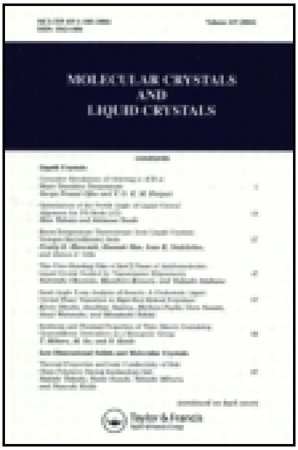

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APPLICATION OF INSULATOR-METAL TRANSITION OF CONDUCTING POLYMERS

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Abstract As example of application of the insulator-metal transition in conducting polymers, electro-optic device utilizing electrochemical doping and radiation induced doping are discussed in detail.

INTRODUCTION

Conducting polymers have attracted much interest not only from the fundamental physical view points, but also from various applications like a solar battery,[1] rechargeable battery[2] and electronic switching element.[3] Recently, we also proposed possible applications of conducting polymers as electro-optic device,[4,5] radiation detector,[6] sensor[7] and etc..

In this paper, we will report details of applications as electro-optic device (Part I), as radiation detector (Part II) and others (Part III) for examples.

Part I ELECTRO-OPTIC DEVICE

The colours of metal and insulator are determined by the plasma reflection and inter-band optical absorption, respectively. Originally, we proposed to use this colour change associated with insulator-metal transition by doping as electro-optic device. However, in the real polymers, the color is also influenced by the formation of electronic states like soliton, polaron and bipolaron etc..

For the construction of the practical device, the polymer must be a high quality thin film with the thickness of 0.1 - 1 μm to obtain clear color change and high switching speed.

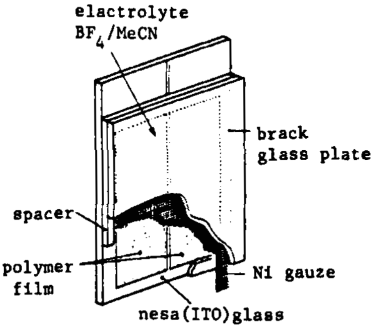

Fig.1 Test cell.

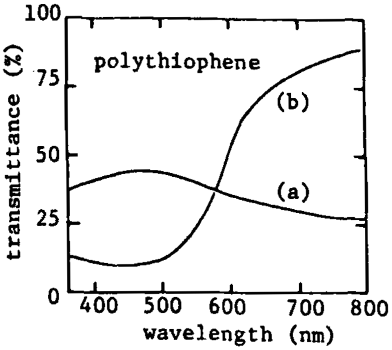

Fig.2 Transmittance spectra of the cell.

Figure 1 indicates one example of the test cell. Electrochemically prepared polythiophene[8] in this case,(thickness:0.1–0.5 μm) on conducting glass was used as working electrode. Either nickel gauze or other conducting glass plate was used as counter electrode. The cell was filled with the appropriate elecrolyte, in this case, ca 0.5 mol/l of $LiBF_4$ in acetonitrile and sealed. By the application of voltage ,$V_a > 0.7$ V, the dopants of acceptor type (in this case BF_4^-) are doped in polymer and metallic colour (blue) appears as shown in Fig.2(a). They are undoped by shortening circuit (or applying the reverse polarity) and the colour as an insulator (red) appears (Fig.2(b)). It can be also used as an optical memory element by opening the circuit after doping or undoping processes. Just the same spectral change was also obtained for the other combination of solvent and solute (Fig.3).

Not only p-type doping by acceptor like ClO_4,BF_4, AsF_6 and PF_6 etc., but also n-type (tetra-butyle ammonium, TBA^+) doping was found to be possible (Fig.4). The spectrum of n-type doped film is just similar to those of p-type doped one, which clearly indicates that these spectra should be originated from the characteristic of polymer itself but not dopants.

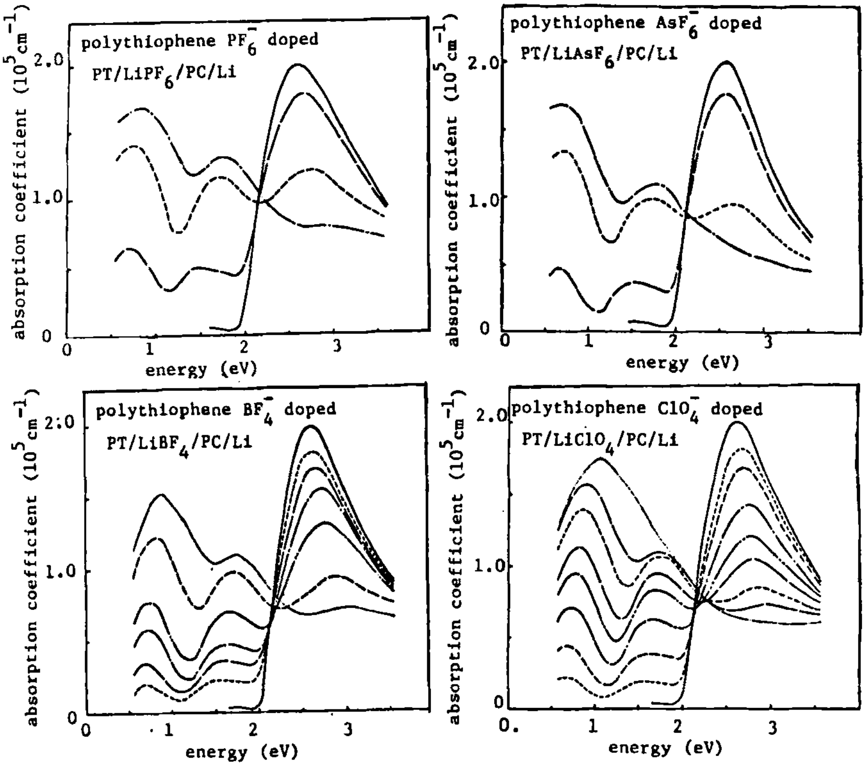

Fig.3 Absorption spectra of polythiophene upon doping in various electrolytes.

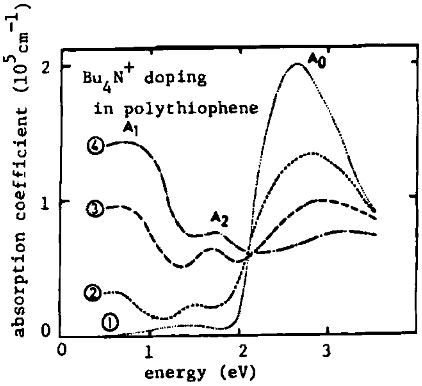

Fig.4 Absorption spectra during TBA doping.

In the electrolyte of $LiBF_4$/acetonitrile, the response time from red to blue, in the case of polythiophene, was ca. 30 msec by the application of 4.5 V and that from blue to red at -2.5 V was 100 msec. The response time remarkably decreases with increasing field strength as shown in Fig.5. At least, at high voltage, the response time becomes of the order of msec, which is faster than the conventional liquid crystal device. Generally, by the application of high voltage, the conducting polymer is considered to start to degrade. However, we can use pulse voltage instead of dc voltage to suppress the succeeding non-effective current flow, which will result in the suppression of degradation.

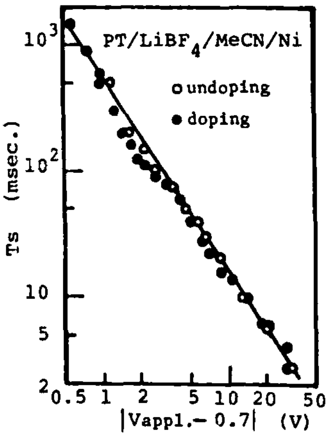

Fig.5 Switching time vs. applied voltage.

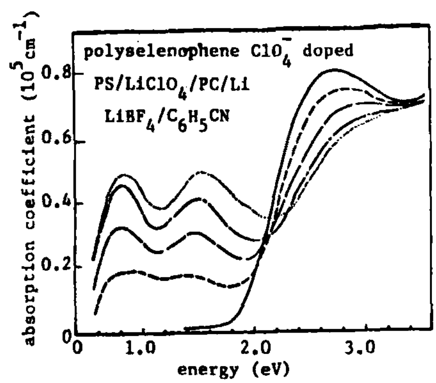

Fig.6 Absorption spectra of polyselenophene during doping.

Switching time is dependent on solvent. For examples, THF and propylenecarbonate indicate much slower response. Though detailed process is not revealed at this stage, perhaps, solvation of dopants molecules may have severe influence on the migration of dopant, diffusion in polymer and interaction at polymer surface.

Similar spectral changes are also observed in many other conducting polymers, for example, polypyrrole, polyfuran, polyselenophene (Fig.6), polyaniline, poly-ortho-azophenylene, poly-para-azophenylene and polypyridazine. Not only solvents usually used for electrolyte like benzonitrile, acetonitrile, THF and PC but also other many conventional solvents like water, alchol, aceton etc. are found to be successfully used for the electro-optic device. In the case of aceton, polymer was relatively stable and swiching was also very fast.

The threshould voltage of this device is comparable or lower than liquid crystal. The swiching speed is also comparable or faster than that of liquid crystal. It should be also noted that the structure is very simple and even optical polarizer is not necessary, which results in the much wider viewing angle compared with liquid crystal TN device. Any special treatment of electrode surface and precise controle of electrode distance are not necessary, which results in the easy construction of large area of panell. We already succeeded to construct the cell with relatively long life of cycle operation.

The range of spectral change is dependent on conducting polymers. Therefore, to cover all the visible spectral range, we are now studying various types of conducting polymers. The study of matrix-type cell etc. is also now in progress.

Part II RADIATION DETECTOR

When the conducting polymer is irradiated under the coexistence of some substance like SF_6, the conductivity increases drastically by electron beam and γ-ray, as shown in Fig.7, which can be explained by the radiation induced doping.[9] Accompanied with this conductivity change, the absorption spectra is also found to change drastically as indicated in Fig.8. ESR linewidth is also found to decrease remarkably. These results are clearly explained in terms of radiation induced doping and resultant insulator-metal transition. This radiation induced doping was also observed in various conducting polymers and with various radiation sources. Therefore, these phenomena can be utilized for the detector of radiation dose. Namely, it can be evaluated by either the change of conductivity or absorption.

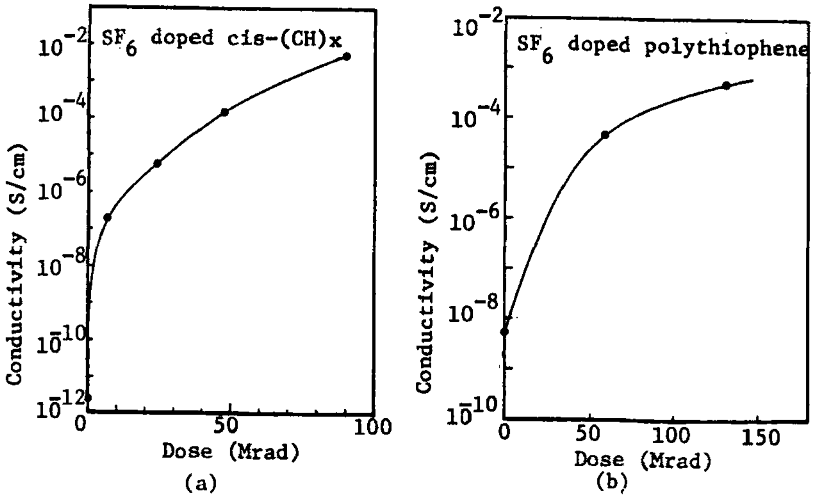

Fig.7 Dependences of electrical conductivity of (a) cis-(CH)x and (b) polythiophene irradiated by electron beam under coexistence of SF_6 on dose.

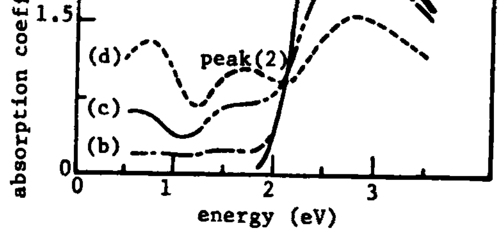

Fig.8 Dependence of absorption spectra of polythiophene irradiated by electron beam under coexistence of SF_6 on dose.

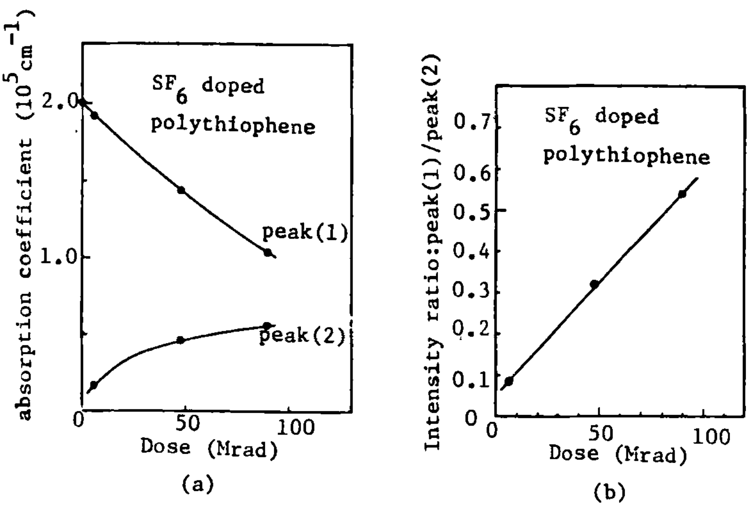

Fig.9 (a) Absorption intensity of peaks (1) and (2) indicated in Fig.(8) as a function of irradiation dose.
(b) Ratio of absorption intensity of peaks (1) and (2) as a function of irradiation dose.

Figure 9 shows dependences of absorption intensities of peak I and peak II in Fig.8 and thier ratio on irradiation dose. The linear dependence of the ratio is convenient for the practical application as detector.

So far, as radiation monitor or detector, CTA (cellulose triacetate) has been used widely. In our new detector, the visible range of light can be used contrary to CTA which are used in ultraviolet and also much higher dose of radiation (>150 Mrad) can be detected compared with conventional CTA detector (<10 Mrad).

Part III OTHER APPLICATIONS

We already reported that conducting polymers and its insulator-metal transition can be used as the detector of humidity[7] and also other gases. Detailed study with the combination of conducting

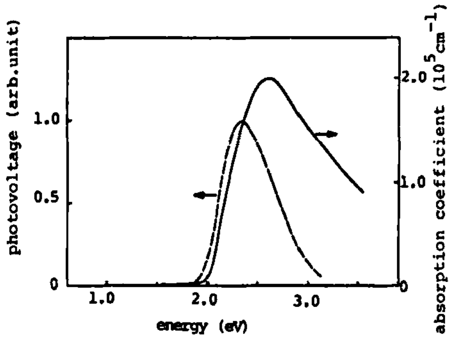

Fig.10 Photovoltaic and absorption spectra of polythiophene.

polmers and various gases are now in progress.

Already, several reports have been reported on the photovoltaic device utilizing polyacetylene, polypyrrole etc.. We found that the Schottky diode prepared with the structure of ITO/pholythiophene/Au also indicates photovoltaic response as indicated in Fig.10. Detailed characteristics of this device will be reported in the near future.

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