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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 aniline and pyrrole using ammonium per sulphate and ferric chloride as oxidants. 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 450 to 850 nm. The copolymers exhibited a lower conductivity compared to the homopolymers due to the unsuccessful complex between PANI and PPy, induced by the use of APS as the oxidant.

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 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].

To date, most of the published research on electrochemical copolymerization of pyrrole and aniline or electrochemical deposition of PANI and PPy layers on different substrates has been developed to obtain PANI–PPy composite [19–23]. It has been reported that PANI–PPy composite coatings on carbon fibres can be formed by using a one-step electrochemical synthesis process [21, 22]. They showed that the behaviour of the current–time (*I*–*t*) transient could be used to understand the formation of PANI–PPy composite coatings on carbon fibres. They also showed that the structure, yield and the morphology of the coatings were dependent on the feed ratio of the monomers (aniline and pyrrole) and the applied potential. On the other hand, Cakmak et al. [23] reported a two step electrochemical polymerization process to obtain conductive homopolymers, composites and copolymers of PANI, PPy and poly(dimethylsiloxane) (PDMS).

It has been reported that the molecular structure of polymer chains play a major role in the conductivity of polymers, whilst the effects of molecular weight and crystallinity are less pronounced [24]. 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

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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 PANI and PPy. 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. [25] 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 [26]. In this study, 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 aniline and pyrrole. The molar ratio of An and Py monomers, in the feed, were kept constant at 1:1.

Experimental details

Materials

Aniline (99%), pyrrole (98%), 2,5-dimethoxyaniline, ammonium persulphate (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.

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. In a 50 mL flask 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 min at room temperature where after 0.48 g of APS and 0.375 g of $FeCl_3$ were added, respectively, in the solution for polymerization initiation. The resultant mixture was stirred for another 3 h. The product was collected by filtration and washed with ethanol and dried at a temperature of 50 °C. The same procedure was followed for PDMA, and poly(2,5 dimethoxyaniline-*co*-pyrrole) synthesis. It should be noted that a feed molar ratio of 1:1 (An:Py) was used since it was reported that by varying the ratios of aniline and pyrrole, copolymers with more PANI or PPy behave similar to those individual homopolymers of anilne or pyrrole, whilst the copolymers from equal molar ratios combined the characteristics of both homopolymers [9, 24, 27].

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 10 mL DMF. Infrared spectra were recorded using a Fourier transform infrared (FT-IR) 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 ($\lambda = 1.54$ Å) radiation source. The diffractogram was in terms of 2θ in the range 5–40°. Conductivity and *I*–*V* characterization were performed on a Keithly 4200 Semiconductor Characterization System. The electrical conductivity of the powder pellets at room temperature was measured using a typical four-probe method.

Results and discussion

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 whilst the peak around 600 nm is attributed to the charge transfer excitons of the quinoid structure [28, 29]. 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), (Fig. 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

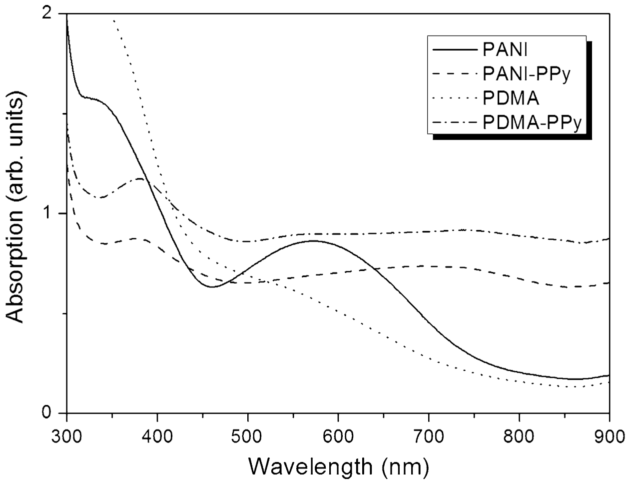

Fig. 1 UV–vis spectra of PANI, PDMA and their copolymers

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.

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 [30]. Figure 2 depicts the photoluminescence spectra of the different polymer powders (PANI, PDMA, PPY and two copolymers) dissolved in DMF. 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 [30, 31]. 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, whilst the peak at around 500 appears [28, 31]. Shimano et al. [30] demonstrated that when PANI is doped from emaraldine base to fully doped emaraldine salt, it exhibits 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.

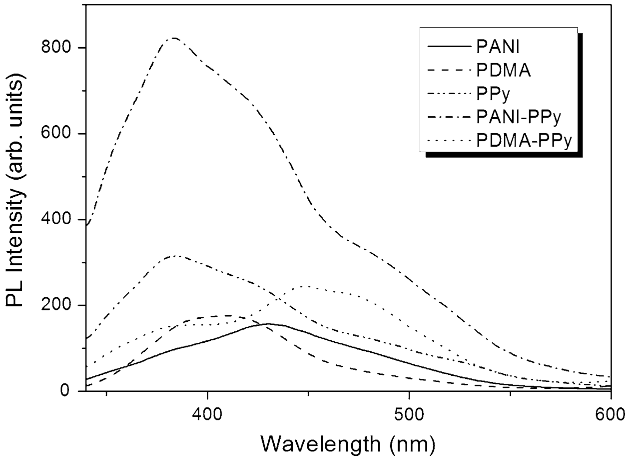

Fig. 2 Photoluminescence of PANI, PDMA and their copolymers

X-ray diffraction analysis

X-ray diffraction was used to probe the structure of the homo and copolymer structures as shown in Fig. 3. PANI shows a sharp peak at around $2\theta = 25.4°$. Additionally, peaks were also observed at 15° and 20°. This indicates that the PANI films are highly crystalline. Similar results were observed in the literature [26, 32]. The peak at 20° and 25.4° can be ascribed to the periodicity parallel and perpendicular to the polymer chains of PANI, respectively [33, 34]. The peak at $2\theta = 15°$ suggests the significant crystallization upon protonation [35]. The broader peaks observed around 25° (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 [36]. Similar results were obtained by Partch et al. [37].

X-Ray diffraction studies show that the PDMA powders are more crystalline compared with PANI powders oxidized with two oxidants, as shown in Fig. 3. Very sharp peaks are observed around $2\theta = 10$, 15, 21, 23 and 26.4°. Skotheim et al. [38] showed that by accommodating large

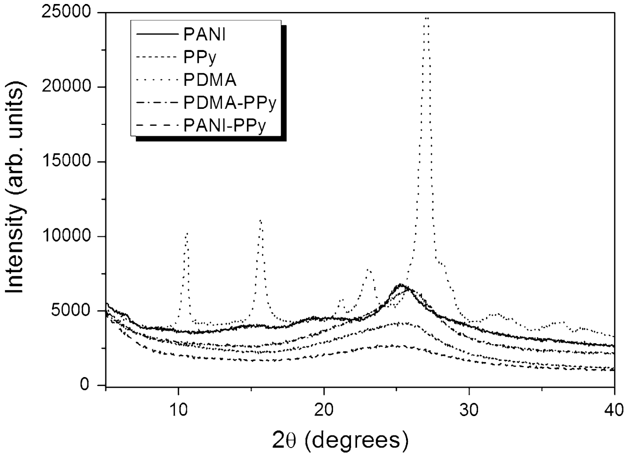

Fig. 3 X-Ray diffraction patterns of the homo and copolymers of PANI, PDMA and PPy

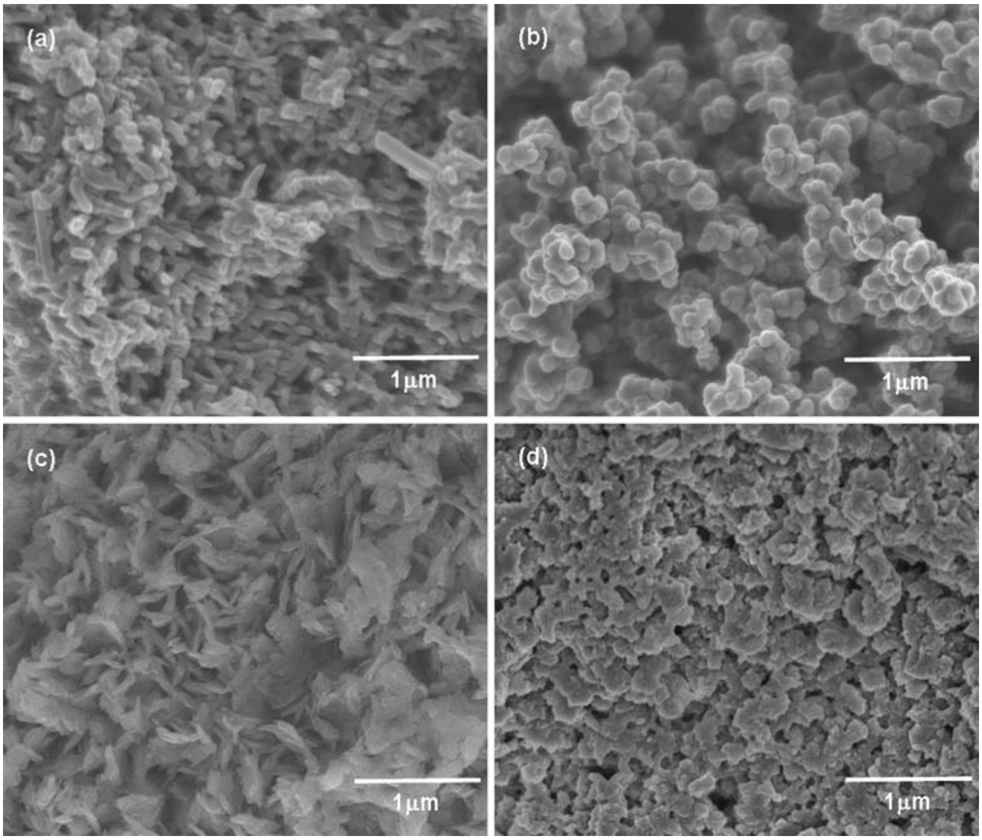

Fig. 4 SEM micrographs of **a** polyaniline, **b**, PANI–PPy, **c** PDMA and **d** PDMA–PPy

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. [39] that the graphite-like diffraction peak at around 25° is common to all the samples and is characteristic of the extent of pi conjugation in PANI. The broad peak at $2\theta = 18–30°$ in the copolymers are indicative of an amorphous behaviour. In both PDMA–PPy and PANI–PPy copolymer a complex behaviour is observed due to the broadness of the peaks. This behaviour is also observed from the SEM micrographs in Fig. 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 Fig. 4, respectively. The micrograph in Fig. 4a 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 (Fig. 4b) showed spherical structures formed by agglomerated particles. The size of the spherical structures varies between 10 and 50 nm in diameter of uniform shape. A flaky structure is observed for the PDMA (Fig. 4c). It can be seen that the pyrrole and dimethoxy aniline monomer in the feed affected the morphology of the obtained copolymer, Fig. 4d. The copolymer obtained shows a more compact surface of spherical agglomerates as seen in Fig. 4d.

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 PPy obtained by the chemical oxidation polymerization [40]. Liu et al. [6] showed that the morphology of PPy is dependent on the reaction time. They showed that granules formed during the initial stages of poymerization which then turned into short and straight fibres after 6.5-h of polymerization.

Fourier transform infrared spectroscopy (FT-IR)

The structure of the different polymers (PANI, PPy and poly(aniline-*co*-pyrrole)) was further studied by FTIR spectroscopy as shown in Fig. 5. It is apparent in Fig. 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 PPy ring structure, respectively [7]. C–N is represented by the band at 1280 cm^{-1} whilst C–H and N–H in-plane deformation vibration are situated at 1130

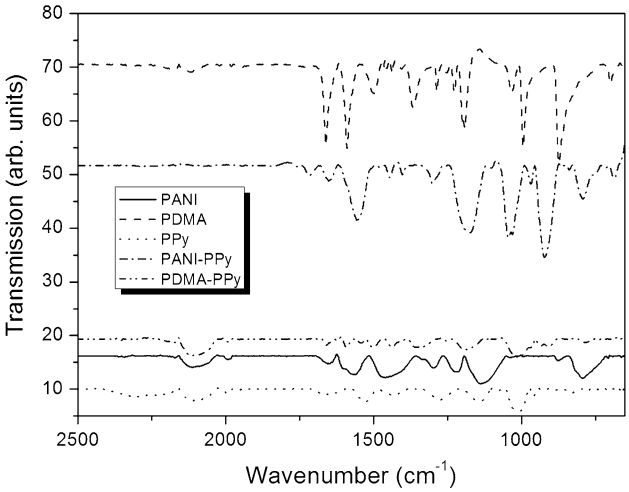

Fig. 5 FT-IR spectra of PANI, PANI–PP and PPY polymers

and 1000 cm^{-1} [7, 8]. The strong bands in the region 900–1800 cm^{-1} indicate that the conductive form of PPy is formed [41]. The spectrum of PANI show bands at 1560 and 1480 cm^{-1} which are attributed to C=C stretching frequencies of quinodic and benzoic ring, respectively, [28]. 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.

I–V measurements

The electrical conductivity measurements of chemically synthesized copolymers and homopolymers were performed on powder pellets by applying a DC voltage sweep from −5 to 5 V and are presented in Fig. 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 PANI and PPy. 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 [42]. 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.

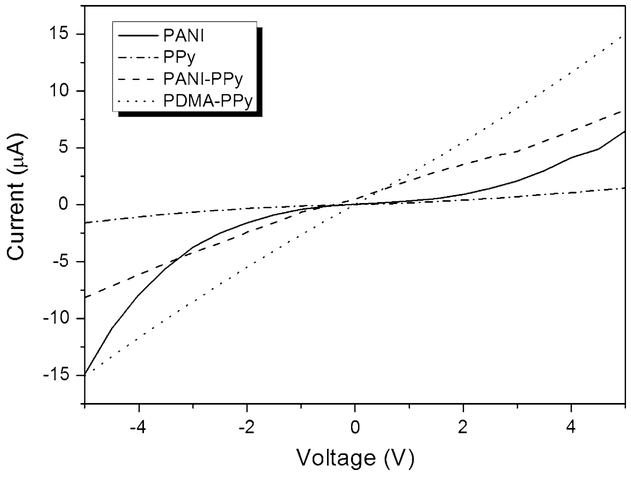

Fig. 6 *I–V* curves of PANI, PDMA–PPy, PANI–PPy and PPy

Table 1 Conductivity of the different polymers

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}

The conductivity of the samples lies on two aspects: microscopic and macroscopic conductivity. The former depends on the doping level, conjugation length and chain length, etc., whereas the macroscopic conductivity is related to some external factors such as the compactness of the samples [43]. It is observed that the conductivity decreases from 10^{-2} to 10^{-5} when aniline is polymerized with pyrrole (Table 1). The lowering of the conductivity may be related to the formation of the complex between PANI and PPy, which could reduce the conjugation or chain length of the composites. It is also suggested that based on the results of SEM observation, one can find that the copolymers (Fig 4e, c, d) show poor ability to form good composites due to weak interactions at the interface between PANI and PPY. When APS has been used as the oxidant, the conductivity of PANI reported in the literature is generally higher than that of PPy [44, 45], as in the present case. However, if similar experiments are carried out with iron(III) salts, the situation is reversed; conductivities over 200 S cm^{-1} have recently been reported for PPy [46], typical values being in the range of tens of S cm^{-1} [47–49]. The conductivity of the PMDA–PPy copolymer is higher than that of PANI–PPy copolymer and is due to the compactness of the sample as shown by the SEM analysis. Therefore, we conclude that the lowering of the conductivity on the copolymers of PANI–PPy is due to the APS, when it is used as the oxidant, which hinder the carrier transport between different molecular chains of PANI and PPy [50].

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. SEM images showed the microfibre and flaky morphology for PANI and PDM, respectively. Otherwise, the SEM results showed that the formed copolymer of poly(aniline-*co*-pyrrole) is spherical with diameters in the microdimensions. An irregular structure is observed for the copolymer of PDMA–PPy. XRD study revealed that the homoploymers of PANI and PDMA powders are crystalline whilst the copolymer of PANI and PDMA are amorphous in nature. The low conductivity is originated from the unsuccessful complex of PANI and PPy and the used of APS as an oxidant.

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