

Synthesis and characterization of nanofibers of conducting polyaniline and its substitute derivatives

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ABSTRACT

Intrinsically conducting polymers have been extensively studied due to their fascinating electronic properties and potential applications. One dimensional conducting polymer nanostructures have been the focus of quite extensive studies worldwide due to their high aspect ratio, high porosity apart from high surface area to volume ratio. In this paper, we report the synthesis of nanofibers of polyaniline and its substitute derivatives and their comparative study in respect of electrical conductivity. Nanofibers of doped polyaniline (PANI), poly(o-methoxyaniline) (POMXA) and poly(o-methylaniline) (POMLA) were synthesized without need of any templates by interfacial polymerization. SEM, TEM, FTIR, UV-VIS and XRD were used to characterize the synthesized conducting polymeric materials. The average diameters of the synthesized nanofibers of conducting polymeric materials were in the range of 70-120 nm. The electrical conductivity was found to be in the range of 0.3 - 1.0 S/cm following the order as POMXA < POMLA < PANI which was found to be closely related to the size dependent electrical properties of the nanofibers. Optical band gap of these polymers was evaluated from UV-VIS absorption studies. Direct and indirect transition energy band gaps were determined from Tauc's plots. Interfacial polymerization was shown to be readily scalable to produce bulk quantities of nanofibers of substitute derivative of polyaniline. Copyright © 2014 VBRI press.

Keywords: Interfacial polymerization; conducting polymers nanofibers; Tauc's plot; polyaniline substitute derivatives.



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interest includes the synthesis of nanofibers of conducting polymers by various techniques and their characterizations for gas sensing applications.

Introduction

Conducting polymers have been widely investigated because of their fascinating electrical and optical properties derived from their conjugated π -electron system. They are attractive class of materials similar to those metals while retaining flexibility and processibility of conventional polymers [1-3]. One can have remarkable scope for tuning of their electrical conductivity between semiconductor and metallic regime, when they are appropriately doped [4]. Among the various conducting polymers synthesized, polyaniline (PANI) occupies a prime position for extensive applications in making devices like polymer light emitting diodes, photovoltaic cells, sensors, batteries and

super capacitors [5]. Nanostructure conducting polymer polyaniline (PANI) has been widely studied for potential applications due to its high surface area, controllable electrical conductivity, color responses with acid/base (doped/dedoped) conditions, good environmental stability and ease of preparation [6]. In recent years, one dimensional (1D) polyaniline nanostructures such as nanorods, nanowires, nanofibers, nanotubes and nanobelts have received intensive interest because they possess the advantages of both low-dimensional system and organic conductors and have potential applications. When PANI and its substitute derivatives are synthesized in the form of one dimensional nanostructure, it may open new avenues for the researchers in creating polymeric nanoscale devices. Several novel methodologies have been developed for the preparation of one dimensional PANI nanostructure [7, 8]. Recently, various authors fabricated nanofibers for novel applications such as gas sensing, super capacitor, filter media, fiber-reinforced plastics, biomedical applications etc. Although some of these applications are in the development stage, a few have been commercially exploited, and fibers loaded with catalysts and chemical indicators [9-12]. The preparation of PANI nanofibers received great development owing to the excellent work by Huang and Kaner et al [13-16]. There are Different methods used to fabricate PANI nanofibers include hard templates, soft templates [17], seeding, interfacial polymerization, rapidly mixing [18] and electrospinning [14].

The chemistry of polyaniline is generally more complex with respect to other conducting polymers, due to their dependence on both the pH value and the oxidation states, described by three different forms known as leucoemeraldine base (fully reduced form), emeraldine base (EB) (50% oxidized form), and pernigraniline base (fully oxidized form). The most important is the EB form and its protonation by means of H^+ ions, generated from protic acids, gives the emeraldine salt form, responsible of the strong increment of the conducting properties. This process is reversible and it is possible for the presence of imine group basic sites located along the conducting polymer backbone. The doping process of polyaniline is always associated to conformational modifications of the polymer chains, due to the local distortions created by the addition of H^+ ions to the basic sites. These distortions are even able to affect the morphology of the deposited films by varying their organization and play an important role in the electrical properties of the conducting polymer. The kind of substituents along the aromatic rings of the polymer backbone seems to affect the molecular rearrangement occurring during the doping process and in some cases; the sterical hindrance generated by “too close” substituents to the aromatic ring is responsible of the spontaneous undoping process [19].

Taking into account these considerations, the aim of the present study was to investigate the possible variations on polyaniline derivatives physical chemistry properties by performing standardized oxidative polymerizations on monomers with different kind of substituents along the aromatic rings. With this background, we report here the synthesis of nanofibers of polyaniline (PANI) and its substitute derivatives such as poly-orthomethoxyaniline (POMXA) and poly-orthomethylaniline (POMLA) by the simple interfacial polymerization method. To the best of our knowledge, direct and indirect band gap of nanofibers of substitute derivatives of polyaniline have not been investigated so far, therefore to find their applicability in optoelectronic devices, the optical properties of PANI, POMXA and POMLA have been presented and compared along with their thermal activation energy and structural characterizations.

Experimental

Materials

The chemicals including aniline (99.5%), o-methylaniline (99.5%) and o-methoxyaniline (99.5%) were purchased from Sigma-Aldrich and purified through distillation under reduced pressure and stored refrigerated before use. Other chemicals such as hydrochloric acid (99.5%), toluene ($C_6H_5CH_3$) (99.5%) and ammonium persulfate (APS) (99.5%) were also purchased from Sigma-Aldrich and used as received. De-ionized water was used for the preparation and dilution of solutions. **Fig. 1** shows the chemical structure of monomers used in the syntheses.

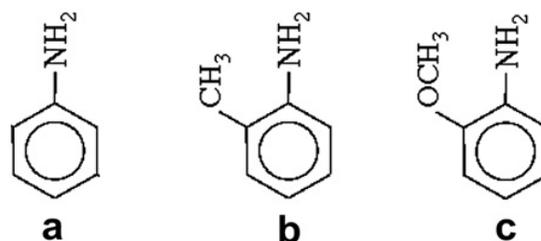


Fig. 1. Chemical structure of monomer used for synthesis of polymer nanofibers, (a) aniline, (b) ortho-methylaniline and (c) ortho-methoxyaniline.

Characterization methods

X-ray diffraction (XRD) was carried on Philips PW1710 automatic X-ray diffractometer with Cu-K α radiation ($\lambda=1.5404\text{\AA}$), with a scanning speed of $10^\circ \text{ min}^{-1}$. FTIR spectra were performed on Shimadzu FTIR-8101A Spectrophotometer in the wavelength range of 400–4000 cm^{-1} . Transmission electron microscopy images were

obtained using PHILIPS-CM200 TEM with resolution 2.4Å. The optical absorption spectra were carried out using UV-1800 double beam UV-VIS spectrophotometer. The electrical conductivity of the compressed pellets of polymer nanofibers was determined by four probe resistivity technique. The pellets were prepared with the help of hydraulic press (Kimaya Engineers, India) by applying a pressure of 5000 kg/cm².

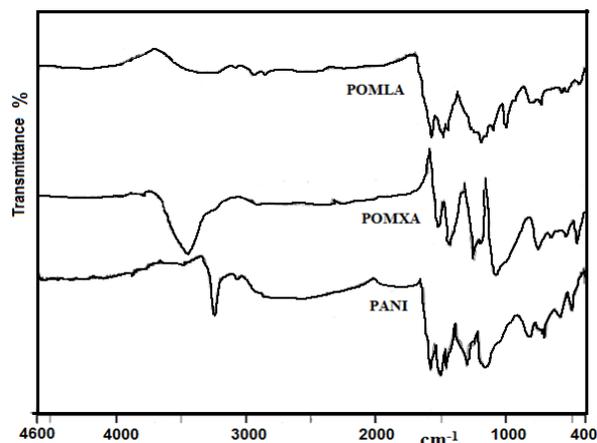


Fig. 2. FTIR spectra of PANI, POMXA and POMLA nanofibers.

Synthesis of PANI nanofibers by interfacial polymerization

The reaction was placed in a heterogeneous biphasic system, where the polymerization occurs primarily at the interface. Since the as-made PANI product was synthesized in its hydrophilic emeraldine salt form, it diffuses away from the reactive interface into the water layer. This made more reaction sites available at the interface and avoids further overgrowth. In a typical process, 1.86 g (3.2 mmol) of aniline was dissolved in 100 ml of organic solvent as toluene in a beaker so as to form organic phase and 4.56 g (0.8 mmol) of Ammonium per sulfate (APS) in 100 ml of hydrochloric acid (1.0 M) in another beaker so as to form aqueous phase. Then the organic phase was carefully added along the side of beaker to the aqueous phase to produce a clear interface of aqueous–organic solutions. As the reaction proceeds, the color of the organic phase becomes darker and finally stops changing, indicating reaction completion. An overnight reaction time is generally sufficient. Upon completion we had vials with toluene organic solvent of polyaniline nanofibers. The synthesis of polyaniline at low temperature (avoid 0° C) favors the formation of longer chains length (and hence, high molecular weight), under this conditions a less amount of structural defect in the polymer can be expected. The dark green precipitate resulting from the polymerization reaction had washed repeatedly with dilute HCl solution and de-ionized water

until the filtrate became transparent. This precipitate was then dried in vacuum oven at 60° C for 24 hours. Solid sample was powdered in a mortar and finally compressed to form pellets. The same polymerization procedures were applied to synthesis of POMXA and POMLA.

Results and discussion

The FTIR spectra of the different samples are shown in Fig. 2. The presence of the characteristic peaks of polymers doped with HCl indicates the successful polymerization of monomers. The peaks at 1560-1610 and 1486-1491 cm⁻¹ are assigned to C=C stretching of the quinoid and benzenoid rings, respectively, and the peak at ca. 1140-1180 cm⁻¹ represents the C-H aromatic in-plane bending. The band falling in the range 800-860 cm⁻¹ is identified with the out-of-plane bending of C-H bond in the 1, 4-disubstituted ring, which has been used as a key to identify this type of substituted benzene. The peak at about 1140-1180 cm⁻¹ is often related to the doped structure; therefore, the results signify that the PANI, POMXA and POMLA nanofibers obtained. [20, 21].

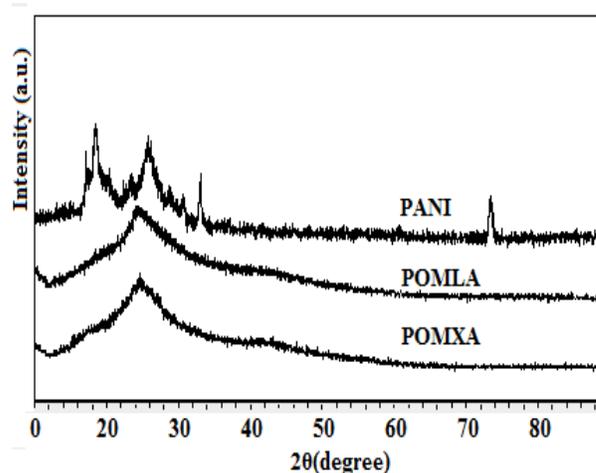


Fig. 3. XRD pattern of of PANI, POMXA and POMLA nanofibers.

The XRD pattern of the polymer generally differs because of uncertainty in the polymeric chains. It depends on the synthetic routes, solvent and ionized state [22]. Fig. 3 shows the XRD pattern of PANI, POMXA and POMLA nanofibers synthesized by interfacial polymerization. The pattern shows sharp and well defined peaks, which indicate semi-crystalline nature of the PANI nanofibers. The diffraction pattern for PANI nanofibers shows the peaks at $2\theta = 19.05^\circ$, 17.86° , 32.26° and 25.75° indicating more crystalline morphology. Whereas POMXA and POMLA for which the single peaks observed at $2\theta = 24.49^\circ$ and 24.27° respectively confirm amorphous morphology. The plains of benzenoid and quinoid rings of PANI chain are responsible for crystalline structure [16]. The average diameter of the

synthesized PANI nanofibers was found to be 60 nm 112 nm and 130 nm for PANI, POMXA and POMLA respectively determined by using Scherer formula [20], quite consistent with TEM results of PANI, POMXA and POMLA.

Fig. 4(A) and (B) show the SEM and TEM images of PANI, POMXA and POMLA nanofibers synthesized by interfacial polymerization respectively. The uniform nanofibrous morphology with the length in few microns and average diameter was found to be 70 nm, 130 nm and 220 nm of PANI, POMLA and POMXA nanofibers respectively.

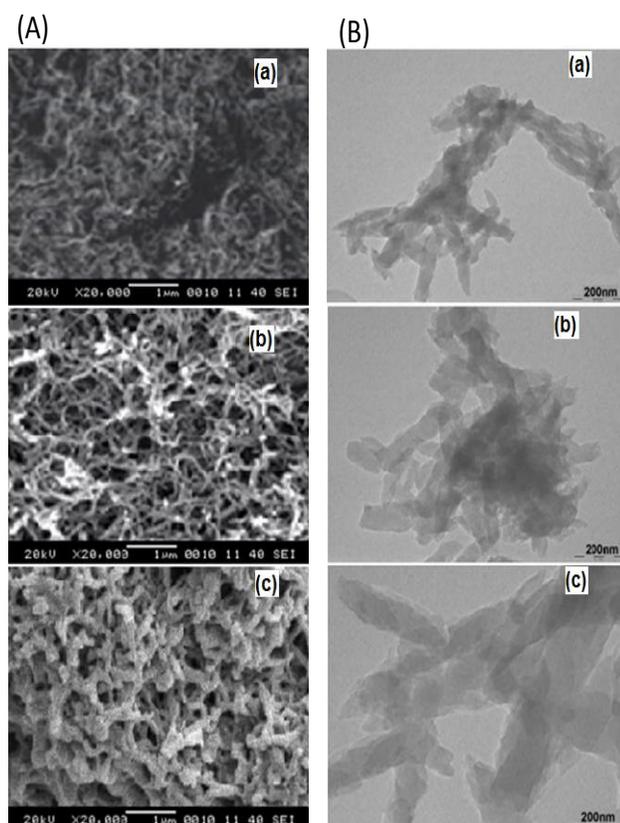


Fig. 4. (A) SEM images of (a) PANI, (b) POMXA and (c) POMLA nanofibers. (B) TEM images of (a) PANI, (b) POMXA and (c) POMLA nanofibers.

Fig. 5 demonstrates UV-visible absorption spectra of PANI, POMXA and POMLA nanofibers. The absorption peak at 310 nm is attributed to the transition of electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) which is related to π - π^* electronic transition [22]. There are two visible region bands one at around 430 nm and the other centered on 800 nm. The peak at a wavelength of around 430 nm is attributed to the transitions between π -polaron band and the second one at 800 nm is due to the polaron- π^* band transitions for PANI [23]. POMXA and POMLA

also showed three bands, for which π -polaron band shifted to 540-550 nm. The absorption bands that have been obtained from the UV-Visible spectra are in good agreement with the results of Yang et al [22] and Jing et al [24] reported in the literature.

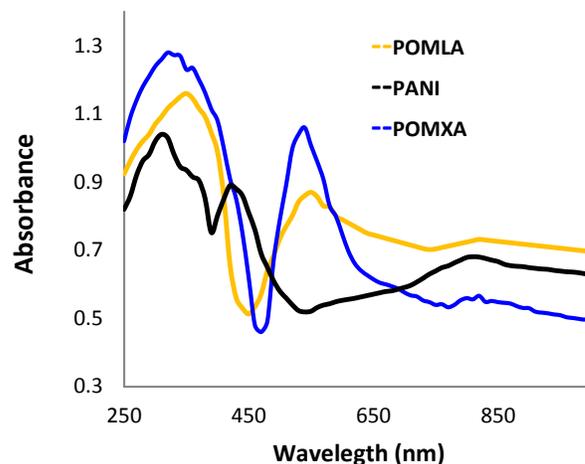


Fig. 5. UV-Vis spectra of PANI, POMXA and POMLA nanofibers.

The valance band or highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) bands are separated by an energy gap is called band gap which is of fundamental important, because the energy gap determines the electrical conductivity and optical absorption character of the polyaniline. The photon absorption in many amorphous materials is found to obey the Tauc relation [22], which is of the form-

$$\alpha h\nu = B(h\nu - E_g)^n$$

where, α is the absorption coefficient, $h\nu$ is the photon energy, B is the band gap tailing parameter, E_g is a characteristic energy which is termed as optical band gap and n is the transition probability index, which has discrete values $n = 1/2, 3/2, 2$ and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden electronic transitions, respectively [23]. The absorption coefficient (α), at the corresponding wavelengths is calculated using the Beer-Lambert's relation,

$$\alpha = \frac{2.303A}{l}$$

where, l is the path length and A is the absorbance [25].

The index $n = 1/2$ represents the direct allowed transition energy gap. To determine the direct transition energy gaps, plot of $(\alpha h\nu)^2$ versus $h\nu$ is linear function existence of direct allowed band transition in polymer samples. Extrapolating of linear dependence of the relation to abscissa yields the corresponding direct allowed band gap. The value of the optical direct

transition energies are 2.54 eV, 2.61 eV and 2.57 eV for PANI, POMXA and POMLA respectively obtained from Fig. 6 (a, b and c). In order to determine the indirect transition energy gap, plots of $(\alpha h\nu)^{1/2}$ as a function of photon energy versus $h\nu$ was plotted and shown in Fig. 6 (d, e and f) for PANI, POMXA and POMLA respectively. The linear portion of the plots at the absorption edge confirms that the material has an indirect optical band gap. The intercept of these curves on the photon energy axis gives the indirect transition energy gap. The value of the optical indirect transition energies was found to be 1.65 eV, 2.45 eV and 2.35 eV for PANI, POMXA and POMLA respectively.

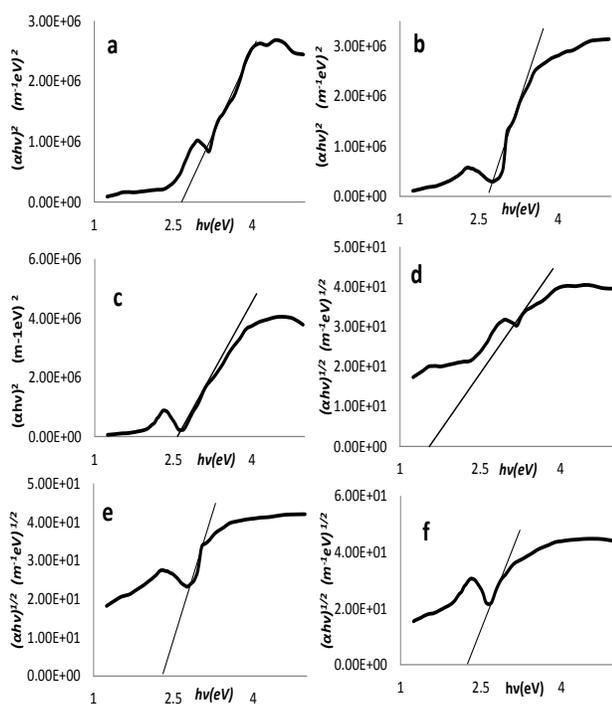


Fig. 6. Direct band gap for PANI (a), POMXA (b), POMLA (c) and indirect band gap for PANI (d), POMXA (e), POMLA (f), obtained from UV-vis spectra by plotting $(\alpha h\nu)^2$ vs $h\nu$ and $(\alpha h\nu)^{1/2}$ vs $h\nu$ respectively.

The analysis of the UV-vis spectra showed a very interesting behaviour on doping with HCl protic acid. The formation of the polaronic state and the presence of the relative bands due to the polaron- π^* and π -polaron transitions were obtained for materials based on poly(o-toluidine) and poly(o-anisidine). The presence of the CH_3^- group along the aromatic rings of the polymer chains seemed to have stronger effect than CH_3O^- group on the doped macromolecules. Since the doping process takes place on the imine groups basic sites nitrogen atoms, characterized by a planar configuration (sp^2 hybridization), and the protonation issues tetrahedral configuration (sp^3 hybridization), this change in the atoms spatial disposition was likely to be mostly affected

by the sterical hindrance for non-electron donor substituents. Moreover, the doping process took place on solid-state films, with consequent diminished degrees of freedom of the polymer chains. Taking into account the major hindrance of CH_3^- substituents than CH_3O^- ones and the strong impediment generated to the modification of the torsion angles on doping.

The measurement of dc conductivity was accomplished through use of the four probe technique. Fig. 7 shows thermal dependence dc electrical conductivity (σ) of PANI, POMXA and POMLA nanofiber respectively. The values of electrical conductivity at room temperature of PANI, POMXA and POMLA nanofibers was found to be 0.99, 0.33 and 0.65 (S/cm) respectively, which are higher than those of the synthesized by conventional polymerization process [26].

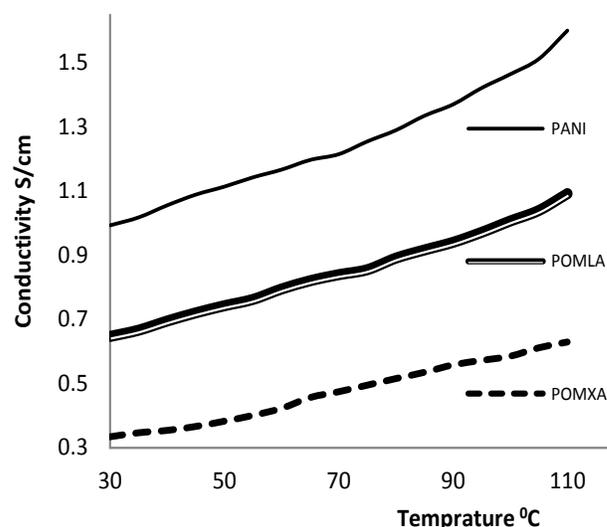


Fig. 7. Thermal dependence electrical conductivity of PANI, POMLA and POMXA nanofibers.

We observed that the temperature dependence for each polymer behaves in the usual activated manner indicating semiconducting property. The increase in conductivity with increase in temperature is the characteristic of “thermal activated behavior” [27]. The increase in conductivity could be due to increase of efficiency of charge transfer between the polymer chains and the dopant with increase in temperature [28]. It is also possible that the thermal curing affects the chain alignment of the polymer, which leads to the increase of conjugation length and brings about the increase of conductivity. There also had to be molecular rearrangement on heating, which made the molecular conformation favorable for electron delocalization [29].

The electrical conductivity of nanofibers was found to follow the order as $\text{POMXA} < \text{POMLA} < \text{PANI}$ indicating the size dependant properties. The electrical conductivity in temperature range 300 to 400 K was found to follow the Arrhenius model [30]. Plots of $\log(\sigma)$

vs $1/T$, gives activation energy for PANI, POMLA and POMXA which was found to be 0.099, 0.124 and 0.167 eV, respectively. The values did not differ significantly from the activation energy of bulk form of PANI reported [31, 32].

Conclusion

Nanofibers of polyaniline and its substitute derivatives PANI, POMLA and POMXA with an average diameter 70-220nm have been successfully synthesized by chemical oxidation using interfacial polymerization method. The XRD study reveals semi-crystalline nature of PANI while POMLA and POMXA shows amorphous nature. Direct and indirect band gap energies of PANI, POMLA and POMXA nanofibers was determined using Tauc plot from UV-VIS spectra. The electrical conductivity was found to be in the range of 0.3 - 1.0 S/cm following the order of POMXA < POMLA < PANI which was closely related to size dependent electrical properties of the nanofibers.

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