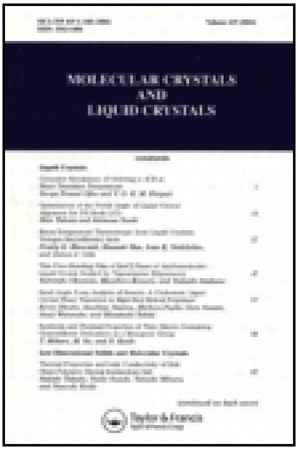

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Polythiophene, Electrochemical Doping and Photoexcitation

Keiichi Kaneto [a] , Yasutaka Kohno [a] & Katsumi Yoshino [a]

[a] Faculty of Engineering, Osaka University, Suita, Osaka, Japan

Version of record first published: 17 Oct 2011.

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 217-220
0026-8941/85/1184-0217/$19.00/0

POLYTHIOPHENE, ELECTROCHEMICAL DOPING AND PHOTOEXCITATION

KEIICHI KANETO, YASUTAKA KOHNO and KATSUMI YOSHINO
Faculty of Engineering, Osaka University, Suita, Osaka, Japan

Abstract Absorption spectra, electrical conductivity and ESR of polythiophene during electrochemical cycles are studied. The existence of a shallow polaron is proposed below the doping level of 3 mol%. Drastic change of conductivity is conjectured to the shallow polaron which is also induced by the photoexcitation. The evolution of gap states at intermediate doping levels is consistent with the picture of polaron → bipolaron.

INTRODUCTION

The generation of charge carriers in conducting polymers with non-degenerate ground state has been explained by the model of polaron (bipolaron).[1] The present experimental work on a polythiophene (PT) suggests the existence of shallow polarons and the (deep) polarons.

EXPERIMENTAL RESULTS

The electrochemically polymerized PT film with the conductivity of $\sigma \simeq 100$ S/cm can be dedoped electrochemically.[2] A neutral PT has $\sigma < 10^{-10}$ S/cm and the ESR spin density (N_s) of ca. 6×10^{17} spins/g which corresponds to ca. 1 spin per 10^4 monomers.

The absorption spectra of PT during electrochemical ClO_4^- doping are shown in Fig.1(a) at dopant concentrations of y > several (in mol%). The peaks at 0.7-0.9 and 1.5-1.8 eV show the blue shift with increasing y and merge into a single peak at ca. 1.1 eV at y ≃ 60. At y < 3, besides, peaks at 1.3 and ca. 1.9 eV are observed to appear in the fractional change of absorption ($\Delta\alpha$) Fig.2(b).[3] The peaks appeared upon n- and p-type dopings are the same energy,[4] suggesting that the evolution of gap states is symmetrical with

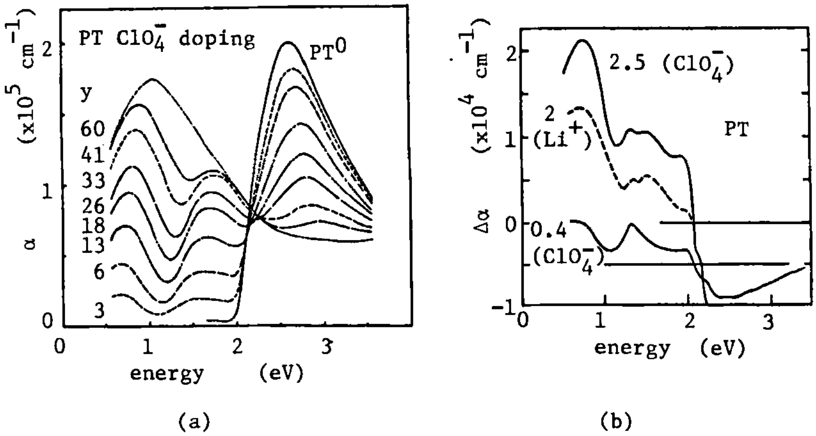

FIGURE 1 Absorption spectra of PT during electrochemical doping of ClO_4^- and Li^+.

respect to the gap center and independent on dopants.

The photobleaching above 2 eV and photodarkening at 1.96 eV with photoluminescence (PL) are observed in the photoexcitated absorption of dedoped PT induced by an Ar ion laser (Fig.2).

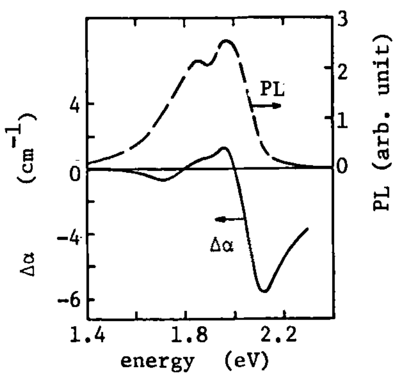

FIGURE 2 Photoexcitated absorption and luminescence in dedoped PT.

The σ and N_s increase remarkably to ca. 1 S/cm and 10^{20}spins/g, respectively, upon doping upto y ≈ 3, followed by the saturation of σ and the decrease of N_s to ca. 10^{19} spins/g.[5] The ESR linewidth decreases sharply from 9 to 0.4 G (motional narrowing), accompanied with the shape change of the Gaussian → Lorenzian. The Pauli-paramagnetic behaviour in the ESR was observed at y > 20.

In the reflectance spectrum of BF_4^- doped (y ≈ 20) PT, a reflectance like plasma edge was observed[5] at ca. 1 eV which gave the plasma frequency of 1.48 eV, the relaxation time of 6.8 x 10^{-16} sec, the core dielectric constant of 2.2 and an optical σ of ca. 300 S/cm. The positive thermoelectric power being ca. 20 μV/K at room temperature depended linearly on the temperature in the BF_4^- (y ≈ 25) doped PT, which gave the density of states of 0.85 states/eV•mono at the Fermi level.[5]

DISCUSSION

The results suggest that three major stages are taking place in PT upon doping, (i) formation of charged carrier with spin at y < 3, (ii) interaction of charged spins at intermediate doping levels and (iii) conversion to the metallic regime at y > 15.

At the stage (i), the energy levels induced in the gap can be drawn as shown in Fig.3(i). SP^+ and SP^- are the bonding and antibonding shallow polarons, respectively, which may come from the weak

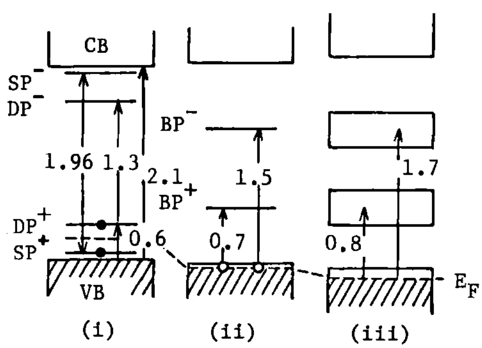

FIGURE 3 Evolution of gap states in PT upon doping, figures; energy in eV, E_F; the Fermi level.

interaction of a dopant and next neighbouring thiophene rings. DP^+ and DP^- are (deep) polarons derived from the strong interaction of a dopant and adjacent rings. The peak observed at 1.96 eV should be originated from the shallow polarons. The peaks of ca. 0.6 and 1.3 eV are ascribed to the transition of the valence band (VB) → DP^+ and DP^+ → DP^-, respectively, since the latter peak becomes obscure due to the bipolaron formation.[1,3]

The charge carrier with spin seems to be related more likely to the shallow polaron. The activation energies of σ are less than 0.15 eV which agree with the binding energy of the shallow polaron.[5]

At the stage (ii), the decrease of N_s implies the formation of spinless charge (bipolaron; BP^+ and BP^-) which locates in the gap as shown in Fig.3(ii).

At the stage (iii), the increased interaction of bipolarons results in the formation of bipolaron bands (Fig.3(iii)). The Pauli-paramagnetic behaviour of ESR, metallic reflection and Positive thermolectric power suggest that the free hole conduction is predominant compared to the bipolaron conduction[1,6] in the case of polythiophene.[3]

REFERENCES

1. J.L. Brédas, R.R. Chance and R. Silbey, Phys Rev. B, 26, 5843 (1982).
2. K. Kaneto, Y. Kohno, K. Yoshino and Y. Inuishi, J. Chem. Soc. Chem. Commun. 382 (1983).
3. K. Kaneto, Y. Kohno and K. Yoshino, Solid State Commun. 51, 267 (1984).
4. K. Kaneto, S. Ura, K. Yoshino and Y. Inuishi, Jpn. J. Appl. Phys. 23, L189 (1984).
5. K. Kaneto, Y. Kohno, S. Hayashi and K. Yoshino, to be publised.
6. J.C. Scott, P. Pfluger, M.T. Krounbi and G.B. Street, Phys. Rev. B, 28,2140 (1983).