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Studies on interfacial and sonochemically synthesized polyaniline nanofibers

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ABSTRACT

Polyaniline, an important conducting polymer, has been synthesized by both interfacial and sonochemical methods. UV-Visible spectra reveal that the degree of polymerization and fiber length highly depend on the method used for synthesis. The fibrous nature of emeraldine base of polyaniline has been studied by SEM micrographs. These fibers are of nano-dimensions with orthorhombic crystal symmetry. The percentage crystallinity of polyaniline has been investigated using powder X-ray diffraction analysis, where the percentage crystallinity of interfacially synthesized polyaniline is 12% more than sonochemically synthesized polyaniline. This paper reveals that with the change in crystallinity, there is a remarkable change in % transmittance, bathochromic shift and fibrous nature of polymer.

Key words: Polyaniline, Nano-fiber, X-ray diffraction, Crystallinity.

INTRODUCTION

Intrinsically conducting polymers like polyacetylene, polypyrrole, polyaniline (PANI), polythiophene, etc., are organic polymers which possess the electrical, electronic, magnetic and optical properties of metals with the retention of mechanical properties. These polymers are easily processable and find suitable utility in various technological applications. These materials are more commonly known as "synthetic metals" [1]. Among these polymers, PANI has elicited the most interest because of its good environmental stability and wide range of electrical conductivity (insulator to metallic regime) found by Mac Diarmid et al [2] in 1985. Significant, scientific and technological interest has been focused on polymer nano particles [3-5]. One dimensional nano-structure of PANI, including fibers [6-7], nanowire, rods, and tubes [8-9] have been studied with great attention by many researchers worldwide because of their importance in manufacturing nano-devices. The PANI nanofibers have been prepared by different methods including chemical, electrochemical as well as physical techniques [10]. Depending on the need of researcher, the conditions for synthesizing the nano-structured PANI are controlled. Due to simple and easy preparation of nanostructured PANI, it has wide applications [11] in industry and laboratories for designing the devices like sensors [12-15], analytical separations [16], electrorhelogical systems [17-18], catalytical supports [19], actuators [20], electrostatic discharge [21], corrosion protection [22-23], field effect transistors and fuel cells etc.

It is well known that the parameters such as melting point, solubility, stability and morphology are dependent on crystallinity of the organic compound. It has been established that the doped and undoped PANI has different crystalline contents [24], i.e., the emeraldine salt (PANI-hydrochloride) is partly crystalline while emeraldine base (undoped PANI) is essentially an amorphous polymer. Such determination of morphology based on X-ray analysis of a powdered sample is a relatively easy and reasonably effective method, although the method has several limitations [25]. The present paper deals with the comparative studies for the degree of crystallinity between interfacially and sonochemically synthesized PANI nanofibers.

MATERIALS AND METHODS

The following materials were used to synthesize nanofibers of PANI: Aniline, HCl, ammonium hydroxide (CDH chemicals India), ammonium persulphate (Merck Ltd., Mumbai, India), dimethylformamide (Qualigen India), and dichloromethane (Spectrochem Pvt. Ltd., Mumbai, India). Aniline was double distilled under reduced pressure and stored at low temperature prior to its use. All other chemicals were AR grade and were used as received. Double distilled and demineralized water from Millipore was used throughout the studies.

Synthesis of PANI by interfacial method

0.2 M of distilled aniline was dissolved in 10 ml of dichloromethane (CH_2Cl_2)to form aniline solution (colorless) in CH_2Cl_2. 0.2 M of APS was dissolved separately in 10 ml of 1 M HCl to form ammonium persulphate (APS) solution (colorless). Both the solutions, i.e., aniline solution and APS solution were kept at low temperature between 1 to 5°C to cool the solutions. This was done to decrease the rate of reaction as the oxidation of aniline by APS is an exothermic reaction. APS solution was poured over the aniline solution which results in the formation of two distinct and separate layers of solutions in contact through an interface. The lower layer was aniline solution while upper layer was APS solution. The beaker containing both the solutions was kept in ice bath to maintain the temperature between 1 to 5°C. Greenish blue colored product started appearing at the interface of the solutions which was an indication of the initiation of the reaction. The product was hydrophilic and therefore it moved upward, i.e., in the APS solution after being formed at interface. After 2 to 2.5 h the changes taking place in the beaker gets stopped which is an indication of the completion of reaction. The product was filtered, washed with distilled water and methanol till the filtrate becomes colorless and then dried at room temperature. The final product was dedoped by 1:1 aqueous ammonia solution for getting emeraldine base (EB) form of PANI. Step-wise schematic representation of interfacially synthesized PANI is given in Fig. 1.

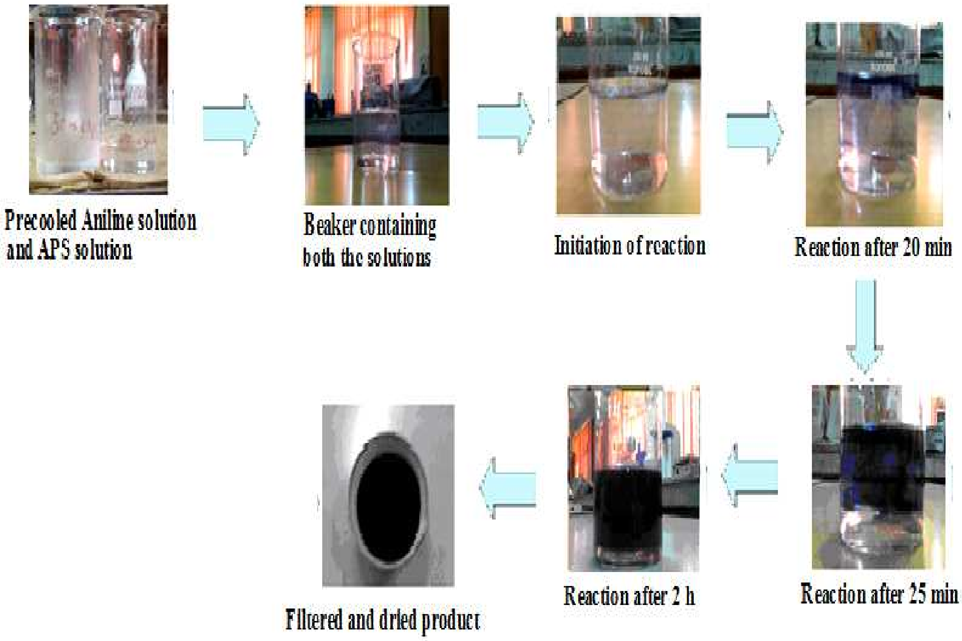

Fig 1. Schematic representation of interfacially synthesized PANI

Synthesis of PANI by sonochemical method

Chemical polymerization of aniline was done with the aid of ultrasonic waves using Ultrasonicator (Model USB-2.25) from Accumax India, Delhi. A solution of freshly distilled aniline (0.2M) was prepared in 1M HCl solution. The solution was cooled at 0-5°C and an aqueous solution of APS (0.2 M) was added drop wise (2.5 µl in one lot) under sonication for 30 min at 5°C. A dark green precipitate so obtained was filtrated and then washed by 1M HCl solution several times followed by deionised water. It was finally dried, and powdered. The final product was dedoped by 1:1 aqueous ammonia solution for getting emeraldine base form of PANI.

RESULTS AND DISCUSSION

UV-Visible spectroscopy

UV-Visible spectra of PANI solutions in DMF were recorded over the range 250-900 nm using double beam UV-Vis spectrophotometer (Model UV5704SS) ECIL, India. The data of UV-Visible spectra confirm the formation of polymer giving characteristic bands. Two absorption bands were appeared in the UV–Vis spectra of PANI in DMF (Fig. 2).

The first absorption band at ca. 350 nm is associated with the π– π* transition of the conjugated ring systems and the second band at ca. 620 nm is assigned to a benzenoid to quinoid excitonic transition in sonochemically synthesized PANI [26]. The much higher absorbance values and bands at 423 and 820 nm are reported for interfacially synthesized PANI owing to its higher solubility. It is reported in the literature that the position of the band about 350 nm correspond to interband π–π* transition and depends on degree of polymerization. Therefore, it is concluded here that an average polymerization degree in sonochemically synthesized PANI is slightly less than the interfacially synthesized PANI. At the same time, relative red shift of the polaron band in interfacially synthesized PANI could argued in favor of comparatively more delocalization of polarons [27]. Additionally, it was found that there is no alteration in the electronic state of the nanofibers of PANI synthesized by two different methods [28].

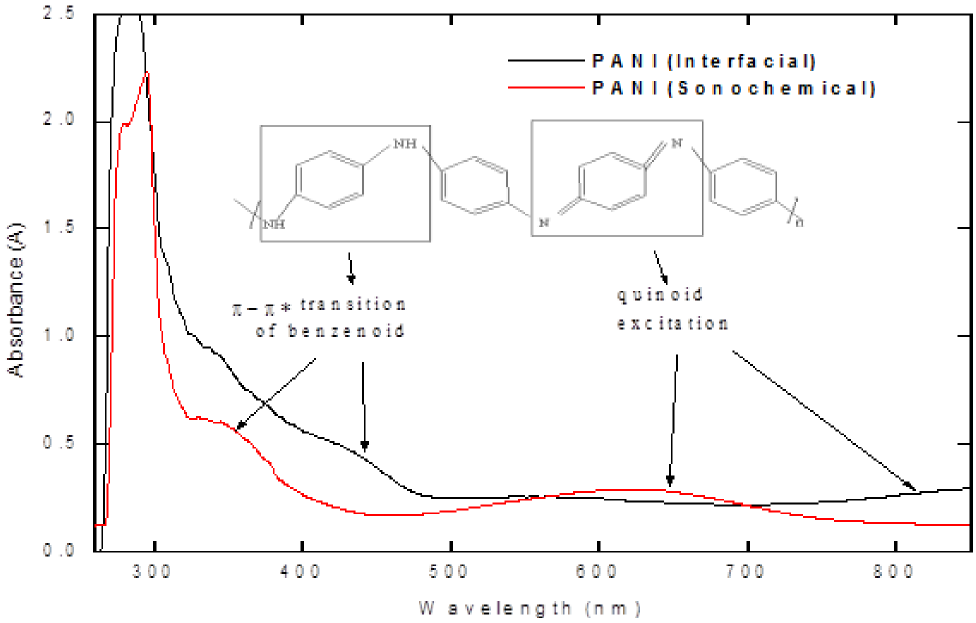

Fig 2. UV-Visible spectra of PANI

FTIR analysis

FT-IR study is useful for characterization of polymers [29-30]. The FT-IR spectra of PANI nanofibers were recorded in KBr medium using a Perkin-Elmer (Model No.2000, UK) spectrometer. The characteristic peaks are observed at 3392, 2922 and 1302 cm^{-1} which attribute due to the –NH stretching, C-H stretching on aromatic ring and C-N stretching while peaks at 1498 and 1590 cm^{-1} show the presence of benzenoid and quinoid structures, respectively. The characteristic peak at 1165 cm^{-1} is due to an aromatic amine stretching. The peak at 828 cm^{-1} attributes due to the out of plane hydrogen deformation of aromatic rings in PANI unit sequences [31]. The characteristics peaks observed for both type of PANI are almost similar which shows that there is no significant difference between the chemical structures of two samples as shown in Fig. 3. The emeraldine base of PANI synthesized by the interfacial method has sharp and intense peaks as compare to PANI synthesized by sonochemical method.

The FTIR spectra show that the change in the percentage transmittance is due to the change in the percentage of crystallinity. Hence, more intense and sharp peak indicates that the sample is more crystalline in nature.

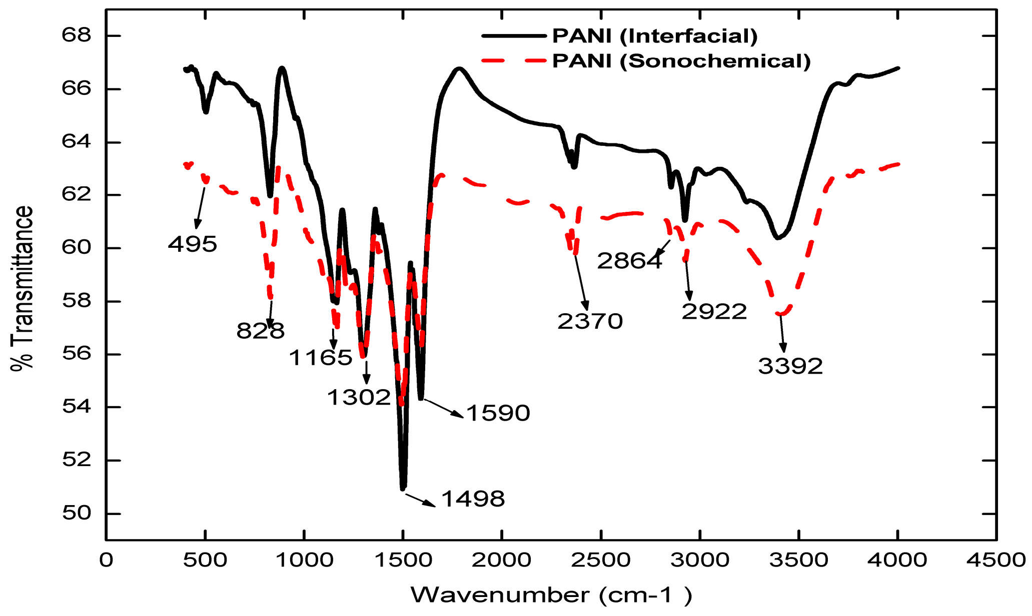

Fig 3. FTIR specra of PANI

XRD analysis

The powder X-ray diffraction patterns were recorded using a Rikagu miniflex diffractometer employing Cu Kα1 radiation at a scan rate of 1°/min and step size 0.02. The X-ray diffraction data for PANI synthesized by interfacial and sonochemical methods are shown in Fig. 4. It has been reported that the crystallinity of the polyaniline sample depends on the conditions set during the synthesis of the polymer. The XRD pattern of polyaniline emeraldine bases with broad diffused peak at approximately 19° indicates that the PANI is amorphous. However, some sharp peaks are also present which indicate that the PANI is little bit crystalline also.

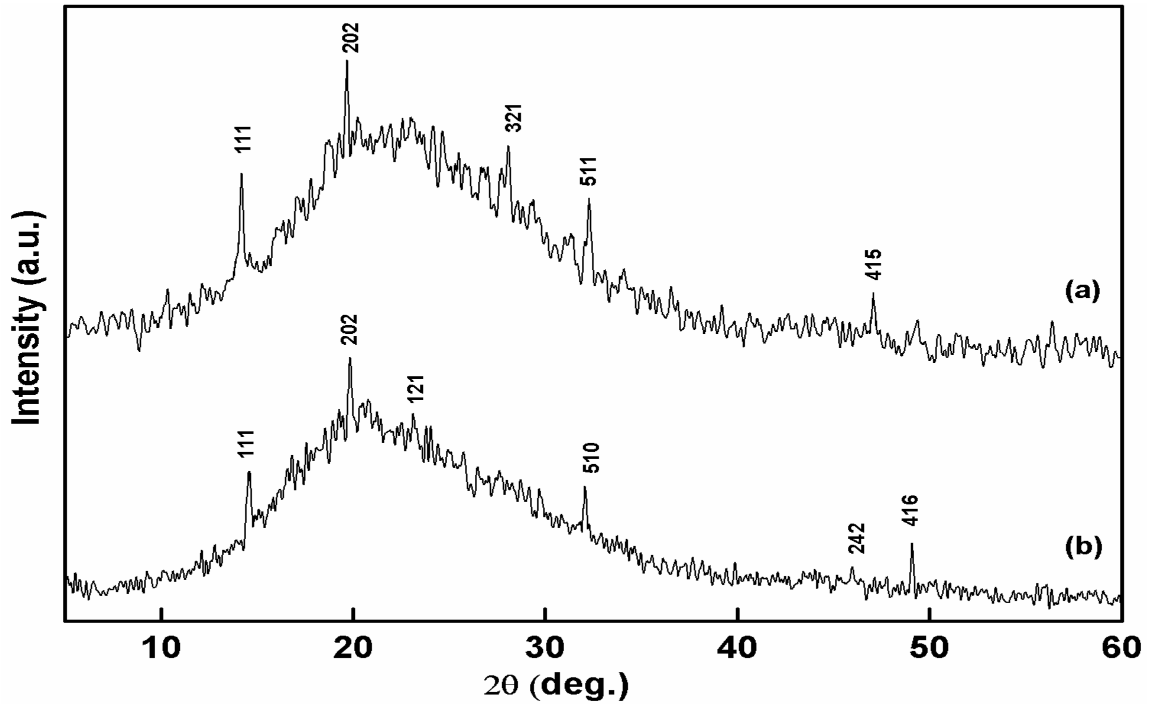

Fig 4. X-ray diffraction spectra of (a) Sonochemically and (b) Interfacial synthesized PANI

Crystallinity index of the sample was calculated by employing a formula given by Manjunath et al. [32] According to this formula, the resolution of the peak R for X-ray spectrum with heights h_1 and h_2 and minima m_1 is given by

$$\mathbf{R} = (2m_1) / (h_1 + h_2) \quad (1)$$

In the case of polymers, where there are more than two peaks as in polyaniline, all the peaks and the minima between them are measured. Thus

$$\mathbf{R} = (m_1 + 2m_2 \ldots\ldots\ldots + m_{n-1}) / (h_1 + h_2 \ldots\ldots\ldots\ldots + h_n) \quad (2)$$

Where m_1, m_2 are the heights of minima between two peaks and h_1, h_2 are the heights of peaks from the base line. The crystalline peaks of PANIs are usually visible in the figures. Hence, for calculating the percentage of crystallinity, appreciably sharp peaks of PANI sample at three different theta values are considered which are presented in Table 1.

Table 1. 2θ value for the peaks, interplanar spacing (d) value and % of crystallinity (R) calculated from X-ray diffraction pattern of PANI (Interfacial) and PANI (Sonochemical)

S. No.	Sample	X-ray data		
		2θ (degree)	**d (A°)**	**R (%)**
1	PANI (Interfacial)	14.383	6.15327	28
		19.841	4.47126	
		28.309	3.14999	
2	PANI (Sonochemical)	14.757	5.99816	16
		19.668	4.51001	
		27.518	3.23876	

Hence, the general formula in (Eq. 2) can be reduced for three peaks as

$$\mathbf{R} = (m_1 + 2m_2) / (h_1 + h_2 + h_3) \quad (3)$$

Then, (1-R) gives the lateral order or the index of crystallinity. The percentage of crystallinity has been estimated by employing the relation (3). It has been found that interfacially synthesized PANI is 28% crystalline while sonochemically synthesized PANI is only 16%. On the other hand, the crystal symmetry for both the samples is orthorhombic and the space group is *pcbn* which is found in agreement with literature value [33]. 2θ values, interplanar spacing values and % crystallinity data have been presented in Table 1.

It is well known that the polymer crystallinity and crystal structure are strongly dependent on the kinetics of polymer formation. The fast growth of the polymer results in disorder orientation of polymer chains and amorphous polymer structure. In this study, the interfacial polymerization is relatively slower than sonochemical polymerization, which is favorable for polymer chains to orient themselves. The higher the degree of regularity in arrangements and ordering of polymer chains, the higher is the crystallinity. This again depends on the type of interaction between the polymer chains during reaction. Due to slow kinetics, the amine group in interfacially synthesized PANI chain leads to strong interchain H-bonding and dipole-dipole interaction, and result in better orientation of chains. Thus, more crystalline nanofibers are obtained. It is believed that high crystallinity will result high conductivity [34].

SEM analysis

In order to confirm the crystallinity of PANI synthesized by different methods, the SEM (Hitachi, S-3700N) micrographs of PANI emeraldine bases are shown in Fig. 5(a) and 5(b). Under careful electron microscopy observations, a large amount of nanofibers is found in both types of samples. But, the amount of nanofibers is relatively more in case of sonochemically synthesized PANI. The length and diameter of the nanofibers are smaller than interfacially synthesized PANI nanofibers. The diameter of interfacially synthesized PANI is 134 nm while sonochemically synthesized have 95 nm. This suggests the possibility of obtaining polyaniline nanofibers without any external structural directing agents. The sonochemically synthesized nanofibers that formed naturally in the early stage of the polymerization reaction are smaller in diameter than interfacially synthesized PANI. Therefore, preparation conditions were designed to “shape” the polymer into nanostructures. One can take advantage of the nanofibrillar morphological unit and focus on modifying the reaction path-way so that nanofiber formation is favored while their overgrowth, which would otherwise lead to agglomeration, is suppressed.

Interfacially synthesized PANI is much more nanofibrillar in nature because of the control over kinetics of reaction. Since, the interfacially synthesized PANI product is in its hydrophilic emeraldine base form, it diffuses away from the reactive interface into the water layer. This makes more reaction sites available at the interface Two basic approaches to separate nanofiber formation from overgrowth in conventional aniline polymerization reactions have been discovered. In the first approach, the reaction is placed in a heterogeneous biphasic system, where the polymerization occurs primarily at the interface and avoids further overgrowth. In this way, the nanofibers formed at the interface are collected in the water layer without severe secondary overgrowth. Therefore, the overgrowth of polyaniline is suppressed due to lack of initiator molecules. From SEM and XRD studies, it is concluded that interfacially synthesized nanofibers of PANI are 12% more crystalline than sonochemically synthesized PANI nanofibers.

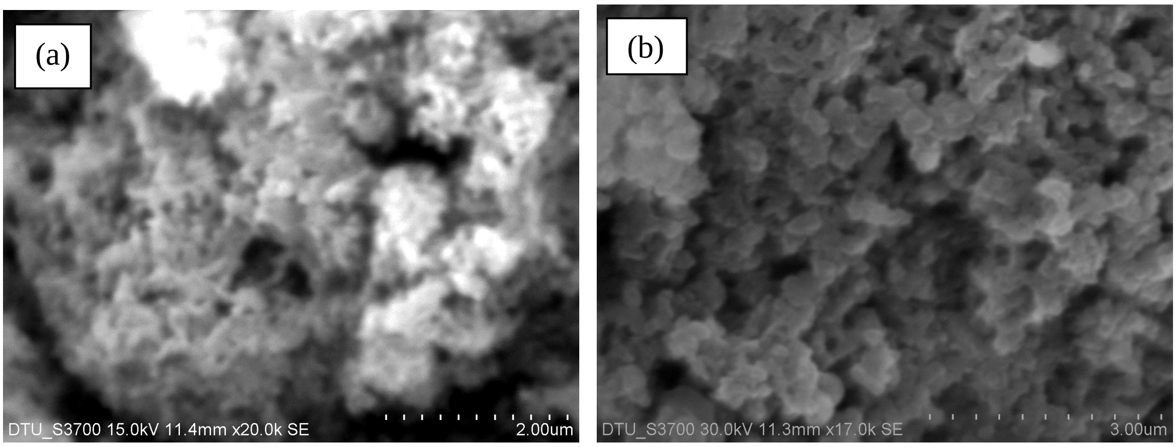

Fig 5. SEM Micrographs of (a) Sonochemically and (b) Interfacially prepared PANI

CONCLUSION

In summary, we can say that the crystallinity of PANI is highly dependent on the method used for synthesis and the kinetics. From UV-Visible spectroscopy, it is found that average polymerization degree in sonochemically synthesized PANI is slightly less than interfacially synthesized PANI. Hence, the nanofibers synthesized by sonochemical method are smaller in length as compare to interfacially synthesized PANI nanofibers. This result is also found in agreement with SEM micrographs. The FTIR spectra suggest that there is no significant difference in the chemical structure of the synthesized PANI nanofibers prepared from either of the method. On the basis of XRD studies, it is concluded that interfacially synthesized PANI is 12% more crystalline than sonochemically synthesized PANI. Further, it is found that with the increase in crystalline nature of polymer, the percentage transmittance, sharpness of peak and batho-chromic shift in the absorption spectra increases while the fiber formation tendency decreases because fibers are irregular patterns and crystallinity is a long range order of unit cells.

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