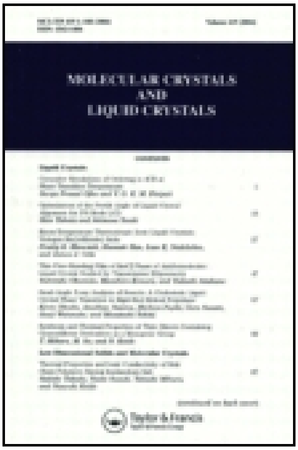

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Solution and Electrical Properties of the Water-Soluble Poly(3-Thiopheneacetic Acid) and its Hydrogel

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Solution and Electrical Properties of the Water-Soluble Poly(3-Thiopheneacetic Acid) and its Hydrogel

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The water-swollen poly(3-thiopheneacetic acid) (P3TAA) gels with various degree of cross-linkage (DCL) were synthesized. Doping behaviors of watersoluble polythiophene and its gel using I_2 and concentrated $HClO_4$ solution as dopants were studied. Electrical conductivity of doped polythiophene gel was investigated. In addition, we have investigated chemomechanical behavior by electric field, and the possibility of polythiophene gel as an electrode is introduced.

Keywords: Polythiophene hydrogel; doping behavior; electrical conductivity

INTRODUCTION

Polymers containing thiophene system have been a subject of research for more than two decades. However, characterization and processing of this material have been limited by their inherent insolubility. Recent progress in the synthesis of new polythiophene derivatives has led to the preparation of processable electroactive polymers which have promising properties for industrial applications [1-2]. The incorporation of relatively long and flexible side chains leads to soluble polymers with a stiff backbone, and this has also been extended to the synthesis of water-soluble polythiophenes by substitution of aromatic hydrogen with hydrophilic groups such as carboxylic acids.

The neutral forms of conjugated polymers generally present a very low conductivity. They can be oxidized chemically or electrochemically accompanied by an insertion of counterions. Most of the I_2-doping for conductive polymers has been performed in vapor state or liquid state using an organic solvent. In this paper, doping behaviors of water-soluble polythiophene and its gel using I_2 and concentrated $HClO_4$ solution as dopants in water were studied by measuring the UV-visible absorption spectra. Electrical conductivity of doped polythiophene gel was investigated. We have investigated chemomechanical behavior by electrical field, and the possibility of polythiophene gel as an electrode was examined.

EXPERIMENTALS

Reagents and Materials: 3-thiopheneacetic acid (3TAA) (Tokyo Kasei) and anhydrous ferric chloride ($FeCl_3$) (Wako Pure) were all used as received. Adipoyl dihydrazide (ADH) (Wako Pure) as a cross-linking agent and N, N '-dicyclohexylcarbodiimide (DCC) (Tokyo Kasei) as a condensation agent were all used as received. Perchloric acid solution ($HClO_4$, 60wt%) (Junsei), I_2 (Junsei) as a dopant, and KI (Wako Pure) were all used as received. Dimethylsulfoxide (DMSO) (Wako Pure) was dried over CaH_2 for 24hr under N_2 and distilled under vacuum before use.

Preparations of the Water-Soluble P3TAA and its Hydrogel: Poly(3-thiopheneacetic acid) (P3TAA) was synthesized by chemical oxidative coupling in dry $CHCl_3$, using anhydrous $FeCl_3$ as a catalyst according to the previously reported method [3]. P3TAA gels with different degree of cross-linkage (DCL) were prepared by cross-linking via a condensation reaction between P3TAA and ADH as a cross-linking agent, using DCC as a condensation agent in DMSO at room temperature for 2 days. The obtained P3TAA gel was washed with fresh DMSO and deionized water repeatedly to remove impurities. DCL was defined as a molar ratio of cross-linking agent to the repeating unit of polymer.

Instrumental Measurements: The structure of polymer was confirmed by FT-IR (Japan Spectroscopic Co., MFT-2000) and ^1H NMR (JEOL JNM-400, 400 MHz). The weight-average molecular weight (M_w) was estimated by gel-permeation chromatography (GPC) with standard polystyrene (Shodex Standard SM-105) as a reference using THF as an eluent at 40°C. M_w and polydispersity were found to be as 1.6×10^4 (repeating unit=35) and 2.81, respectively. UV-visible absorption spectra were obtained with a Hitachi UV-visible spectrophotometer (Model U-3000) at various conditions. The conductivity was measured by an ac two-terminal method using an LCZ meter at 20°C. The polythiophene gel was cut into 5×5×2 mm rectangular solid shape and was sandwitched between a pair of parallel-plate electrode.

RESULTS AND DISCUSSION

It has been carried out I_2-doping in the aqueous state by mixing P3TAA solution with I_2 in the buffer solution (pH=7.0; using a phosphate buffer solution) containing 0.2 M KI. Figure 1 shows UV-visible absorption spectra of the neutral (B) and oxidized (C) states of water-soluble P3TAA. A new broad spectrum appears at around 749 nm, which is contributed to polaron after doping and corresponds to localization of electron. This change in the visible range of absorption spectrum corresponds to a change of the color of polymer solution from red (neutral state) to black (oxidized state). The I_2-doping on water-swollen P3TAA gel has also been attempted. However, no characteristic peak due to the doped state was observed.

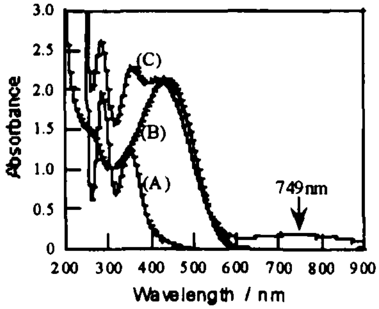

FIGURE 1. UV-visible absorption spectra of (A) 2x10^{-3} wt% I_2 solution in the presence of 0.2 M KI, (B) 5x10^{-4} M P3TAA in a phosphate buffer solution of pH=7, and (C) I_2 doped P3TAA solution at 25 °C.

We have further studied the doping behaviors of water-soluble P3TAA and its gel using a concentrated $HClO_4$ solution as a dopant. When 60 wt% $HClO_4$ solution was added into the P3TAA aqueous solution, the solution turned to black (oxidized state) to give a precipitate. When a P3TAA gel was immersed in

$HClO_4$ solution, the gel became black and shrunk to some extent. When absorption spectrum was measured, a new broad peak centered at 749 nm appeared in addition to the maximum of absorption around 405 nm.

To investigate these doping effects further, electrical conductivities of P3TAA gels doped with 60 wt% $HClO_4$ solution was measured. Undoped wet and dry P3TAA gels showed the electrical conductivities of 7×10^{-4} S/cm and 7×10^{-8} S/cm, while doped P3TAA gels showed 2×10^{-2} S/cm and 1×10^{-3} S/cm, respectively. Though the electrical conductivity of doped P3TAA gels is lower than that of electrochemically doped poly(3-alkylthiophene), the obtained results clearly demonstrate that the increase in the conductivity of doped P3TAA gel, both in the dry and wet state, is attributed to the successful doping of water-soluble P3TAA gel.

Gel changes its size and shape in response to environmental stress to other stimuli. These unique characteristics of gels allow them to be used as chemomechanical systems [4], which convert chemical free energy into mechanical work. Here, we introduce a newly polymer gel, polythiophene gel, responding both to the electronic and ionic signals due to its electronically and ionically conductive nature. P3TAA gels (15mm long, 1mm wide, 1mm thick) showed bending motion to an ionic stimuli like the polymer gel-surfactant assembly reaction. The extent of bending from center point in 0.2 M KI solution including I_2 was larger than that of in 0.2 M KI solution without I_2. This result suggests that I_2 plays a certain role on bending motion of a polythiophene gel. The bending motion of P3TAA gel to an electronic stimuli was also observed when a P3TAA gel was used as an working electrode in 0.2 M KI solution with I_2 Bending direction was constant regardless of changing the direction of electric field.

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