SYNTHESIS AND CHARACTERIZATION OF COMPLETELY SOLUBLE POLYPYROLE SALTS VIA INVERSE EMULSION POLYMERIZATION USING A MIXTURE OF CHLOROFORM AND 2- BUTANOL AS A DISPERSING MEDIUM

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ABSTRACT

Polypyrole (PPy) is one of the most promising candidates for possible technological applications. However, its insolubility in common organic solvents limits its range of applications. In the present study an attempt has been made to synthesize soluble polypyrole salt via inverse polymerization pathway using benzoyl peroxide as oxidant and dodecylbenzenesulfonic acid (DBSA) as dopant as well as a surfactant. A mixture of chloroform and 2-butanol was used as dispersion medium for the first time for the synthesis of polypyrole. The influence of synthesis parameters such as concentration of pyrrole, benzoyl peroxide and DBSA on the yield and other properties of the resulting PPy salt was studied. The synthesized PPy salt was found to be completely soluble in DMSO, DMF, m-cresol, chloroform and in a mixture of toluene and 2-propanol. The synthesized polymer salt was also characterized with SEM, UV-Vis spectroscopy and TGA. The extent of doping of the PPy salt was determined from UV-Vis spectra. The activation energy for the degradation of the polymer was calculated with the help of TGA.

Keywords: PPy-DBSA salt, common organic solvents, XRD, UV-Vis spectroscopy.

1. INTRODUCTION

Conductive polymers (CPs) for the first time prepared in the 1970's, as a new group of organic compounds that possess both electrical conducting and visual properties like metals and inorganic semiconductors[1]. Among the conducting polymers a well-known polymer is polypyrrole (PPy) first synthesized in 1916[2]. This polymer has attracted unique attention due to its good environmental stability[3], simplicity in synthesis[4], high electrical conductivity and fine mechanical properties[2]. The current technical uses of polypyrrole e.g. in counter electrode in electrolytic capacitors, electrochromic devices, chromatographic inactive phases, sensors, membrane partition, light-weight batteries accordingly, have attracted a vast deal of attention in recent years and is now one of the most dynamic areas of investigation in polymer science and engineering[5-6]. PPy can simply be synthesized either by oxidative chemical or electrochemical polymerization of pyrrole monomers[7]. Chemical polymerization is an easy and rapid process with no requirement of particular instruments. Large amount of polypyrrole can be prepared as fine powder by means of oxidative polymerization of the monomer pyrrole by using chemical oxidants in aqueous or non-aqueous solvents[2], or through chemical vapour deposition[8]. Due to the extended conjugated chain structure, PPy is insoluble in different aqueous non-aqueous solvents and as a consequence it is not easily processable. Recently a soluble polypyrrole (PPy) has been prepared chemically[9]. It was reported that PPy doped with anionic surfactant, dodecylbenzen-sulfonic acid $[(Py_3)^+ (DBSA)^-]_x$ showed little solubility in organic solvents such as DMSO, DMF, THF, chloroform and m-cresol etc. It is due to the overall interaction of the surfactant anion with the solvent. It has also been observed that the solubility of PPy increases in the poor solvents by the addition of excess dodecylbenzenesulphonic acid (DBSA). It has been found that this type of sulfonic acid affect the solubility of polypyrrole when soluble PPy is prepared by the doping method[10].

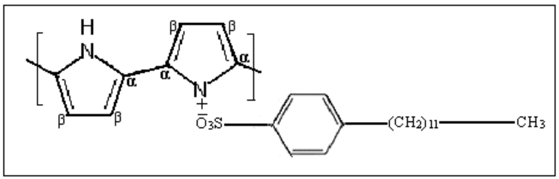

Figure 1. Proposed chemical structure of PPy-DBSA.

In this study we have synthesized PPy-DBSA salt via inverse emulsion chemical polymerization using chloroform and 2-butanol as dispersion medium for the first time. The prepared sample was completely soluble in a number of common organic solvents. Conducting properties, morphology, and thermal stability were determined by using different physicochemical techniques.

2. EXPERIMENTAL

Materials

All chemicals used were of analytical reagent grade. Pyrrole (Fluka Chemie), benzoyl peroxide (Scharlab), dodecyl-benzenesulphonic acid (Acros), 2-butanol (Aldrich), 2-propanol (Merck) and tetra-hydrofuran (Scharlab) were used as received.

Synthesis

PPy salt was synthesized by inverse emulsion polymerization using monomer pyrrole. The process was carried out in a 250 mL round bottom flask by taking chloroform in the flask. Then benzoyl peroxide was added to it under slow mechanical stirring. Then 2-butanol, DBSA and pyrrole were added to the above solution. After adding distilled water to the mixture, it was allowed to proceed for 24 hours upon vigorous stirring. Then the prepared product was washed three times with 20ml of acetone and distilled water subsequently. After drying dark brown amorphous powder of PPy-DBSA salt was obtained (Figure 1).

3. RESULTS AND DISCUSSION

3.1. Solubility

The solubility of the synthesized PPy-DBSA salt was investigated in a number of organic solvents such as chloroform, DMSO, THF, DMF, and m-cresol and was found to give homogeneous solutions (Table. 1). There is a proposal that the long chain dopant DBSA in polymerization media hinders the cross-linking among polymer chains and thus, increases its solubility leading to an improvement in process-ability[11].

Table 1. Solubility of PPy-DBSA salt in common organic solvents

S. No	Organic Solvent	Temperature (ºC)	Effect
1	DMSO	25	Completely soluble
2	DMF	25	-do-
3	THF	25	-do-
4	m-cresol	25	-do-
5	Toluene/2-propanol	25	-do-
6	Chloroform	25	Partially soluble

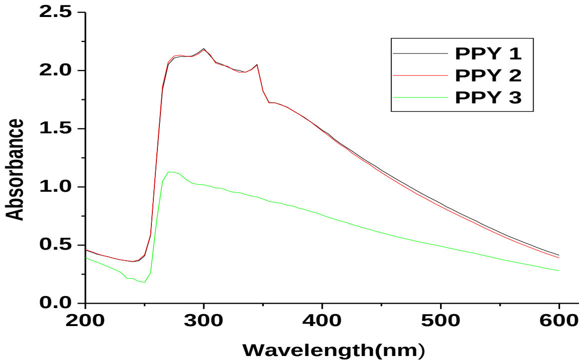

Figure 2. UV-Vis Spectra of PPy samples in DMSO.

3.2. UV-Vis Analysis

Figure 1 shows UV-Vis spectra of PPy-DBSA salts in THF solvent. All the three samples with varying concentrations of pyrrole monomer exhibited three characteristic bands. Band 1 in the range of 265-280nm is attributed to π—π* transition of the aromatic ring in the polymer chain. Band 2 at 290-370nm is due to polaron transition. Band 3 at 400-460nm is due to bipolaron transition[12].

3.3. TGA Analysis

The TGA characteristics of PPy-DBSA salts were obtained in the range from room temperature to 650 ˚C (TA Instrument Co.) under nitrogen (100 cc/min). Fig. 2 shows the thermograms of PPy samples synthesized with varying concentrations of pyrrole monomer. All the samples were observed to exhibit three distinct weight losses[13]. Weight loss at 90-100 °C (~30 %) is due to the elimination of moisture, solvents, oligomers and unreacted monomers. These polymers started to lose their weights (~40-50%) at 200°C probably losing the dopant anions $(DBSA)^-$ from the polymer chain. At higher temperature (>450 °C) the decomposition of polymer chain can lead to the production of volatile gases[14]. The synthesized PPy-DBSA salts are thermally stable in the range of 10 to 450 °C and beyond this temperature range, the decomposition process become very rapid.

3.4. SEM Analysis

Scanning electron microscopy was performed to know about the morphology of PPy-DBSA salt in various concentration of the monomer as shown in Fig. 4. It is seen from the micrograph that the salt has uniform granular morphology and the average grain size is ~ 0.7 μm. Such uniform and minor structure makes possible the formation of electrical conductive network within the PPy-DBSA and is preferred for sensing applications[15].

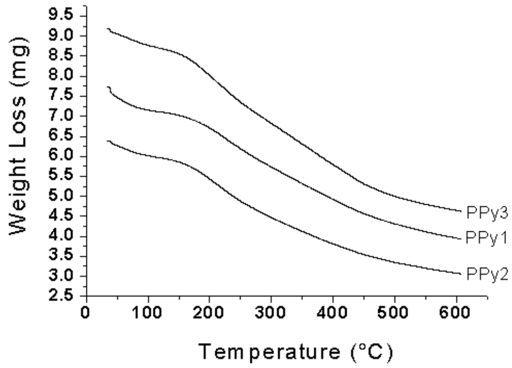

Figure 3. TGA curves of PPy 1, PPy 2 and PPy3.

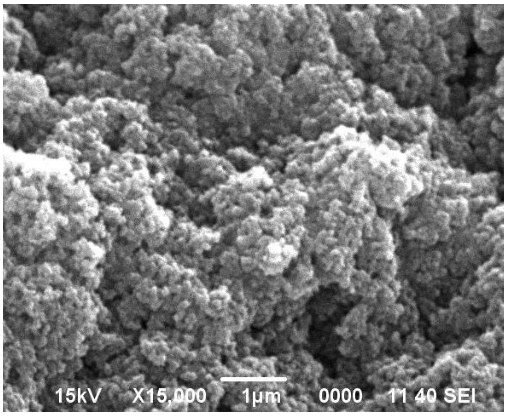

Figure 4. SEM micrograph of PPy-DBSA synthesized at ambient temperature

CONCLUSIONS

Completely soluble PPy-DBSA salts were prepared by inverse emulsion chemical polymerization. From the UV-Vis absorption spectra it was suggested that the electrical conductivity mechanism of PPy-DBSA should be polaron and bipolaron hopping. SEM analysis shows the uniform granular morphology of the PPy-DBSA while TGA indicates its high thermal stability up to 450ºC.

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