

Undoping Effect of Electropolymerized Polymer for Two-Layer Organic Photovoltaic Cells Based on Polymer/Dye Junction

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SYNOPSIS

The undoping effects of electropolymerized poly(3-methylthiophene) (PMeT) and poly(*N*-methylpyrrole) (PMPy) on the open-circuit photovoltage V_{OC} and on short-circuit photocurrent J_{SC} were investigated for two-layer organic photovoltaic cells based on the PMeT or PMPy/vacuum-evaporated rhodamine B (RB) under the electrochemical doping level between -3 and $+3$ V. The value of V_{OC} of the undoped-polymer/RB cell was larger than that of the doped-polymer/RB cell. PMeT/RB and PMPy/RB cells gave the minimum value of J_{SC} at a doping level of 0 V. It was suggested that polarons and bipolarons states formed at a doping level of 0 V may work as a trap site for the carrier to decrease in J_{SC} . Undoping of the PMeT improved V_{OC} and J_{SC} of the PMeT/RB two-layer organic photovoltaic cell together with its durability. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The conducting polymers such as polythiophene (PT) and polypyrrole can be synthesized easily by electropolymerization and behave as a *p*-type semiconductor.¹ On the basis of these properties, many photovoltaic cells utilizing polymer/inorganic,² polymer/metal,³ and polymer/polymer⁴ interfaces have been studied. However, there are some problems with these photodiodes. One of them is that the electrolyte anions (dopant anions) such as ClO_4^- , which are incorporated into the conducting polymer films through electropolymerization, decrease the durability of the cells.

We have studied the Au/polymer/dye/Al two-layer organic photovoltaic cells using the conducting polymer such as polypyrrole, poly(*N*-methylpyrrole) (PMPy), and poly(*N*-vinyl carbazole) prepared by electropolymerization.^{5,6} But these cells were unstable and had a short life because the diffusion of doped anions through the dye layer induced corrosion of the aluminum electrode.

Poly(3-methylthiophene) (PMeT) synthesized electrochemically is known to be very stable in both the doped and undoped states.⁷ However, the two-layer photovoltaic cell using doped PMeT as a polymer layer was still unstable and had a short life because corrosion of aluminum was induced by the diffusion of dopants through the dye layer. Therefore, we fabricated the two-layer photovoltaic cell using undoped PMeT as a polymer layer to improve the instability of the cell arising from the migration of dopants.⁸ As a result, the performance of the cell was improved by use of the undoped PMeT. The electrochemical undoping of the polymer is very significant in improving the characteristics of the cell. In this paper, we report an interesting undoping effect of PMeT, PT, and PMPy on the photovoltage and photocurrent of the two-layer organic photodiode.

EXPERIMENTAL

Materials

N-Methylpyrrole (MPy), thiophene (T), and 3-methylthiophene (MeT) as a monomer, tetraethyl perchlorate (TEAPC) as an electrolyte, and pro-

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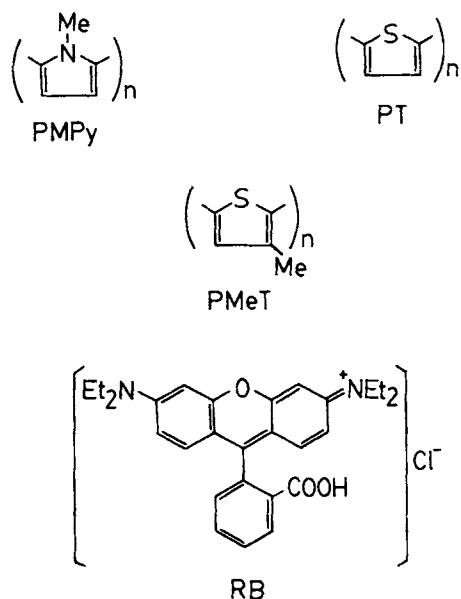


Figure 1 Chemical structures of polymers and dye used in the photovoltaic cells.

pylene carbonate (PC) as a solvent in a GR grade were purchased from Wako Pure Chemical Industries (3-10, Doshomachi, Higashi-ku, Osaka 541, Japan) and were used without further purification. Rhodamine B (RB) as a dye in a specially prepared analytical reagent-grade "TCI-Ace" was purchased from Tokyo Kasei Kogyo Co. (3-1-13, Nihonbashi-Honcho, Chuo-ku, Tokyo 103, Japan) and was used without further purification. Chemical structures of the polymers and RB are shown in Figure 1.

Electropolymerization and Undoping

The electropolymerization was carried out galvanostatically in the single-compartment cell with a Au-sputtered slide glass as a working electrode and platinum plate as a counterelectrode. The condition

of electropolymerization is shown in Table I. The obtained polymer was undoped electrochemically at the fixed voltage for 2–3 min under the conditions shown in Table II. The undoped polymer was rinsed with a large amount of PC and was dried *in vacuo*.

Preparation of the Cell

Rhodamine B (RB) as a dye layer was sublimed in a vacuum onto the polymer layer. Finally, an aluminum layer was evaporated on the top of the RB layer to form the front electrode with an effective area of 1 cm². The cell structure is depicted in Figure 2.

Measurements

Absorption spectra were measured with a Shimadzu UV-2100 spectrophotometer at room temperature. Electron spin resonance (ESR) spectra were recorded on JEOL JES-RE2X spectrometer using the X-band at room temperature.

All the electrical measurements were carried out in air at room temperature. The cell was illuminated by a 300 W tungsten projector lamp with a neutral density and/or interference filter. Usually, the cell was illuminated through the aluminum electrode. The short-circuit photocurrent J_{SC} obtained by the light through each interference filter was normalized and plotted against the corresponding wavelength to draw the action spectra.

RESULTS AND DISCUSSION

Current–Voltage Characteristics

The dark current–voltage (J – V) characteristics of the undoped-polymer/RB cells are illustrated in Figure 2. All the cells exhibited a clear rectifying

Table I Condition of the Electropolymerization

Monomer	Solvent	M. Concn ^a (mol/L)	S. E. Concn ^b (mol/L)	C. D. ^c (mA/cm ²)	P. T. ^d (°C)
MPy	99% aq PC ^e	0.1	0.1	1.5	0
T	PC	0.3	0.1	5.0	5–10
MeT	PC	0.3	0.1	5.0	5–10

^a Concentration of the monomer.

^b Concentration of the supporting electrolyte (Et₄NClO₄).

^c Current density of the electropolymerization.

^d Polymerization temperature.

^e 99% PC + 1% water.

Table II Conditions of the Electrochemical Undoping

Polymer	Solvent	S. E. Concn ^a (mol/L)	U. D. Level ^b (V)	U. T. ^c (°C)
PMPy	99% aq PC ^d	0.1	-2	r.t. ^e
PT	PC	0.1	-3	r.t.
PMeT	PC	0.1	-3	r.t.

^a Concentration of the supporting electrolyte (Et₄ClO₄).

^b Undoping level.

^c Undoping temperature.

^d 99% PC + 1% water.

^e Room temperature.

effect: A forward current was observed when the gold electrode was positively biased with respect to the aluminum electrode. This suggests that an effective barrier is formed inside the organic bulk layer for each cell. The rectifying effect is quite similar to those of the doped-polymer/RB cells that we reported previously.⁶ In the case of the doped-polymer/RB cells, the interface region between doped-polymer and RB was considered to form such an effective barrier.⁶ We confirmed that the Au/undoped-polymer/Al single-layer cells exhibited a similar rectifying effect and that the undoped-polymer/Al interface was the active area.⁹ These facts show that the undoped polymers behave as a *p*-type semiconductor in the same way as do the doped polymers. Accordingly, both undoped-polymer/RB

and doped-polymer/RB cells can have the same electrical characteristics. It is well known that the Au/PMeT interface shows ohmic contact¹⁰ and that the RB/Al interface also shows good ohmic contact and has no effective barrier for photocurrent generation.¹¹ The observed rectifying effect might be derived from the interface between the undoped polymer and RB, which is presumed to form an effective barrier.

Effect of Undoping on Photovoltaic Effect

Under illumination, these cells exhibited the photovoltaic effect. The photocurrent action spectra for the Au/undoped-PMeT/RB/Al cell⁸ showed that the effective region of the cell is the interface between the undoped polymer and RB.

Table III summarizes the photovoltaic device parameters of the undoped-polymer/RB and doped-polymer/RB cells. The doped-PMeT/RB cell was very unstable as were the earlier cells that the Al electrode corroded (see the pictures in Fig. 2 in Ref. 8) and data could not be obtained. It is interesting to note that the value of the open-circuit photovoltage V_{OC} of the undoped-polymer/RB cell is larger than that of the doped-polymer/RB cell. Lowering of the doping level of the polymer might make the barrier more effective. Hiramoto et al.¹² reported that the doping into the *p*-type organic dye led the V_{OC} of the two-layer organic photovoltaic device to become larger. Polymer and dye each showed a reverse doping effect on V_{OC} . The mechanism of increase in the V_{OC} for the undoping of the polymer might be different from that for the doping of the dye.

Effect of Doping Level on the Photocurrent

As shown in Table III, the J_{SC} of the doped-polymer/RB cell is larger than that of the undoped-polymer/RB

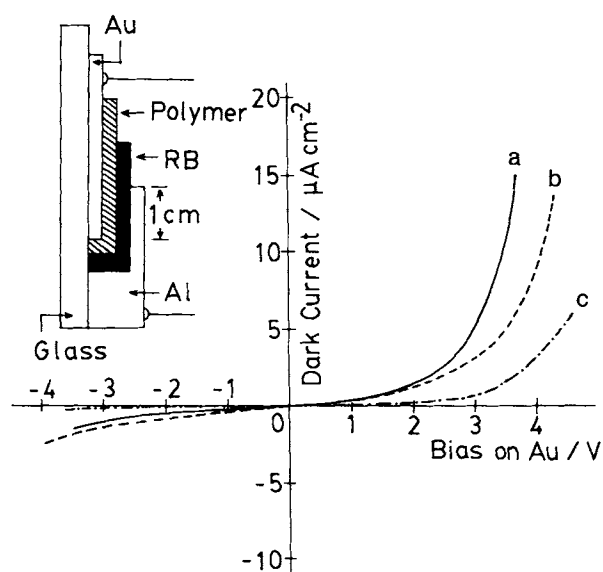


Figure 2 Schematic diagram of the polymer/RB sandwich cell structure and typical dark current-voltage characteristics of the cell: (a) PMPy; (b) PT; (c) PMeT.

Table III Photovoltaic Device Parameters of Polymer/RB Cells

Cell	I_T (mW/cm ²)	J_{sc} (μ A/cm ²)	V_{oc} (mV)	FF	η' % ($\times 10^3$)
Undoped PMPy/RB	1.0	0.08	690	0.23	1.3
Undoped PT/RB	1.0	0.20	780	0.14	2.2
Undoped PMeT/RB	1.5	0.57	860	0.14	4.8
Doped PMPy/RB	7.0	2.20	540	0.13	2.2
Doped PT/RB	1.4	1.00	340	0.20	4.9

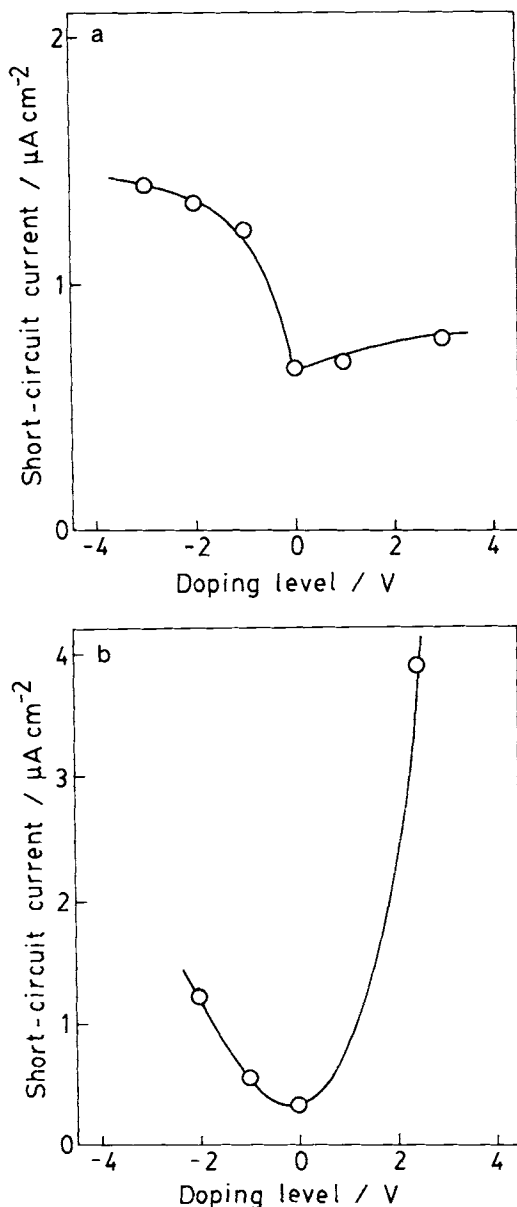


Figure 3 (a) Dependence of J_{sc} for the PMeT/RB cell on the doping level of PMeT. Irradiation power: 10 mW/cm². (b) Dependence of J_{sc} for the PMPy/RB cell on the doping level of PMPy. Irradiation power: 10 mW/cm².

RB cell except for a set of PMeT/RB cells in which the doped-PMeT/RB cell is very unstable. This seems to be reasonable because the doped polymer is more conductive than is the undoped polymer.¹⁰

Figure 3 shows the relationships between the short-circuit photocurrent J_{sc} of the cell and the doping level of the (a) PMeT and (b) PMPy, respectively. The doping level is defined as a biased voltage to control the concentration of ClO_4^- in PMeT or PMPy film. The value of J_{sc} gave the minimum at the doping level of 0 V for both cells. This might not be explained only by a high photoconductivity observed for undoped polymer under illumination.¹⁰ Localized electronic states arising in the band structure of the conducting polymer as polarons or bipolarons states must be considered to explain the minimum J_{sc} at the doping level of 0 V, as described below.^{13,14}

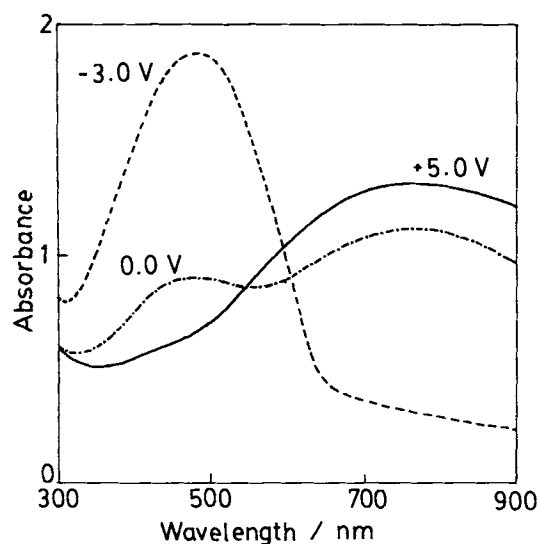


Figure 4 Absorption spectra of PMeT on the various doping levels. (solid) +5.0 V; (dot-dash) 0.0 V; (dash) -3.0 V.

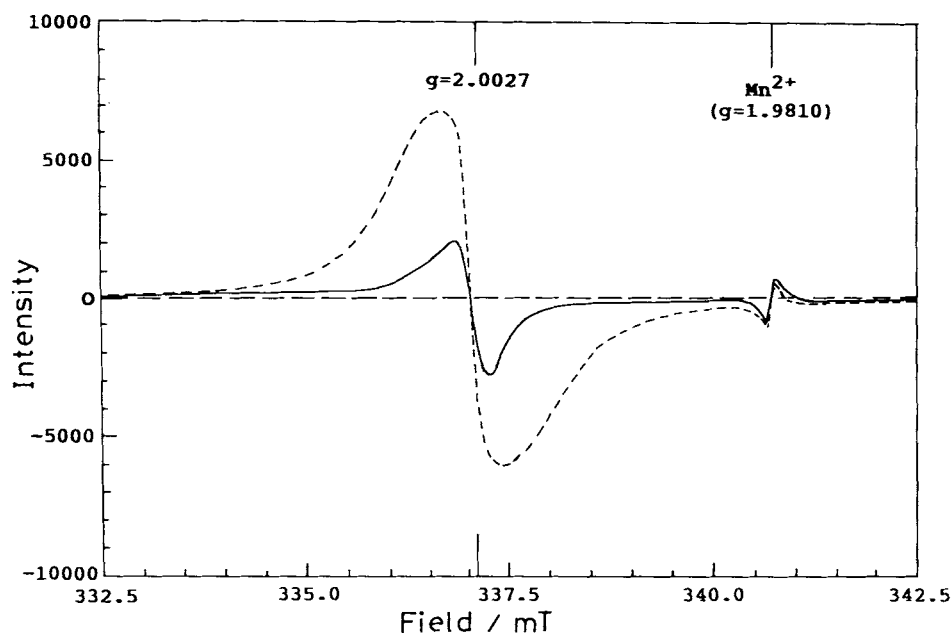


Figure 5 ESR spectra of doped and undoped PMeT with the Mn^{2+} marker: (dash) doped (no undoping); (solid) undoped at -3.0 V.

The Band Structures of Polymer for Various Doping Levels

Figure 4 shows absorption spectra of PMeT at the various doping levels, suggesting the formation of polarons or bipolarons above 0 V. The evidence for the formation of polarons was supported by the ESR data (Fig. 5). Figure 6 illustrates the evolution of the band structure of the polymer on doping. The left side (1) is the undoped state and the right side (4) is the hypothetical 100% doping level, with quasi-metallic behavior. The middle (2) and (3) are

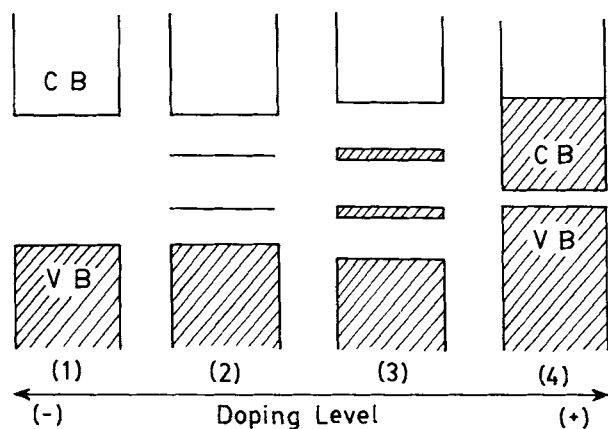


Figure 6 Evolution of the band structure of polymer for various doping levels (modified from Skotheim¹⁴): (1) undoped; (2, 3) intermediate doping level; (4) hypothetical 100% doping level.

intermediate states, and the former consists of polaron and bipolaron states, and the latter, of overlapped bipolaron states forming two bands. At the 0 V doping level, a number of localized electronic states should form. The localized electronic states may work as a trap site for the carrier, so that J_{SC} shall decrease in proportion to the number of the localized electronic states. As shown in Figure 3(a), the J_{SC} of the undoped-PMeT/RB cell is larger than that of the doped-PMeT/RB cell. Because of the instability of doped-PMeT photovoltaic cells,⁸ its J_{SC} is considered to be decreased. Undoped PMeT is well known as a high photoconducting polymer.¹⁰ We have reported that the Au/undoped-PMeT/RB/Al cell is very stable.⁸ The present paper reports that the undoped-PMeT/RB cell provides larger V_{OC} and J_{SC} besides the stability of the cell.

CONCLUSIONS

Polymer/RB two-layer organic photovoltaic cells using doped and undoped conducting polymers (Au/polymer/RB/Al) exhibited a clear rectifying effect and showed the photovoltaic effect on illumination. The open-circuit voltage V_{OC} of the undoped-polymer/RB cell is much larger than that of the doped-polymer/RB cell. The cell for the doping level of 0 V had the minimum J_{SC} . This was explained by the change in the band structure of the polymer. Undoping of the PMeT improved the V_{OC} and J_{SC} of

the PMeT/RB two-layer organic photovoltaic cell together with durability.

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