# p-Doping of Poly(3-hexylthiophene-2,5-diyl) with Sulfonic Acids and Oxygen Related to Self-doping of Sulfonated Polythiophenes

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Poly(3-hexylthiophene-2,5-diyl), P3HexTh, was p-doped by sulfonic acids such as $CH_3SO_3H$ in the presence of $O_2$. In the case of regioregular head-to-tail type P3HexTh, molecular assembly took place prior to the p-doping. Tetramer and pentamer of thiophene underwent similar oxidation.

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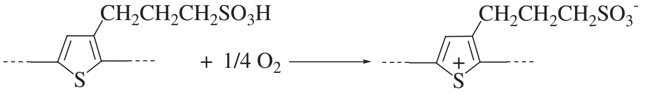
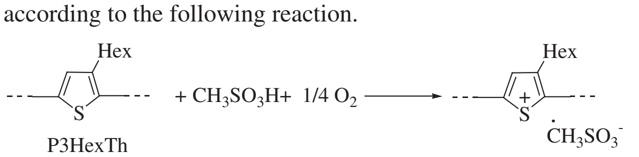
π-Conjugated polymers are the subject of recent interest,[1] and π-conjugated polymers with pendant $–SO_3H$ groups have attracted special attention.[2] They receive so-called "self-doping" and have found practical applications. However, there still remain unclear parts about the self-doping. Previously, we proposed the following chemical reaction for the self-doping of poly[3-(3′-sulfopropyl)thiophene], $P3(PrSO_3H)Th$, under air:[3]



$P3(PrSO_3H)Th$ + 1/2 $H_2O$ (1)

If the self-doping can be expressed as this, use of free sulfonic acid, instead of the pendant sulfonic acid, would also lead to similar p-doping of polythiophenes. In order to get more information about the self-doping and for better understanding of chemical doping of π-conjugated polymers, we followed reactions of poly(3-hexylthiophene-2,5-diyl), P3HexTh, with sulfonic acids under air by UV-vis spectroscopy, and herein report the results. Two types of P3HexTh were used in this study. P3HexTh(Fe) with a head-to-tail unit content of 80% and number average molecular weight, *M*n, of 13500 (vs polystyrene standards; determined by gel permeation chromatography) was prepared by oxidative polymerizatoin of 3-hexylthiophene and dedoped as previously reported, whereas commercially available head-to-tail type P3HexTh(Zn/Ni) with a head-to-tail content of 98.5% and *M*n of 17900 was used as another sample.[4]

Figure 1 shows changes of UV-vis spectrum of P3HexTh(Fe) during the reaction with $CH_3SO_3H$ ($pK = -6.0$)[5] in chloroform under air. The original peak of neutral P3HexTh(Fe) at 429 nm decreases with time, and the new peak at 832 nm is assigned to p-doped polythiophenes.[1–3,6] The spectroscopic change is similar to those observed during the self-doping of $P3(PrSO_3H)Th$[3] and electrochemical oxidation of polythiophenes.[6c] These results suggest that p-doping of P3HexTh(Fe) occurs with $CH_3SO_3H$ according to the following reaction.



P3HexTh

+ 1/2 $H_2O$ (2)

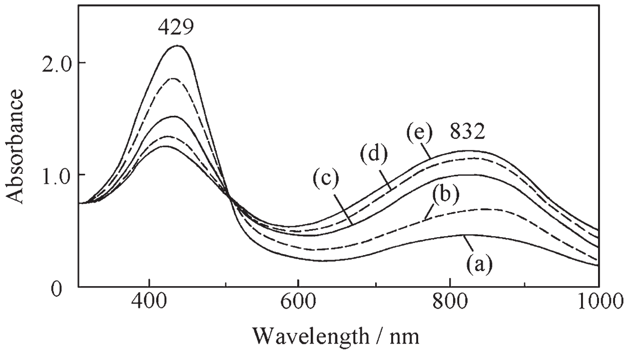


**Figure 1.** Changes of UV-vis spectrum of P3HexTh(Fe) in the reaction with methanesulfonic acid (0.27 M) in chloroform at 24 °C under air. Time after the first scan to obtain curve (a)/s: (b) 360; (c) 1440; (d) 4300; (e) 9500.

The p-doping with $CH_3SO_3H$ did not proceed under $N_2$, similar to the case of $P3(PrSO_3H)Th$ under $N_2$;[3] the reaction of P3HexTh(Fe) with $CH_3SO_3H$ did not show significant changes of the UV-vis spectrum under $N_2$, supporting necessity of $O_2$ in the p-doping. The p-doping was accelerated under $O_2$. Without $CH_3SO_3H$, P3HexTh(Fe) did not receive the p-doping even under $O_2$.

Concentration of $CH_3SO_3H$ is crucial for the p-doping, suggesting that the distance between the polymer and $CH_3SO_3H$ is important for the p-doping. The data shown in Figure 1 were obtained with 0.27 M of $CH_3SO_3H$, whereas at 0.18 M of $CH_3SO_3H$ the rate of the p-doping became very slow and the p-doped state near that expressed by the curve (b) in Figure 1 was attained after 1 day. The degree of p-doping finally attained also depended on the concentration. The concentration of 0.27 M indicates that the solution contains $CH_3SO_3H$ every 18 Å, whereas the increase in the average distance from 18 Å of 0.27 M to 21 Å of 0.18 M seems to give a severe retardation of the p-doping due to a decrease in the chance for the acid molecule to approach the redox active thiophene unit in the polymer. For this reason, $P3(PrSO_3H)Th$ seems to have advantages to form the stable p-doped state. Even when the $PrSO_3H$ group in $P3(PrSO_3H)Th$ assumes a linear stiff structure, the distance between the $SO_3H$ group and the thiophene unit is shorter than about 5 Å; for this reason the so-called self-doping of $P3(PrSO_3H)Th$ is considered to proceed smoothly.

$C_2H_5SO_3H$ (0.27 M) with weaker acidity ($pK = -5.5$)[5] also caused similar p-doping under air. However, the rate of the reaction was considerably (by one order of magnitude) slower. The degree of p-doping finally attained was about half of that attained with $CH_3SO_3H$. These results indicate importance of acidity of the sulfonic acid in the p-doping. $CH_3COOH$ (0.83 M), which had p*K*a of 4.56 and showed p*K*a by about 12 larger than $CH_3SO_3H$ in organic solvents,[5] did not lead to the p-doping under air. $CF_3COOH$ (0.36 M) with p*K*a of 0.52 led to the p-doping at a rate comparable to that observed with $C_2H_5SO_3H$ (0.27 M). These results suggest the presence of a favorable interaction between the thiophene unit and anions of strong acids, especially with sulfonic acid. It is noted that most of industrialized electrically conducting π-conjugated polymers have sulfonate (e.g., alkylnaphthalenesulfonate for polypyrrole,[7] polystyrene sulfonate for poly(ethylenedioxythiophene),[6] and the self-doping polymers) as the dopant (or the counter anion).

The spectroscopic changes shown in Figure 1 did not obey simple first order kinetics, although the self-doping of $P3(PrSO_3H)Th$ under air obeyed pseudo-first-order kinetics with respect to the concentration of the non-doped thiophene unit.

α-Terthiophene did not undergo the p-doping with $CH_3SO_3H$, whereas α-quaterthiophenes (α-$Th_4$'s), α-quinquethiophene (α-$Th_5$),[8] and ferrocene received a similar p-doping or oxidation with $CH_3SO_3H$ (0.27 M) under air: for α-$Th_4$'s and α-$Th_5$ at slower reaction rate (by two order of magnitude and one order of magnitude slower, respectively,) than that observed with P3HexTh(Fe). These results reveal importance of the π-conjugation length or redox potential of the compound in the p-doping or the oxidation.

Figure 2 shows changes of the UV-vis spectrum during the p-doping of P3HexTh(Zn/Ni) with $CH_3SO_3H$ (0.27 M) under air. As shown in Figure 2, the new absorption peak characteristic of p-doped polythiophenes appears at 822 nm. In the case of P3HexTh(Zn/Ni), the addition of $CH_3SO_3H$, however, causes additional changes of the spectrum. The new peaks around 550 nm seem to be assigned to π-stacked P3HexTh(Zn/Ni),[4] and changes of nature of the solvent led by addition of $CH_3SO_3H$ and/or occurrence of partial p-doping is considered to cause the π-stacking. It was reported that addition of poor solvents such as acetone to the chloroform solution of P3HexTh(Zn/Ni) led to formation of colloidal π-stacked P3HexTh(Zn/Ni).[4] Rise of the base line in the UV-vis spectrum supports formation of colloidal particles. ESR data showed difference between the p-doped P3HexTh(Fe) and P3HexTh(Zn/Ni). The former gave two ESR signals at g = 1.9989 and 1.9997, whereas the latter gave an ESR signal at g = 2.0000. Their intensity increased with time, supporting formation of radical species due to the p-doping. For P3HexTh(Zn/Ni), the p-doping is considered to occur with assembled polymer molecules.

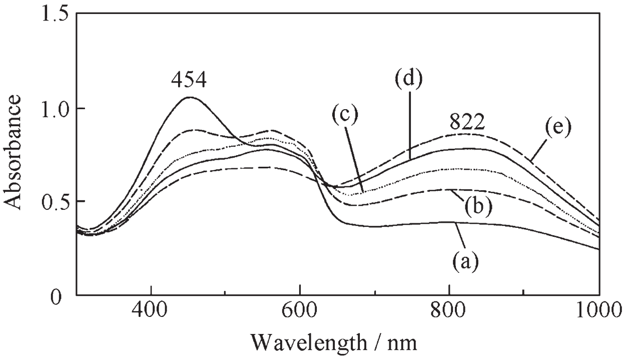


**Figure 2.** Changes of UV-vis spectrum of P3HexTh(Zn/Ni) in the reaction with methanesulfonic acid (0.27 M) in chloroform at 24 °C under air. Time after the first scan to obtain curve (a)/s: (b) 840; (c) 1920; (d) 5600; (e) 7300.

The results described above give better understanding for the self-doping of π-conjugated polymers with the pendant sulfonic group and reveal that P3HexTh can also be p-doped in the presence of special acids under air.

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8 Commercially available α-$Th_4$ and synthesized α-$Th_4$ and α-$Th_5$ with 3-hexyl units at the both terminal thiophene units. Details of the synthesis of the latter two compounds will be reported elsewhere.