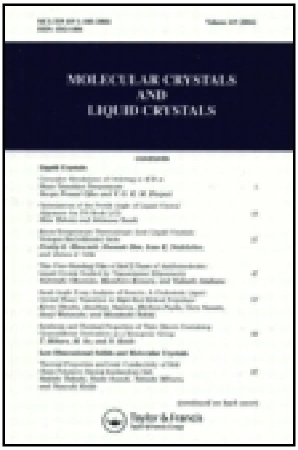

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Synthesis and Characterization of Soluble Polyaniline and Its Derivatives Doped with Dialkylsulfates

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Synthesis and Characterization of Soluble Polyaniline and Its Derivatives Doped with Dialkylsulfates

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Soluble polyaniline and its derivatives doped with dialkylsulfate (DAS : dimethylsulfate, diethyl sulfate, dipropylsulfate etc.) were chemically synthesized. Solubilities of polyaniline doped with DAS (PANI·DAS) powders in polar solvents and polyethoxy aniline doped with DAS (PEtOANI·DAS) powders in various alcohols were observed in the range of 3-8 wt.% and 2-5 wt.%, respectively. This improved solubility in organic polar solvents was explained with the interactions between the hydrophilic sulfonate group, polar substituent and polar solvents. Compared to that of HCl doped polyaniline, PANI·DAS showed improved thermal stability upon heat treatment at 160 ℃. The electrical conductivities of PANI·DAS and PEtOANI·DAS films appeared in the range of 1.2~2.3 S/cm and 10^{-2}~10^{-4} S/cm, respectively.

Keywords soluble polyaniline; polyethoxyaniline; dialkylsulfate; protonic acid doping; nucleophilic addition

INTRODUCTION

For many years, it has been known that polyaniline was intractable material in polar solvents including water and alcohols[1,2]. Recently, the poor solubility of polyaniline salt (emeraldine salt, ES) was explained with the strong molecular interaction (hydrogen bonding) between intra and inter chain[3,4]. Cao et al[5] reported that polyaniline doped with functionalized protonic acids [camphorsulfonic acid (CSA), dodecyl benzenesulfonic acid (DBSA) etc.] showed the improved solubility in organic solvents due to the interaction between counter ion and solvent and especially, polyaniline doped with polar dopant, CSA, was soluble

in weakly polar solvents such as *m*-cresol, phenol etc.
In this study, polyaniline soluble in polar solvents [DMF, DMSO, EG, NMP etc.] and polyethoxyaniline soluble in alcohols [2-propanol, butanol, benzyl alcohol) etc.] were synthesized using dialkylsulfate (dimethylsulfate, diethyl sulfate, dipropyl sulfate) dopants and their physical properties including solubility, thermal stability and electrical conductivity etc. were examined.

EXPERIMENTAL

Polyaniline and polyethoxyaniline were synthesized by conventional methods. 1 mol Polyaniline (EB) and 1 mol polyethoxyaniline powders were mixed with 2 mol DAS, respectively, to make soluble, conducting polyaniline and polyethoxyaniline. The resulting PANI·DAS and PEtOANI·DAS powder were dissolved in polar solvents for use.
UV-Vis./NIR (Shimadzu UV-3100) spectra were recorded in the range of 260 to 2600 nm with the homogeneous solution. XRD patterns were obtained using Philips diffractometer (PW 1825/00) to examine the degree of crystallinity for the free standing films. Four-probe method was used to measure the electrical conductivities of free standing films.

RESULTS AND DISCUSSION

To improve the solubility of conducting polymer in polar solvent, many factors such as the polarity and structure of dopant and solvent, the degree of crystallinity in the polymer, the structural similarity between solvent and polymer unit etc. should be taken into considerations.
The protonic acid doping in polyaniline was based on the basicity of imine group. In this study, however, the reaction between polyaniline and DAS is based on the nucleophilic addition in which imine group act as a strong electron donor and alkyl groups were attached to polyaniline as nucleophiles. In Figure 1, the mechanisms for doping of polyaniline with HCl and dimethyl sulfate (DMS) are compared.
To examine the solvent effect on the chain conformation of PANI·DAS, UV-Vis./NIR spectra and XRD patterns were measured and the results are shown in Figure 2. For most of solvents, localized polaron peaks were observed at 820 nm. These peaks are attributed to the localization of charge carriers caused by introduction of methyl group which lead to the increase in torsion angle between the rings. However, in DMF or *m*-cresol, the absorption peaks at NIR region (2600nm) which are related to delocalization of charge carrier were observed with medium intensity.
In XRD patterns, PANI·DMS film cast in DMF showed improved

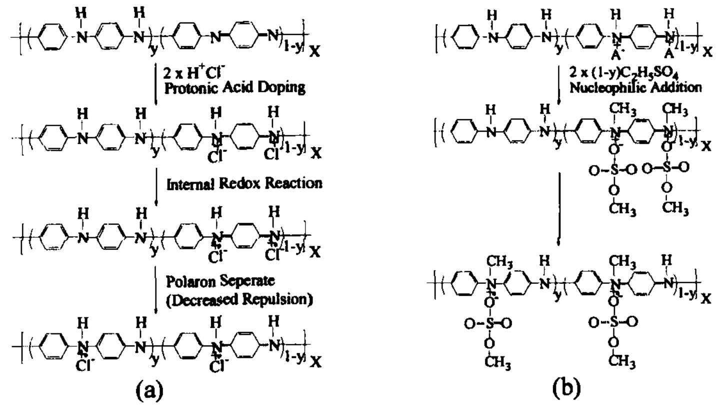

FIGURE 1. (a) Protonic acid doping of polyaniline (EB) with HCl and (b) Nucleophilic addition of polyaniline (EB) to DMS.

crystallinity compared to that of the film cast in NMP solvent. From these results, it is believed that DMF and *m*-cresol are good solvents which solvate the counter ion and polymer chains effectively.

Free standing films were cast from NMP and were doped with DMS, DES and DPS. Their room temperature conductivities were 2.3 S/cm, 1.8 S/cm and 1.2 S/cm, respectively. When the films were heated at 160 °C for 2 hours, the conductivities was decreased to 1.5 x 10^{-1} S/cm. These results represent that PANI·DAS films show higher thermal stability compared to that of PANI·HCl film (1.5 x 10^{-2} S/cm) after the heat treatment under same condition. These results seem to be due to the higher boiling point of DAS than that of HCl and the increase in interaction between DAS and imine group.

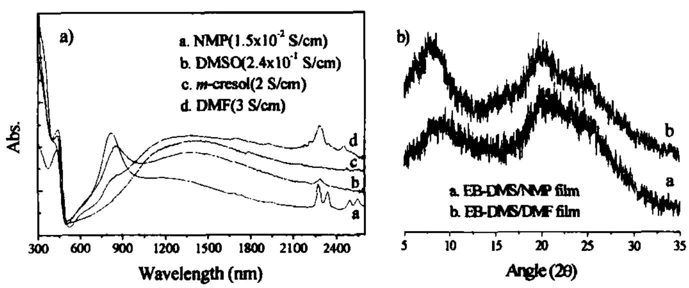

FIGURE 2. UV-Vis./NIR spectra of DMS doped polyaniline in various solvents (a. THF, b. NMP, c. *m*-cresol, d. DMF).

Polyethoxyaniline doped with hydrophilic dopant DAS, PEtOANI·DAS showed excellent affinity with polar solvents including various alcohols. Solubilities of PEtOANI· DAS in various alcohols appeared in the range of 2~5 wt.%. The results may be due to the interaction between the solvent, dopant and polar ethoxy group in the polymer.
To examine the solvent effect for PEtOANI·DAS, UV-Vis./NIR spectra were measured. In the spectra, the strong localized polaron peaks at ~770 nm which are due to the localization of charge carriers appeared. PEtOANI·DAS films cast from various alcohols showed amorphous XRD patterns due to the structural disorder. Solution UV-Vis./NIR spectra of PEtOANI·DMS in alcohols and XRD patterns of PEtOANI·DMS films cast from various alcohols are shown in Figure 3. The film cast from benzyl alcohol and butyl alcohol solution showed the conductivity of 3.4 x 10^{-2} S/cm, 1.2 x 10^{-2} S/cm, respectively.

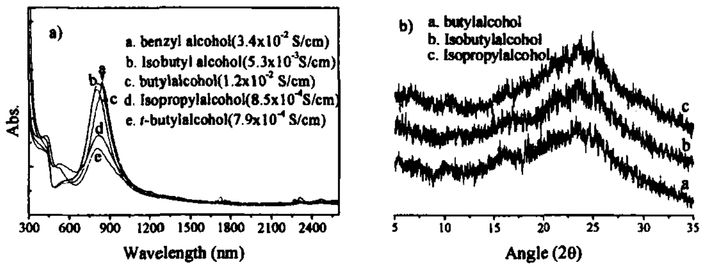

FIGURE 3. (a) UV-Vis./NIR spectra of PEtOANI·DMS/alcohols and (b) XRD patterns of PEtOANI·DMS films cast from various alcohols.

In conclusion, soluble polyaniline in polar solvents and soluble polyethoxyaniline in various alcohols were synthesized successfully using dialkylsulfate dopants.

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