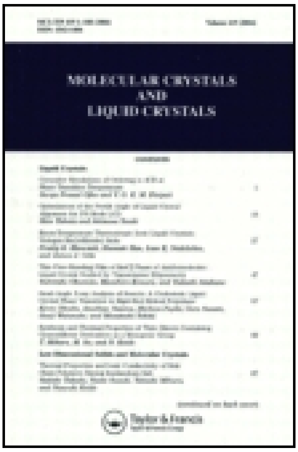

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Optical Properties of Poly(Isothianaphthene)

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Abstract The optical properties in poly(isothianaphthene), PITN, have been investigated by photoconductivity measurements and *in situ* optical absorption spectroscopy measurements during electrochemical n-type doping. Irradiation of the anode induces photoconductive response for a photon energy neighboring the band-gap and upon irradiation of the cathode photoconduction was observed for light of photon energies higher than the band-gap. The origin of this anomalous polarity effect of photoconduction in PITN has been discussed.

INTRODUCTION

Poly(isothianaphthene), PITN is one of the most attractive polythiophene, PT derivative, since PITN in the undoped state has the smallest band-gap of about 1.0 eV in the family of conjugated polymers.[1] This small band-gap polymer is dark blue-black when undoped and becomes greenish-yellow and transparent upon doping.[1] This fact indicates that transparent conducting films can be prepared even with organic conducting polymers by low-temperature processing.

It is also desirable from practical view points that the conducting polymers can be doped by p-type and n-type dopants in a reversible manner. Therefore, it is very interesting to clarify whether n-type doping is possible in PITN or not. Moreover, optical properties of PITN such as photoconduction have not been studied so far. This article is concerned with the fundamental electrochemical and optical properties of PITN.

EXPERIMENTALS

PITN was prepared according to a similar procedure that was described in details in our previous publications.[2] The electrochemical investigations were carried out in a three-compartment cell. The *in situ* optical absorption spectroscopy measurements during electrochemical doping were carried out using a Hitachi 330 spectrophotometer.

Photoconductivity induced by irradiating with a Xe arc lamp light passing through a monochromator was measured utilizing a programmable electrometer (Keithley 617S). The sample was sandwiched between two ITO glass electrodes.

RESULTS AND DISCUSSION

The electronic band structure of PITN was deduced, as illustrated in Figure 1.[2] In the undoped state, the band-gap of PITN is about 1.0 eV. The top of the valence band of PITN is located at an energy state higher than that of PT by about 0.5 eV. This result indicates that the dopant in PITN is relatively stable compared with that in PT. The smaller band gap of PITN by about 1.1 eV compared to that of PT should indicate that the bottom of the conduction band of PITN is located at an energy state lower than that of PT by about 0.6 eV. In such a case, successful n-type doping in PITN is expected.

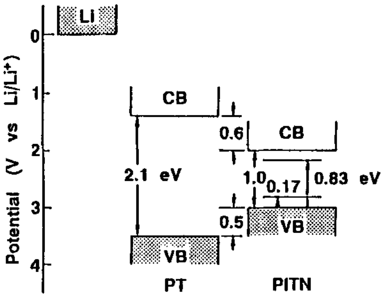

FIGURE 1 Experimental energy-level diagram in p-type doped PITN.

Figure 2 shows a typical cyclic voltammogram of PITN obtained after repeating several redox cycles. The cyclic voltammogram is quite unique compared to that in other conducting polymers. In the cyclic voltammetry of PITN two steps were observed for the reduction and oxidation processes. If the applied potential is reversed at around -0.3 V vs Ag/Ag^+ after the n-type doping, then the peak Ep,c1 disappears nearly totally.

This indicates that the pre-p-type doping is necessary for the appearance of Ep,c1 peak. That is, the PITN film is in p-type doped state at the Ep,a2 potential and the reduction of the p-type doped PITN after the partial discharge occurs at the Ep,a potential. The remaining residual charge by p-type doping is reduced at the Ep,c1 potential. The origin of the Ep,a1 peak can also be explained similarly. The first step (Ep,c1) is interpreted to be due to the reduction of the residual charge in the polymer (irreversible p-type charge). Moreover, the second totally reversible wave (Ep,c2) corresponds to the n-type ($Bu4N^+$) doping in PITN and current peak Ep,c is ascribed to the $Bu4N^+$ undoping. Recurrent sweeps between the undoped state and the Ep,c2 wave appear very similar and show that the n-type doping is a nearly totally reversible process. It should be noted that similar effects of residual charge remain in the polymer after dedoping in the p-type doping process. This residual charge can be completely eliminated only by means of an positive sweep up to Ep,a1 as shown in Figure 2. That is, a sweep to a high positive potential subsequent to a sweep to the Ep,c1 or Ep,c2 potentials results in a new irreversible positive peak Ep,a1 that appears at the threshold of the Ep,a2 p-type (BF4$^-$) doping step. A current peak Ep,a is ascribed to the BF4$^-$ undoping. There exists a hysteresis depending on whether the potential was swept beyond Ep,c1 in the negative cycle and Ep,a1 in the positive cycle.

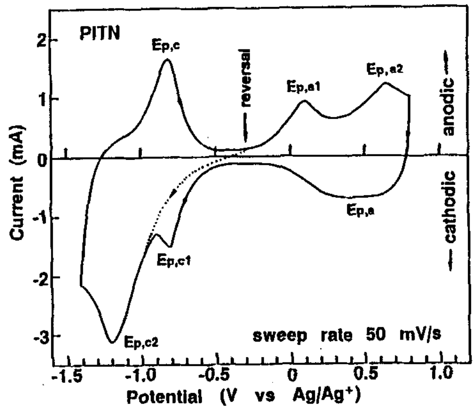

FIGURE 2 Cyclic voltammograms of PITN obtained after repeating the redox cycles several times in acetonitrile 0.2 mol/l Bu4NBF4.

We have also carried out *in situ* optical absorption spectroscopy measurements of the PITN to obtain other evidence of n-type doping. The evolution of the absorption spectra during the negative polarity of a PITN film is shown in Figure 3. Such a feature corresponds to a continuous reduction sweep performed between 0.1 (a rest potential) to -1.4 V vs Ag/Ag$^+$. In the low applied potential region, an absorption peak at about 750 nm which may be interpreted as originated in the interband transition of PITN gradually became larger and was slightly shifted to the long wavelength side, whereas the slight absorption at the near-infrared region was suppressed simultaneously. Such spectral changes can be explained by the existence of a residual charge (p-type dopants). That is, this small modification of the absorption spectrum in the low potential range is interpreted to be due to the compensation of residual charge. With increasing applied potential, their change is not different from that already observed during the p-type doping process.[2] That is, interband transition was suppressed and new absorption band evolved in the infrared region. The undoped PITN film is blue in color, while the polymer in the reduced state is colorless and transparent like a p-type doped PITN. Thus, application to electrochromic displays has been suggested.

From these experimental observations by means of different consecutive sweeps, it should be noted that the appearance of the pre-peaks Ep,c1 or Ep,a1 was only caused in dedoping process of the residual charge stored in the fully doping stages at Ep,a2 or Ep,c2 and partially dedoped at Ep,a or Ep,c. Accordingly, the voltammetric response of the PITN film is affected intensely by their background.

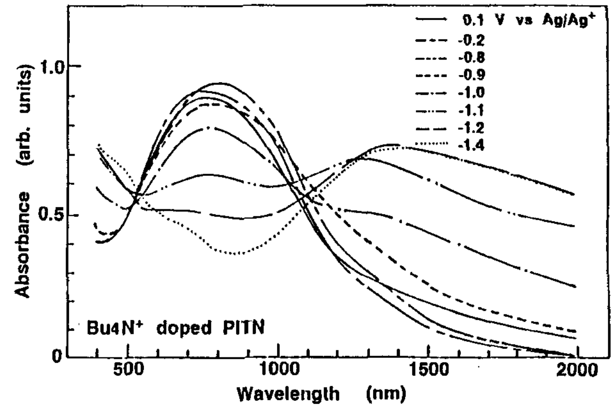

FIGURE 3 Optical absorption spectral change of PITN taken *in situ* during electrochemical Bu4N$^+$ doping as a function of the applied potential.

Figure 4 shows photoconduction spectra of PITN at room temperature for the light irradiations through the cathode and anode electrodes. When the irradiating light was penetrating from the negatively biased electrode (cathode irradiation), it should be noted that the photoconduction was observed in a relatively wide photon energy range. Photoconduction at energy higher than the band-gap was enhanced and only a small peak appears at the band-gap. On the other hand, for the light irradiation from the anode side, a photoconduction signal appeared only at the photon energy corresponding to the band-gap; but at photon energies exceeding the band-gap, only negligible photoconduction was observed. The origin of this anomalous polarity effect of photoconduction in PITN has not been conclusively determined. However, we are speculating several possibilities in its origin as follows at this stage. Usually undoped PITN is a p-type semiconductor throughout the entire temperature range; this was confirmed by the observation of positive thermoelectric power.[1]

Possibility (1). As evident in Fig. 4, the photoconduction spectrum seems to be divided in two parts of different origin, the response at around the band-gap of PITN (about 1.0 eV) and that at higher energy. The former response at around 1.0 eV is much larger for the anode irradiation than that for the cathode irradiation. In many inorganic semiconductors such a large photoresponse was also observed at the band-gap energy. The carrier generation through photoexcited excitons should be effective in the photon energy of the band-gap but at higher photon energy the efficiency of photo-carrier generation may be smaller because of the shorter penetration depth of light and the higher density of defects at the surface area. The larger response for the anode irradiation in the former region suggests that the positive photo-carriers either holes or positive polarons are playing major contribution in consistent with the result of thermoelectric power. On the other hand, the latter response in the higher photon energy range is dominant for cathode irradiation but negligible for the anode irradiation, which suggests that the photo-induced electron injection from the cathode into the sample and the resultant migration of negative carriers such as electrons or negative polarons are the origin of the latter response.

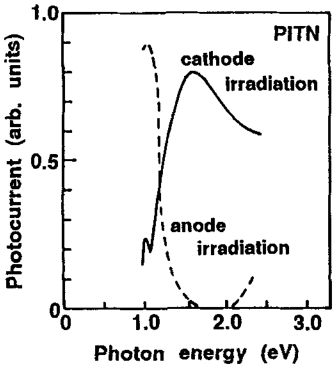

FIGURE 4 Photoconduction spectra of PITN at room temperature.

Possibility (2). By the incident photon with an energy larger than the band-gap, carriers should be excited only in the surface area near the electrode. At the interface between electrode and PITN an inversion layer in which accumulation of negative carriers is expected should be formed. If the carrier is excited in this inversion layer, the hole concentration should be much smaller, due to the recombination, compared with the electron. Therefore, when the irradiated side electrode is positively biased, photoexcited negative carriers will be extracted into the anode, resulting in negligible photoconduction for the light with photon energy larger than the band-gap. When the electrode is negatively biased, the electron should migrate into the bulk, resulting in the photoconduction signal.

Possibility (3). In this conducting polymer the excitation of carrier generation process may be highly complicated. Upon light irradiation, interband absorption by interchain excitation and also intrachain excitation may play role. It is also considered that in the initial step of carrier generation exciton process and direct excitation by band to band may contribute. These complex situation may occur in the range of photon energy as observed in this experiment.

The photoexcitation with light of photon energy smaller than the band-gap energy was not clearly confirmed because of the restricted resolution of used photodiode in this experiment. Detailed experimental studies will be carried out in the future.

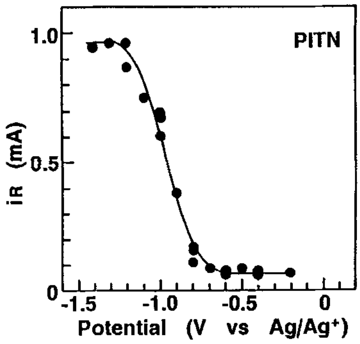

FIGURE 5 Relation between the negative limit potential and the Ep,a1 peak currents (iR).

A reversible redox reaction of the conducting polymers may be also a candidate for application to electronic devices such as memories with learning effect. Especially, the properties of PITN film clarified in this study can also be applied to a writing-reading device in principle, since the appearance of the two pre-peaks Ep,c1 and Ep,a1 suggests that the residual charge (positive or negative) is relatively stable.

Figure 5 indicates the corresponding change of the Ep,a1 peak current (iR) by shifting of the negative potential limit. The reading current is iR (the oxidation current of the residual charge of the polymer) as a function of this negative limit. That is, this result suggests that a part of the record written by n-type doping process of PITN can be wiped out from a residual negative charge which remains in the polymer after the dedoping process. A similar property was also observed in the p-type doping process of PITN. A detailed further experimental study is being performed to achieve a good memory state of the device.

CONCLUSIONS

The fundamental electrochemical and optical properties of PITN have been investigated. A writing-reading device using a residual charge which remains in PITN after the dedoping has also been proposed.

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