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An impressive emulsion polymerization route for the synthesis of highly soluble and conducting polyaniline salts

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ABSTRACT

We report a sophisticated emulsion polymerization route for the synthesis of polyaniline (PANI) salts. In this process, the chemical oxidative polymerization of aniline was carried out in the presence of two dopants i.e., dodecylbenzenesulfonic acid (DBSA) and sulfuric acid (H_2SO_4). The synthesized PANI salts were highly soluble in a large number and variety of common organic solvents (so far highest number of solvents including the less hazardous ethanol) and showed very good conductance. Presumably the presence of DBSA and sulfuric acid moieties, respectively, contributed toward the improvement in solubility and conductance. After optimization of the reaction parameters, the obtained polymers were systematically characterized with cyclic voltammetry, in situ conductance, in situ UV–vis spectroelectrochemical and intrinsic viscosity measurements. X-ray diffraction, TGA and SEM were used for further analysis. The materials showed very good electrochemical and electrochromic reversibility and high thermal stability (up to 500 °C). Moreover, potentiodynamic measurements revealed that coatings of this polymer can provide extra ordinary resistance to the steel surfaces particularly against the harsh corrosive environment of the oceans.

1. Introduction

Polyaniline and its derivatives are the subject of considerable research interest around the globe. The versatile technological applications of this fascinating material in various fields are broadly associated with its good conducting properties. Depending upon the mode of synthesis, nature and concentration of dopants and supporting electrolyte, PANI is collected in different states; leucoemeraldine, emeraldine base, emeraldine salt or pernigraniline. Emeraldine salt is the most promising and the only electrically conducting form of PANI [1].

Although, PANI is a promising candidate for various technological applications such as corrosion protections of metals, rechargeable batteries, capacitors, actuator and sensors [2], it has the drawback of poor processability and solubility in commonly used organic solvents. This limits the applications of PANI to a greater extent. Literature reveal that the properties of PANI greatly depend upon the method of synthesis, types of dopants, oxidants and the solvent system used during its synthesis. For instance, the processability of PANI was reported to be improved significantly by grafting copolymerization of aniline onto a modified surfactant [3]. Considerable progress has been made by the preparation of polymer blends and composites [2]. The solubility of PANI was also reported to be improved considerably by adopting chemical oxidative polymerization routes for the synthesis of substituted PANIs or copolymerization of aniline with substituted anilines and synthesis of PANI by emulsion/inverse emulsion polymerization techniques [4]. In emulsion/inverse emulsion polymerization pathways, different types of surfactants are employed. These surfactants are believed to help in improvement of solubility. At the same time they also act as dopants.

Dodecylbenzenesulfonic acid (DBSA) has emerged as a promising dopant and surfactant and is frequently applied in different protocols for the synthesis of soluble PANI. Some examples are polymerization in solution [5], emulsion/inverse emulsion polymerization [6] and re-doping of emeraldine base (EB-PANI) [7]. The solubility of PANI, doped with dodecylbenzenesulfonic acid (DBSA) or camphor sulfonic acid, in chloroform and xylene has been reported [8]. Yu et al. [9] fabricated a honeycomb-structured film of PANI–DBSA, which was electroactive and semi-conducting in the appropriately doped state. Han et al. [10] reported the synthesis of PANI nanoparticles using DBSA in aqueous DBSA micellar solution. Earlier a new inverse emulsion polymerization

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pathway was reported for the synthesis of PANI doped with DBSA using benzoyl peroxide as the oxidizing agent [11]. It was reported that the synthesized PANI was soluble in chloroform but did not show any electrical conductance in aqueous acidic media.

These reports demonstrate that the efforts for enhancing the solubility of PANI in commonly used solvents via different approaches always result in the reduction in the conductance of PANI to different levels [4,12].

Reports are also available on several chemical oxidative polymerization routes adopted for the synthesis of PANI having good conductance. But the results are not impressive. Stejskal et al. [13] studied the effect of various acids on the conductance of PANI. They observed that among various acids such as sulfuric acid, hydrochloric acid, sulfonic acid and carboxylic acid, only hydrochloric acid and sulfuric acid appreciably enhance the conductance of PANI. Borole et al. [14] compared the effect of and Cl^- anions on the conductance of PANI. They found highest conductance for sulfate-doped PANI. However, they did not achieve appreciable solubility. Rao et al. [15] used benzoyl peroxide as a novel oxidizing agent for the synthesis of PANI. The PANI salts synthesized by this pathway showed good conductance but low solubility.

Here we report an emulsion polymerization pathway for the synthesis of PANI. The beauty of the route arises from the fact that the synthesized PANI salts were found to be highly soluble and conducting. To the best of our knowledge there is no report on the synthesis of PANI, neither via electrochemical polymerization nor via chemical oxidative polymerization, where the synthesized PANI is highly soluble in a large number of common organic solvents and at the same time exhibits good conductance. In this process dodecylbenzenesulfonic acid (DBSA) and sulfuric acid, were both used together as dopants, resulting in the formation PANI–DBSA–H_2SO_4. The long alkyl chain of DBSA is supposed to impart solubility to the synthesized polymer in common organic solvents. The sulfate moiety can provide a good conductive structure because it may cause less hindrance as compared to bulky alkyl group of DBSA. The synthesized PANI–DBSA–H_2SO_4 salts seem to deserve their application in various technologies such as corrosion protection of metals.

2. Experimental

2.1. Materials and chemicals

All chemicals were of analytical grade. Aniline (Riedel-de Häen) was distilled under reduced pressure and stored under nitrogen in a refrigerator. H_2SO_4 (Riedel-de Häen), chloroform (Scharlau), DBSA (Aldrich), ammonium persulfate, APS (Riedel-de Häen) were used as received, Ultrapure water (Millipore) was used for solution preparation and natural water of Indian and Pacific Oceans was used for corrosion tests.

2.2. Synthesis of polyaniline

In a typical experiment, 7.47 mmol of DBSA was slowly added to 50 mL of chloroform under constant stirring. Then 16.42 mmol of aniline was added to this mixture. It was followed by the drop wise addition of 25 mL of an aqueous solution of sulfuric acid (12.50 mmol) and 25 mL of an aqueous solution of the oxidant, APS, (1.25 mmol). Consequently the formation of a milky white emulsion was observed. The stirring was continued at room temperature. The content of the round-bottom flask gradually turned green. After about 24 h, the mixture was transferred in to a separating flask and kept for 15 min to separate the organic and aqueous phases. Afterwards, the organic phase was washed repeatedly with deionized water and added to 50 mL of acetone in order to precipitate out the polymer. The obtained green precipitate was filtered under suction and washed with excess of acetone. It was then kept overnight in an oven at 60 °C for drying.

By following the above mentioned procedure, the amounts of reactants (i.e., sulfuric acid, aniline and APS) were stepwise changed in the feed for optimization. Details of the synthesized samples are listed in Table 1.

2.3. Characterization

Percent yield of PANI was calculated by using the following formula:

$$\text{Percentyield} = \frac{\text{Weightofpolyaniline}}{\text{Weightofaniline}} \times 100 \quad \text{(i)}$$

As basically we wanted to observe the effect of the amount of the H_2SO_4 on the properties of the resulting polyaniline salts, seven samples (sample numbers 1–7 in Table 1) were synthesized with varying amounts of H_2SO_4. Of these samples, sample number 1 (with 3.75 mmol of H_2SO_4) sample number 4 (with 12.5 mmol of H_2SO_4) and sample number 7 (with 25.00 mmol of H_2SO_4) were selected for further studies. The amounts of aniline, APS and DBSA were kept constant as 16.42 mmol, 1.25 mmol and 7.47 mmol, respectively. For the sake of convenience and clarity, samples number 1, 4 and 7 were further labeled as PANI 1, PANI 2 and PANI 3, respectively. These samples demonstrate the lowest, intermediate and highest amounts of the acid in presently studied range, while keeping all the other parameters constant.

The following procedure was adopted for the determination of maximum attainable concentration of the synthesized materials in a particular solvent (e.g., in chloroform). For this purpose 10 mL of chloroform was taken and 1 g of the sample was gradually added to it. When some of the polymer did not dissolve, further 3 mL of chloroform was added to dissolve it. The solubility was then calculated in percent weight/volume (w/v%). In this way, the solubility of the synthesized materials was determined in a variety of organic solvents as demonstrated in Fig. 2.

Cyclic voltammetry was performed by means of 3000 ZRA potentiostat/galvanostat Gamry (USA). Cyclic voltammograms were recorded in a three electrode cell containing 0.5 M H_2SO. PANI dissolved in ethanol was dip-coated onto a gold sheet and it was used as working electrode. A gold coil and a saturated calomel

Table 1
Composition of various samples of PANI–DBSA–H_2SO_4 salts. Samples 1–7 were synthesized with varying amounts of H_2SO_4. Samples 8–13 were synthesized with varying amounts of aniline while in samples 14–19 the amount of APS was changed.

S. No	H_2SO_4 (mmol)	Aniline (mmol)	APS (mmol)
1	3.75	16.42	1.25
2	5.00	16.42	1.25
3	7.50	16.42	1.25
4	12.50	16.42	1.25
5	17.50	16.42	1.25
6	22.50	16.42	1.25
7	25.00	16.42	1.25
8	12.50	1.09	1.25
9	12.50	5.47	1.25
10	12.50	10.95	1.25
11	12.50	16.42	1.25
12	12.50	21.90	1.25
13	12.50	27.38	1.25
14	12.50	16.42	0.25
15	12.50	16.42	0.50
16	12.50	16.42	0.75
17	12.50	16.42	1.00
18	12.50	16.42	1.50
19	12.50	16.42	1.75