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Preparation and Characterization of a Water-Soluble Conjugated Polymer-Iron(III) Chloride Complex

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A water-soluble ionic polyacetylene, poly(2-ethynyl-N-pentylpyridinium iodide) [PEPPI] was prepared by the uncatalyzed polymerization of 2-ethynylpyridine by using 1-iodopentane in high yield. PEPPI-iron(III) chloride complex was prepared by the reaction of PEPPI and iron(III) chloride in DMF and its properties were characterized. The electrical conductivity of PEPPI-iron(III) chloride complex was 4.3 × 10^{-4} S/cm. The photoluminescence (PL) spectra of PEPPI-iron(III) chloride complex showed that the photoluminescence peak is located at 578 nm, corresponding to a photon energy of 2.15 eV. The cyclic voltammograms of PEPPI-iron(III) chloride complex exhibited irreversible electrochemical behaviors between the doped and undoped peaks. It was found that the kinetics of the redox process of polymer is controlled by the reactant diffusion process.

Keywords Polyacetylene; 2-ethynylpyridine; poly(2-ethynyl-N-pentylpyridinium iodide); iron(III) chloride; electro-optical; cyclovoltammogram

1. Introduction

Since the initial discovery in 1977, that polyacetylene, now commonly known as the the simplest conjugated polymer and a prototypical conjugated polymer exhibiting metallic conductivity in its p- or n-doped states by either chemical or electrochemical method [1–5], great progresses in organic semiconductors with electrical, electronical, magnetic, and optical properties and knowledge of their physical and chemical properties drive the development of low-cost optoelectronic applications such as light-emitting devices [6–8], biological and chemical sensors [9,10], nonvolatile memory devices [11–13], solar cells [14–16], field-effect transistors [17,18], and photosensing devices [19,20].

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Polyacetylene has been widely studied for both fundamental understanding of its properties and for potential applications [3–5]. However, despite a high conductivity, its instability in atmospheric conditions constitutes a major obstacle to practical applications. On the other hand, substituted polyacetylenes have exhibited improved solubility, leading to processibility, and improved stability but with considerable sacrifice of electrical properties [21–28].

The progress of various transition metal-based polymerization catalysts enabled the synthesis of a wide variety of conjugated polymers from monosubstituted and disubstituted acetylenes [21,22,26], and nonconjugated diynes [23,24,27]. Polyelectrolytes have been actively investigated for several decades. Various conjugated polyelectrolytes had been prepared from the linear polymerization of ionic acetylene monomers by the metathesis catalysts [23]. A new class of ionic conjugated polymers was prepared by the spontaneous polymerization of ethynylpyridinium salts without any additional initiator or catalyst [30,31]. The advantage of this polymerization was known to originally eliminate the contamination of catalyst or initiator impurities. We have also reported the synthesis of various functional ionic polyacetylenes via the uncatalyzed polymerization of ethynylpyridinium salts produced in the initial stage of reaction by the quaternarization reaction of ethynylpyridines and functional alkyl halides or ring-openable cyclic compounds [32–36].

In recent years, we prepared a new water-soluble ionic polyacetylene (PEPPI) by the uncatalyzed polymerization of 2-ethynylpyridine by using 1-iodopentane [37]. Here, we report the preparation of PEPPI-iron(III) chloride complex and characterized its electro-optical and electrochemical properties.

2. Experimental

2-Ethynylpyridine was prepared as reported in literature [38]. The resulting 2-ethynylpyridine was purified by vacuum distillation after drying with calcium hydride. Iron(III) chloride (Aldrich Chemicals., anhydrous, powder, 99.99 + %) and 1-iodopentane (Aldrich Chemicals., 98%) were used as received. PEPPI was prepared by the uncatalyzed polymerization by heating the equimolar mixture of 2-ethynylpyridine and 1-iodopentane in DMF solvent as reported in our previous paper [37].

PEPPI-iron(III) chloride complex was prepared as following procedure. In 100 mL reactor containing 40 mL DMF, 1.0 g of PEPPI (3.33 mmol per monomeric unit) and 0.270 g of iron(III) chloride (1.67 mmol) was added and stirred at 30°C for 6 hrs. Then the black reaction solution was precipitated into a large excess of ethyl ether. The precipitated material was filtered and dried in vacuum oven at 40°C for 24 hrs. 1.20 g of PEPPI-iron(III) chloride was isolated in a lustrous black powder.

Electrical conductivity measurements were performed on pressed pellets employing the standard four-probe technique with an a Hewlett-Packard 3490 multimeter and a Keithley 616 Digital Electrometer. Pellets with diameter of 13 mm and thickness of around 0.5 mm were prepared by hydraulic pressing with pressure of 40 Mpa. Energy dispersive X-ray (EDX) analyses were performed by Hitachi JEOL system (S-4200).

The UV-visible absorption spectra were measured by a HP 8453 UV-visible Spectrophotometer. Electrochemical measurements were carried out with a Potentionstat/Galvanostat Model 273A(Princeton Applied Research). To examine electrochemical properties, polymer solution was prepared and the electrochemical measurements were performed under 0.1M tetrabutylammonium tetrafluoroborate solution containing DMF. ITO, $Ag/AgNO_3$ and platinum wire were used as a working, reference and counter electrode,

respectively. The photoluminescence spectra were obtained by Perkin Elmer luminescence spectrometer LS55 (Xenon flash tube) utilizing a lock-in amplifier system with a chopping frequency of 150 Hz.

3. Results and Discussion

PEPPI was easily prepared by the uncatalyzed polymerization of 2-ethynylpyridine by using 1-iodopentane under mild reaction condition. The resulting PEPPI was dark brown powder and completely soluble in water and such organic solvents as DMF, DMSO, NMP. PEPPI-iron(III) chloride complex was also easily prepared by the reaction of PEPPI and iron(III) chloride in DMF solvent under mild reaction condition. The complex solution was easily precipitated into a large excess of ethyl ether. A lustrous black powder was obtained.

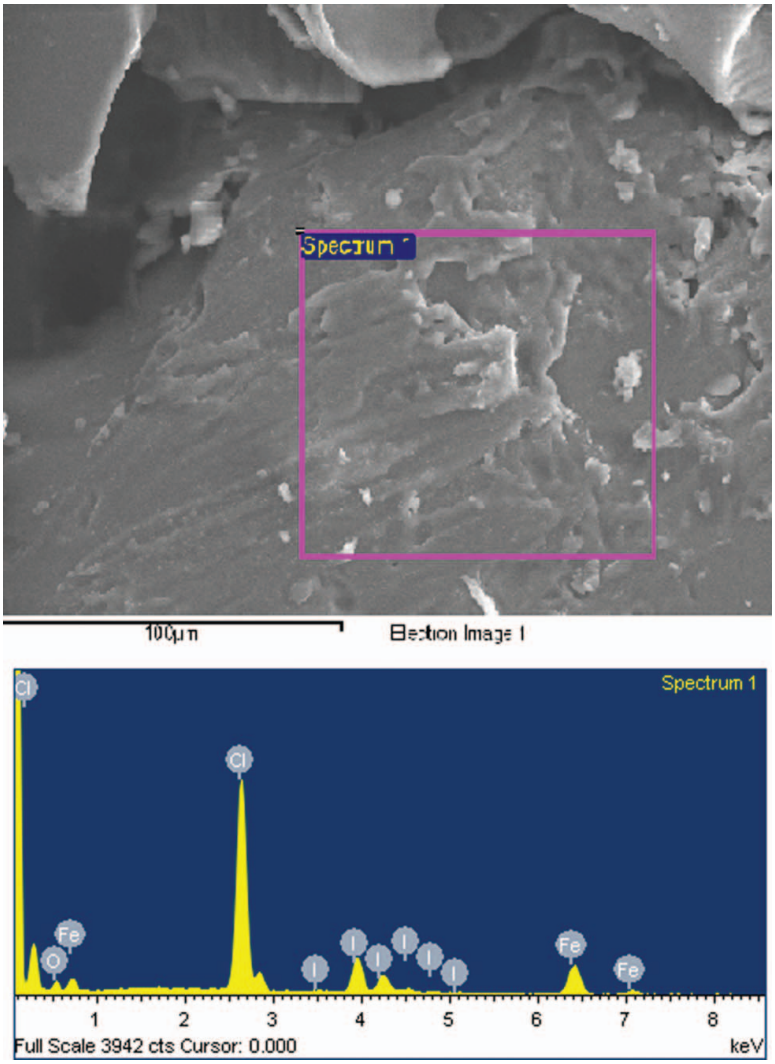

Figure 1. EDX spectrum of PEPPI-iron(III) chloride powder.

The results from EDX analysis (Figure 1) confirmed the presence of Fe, Cl, and I atoms. The multiple iodine peaks means that the iodide atoms have many different form and/or different environments although the exact form of iodide atom is not able to be interpreted. TGA thermogram of PEPPI-iron(III) chloride complex retains 95% of its original weight at 100°C, 89% at 200°C, 71% at 300°C, 66% at 400°C, and 45% at 700°C. Although the conductivity of PEPPI itself is lower than the lower limit of the four-probe meter, the electrical conductivity of the present PEPPI- iron(III) chloride complex was 4.3×10^{-4} S/cm.

The electro-optical properties of PEPPI doped with iron(III) chloride complex were measured and discussed. Figure 2 shows the UV-visible spectrum and photoluminescence (PL) spectrum of PEPPI-iron(III) chloride complex solution (0.1 wt.%, DMF). This material showed characteristic UV-visible absorption band at up to 650 nm and PL peak at 578 nm corresponding to the photon energy of 2.15 eV. Considering the changed PL maximum wavelength values after doping, PEPPI-iron(III) chloride complex exhibited 5 nm blue-shift compared to PEPPI compound of 583 nm. In our previous paper[37], PL maximum value of PEPPI compound was also blue-shifted 28 nm from PEHPI including hexyl side group and it was due to the decreased planarity [37]. Therefore, it would be explained by that iron(III) chloride dopant could also break the main chain planarity.

To examine the electrochemical redox property, cyclic voltammograms (CVs) of PEPPI -iron(III) chloride complex were measured with various methods. The measured cyclic voltammograms of PEPPI-iron(III) chloride complex with the various scan rates (30 mV/s ∼150 mV/s) are shown in Fig. 3(a). The peak potentials are constant and are not changed as the scan rate is increased. Also, very stable cyclic voltammograms of PEPPI-iron(III) chloride complex under the consecutive scans up to 30 cycles were observed in Fig. 3(b), which means that this material has relatively stable redox process in this electrochemical condition. In Fig. 3, the oxidation of PEPPI-iron(III) chloride complex was occurred at

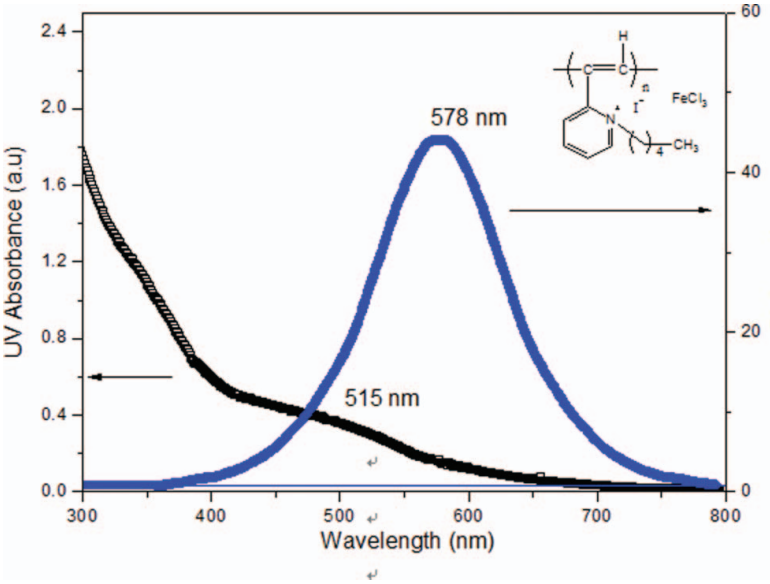

Figure 2. Optical absorption and photoluminescence spectra of PEPPI-iron(III) chloride complex solution.

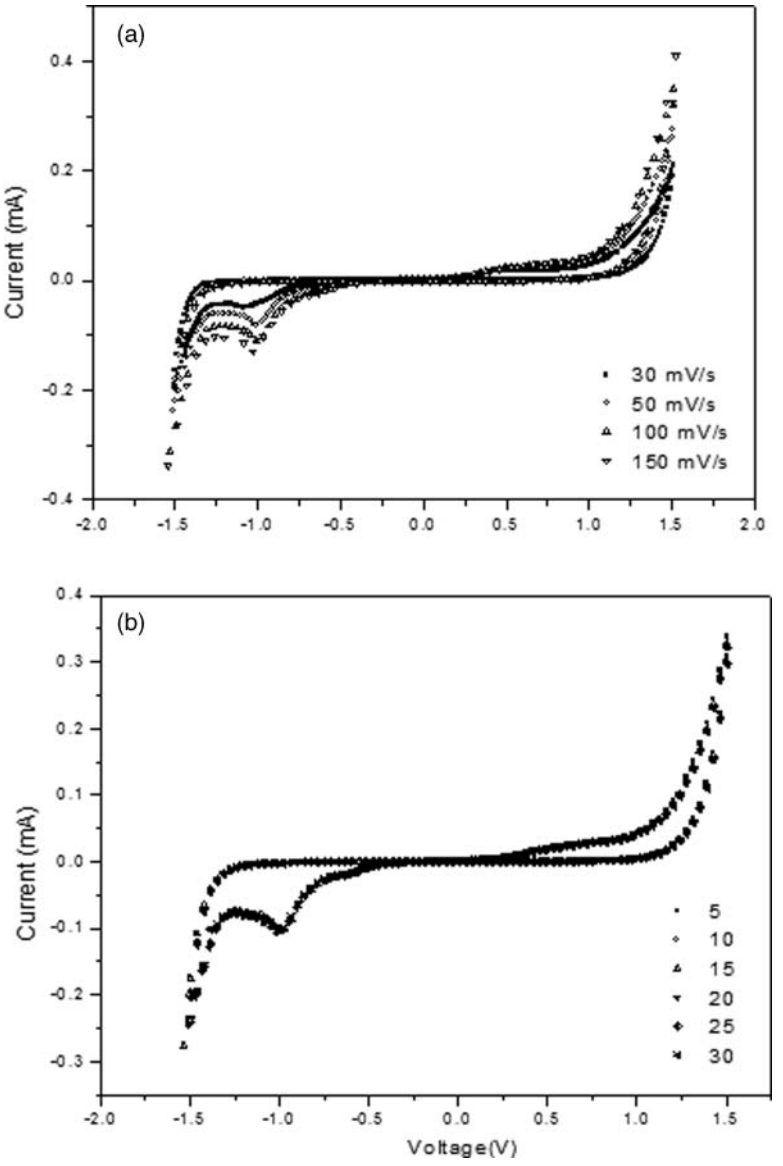

Figure 3. Cyclic voltammograms of PEPPI-iron(III) chloride complex [0.1M $(n\text{-}Bu)_4NBF_4$/DMF] (a) 30 mV/sec ∼150 mV/sec with various scan rates and (b) consecutive 30 scans under 100 mV/s.

0.22 V (vs $Ag/AgNO_3$) and it also showed the irreversible reduction peak starting at −0.39 V. The most interesting point is peak potential and current amount of reduction peak in CV result of PEPPI-iron(III) chloride. Comparing the oxidation and reduction peak of nondoped PEPPI with doped PEPPI. PEPPI itself showed vivid two oxidation peaks and those are relatively stronger than reduction, which means that larger current amount during oxidation [37]. However, PEPPI-iron(III) chloride showed stronger reduction peaks at around −1.0 V than oxidation. It indicates that this material was doped and oxidized by iron(III) chloride acid from PEPPI. Oxidized form caused easier reduction during

redox scans and increased the reduction current compared to pure PEPPI. Based on the empirical equation, scan rate exponent was 0.4061, indicating close to diffusion process. This result suggests that the electrochemical process of PEPPI-iron(III) chloride complex is reproducible in the potential range of $-1.50 \sim +1.50$ V vs $Ag/AgNO_3$.

4. Conclusions

In this article, we prepared ionic conjugated polymer (PEPPI)-iron(III) chloride complex by the reaction of PEPPI and iron(III) chloride in DMF solvent. The product was easily isolated in a lustrous black powder. The electrical conductivity of PEPPI-iron(III) chloride complex was 4.3×10^{-4} S/cm. The photoluminescence spectra of PEPPI-iron(III) chloride complex showed that the photoluminescence peak is located at 578 nm, corresponding to a photon energy of 2.15 eV, which exhibit slightly blue-shifted compared to non-doped pure PEPPI. The cyclic voltamogram of PEPPI-iron(III) chloride complex exhibited irreversible electrochemical behavior between the oxidation and reduction peaks as well as stable redox window in the range of -1.50 to $+1.50$ V. Also, reduction current in CV result was larger than oxidation due to the doped PEPPI form. The redox process kinetics of PEPPI-iron(III) chloride complex were close to a diffusion process.

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