

INFLUENCE OF POLYMERIZATION ROUTES ON THE CRYSTALLINE BEHAVIOR OF POLYANILINE SALT

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ABSTRACT

The effects of polymerization routes on the crystalline nature of polyaniline (PANI) salts were investigated. PANI salts were prepared by two effective pathways, i.e. emulsion polymerization (Bilal, et al., 2014) and inverse emulsion polymerization (Bilal, et al., 2012). Scanning electron micrographs (SEM) present the irregular granular morphology of these PANI salts having different particle sizes. The effect was further assessed by X-ray diffraction (XRD) in detail. The results showed that interchain separation and crystallite size of the PANI salts were affected by the synthesis methods. The small crystallite size and interchain separation of PANI salt prepared by emulsion polymerization suggested its good electrical properties compared to the PANI salt prepared by inverse emulsion polymerization. The results were further supported by energy band gap values calculated by using UV-Vis spectra. All these results demonstrate that emulsion polymerization enhanced the crystalline behavior by inducing more ordered structure of PANI salt, which can be readily used in optoelectronic devices.

Keywords: Polyaniline, polycrystalline nature, SEM, XRD, UV-Vis spectra

1. INTRODUCTION

Polyaniline (PANI), one of the most thoroughly studied intrinsically conducting polymers, has received great attention due to its excellent chemical stability combined with admirable levels of electrical conductivity in its doped or protonated form, known as PANI salt (Kim, Kwon and Ihm, 2007). Infact, the highly order crystalline structures (with π -conjugated system) of PANI salt is expected to have metal-like electrical conductivity (Kondawar, et al., 2012).

PANI has wide range of potential applications in sensors (Liu, Hayashi and Toko, 2012), rechargeable batteries (Xiao, et al., 2012; El-Shazly and Al-Turaif, 2012), capacitors (Ghenaatian, et al., 2011) and in optical and electronic devices (He, et al., 2001). However, processing of PANI into useful objects and devices has been problematic because of its insolubility in common organic solvents. Therefore, attempts have been made to modify PANI structure and to overcome the difficulties associated with the use of PANI by using different approaches. The successful strategies include the synthesis of

substituted polyaniline (Chan, et al., 1995; Watanabe, et al., 1989; Bilal, Shah and Holze 2011), co-polymerization of aniline with substituted anilines (Bilal and Holze, 2006) and synthesis of PANI salt by emulsion/inverse emulsion polymerization technique (Palaniappan and Nivasu, 2002; Palaniappan and John, 2008). In case of synthesis of substituted PANIs or co-polymers the solubility improves; however, its electrical conductivity is always sacrificed (Palaniappan and John, 2008). Therefore, among these methods emulsion/inverse emulsion polymerization pathways are more useful for improving both the solubility and electrical conductivity of the PANI (Palaniappan and John, 2008).

In the emulsion polymerization, the monomer is dispersed in an aqueous phase in the presence of a surfactant. For the synthesis of PANI by emulsion polymerization, aniline, a protonic acid and an oxidant are combined with a mixture of water and a nonpolar/weakly polar solvent (sparingly soluble or insoluble in water). The product of the above reaction cannot be isolated directly, since the PANI salt and by-products exist in the emulsion together and generally the product is isolated by destabilizing the emulsion through the addition of acetone. The PANI salt is then collected and subjected to repeated washing to free it from other constituents. The mechanism of an inverse emulsion polymerization is similar to that of emulsion polymerization. The difference is that in an inverse emulsion polymerization system, the product is in a dispersion of an aqueous solution of water-soluble polymer in a nonpolar/weakly polar organic solvent. However, synthesizing by these emulsion methods, electrical conductivity of PANI is not going to be high enough to get useful products (Yin and Ruckenstein, 2000).

Therefore, a systematic study aimed at establishing effective polymerization pathway for the synthesis of processable PANI salts was started. Recently, two novel methods i.e., emulsion polymerization (Bilal, et al., 2014) and inverse emulsion polymerization (Bilal, et al., 2012) for the synthesis of completely soluble and highly electrically conducting polyaniline salts were successfully developed. The purpose of this study is to analyze and compare the crystalline behavior of these polymers in details because appreciable connectivity between the microcrystalline domains of PANI chain (i.e. crystallinity of PANI) is one of its very important properties. Hence, the knowledge of crystalline quality of the synthesized PANI salts will

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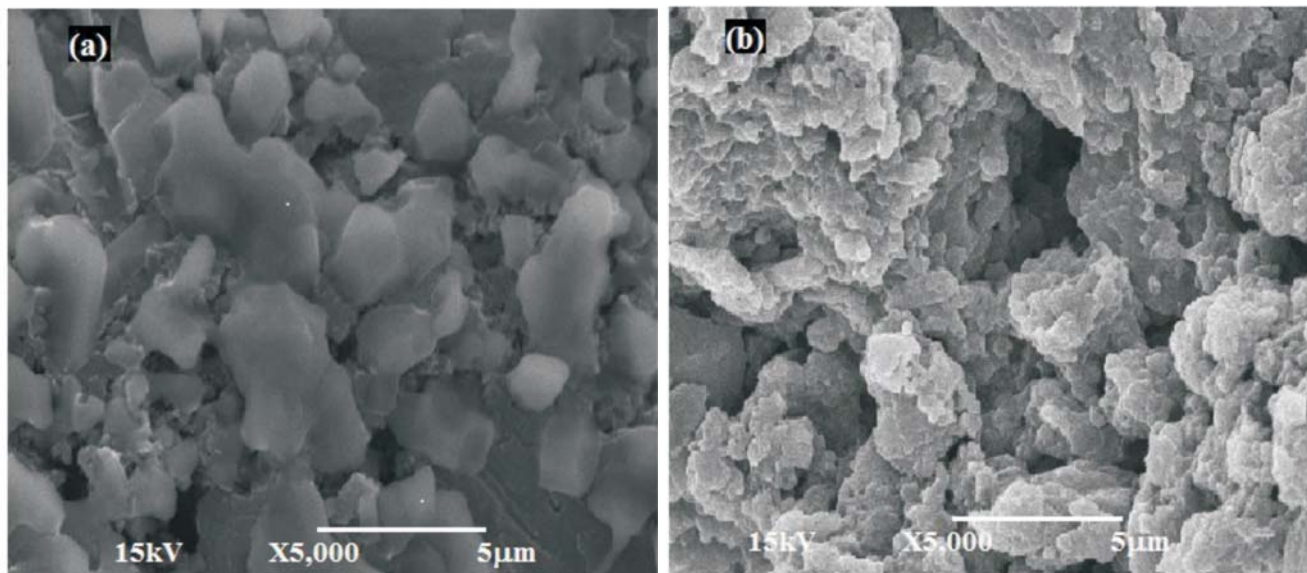


Figure-1: Scanning Electron Micrographs of (a) PANI 1 and (b) PANI 2

provide the scope for its utilization in electronic applications and future re-search

2. MATERIALS AND METHODS

2.1 Chemicals

All chemicals were of analytical grade. Aniline (Riedel-de H en) was distilled under reduced pressure and stored in a refrigerator. H_2SO_4 (Riedel-de H en), Chloroform (Scharlau), Dodecyl Benzene Sulfonic Acid, DBSA, (Aldrich), Ammonium persulfate (Riedel-de H en), Benzoyl peroxide (Merck), 2-Propanol (Merck) were used as received. Water (Millipore) was used for solution preparation.

2.2 Synthesis of Polyaniline Salts

Polyaniline salts were prepared by the following two methods reported elsewhere (Bilal, et al., 2012; Bilal, et al., 2014).

In a typical experiment, 0.10 M DBSA was slowly added to 50 mL of the solvent chloroform under constant stirring. To this mixture, 0.05 M aniline was added followed by the drop wise addition of 25 mL of the dopant H_2SO_4 (0.5 M) and 25 mL of an aqueous solution of the oxidant, ammonium persulfate (0.05 M) in order to get a milky white emulsion. The content of the round-bottom flask gradually turned green and the stirring was continued at room temperature. After about 24 hours, the reaction was stopped, the organic phase was separated and washed repeatedly with de-

ionised water. It was then added to 200 mL of acetone to precipitate out the polymer. The green precipitate obtained was filtered under suction, washed with excess of acetone and dried overnight in an oven at 60°C. The synthesized polymer was labelled as PANI 1.

In a typical experiment 0.29 mol of chloroform was taken in a 100 mL round bottom flask. Then 1.25×10^{-3} mol benzoyl peroxide was added to it under mechanical stirring. To the above solution 0.13 mol of 2-butanol, 3.73×10^{-3} mol DBSA, and 9.66×10^{-4} mol of aniline were added. To the resulting mixture 0.28 mol of de-ionized water (Millipore) was added to form a milky white emulsion. The mixture turned green in 5 hours and polymerization reaction was allowed to proceed for 24 hours. In the end, the organic phase containing Polyaniline salt was separated and washed four times with 50 mL of acetone. After thorough washing, a dark green highly concentrated polyaniline salt was obtained. Then it was dried at room temperature for 24 hours in a petri dish. On addition of small amount of acetone to the petri dish the film broke into flakes. Then PANI salt was separated by filtration and dried in a desiccator. The synthesized polymer was labelled as PANI 2.

2.3 Characterizations

Morphological features and size of particles were analyzed with a scanning electron microscope (JSM-5910, JEOL). In every case, the sample was made by mounting a little amount of the given powder on an

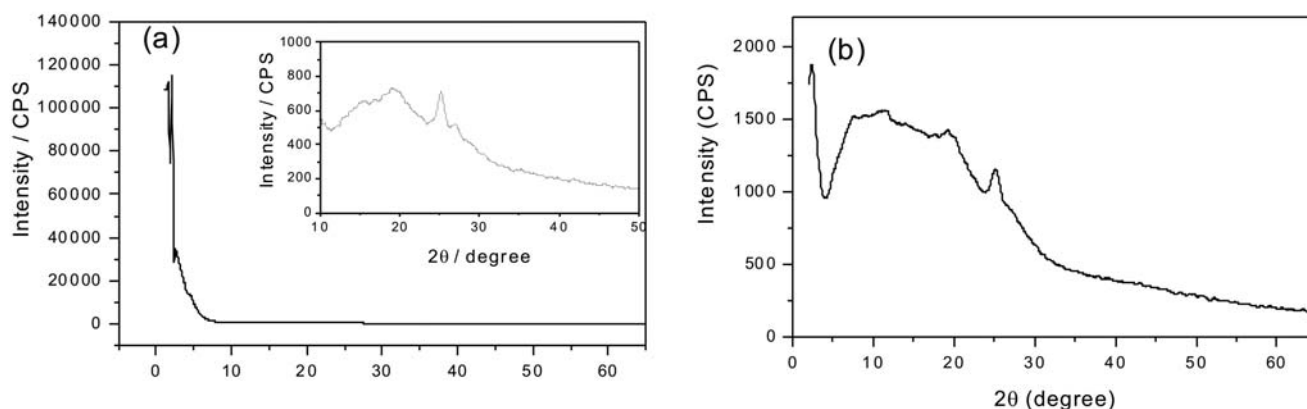


Figure-2(a): X-ray Diffraction Pattern of PANI 1. The Insets of the Figure Represent the Enlarged Parts of the XRD Patterns between $2\theta = 10-50^\circ$, (b) X-ray Diffraction Pattern of PANI 2.

aluminum stub using double-coated conducting carbon adhesive tape. Samples were coated with gold by using auto fine coater [JEOL, JFC-1600] for the duration of 30 seconds. The working distance was kept 10 mm from the sample to electron gun tip and the accelerating voltage was adjusted to 15 kV.

The X-ray diffraction patterns of PANI samples were recorded in the range 1° to 70° using a Rigaku X-ray diffractometer (Japan) at room temperature, having copper $K\alpha$ radiation with wavelength of 1.5405 \AA and a continuous scan speed of $0.05^\circ/\text{s}$.

UV-Vis spectrum was collected using Perkin Elmer 650 (UK) Spectrophotometer. A quartz cell of 1 cm path length was used for recording spectra of different samples of PANI dissolved in chloroform.

3. RESULTS AND DISCUSSION

3.1 SEM Images

The morphologies of soluble PANI samples were analyzed by SEM and their photographs are shown in Figure-1. It demonstrates that all PANI samples are highly aggregated and irregularly shaped particles, with average size $2.3 \mu\text{m}$ and $2.5 \mu\text{m}$ for PANI 1 and PANI 2, respectively. Large particles might contain several crystallites. In order to understand whether the particle is a single crystal or a polycrystalline, Scherrer relation was applied to XRD patterns (discussed in section 3.2) to predict the size of the crystallites (Abdullah and Khairurrijal, 2008).

3.2 X-ray Diffractometry

XRD is a useful technique for the estimation of crystallinity, crystallite size and interchain separation.

Figure-2(a) and Figure-2(b) represent the XRD patterns of the PANI 1 and PANI 2, respectively. In both samples, the peak located around $2\theta = 2.5$ indicates intermolecular spacing of layered structure of the polyaniline chain which is separated by long alkyl tails of DBSA (Han, et al., 2002). This is the characteristic peak of PANI salts (emeraldine salt) indicating that surfactant groups are properly inserted into the PANI chain (Palaniappan and Devi, 2006). In case of PANI 1, the overall sharpness of the characteristic peaks indicates the good crystalline nature of the polymer. The peak centered at $2\theta = 25^\circ$ (shown in the inset of the Figure-2(a)) is assigned to the van der Waals distance between stacks of phenylene rings (Saravanan, Palaniappan and Chandezon, 2008).

Since the polymer crystals are imperfect. Therefore, the descriptive term used for these is "crystallite" and hence the degree of order in polymers is determined from the measurement of the crystallite size. The degree of order of a polymer increases with increase in the crystallite size (Hussain and Mohammad, 2004). The crystallite size was determined from Scherrer relation (Abdullah and Khairurrijal, 2008).

$$t = k\lambda / B \cos \theta \quad (1)$$

where 't' is the crystallite size, 'k' is the shape factor for the average crystallite, 'B' is the full width at half maxima of the crystalline peak in radians.

For calculation of crystallite size, main crystalline peak at around $2\theta = 25^\circ$ was selected for both samples. Crystallites size of the PANI salts calculated from equations 1 are given in Table-1. Based on SEM pictures (Figure-1), the particle sizes of the polymers are several times greater than the crystallite size which confirmed that the polymers are polycrystalline

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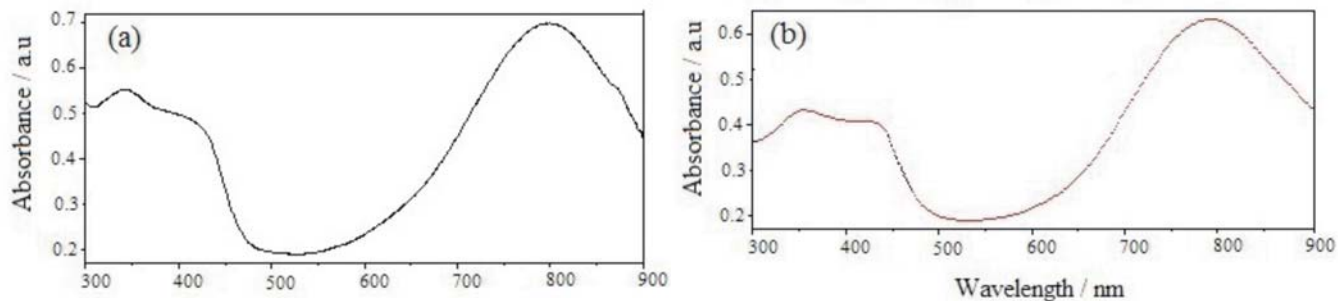


Figure-3: UV-Vis Spectra of (a) PANI 1 and (b) PANI 2

Table-1: Crystallite Size (t), Interchain Separation (R) and Energy Band Gap of the PANI Salts

Name of sample	t (nm)	R (nm)	Band gap (ev)
PANI 1	22	0.21	3.59
PANI 2	21	0.22	3.63

(Abdullah and Khairurrijal, 2008). In the present study, it was found that the crystallite size of PANI 1 is greater than in PANI 2, which represents that the former polymer has more order structure than the latter one (Hussain and Mohammad, 2004).

Furthermore, by using XRD data, the interchain separation 'R' of the synthesized PANI salts was determined from the following relation (Bhadra and Khastgir, 2007):

$$R = 5\lambda / 8 \sin\theta \quad (2)$$

The values of the interchain separation (R) are given in Table-1 which demonstrates that the 'R' value of PANI 1 is less than that of PANI-2. It seems that PANI 2 is highly doped as compared to PANI 1, as a result the dopant molecules exert more force against ordering and closing of the polymer chains leading to a higher interchain separation that affects electrical properties of the polymer (Bhadra, et al., 2007). The increased crystallite size and small interchain separation of PANI 1 demonstrates that method 1 is more promising for improvement of crystalline nature of PANI.

3.3 Band Gap / Energy Gap

Figure-3(a) shows three peaks at $\lambda = 345, 421, 798$ nm for PANI 1 and at $\lambda = 345, 542, 799$ nm for PANI 2. The first absorption band arises from $\pi - \pi^*$ electron transition within benzoid (B) ring, the second and third absorption peaks are attributed to the polaron transition (quinoid, Q, ring) and bipolaron transition (Exiton), respectively.

The first absorption band in the UV-Vis spectra corresponding to $\pi - \pi^*$ transition. The π orbital form the valance band whereas conduction band is produced by π^* orbital. An energy difference between these two bands is known as band gap or energy gap. The knowledge of the positions of highest occupied molecular orbital (HOMO, π^*) and the lowest unoccupied molecular orbital (LUMO, π) and the energy gap between them is crucial and play an important role in determining their electrical conductivity and band structure (Senevirathne, Nanayakkara and Senadeera, 2007). The band gap for $\pi - \pi^*$ electron transition of the PANI salts was calculated by using the following equation (3) (Sinha, Bhadra and Khastgir, 2009).

$$\Delta E = hc / \lambda_{\max} \quad (3)$$

Where,

h = Plank's constant

c = velocity of light

λ_{\max} = wave length of first absorption band

The values are tabulated (Table-1) which shows that the band gap of PANI 1 (synthesized by Method 1) is smaller than PANI 2 (synthesized by Method 2). This would make the transition easier and as a result the conductivities have been increased which can be readily used in optoelectronic devices (Shao, et al., 2010).

4. CONCLUSIONS

In this study, the influence of the polymerization

pathways on the crystalline nature of the polyaniline (PANI) salts has been investigated. PANI salts were prepared by emulsion and inverse emulsion polymerization methods (Bilal, et al, 2012; Bilal, et al, 2014). Morphology and particle size of the synthesized PANI salts were characterized by scanning electron microscopy (SEM). The crystallite size and interchain separation were determined from X-ray analysis. The energy band gaps of the prepared PANI salts were calculated from ultra-violet visible spectroscopy and were correlated with the X-ray analysis. The results showed that the aforementioned polymerization methods controlled the crystalline behavior of the synthesized PANI, which in turn affect its electrical properties. The whole results revealed that emulsion polymerization route is quite effective for synthesis of PANI with good crystalline etiquette and is useful for electronic applications.

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