

# Temperature dependent electrical conductivity of *p*-doped poly(3,4-ethylenedioxythiophene) and poly(3-alkylthiophene)s

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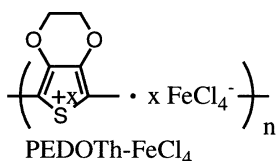
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## Summary

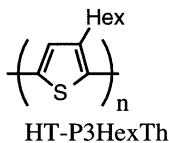
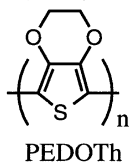
Temperature dependent electrical conductivity of substituted polythiophenes (poly(3,4-ethylenedioxythiophene) PEDOT<sub>h</sub> and head-to-tail type poly(3-alkylthiophene) HT-P3RTh) has been measured. The electrical conductivity ( $\sigma$ ) of *p*-doped PEDOT<sub>h</sub> and HT-P3RTh obeys equations of a type,  $\ln \sigma = \ln \sigma_0 - (T_0/T)^{0.25}$ , with the  $T_0$  value of about  $10^5$ - $10^7$  K.

## Introduction

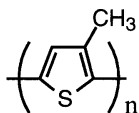
Although chemical and physical properties of  $\pi$ -conjugated polythiophene and its derivatives have been the subject of many papers (1-9), investigations of their electrically conducting properties at low temperatures have been limited (8). We have measured temperature dependent electrical conductivity of the *p*-doped state of the following five kinds of polythiophene derivatives between room temperature and liquid helium temperature, and herein report the results.



$x = 0.20$  as estimated from Cl analysis

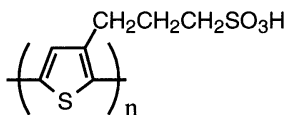


regioregular head-to-tail type poly(3-hexylthiophene)



HT-P3MeTh

regioregular head-to-tail  
type poly(3-methylthiophene)

P3(PrSO<sub>3</sub>H)Th

PEDOT<sub>x</sub>-FeCl<sub>4</sub> (6) and P3(PrSO<sub>3</sub>H)Th (7) have already found practical uses and are industrially produced. P3(PrSO<sub>3</sub>H)Th is considered to take a so-called self-p-doped state (7). Neutral PEDOT<sub>0</sub> was prepared by dehalogenation polycondensation of the corresponding dichloro monomer with a zerovalent nickel complex (9, 10) and p-doped with iodine. Recently regiocontrolled synthesis of poly(3-alkylthiophene)s such as HT-P3HexTh and HT-P3MeTh has become possible (4, 5, 9), and the polymers have attracted strong interest. These polymers were also p-doped with iodine and used for the present research.

## Experimental

### Materials

PEDOT<sub>x</sub>-FeCl<sub>4</sub> (6) and HT-P3MeTh (9) were prepared according to the literature. PEDOT<sub>x</sub>-FeCl<sub>4</sub> contained 15.6% chlorine, which corresponds to a doping level ( $x$  in the above shown molecular structure) of 0.2. HT-P3HexTh was purchased from Rieke Metals Inc. An aqueous solution of P3(PrSO<sub>3</sub>H)Th (0.9 wt%) was kindly donated from Showa Denko Co. Ltd. 2,5-Dichloro-3,4-ethylenedioxythiophene was prepared by a reaction of 3,4-ethylenedioxythiophene with *N*-chlorosuccinimide. Anal. Calcd for C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>O<sub>2</sub>S: C = 34.1%, H = 1.9%, Cl = 33.6%, S = 15.2%. Found: C = 34.5%, H = 2.1%, Cl = 33.5%, S = 14.9%. Neutral PEDOT<sub>0</sub> was prepared by dehalogenation polycondensation of 2,5-dichloro-3,4-ethylenedioxythiophene with a mixture of bis(1,5-cyclooctadiene)nickel(0), 2,2'-bipyridyl, and 1,5-cyclooctadiene in a manner similar to those previously reported (10). Yield = 82%. Anal. Calcd for (C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>S·0.2H<sub>2</sub>O)<sub>n</sub>: C = 50.1%, H = 3.1%, S = 22.3%. Found: C = 49.7%, H = 3.0%, S = 22.7%, Cl = 0%.

### Iodine doping and measurements

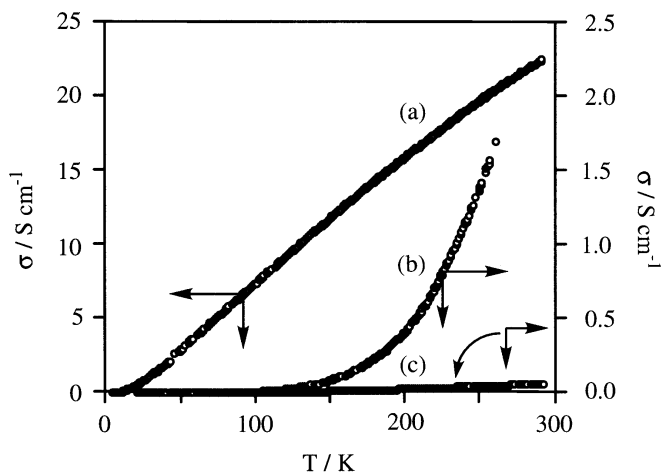
Iodine-doping of neutral PEDOT<sub>0</sub> was carried out by exposure of the sample to vapor of iodine in a manner similar to those previously reported (10). The following  $y$  value was defined,  $y$  = (molecules of I<sub>2</sub> taken by the polymer)/(monomer unit), and the  $y$  values observed with the iodine-doped PEDOT<sub>0</sub> and HT-P3MeTh were 0.60 and 0.25, respectively. The iodine doping of HT-P3HexTh was carried out in an aqueous medium as previously reported (11), and a  $y$  value of 1.11 was observed for the sample. PEDOT<sub>x</sub>-FeCl<sub>4</sub> and these iodine-doped samples were compressed into a pellet at about 2000 kg cm<sup>-2</sup>, and a bar specimen was cut from the pellet and used for the measurement of the electric conductivity. The aqueous solution of P3(PrSO<sub>3</sub>H)Th was cast on a glass substrate and dried under vacuum. The obtained film was used for the measurement of the electrical

conductivity. The electrical conductivity was measured with the four probe method using a cryostat system prepared by Fuso Co. Ltd.

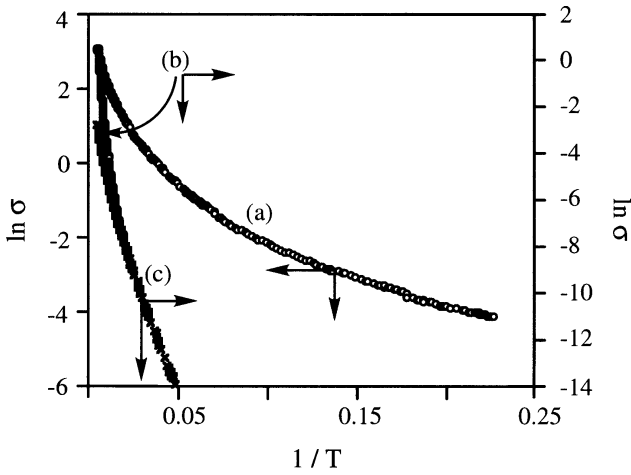
## Results and discussion

Figures 1-3 exhibit temperature dependences of the electrical conductivity ( $\sigma$ ) of PEDOT<sub>h</sub>-FeCl<sub>4</sub> and iodine doped HT-P3RTh, their Arrhenius plots, and plots according to a variable range hopping (VRH) model proposed by Mott (8, 12), respectively. The  $\sigma$ -T profiles depicted in Figure 1 resemble that reported for iodine-doped polythiophene (8).

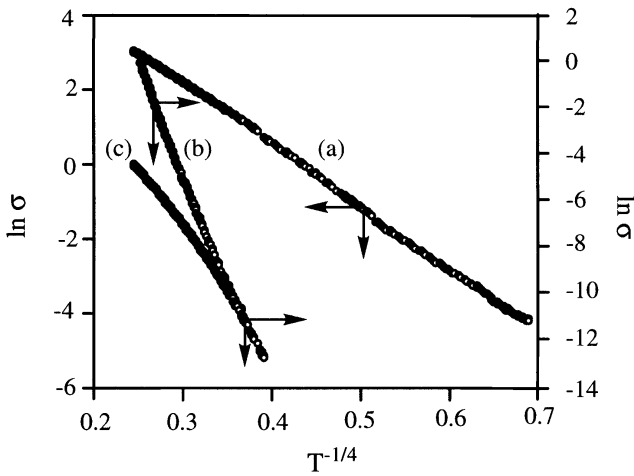
As shown in Figures 2 and 3, the Arrhenius plot did not give a linear line, whereas the data fall on a straight line when plotted as  $\ln \sigma$  vs  $T^{-1/4}$



**Figure 1** Temperature dependence of the electrical conductivity of (a) PEDOT<sub>h</sub>-FeCl<sub>4</sub>, (b) HT-P3HexTh (iodine-doped), and (c) HT-P3MeTh (iodine-doped).



**Figure 2** Arrhenius plots of the data shown in Figure 1. (a) PEDOTTh-FeCl<sub>4</sub>, (b) HT-P3HexTh (iodine-doped), and (c) HT-P3MeTh (iodine-doped).



**Figure 3** Plots of  $\ln \sigma$  vs  $T^{-1/4}$ . (a) PEDOTTh-FeCl<sub>4</sub>, (b) HT-P3HexTh (iodine doped), and (c) HT-P3MeTh (iodine-doped).

$$\ln \sigma = \ln \sigma_0 - (T_0/T)^{1/4} \quad (1)$$

This equation corresponds to a three dimensional VRH model, and the data depicted in Figure 3 give the  $\sigma_0$  and  $T_0$  values of  $1.3 \times 10^4 \text{ Scm}^{-1}$  and  $7.8 \times 10^4 \text{ K}$ , respectively, for PEDOT<sub>h</sub>-FeCl<sub>4</sub>. The VRH mechanism includes hopping of carrier to a site accepting the carrier (8, 12), and the applicability of eq. 1 for PEDOT<sub>h</sub>-FeCl<sub>4</sub> is considered to originate from microscopic variable range hopping mechanism of the carrier in the polymer chain (12, 13). However, hopping of the carrier between interparticle contacts in the compressed powder sample is also to be taken into account. A two-dimensional VRH model gives a somewhat different type of temperature dependence (8, 12),  $\ln \sigma = \ln \sigma_0' - (T_0'/T)^{1/3}$  (eq. 2), and plots according to this equation also afford an apparently linear line, and it is difficult to determine whether the electrical conduction obeys the three dimensional or two dimensional VRH mechanism, similar to the case of p-doped polythiophene (8).

Temperature dependence of the electrical conductivity of the iodine-doped PEDOT<sub>h</sub>, HT-P3HexTh, and HT-P3MeTh also deviates from the Arrhenius type equation, and plots according to eq. 1 give linear lines. Table 1 summarizes the  $\sigma_0$  and  $T_0$  values obtained with the p-doped samples, together with the values previously reported for p-doped polythiophene (8) and p-doped tetrathiafulvalene (TTF) -based  $\pi$ -conjugated polymer (13).

Table 1  $\sigma_0$  and  $T_0$  values of p-doped polythiophenes

no	polymer	$\sigma_0/\text{Scm}^{-1}$	$T_0/\text{K}$	Temperature range <sup>a</sup> /K
1	PEDOT <sub>h</sub> -FeCl <sub>4</sub>	$1.3 \times 10^3$	$7.8 \times 10^4$	5 - 300
2	PEDOT <sub>h</sub> (iodine-doped)	$2.9 \times 10^5$	$4.4 \times 10^7$	95 - 300
3	HT-P3HexTh (iodine-doped)	$1.2 \times 10^8$	$2.8 \times 10^7$	45 - 300
4	HT-P3MeTh (iodine-doped)	$2.4 \times 10^6$	$1.4 \times 10^7$	15 - 85 <sup>c</sup>
5	polythiophene (AsF <sub>5</sub> -doped) (8a)	$1.1 \times 10^4$	$7.3 \times 10^5$	ca. 10 - 300
6	TTF-based p-doped polymer (13) <sup>b</sup>	$3.9 \times 10^7$	$8.1 \times 10^7$	100 - 300

<sup>a</sup> Below the temperature range, the electrical conductivity became lower than that measurable with the apparatus.

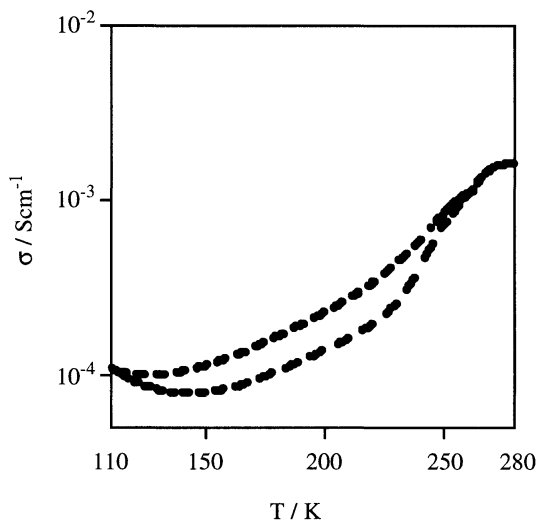
<sup>b</sup> The  $\sigma_0$  value of the polymer in the previous paper is corrected.

<sup>c</sup> Above 85 K, the plots deviate from eq. 1.

The observed  $T_0$  values are in a reasonable range (12) for the VRH model. Although detailed discussion for the meanings of the  $\sigma_0$  and  $T_0$  values requires further information such as packing state and grain size of the doped sample, a larger  $T_0$  value may be associated with a smaller state of density at the Fermi level and a shorter localization length (12).

The electrical conductivity of the film of P3(PrSO<sub>3</sub>H)Th showed a different type of temperature dependence, which is exhibited in Figure 4. The electrical conductivity was somewhat unstable and the sample gave different electrical resistance between the measurements during cooling and warming, as shown in Figure 4. The unique temperature dependence of P3(PrSO<sub>3</sub>H)Th may be attributed to a stronger influence of environment on the p-doped state of P3(PrSO<sub>3</sub>H)Th than that on the p-doped state of PEDOT<sub>h</sub> (14). The self-p-doped state of P3(PrSO<sub>3</sub>H) seems to be affected by delicate environmental changes

(14), and varying the temperature may cause such a change in the self-p-doped state (e.g., the degree of the p-doping (14)).



**Figure 4** Temperature dependence of the electrical conductivity of P3(PrSO<sub>3</sub>H)Th  
The lower curve: data measured during warming. The upper curve: data measured during cooling.

As described above, new examples have been provided for the VRH type temperature dependence of the electrical conductivity of substituted polythiophenes, in addition to the previously reported example of non-substituted polythiophene (8).

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