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Polypyrrole synthezited with oxidative cerium(IV) ions

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SUMMARY

The chemical oxidation of pyrrole by Ce(IV) salts in aqueous solutions or water-acetonitrile system has been studied. Products were characterized by elementel analyses, FT-IR and conductivity measurements. Conductivity values of polypyrrole complexes synthesized in aqueous solutions are comparable with those in acetonitrile-water, if suitable oxidant/monomer ratio and [H^+] are selected.

INTRODUCTION

Among the conducting polymers, polypyrrole (PPy) has received a good deal of attention because of its high electrical property, enviromental stability and ease of synthesis [1,2]. Highly conductive PPy has been prepared by various methods, such as electrochemical polymerization [3-4], chemical polymerization, by mild oxidative transition metal ions [2,5].

Since Ce(IV) is capable of polymerizing vinyl monomers effectively [6-8], it was challenging to study polymerization of pyrrole by the use of strong oxidants such as Ce(IV) ions, namely ceric(IV) ammonium nitrate (CAN) and ceric(IV) sulphate (CS) in some detail. So, in this study, the effect of monomer, ligand and metal ion concentration, and solvent were investigated. The conductivities of PPy complexes obtained showed variations in the range of literature values [9,10], depending on the conditions.

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EXPERIMENTAL PART

a) Materials

$(NH_4)_2[Ce(NO_3)_6]$, $Ce(SO_4)_2.4H_2O$, pyrrole, acetonitrile, H_2SO_4 and HNO_3 were all Merck reagent grade chemicals of the highest purity and were used without further purification.

b) Polymerization Procedure

Cerium(IV) salts were dissolved in acetonitrile-water (80:20) mixture and water in the presence of nitric acid or sulphuric acid. Monomer was slowly added to the Cerium(IV) solution which was being continuously stirred during the polymerization process. A black powder formed almost instantaneously and further aeration of the solution resulted in additional products. The black powder was thoroughly and repeatedly washed with copious amounts of pH=1 distilled water, until the filtrate was colorless. The powder was then dried at about 9-10°C.

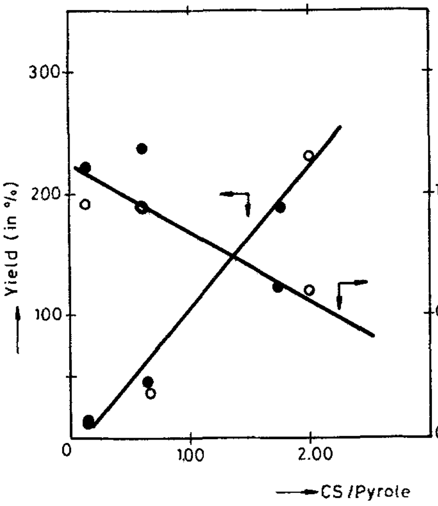
c) Polymer Characterization

In order to measure the electrical conductivity, the polypyrrole powder was compacted under pressure to obtain a thin pellet. Typical sample dimensions were 13 mm and the thickness was 0.30 mm. Conductivity measurements were performed in air by use of a Four Probe Technique. Jasco 5300 FT-IR spectrophotometer was used for spectral analysis. The elemental analysis of four samples synthesized in the aqueous and acetonitrile-water media were carried out on a Carlo-Erba 1106 elemental analyzer.

RESULTS AND DISCUSSION

Increase in CS/pyrrole and CAN/pyrrole concentration ratios cause a linear increase on the yields but as an oxidant CS gives an about two or three times higher yield than CAN in aqueous solutions (Fig. 1 and 2).

The higher than 100 % yields obtained at high CS/pyrrole ratios is probably due to CS complexation of pyrrole rather than only SO_4^- and NO_3^- ligands.



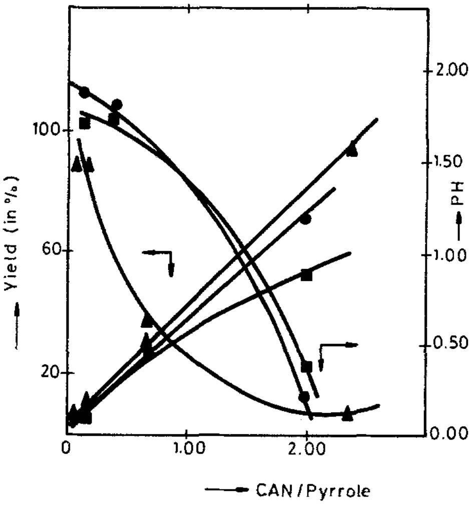
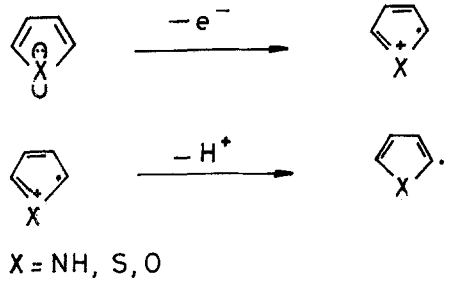


Fig.1 : The relationship between the yields of PPy complexes and pH of rinsing water, and CS/pyrrole ratio in 0.05 M (o) and 0.1 M H_2SO_4 solution (o).

Fig.2 : The relationship between the yields of PPy complexes and pH of rinsing water, and CAN/pyrrole ratio in water (o), acetonitrile-water (▲) and 0.005 M HNO_3 solution (■).

The pH of rinsing water decreases in CAN and CAS by increasing the Ce(IV) concentration indicating a similar mechanism in both cases; this indicates acid formation by proton loss of the pyrrole ring, according to an analogous mechanism [11].

Scheme I



monomer oxidation

proton loss

Some important conclusions have been reached by discussing conductivity measurements and FT-IR spectra, and comparison with literature data (Table I).

Table I : FT-IR and conductivity results of PPy complexes synthesized from CAN and CS under various conditions

No	Pyrrole (Mol/lt)	CAN (Mol/lt)	CS (Mol/lt)	SOLVENT	CONDUCTIVITY (S)
4	0.150	0.3		H_2O	$3.76.10^{-5}$
7	0.015		0.01	0.05 M H_2SO_4	$2.08.10^{-4}$
8	0.075		0.01	"	$6.13.10^{-5}$
2	0.075	0.01		Acetonitrile-H_2O	$3.91.10^{-2}$
5	0.015	0.01		H_2O	$3.5.10^{-3}$

First, the higher Ce(IV)/pyrrole ratio gave PPy complexes which have lower conductivity even by different ligands and solvent media. In these samples C=O streching vibrations are also observed (1,3,4,5). Second, for two different experiments (1,2) carried out at the same Ce(IV)/Py ratio (1:7.5) and medium (acetonitrile/water), the band at 1700 cm^{-1} for the pyrrolidinone carbonyl group was not observed. One of these samples has lower conductivity because of waiting for 40 days. This might be due to insertion of the PPy/NO_3^- complexes which diffused to the polymer when incorporated in a PPy chain. The sample containing p-toluene sulfonic acid (p-TSA) showed higher conductivity than the PPy/NO_3^- and PPy/$SO_4^=$ complexes. This behaviour could be explained by a high interaction of the p-TSA molecules with neighbourig pyrrole rings. The slow diffusion has also been explained by a decreased mobility of these ions (10,12,13).

Elementel analyses of samples showed that PPy prepared by CS and CAN contain $SO_4^=$ and NO_3^- respectively in addition to nitrogen of PPy (Table II). As expected the nitrogen content is higher than in $SO_4^=$ synthesized products, and the number of pyrrole rings change from $\sim$3 to $\sim$6 for every counter ion, according to ligand and solvent effect. (Table II).

Table II : Elemental analysis results of PPy complexes synthesized from CAN and CS under various conditions

No	ELEMENTAL ANALYSIS
4	$C_4H_{3.44}N_{0.98}(SO_4)_{0.33}$
2	$C_4H_{3.14}N_{1.17}O_{1.33}$
5	$C_4H_{3.4}N_{0.85}(SO_4)_{0.24}$

FT-IR spectroscopy of samples prepared by aqueous solutions containing nitric acid and sulphuric acid, gave C=O streching vibration(Table I and Fig. III). In contrast, the conductivity of these polymers were comparable with polymers synthesized in acetonitrile/water which have not shown C=O vibration and thus have higher conjugation (Fig.3). Consequently, if the Ce(IV)/pyrrole ratio and pH are suitably selected, fairly conductive PPy complexes could be synthesized in water systems also.

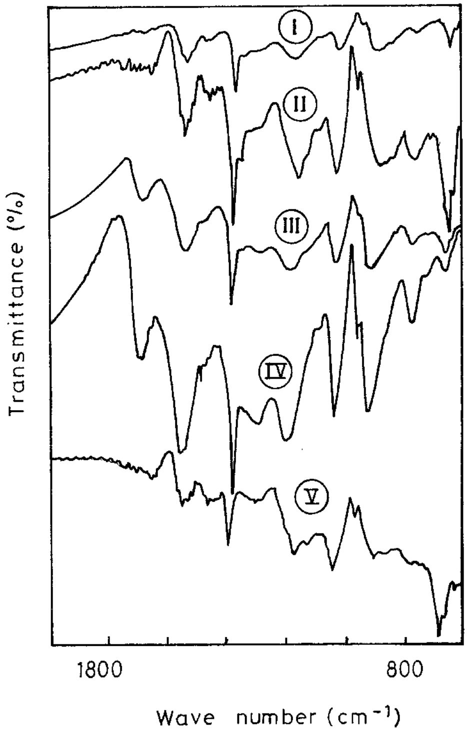


Fig.3 :FT-IR spectra of PPy complexes prepared by using the following oxidants and solvents, respectively : I, II-,III- CAN,acetonitrile-water; IV-, V- CAN, water.

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