Radical Polymer and its Nano-sized Thin Film Device

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1. Introduction

Organic radical molecules bear unpaired electrons and are oxidized and reduced by applying voltage. For example, 2,2,6,6-tetramethylpiperidinyloxy radical releases one electron to become the corresponding oxoammonium salt, returning to the TEMPO radical by one-electron reduction [1]. These radical molecules had been extended to radical polymers, which are characterized by their transparency, film-forming property, etc., besides the redox property [2]. On the other hand, the devices and polymer memory consist of the redox activity materials were reported [3–6]. In this paper, poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) was selected as a radical polymer, and *I-V* characteristics of a PTMA device as well as the electrochemical characteristics of PTMA were studied.

Fig. 1 Redox of the TEMPO radical

2. Experimental

PTMA (molecular weight: 89000 and radical concentration: 70%) was prepared according to our previous paper [2].

The cyclic voltammetry was measured by using a conventional cell under an atmosphere of dry argon. The electrolyte solution was consisted of 0.1 M tetrabutylammonium tetrafluoroborate in dichloromethane. A platinum disk and a coiled platinum wire were used as the working and the

Fig. 2 Configuration of the nano-sized thin film device and chemical structure of PTMA

counter electrode, respectively. The reference electrode was Ag/AgCl.

Electron spin resonance (ESR) spectra and surface of the PTMA layer were observed by using a JEOL JES-TE200 ESR spectrometer with 100 kHz field modulation and by a Nanoscope III a atomic force microscope (AFM) (Digital Instruments), scanning electron microscope (SEM) (Keyence), stylus-type film thickness meter (KLA-Tencor).

PTMA was dissolved in chloroform (5 g/l), the solution was spin-coated on an ITO glass substrate, and aluminum was deposited onto it as the cathode. The thickness of the PTMA layer was 15 nm, and the ITO and aluminum layers were 150 nm.

A positive voltage and a negative voltage were ramped from -8 to 8 V. The device was electrically characterized by using a 2400-C digital source meter (Keithley).

3. Results and Discussion

The cyclic voltammetry of PTMA in the dichloromethane solution gave a unimodal and sharp wave which was repeatedly recorded in the potential sweeps of 100 times at room temperature (Fig. 3). The voltammogram means that the redox

Fig. 3 Cyclic voltammogram of PTMA (scanning rate = 100 mV/s) in CH_2Cl_2 with 0.1M $(\text{C}_4\text{H}_9)_4\text{NBF}_4$ as a supporting electrolyte

Fig. 4 ESR spectrum of the dichloromethane solution of PTMA at room temperature

of PTMA was reversible and stable. Redox potential of the PTMA was observed at ca. 0.8 V vs. Ag/AgCl. The redox of PTMA which agreed with that of the TEMPO radical was ascribed to the reaction between the radical and the oxoammonium salt. The small separation of redox peaks suggested a very rapid and reversible electron transfer reaction for PTMA.

Fig. 4 shows the ESR spectrum of the dichloromethane solution of PTMA. The broad ESR signal at $g = 2.00$ indicated both the oxygen-centered radical and the high concentration of the unpaired electron along the polymer chain.

AFM image (Fig. 5) of the PTMA layer formed on the ITO substrate elucidated a smooth and homogeneous polymer layer formation. Both SEM and a stylus-type film thickness meter measurement indicated the 15 nm thickness of the PTMA layer on the substrate.

Current - voltage (I - V) curves of the PTMA device displayed a nonvolatile behavior. Typical I - V curves are shown in Fig. 6. When the bias was

Fig. 5 AFM image of the spin-coated PTMA

Fig. 6 I - V characteristics the device with the configuration of ITO / PTMA / Al

ramped from 0 to 8 V, the current injection appeared with a high resistance upon the range of 0 - 4 V. However, the conductivity of the device was switched to a low resistance state at the 5 V (first bias). Upon the second bias, the I - V relation was almost linear from the low given voltage. After the bias was negatively ramped from 0 to -8 V (third bias), the state of the device remained the low resistance one (fourth bias).

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