Unique Temperature Dependence of NMR and UV-visible Spectra of Poly(3-hexylthiophene-2,5-diyl) and Its Related Compounds

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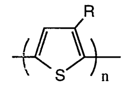
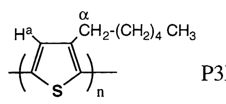
Lowering temperature of solutions of poly(3-hexylthiophene-2,5-diyl) P3HxTh below -10 - -20 °C leads to decrease in signal intensity of aromatic-H and α-CH_2 in ^{1}H-NMR spectrum. A shift of the π-π* absorption band to a longer wavelength by 26-60 nm is also observed. These results are accounted for by aggregation of P3HxTh through intermolecular interaction of the π-conjugated system.

Numerous reports have been published on NMR and UV-vis. spectra of π-conjugated poly(3-alkylthiophene-2,5-diyl) P3RTh.[1-4] However, NMR and UV-vis. spectroscopic behavior of P3RTh at low temperature has received much less



P3RTh


P3HxTh

attention. In the course of our recent studies on solution properties of P3RTh and its iodine adduct,[5] the author has noticed that P3RTh and its iodine adduct show unique NMR and UV-vis. spectroscopic behavior. This paper deals with such spectroscopic behavior of three kinds of poly(3-hexylthiophene-2,5-diyl) P3HxTh, which are prepared by (a) dehalogenation polycondensation of 2,5-dibromo-3-hexylthiophene by using an Ni(0) complex (P3HxTh(Ni)), (b) oxidative polymerization of 3-hexylthiophene with $FeCl_3$ (P3HxTh(Fe)), and (c) a Rieke's method using zinc and a nickel catalyst (P3HxTh(Zn/Ni)).[2-5] They contain the head-to-tail (HT) and head-to-head (HH) units in the following ratios:

P3HxTh(Ni) HT/HH = 3/7; P3HxTh(Fe) HT/HH = 6.3/3.7; P3HxTh(Zn/Ni) HT/HH = 10/0

Lowering temperature (e.g., to -20 °C) of solutions ($CHCl_3$ or CH_2Cl_2 solution) of these polymers gives jelly-like very viscous solutions which recover the original solutions on warming to room temperature. Charts (a) and (b) in Figure 1 compare ^{1}H-NMR spectra of P3HxTh(Zn/Ni) at 0 °C and -20 °C. Assignment of the signals are shown in the chart (a), and the peak area ratios at 0 °C agree with the structure of P3HxTh. However, at -10 °C the areas of H^a (aromatic-H) and α–CH_2 signals[6] decrease to about 72%, and at -20 °C they decrease to about half. P3HxTh(Ni) and P3HxTh(Fe) give similar decrease in the peak area of H^a and α-CH_2 in CD_2Cl_2 at low temperatures. Such unique effects of temperature on the H^a and α-CH_2 signals have not been reported.

These results strongly suggest aggregation of P3HxTh at the low temperature. Stacking of P3HxTh molecules seem to occur by interaction between the main chain π-conjugation systems, and it will bring about a magnetically special circumstances at the H^a and α-CH_2 protons. On the other hand, the other parts of the hexyl group are apart from the aggregation site and seem to maintain freedom of motion to give magnetically homogeneous

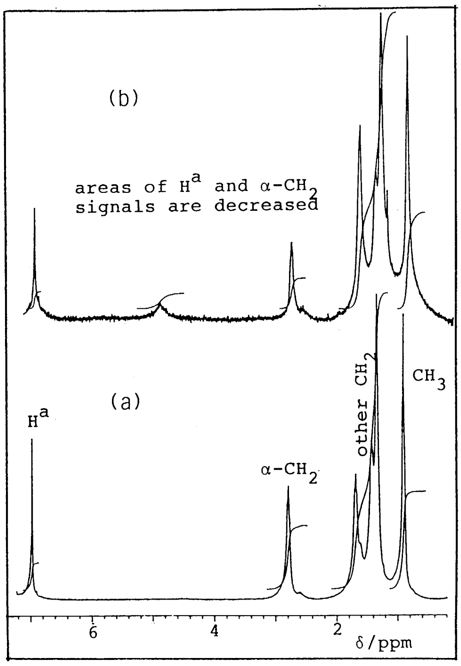
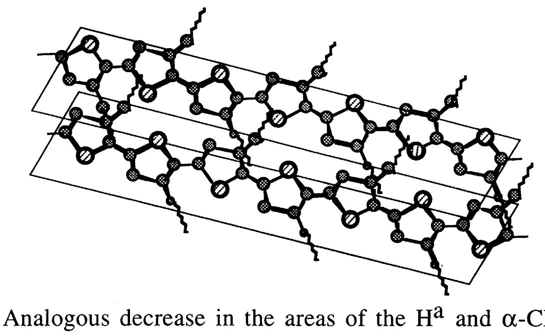
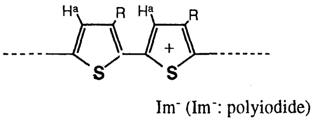


Figure 1. ^{1}H-NMR spectra of P3HxTh(Zn/Ni) in $CDCl_3$ at (a) 0 °C and (b) -20 °C.

environment and normal signals. Broad new signals observed at about δ 4.9 ppm at -20 °C (chart (b)) may originate from the H^a or α-CH_2 protons in the stacked cluster. A model for the aggregation of the P3HxTh molecules is shown below.

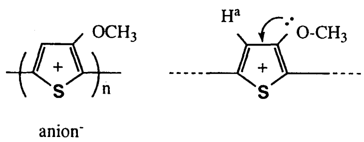


Analogous decrease in the areas of the H^a and α-CH_2 is observed on addition of iodine (0.25 mol I_2/monomer unit) to a CD_2Cl_2 solution of P3HxTh(Ni) at room temperature.[7] The addition of iodine will generate delocalized positive carrier (p-doped state) in the polymer chain, and this great change in the electronic state and/or Im^--assisted aggregation of P3HxTh seems to cause the decrase in the peaks areas of H^a and α-CH_2.



Intensity of H^a and α-CH_2 signals is decreased to 32%.

The strong effect of the iodine-doping on the H^a proton is in contrast to the effect of p-doping of poly(3-methoxythiophene-2,5-diyl) P3MeOTh.[8] In this case, the p-doping causes disappearance of the ^{1}H-NMR OCH_3 signal, whereas the H^a



A ^{1}H-NMR signal of OCH_3 disappears almost completely on the p-doping,[8] whereas a H^a signal is only broadened.

signal receives only minor effect from the p-doping. Migration of the lone pair electron of the OCH_3 group explains the results as shown above. However, in the case of P3RTh, such mobile lone pair electrons are absent and the H^a proton receives the strong effect from the p-doping.

Temperature dependence of UV-vis. spectrum of P3HxTh also supports the formation of an aggregated cluster of P3HxTh at the low temperature. In the concentration range for the UV-vis. measurement (about 10^{-4} M monomer unit), the solution of P3HxTh looks homogeneous up to about -60 °C. Figure 2 depicts temperature dependence of the UV-vis. spectrum of P3HxTh(Fe), and Figure 3 exhibits temperature dependence

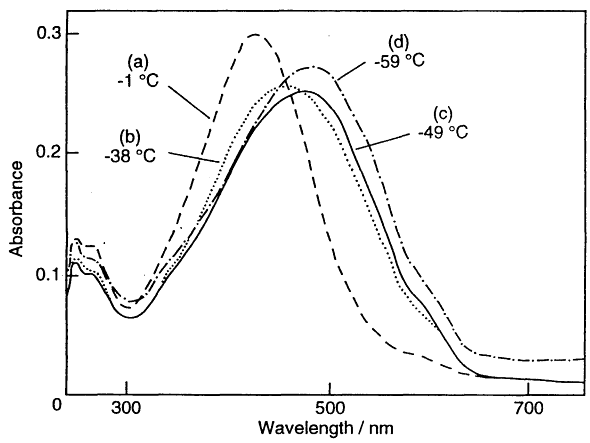


Figure 2. UV-vis. spectra of PHxTh(Fe) at various temperature in CH_2Cl_2 under air.

of λ_{max} of the π-π^* absorption band.

Detailed studies have been made on thermochromism of P3RTh in solutions at temperatures above 0 °C,[3a] and the thermochromism has been accounted for by a conformational change of single P3RTh molecule. However, such a large shift of λ_{max} at low temperatures and dependence of the shift on the microstructure (HT and HH content) of P3RTh have not been reported, and the present results are explained by a strong change in electronic state of the polymer by formation of the aggregated cluster through the π-conjugated system. It has been reported that formation of clusters often leads to strong bathochromic

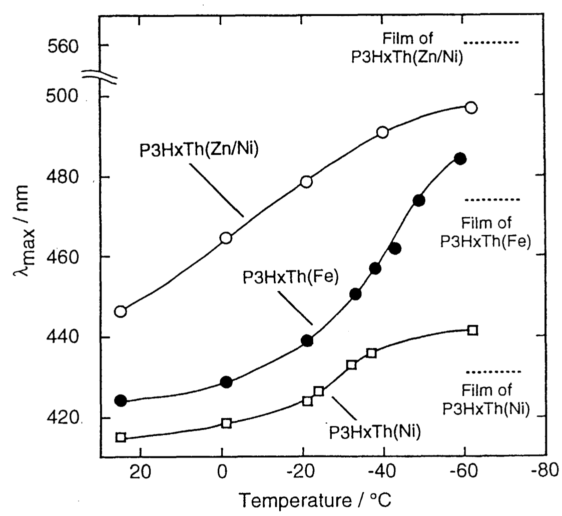


Figure 3. Temperature dependence of λ_{max} of CH_2Cl_2 solutions of PHxTh's under air. Broken lines indicate λ_{max} of films.

shifts of absorption bands of metal complexes. Microstructure of P3RTh seems to affect strongly the ease of the aggregation.

As shown in Figure 3, at the low temperature, the solution give the λ_{max} near the λ_{max} of the corresponding P3HxTh films,[2] although a film of P3HxTh(Zn/Ni) gives the λ_{max} at a considerably longer wavelength presumably due to its highly ordered structure in the solid film. At about -60 °C, rise of the base line is observed for all cases of P3HxTh's (cf. Figure 2), suggesting that at this temperature, the size of the aggregated cluster becomes comparable to the wavelength of light (ca. 1000 nm). The λ_{max} position was stable during the measurement. $CHCl_3$ gave smaller changes in the ^{1}H-NMR and UV-vis. spectra with temperature than $CHCl_2$, in accord with higher solubility of P3HxTh in $CHCl_3$ than in CH_2Cl_2.[5]

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References and Notes

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6 Areas of other CH_2 and CH_3 signals are used as the standard. At -30 °C, the areas of H^a and α-CH_2 signals decreases to 27%, whereas an area ratio of 1:2 is maintained between the H^a and α-CH_2 signals.
7 Iodine adducts of P3HxTh(Zn/Ni) have very low solubility, however, iodine adducts of P3HxTh(Ni) are soluble.
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