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CONTROLLED SYNTHESIS OF NANOSIZED POLYANILINE *VIA* UNSTIRRED, LIQUID-LIQUID INTERFACIAL POLYMERIZATION PROCESS

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Abstract. Nanorods/nanofibers of polyaniline were synthesized *via* liquid-liquid interfacial polymerization process using ammonium persulphate as an oxidizing agent. *Para*-toluene sulphonic acid (*p*-TSA) was used as a dopant during the polymerization process. The spectroscopic characterization (UV-Vis and FT-IR) confirms the presence of conducting emeraldine salt phase of the polymer. The morphological studies were carried out using FE-SEM analysis.

Keywords: nanomaterial, polyaniline, interfacial polymerization.

1. Introduction

The intrinsically conducting polymers (ICPs), more commonly known as “synthetic metals”, forms the third class of molecular conductors. Initially, the study of conjugated polymers was hampered owing to their insolubility, infusibility and instability in the air. However, due to incorporation of substituent and the use of various dopants these materials are found to be soluble in common organic solvents and hence processable.

Polyaniline (PANI) is one of the most important conducting polymers owed to its easy preparation and doping process, good electrical conductivity and environmental stability, and potential use as electrochromic device, as sensor and as corrosion protecting paint [1]. These properties turned PANI attractive to use in solar cells, displays, lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings and sensors. Conventional polyaniline synthesis methods are known to produce particulate products with irregular shapes and size. Therefore, many methods have been

developed to make nanostructures of polyaniline. The recent research efforts deal with the control and the enhancement of the bulk properties of PANI, mainly by formation of organized PANI chains and nanofibers.

Nanostructured polyanilines have attracted much attention because of their potential applications such as chemical and biological sensors [2, 3], surface modified electrode [4], biocompatible material [5], artificial muscles [6], and anticorrosion coating [7]. Many synthesis methods [8–13] have been reported to prepare nanosized polyaniline. The morphology of polyaniline nanofibers can be modified by introducing hard templates [14, 15] or structure directing molecules [16, 17].

Recently, novel interfacial polymerization process has been introduced for the synthesis of nanosized polyaniline. Interfacial polymerization is an alternative to bulk polymerization or condensation polymers, which would require high temperatures. Two immiscible solvents are used in this method, with monomer dissolved in one solvent (organic) reacting with oxidizing agent and protonic acid dissolved in the other solvent (aqueous). Reactions often occur on a time scale that so fast that for our purposes they might as well be called instantaneous. Higher molecular weights are obtained because monomer is more likely to encounter a growing chain than the opposing monomer. A rapid, but more controlled approach is to take advantage of the fast kinetics of the polymerization at the interface between two immiscible phases. Interfacial polymerization involves the reaction of monomer dissolved in an organic phase with an oxidizing agent dissolved in an aqueous phase at the interface between the two non-miscible phases. Interfacial polymerization can be of two types. In one case, there are two separate macroscopic layers in contact with each other.

This is called “unstirred interfacial polymerization” and is the subject of study under this project. Unstirred interfacial polymerization is used to produce membranes and to create polymer by continuous removal in a single rope. The other case is the one where one phase is dispersed as tiny droplets in the other (continuous) phase by using high speed stirring. This is called “stirred interfacial polymerization”. Stirred interfacial polymerization is used to produce tiny microcapsules (hollow inside) and microspheres (not hollow) for various applications like controlled release of drugs and pesticides.

Herein, we report the simple and scalable techniques for the preparation of nanosized polyaniline *via* novel unstirred, interfacial polymerization technique and complete physico-chemical characterization of the synthesized polyaniline nanofibers using various analytical tools.

2. Experimental

All chemicals were of analytical reagent (AR) grade and used as received. *p*-Toluenesulfonic acid (*p*-TSA) was obtained from Thomas Baker Pvt. Ltd. Monomer, aniline was supplied by S.D.Fine-Chem Ltd. and distilled prior to use. Monomer – aniline (99 % purity, molecular weight 93.12, boiling point 457 K, density 1.02 g/ml) – was distilled under reduced pressure and stored at low temperature prior to use. Ammonium persulfate (APS) – oxidizing agent – was procured from S.D.Fine-Chem Ltd. and used as received. Chloroform, as an organic solvent was also supplied by S.D.Fine-Chem Ltd. and used as received. All solutions were prepared in double distilled water. In a typical polymerization process, the appropriate amount (0.553 mol) of the monomer (aniline) was dissolved in the organic solvent (chloroform) to form the organic phase. The aqueous phase consists of the oxidizing agent, ammonium persulfate (0.554 mol) dissolved in double distilled water together with *p*-toluenesulfonic acid (PTSA) (1.33 mol) as a protonic acid. The monomer to oxidizing agent ratio was kept as 1:1. After complete addition of the oxidizing agent (aqueous phase) to the reaction mixture (organic phase) slowly, the two phases are formed and the polymerization is observed to be initiated at the boundary or at the junction of the two phases.

Fig. 1 shows different steps involved during the polymerization process. After completion of the reaction the polymer was separated and washed with distilled water until the filtrate was colourless. Finally, the polymer was dried in an oven at 353 K for 12 h. Free flowing, dark greenish-black powder was then subjected for the physico-chemical characterization.

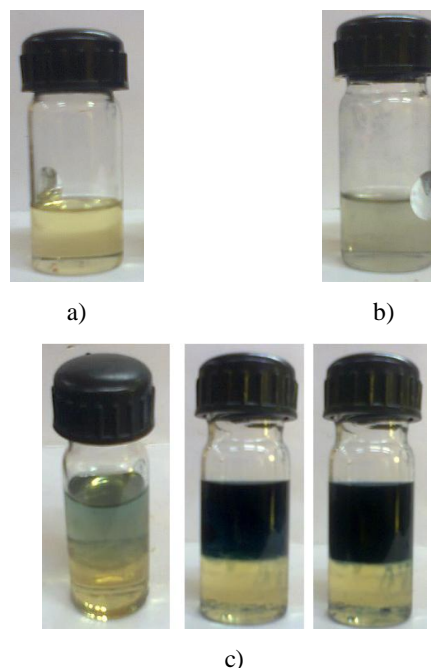


Fig. 1. Photographs of sample bottles containing: organic phase (a); aqueous phase (b) and various steps involved during the interfacial polymerization process after mixing of two phases (c)

In order to achieve proper washing and isolation of the synthesized material without any loss, we have carried out the similar reaction using separating funnel and the stages involved during this are presented in Fig. 2.

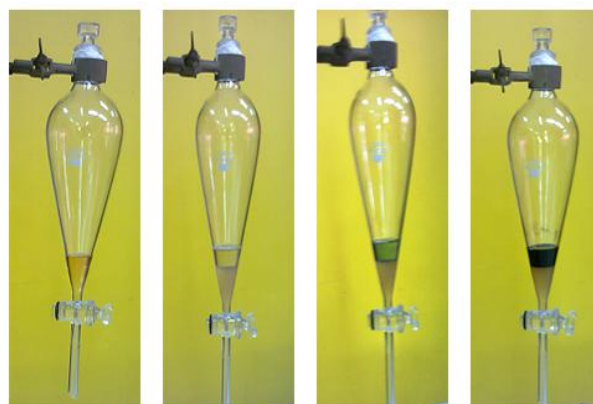


Fig. 2. Photographs of various steps involved during the interfacial polymerization process using separating funnel

The isolation of the material after completion of the reaction is comparatively much easier as one can discard the organic phase through the knob of separating funnel without the need of filtration. The repeated washing of the product is also found to be easy and efficient as compared with the reaction carried out in small sample bottles. Also, there is an advantage in using the separating funnel for the

reaction and subsequent washing and isolation, due to minimized/almost no loss in the product, which usually takes place in isolation and washing of the product using filter paper by vacuum filtration.

3. Results and Discussion

3.1. UV-Visible Spectroscopy

The UV-Visible spectrum of the polymer solution was recorded using “Perkin Elmer Lambda 950” spectrophotometer in the range of 300–900 nm. Electronic absorption of conducting polymers is useful in investigating the oxidation and doping state of the polymer.

The optical absorption spectra of the polyaniline doped with *p*-TSA is presented in Fig. 3.

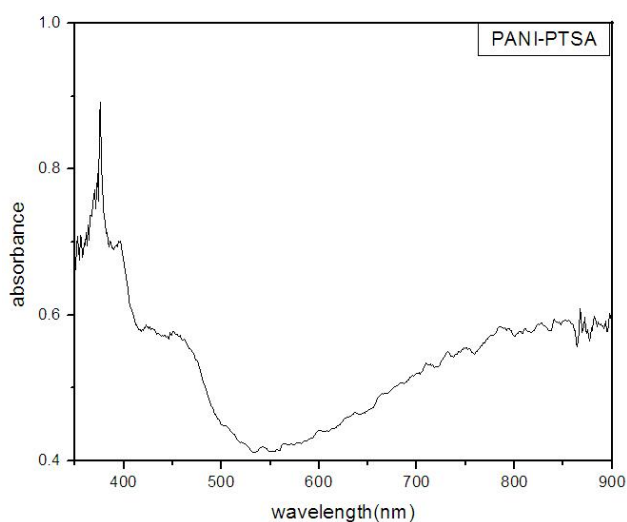


Fig. 3. UV-Vis spectrum of nano-polyaniline

The spectrum exhibits sharp peaks at 320 nm which corresponds to the π - π^* transition of the benzenoid rings, while the shoulder at 420 nm is attributed to the localized polarons, which is the characteristic of the protonated polyaniline. The increasing absorption at higher wavelength (\sim 800 nm) confirms the presence of conducting emeraldine salt (ES) phase of the polymer [17].

3.2. XRD Analysis

X-ray diffraction was used to further probe the structure of the polyaniline nanofibers and the XRD spectrum is presented in Fig. 4.

From Fig. 4 it is observed that two broad bands centered at $2\theta \sim 20^\circ$ and $\sim 25^\circ$ show that these nano-fibers are partially crystalline. The sharp peak at $\sim 25^\circ$ is a characteristic peak of the extent of π conjugation in the polyaniline. This sharpness of the peak shows the longest order of π conjugation.

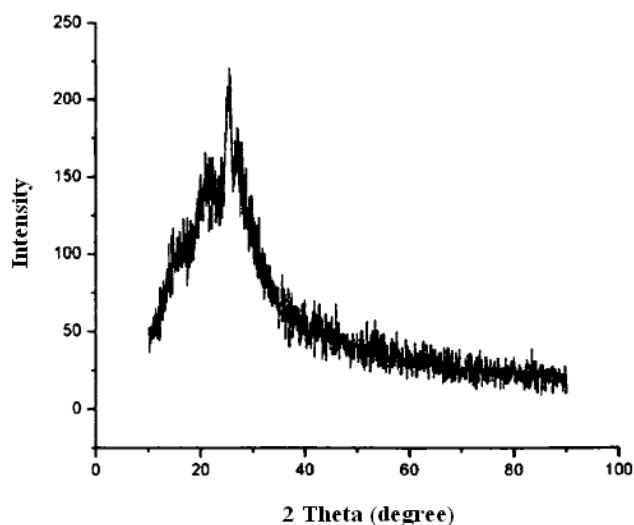


Fig. 4. XRD pattern of the *p*-TSA doped nanosized polyaniline

In short it is observed that the benzenoid and quinonoid units are more orderly arranged in *p*-TSA doped polyaniline synthesized *via* interfacial polymerization.

3.3. FT-IR Spectroscopy

Fig. 5 represents the FT-IR spectrum of the polyaniline nanorods/nanofibers synthesized by unstirred, interfacial polymerization technique and the peak positions related to the corresponding chemical bonds are listed in Table 1.

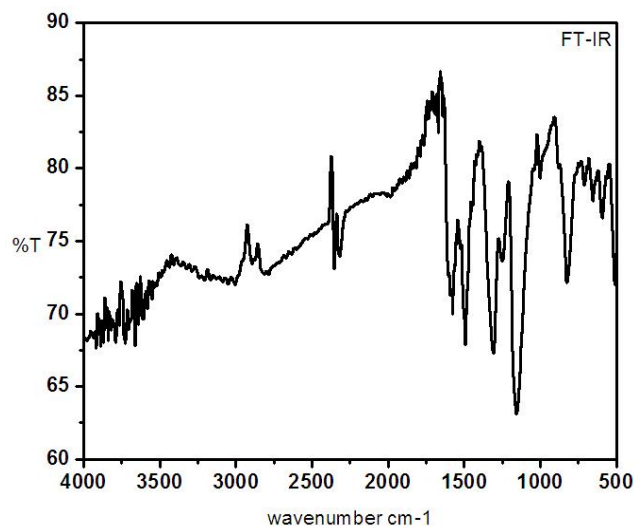


Fig. 5. FT-IR spectrum of polyaniline nanorods/nanofibers doped with *p*-TSA

The presence of two bands in the vicinity of 1500 cm^{-1} and 1600 cm^{-1} are assigned to the non-

symmetrical C6 ring stretching modes. The higher frequency vibration at 1600 cm^{-1} has a major contribution from the quinoid rings while the lower frequency mode at 1500 cm^{-1} depicts the presence of benzenoid ring units [17]. The presence of these two bands clearly shows that the polymer is composed of amine and imine units. Furthermore, this supports our UV-Vis characterization, discussed earlier, where, different phases are observed in the spectrum. The presence of other characteristic bands confirms the presence of conducting emeraldine salt phase in the polymer.

3.4. FE-SEM Analysis

Fig. 6 shows the micrographs of nanosized polyaniline synthesized *via* interfacial polymerization method. The magnifications were selected such that the morphology could be seen clearly. Interfacial polymerization is a non-template approach in which monomer gets linearly polymerized at the interface of the two immiscible solvents thus offering very interesting morphological features, with observed fibrillar/rod type of structure with thickness of the fibers/rods $\sim 90\text{--}100\text{ nm}$ and length up to few microns.

Table 1

Characteristic frequencies of *p*-TSA doped nanosized polyaniline

Wavenumber, cm^{-1}	Band characteristics
668	C–S stretching of the benzenoid ring of <i>p</i> -TSA
825	C–H stretching indicating <i>para</i> -coupling
1001	S–O stretching of <i>p</i> -TSA
1155	NH $^{+\bullet}$, indicating PANI nanofibers is in the doped state
1160	Stretching vibrations of the SO $_3$ H group
1247	C–N $^{+\bullet}$ stretching
1307	C–N stretching of the secondary aromatic amine
1493	C=C stretching of benzenoid ring.
1573	C=C stretching of quinoid ring
3005	O–H stretching of PTSA
3550	Free N–H stretching

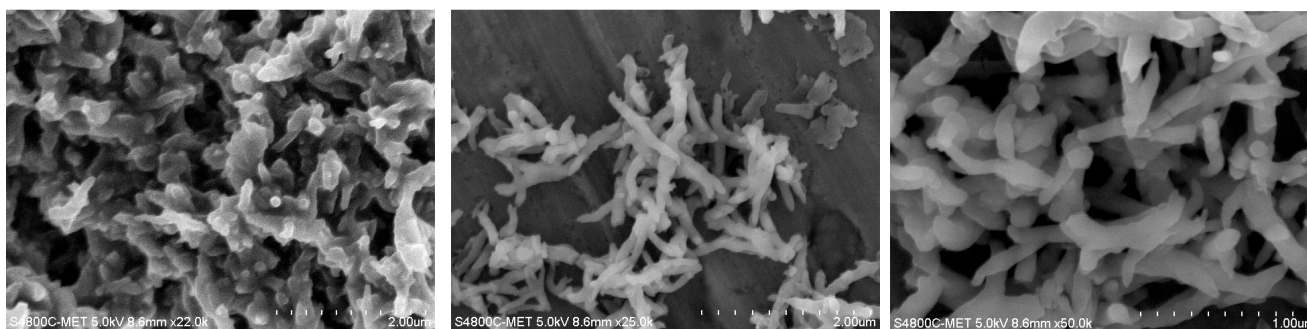


Fig. 6. FE-SEM micrographs of polyaniline nanorods/nanofibers doped with *p*-TSA

In the present investigation, nanostructured polyaniline is prepared by chemical oxidative polymerization of aniline in aqueous acidic medium via interfacial polymerization process. Ammonium persulfate (APS) being the most common oxidizing agent was used to initiate the polymerization reaction. The process of interfacial polymerization and growth of the nanorods/nanofibers of polyaniline and chemical reaction involved during the polymerization is schematically demonstrated in Figs. 7 and 8.

As shown in Fig. 7 the formation of the nanorods/nanofibers by the interfacial polymerization

process is due to the controlled availability of the monomer at the junction of the organic and aqueous phase during the polymerization. It is expected that a very limited amount of monomer molecules present in the organic phase are interacting with the oxidizing agent, present in the aqueous phase. Since the as-made polyaniline product is synthesized in its hydrophilic emeraldine salt form it diffuses away from the reactive interface into the water layer. This makes more reaction sites available at the interface and thus avoiding further overgrowth or polymerization proceeds without severe secondary overgrowth.

After complete addition of the oxidizing agent (aqueous phase to organic phase) formation of the boundary between the two different phases takes place. The density of the water is less than that of the organic solvent, chloroform, thereby forming the upper phase in the reaction media. At the boundary, the oxidizing agent reacts with the monomer molecule and initiates polymerization, which proceeds further till complete polymerization of the monomer present in the non-aqueous media resulting in a linear structure of the polymer. On the contrary, during the bulk polymerization process all the monomer molecules present in the reaction media interact with the oxidizing agent and the reaction initiates at all monomer sites and proceeds further. The initially formed granular polyaniline further reacts with the monomers present in the reaction flask (secondary growth stage) and the size of the granules increases to form a sponge-like structure at the end of reaction. In contrast, in interfacial polymerization controlled availability and interaction of monomer and oxidant at the interface as well as the fast movement of initially formed PANI chains lead to the formation of PANI nanofibers/nanorods. Therefore, only polyaniline nanofibers/nanorods are generated without further secondary growth as shown schematically in Fig. 7.

Fig. 9 displays the thermal profile (TG/SDTA) of the polyaniline nanorods/nanofibers synthesized by interfacial method using *p*-TSA as a dopant.

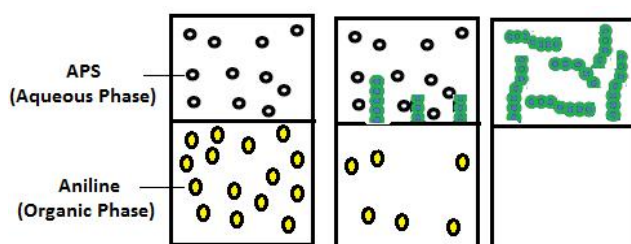


Fig. 7. Schematic interfacial polymerization of aniline and formation of nanorods/nanofibers

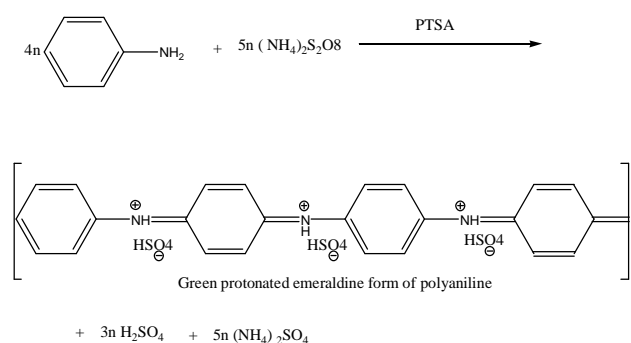


Fig. 8. Chemical scheme of polymerization of aniline using ammonium persulfate (APS) as an oxidizing agent to form polyaniline

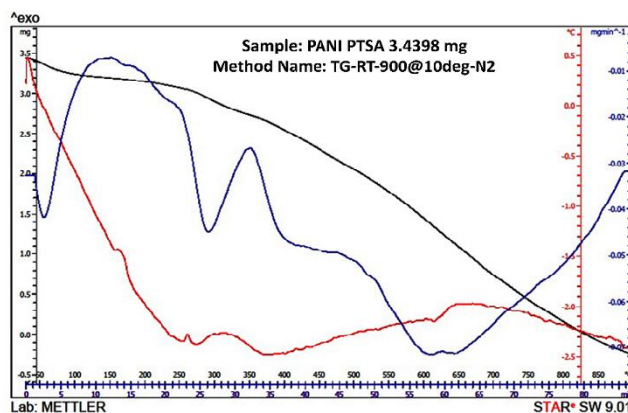


Fig. 9. Thermogram of nano-polyaniline

It is observed from Fig. 9 that the polymer exhibits a three-step decomposition pattern similar to that of polyaniline synthesized by bulk polymerization process. The first step in the decomposition pattern, starting from RT – 373 K, is obviously due to the removal of free water molecules/moisture present in the polymer matrix.

The second step starting from 373 to 573 K is mainly due to the loss of the dopant ion from the polymer chains (thermal dedoping), as well as loss of more strongly bound water between the polymer chains, whereas the third step starting from 573 K onwards is accounted for the degradation and decomposition of the skeletal polymer backbone after the elimination of the dopant ion [17]. The first derivative plot also reveals the similar weight loss pattern.

The room temperature solid state conductivity of the polymer was measured on pressed pellets having a diameter of 1.5 cm using the two-probe conductivity measurement technique. The conductivity of *p*-TSA doped polyaniline nanofibers is found to be $1.01 \cdot 10^{-4}$ S/cm, which is higher than that of synthesized by bulk polymerization process.

4. Conclusions

Nanostructured conducting polymer polyaniline was synthesized by unstirred, liquid-liquid interfacial polymerization method using ammonium persulfate as an oxidizing agent and *p*-toluene sulfonic acid (*p*-TSA) as a dopant. The monomer was dissolved in chloroform forming an organic phase while aqueous phase comprises an acid and oxidizing agent dissolved in water. The presence of conducting emeraldine salt phase of the polymer was confirmed by the UV-Visible and FT-IR spectroscopy and is supported by X-ray diffraction analysis. The FE-SEM analysis revealed the nanorods/nanofibrillar structure of the polymer having the diameter (width) of 90–100 nm and the of length up to

few microns. Thermogravimetric analysis shows the three-step decomposition pattern similar to the polyaniline synthesized by bulk polymerization method. The synthesized polyaniline nanofibres will have potential for application in sensors and other fields of electronics.

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КОНТРОЛЬОВАНИЙ СИНТЕЗ НАНОРОЗМІРНОГО ПОЛІАНІЛІНУ ЗА ДОПОМОГОЮ НЕПЕРЕМІШУВАНОВОГО ПРОЦЕСУ ПОЛІМЕРИЗАЦІЇ НА МЕЖІ РІДИНА-РІДИНА

Анотація. Полімеризацією на межі розподілу фаз рідина-рідина з використанням як окиснювача персульфату амонію синтезовані наностержні/нановолокна поліаніліну. Як легуючу домішку використано *p*-толуолсульфонову кислоту. Присутність в полімері емералдінової солі підтверджено УФ-спектроскопією та ІЧ-спектроскопією Фур'є. Морфологічні дослідження проведені з використанням скануючої електронної мікроскопії.

Ключові слова: наноматеріал, поліанілін, міжфазова полімеризація.