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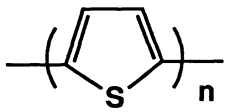
Reversible Doping and Undoping Behavior of Poly(2,5-thienylene) Studied by X-Ray Diffractiometry

Takakazu YAMAMOTO,* Atsushi MORITA, and Takaki KANBARA
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227

Extensive doping of poly(2,5-thienylene) (PTh) with iodine gives rise to a new crystal form with d value of 1.00, 0.49, 0.32, and 0.25 nm. Undoping of the iodine-doped PTh with N_2H_4 leads to recovery of original crystal structure of PTh, showing that rearrangement of PTh molecules after the undoping is very smooth.

Revealing of doping and undoping processes of π-conjugated electrically conducting polymers is important for utilization of the π-conjugated polymers in devices such as batteries and electrochromic device. The doping leads to change of crystal structures of the π-conjugated polymers,[1-3] whereas p-type doped polymers are undoped by treatment with reducing reagents and this undoping is expected to recover the original crystal structure of the π-conjugated polymer. However, to our knowledge, there has been no report that the original crystal structure is actually recovered by the undoping. Doping with strong oxidizing reagents like iodine may causes some chemical reactions on the polymer and rearrangement of the polymer molecules after the undoping may be difficult.

We now report that doping and undoping processes of PTh are reversible as revealed by powder X-ray diffractometry.



poly(2,5-thienylene) (PTh)

PTh was prepared by a reaction of 2,5-dibromothiophene with zerovalent nickel complex;[4] the sample is suitable for the present study since it has high crystallinity due to well-defined linkage between the monomer units and is easily doped with a variety of dopants. Since $CHCl_3$-extractable fraction was removed by Soxhlet extraction, the polymer is considered to have degree of polymerization higher than about 30.[5] Doping of PTh with iodine caused change of color from reddish brown to dark brown (almost black), and the original reddish brown was recovered on the undoping with N_2H_4. As shown in Fig. 1, the IR spectrum after undoping shows the same pattern as that of non-doped original PTh.

Figure 2 shows change of powder X-ray diffraction pattern of PTh during the doping and undoping processes. The X-ray diffraction pattern of the non-doped PTh shows reasonably sharp peaks.[4] Doping with iodine lead to

not only the increase in electrical conductivity of the sample, but also broadening of the diffraction peaks. When extensively doped ((C) in Fig. 2), the sample gave rise to new diffraction peaks at d value of 1.00, 0.49, 0.32, and 0.25 nm (d = 1.00/n (n = 1-4)). Although formation of new crystal forms of poly(acetylene)[1] poly(1,4-phenylene)[2,3] by p-type doping has been reported, this is the first report for the formation of the new crystal structure of PTh by doping.

When the extensively iodine-doped PTh was treated with an aqueous solution of N_2H_4, the polymer was undoped completely as judged from color, IR spectrum (Fig. 1), and analytical data. The powder X-ray diffraction pattern of the undoped PTh ((d) in Fig. 2) is essentially the same as that of original non-doped PTh, showing the diffraction peaks at the same position and with the same sharpness in experimental error. Thus, the present data unequivocally indicate that the reversibility of the doping and undoping processes of PTh using iodine and N_2H_4 is very good, in view of not only the chemical structure of the polymer but also the crystal structure of the polymer.

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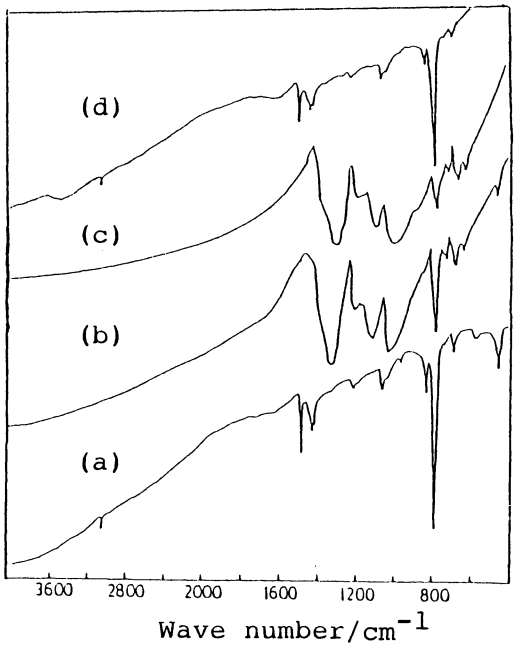

Fig. 1. Change of IR spectra on the doping and undoping. (a): non-doped PTh, (b): wt-% of iodine/PTh = 40, (c): wt-% of iodine/PTh = 120, (d): undoped PTh.

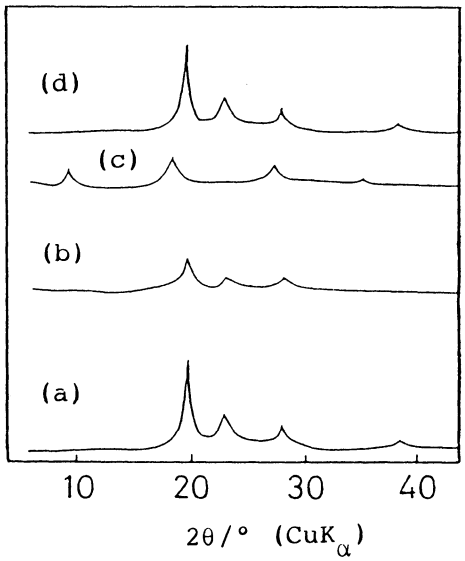

Fig. 2. Change of X-ray diffraction patterns on the doping and undoping. (a)-(d): as in Fig. 1.

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