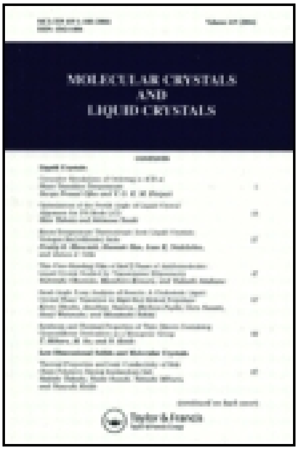

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Photoluminescence Phenomena of Functional Dopant Doped Soluble Polypyrroles in Organic Solvents

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We have investigated the photoluminescence (PL) phenomena of functional dopant doped polypyrroles (Ppy-DEHS, Ppy-BNS) in organic solvents with various conditions. From the results of UV-Vis. and PL spectra, we found that the change in polymer chain conformation from expanded to coil-like structure resulted in blue-shifted emission and reduced PL intensity. Addition of small amount of non-polar solvent to polar solvent media did not influence the shapes of PL curves but reduced the PL intensity under photo-excitation at 380 nm.

Keywords: functional dopant; photoluminescence; polypyrrole; UV-Vis

INTRODUCTION

Recently, a structure having the electron transportation part and the hole transportation part at the same time at the main chain of polymer for radiation material (EL) to increase the radiation efficiency of ELD has been synthesized and the way of improving the EL efficiency by introducing hole • electron transporting layer of polymer thin membrane between the radiation layer and the metal electrode has been reported.

Among conducting polymers, polypyrrole which has excellent heat stability and atmospheric stability, high conductivity is a material having a lot application possibility [1–3], as well as polyaniline, because it's easy to be synthesized. Polyaniline has solubility to various organic solvent agents in accordance with the various change

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of dopants [4,5], however, polypyrrole has a weak point of not being easily dissolved in general organic solvent agents due to strong attraction and combination between and withing chains [6].

In this study, we have synthesized polypyrrole which has high solubility to various organic solvents by using butylnaphthalene sulfonic acid sodium salt (BNSNa), a dopant that has more effect of the non-polarity activator than that of polarity or di(2-ethylhexyl) sulfosuccinate sodium salt (DEHSNa) [7–9], a functional dopant which has the polarity activator and the non-polarity activator at the same time to overcome the problem of polypyrrole having lower solubility in the limited organic solvents. We have investigated the spectroscopic phenomenon of polypyrrole by various polarity solvents, functional dopant and the interaction between the polymer after producing fine solution by melting the functional dopants doped soluble polypyrrole (Ppy-DEHS, Ppy-BNS) to various organic solvents.

EXPERIMENTAL

Synthesis

Pyrrole (Tokyo Chemical Industry Co.) was vacuum distilled prior to use. Sodium di(2-ethylhexyl) sulfosuccinate (DEHSNa) and butylnaphthalene sulfonic acid sodium salt (BNSNa) were purchased from Tokyo Chemical Industry Co. The structure of dopant is shown in Figure 1. Ammonium peroxydisulfate (APS), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidinone (NMP), ethanol, toluene, tetrahydrofuran (THF), and chloroform were purchased from Aldrich and used as received.

A mixture of pyrrole (0.4 mol) and DEHSNa (or BNSNa:0.15 mol) in distilled water (900 mL) and a solution of APS (0.10 mol) in distilled water (100 mL) were cooled to 0°C. The APS solution was slowly added to the pyrrole mixture for 2 minutes at 0°C while stirring. The reaction was continued for 20 h at 0°C. The resulting precipitate was filtered and washed with 2 L of distilled water and dried in vacuum to give the product.

Measurements

UV-Vis. and PL spectra of homogeneous solutions were recorded using Shimadzu UV-3100 and Shimazu RF-5301 PC, respectively. We also investigated the photoconductivity of Ppy-DEHS film upon irradiation of light of 366 nm at 18 W.

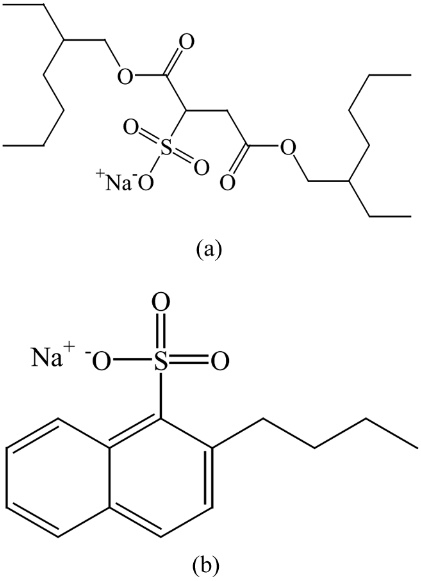


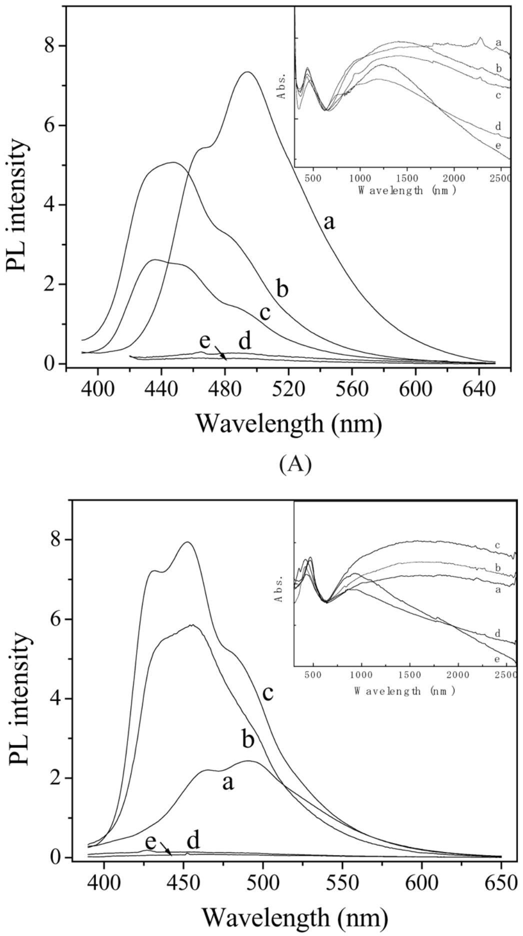
FIGURE 1 The molecular structures of the dopants.

RESULTS AND DISCUSSION

UV-Vis. and PL spectra of Ppy-DEHS and Ppy-BNS solutions in various organic solvents were obtained (Fig. 2). While the absorbance of Ppy-DEHS solutions in the range 300–500 nm did not change significantly, that in the NIR range corresponding to free carrier tail decreased as the solvent polarity reduced. In PL spectra, Ppy-DEHS solutions in polar solvents such as DMSO, DMF, and NMP exhibited significant PL intensity. The less polarity in solvents was, the less PL intensity was. In the case of THF, the polymer solution decreased significantly in PL. Moreover, PL of Ppy-DEHS was not observed in chloroform.

Meanwhile, the absorbance of Ppy-BNS in polar solvents decreased in the NIR range in the order of NMP, DMF, DMSO. The order was in the contrary to that of the Ppy-DEHS solutions. In PL spectra, Ppy-BNS solution exhibited PL phenomenon. The PL intensity decreased as the free carrier tail decreased. The PLs of Ppy-BNS solutions were not observed in nonpolar solvents (THF, chloroform).

The solvent-dependant PL intensity can be explained by the change of the polymer chain conformation. It is well known that the conformation change occurs by the interaction between the polypyrrole doped



(A)

(B)

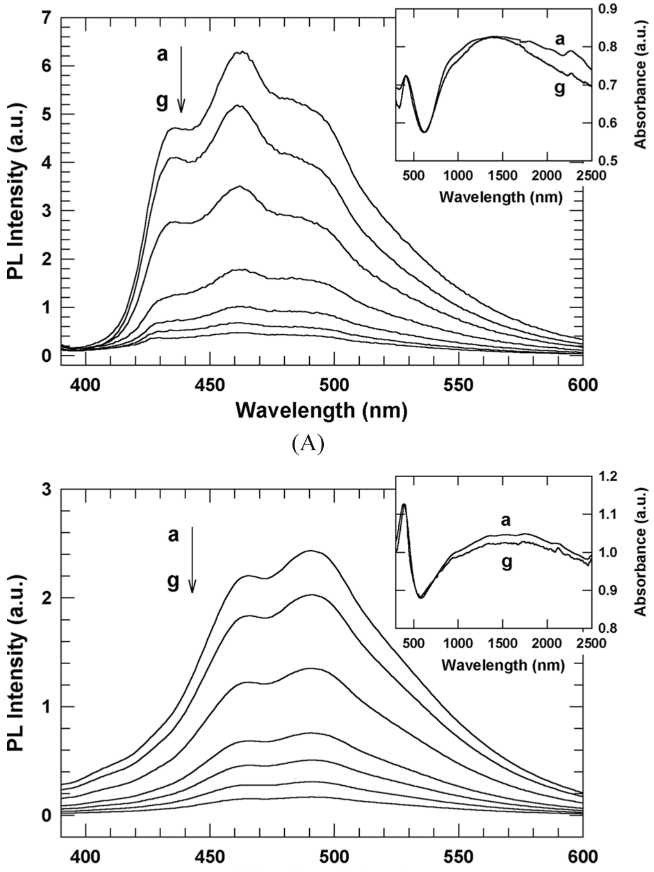
FIGURE 2 PL spectra and electronic absorption of Ppy-DEHS (A) and Ppy-BNS (B) in various solvents; (a) DMSO, (b) DMF, (c) NMP, (d) THF, and (e) chloroform. All the polymer concentrations were same as 4×10^{-3} wt%. The excitation wavelength was 380 nm.

with a dopant and organic solvent. The polymer in a good solvent has expanded structure resulting in significant increase of free carrier tail in the range of NIR. In the case of a poor solvent, it has coil-like structure with decrease of free carrier tail. The coincidence between the intensity of free carrier tail and the PL intensity in Figure 2 confirms that the strong relationship between the chain conformation and PL phenomena. From the fact that the free carrier tail increased in polar solvents, it can be deduced that Ppy-DEHS and Ppy-BNS in polar solvents (DMSO, DMF, NMP) would have expanded structures. However, the polymers in non-polar solvents (chloroform, THF) may have coil-like structures. Upon photo-excitation, the possibility in irradiative decay of the exiton would depend on its surroundings. The quenching site in the coil-like structure would be more than that in the expanded structure due to the intrachain interaction.

In Figure 2, it was also observed that the maximum wavelength in PL was red-shifted when the polarity of the solvents increased. This PL phenomenon occurs because the $\pi \rightarrow \pi^*$ interaction between the polarity of solvent and the polymer chain are different. Generally speaking, the emission spectra in molecule shows red shift as the polarity of aliphatic solvents increased at excite state, due to the dipole-dipole interaction.

We also obtained UV-Vis. electronic absorption and PL spectra of Ppy-DEHS in various compositions of co-solvents (DMSO and chloroform) (Fig. 3A and 3B), to know how much small amount of non-polar solvent (chlorform) in the polymer solution would influent on the changes in the polymer chain conformation and PL intensity. The magnitude of free carrier tail did not decreased up to the composition of (chloroform/DMSO; 1/99 by wt%) (f in Fig. 3A). This indicates that significant change in the polymer conformation did not occurred. The free carrier tail somewhat decreased when the chloroform ratio increased up to 2 wt% (g in Fig. 3A) indicating that the amount started to effect on the polymer conformation from expanded structure to coil-like structure. However, the PL intensity somewhat decreased after adding just small amount (0.2 wt%) of chloroform (b in Fig. 3B) in which free-carrier tail did not decreased (b in Fig. 3A). In the solvent composition of 0.4 wt% chloroform, the PL intensity reduced to almost half magnitude of the original value (c in Fig. 3). The PL intensity reduced almost 1 order of the original value in the composition of 1 wt% chloroform (f in Fig. 3). The PL intensity reduced more that 1 order of the original value when the amount of chloroform consisted more than 2 wt% (g in Fig. 3). As a result, the contents of chloroform increased up to 1 wt%, the magnitudes in PL intensity dramatically reduced while no significant change of the UV-Vis absorption spectra were observed.

The conductivities of Ppy-DEHS and Ppy-BNS films without photo-irradiation were ca. 0.8 and ca. 0.09 S/cm, respectively. The higher value in Ppy-DEHS film is presumably because the polymer chains of Ppy-DEHS have more expanded conformation in DMSO than those of Ppy-BNS polymer chains. The chain conformation in a



(A)

(B)

FIGURE 3 PL spectra of (A) Ppy-DEHS and (B) Ppy-BNS solutions in co-solvents (DMSO/chloroform). The chloroform contents in (A) and (B) are (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, (f) 1.0, and (e) 2.0 wt%. All the polymer concentrations were same as 4×10^{-3} wt%. The excitation wavelength was 380 nm.

polymer solution impacts on the morphology of the corresponding film after free-standing casting. It is well known that the expanded structure in conductive polymers usually enhances their conductivity. After photo-irradiation at 366 nm, the conductivities increased up to ca. 10 and 5 times more than those without photo-irradiation in the Ppy-DEHS and Ppy-BNS films, respectively. The enhancement in conductivity by photo-irradiation can be explained by two factors.

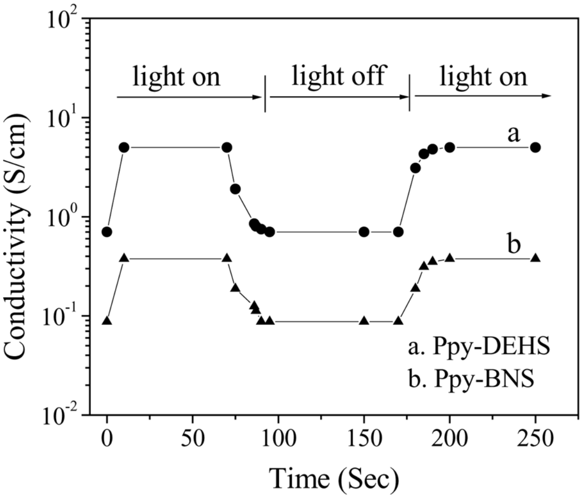


FIGURE 4 Photoconductivity of Ppy-DEHS film and Ppy-BNS film.

One is that charge carrier such as polaron was accumulated by photo-excitation. Figure 4 shows the result of measuring the photoconductivity of Ppy film.

Current-voltage (I-V) characteristic of ITO/Ppy/Al device (A) and ITO/Ppy/AlQ$_3$/Al device (B) were shown in Figure 5. Ppy doped with DEHSNa (Ppy-DEHS) or BNSNa (Ppy-BNS) were used as a hole transport material in the organic light emitting devices. ITO/Ppy/Al

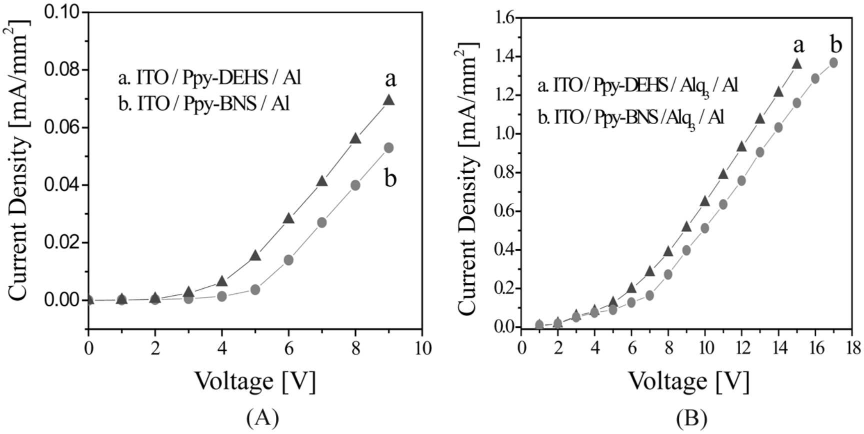


FIGURE 5 Current-voltage characteristic of ITO/Ppy/Al device (A) and ITO/Ppy/AlQ$_3$/Al device (B).

device (A) and ITO/Ppy/AlQ_3/Al device (B) had a operating voltage of 3 V ~ 4 V.

CONCLUSIONS

The PL of doped polypyrrole (Ppy-DEHS and Ppy-BNS) solutions was influenced by three conditions; concentration, polarity of solvent media. The polarity of the solvents induced conformational change of polymer chains. Polymer chains have expanded conformation in polar solvents but coil-like conformation in non-polar solvents. The change from expanded to coil-like conformation resulted in blue-shifted emission and reduced PL intensity. Addition of small amount of non-polar solvent to polar solvent media did not influence the shapes of PL curves but reduced the PL intensity.

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