 ($CHCl_3$-soluble part): 4.2−4.6 (m, 8H, $-C_5H_4-Fe-C_5H_4-$), 7.2−7.5 (m, 4H, Ph−H). PAE-Fc-2 ($CHCl_3$-soluble part): 4.2−4.6 (m, 8H, $-C_5H_4-Fe-C_5H_4-$), 7.2−7.7 (m, 2H, 3,4-Py−H), 8.5−8.6 (br, 1H, 6-Py-H). PAE-Fc-3: 0.9 (s(br), 3H, $-CH_3$), 1.3 (s(br), 6H, $-(CH_2)_3-CH_3$), 1.6 (m, 2H, Th$-CH_2CH_2-$), 2.7 (m, 2H, Th$-CH_2-$), 4.2−4.5 (m, 8H, $-C_5H_4-Fe-C_5H_4-$), 6.9−7.0 (m, 1H, Th−H). PAE-Fc-4: 0.8 (s(br), 6H, $-CH_3$), 1.2 (s(br), 36H, $-(CH_2)_9-CH_3$), 1.6 (s(br), 4H, Ph$-CH_2CH_2-$), 2.6 (s(br), 4H, Ph$-CH_2-$), 4.2−4.5 (m, 8H, $-C_5H_4-Fe-C_5H_4-$), 7.2−7.3 (br, 2H, PhH). PAE-Fc-5: 0.8 (s(br), 6H, $-CH_3$), 1.2 (s(br), 36H, $-(CH_2)_9-CH_3$), 1.6 (s(br), 4H, $PhCH_2-CH_2-$), 2.6 (s(br), 4H, Ph$-CH_2-$), 3.9−4.4 (m, 16H, $-(C_5H_4-Fe-C_5H_4)_2-$), 7.2−7.3 (br, 2H, Ph−H). IR data for the $\nu(C{\equiv}C)$ vibration (cm^{-1}, in KBr): PAE-Fc-1, 2202; PAE-Fc-2, 2204; PAE-Fc-3, 2202; PAE-Fc-4, 2212; PAE-Fc-5, 2208.

Measurements. IR spectra were recorded on a JASCO IR-810 spectrometer. NMR spectra were taken by using JEOL JNM-EX90 and JNM-400 spectrometers. TGA curves and UV−visible spectra were obtained with a Shimadzu thermoanalyzer and a Hitachi Model 200-20 spectrometer, respectively. Light scattering analysis was carried out as previously reported by using a He−Ne laser (λ = 632.8 nm).[11] GPC traces were obtained with a Tosho HLC-8020 gel permeation chromatograph; eluent = DMF. Cyclic voltammetry was carried out with a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko KB-104 function generator. Mössbauer spectra were obtained by using a Wissel Mössbauer spectrometer in constant acceleration mode. Electrical conductivity was measured with a Advantest R8340 A meter. Powdery polymer sample was compressed into a pellet (o.d. = 13 mm; thickness = about 1 mm) at 100 MPa. From the pellet a bar was obtained by cutting the pellet. Two electrodes were put at both the ends of the bar by carbon paste, and the dc electrical conductivity was measured.

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