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Note

Electrochemical determination of diffusion coefficient of π-conjugated polymers containing ferrocene unit

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Abstract

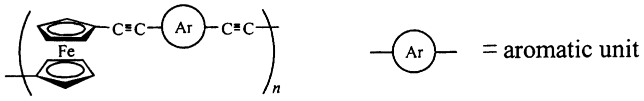
The diffusion coefficient (*D*) of π-conjugated polymers containing ferrocene unit in the polymer main chain in a 1:1 mixture of CH_2Cl_2 and CH_3CN was determined from peak oxidation current observed in cyclic voltammetry of the polymers. The *D* value of the polymers was in a range of about 1×10^{-12}–5×10^{-12} $m^2\,s^{-1}$, which was considerably smaller than those of ferrocene ($D = 470 \times 10^{-12}$ $m^2\,s^{-1}$) and 1,1′-bis(phenylethynyl)ferrocene (**2**) ($D = 68 \times 10^{-12}$ $m^2\,s^{-1}$) in accordance with the higher molecular weight of the polymer. Effects of the structure of the π-conjugated polymers on the *D* value are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene-containing polymers; π-Conjugated polymers; Diffusion coefficient

1. Introduction

Ferrocene is one of the most famous and important organometallic compounds not only in the field of organometallic chemistry but also in the area of electrochemistry. Electrochemical redox potentials of materials are determined against reference electrodes such as the normal hydrogen electrode (NHE) and the saturated calomel electrode (SCE); a ferrocene/ferrocenium (Fe(II)/Fe(III)) couple is also often used as the standard reference electrode in electrochemistry due to its stability, excellent electrochemical response, and solvent independent redox behavior [1].

Although numerous polymers containing ferrocene units in their main chain or side chain have been prepared [2], studies on their electrochemical response have been limited [3]. Diffusion process of the ferrocene polymer in the electrochemical reaction has mainly been analyzed with polymers containing ferrocene units in the side chain, and analysis of the diffusion process of the ferrocene polymer containing the ferrocene unit in a π-conjugated main chain has received little attention. In our previous paper, we reported synthesis of poly(aryleneethynylene) (PAE) type polymer constituted of 1,1′-ferrocenylene units and π-conjugated units connecting the 1,1′-ferrocenylene units [4]. The polymers were electrochemically active, and the electrochemical data revealed the presence of an electronic interaction between the 1,1′-ferrocenylene units through the π-conjugated unit.



PAE type polymer containing 1,1'-ferrocenylene unit

Now we are interested in the diffusion process of the PAE type polymer containing the 1,1′-ferrocenylene units [4], and have determined diffusion coefficients of the polymers based on the electrochemical behavior of the polymers.

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2. Experimental

2.1. Materials and chemicals

Preparation of the PAE type polymers constituted of the 1,1′-ferrocenylene unit (**1a**–**1d**) was already reported [4]. 1,1′-Bis(2-phenylethynyl)ferrocene (**2**) was synthesized according to the literature [5].

2.2. Cyclic voltammetry (CV)

Cyclic voltammetry (CV) was performed using Hokuto Denko HA-301 potentiostat and HB-104 function generator with an *X*–*Y* recorder. A three-necked Schlenk tube type H-shaped cell was used in the measurement. The potential was referred to 0.10 M of Ag^+/Ag ($AgNO_3/Ag$ wire). A 1:1 (v/v) mixture of CH_2Cl_2 and MeCN was employed as the solvent under nitrogen atmosphere. Cyclic voltammograms were obtained by using a solution containing $[^n Bu_4N]BF_4$ (0.10 M) as the electrolytic solution. Concentration of the ferrocene unit was 1.0×10^{-3} M for the polymers as well as for ferrocene and **2**. Working and counter electrodes were Pt wire and Pt plate, respectively.

2.3. Determination of diffusion coefficients

The diffusion coefficient (D) was calculated using the following electrochemical equation [6]:

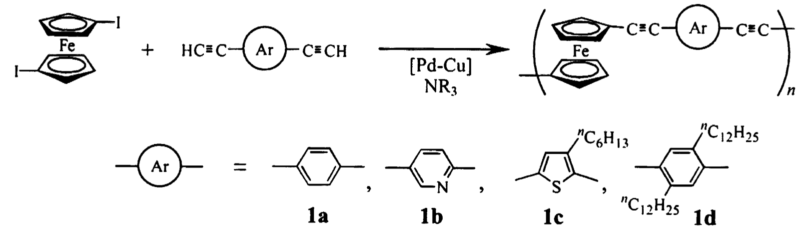
$$i = 0.4463 \times n^{3/2} F^{3/2} A (RT)^{-1/2} D^{1/2} C v^{1/2} \qquad (1)$$

where i is the peak current of the CV peak, A denotes the area of electrode (m^2), C represents the concentration of the electrochemically active species ($mol\ m^{-3}$), and n is the number of electron moved during electrochemical reaction per the active species; $n = 1$ for the ferrocenic compounds. v expresses the sweep rate ($V\ s^{-1}$), and the diffusion coefficient, D, in units of $m^2\ s^{-1}$ can be determined from Eq. (1). At 25 °C, the RT value becomes 2480 $J\ mol^{-1}$, and Eq. (1) gives the following Eq. (2) by using the Faraday constant of $F = 96\,500\ C\ mol^{-1}$.

$$i = 2.69 \times 10^5 \times A D^{1/2} C v^{1/2} \qquad (2)$$

3. Results and discussion

The PAE type π-conjugated polymers containing the 1,1′-ferrocenylene units (**1a**–**1d**) were prepared as previously reported. The ferrocenic compound **2** was synthesized according to the literature [5] (Eq. (4)).



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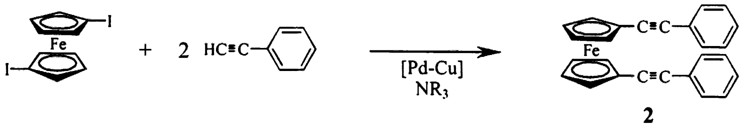

(4)

Fig. 1 shows the cyclic voltammograms of ferrocene, **2**, and **1a**–**1d** at various scanning rates. All cyclic voltammograms showed one couple of Fe(II)/Fe(III) redox peaks, and the CV charts showed good reversibility. Redox potentials of the materials are summarized in Table 1. Due to the attachment of the electron-withdrawing ethynylene unit –C≡C–, the oxidation potentials of **2** and **1a**–**1d** are shifted to higher potentials, compared with that of ferrocene.

The peak current (i) increased with an increase in the scanning rate as shown in Fig. 2. It is known that the peak current (i) of the CV peak of low molecular weight compounds is usually controlled by diffusion of the compound to the surface of the working electrode [6]. In this case, i increases proportionally to square root of the scanning rate, $v^{1/2}$ (cf. Eq. (2)). The linear correlation observed for **1a**–**1d** suggests that the rate of the electrochemical reaction of the polymers is also controlled by the diffusion of the polymer. In this case, the diffusion coefficients (D) of **1a**–**1d** can be obtained from Eq. (2). The D values of **1a**–**1d** thus calculated are summarized in Table 2 together with those of ferrocene and **2**. To our knowledge, D value of some pendant type ferrocenic polymers has been reported [3], however, determination of the D value of main chain type ferrocenic polymer has no precedent.

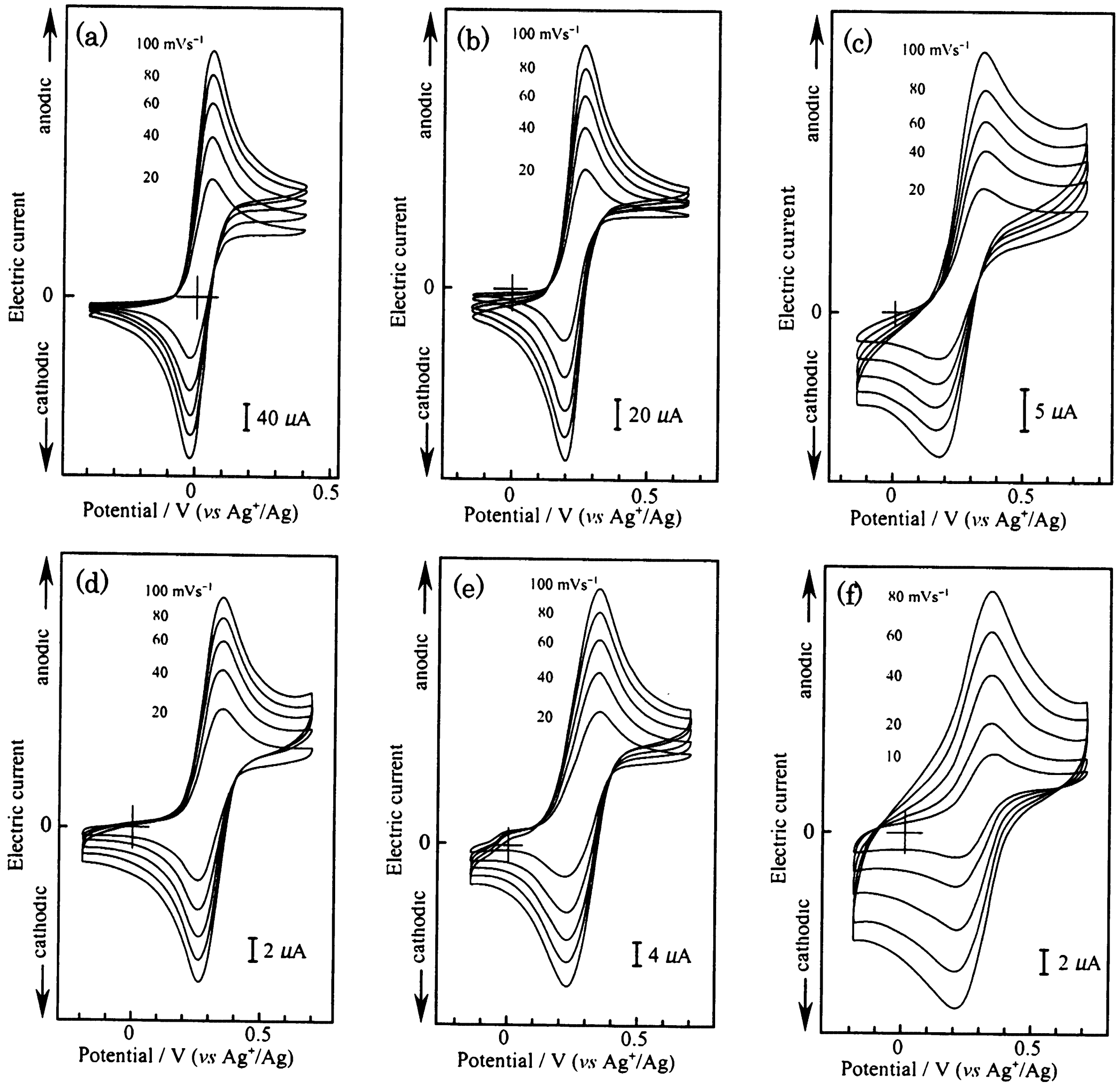

Fig. 1. Cyclic voltammograms of: (a) ferrocene; (b) **2**; (c) **1a**; (d) **1b**; (e) **1c**; and (f) **1d** in a 1:1 mixture of CH_3CN and CH_2Cl_2 containing 0.10 M $[^{n}Bu_4N]BF_4$ under N_2. Concentration of the ferrocene unit = 1.0×10^{-3} M. The figure attached to each CV curve represents the scanning speed in mV s^{-1}. Potential is given vs. $AgNO_3/Ag$.

The diffusion coefficient usually decreases with an increase in the molecular weight of the compound and the size of the molecules [7], and the considerably smaller D value of **1a**–**1d**, compared with those of ferrocene and **2** agrees with this concept. Among the polymers, **1c** gave a larger D value compared with other polymers, in spite of its larger molecular weight. It may be due to the coiled structure of **1c** and to its flexible structure because of the bending at the thiophene unit. Other polymers may have a more rigid main chain and give a rigid rod-like structure with larger effective volume, which brings about larger effective friction in moving the solution. Another possible explanation is that the thiophene unit is suited to convey electronic information between the ferrocenic units along the polymer chain, and even if a part of the polymer (e.g. end of the polymer) touches the working electrode, it brings about an electrochemical redox reaction of all the 1,1′-ferrocenylene units in the polymer. Thiophene unit is known as a superior electron-conveying unit [8] especially under oxidation conditions. Further studies

Table 1
Redox potentials obtained from cyclic voltammograms

Compound	E_{pa} (V) [a]	E_{pc} (V) [a]	$E°$ (V) [b] vs. Ag^+/Ag
Ferrocene	0.06	−0.03	0.02
2	0.27	0.20	0.23
1a	0.34	0.17	0.25
1b	0.35	0.27	0.31
1c	0.35	0.27	0.31
1d	0.33	0.20	0.27

Measured in a CH_3CN–CH_2Cl_2 (v/v = 1:1) solution containing 1.0×10^{-3} M of the ferrocenic unit and 0.10 M of $[^{n}Bu_4N]BF_4$ at room temperature. Working electrode: Pt wire; counter electrode: Pt plate. Sweep rate = 80 mV s^{-1}.

[a] E_{pa} = peak anode potential; E_{pc} = peak cathode potential.

[b] $E°$ value is calculated as an average of E_{pa} and E_{pc}.

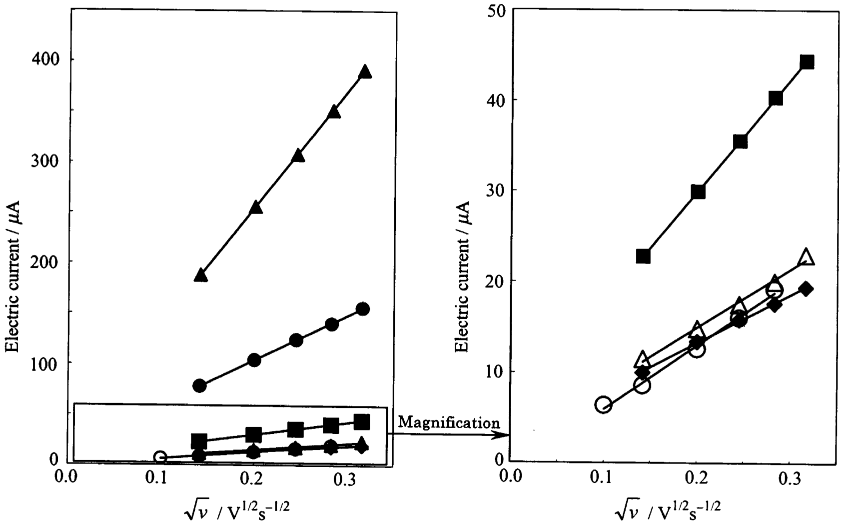

Fig. 2. Plots of anodic peak electric current of: ferrocene (▲); **2** (●); **1a** (△); **1b** (◆); **1c** (■); and **1d** (○), against $v^{1/2}$ (v = scan rate) taken from Fig. 1 (left). Magnification of the plots about **1a**–**1d** (right).

Table 2
Diffusion coefficients

Compound	M_w [a]	$10^{12}D$ ($m^2 s^{-1}$)
Ferrocene	186	470
2	330	68
1a	1500 [b]	1.6
1b	10 500 [c]	1.0
1c	17 000 [c]	5.3
1d	10 000 [d]	2.1

[a] Molecular weight.

[b] Number average molecular weight (M_n) determined by gel permeation chromatography [4a].

[c] M_n calculated based on the assumption that M_n of polymers [4a] prepared by polycondensation is half of the weight average molecular weight determined by light scattering method [9].

[d] M_n determined from ^1H-NMR peak areas of the terminal C≡CH proton and α-CH_2 proton in the alkyl side chain.

on the electrochemical process of ferrocene polymers will reveal interesting features of such polymers.

4. Summary

The peak current (i) observed in the cyclic voltammograms of redox-active π-conjugated polymers containing 1,1′-ferrocenylene units was proportional to the square root of the scanning rate ($v^{1/2}$). Based on this observation, the diffusion coefficient (D) of the polymers was determined. The D value was reasonably smaller than those of ferrocene and the ferrocenic compound **2**.

Acknowledgements

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References

[1] G. Gritzner, J. Kuta, Pure Appl. Chem. 56 (1984) 461.

[2] (a) K.E. Gonsalves, X. Chen, in: A. Togni, T. Hayashi Jr. (Eds.), Ferrocenes, Wiley-VCH, Weinheim, 1995 (chap. 10);
(b) C.U. Pittman Jr., in: E.J. Becker, M. Tsutsui (Eds.), Organometallic Reactions and Syntheses, Plenum Press, New York, 1977;
(c) N. Hagihara, K. Sonogashira, S. Takahashi, Adv. Polym. Sci. 41 (1980) 149;
(d) M. Kurihara, M. Kurosawa, T. Matsuda, H. Nishihara, Synth. Met. 102 (1999) 1517;
(e) T. Yamamoto, K. Sanechika, A. Yamamoto, M. Katada, I. Motoyama, H. Sano, Inorg. Chim. Acta 73f (1983) 75.

[3] (a) T.W. Smith, J.E. Kuder, D. Whchick, J. Polym. Sci. 14 (1976) 2433;
(b) A.L. Crumblis, D. Cooke, J. Castillo, P. Wisian-Nelson, Inorg. Chem. 32 (1993) 6088;
(c) B.B. Gnedenko, A.D. Ryabov, Anal. Chem. 66 (1994) 2240.

[4] (a) T. Yamamoto, T. Morikita, T. Maruyama, K. Kubota, M. Katada, Macromolecules 30 (1997) 5390;
(b) T. Morikita, T. Maruyama, T. Yamamoto, K. Kubota, M. Katada, Inorg. Chim. Acta 269 (1998) 310.

[5] (a) S.L. Ingham, M.S. Khan, J. Lewis, N.J. Long, P.R. Raithby, J. Organomet. Chem. 470 (1994) 153;
(b) M. Rosenblum, N. Brawn, J. Papenmeier, M. Applebaum, J. Organomet. Chem. 6 (1966) 173.

[6] (a) A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley, New York, 1982;
(b) H. Matsuda, Y. Ayabe, Z. Electrochem. 59 (1955) 494.

[7] S. Kambara (Ed.), Kobunshi Jikkengaku 11, Kobunshi Yoeki, Kyoritu Syuppan, 1982, p. 442.

[8] (a) T.A. Skotheim, R.L. Elsenbaumer, J.R. Reynolds (Eds.), Handbook of Conducting Polymers, 2nd ed., Marcel Dekker, New York, 1977;
(b) H.S. Nalwa (Ed.), Handbook of Organic Conductive Molecules and Polymers, Wiley, Chichester, 1997;
(c) T. Yamamoto, Bull. Chem. Soc. Jpn. 72 (1999) 621.

[9] P.J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY, 1953.