

Influence of surfactant concentration on counter-ion induced solubility of poly(pyridine-2,5-diyl)

IMIT Mokhtar (木合塔尔·依米提)^{†1,2}, YAMAMOTO Takakazu², IMIN Patigul (帕提古丽·依明)¹

⁽¹⁾*School of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, China*

⁽²⁾*Chemical Resources Laboratory, Tokyo Institute of Technology, 4259, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

[†]E-mail: mokhtarjan@sohu.com

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Abstract: Protonating the pyridine rings of poly(pyridine-2,5-diyl) with dodecylbenzenesulfonic acid and camphorsulphonic acid produces polymer materials which can be dissolved in chloroform (in contrast to the unprotonated polymer, which can only be dissolved in strong acids such as formic acid) and allows mixing the protonated polymers with other chloroform soluble conjugated polymers for use in electronic devices. The protonating behavior of poly(pyridine-2,5-diyl) with two kinds of surfactants is different in some levels. Dodecylbenzenesulfonic acid has higher protonating ability than camphorsulphonic acid.

Key words: Poly(pyridine-2,5-diyl), Counter-ion solubility, Surfactants

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INTRODUCTION

Preparation and electrical properties of poly(arylene)s having π -conjugation system along the polymer chain are the subject of recent interest (Skotheim *et al.*, 1997; Nalwa, 1997; Yamamoto, 2002). Among the poly(arylene)s, poly(p-phenylene), poly(pyridine-2,5-diyl) and poly(thiophene-2,5-diyl) are the most fundamental polymers and had been extensively studied (Skotheim *et al.*, 1997; Yamamoto, 2002; Nurulla *et al.*, 2001). However, these polymers show only low solubility due to their rigid rod-like structure. Poly(pyridine-2,5-diyl) (PPY) dissolves only in strong acids such as sulfuric acid, trifluoroacetic acid, and formic acid. Several attempts have been reported to enhance the solubility of PPY by modifying the polymer structure (Yamamoto *et al.*, 1994; 2001). We introduced flexible side chains in the polymer backbone to improve solubility of PPY in common organic solvents; however, the modification partly interrupted the conjugation. Significant progress in tackling the intractability of PPY has been recently reported by Jonforsen *et al.* (1999) and Ikkala

and co-workers (Ikkala and ten Brinke, 2002; Knaapila *et al.*, 2001). Because PPY contains sites needed to construct supramolecules, it forms self-organized supramolecules with dodecylbenzenesulfonic acids (DBSA) and octyl gallate in formic acid to yield better processability and to tune chemical and physical properties of the polymer. It was also reported that the complexation with dodecylbenzenesulfonic acids achieved solubility of PPY in chloroform, although the effect of concentration of the surfactants, DBSA and camphorsulphonic acid (CSA), on the solubility of PPY in chloroform has not been studied yet. In this paper, we report the influence of the DBSA and CSA to yield the soluble product of PPY in chloroform.

EXPERIMENTAL DETAILS

Materials and measurements

Dodecylbenzenesulfonic acids and camphorsulphonic acid were purchased from Aldrich Chemical Co. Inc. Bis(1,5-cyclooctadiene)nickel(0),

Ni(COD)₂, was prepared according to the literature (Yamamoto, 2002; Yamamoto *et al.*, 1988; 1994).

Changes in the UV-Vis spectrum of the polymer solution were followed with a Shimadzu UV-8000 spectrometer. The photoluminescence (PL) spectrum in solution was measured with a Hitachi F4010 spectrometer. IR spectra were recorded on a Jasco IR-810 spectrometer. All of the measurements were performed at room temperature.

Preparation of poly(pyridine-2,5-diyl) and its complexes with DBSA and CSA

The synthesis of poly(pyridine-2,5-diyl) was based on a method reported by our group as shown in Fig.1 (Yamamoto *et al.*, 1988; 1994).

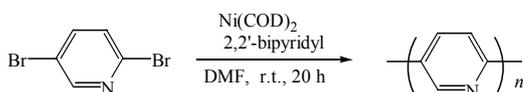


Fig.1 Synthesis of poly(pyridine-2,5-diyl)

In a typical preparation, a mixture of 2,5-dibromopyridine and the Ni(0) complex (1.0~1.2 mol/mol of the monomer) in a solution of N,N-dimethylformamide (DMF) at 60 °C yielded a yellowish orange precipitate of PPY. The precipitate was washed repeatedly with hot toluene, warm aqueous solutions (pH=3) of Ethylenediamine tetraacetic acid (EDTA), warm aqueous solutions (pH=9) of EDTA, warm aqueous solutions (pH=9) of NaOH, hot water, and hot methanol, and dried under vacuum; yield was about 90%. PPY thus obtained was reported to have a molecular weight of 4300 g/mol and is constituted of a random mixture of head-to-tail and head-to-head units (Yamamoto *et al.*, 1988).

Complexation of PPY with DBSA and CSA to form PPY(DBSA)_x and PPY(CSA)_x was performed in chloroform (5 ml) at room temperature, by overnight stirring of PPY and corresponding surfactants in chloroform. After filtering through a 0.2 μm membrane, UV-vis spectrum and photoluminescence spectrum were obtained using the filtrate. IR spectra were obtained after drying the filtrate and washing with plenty of water to remove the sulfonic acids. The molar ratio of PPY and surfactants are shown in Table 1.

RESULTS AND DISCUSSIONS

PPY forms complexes with sulfonic acids (Monkman *et al.*, 1998). When the acid molecule is amphiphilic, the polymer backbone can be complexed with the DBSA and CSA molecules, and complex forms are reported to form lamellar self-organized structures with alternating polar and nonpolar layers (Jonforsen *et al.*, 1999; Ikkala and ten Brinke, 2002). Complexation of PPY with sulfonic acids was regarded to be through hydrogen bonding between the sulfonic acid and the nitrogen of PPY (Jonforsen *et al.*, 1999; Knaapila *et al.*, 2001), and the protonation is considered to occur on the nitrogen atom of PPY as shown in Fig.2.

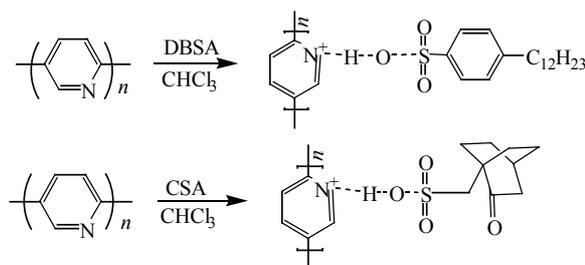


Fig.2 Protonation of PPY with DBSA and CSA

Table 1 Molar ratio of PPY and surfactants in 5 ml CHCl₃

Entry	PPy(CSA) _x			PPY(DBSA) _x		
	PPY (mmol)	CSA (mmol)	r* (ca.)	PPY (mmol)	DBSA (mmol)	r* (ca.)
1	0.062	0.067	1:1	0.061	0.069	1:1
2	0.065	0.138	1:2	0.062	0.136	1:2
3	0.068	0.221	1:3.5	0.069	0.242	1:3.5
4	0.068	0.297	1:4.4	0.066	0.405	1:6
5	0.064	0.387	1:6	0.073	0.517	1:7
6	0.063	0.508	1:8	0.065	0.530	1:8

*r is molar ratio of PPY and CSA

To make the PPY soluble in chloroform it was protonated with DBSA and CSA. In the case of DBSA, addition of one mol of DBSA per monomer unit was sufficient to dissolve the polymer in chloroform. Sometimes an emulsion was formed when the polymer and DBSA were stirred in chloroform. Addition of a few drops of formic acid (about 0.1 ml) was enough to break this emulsion. Once a stable complex was formed between PPY and the DBSA, addition of formic acid is not necessary to re-dissolve the isolated complex. The isolated complex was obtained by drying the solution under vacuum; with the IR spectrum indicating that the complex did not contain formic acid.

In contrast to the case of DBSA, addition of a larger amount of CSA was needed to make the complex soluble in chloroform. When a mixture of PPY and CSA was stirred in chloroform, it was impossible to obtain a clear solution until the molar ratio of CSA between PPY (CSA/the pyridine unit) reached to 6.

As shown in Fig.3, the protonation degree of PPY observed with these two surfactants is different.

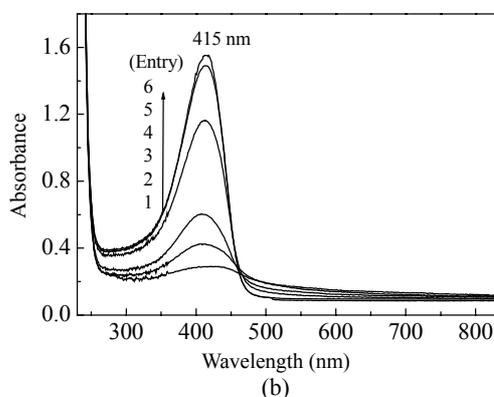
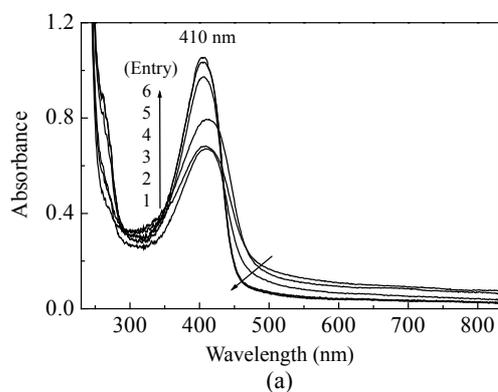


Fig.3 UV-vis spectra variation of PPY following the increase of surfactants concentration in chloroform (a) PPY-DBSA; (b) PPY-CSA

Since PPY was insoluble, the filtrate obtained from the dispersed chloroform solution of PPY showed no absorption peak of PPY at about 380 nm (Yamamoto et al., 1994). However, the filtrate obtained from the chloroform solution containing PPY and the sulfonic acid showed a peak at about 410 nm which was assigned to the $\pi-\pi^*$ transition of the protonated PPY. The amount of the solubilized PPY or the degree of the protonation was estimated from the height of the absorption peak at about 410 nm. As seen from Fig.3a, the DBSA filtrate has an absorbance of about 0.6 even at the 1:1 ratio (entry 1). On the contrary, the CSA filtrate has minor absorption at 415 nm at the 1:1 ratio. These data indicate that DBSA has higher protonating ability than that of CSA. However as shown in these figures, even after the molar ratio of PPY and surfactants reached to 1:8 the absorption peaks were not changed obviously, this indicates that all of the PPY have completely dissolved.

Because DBSA has a long alkyl chain, its solubility in organic solvents is considered to be higher than that of CSA, which may be the reason for the lower ability of CSA as surfactant for solubilizing PPY.

Fig.4 is the IR spectra of PPY and its protonated compounds. PPY has strong characteristic peaks at 1582 cm^{-1} and 1449 cm^{-1} . After the protonation with DBSA and CSA, these peaks became very weak, and new peaks of the surfactants appear as shown in Figs.4b and 4c, supporting the complex formation of PPY protonated with the surfactants. The strong broad absorption peak around 1172 cm^{-1} is characteristic of the sulfonic group.

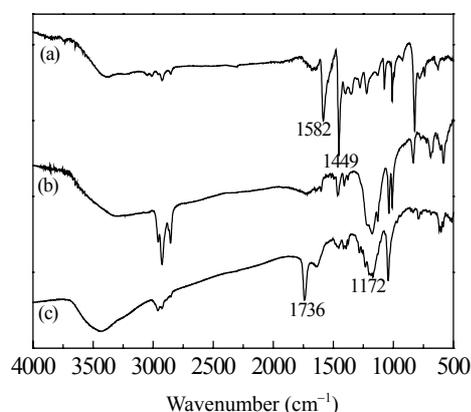


Fig.4 IR spectra of (a) PPY, (b) the PPY-DBSA complex, and (c) the PPY-CSA complex

Figs.5a and 5b depict photoluminescence (PL) data of the protonated states of PPY with DBSA and CSA, respectively. As depicted in Fig.5, the PPY-DBSA complex has an emission (EM) peak at 510 nm, whereas the PPY-CSA complex has an EM peak at 540 nm. When CSA was used, the photoluminescence peak shifted to a longer wavelength compared with the case of DBSA.

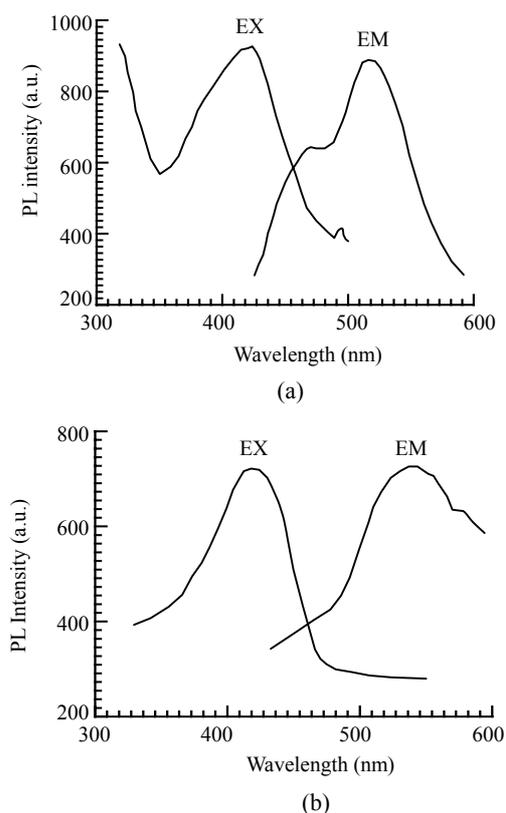


Fig.5 PL data of PPY in chloroform after protonation with (a) DBSA and (b) CSA

EX: excitation spectrum; EM: emission spectrum

CONCLUSIONS AND SCOPE

The complexes formed between poly(pyridine-2,5-diyl) and sulfonic acids such as dodecylbenzenesulfonic acid and camphorsulfonic acid are soluble in chloroform. Docecylbenzenesulfonic acid undergoes complex forming reaction at lower concentration than camphorsulfonic acid. Because of the increase in the solubility, it will be possible to make mixtures

of the PPY-sulfonic acid complex with other chloroform soluble conjugated polymers. Other nitrogen containing π -conjugated polymers might yield similar soluble complexes when proper sulfonic acid and organic solvent are used.

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