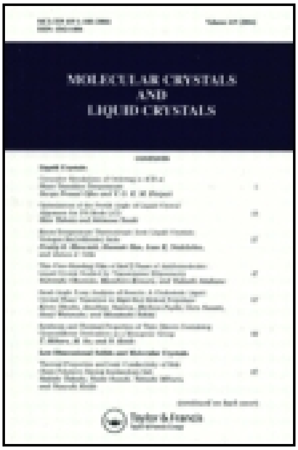

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Synthesis and Characteristics of Soluble Polypyrroles with Mixed Dopants

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Soluble conducting polypyrroles(Ppy) were prepared by the oxidative polymerization of pyrrole using mixed dopants. Compared to the dodecylbenzenesulfonic acid doped polypyrrole [Ppy-DBSA (σ_{RT}~10^{-1} S/cm)], the Ppy with mixed dopants (Ppy-mixed dopants) showed higher absorption intensity in near IR region in UV-Vis./NIR solution spectra and partly crystalline X-ray diffraction (XRD) patterns and higher conductivity of ~20 S/cm for free standing films. The Ppy-DBSA film showed three dimensional variable range hopping (3D-VRH) conducton while Ppy-mixed dopant systems 1D-VRH conduction. These results are explained by the packing effect of planar dopant between the polymer chains.

Keywords: soluble polypyrrole; mixed dopant; electrical conductivity; conduction mecahanism; packing effect

INTRODUCTION

Polypyrrole(Ppy) is an interesting material because of its thermal, environmental stability, relatively high electrical conductivity (<400S/cm) and ease of synthesis etc. Until few years ago, Ppy had been known as insoluble material in organic solvents. Recently, it was reported that Ppy-DBSA with long alkyl chain is soluble in common organic solvent [1,2]. However soluble Ppy-DBSA showed relatively low electrical conductivity (10^{-1} S/ cm) compared to that of Ppy that was prepared by a conventional synthetic route[3]. It is, therefore, necessary to improve the electrical conductivity as well as the solubility for the practical applications.

Recently, two factors which affect on the properties of Ppy were suggested and proved by XPS results[4,5]. The first is the disordered effect caused by interchainlinks due to 2,3 coupling and side chains. The second is the electrostatic effect between polymer chain and dopants. So, it is expected that the physical properties such as solubility, conductivity and conduction mechanism can be controlled by varying these two effects.

In this study, we report the synthesis of soluble Ppy which has the improved conductivity as well as processibility using mixed dopants. And the characteristics of Ppy-mixed dopant systems in solution and solid states are investigated by UV-Vis./NIR spectra, XRD pattern, and electrical conductivity measurements.

EXPERIMENTAL

Pyrrole and DBSA were weighed [the molar ratio of pyrrole : DBSA equal to 4:1] and dissolved in 80ml of distilled water. In another beaker, various dopants [hydrochloric acid (HCl), camphorsulfonic acid (CSA), naphthalenesulfonic acid (NSA), toluenesulfonic acid (TSA), antraquinone-2-sulfonic acid (AQ_2SA) etc.] and $(NH_4)_2S_2O_8$ as an oxidant were dissolved in 20ml distilled water[the molar ratio of acid : oxidant equal to 4 : 1}. Then these solutions were well mixed under magnetic stirring at 0°C for 20 hrs. After the precipitates were filtered and washed with mathanol, the filter cake was dried in vacuum to prepare Ppy powder. Ppy powder was added to the selected solvent under magnetic stirring to make 1~3% homogeneous solution. Free standing films were cast from the solution onto the slide glass plate placed in drying oven (60°C). After drying, the film was peeled off from the glass plate.

UV-Vis./NIR(Shimadzu UV-3100) spectra were recorded in the range of 260 to 2600nm with the homogeneous solution. XRD patterns were obtained using Philips PW 1825/00 diffractometer to examine the degree of crystallinity for the free standing films. Four probe method was employed for the conductivity measurement in the temperature range of 10~300K.

RESULTS AND DISCUSSION

In this study, mixed dopants were prepared with DBSA and other dopants (HCl, CSA, TSA, NSA and AQ_2SA). DBSA was used to provide the Ppy with the soluble functionality and other dopants were used to improve the electrical conductivity. Fig. 1(a) shows UV-Vis./NIR spectra of Ppy-DBSA solution prepared in various solvents. The strong effects of various solvent on absorption were detected in the Ppy-DBSA system. Absorption intensity around 2600nm (NIR region) related to the mobility of charge carrier appears very low in Ppy-DBSA. However, Ppy-DBSA/NSA (DMSO) solution shows free carrier tail. [Fig. 1(b)] It is obvious that the type of dopant affect the conformation of Ppy chain. In DMSO, Ppy-DBSA may have collapsed coil conformation while Ppy-DBSA/NSA or Ppy-DBSA/TSA may have loosened

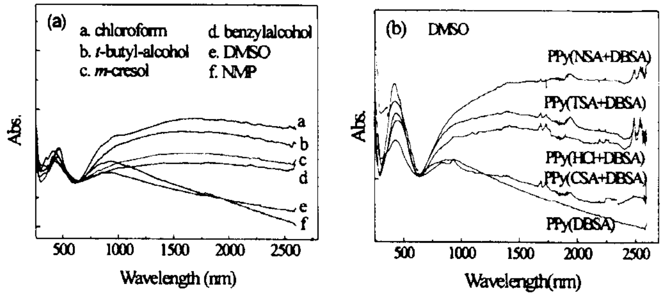

FIGURE 1. UV-Vis./NIR solution spectra of (a) PPy-DBSA (b) PPy-mixed dopant systems in various solvents.

coil conformation, which cause the difference in carrier mobility and electrical conductivity.

Fig. 2 shows the XRD patterns for various Ppy free standing films. The XRD result for the Ppy-DBSA(DMSO) free standing films show amorphous pattern, while Ppy-mixed dopant (DMSO) films show partly crystalline patterns. In particular, the improved crystallinity was observed in Ppy systems doped with planar structure dopant. It seems that the planar structure dopants such as NSA and TSA improve the array regularity of the polymer chain.

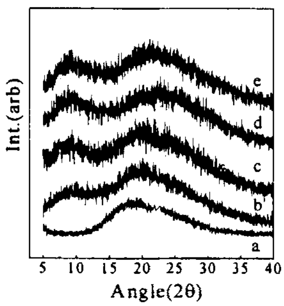

Figure 2. XRD patterns of various Ppy free standing films cast from DMSO solution doped with (a) DBSA, (b) DBSA/NSA, (c) DBSA/TSA (d) DBSA/CSA, and (e) DBSA/HCl.

The temperature dependence of electrical conductivities of Ppy-DBSA and Ppy-DBSA/NSA free standing films prepared in DMSO is shown in Fig. 3.

Ppy-DBSA (DMSO) films with 3D-VRH conduction show a conductivity of 10^{-1} S/cm at room temperature, whereas Ppy-DBSA/NSA (DMSO) films with 1D-VRH conduction show a conductivity of 12 S/cm at room temperature. These results of UV-Vis./NIR spectra, XRD pattern, electrical conductivity data suggest that the packing effect of planar structure dopants added to DBSA induce the aromatic interacton between polymer chains resulting in array regularity of polymer. This leads to the increase in the mobility of charge carrier along the polymer chain. As a result, electrical conductivity is increased up to 20 S/cm for Ppy-AQ_2SA (DMSO) system and thus 1D-VRH conduction behavior is observed.

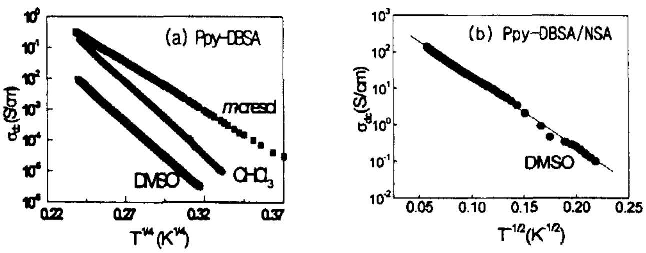

FIGURE 3. Temperature dependence of electrical conductivities for (a) Ppy-DBSA (DMSO) and (b) Ppy-DBSA/NSA (DMSO) free standing films.

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