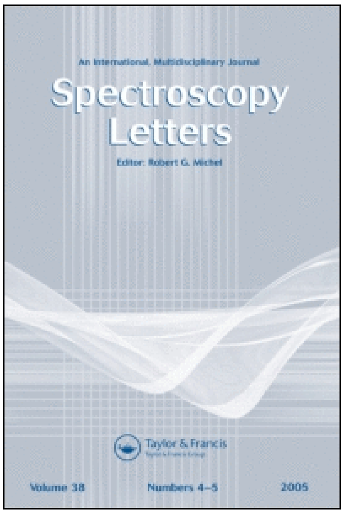

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Spectroscopic Studies of the Stability of Doped Polythiophenes Under Air

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SPECTROSCOPIC STUDIES OF THE STABILITY OF DOPED POLYTHIOPHENES UNDER AIR

Keywords: Infrared spectroscopy, UV-visible spectra, conductive polymer, polythiophenes, air

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ABSTRACT

The stability of the doped state of conductive polythiophenes under air was investigated by the use of Infrared (IR) and UV-visible (UV) spectroscopies. Poly(3-methyl thiophene) doped with BF_3-ethyl ether (BFEE). shows higher stability due to its stereoregularity-chain structure. While the doped polythiophene (PT) degrades easily under the moisture.

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INTRODUCTION

Recent years have witnessed the emergence of growing class of conductive polymers with π-conjugated electronic structure.[1,2] The enviromental stability of conductive polymers is the most crucial problem that must be concerned before they can be widely used. In this letter, we describe the spectroscopic studies of the stability of polythiophene (PT) and poly(3-methyl thiophene) (PMT) doped with BF_3-ethyl ether (BFEE).

EXPERIMENTAL

Electrochemical polymerization of PT and PMT were performed in a one-compartment three-electrode cell with the use of a PARC M273 potentiostat under the control of a computer. To obtain a free-standing film, stainless steel sheets (1.5 x 7 cm^2) were employed as working electrodes and counter electrodes. The galvanostatic method was used for electrochemical polymerization at a current density of 1 mA cm^{-2} and the thickness of the deposited films was controlled by the electric charge passed during film growth. All potentials were measured versus an Ag/AgCl (3.5 M KCl) reference. Each solution containing 0.1 mol L^{-1} thiophene was degassed by bubbling dry argon before the experiment and maintained a slight argon overpressure during the experiment.

IR spectra of PT and PMT were recorded by a Bruker IFS-66V spectrometer. UV-visible spectra weremeasured with a Shimadaza UV-3100 spectrometer.

RESULTS AND DISCUSSION

As the BFEE-doped PMT film was exposed to air with 32% relative humidity at room temperature for 80 days, it maitained its dark color.

Figure 1 shows its UV spectra recorded before and after the exposure respectively. A very broad band extending from 600 to 900 nm, characteristic of the existence of polaron (or bipolaron) absorption could be observed in Figure 1A. This indicates that the filled valence band of the polymer became partially empty, as the film was doped. After exposure in air for 180 days, there is no significant changes in the UV spectrum in Figure 1B, indicating that BFEE-doped PMT film is fairly stable in air.

In contrast to PMT, where the doped state is stable in air, the BFEE-doped PT is unstable. Figure 2A and 2B show the UV spectra of doped PT recorded before and after exposure to air for 180 days, respectively. After exposure, a broad band in region of 400 to 550 nm, corresponding to a neutral PT state increased in intensity[3]. While the absorption band in region of 600 to 900 nm, which is due to polaron (or bipolaron) reduced in intensity[4]. The color of PY film changed from blue to red after exposure. These changes indicate that the doped PT is reduced from its oxidation state to the reduced state.

Figure 3 illustrates IR spectra of doped PT film exposed to air with 32% humidity for various times. After exposure, the bands near 1034, 1196, 1340 cm^{-1} bands, which are characteristic absorption of BFEE still exist but reduced in relative intensity, compared with the C-H vibration model at 787 cm^{-1}.

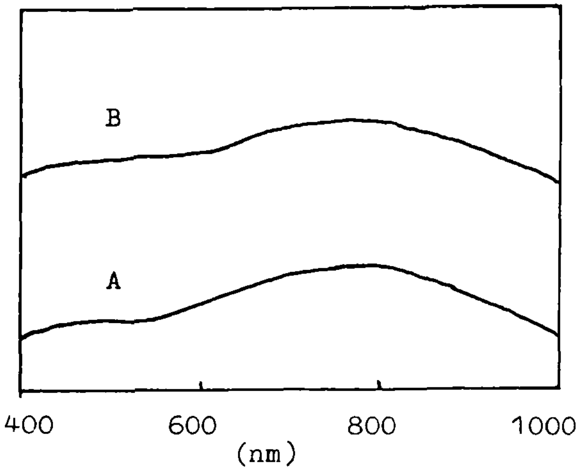

Figure 1. UV spectra of BFEE-doped PMT film recorded before (1A) and after (1B) exposure in air for 80 days respectively.

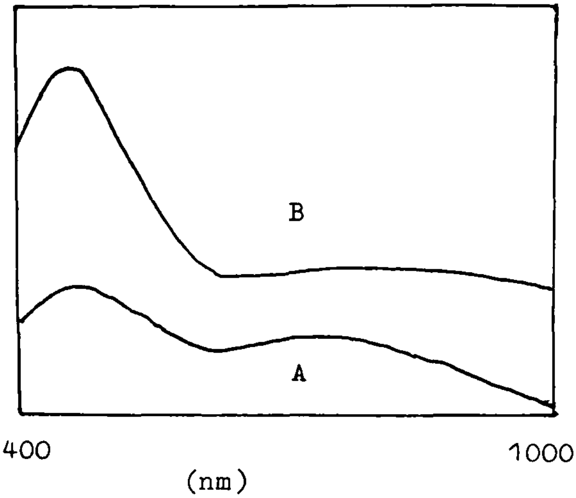

Figure 2. UV spectra of PT film recorded before (2A) and after (2B) exposure in air for 180 days respectively.

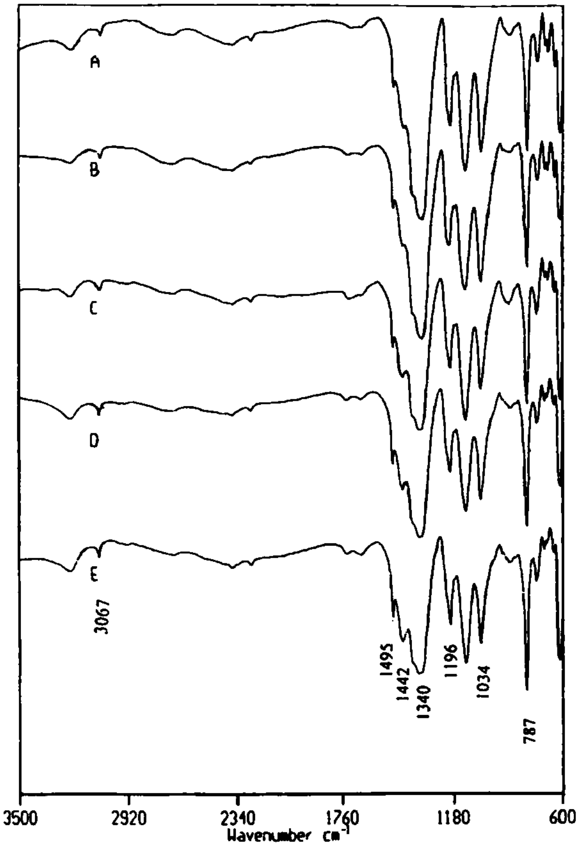

Figure 3. IR spectra of PT film exposed in air with 32% humidity for 1 day (A), 14 days (B), 35 days (C), 50 days (D) and 80 days (E).

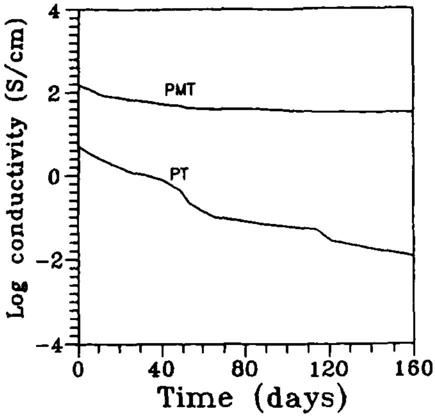

Figure 4. Conductivity changes of PT and PMT upon exposure in air.

The spectral changes shown in Figures 2 and 3 indicate the partial dedoping of PT during exposure. While the spectra of PMT do not show any significant changes after exposure.

The time dependence of electric conductivity of doped PMT and PT film is illustrated in Figure 4. For PT film, the conductivity droped continuously during 160 days. While PMT film is rather stable during exposure in air.

PMT shows not only higher conductivity but also better stability in air than PT film. These values indicate that PMT is a better film for the possible application in microelectronic industries.

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