

Morphological controlled synthesis of micro-/nano-polyaniline

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Abstract A novel, highly efficient and economical route is developed for the synthesis of polyaniline micro-/nanostructure. Materials were characterized by a complementary combination of X-ray diffraction, Scanning electron microscopy, Fourier-transform infrared, and UV-visible spectrophotometer. Morphology of polyaniline can be tailored by varying the structure-directing agents and pH of the synthesis condition. Ethylene glycol and polyethylene glycol formed a three-dimensional flower-like structure whereas block-copolymer (ethylene oxide and propylene oxide based copolymer EO₂₀PO₇₀EO₂₀) formed leaf-like structure when the synthesis was performed at pH 7. Using these structure-directing agents, nanorod and granular morphologies were obtained when the samples were synthesized at pH 3 and 1, respectively.

Keywords Morphological controlled synthesis · Structure directing agents · Ethylene glycol · Polyaniline

Introduction

Conducting polymers have been observed as a frontier area of research and prospective materials for technological applications since last decade [1, 2]. The importance of conducting polymer was celebrated in the form of Nobel Prize in Chemistry to MacDiarmid, Heeger and Shirakawa. Conducting polymers have received great attention as functional materials because of their high π -conjugated length, unique electrical properties that cover the whole

insulator–semiconductor–metal range, their reversible doping/de-doping process, and controllable chemical and electrochemical as well as physical properties [3–9]. These unique properties not only suggest promising applications of conducting polymers in technology, but also hold an important position in basic materials science research. Among the conducting polymers, polyaniline (PANI) has found significant attention in recent years. PANI exhibits many potential applications such as rechargeable batteries, molecular sensors, gas separation devices, light-emitting diodes, electrorheological material etc. [10–15]. PANI is thermally and environmentally stable materials, which makes it relatively easy to handle and when doped with protonic acid, metallic conduction can be achieved. PANI nanostructures, such as nanofibers/wires/rods/tubes can be made by introducing structure-directing agents into chemical polymerization. Both, soft templates and hard templates can be used to fabricate PANI nanostructures [16–23]. Nanostructures of PANI are of great current interest because they combine the properties of low-dimensional organic conductors with high surface area materials. This situation can lead to enhanced properties in applications such as chemical sensors.

Morphology is a key factor in controlling the physico-chemical properties of materials [24]. Alan MacDiarmid (Nobel Laureate), one of the pioneers in PANI research stated that “there are as many different types of polyaniline (s) as there are people who make it [25].” Among the various morphologies of PANI, 1D nanostructures have attracted increasing interest due to the advantages of low-dimensional systems. Usually, a template is used to obtain PANI with different morphology. Both hard templates (nanochannels of zeolite [26] or nanoporous membranes [27]) and soft templates (micelles [28–31], emulsions [32] or liquid crystals [33]), have been used. Synthesis of PANI

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with unique morphologies have also been reported using ethylene glycol, polyethylene glycol and block copolymers, in which these compounds have been used either as a solvent or in large excess [34–36]. However, it may be noted that PANI nanofibers and nanotubes can also be obtained in aqueous solution without any template, which provides facile and environmentally friendly ways to synthesize 1D PANI nanostructures [37, 38]. The synthesis of PANI nanostructures including nanosheets, nanofibers, and nanoparticles at organic/aqueous interfaces was carried out by controlling the diffusion rate and the polymerization induction time of aniline [39]. However, the use of an organic phase limits the large-scale synthesis of PANI materials. Therefore, the synthesis of multi-dimensional PANI nanostructures is very challenging to material scientists and chemists.

Though various synthetic pathways are reported for the synthesis of PANI, but it is still highly desirable to develop novel and smart synthetic procedures for building PANI materials with different morphology. In this study, a direct one-step synthetic protocol for PANI micro-/nano-structured materials by using soft-templating (ethylene glycol, polyethylene glycol and block copolymers such as pluronic 123) method has been reported. Due to its simplicity, high efficiency, low cost synthesis reported here proves to be a promising protocol for micro-/nano-structured PANI materials.

Experimental

Materials

Aniline, ammonium peroxodisulphate (APS), HCl, ethylene glycol (EG), polyethylene glycol (PEG) were obtained from Spectrochem India Pvt. Ltd. $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$ ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, MW=5,800, designated Pluronic P-123) (hereafter represent as P123) was obtained from Aldrich.

Sample preparation

Except aniline, all reagents were used as received without any further purification. Aniline was distilled prior to use. In a typical synthesis, 20 mmol of aniline and 0.2 mmol of structure directing agents (SDA) were dispersed in 100 mL of deionized water (pH 7) with magnetic stirring at room temperature for 1 h and then with ultrasonication for another 0.5 h to obtain a uniform solution. After that, the mixture was maintained at 15 °C for 0.5 h before oxidative polymerization. Then the aqueous solution of APS (20 mmol APS and 100 mL of deionized water) was added to the above mixture in one portion. The resulting solution

was stirred for another 0.5 min to ensure complete mixing and then the reaction was allowed to proceed without agitation for 24 h at 15 °C. The products were washed with deionized water and acetone until the filtrate became colorless. Any short chain oligomers formed during the reaction was washed out during this process. Finally, the product was dried in vacuum at 60 °C for 24 h. In order to understand the effect of acid concentration, samples were also prepared at pH 3 and pH 1.

To confirm, whether the product is polyaniline or oligo-aniline, as-synthesized materials obtained under different conditions were washed with methanol. 500 mg of sample and 50 ml of methanol were taken in a 100 ml round bottom flask and stirred for 10 min. Organic layer was removed just by filtration. Solid material was dried in oven. Similar procedure was repeated three more times. Methanol portions were combined and evaporated to get dry aniline-oligomers. Weight of insoluble portion and dry aniline-oligomers were measured. Insoluble PANI materials and aniline-oligomers were subjected to X-ray diffraction (XRD) and Fourier-transform infrared (FT-IR) investigations. To confirm the morphology of the materials after washing with methanol, Scanning electron microscopy (SEM) images of insoluble PANI were taken. PANI samples (after washing with methanol) are not soluble in water. They are soluble in NMP (N-methyl-2-pyrrolidone), whereas partially soluble in DMSO (dimethyl sulfoxide) and DMF (N,N'-dimethylformamide).

Characterization

XRD patterns were recorded on a PANalytical X'PERT PRO (using Cu K α radiation, graphite monochromator). Diffractograms were recorded between 5° and 50° with a step of 0.2° (2 θ). SEM measurements were carried out on a JEOL JSM-6610LV, to investigate the morphology of samples. FT-IR was recorded on Bruker Tensor-27 spectrometer using ATR in the range of 600–4,000 cm^{-1} (spectral resolution=4 cm^{-1} ; number of scans=100). UV-visible spectra were recorded on Analytikjena Specord 250 PLUS spectrophotometer with the PANI dispersed in deionized water. UV-visible spectra were also recorded in NMP. Molecular weight of polymers was measured through gel permeation chromatography (Shimadzu GPC). Polymers were dissolved in NMP, and the carrier solvent was NMP containing 0.1% LiCl. Polystyrene standards were used as the reference.

Results and discussion

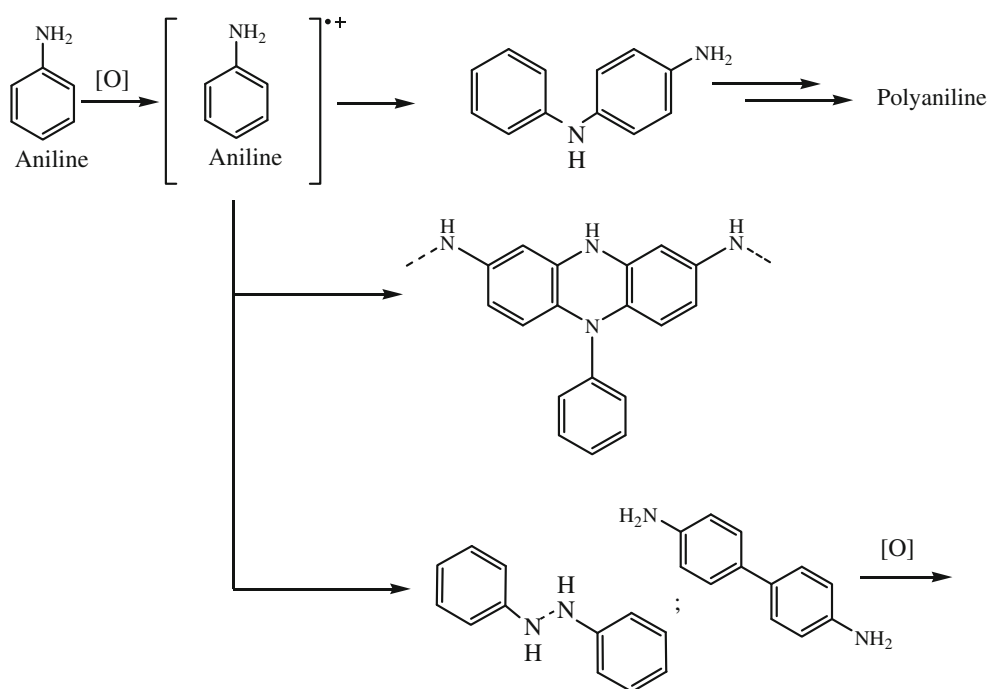
The present study describes the morphologically controlled synthesis of PANI materials by using non-ionic SDA at

different pH (1, 3, and 7). Nonionic surfactants possess the hydrophile–lipophile balance, which varies with the relative lengths of the hydrophilic and hydrophobic moieties in the surfactant [40]. In this study, the hydrophile–lipophile balance was systematically varied by varying the SDA. Following section describes the role of different SDA (EG, PEG and P123) on the morphological controlled synthesis of PANI materials at different pH conditions.

First, the role of EG was investigated in the synthesis of PANI. Different morphologies were obtained at different pH conditions. When no acid was used (pH 7) in the system, the reaction rate was slow. At the early stage of polymerization, aniline exists mainly as a neutral molecule, which can be easily oxidized to form ortho-coupled and para-coupled aniline molecules by the reduction of APS. The oxidation of ortho-coupled aniline molecules yielded oligomers that are composed of phenazine-like segments (Scheme 1) [41, 42], which was confirmed by FT-IR (discussed later in the following section). Furthermore, aniline can also be sulfonated easily at low acidity by the electrophilic attack of APS. The newly formed phenazine-like segments form intra-/inter-molecular hydrogen bonding with EG. These hydrogen bonded phenazine-ethylene glycol moiety self-assemble and form curved three-dimensional flower like network structure. The low-magnification SEM image in Fig. 1(a) reveals that flower-like polyaniline micro-/nano-structures were formed in the resulting product. The high-magnification SEM image (Fig. 1(b)) shows that the flower-like nanostructures are composed of polyaniline nanodisks. The thickness and

lateral dimensions of the polyaniline nanodisks are in the range of 8–10 nm and 0.5–1 μm , respectively. It seems that, in the first step, the aniline was exhausted by the formation of oligomers. Oligomer does not participate into the polymerization because the intermediate pernigraniline [43] like structure was not protonated at $\text{pH} > 3$ in the reaction medium. It may be noted that the protonation of pernigraniline like structure takes place only at $\text{pH} \leq 3$ [44]. There is only a single unpaired electron at the growing end of the PANI chain (Scheme 2). The unpaired electron at the end of the molecule becomes more and more delocalized along the chain as the degree of polymerization increases. That is why, it soon loses its reactivity, and the polymerization stops at the oligomer stage. When the pH of the reaction mixture gradually reached a value where pernigraniline started to be protonated (this increase in pH is due to the formation of H_2SO_4 by the reduction of APS), the concentration of electrons with unpaired spins on pernigraniline chains dramatically increased. The unpaired electrons at the end of oligomer molecules became re-localized and, because of that, were re-activated so that they could again participate in polymerization reactions. It seems that no aniline monomer available any more, the existing ethylene glycol hydrogen bonded aniline oligomers were likely to be coupled into polymer chains. Not well-aligned nanorod like structure was obtained when the synthesis was performed at pH 3 (Fig. 1(d)). Although, here also intra-/inter-molecular hydrogen bonding exists amongst pernigraniline like moiety and EG, but the pernigraniline keeps

Scheme 1 Different oligomers produced from the oxidation of aniline



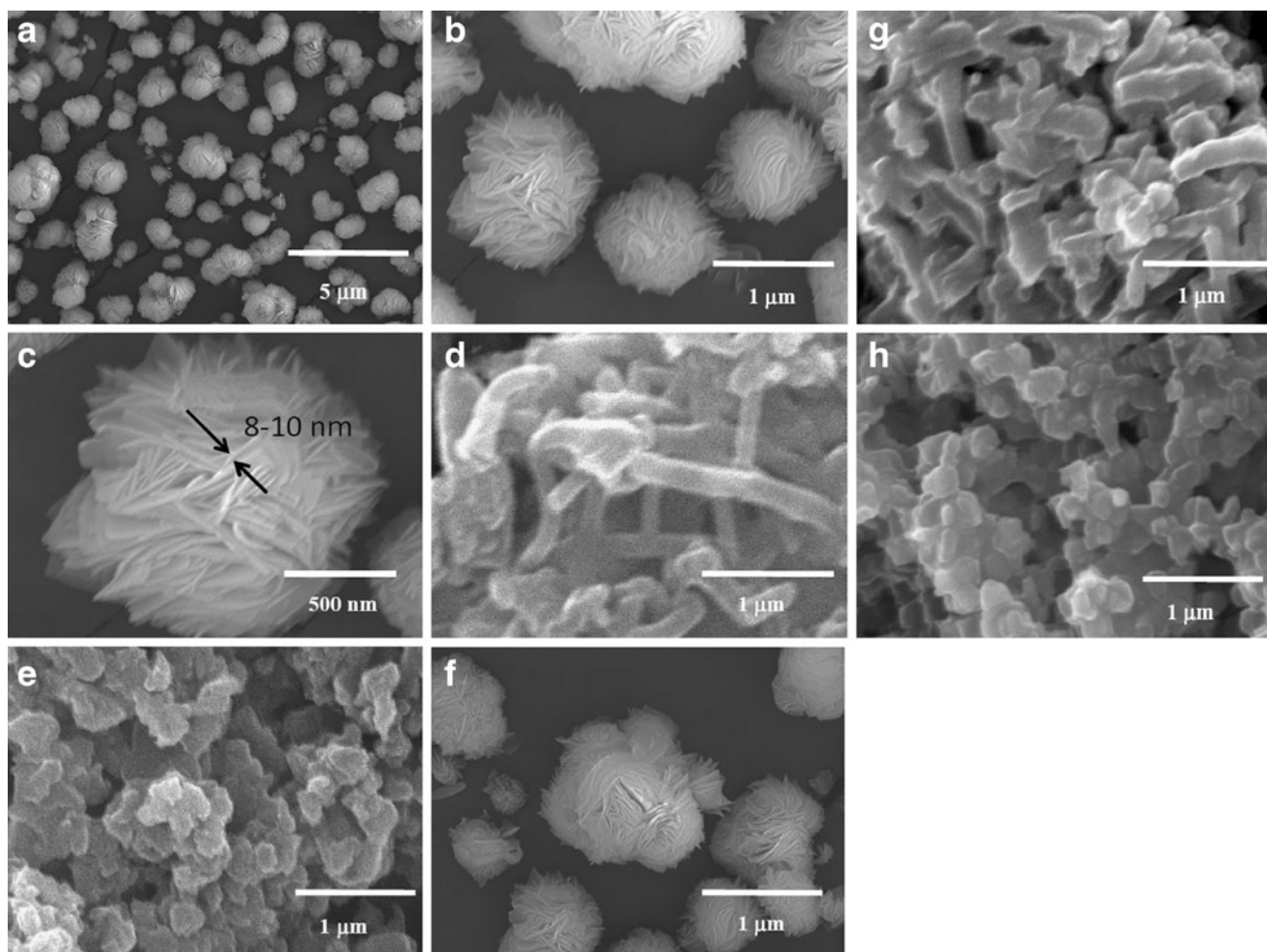
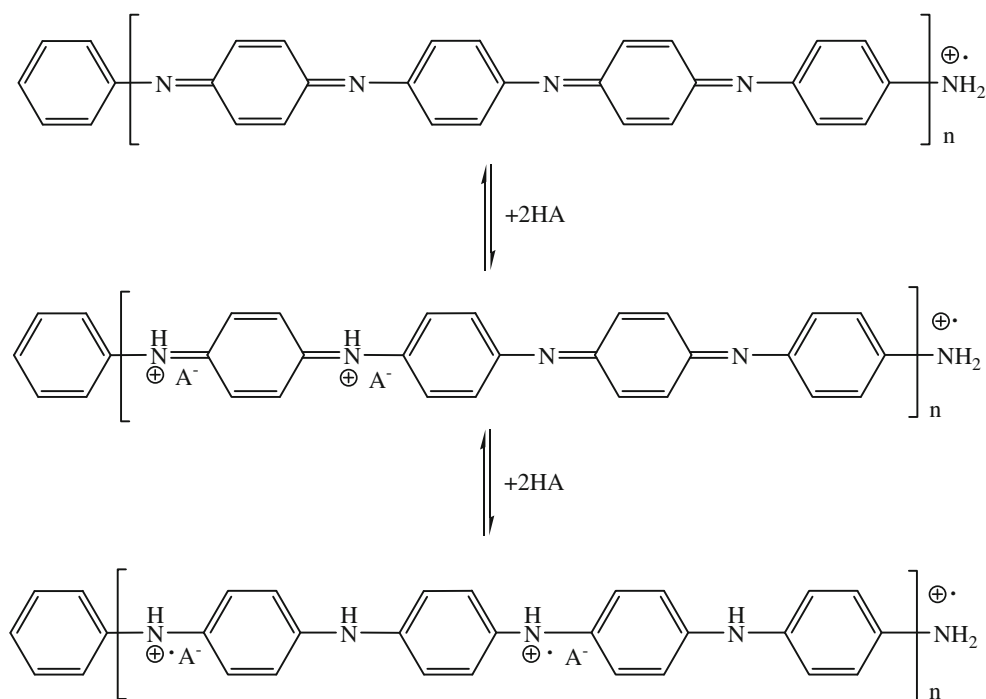


Fig. 1 SEM images of PANI synthesized using EG at **a-c** pH 7, **d** pH 3, **e** pH 1, **f** methanol washed PANI synthesized using EG at pH 7, **g** methanol washed PANI synthesized using EG at pH 3 and **h** methanol washed PANI synthesized using EG at pH 1

protonating from the beginning of the reaction (at the beginning of the reaction pH of the medium was 3). This protonation helps growing the chain in the elongated form, from the start of the reaction and produces a nanorod like structure. It may be noted that due to significant hydrogen bonding, the nanorods are not properly aligned but mixed with one another as shown in the SEM images. There seems to be a link among the course of polymerization and the supramolecular PANI morphology that was produced. Aniline oligomers produced in the early stages of the polymerization are hydrophobic. They may assemble to constitute a template-like structure that further predetermines the directional growth of PANI. Again, once they become protonated at low pH, their hydrophobicity is reduced and they become soluble in the reaction medium. This may result in a lower extent and altered procedure for oligomer aggregation and, consequently, in the change in the produced morphology. This concept may also explain why disordered nanorod like structures was obtained at

lower acidity (pH 3), and disordered granular ones at high acidity (pH 1) of the reaction medium (Fig. 1(e)) [45].

When the synthesis was carried out in the presence of PEG at pH 7, flower like structure was obtained. However, it may be noted that the flower like structure obtained using PEG was less crosslinked than it was obtained using EG (Fig. 2(a)). This may be due to the fact that highly ordered hydrogen bonded oligomeric network was formed in EG to yield highly cross-linked curved 3D network structure, whereas in PEG, the polymeric backbone provides only limited hydrogen bonding and thus forms less ordered oligomeric structure to produce flowerlike structure with less cross-linked network 3D structure. Sample prepared at pH 3 produces highly ordered nanorod like structure, which is better in quality and size when compared with the sample synthesized from EG (Fig. 2(b)). The diameter and length of the PANI nanorod are in the range of 120–150 nm and 1–4 μm, respectively. The long PEG chains help forming the nanorod structure following the same mechanism as it was

Scheme 2 Growth of PANI chains in the pernigraniline form

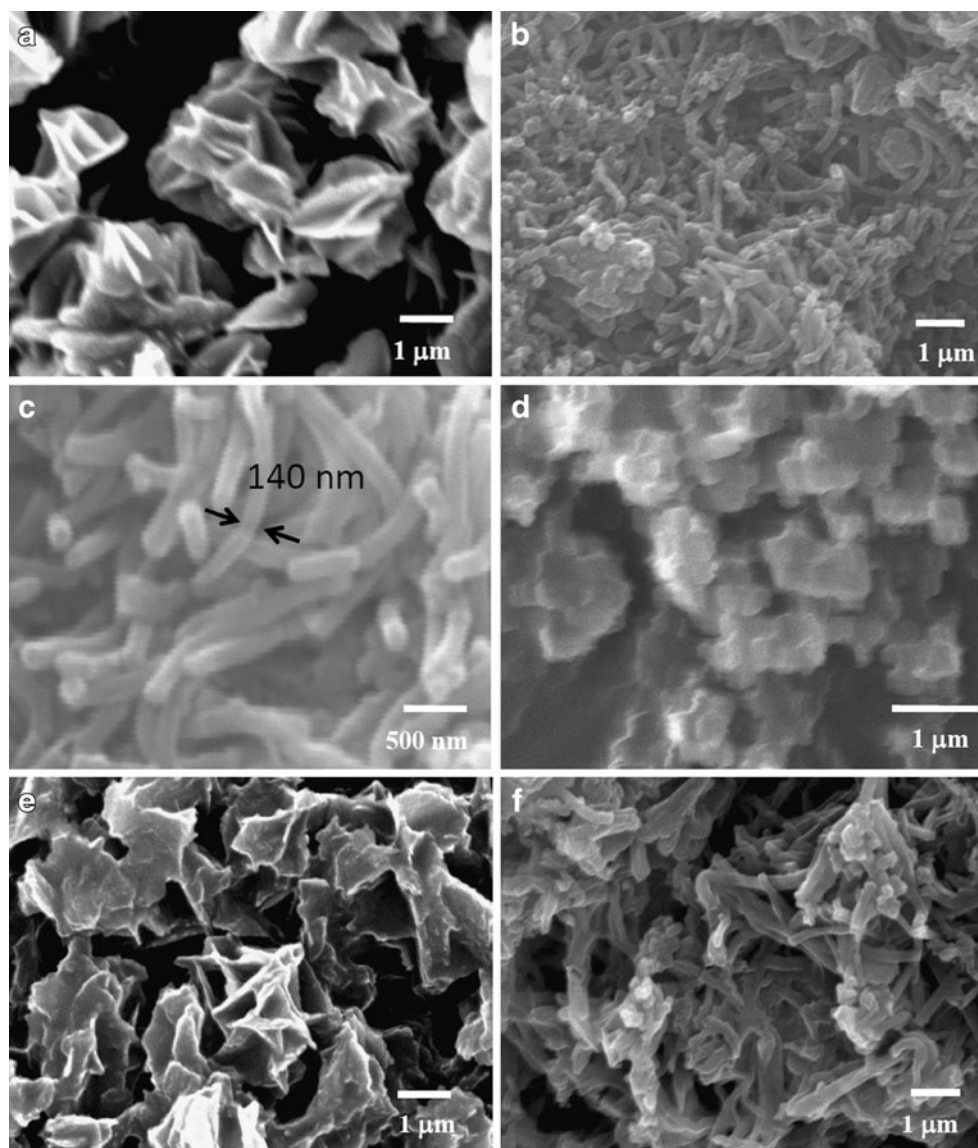
discussed for EG. Again in this case also at pH 1, disordered granular like structure was obtained (Fig. 2(d)) [45].

When the synthesis was carried out in the presence of P123 under neutral condition, a leaf like structure was obtained (Fig. 3(a)). P123 (an amphiphilic molecule) forms micelles in aqueous solution in which EO chains are located in the outer parts of the micelles due to their hydrophilic features. When aniline is added, the hydrogen bonds among anilines and the EO groups of P123 drive the aniline molecules to be adsorbed on the EO chains. As the polymerization proceeds, the long EO chains of P123 may act as “structural directors” for the chemical polymerization. Aniline has an amphiphilic structure of hydrophilic -NH_2 and hydrophobic $\text{-C}_6\text{H}_5$, therefore there would be droplets formed by aniline, and such droplets would be adsorbed on the EO chains of P123 owing to the hydrogen bonds among the aniline and EO groups [46]. After adding APS to the reaction system, the droplets will act as a template for the formation of nanorods because EO chains in PANI have a tendency to elongate in the direction of the EO chains, which results in the formation of PANI nanorod [28]. As the polymerization proceeds, the growth of building blocks of nanorods and the aggregation along with fusing process of micelles will lead to the formation of micrometer-sized leaf-like PANI (Fig. 3(a)). When the sample was prepared at pH 3, the resultant morphology of PANI is agglomerated nanorods (Fig. 3(b)). The diameter and length of the PANI nanorods are in the range of 150–170 nm and 3–5 μm , respectively. The results show that the addition of very minute amount of HCl as a doping acid

prevents the self-assembly behavior of nanorods. As commonly known, aniline may exist as aniline hydrochloride after the addition of HCl to the reaction system. Such a salt form of aniline is unfavorable for the formation of droplets that lead to the formation of nanorods. Using P123 at pH 1, disordered granular-like structure was obtained which is similar to the case of EG/PEG (Fig. 3(c)).

To further confirm the morphological changes and solid state behavior of the PANI nanomaterials, finely powdered samples were subjected to wide angle X-ray diffraction analysis. In the presence of SDA, the SDA-polymer undergoes various interactions, which tend to organize the polymer chains in three-dimensional highly ordered fashions. XRD pattern shows that the sample prepared at pH 7 exhibit highly crystalline ordered structure (Figs. 4(a), 5(a) and 6(a)). With decrease in pH (from 7 to 1), crystallinity decreases. Sample prepared at pH 7 shows an intense peak at $2\theta=6.4^\circ$ (d-spacing 13.3 Å) [31, 47], which indicates that the flower like or leaf like morphology possess more ordered conformation which increased solid state ordering compared to that of the nanorods. Several sharp peaks at $2\theta=18.5, 19.8, 23.4, 25.5, 26.4, 28.4$ were observed in addition to the peak at $2\theta=6.4^\circ$. This further confirms the existence of highly ordered structure of PANI obtained at pH 7. Although the peak at $2\theta=6.4^\circ$ is present in the sample prepared at pH 3 but its intensity was very less compared to the sample prepared at pH 7, which further confirms the lowering in the order of the materials (Figs. 4(a), 5(a) and 6(a)). It may be noted that peak at $2\theta=6.4^\circ$ is absent for the sample prepared at pH 1. However, broad nature of the peaks at 20.4 and 25.5

Fig. 2 SEM images of PANI synthesized using PEG at **a** pH 7, **b-c** pH 3, **d** pH 1, **e** methanol washed PANI synthesized using PEG at pH 7 and **(f)** methanol washed PANI synthesized using PEG at pH 3

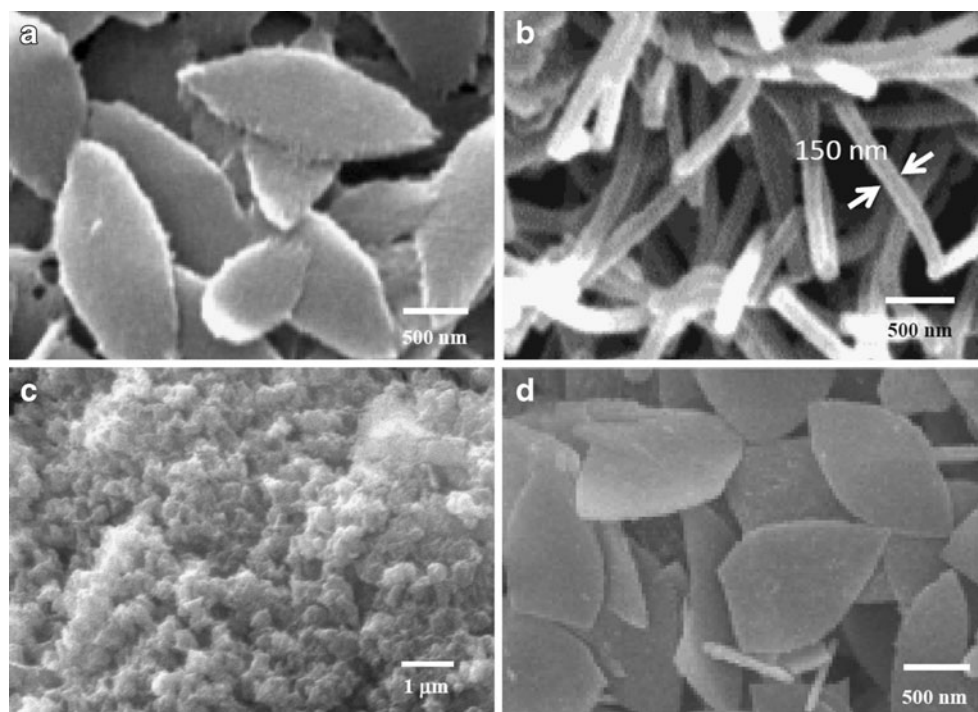


were observed for the samples prepared at pH 3 and pH 7. This also confirms that the samples prepared at low pH (pH 1 and pH 3) condition are semi-crystalline to amorphous in nature [48, 49]. The peak centered at $2\theta=20.4^\circ$ is ascribed to periodicity parallel to the polymer chain and the later peak at $2\theta=25.5^\circ$ may be ascribed to periodicities perpendicular to the PANI chains, respectively [50]. Sample synthesized using EG are more crystalline in nature compared to the samples prepared using PEG and P123 (Figs. 4(a), 5(a) and 6(a)).

The chemical structure of PANI was confirmed by FT-IR and UV-visible spectroscopy. FT-IR confirmed the formation of phenazine-like segments for the sample prepared using EG at pH 7 (Fig. 7(a)). No peak was observed in the region of $3,600\text{--}3,300\text{ cm}^{-1}$ (Fig. 7(a), inset). This confirms that the sample does not contain any free NH or OH group. Sharp peak at $3,120\text{ cm}^{-1}$ confirms the existence of strong intra-/inter-molecular hydrogen bonding among the phenazine

like oligomers with EG (Fig. 7(a), inset) [51]. Peak at $3,060\text{ cm}^{-1}$ confirms the presence of aromatic hydrogen due to phenazine like segment (consist of quinonoid and benzenoid rings). The aromatic C—C stretching vibrations of the phenazine-like segments appear at $1,445\text{ cm}^{-1}$. The peaks at $1,375$, $1,280$ and $1,170\text{ cm}^{-1}$ are a result of the stretching vibrations of secondary aromatic C—N [52]. Peaks at $1,230$ and $1,060\text{ cm}^{-1}$ are due to the C—O stretching frequency, which confirm the existence of EG in the PANI structure (Fig. 7(a)). The above evidence clearly states that the chemical structure of PANI obtained at pH 7 is made up of phenazine like oligomeric segment, which is in a crystalline state. This high crystallinity is due to highly ordered packing arrangement of phenazine like segment with strong hydrogen bonding. Peaks at $1,070$ and 700 cm^{-1} (due to S=O and S—O) confirm the incorporation of sulfonate groups attached to the aromatic rings in PANI

Fig. 3 SEM images of PANI synthesized using P123 at **a** pH 7, **b** pH 3, **c** pH 1 and **d** methanol washed PANI synthesized using P123 at pH 7



structure [53]. Sample prepared at pH 3 also exhibited similar FT-IR spectra as it was obtained in case of the sample prepared at pH 1 except a less resolved broad peak at $3,300\text{ cm}^{-1}$ (Fig. 7(a), inset). This shows the existence of some free NH group in the PANI structure. As discussed above, the packing arrangement of pernigraniline like segment are less ordered in the rod like structure compared to 3D flower like structure, which was reflected in the FT-IR spectrum as free NH group. This result is consistent with the SEM and XRD observation. Sample prepared at pH 1 shows broad peak at $3,430\text{ cm}^{-1}$ which corresponds to the

N–H stretching vibrations of the leucoemeraldine component [54]. The peak at $3,225\text{ cm}^{-1}$ is the result of different types of intra-/inter-molecular hydrogen-bonded N–H stretching vibrations of secondary amines (Fig. 7(a)). This N–H vibration appears at higher vibration indicates that the hydrogen bonding in this case was much weaker than in case of the sample prepared at pH 7. Other part of the IR spectrum is similar for PANI materials reported in the literature. FT-IR spectra of samples prepared using PEG at different pH conditions are similar as it was discussed above for the samples prepared using EG (Fig. 8(a)). FT-IR

Fig. 4 XRD patterns of **a** PANI synthesized using EG at different pH conditions and **b** methanol washed PANI synthesized using EG at different pH conditions

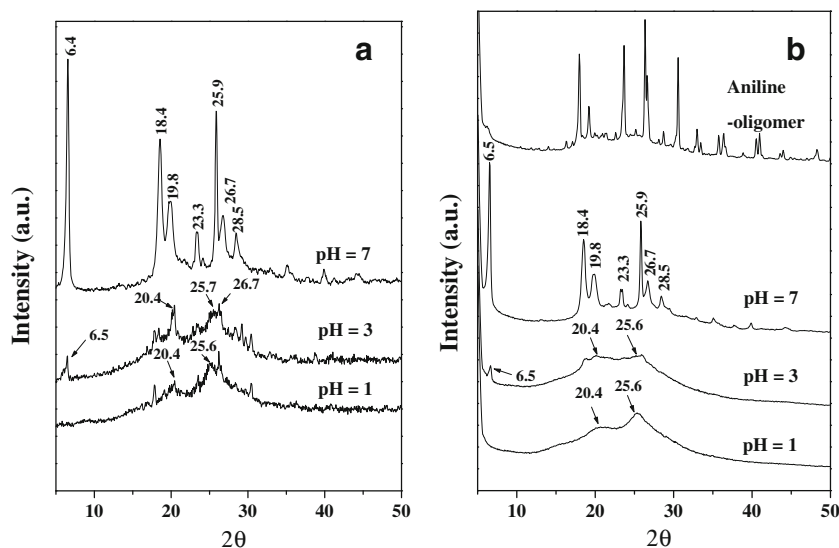
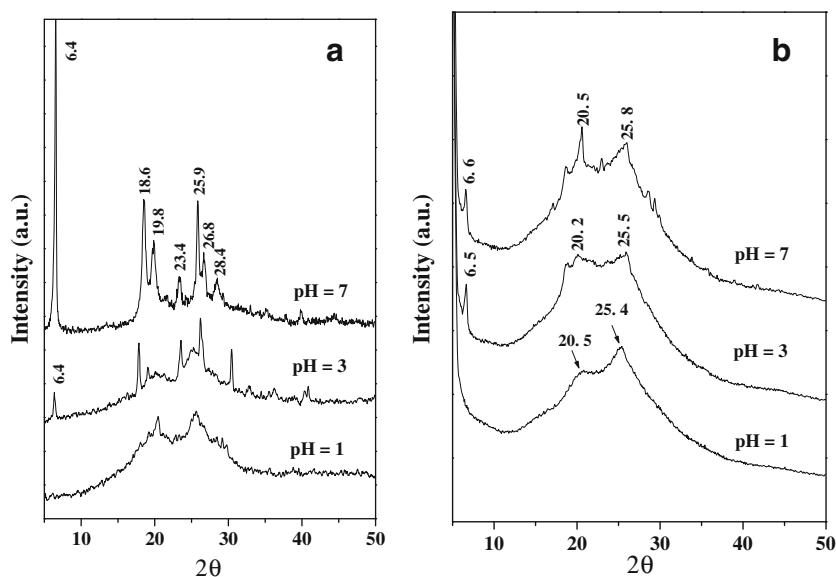


Fig. 5 XRD patterns of **a** PANI synthesized using PEG at different pH conditions and **b** methanol washed PANI synthesized using PEG at different pH conditions



spectra of samples prepared using P123 at different pH conditions are similar to that of samples prepared using EG/PEG. Peaks at 1,605, 1,241 and 1,038 cm^{-1} confirm incorporation of p123 moiety in the PANI structure for the sample prepared at pH 7 using P123 (Fig. 9(a)).

UV-visible spectra are believed to be similar for all kinds of samples using different SDA. Hence, the UV-visible study was performed for one set of samples. We have chosen the PANI samples prepared using PEG at different pH conditions (Fig. 10(a)). The UV-visible spectra of PANI were measured with samples dispersed in water [3, 36]. Only two peaks at 307 nm and 445 nm, which are assigned to the π - π^* benzenoid transition and the benzenoid to

quinoid excitotic transition, respectively were observed [55], indicating that PANI is in the emeraldine base form. Besides the two peaks mentioned above, one additional peak ($\lambda_{\text{max}}=700$ nm for pH 3 and $\lambda_{\text{max}}=750$ nm for pH 1) was also observed for the samples prepared at pH 3 and pH 1 (Fig. 10(a)). Third peak represents the π -polaron transition, indicating that the materials are in the conductive state [56]. Shifting of λ_{max} from 700 nm to 750 nm for the material synthesized at pH 1 shows that the material has high conductivity when it was synthesized in high acidic condition (pH 1) [56]. Samples prepared using PEG at different pH was doped using 1 M HCl and subjected to UV-visible study (Fig. 10(b)). UV-visible spectra of doped

Fig. 6 XRD patterns of **a** PANI synthesized using P123 at different pH conditions and **b** methanol washed PANI synthesized using P123 at different pH conditions

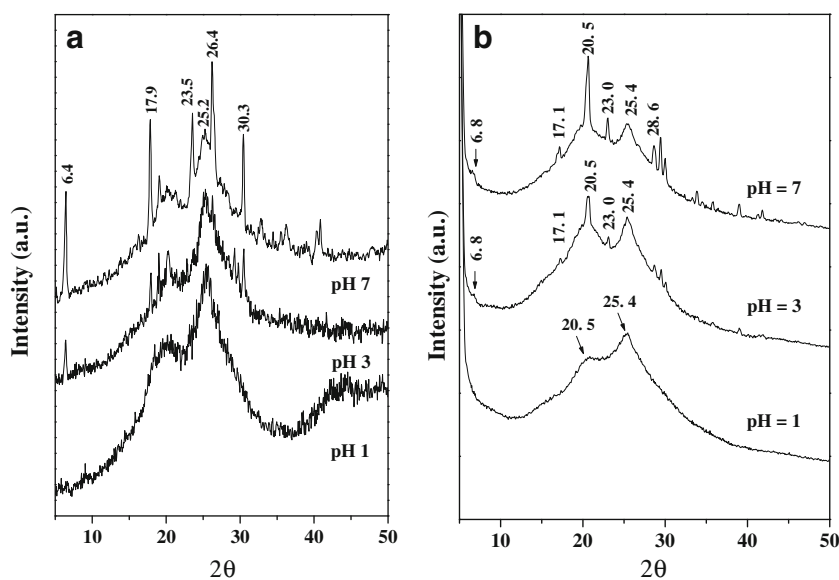
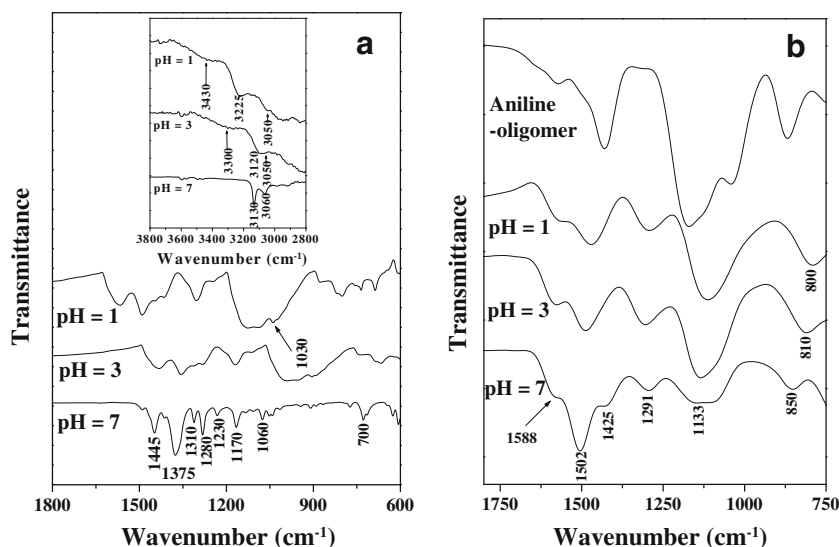


Fig. 7 FT-IR spectra of **a** PANI synthesized using EG at different pH conditions and **b** methanol washed PANI synthesized using EG at different pH conditions



samples exhibit same patterns as it was observed for the sample prepared using pH 1, except that the last peak which occurred at different λ_{\max} (Fig. 10(b)). λ_{\max} of 835 nm, 855 nm and 920 nm were obtained for samples prepared at pH 7, pH 3 and pH 1 respectively. This confirms that the conductivity of the materials prepared at pH 1 further increased after doping with 1 M HCl. It may be noted that the electrical conductivity of the products depends not only on morphology, but also on the degree of doping. For comparison, UV-visible spectra of PANI synthesized using PEG at different pH conditions and PANI synthesized using only APS (without any SDA) in NMP solvent were measured (Fig. 11). Spectra obtained of PANI samples in NMP matched well with the reported spectra in literature [34].

Samples prepared at pH 7 using EG/PEG/P123 have IR peaks at 1,230 and 1,060 cm^{-1} are due to C-O stretching, which signify that the EG/PEG/P123 is still present within the as-synthesized sample and is attached most probably due to hydrogen bonding [34, 57]. To confirm whether the product is polyaniline or oligo-aniline, materials synthesized under different conditions were washed with methanol. Materials synthesized using EG at pH 7, pH 3 and pH 1 had 30.2%, 20.7% and 4.5% aniline-oligomers, respectively, in the as-synthesized PANI samples. Sample prepared at pH 7 has almost similar XRD pattern before and after washing (Fig. 4(b)). After washing, peak intensity has been reduced, which clearly shows that methanol washing did not disturb the ordering in the materials. Sample prepared at pH 3 and pH 1 show smooth XRD pattern

Fig. 8 FT-IR spectra of **a** PANI synthesized using PEG at different pH conditions and **b** methanol washed PANI synthesized using PEG at different pH conditions

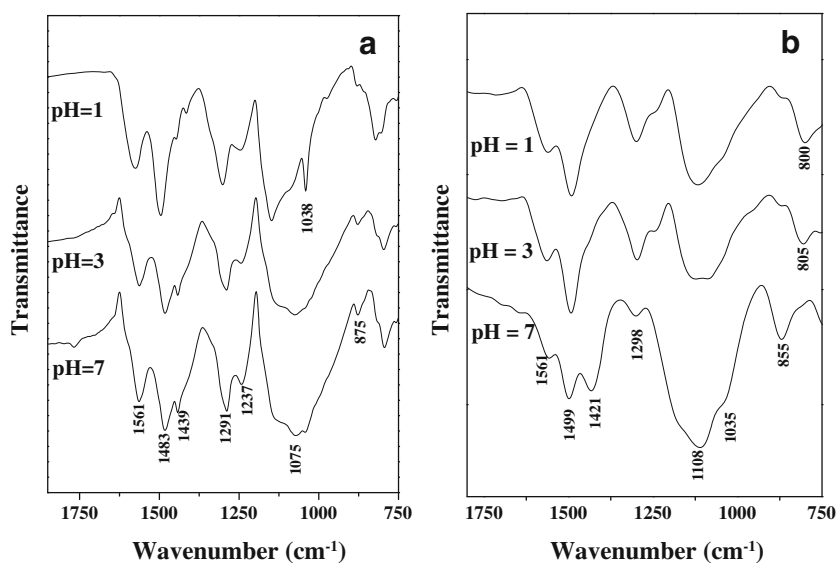
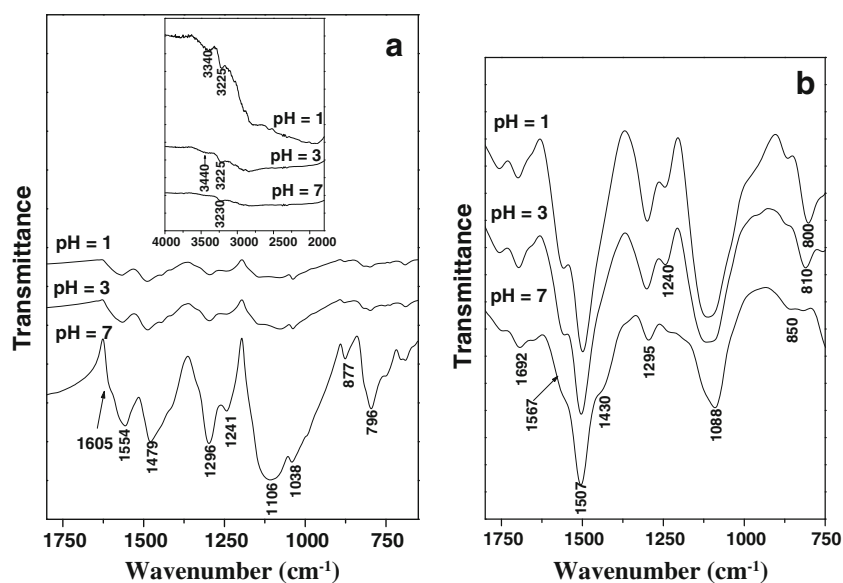


Fig. 9 FT-IR spectra of **a** PANI synthesized using P123 at different pH conditions and **b** methanol washed PANI synthesized using P123 at different pH conditions



after methanol washing (Fig. 4(b)). Noise present in the XRD pattern before washing is due to the aniline-oligomers present in the as-synthesized sample. XRD profile of aniline-oligomers is also provided in Fig. 4 (b). FT-IR spectra of aniline oligomer and PANI synthesized using EG at different pH after washing with methanol is shown in Fig. 7(b). FT-IR clearly shows that phenazine moiety is only present in the sample prepared at pH 7 (1,425 cm⁻¹). For methanol washed samples, a distinguish IR peak was observed at 850 cm⁻¹ (represents the phenazine moiety) for materials synthesized at pH 7, where as for materials synthesized at pH 3 and pH 1, this peak was observed at 810 cm⁻¹ and 800 cm⁻¹, respectively (represents 1,4-disubstituted benzene) [58]. Materials synthesized at pH 7

after washing did not show any peak at 1,060 cm⁻¹, which confirms that ethylene glycol had been removed from the as-synthesized sample after washing. Other characteristic peaks match well with the PANI materials. SEM images taken after washing with methanol did not show any change in the morphology (Fig. 1(f-h)).

Materials synthesized using PEG at pH 7, pH 3 and pH 1 had 26.2%, 18.6% and 3.8% aniline-oligomers, respectively, in the as-synthesized PANI samples. Materials prepared at different pH condition exhibited smooth XRD pattern after washing with methanol (Fig. 5(b)). Noise present in the XRD pattern before washing is due to the aniline-oligomers present in the as-synthesized sample. FT-IR spectra of PANI synthesized using PEG at different pH after washing with

Fig. 10 UV-visible spectra of PANI synthesized using PEG at different pH conditions in water **a** as-synthesized and **b** after doping with 1 M HCl solution

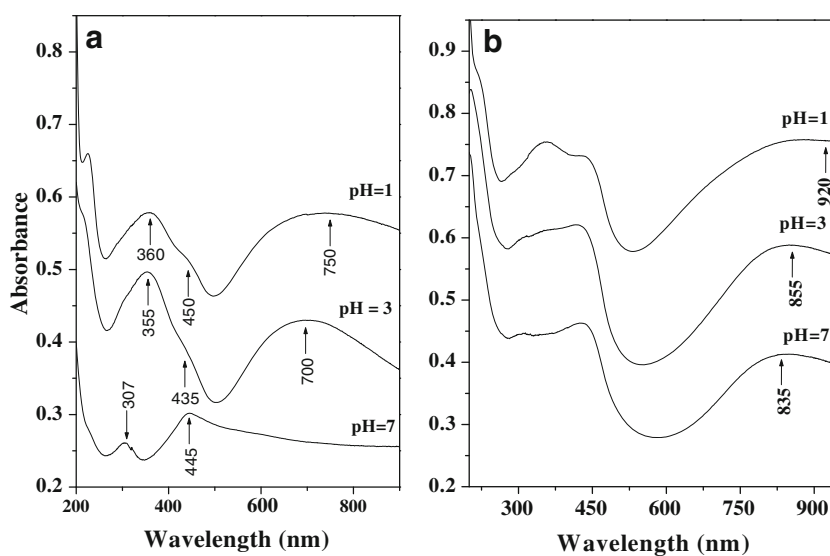
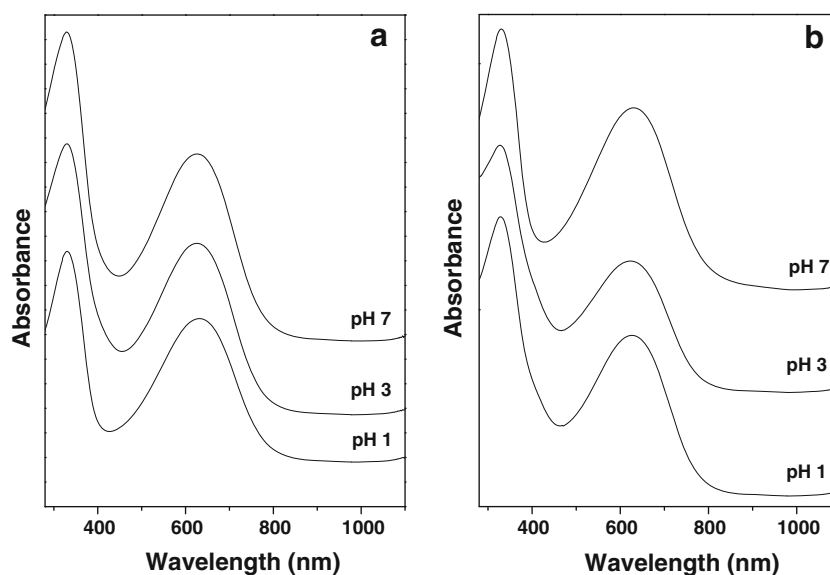


Fig. 11 UV-visible spectra of **a** PANI synthesized using PEG at different pH conditions in NMP and **b** PANI synthesized using only APS at different pH conditions in NMP



methanol are shown in Fig. 8(b). FT-IR clearly shows that phenazine moiety is only present in the sample prepared at pH 7 ($1,421\text{ cm}^{-1}$). For methanol washed samples, a distinguish IR peak was observed at 855 cm^{-1} (represents the phenazine moiety) for materials synthesized at pH 7, where as for materials synthesized at pH 3 and pH 1, this peak was observed at 805 cm^{-1} and 800 cm^{-1} , respectively (represents 1,4-disubstituted benzene) [58]. Materials synthesized at pH 7 and after washing with methanol exhibited very weak band at $1,035\text{ cm}^{-1}$ confirmed that PEG has almost been removed from the sample. This peak was absent in the two samples prepared at pH 3 and pH 1 after washing with methanol. Other characteristic peaks match well with the reported literature. SEM images taken after washing with methanol did not show any change in the morphology (Fig. 2(e), (f)).

Materials synthesized using P123 at pH 7, pH 3 and pH 1 had 23.7%, 16.4% and 3.5% aniline-oligomers, respectively, in the as-synthesized PANI samples. Materials prepared at different pH condition exhibited smooth XRD pattern after washing with methanol (Fig. 6(b)). Noise present in the XRD pattern before washing is due to the aniline-oligomers present in the as-synthesized sample. FT-IR spectra of PANI synthesized using P123 at different pH after washing with methanol are shown in Fig. 9b. FT-IR clearly shows that phenazine moiety is only present in the sample prepared at pH 7 ($1,430\text{ cm}^{-1}$). For methanol washed samples, a distinguish IR peak was observed at 855 cm^{-1} (represents the phenazine moiety) for materials synthesized at pH 7, where as for materials synthesized at pH 3 and pH 1, this peak was observed at 805 cm^{-1} and 800 cm^{-1} , respectively (represents 1,4-disubstituted benzene) [58]. Materials synthesized at pH 7 and after washing with methanol exhibited no peak in the range $1,000\text{--}1,050\text{ cm}^{-1}$, which confirmed that P123 has been completely removed from the sample. Whereas one sharp peak at $1,240\text{ cm}^{-1}$ was observed in the

samples prepared at pH 3 and pH 1 even after washing with methanol, confirming the incorporation of p123 moiety in the PANI nanostructure. Other characteristic peaks match well with the reported literature. SEM image taken after washing with methanol did not show any change in the morphology (Fig. 3(d)). Molecular weights of methanol washed PANI samples prepared under different conditions are given in Table 1.

Conclusions

A simple and economical route based on EG/PEG/P123 mediated self-assembly process was adopted to synthesize PANI micro-/nano-structured PANI of different morphology. Micro-/nano-composite structure is highly dependent on the

Table 1 Weight-average molecular weight of PANI synthesized in this study

S. No.	SDA used for the synthesis	pH of the medium	Molecular weight of PANI obtained
1	Nil	1	73,920
2	Nil	3	70,230
3	Nil	7	67,610
4	EG	1	31,040
5	EG	3	28,270
6	EG	7	25,450
7	PEG	1	34,370
8	PEG	3	32,140
9	PEG	7	29,680
10	P123	1	38,120
11	P123	3	35,470
12	P123	7	30,050

SDA and synthesis condition. Flower-like and leaf-like micro-/nano-structure were obtained using EG/PEG and p123, respectively for the sample synthesized at pH 7. Rod-like and granular-like morphologies were obtained for the samples synthesized at pH 3 and 1 respectively, using all kinds of SDA investigated in this study. Electron microscopy analysis shows that micro-/nano-structure is composed of hierarchically arranged nanosized building blocks. Hydrogen bonding plays a key role for the self-assembly process to form different morphology at different pH conditions.

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