電解合成導電性高分子のキャラクタリゼーション および電子デバイスへの応用*

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Characterization of Electrochemically Synthesized Conductive Polymers and Their Application to Electronic Devices

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要　旨

A new class of organic polymers synthesized either chemically or electrochemically has been devised with remarkable ability to conduct electrical current. Their conductivity can be controlled either by chemical or electrochemical doping from metal to insulating region. Types of conductance can also be controlled by doping either with acceptor or donor to give rise *p*- or *n*-type conductance of the polymer film, respectively. As a result, wide application of the doped polymers in the electronic devices have been launched.

In contrast to the anion (acceptor)-doped poly(heterocycles), only few examples of the cation (donor)-doped ones have been studied. To our knowledge, however, detailed investigation of the *n*-type conductance for electrochemically cation-doped polymers has not been carried out so far, although *p*-type conductance of anion-doped ones seems to be well established. As for polymer devices, most works were concerned with Schottky-type ones, although devices based on *p*-*n* junction constructed by pressure contact of *p*- and *n*-doped poly(acetylene) films have been reported. Fabrication of a *p*-*n* homojunction polymer diode would be a new approach to examine the possibility of using a conducting polymers to an electronic device.

In this work, detail clarification of *p*- and *n*-type conductance for anion- and cation-doped poly(thiophene) PT and its derivatives has been made based on the measurements of work function and conductivities together with the current-voltage (J-V) measurements with and without illumination. In addition, a novel method for fabricating a *p*-*n* homojunction in a

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**現在の所属：Bangladesh University of Engineering and Technology, Chemistry Department single strip of poly(3-methyl thiophene) (PMT) film has been proposed which might open a new technology for using conductive polymers in the electronic devices.

Characterization of anion- and cation-doped polymers as *p*- and *n*-type semiconductors : Cyclic voltammograms for PT, PMT and poly(2, 2'-bithiophene) (PBT) films showed that oxidation and reduction of these films lead to color change from deep blue to orange-violet indicating anion- and cation-doping, respectively. When the potential was switched to 0.0V*vs.* saturated calomel electrode (SCE), color of these films turned to red, indicating dedoped states of these polymers.

Determination of the doping levels were done by the measurement of charge *vs.* time (Q-t) during doping and its reverse process. The maximum doping level evaluated from the analysis of a Q-t plot for the anion-doping process was in good agreement with the value from a similar plot obtained for the dedoping process by stepping the potential from +1.4 V to 0.0V. With the cation-doping process, in contrast, the effective dedoped charge from the films, calculated from a Q-t plot in stepping the potential back from −2.4V to 0.0V, was much smaller than the doped charge for cations at -2.4V. Evidently, the finding suggests instability of the cation-doped films although a mechanism for deactivation of the cation-doped films has not been investigated further in the present work.

Work function measurements of PT, PMT and PBT films at their different anion- and cation-doped state indicated that the anion-doped films exhibited work function values greater than that of the dedoped film. On the other hand, work functions of the cation-doped films are smaller than the dedoped film. The finding implies that with anion-doping Fermi level of the film shifts downwards while the cation-doping leads it to move upwards. This trend is consistent with the change of a Fermi level expected for traditional inorganic semiconductors when acceptors or donors are doped.

The changes of the work functions for doped and dedoped films while standing in air have been investigated and the result showed that the change in work function of the cation-doped film with time is fast for the initial couple of hours and stops afterward. A similar trend can be seen for dedoped and anion-doped films although the magnitudes of the changes are relatively small. We also notice that the direction of the work function change for the dedoped and cation-doped PMT films is opposite to that for the anion-doped film. Undoubtedly, a lowering of the Fermi level in the cation-doped film with time is ascribable to the effect of oxygen in air so as to compensate the *n*-type conductance of the cation-doped films. Likewise, a slight lowering of the Fermi level of the dedoped film may be explained in terms of an electron accepting properties of oxygen. The result suggests also that *p*- and *n*-type characters of the anion- and cation-doped films, respectively, remain unchanged even after standing for 24 hours in air.

The above argument on the conductance type of the doped films was further examined by the conductivity measurement. The change in conductivity with a doping level showed that the conductivity increases by more than 5 orders of magnitude when the films were doped with anions. A cation-doping also leads to the conductivity increase, although the maximum conductivity for the cation-doped films is lower than that of anion-doped ones.

The observed increase in conductivity of the polymer films by doping with anions or cations is consistent with the view that the type of conductance can be switched between *p*-type and *n*-type with an intrinsic state for the dedoped film by the electrochemical doping.

J-V characteristics of the sandwich-type cells (i) ITO/(anion-doped film)/In and (ii) ITO/ (cation-doped film)/In showed clear rectification. On the other hand, symmetrical cells such as ITO/(anion-doped film)/ITO and In/(cation-doped film)/In showed ohmic behavior, suggesting that the junctions In/(anion-doped film) and ITO/(cation-doped film) have a blocking nature. Formation of a blocking contact of the cation-doped films with a high work function metal ITO indicates that the films have *n*-type conductance. Similarly, a blocking contact formed between the anion-doped film and a low work function metal In provides an evidence for *p*-type conductance of the films. In addition, appreciable photocurrents were induced while the cells (i) and (ii) were illuminated from In and ITO sides, respectively. The J-V characteristics with and without illumination are in good agreement with the measured work function values of the anion-doped film, cation-doped film, ITO and In.

J-V characteristics of a cell having a configuration ITO/(anion-doped film)/(cation-doped film)/In showed rectification and induced photocurrent while the junction anion-doped film/cation-doped film was illuminated. In view of the fact that the ITO/(anion-doped film) and In/(cation-doped film) junctions exhibit ohmic behavior, the rectifying behavior and photocurrents may be ascribed to the formation of the *p-n* junction at the interface (anion-doped film)/(cation-doped film).

Application of doped-polymers to the electronic devices : An organic *p-n* homojunction has been successfully constructed in a single strip of PMT film by electrochemical cation-doping on one side and photosensitized anion-doping on the other side. Photochemical anion-doping was done by contacting an electrochemically cation-doped PMT film with a degassed mixture of CH_3CN/water (3:1) containing 5×10^{-2} mol dm^{-3} Me_4NPF_6, 1×10^{-4} mol dm^{-3} $[Ru(bpy)_3]^{2+}$ and 1×10^{-2} mol dm^{-3} $S_2O_8^{2-}$. $[Ru(bpy)_3]^{2+}$ and $S_2O_8^{2-}$ act as a sensitizer and a sacrificial oxidant for photochemical anion-doping. The contacting surface between the polymer and the solution was illuminated with white light. The photoexcited CH3CN/water species, $[Ru(bpy)_3]^{2+*}$, was quenched with $S_2O_8^{2-}$ to generate $[Ru(bpy)_3]^{3+}$, SO_4^{-} and SO_4^{2-}. These intermediates, except SO_4^{2-}, have sufficient oxidizing power to dedope and oxidize the cation-doped PMT, because the standard redox potentials of the couples of $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ and SO_4^{-}/SO_4^{2-} are 1.48 V and $>$ 3.42 V *vs.* SCE, respectively. Consequently, the irradiated side of the polymer contacting the solution was oxidized to the anion-doped state, whereas the other side of the film remained in the cation-doped state under appropriate experimental conditions.

The rectifying effect observed with the Al/cation-doped PMT/anion-doped PMT/Au cell provides an evidence for the formation of a *p-n* homojunction in the PMT film since both Al/cation-doped PMT/Al and Au/anion-doped PMT/Au cells exhibit ohmic behavior. The formation of *p-n* homojunction can be inferred from measured work functions of the electrochemically cation-doped PMT, photochemically anion-doped PMT, Al and Au films. The *p-n* homojunction cell yields a short-circuit photocurrent of 0.16 μA cm^{-2}, an open-circuit photovoltage of 0.23 V and a fill factor of 0.30.

The study developed in this thesis shows that PT, PMT and PBT films with *p-* and *n*-type conductance can be prepared by electrochemical doping with anions and cations, respectively. A noble technique for the fabrication of a *p-n* homojunction in a single strip of PMT film has been demonstrated. However, stability of the cation-doped polymer in ambient atmosphere might hinder the efficiency of the photovoltaic devices. Long-term research probably is necessary to develop a commercial potential for conducting polymers and to improve the efficiency and stability of the photovoltaic devices. Research on new conducting polymers is also necessary to discover new, stable materials having better properties. Therefore, future investigation will reveal whether or not polymeric devices will meet the stringent efficiency and stability requirements necessary for practical applications.