

SHORT COMMUNICATIONS

Iodine Doping of Poly(thiophene-2,5-diyl) and Poly(3-alkylthiophene-2,5-diyl)s in Aqueous Media

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Poly(thiophene-2,5-diyl)^{1–5} and poly(3-alkylthiophene-2,5-diyl)s^{6–12} have attracted great interest, because these π -conjugated polymers not only possess unique electrical and optical properties but also have high stability toward air both in undoped and doped states. In addition, poly(3-alkylthiophene-2,5-diyl)s containing a long alkyl chain in the monomer unit show good processibility. Doping of the π -conjugated polymers with I₂ is a convenient method to turn the low electrically conductive polymers to semiconductive or conductive organic materials. The iodine-doping has been usually carried out with vapor of I₂. Another type of iodine-doping using aqueous media has received less attention, although it may be suited to a large scale doping and does not require organic solvents. In addition, the doping in aqueous media is expected to give information about the dependence of the amount of absorbed iodine on the concentration of iodine. In this paper, we report results of the aqueous doping of poly(thiophene-2,5-diyl) and poly(3-alkylthiophene-2,5-diyl)s with I₂.

EXPERIMENTAL

Materials

Poly(thiophene-2,5-diyl) (PTh) was prepared as described in the literature.^{6c} Poly(3-hexylthiophene-2,5-diyl)s were prepared by two already reported methods: oxidative polymerization of 3-hexylthiophene using FeCl₃ as the oxidant¹² and dehalogenative polycondensation of 2,5-diiodo-3-hexylthiophene using a Ni(0) complex.^{6c,d} Both polymers were characterized spectroscopically and have molecular weights of $M_n = 3.8 \times 10^4$ (FeCl₃; P3HexTh(Fe)) and $M_n = 3.9 \times 10^4$ (Ni(0); P3HexTh(Ni)), respectively, which were determined by GPC using polystyrene standards. The ratios of HT and HH linkage of P3HexTh(Fe) and P3HexTh(Ni) were determined by the ¹H NMR peak area as 80 : 20 and 40 : 60, respectively. Commercially available poly(3-hexylthiophene-2,5-diyl)(P3HexTh(Zn/Ni)) prepared by using Zn and Ni) with $M_n = 1.7 \times 10^4$ (GPC) and the HT-HH ratio higher than 98 : 2 (Rieke Metals, Inc.) was also used.¹⁰

Doping of Poly(thiophene-2,5-diyl) and Poly(3-alkylthiophene-2,5-diyl)s by I₂

In nitrogen atmosphere, the powdery polymer was added to an aqueous solution containing KI (0.50 M) and I₂ with several concentrations. The mixture was thermostatted at 25°C and stirred for 24 h. The color of the polymer turned from brown to black during the reaction and this doped polymer was separated by filtration. The product was washed with distilled water, and dried under air at ambient temperature. This sample was then applied to elemental analysis, which was carried out by ion chromatography for iodine. Samples after drying more than 1 month under ambient conditions were used for conductivity measurement by a 2 probe method under Ar. The concentration of iodine in the remaining aqueous solution was determined by titration with an aqueous solution of Na₂S₂O₃. The amount of iodine absorbed by the polymer was calculated from the difference between the initial concentration of iodine and its final concentration after absorption by the polymer, similar to the method reported in the literature.¹³ For the sample obtained with P3HexTh(Fe) at [I₂] = 0.090 M, the amount of iodine thus estimated (I₂/monomer unit = 0.16) roughly agrees with data of the elemental analysis: Found: C, 57.9; H, 7.1; I, 16.8%. Calcd.: C, 58.1; H, 6.8; I, 19.6%. For comparison, doping of the polymers with vapor of I₂ was carried out according to the literature method.^{1,6} After the doping, excess I₂ was removed under vacuum, and the amount of iodine taken was determined by the weight increase of the sample.

RESULTS AND DISCUSSION

The amount of iodine taken by the polymers is plotted in Figure 1. The results indicate efficient doping by contact of the polymer with the aqueous solution of I₂. I₂ doped poly(thiophene-2,5-diyl) obtained by exposing the polymer to I₂ vapor has been studied in detail by means of resonance Raman and ¹²⁹I Mössbauer spectroscopy which reveals the presence of the dopant in a [I-I-I...I-I]⁻ (I₅⁻) form.^{6c,14} The aqueous doping of poly(thiophene-2,5-diyl)s in the present study is considered to cause similar doping with I₅⁻ according to eq 1 and 2. Iodine is dissolved mainly as KI₃ in the aqueous solution of KI and I₂, and I₂ partly released is considered to be absorbed by the polymer. As

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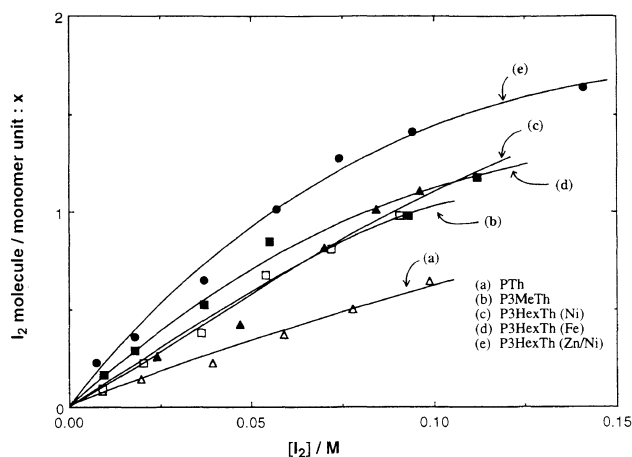
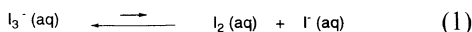


Figure 1. Plots of molar ratio of I_2 to the monomeric unit of the polymer vs. equilibrated concentration of $[I_2]$. In an aqueous medium containing KI (0.50 M) at 25°C. (a) PTh (Δ); (b) P3MeTh (\square); (c) P3HexTh (Ni) (\blacktriangle); (d) P3HexTh (Fe) (\blacksquare); (e) P3HexTh (Zn/Ni) (\bullet).



shown in Figure 1, at a high concentration of I_2 , the curve (a) for PTh gives about 200 g of iodine absorbed per 100 g of PTh, which corresponds to the doping level (a) of 0.26 in eq 2 if all of iodine absorbed participates in the p -doping. The observed doping level thus estimated was somewhat higher than that attained by electrochemical doping of PTh.¹⁵

$$x = \frac{(\text{mol of } I_2 \text{ absorbed})}{(\text{mol of the monomer unit})}$$

As shown in Figure 1, P3HexThs take a larger amount of iodine per the monomer unit than PTh under the same conditions. The slope for the curves of P3HexTh in a range of low concentrations of I_2 in Figure 1 is notably larger than that for PTh. It may be related to a lower oxidation potential of P3HexTh (0.58–0.61 V vs. Ag/Ag⁺)^{6c,d} than that of PTh (0.71 V vs. Ag/Ag⁺)^{15b} determined in the electrochemical study of the polymers. As seen in Figure 1, the regioregular P3HexTh(Zn/Ni) absorbs a higher amount of iodine than regiorandom P3HexTh(Fe) and P3HexTh(Ni) at the same I_2 concentration. Regioregular P3HexTh(Zn/Ni) tends to form a stacked structure in the solid state,^{10,11,16} and may provide circumstances for easy absorption of iodine by ordering of the polymer molecules. The data obtained from the titration (Figure 1) essentially agree with data obtained from elemental analysis at low doping levels (below an x value of 0.2).

It was previously reported that iodine doping of P3HexTh(Ni) led to a severe decrease in the strength of aliphatic $\nu(\text{CH})$ absorption bands in its IR spectrum.^{6d} Recently, it was also reported that an anion dopant (PF_6^-) was located near an alkyl group in a p -doped oligothiophene having the alkyl substituent.¹⁷ These results suggest effects of the alkyl side chain on the iodine-doping and the importance of the stereoregularity to determine the degree of the doping. IR spectra of the present P3HexThs-iodine adducts also showed severe

decrease in the intensity of the aliphatic $\nu(\text{CH})$ absorption bands, similar to the case of the vapor doping.^{6d}

The x value observed with the sample was considerably higher than that of iodine-doped poly(thiophene-2,5-diyl) and poly(3-alkylthiophene-2,5-diyl)s obtained by the vapor doping. For example, the vapor doping of poly(thiophene-2,5-diyl) gave the maximum x value of 0.4,^{6c} whereas the aqueous doping gave the x value of 0.6. Similar trend was observed for poly(3-alkylthiophene-2,5-diyl)s. Both P3HexTh(Zn/Ni) and P3HexTh(Fe) gave the x value of 0.36 in the vapor doping. The highly absorbed iodine in the aqueous doping, however, may include physically absorbed iodine in addition to iodine used for the p -doping expressed by eq 2. The absorption curves shown in Figure 1 do not show enough saturation, and the aqueous doping at higher $[I_2]$ may show leveling off of the x value. However, such doping at higher $[I_2]$ was not possible due to the limited solubility of I_2 .

The aqueous doped polymers showed electrical conductivity similar to or somewhat lower than that of vapor doped polymers. For example, iodine-doped PTh, P3HexTh(Fe), and P3HexTh(Ni/Zn) obtained at a high concentration of I_2 (ca. 0.1 M; Figure 1) gave the electrical conductivity of $2 \times 10^{-1} \text{ S cm}^{-1}$, $8 \times 10^{-1} \text{ S cm}^{-1}$, and 4 S cm^{-1} , respectively, at room temperature.

As described above, the aqueous doping can be easily achieved with poly(thiophene-2,5-diyl) and its alkyl derivatives to prepare the electrically conductive materials. The reactivity of the polymer toward I_2 is correlated with relative oxidation potential of the polymer and the microstructure of the polymer.

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