

Polymer Communication

# Electrochemical behavior of poly(3-hexylthiophene). Controlling factors of electric current in electrochemical oxidation of poly(3-hexylthiophene)s in a solution

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## Abstract

Electrochemical response of regio-random and regio-controlled poly(3-hexylthiophene), P3HexTh, was investigated by cyclic voltammetry. P3HexTh underwent electrochemical oxidation at about 0.4 V vs. Ag<sup>+</sup>/Ag in a THF solution, and the peak anode electric current,  $i_{pa}$ , was proportional to the sweeping rate  $v$ ;  $i_{pa} = \text{const} \times v^{1/2}$ . These data indicated that diffusion of the P3HexTh molecule in the solution was important to determine  $i_{pa}$ . Application of a Matsuda's equation with assumptions gave a diffusion coefficient,  $D$ , of about  $1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  at molecular weight of about 5000, and the  $D$  value steeply decreased with increase in the molecular weight.

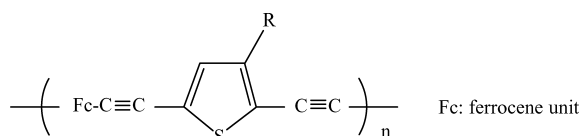
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**Keywords:** Poly(3-hexylthiophene); Electrochemical response; Diffusion

## 1. Introduction

Electrochemically active polymers such as  $\pi$ -conjugated polymers [1–3] are the subject of recent interest. Electrochemical responses of such polymers have actively been studied to reveal basic electronic states of the polymers and to develop electrochemical devices such as sensors of bio-materials, electrochromic polymer device, and battery [4–12]. These researches, however, have mainly carried out with polymer films laid on electrodes, and researches using solutions of the polymers have been limited.

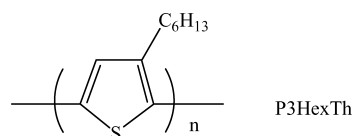
Previously we measured cyclic voltammograms (CVs) for electrochemical oxidation of main-chain type polyferrocenes consisting of ferrocene units connected by  $\pi$ -conjugated organic bridges, e.g.



in solutions [13,14], and reported that the peak anodic

current,  $i_{pa}$ , was proportional to the square root of the scanning rate,  $v^{1/2}$ . This result suggested that diffusion of the electrochemically active polymer in the solution was important to determine  $i_{pa}$  in the CV process.

As an extension of the study, we examined CV behavior of poly(3-hexylthiophene), P3HexTh, in a solution, and now report the results.



In the case of P3HexTh, the  $\pi$ -conjugated system along the polymer chain is expanded to a higher degree than that of the ferrocene-based polymers, and P3HexTh will give more direct information about electrochemical behavior of the  $\pi$ -conjugated polymer in the solution.

## 2. Experimental part

### 2.1. Materials

Regio-random poly(3-hexylthiophene), P3HexTh(Fe),

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was prepared by oxidative polymerization of 3-hexylthiophene with  $\text{FeCl}_3$ , according to the literature [15]. Regio-regular head-to-tail type poly(3-hexylthiophene), HT-P3HexTh(Zn/Ni), which was prepared via organometallic polycondensation using a zinc compound and nickel complex [16], was purchased from Rieke Metals Inc. P3HexTh(Fe) and HT-P3HexTh(Zn/Ni) were fractionated into several parts with different  $M_n$  (number average molecular weight) and  $M_w$  (weight average molecular weight) values, according to solubility of the polymers in chloroform (solubility = high), methylene chloride (solubility = medium), THF (solubility = medium), hexane (solubility = low), and methanol (solubility = poor) [17], in manners similar to that previously applied [18].  $M_n$  and  $M_w$  values were obtained by GPC (eluent = chloroform) by using a Shimadzu LC-9A liquid chromatograph (vs. polystyrene standards).

## 2.2. Measurements

The CV measurements were carried out by using a dry THF ( $5 \text{ cm}^3$ ) solution containing P3HexTh ( $2.0 \times 10^{-3} \text{ M}$ , based on the repeating monomeric unit) and tetrabutylammonium tetrafluoroborate  $[\text{NBu}_4]\text{BF}_4$  (0.10 M) under  $\text{N}_2$  atmosphere. A Hokuto Denko HABF501 potentiostat/galvanostat was used for the CV measurement at room temperature (about  $25^\circ\text{C}$ ). A platinum plate ( $\phi = 1.6 \text{ mm}$ ; area =  $0.020 \text{ cm}^2$ ), a platinum wire, and  $\text{Ag}^+/\text{Ag}$  were used as the working, counter, and reference electrodes, respectively.

## 3. Results and discussion

Fractionation of regio-random P3HexTh(Fe) and regio-regular P3HexTh(Zn/Ni) gave the fractions listed in Table 1. The results shown in Table 1 reveal a trend that regio-regularity of both P3HexTh(Fe) and P3HexTh(Zn/Ni) increases with increase in the molecular weight of the polymer. This seems to indicate that the regio-selection during the polymerization occurs more effectively after the propagating polymer species obtains certain chain length, and suggests that formation of a  $\pi$ -stacked crystalline assembly between regio-regular segments [16,17,19,20] is enhanced after the polymer attains the enough chain length and this brings about the effective regio-selection in the polymerization.

Fig. 1 shows examples of the CV charts. As seen in Fig. 1, the oxidation (or p-doping) of P3HexThs took place with a peak anodic potential  $E_{\text{pa}}$ , at about 0.4–0.5 V vs.  $\text{Ag}^+/\text{Ag}$ , and this oxidation potential is comparable to those observed with films of polythiophenes [1–3,21,22]. The corresponding p-dedoping peak appears at  $E_{\text{pc}} = \text{about } 0.25 \text{ V vs. } \text{Ag}^+/\text{Ag}$ , similar to cases of films of polythiophenes [1–3,21,22]. These results indicate that the electrochemical p-doping or oxidation of P3HexTh in the solution can also be

Table 1

Fractionation of P3HexTh(Fe) and HT-P3HexTh(Zn/Ni)

No	Fraction <sup>a</sup>	$M_n$	$M_w/M_n$	HT-content (%) <sup>b</sup>	$\lambda_{\text{max}}$ (nm) <sup>c</sup>
Fe-1		5000	1.60	75	437
Fe-2		10,000	1.40	75	437
Fe-3		17,000	1.47	78	439
Fe-4		21,000	1.52	81	441
Fe-5		23,000	1.74	83	442
Fe-6		33,000	2.61	83	442
Fe-7		34,000	2.62	85	443
Zn/Ni-1		3000	1.33	81	433
Zn/Ni-2		9000	1.67	91	446
Zn/Ni-3		9000	1.56	91	447
Zn/Ni-4		14,000	1.86	94	449
Zn/Ni-5		25,000	1.80	97	452
Zn/Ni-6		33,000	1.76	98	452

<sup>a</sup> Fe: P3HexTh(Fe). Zn/Ni: HT-P3HexTh(Zn/Ni).

<sup>b</sup> Calculated based on the peaks at  $\delta$  2.80 (HT-unit) and 2.58 (HH-unit) of the  $\alpha$ -CH<sub>2</sub> group [16]. HT-content = (peak area of the peak at  $\delta$  2.80)/(peak area of the peak at  $\delta$  2.80 + peak area of the peak at  $\delta$  2.58).

<sup>c</sup> In chloroform.

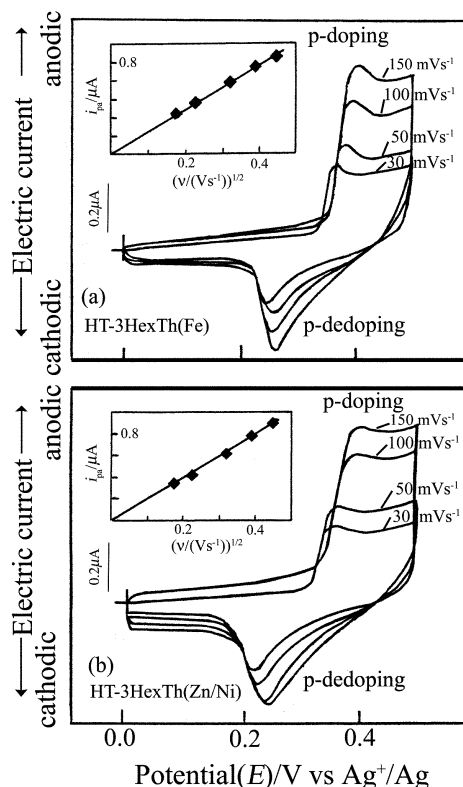
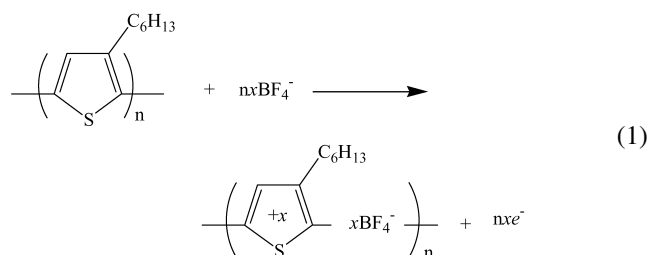


Fig. 1. Cyclic voltammograms of (a) P3HexTh(Fe) (Fe-4 in Table 1) and (b) HT-P3HexTh(Zn/Ni) (Zn/Ni-4) dissolved in a THF solution of  $[\text{NBu}_4]\text{BF}_4$  (0.10 M). At scanning velocity ( $v$ ) of 30, 50, 100, and  $150 \text{ mV s}^{-1}$ . The inset depicts the dependence of the peak anodic current,  $i_{\text{pa}}$ , on  $v^{1/2}$ . Working electrode = Pt plate (area =  $0.020 \text{ cm}^2$ ).

expressed as:



The p-doping potential seems to be affected by effective  $\pi$ -conjugation length in the polymer, which is also considered to be reflected in the  $\lambda_{\text{max}}$  positions listed in Table 1.

When P3HexTh has a higher HT-content, the effective  $\pi$ -conjugation length in the polymer is considered to be longer due to less steric repulsion between the hexyl groups at a head-to-head junction in the polymer [23]. Higher molecular weight will also contribute to a longer  $\pi$ -conjugation length. The longer effective  $\pi$ -conjugation will give a lower LUMO and a higher HOMO levels [24] to afford the  $\lambda_{\text{max}}$  position at a longer wavelength and a lower oxidation or p-doping potential. The  $\lambda_{\text{max}}$  data listed in Table 1 agree with the view described above, and the p-doping potential also shifts agreeing with the view. The Fractions Zn/Ni-1 and Fe-1 (cf. Table 1) showing at a shorter wavelength gave the  $E'_{\text{pa}}$ s at 0.53 and 0.46 V vs.  $\text{Ag}^+/\text{Ag}$ , respectively. On the other hand, the other fractions exhibited  $E_{\text{pa}}$  at a lower potential of 0.40–0.43 V vs.  $\text{Ag}^+/\text{Ag}$  (cf. Fig. 1) in accord with the discussion given above.

Since polythiophenes usually undergo chemical and electrochemical oxidation to accept one-electron oxidation per about 5 units of the thiophene ring [21,22], the doping level,  $x$  in Eq. (1), is assumed to be 0.2 in the present electrochemical reaction.

The linear correlation between  $i_{\text{pa}}$  and  $v^{1/2}$ , which is shown in the insets in Fig. 1, suggests that diffusion of the P3HexTh molecule to the surface area of the platinum electrode is an important factor to determine  $i_{\text{pa}}$ , similar to cases of electrochemical reactions of low molecular compounds.

If one applies the following Matsuda's equation [25,26] for  $i_{\text{pa}}$  (in A)

$$i_{\text{pa}} = 0.4463 \times 10^{-3} \times n^{3/2} F^{3/2} A (RT)^{1/2} D^{1/2} C v^{1/2} \quad (2)$$

or

$$i_{\text{pa}} = 269An^{3/2}D^{1/2}Cv^{1/2} \text{ at } 298\text{K} \quad (3)$$

( $A$  = area of the electrode (in  $\text{cm}^2$ ) = 0.020  $\text{cm}^2$  for the present case;  $n$  = number of electrons participated in the electrochemical reaction when the P3HexTh molecule reaches the platinum electrode;  $D$  = diffusion coefficient (in  $\text{cm}^2 \text{s}^{-1}$ );  $C$  = number concentration (in M) of the electrochemically active species (P3HexTh);  $v$  = scanning velocity (in  $\text{V s}^{-1}$ )), the diffusion coefficient,  $D$ , can be evaluated from the CV data shown in Fig. 1.

For the present study, the concentration of the monomeric 3-alkylthiophene unit was  $2 \times 10^{-3}$  M. Consequently, the  $C$  value in Eq. (3) was calculated by the following equation;  $C = 2.0 \times 10^{-3} \times (166/M_n)$  or  $(2.0 \times 10^{-3})/dp$  ( $dp$  = degree of polymerization; 166 = molecular weight of the monomeric unit). Based on the above described doping level,  $x$  of 0.2 in Eq. (1),  $n$  was calculated as  $0.2(M_n/166)$ .

Based on the assumptions described above, the diffusion coefficient,  $D$ , is calculated from Eq. (3) and  $i_{\text{pa}}$  (or the slope of the line given in the inset of Fig. 1), and Fig. 2 depicts plots of the  $\log D$  value against  $\log M_n$ . As seen in Fig. 2, a roughly linear correlation is observed between  $\log D$  and  $\log M_n$  in a  $M_n$  range of about 3000–17,000. The data points of P3HexTh(Fe) and HT-P3HexTh(Zn/Ni) seem to fall on the same line. The regioregular, high molecular weight polymers, Zn/Ni-5 and Zn/Ni-6 listed in Table 1, seemed to cause electrochemical deposition of the polymer on the Pt plate due to decrease in the solubility after the p-doping [27], and the data for these two polymers were omitted in the  $i_{\text{pa}}$  vs.  $v^{1/2}$  plots.

Diffusion coefficients of polymers such as polyacrylonitrile and polystyrene in solutions have been reported [28–33], and linear correlations between  $\log D$  and  $\log M$  have been observed. However, estimation of the  $D$  value of electrically conducting  $\pi$ -conjugated polymer and dependence of the  $D$  value on  $M_n$  have not been reported to our knowledge.

The observed slope of about  $-1$  for the straight line in Fig. 2 is considerably larger than those (e.g. slope = about  $-0.5$  for polystyrene [28–30,33]) observed with usual polymers. The slope has been related to stiffness of the polymer molecule in the solution [28–33], and the negatively large slope observed with P3HexTh implies that P3HexTh assumes a stiffer molecular structure than usual polymers presumably due to the all heteroaromatic main chain.

Light scattering analysis of regioregular P3HexTh with a high HT content and respective  $M_n$  and  $M_w$  values of 17,000

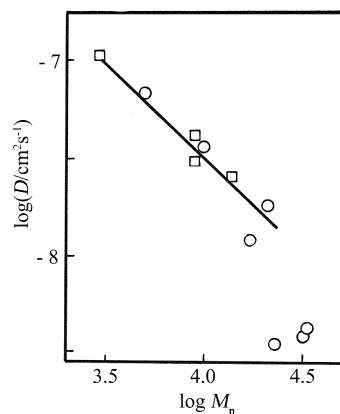


Fig. 2. Dependence of the diffusion constant,  $D$ , on the  $M_n$  value. ○: data for P3HexTh(Fe) □: data for HT-P3HexTh(Zn/Ni).

and 28,000 (determined by GPC) [34] indicates that the polymer has a stiff structure even in a good solvent (chloroform) with a very large  $\rho_v$  (degree of depolarization value) of 0.27 and a radius of gyration  $R_g$  of 36 nm and a hydrodynamic radius  $R_h$  of 25 nm in the good solvent (chloroform) [17]. These data support a view that the polymer has a similar or stiffer structure, compare with all aromatic *p*-phenylene type polyamides such as Kevlar which shows a  $\rho_v$  value of about 0.1 [35], and a persistence length of about 30 nm has been estimated for the regioregular P3HexTh from the light scattering data [36].

The  $D$  value of  $10^{-7} \text{ cm}^2 \text{ s}^{-1}$  at  $M_n$  of about 3000 (Fig. 2) is by one order of magnitude smaller than those observed with usual polymers such as polystyrene and glycoproteins [28–30,31] in various solutions. This also seems to suggest that P3HexTh assumes a stiffer structure, although further investigation to evaluate the  $M_n$  value (e.g. by ultracentrifugal analysis of molecular weight [32]) may be necessitated in future; the data obtained in the ultracentrifugal analysis has been directly correlated with the diffusion coefficient [32]. In Fig. 2, a steep decrease in the log  $D$  value is observed in the larger  $M_n$  region. The reason for this is not clear now. However, molecular assembly of P3HexTh [17] in the THF solution to increase the effective mass of the polymer is conceivable. The GPC analysis was carried out with a dynamically flowing solution, whereas the diffusion in the electrochemical process takes place in a non-flowing medium where the molecular assembly is considered to occur more easily. The increase in the regioregularity with the increase in  $M_n$  (*vide ante*) seems to assist the molecular assembly to increase the effective mass.

As described above, the dependence of  $i_{pa}$  in the electrochemical reaction of P3HexTh was for the first time analyzed. The  $i_{pa}$  value increased proportionally with  $v^{1/2}$ , and the diffusion coefficient obtained on the basis of the electrochemical equation, Eq. (2), was discussed. The obtained results are considered to contribute to better understanding of electrochemically active P3HexTh.

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