Physicochemical and morphological properties of poly (aniline-*co*-pyrrole)

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ABSTRACT

Copolymers of aniline and pyrrole have been prepared by chemical oxidative polymerization of 1:1 mixture of aniline and pyrrole monomer with ammonium per sulphate and ferric chloride. The structural and morphological properties were studied by X-ray diffraction and scanning electron microscopy. Both copolymers showed an amorphous behaviour compared to their homopolymers. SEM micrographs of poly(aniline-pyrrole) copolymer showed agglomerated spherical structures where as poly(2,5 dimethoxyaniline-pyrrole) showed disordered structures of spherical agglomerates. The copolymers showed improved UV-Vis absorption with the broad peak from

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450-850 nm. The copolymers exhibited a lower conductivity compared to the homopolymers. It is also observed that the PDMA-PPY copolymer obeyed ohms law where as PANI-PPY behaved like a diode.

1. INTRODUCTION

Electronically conducting polymers have been the subject of numerous investigations in the past two decades **[1-5]**. Among conducting polymers, polyaniline (PANI) and polypyrrole (PPy) are the most promising materials because of their high electrical conductivity, environmental stability, low cost of production and favourable physiochemical properties **[6-8]**. These properties provide favourable conditions for potential applications in light-emitting diodes, solar cells, sensors, batteries, and electrochemical supercapacitors **[9]**. PANI and polypyrrole (PPy) can be prepared by electrochemical **[10-12]** and chemical oxidative-polymerization methods **[13-17]** and can also be doped or undoped between their conducting and insulating states **[18]**. The chemical oxidative polymerization of pyrrole is very important as it is a more feasible route for producing polypyrrole on a large scale.

It has been reported that the molecular structure of polymer chains play a major role in the conductivity of polymers, while the effects of molecular weight and crystallinity are less pronounced **[19]**. The molecular structure of

a conducting polymer chain can be controlled in three ways: (1) changing the degree of protonation and the sort of an acid, (2) by the chemical substitution of constitutional units in the PANI, (3) by copolymerization of aniline with suitable co-monomers.

Recently, a great deal of attention has been paid to synthesize aniline-based copolymers. A possible reason is probably attributed to great difficulty to synthesize new conducting polymers with electric properties and stability better than polyaniline and polypyrrole. The copolymerization of aniline and other monomers offers a possibility to prepare a new PANI type of copolymer that not only retains the good properties of PANI itself but also possesses new properties. However, Fusalba *et al.* [20] reported that the main motivation for preparing copolymer composites lies in the possibility that these materials overcome the limitation of the rareness of new conjugated π-bond-containing monomers. It is believed that copolymerization of a pair of monomers will lead to an increase in the number of conductive polymers that can be made from the same set of monomers [21].

In this article we report on the morphological evolution, optical and structural properties of poly (aniline-*co*-pyrrole) prepared by a chemical oxidative copolymerization process from monomer mixtures of An and Py. The molar ratio of An and Py monomers, [An:Py], were kept constant at 1:1.

2. EXPERIMENTAL DETAILS

2.1. Materials

Aniline (99 %), Pyrrole (98 %), 2, 5 dimethoxyaniline, Ammonium per sulphate (APS, $(NH_4)_2S_2O_8$, 98 %), dimethylformamide (DMF, 99 %) and ferric chloride ($FeCl_3$) were purchased from Sigma Aldrich. All chemicals were used as received without further purification.

2.2. Synthesis of PANI, PPy, Poly (aniline–co-pyrrole), PDMA, and poly (2,5 dimethoxyaniline-co-pyrrole)

PANI, PPy, Poly (aniline-co-pyrrole) (PANI-PP) was synthesized by chemical oxidation of their respective monomer. The molar ratios of An and Py monomers were kept constant at 1:1. In a 50 mL flask a 0.2 ml aniline and 0.2 mL of pyrrole were dissolved in a solution of 2 mL HCl in 20 mL distilled water. The solution was stirred for 30 minutes at room temperature where after 0.48 g of APS and 0.375 g of $FeCl_3$ was added respectively in the solution for polymerization initiation. The resultant mixture was stirred for another three hours. The product was collected by filtration and washed with ethanol and dried at a temperature of 50 ^{o}C. The same procedure was followed for PDMA, and poly((2,5 dimethoxyaniline-co-pyrrole) synthesis.

2.3. Characterization

Scanning electron microscopy (SEM) samples were prepared by placing some of the synthesized materials onto an aluminium stub using adhesive carbon tape. The samples were sputter-coated with gold to prevent

charging effects inside the microscope. The morphology of powder samples was investigated by using JEOL 7500F high resolution field emission SEM. Ultraviolet-visible (UV-vis) spectra were recorded on a PerkinElmer Lamda 750S spectrometer from 320 to 900 nm. Photoluminescence (PL) measurements were recorded on PerkinElmer LS 55 spectrometer by exciting the samples with a 320 nm line of deuterium lamp. The UV-vis and PL samples were prepared by dissolving about 0.005 g of a material in 10mL DMF. Infrared spectra were recorded using a Fourier transform infrared (FTIR) spectrometer (PerkinElmer Spectrum 100) to identify the chemical structure of PDMA respectively. A small amount of material was placed on the diamond coated detector and pressed onto the electrode for FTIR measurements. The X-ray diffraction patterns of powders were recorded on a Phillips (PANalytical) X-ray diffractometer using Cu Kα (λ = 1.54 A°) radiation source. The diffractogram was in terms of 2θ in the range 5–40°. Conductivity and I-V characterization were performed on Keithly 4200 Semiconductor Characterization System on 12.92 mm diameter pellets.

3. RESULTS AND DISCUSSION

3.1. Ultraviolet Visible spectral analysis

Figure 1 shows the UV-Vis spectra of the chemically prepared homopolymers of PANI and PDMA and their respective copolymers. The spectral characteristics of the copolymers were found to be noticeably different from the individual homopolymers, PANI and PDMA. The UV-vis

spectrum of PANI shows absorption peaks at around 340 and 600 nm. The peak around 340 nm is due to π-π* transition of benzoid rings while the peak around 600 nm is attributed to the charge transfer excitons of the quinoid structure [22, 23]. When aniline is copolymerized with pyrrole, the absorption peak shifted to higher wavelengths. A similar shift is observed in the UV-vis spectra of the copolymerized poly (2, 5 dimethoxy-co-pyrrole) (PDMA-PPY), (Figure 1). These shifts suggested that the inclusion of pyrrole in PANI and PDMA matrix reveals an increase in conjugation length for copolymers. The UV-vis spectra of the copolymers also shows a broad peak between 450-800 nm (PANI-PPY) and 500-850 nm, indicating that it can possibly be used for electron harvest in photovoltaic applications, since the maximum absorption of the sun is at 750 nm. The coexistence of peaks around 340 nm for PANI and PDMA reveals that the polymers are having an emeraldine structure.

3.2. Photoluminescence analysis

It has been reported that in most polymers the chromophore responsible for luminescence is the benzoic group and it was also found that quinodic groups are responsible for the quenching effect of photoluminescence [24]. Figure 2 depicts the photoluminescence spectra of the different polymer powders (PANI, PDMA, PPY and two copolymers) dissolved in NMP. The PL spectrum shows two peaks at around 390 and 420 nm. A broad peak is observed between 450 and 500 nm. The peak at ~ 390 and ~420 nm is attributed to the benzenoid groups causing the emission in the different polymers, whereas the broad peak at 500 nm is assigned to the

protonating form or the dope state of the polymer **[24, 25]**. The PL spectrum confirms the semi-conducting behaviour of the different polymers because of the presence of a weak peak at ~420 nm. For a fully doped state, the peak at ~420 nm disappears completely, while the peak at around 500 appears **[24, 25]**. Shimano *et al.* **[24]** demonstrated that when PANI is doped from emaraldine base to fully doped emaraldine salt, it exhibit a decrease in highest occupied molecular orbital (HOMO)/lowest un-occupied molecular orbital (LUMO) energy gap. This is due to a doping/protonation of leucoemaraldine base.

3.3. X-ray diffraction analysis

X-ray diffraction was used to probe the structure of the homo and copolymer structures as shown in Figure 3. PANI shows a sharp peak at around 2θ = 25.4 ^{o}. Additionally peaks were also observed at 15 and 20 ^{o}. This indicates that the PANI films are highly crystalline. Similar results were observed in the literature **[21, 26]**. The peak at 20 and 25.4 ^{o} can be ascribed to the periodicity parallel and perpendicular to the polymer chains of PANI respectively **[27, 28]**. The peak at 2θ=15 ^{o} suggests the significant crystallization upon protonation **[29]**. The broader peaks observed around 25 ^{o} (Fig. 3) for PANI-PP copolymer and PPY are characteristic of amorphous PPy, as well as the scattering of PPy chains at the interplanar spacing **[30]**. Similar results were obtained by Partch *et. al.* **[31]**.

X-Ray diffraction studies show that the PDMA powders are more crystalline compare with PANI powders doped with two protonic acids, as shown in Fig. 3. Very sharp peaks are observed around 2θ = 10, 15, 21, 23 and 26.4 ^{o}. Skotheim *et. al.* [32] showed that by accommodating large sized dopant ions, such as PO_4- demands greater rearrangement of bonds along the polymer backbone, can lead to better crystallinity. It has also been shown by Zhang *et. al.* [33] that the graphite-like diffraction peak at around 25 ^{o} is common to all the samples and is characteristic of the extent of pi conjugation in PANI. The broad peak at 2θ = 18-30° in the copolymer (PDMA-PPy) are indicative of an amorphous behaviour.

In both PDMA-PPY and PANI-PPY copolymer amorphous behaviour are observed due to the broadness of the peaks. The amorphous behaviour is also seen from the SEM micrographs in Fig. 4.

3.4. Scanning electron microscopy analysis

SEM morphology of the homopolymers of PANI and PDMA and copolymers of PANI-PPy and PDMA-PPy are shown in Figure 4, respectively. The micrograph in Figure 4(a) shows either a "rod-like" or a fibrillar structure. It is known that a fibrillar growth is intrinsic to PANI. During the copolymerization process the poly (aniline-co-pyrrole) PANI-PP SEM image (Figure 4(b) showed that spherical structures formed by agglomerated particles. The size of the spherical structures varies between 1 and 2 μm diameter of uniform shape. A flaky structure is observed for the PDMA (Fig. 4 c). It can be seen that the pyrrole and dimethoxy aniline monomer in the feed

affected the morphology of the obtained copolymer, Figure 4 (d). The copolymer obtained shows more irregular, disordered structures (amorphous) of spherical agglomerates as seen in Fig. 4 (d).

It is known that the π^* interactions between the pyrrole main chain is very strong. Therefore it has a tendency to aggregate into the irregular morphology, which is commonly observed in the poly pyrrole obtained by the chemical oxidation polymerization [34]. Liu *et al.* [6] showed that the morphology of polypyrrole is dependent on the reaction time. They showed that granules formed during the initial stages of poymerization which then turned into short and straight fibbers after 6.5 hours of polymerization.

3.5. Fourier Transform Infrared spectroscopy (FT-IR)

The structure of the different polymers (polyaniline, polypyrrole and poly(aniline-co-pyrrole)) was further studied by FTIR spectroscopy as shown in Figure 5. It is apparent in Figure 5 that, PANI, PDMA and PPY show their characteristic peaks of their homopolymers. The bands at 1530 and 1441 cm^{-1} in the PPy spectrum are due to C=C and C-C stretching vibrations in the polypyrrole ring structure, respectively [7]. C-N is represented by the band at 1280 cm^{-1} while C–H and N–H in-plane deformation vibration are situated at 1130 and 1000 cm^{-1} [7, 8]. The strong bands in the region 900-1800 cm^{-1} indicates that the conductive form of PPy is formed [35]. The spectrum of PANI show bands at 1560 and 1480 cm^{-1} which are attributed to C=C the stretching frequencies of quinodic and benzoic ring respectively [22]. The bands at 1287 and 1239 cm^{-1} are due to several stretching forms of C-N

bonds. PDMA spectrum shows peaks at 1660, 1540 and 1500 cm-1, which are due to C=O, the stretching vibrations of quinodic and benzoic groups, respectively. The peaks at 1363 1283 and 1195 cm^{-1} are due to various C-N stretching vibrations. It is observed that the peaks shifted to a lower wave-numbers for the copolymer (poly (aniline-co-pyrrole)) demonstrating the presence of neighbouring aniline and pyrrole constitutional units.

3.6. I-V Measurements

The electrical conductivity measurements of chemically synthesized copolymers and homopolymers were performed on pellets by applying a DC voltage sweep from -5 to 5 V and are presented in Figure 6 and Table 1. As shown in Fig. 6, the current–voltage characteristics of the copolymers are ohmic at room temperature. Current – voltage characteristics of the homopolymers show a non-linear (non-ohmic) behaviour. This behaviour can be explained by conduction mechanism of polyaniline and polypyrrole. In intrinsic semiconductors the charge conduction is only carried out by free electrons carriers but, in these polymers the formation of polarons and bipolarons also takes part in charge conduction **[36]**. When the applied voltage is increased the formation of polarons and bipolarons also increases resulting in the higher current values through the sample. It can also be noted that during forward bias the PDMA-PPY has the highest current followed by PANI-PPY, PANI and then PPY.

It is observed that the conductivity decreases from 10^{-2} to 10^{-5} when aniline is polymerising with pyrrole (Table 1). The lowering of the conductivity from the copolymer than PANI is expected to arise from the steric effect of the bulky substituent ($-OCH_3$) that can provide torsional twists in the polymer backbone, reducing the coplanarity and average electron delocalization length. Such type of observations has been noted for substituted polyaniline and copolymers of anilines with substituted anilines **[37, 38]**. The results indicate that when polymerising aniline with pyrrole the conductivity decreases for polyaniline and improve for polypyrrole. This means copolymerisation can increase the conductivity of polypyrrole. This is evidence that the copolymer formed is not just the combination of polypyrrole and polyaniline but a completely new material with new properties. This is confirmed by UV-Vis results where PDMA-PPY has improved the wavelength window to up to 850 nm.

CONCLUSION

Copolymers of aniline and pyrrole were successfully synthesized using a conventional chemical oxidative polymerization process. The polymer displayed a strong optical absorption in the visible region and exhibited photoluminescence as determined by UV–vis and fluorescence spectrum analysis. The morphology of the homopolymers has fibrillar and flaky structures for PANI and PDM, respectively. The SEM results showed that the formed copolymer of poly(aniline-*co*-pyrrole) is spherical with diameters in the

micro/sub micro dimensions.   An irregular structure is observed for the copolymer of PDMA-PPy.   XRD study revealed that the homoploymers of PANI and PDMA powders are crystalline while the copolymer of PANI and PDMA are amorphous in nature.

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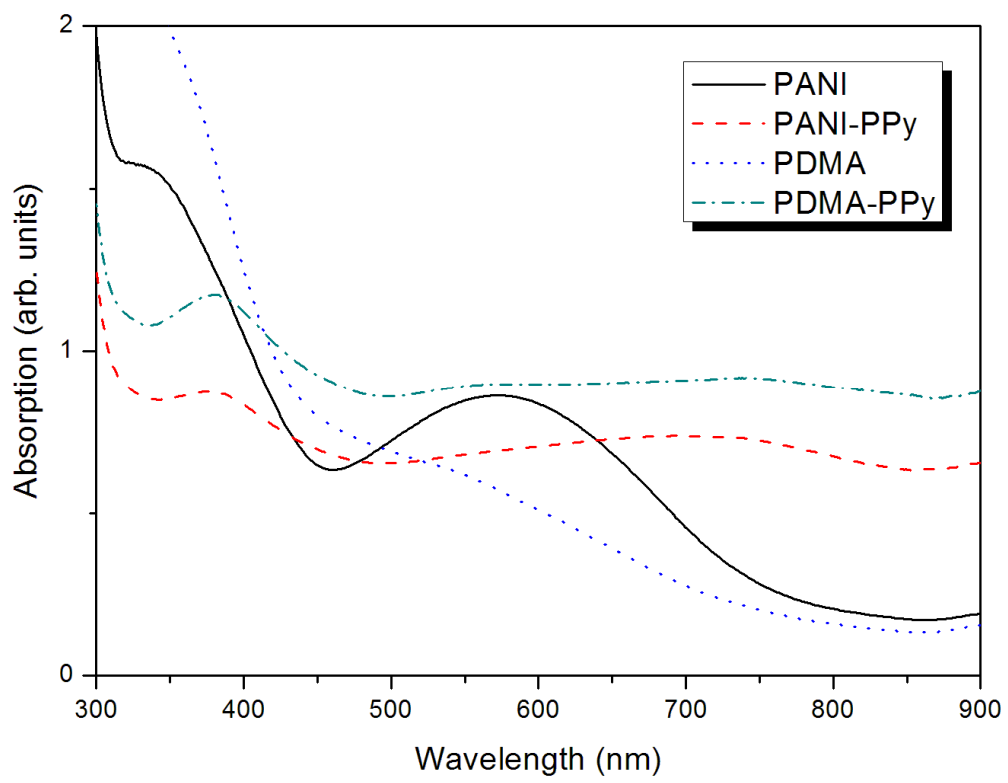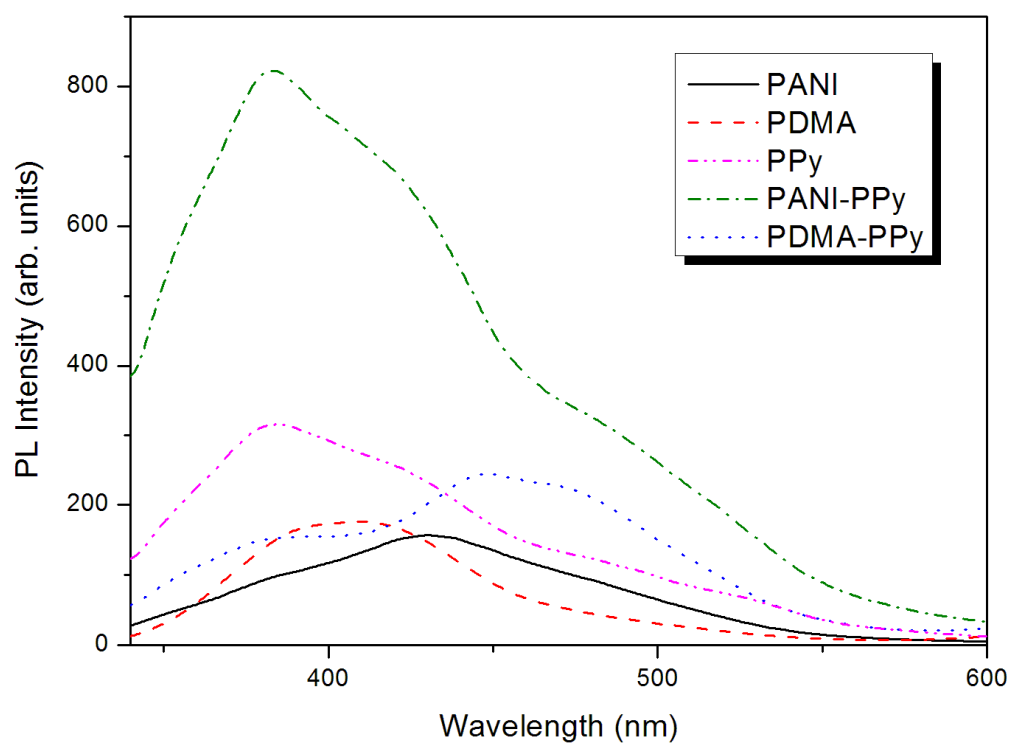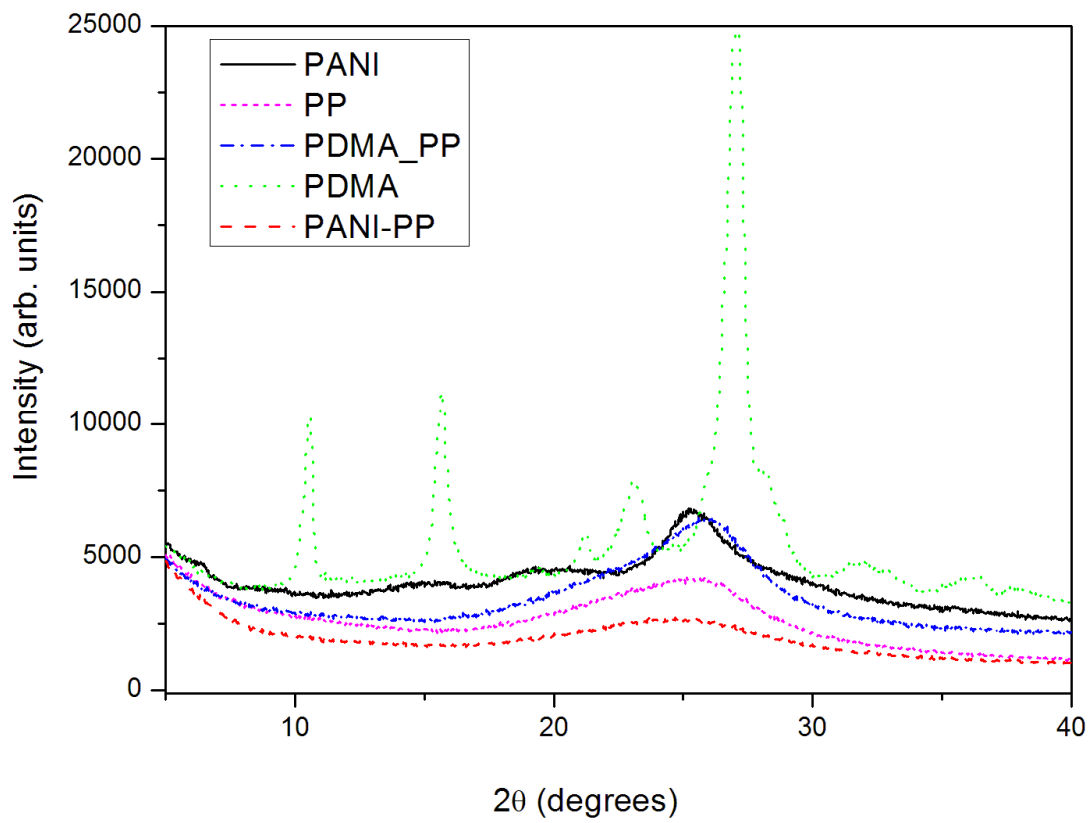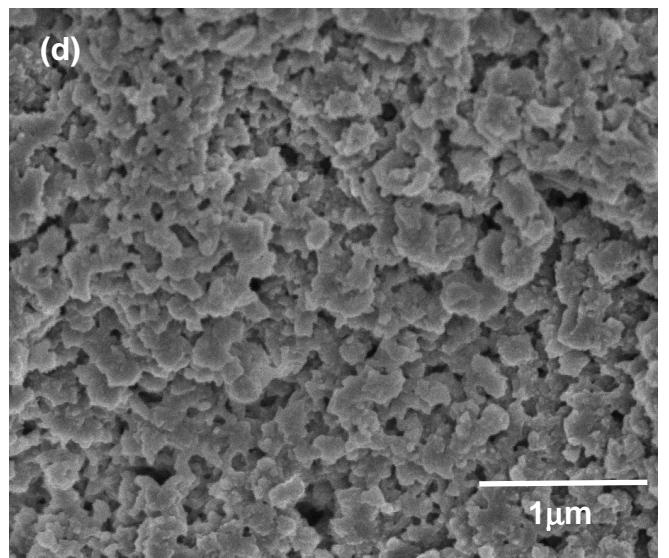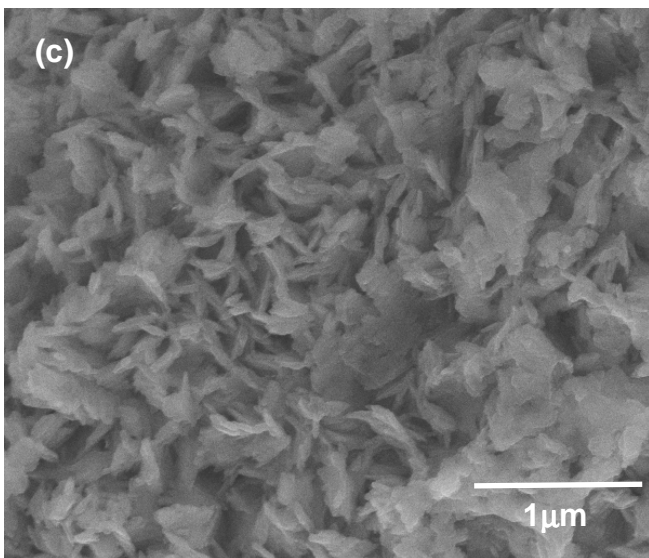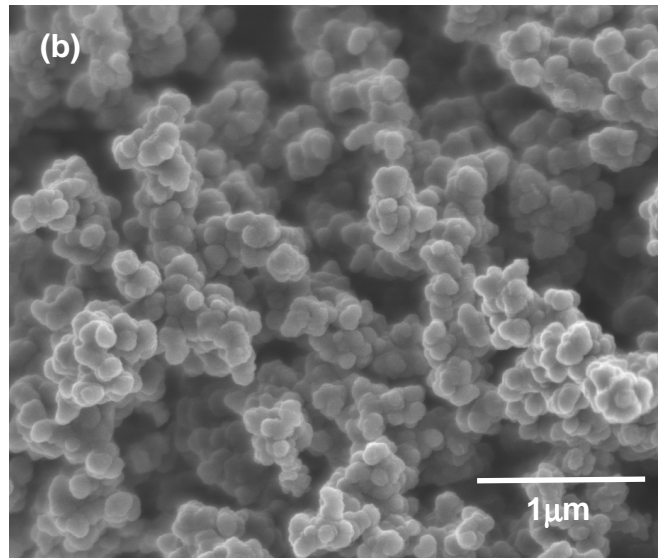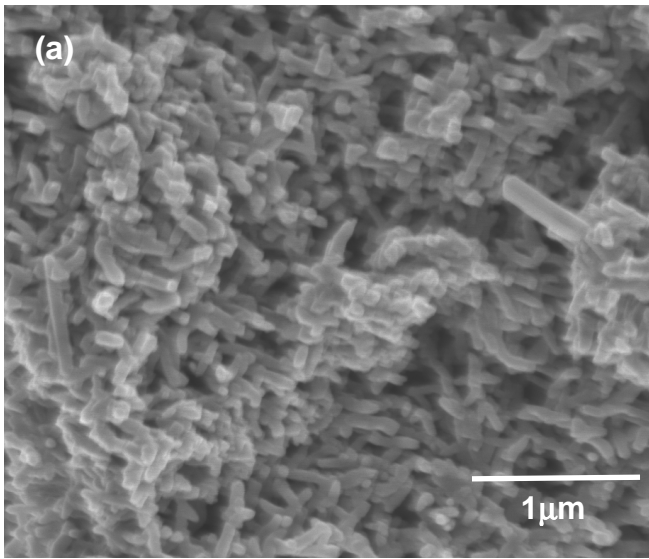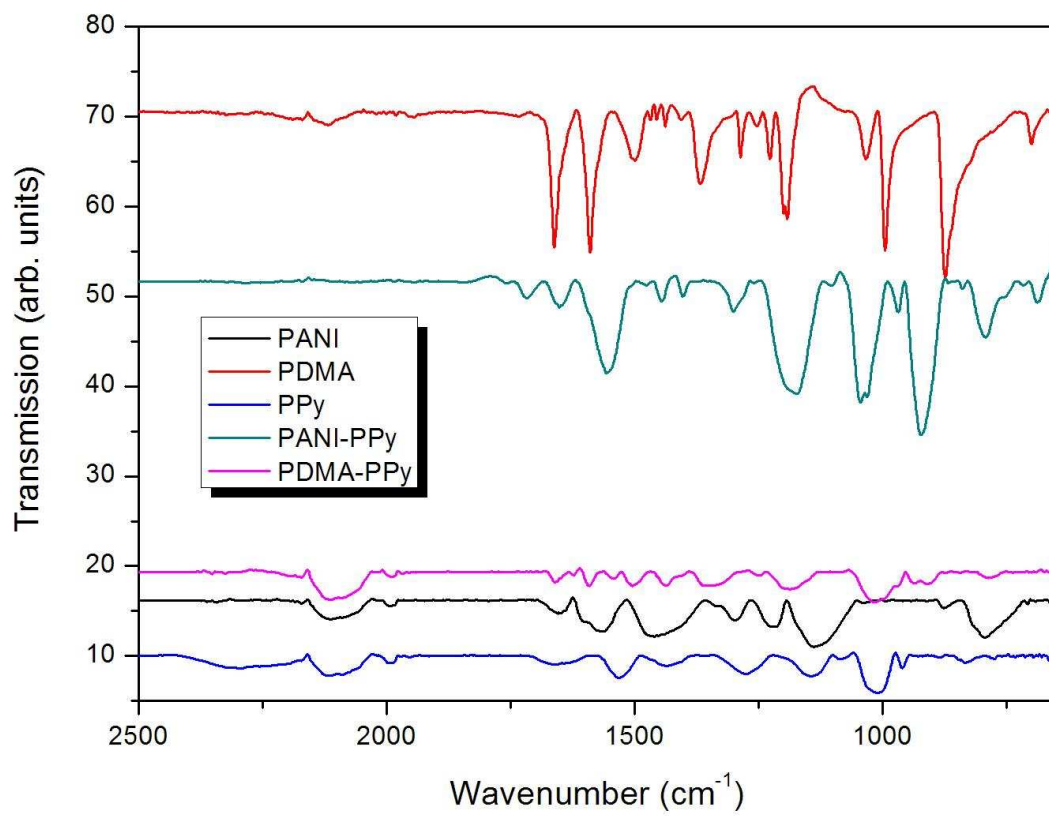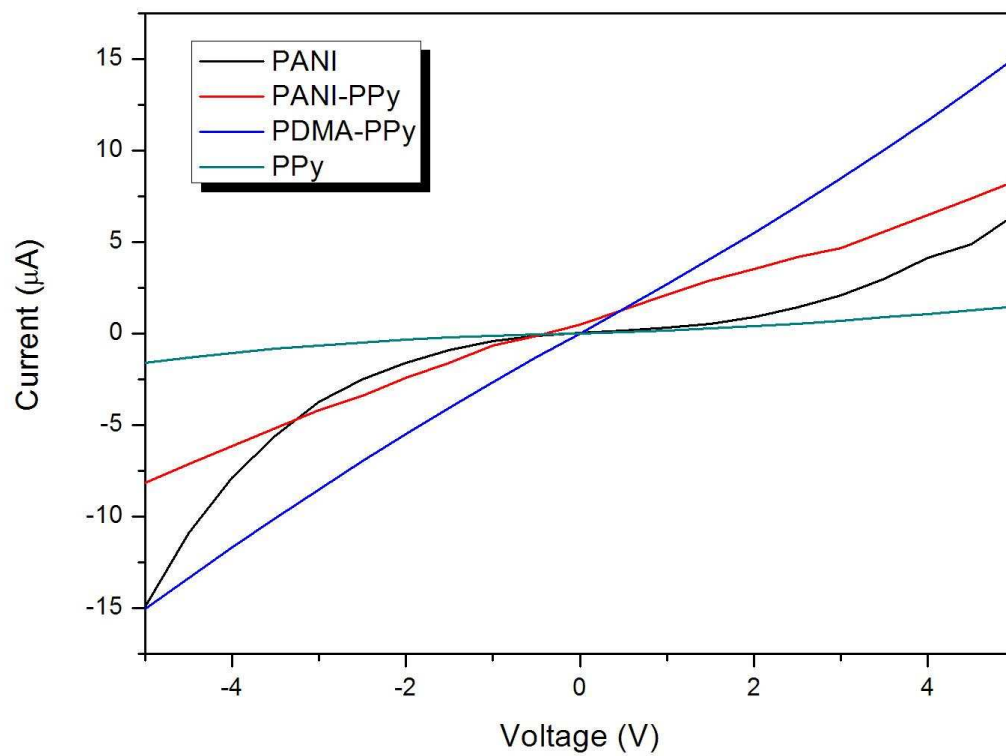
Sample	Conductivity (S/cm^2)
PANI	4.1×10^{-2}
PANI-PPY	2.5×10^{-5}
PDMA-PPY	5.2×10^{-4}
PPY	4.8×10^{-6}