Combined Experimental and Theoretical Study of Poly(Aniline-*co*-Pyrrole) Oligomer

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Abstract

Quantum mechanical calculations are performed to establish the structure of an oligomer of aniline and pyrrole [Poly(Ani-*co*-Py)], through comparison of experimental and theoretically calculated properties, including conductivity. The copolymer was synthesized through chemical oxidative polymerization and then confirmed from the experimental IR, UV-vis, mass spectra, elemental, XRD, TGA, and SEM analysis. Quantum mechanical calculations are performed at Density Functional Theory (DFT) and Time dependent DFT (TD-DFT) methods for the electronic and spectroscopic properties of the oligomer. A very nice correlation is found between the theory and experiment which consequences the structure of Poly(Ani-*co*-Py). Poly(Ani-*co*-Py) is not explored like other conducting polymers; however, by tuning this molecular structure, the electro-active nature of this material can be enhanced adequately.

KEYWORDS: DFT, Poly(Ani-*co*-Py), PPy, PANI, Band gap, IR, UV-vis, IP, EA, HOMO-LUMO

1. Introduction

Advanced functional macromolecules such as conjugated organic polymers (COPs) [1-3] are promising due to their wide range of technological applications in the area of rechargeable batteries [4], optoelectronic devices [5], light emitting diodes [6], photovoltaic, sensors [7], biosensors [6, 8], electrochromic display material, electromagnetic shielding [9], artificial muscles, and solar cell. Among COPs; poly (*o*-phenylene-diamine) (POPD) [9], poly (*3*, *4*-ethylenedioxythiophene) (PEDOT), polyparaphenylene (PPP), polypara-phenylenevenylene (PPV), polythiophene (PT), polypyrrole (PPy) [10], and polyaniline (PANI) have been studied both theoretically [11, 12] and experimentally for efficient synthesis, characterization and applications [13-15]. Physical, electronic and mechanical properties of the conducting polymers can be enhanced by doping, de-doping [12], nanotube additives, and copolymerization [16-18]. Poly(Ani-*co*-Py) double-walled nanotube arrays for electrochemical energy storage (high-performance supercapacitor) have been fabricated by Z. –L. Wang *et al* [18]. Composites formation is another efficient way to tune the properties of COPs. Compared to pure COP, composites of COP with other materials such as metals are gaining attentions due to unique properties and applications. Blinova *et al* [19, 20], synthesized PANI-silver nano-composites and reported higher conductivity of the nanocomposites as compared to pure PANI.

On the other hand, copolymerization is an efficient way to get some new unique properties which are non-existent for homo polymer [21-24]. Solanki *et al.* [24] has efficiently electropolymerized Poly(Ani-*co*-Py)-immobilized cholesterol oxidase (ChOx) film (Poly(Ani-*co*-Py)/ChOx), and used as biosensor (bioelectrode) with sensitivity of 93.3 mA/mM. A remarkable increase of sensitivity in Poly(Ani-*co*-Py)/ChOx is observed compared to their homo polymer-immobilized ChOx, i.e. PANI/ChOx (69.0 mA/mM) and PPy/ChOx (32.2 mA/mM). S. E. Mavundla *et al*. [25] has chemically synthesized Poly(Ani-*co*-Py) using ammonium persulphate (APS) and ferric chloride as oxidants. They reported the physicochemical and morphological properties of Poly(Ani-*co*-Py), with amorphous, disordered structure, and lower conductivity compared to their homo polymers of PANI and PPy. These authors had assigned the lower conductivity of

Poly(Ani-*co*-Py) due to ineffective complex formation between PANI and PPy, induced by the use of APS as the oxidant. These authors has described the structural properties with different characterizations but did not mention the proper structure of Poly(Ani-*co*-Py). Poly(Ani-*co*-Py) is an interesting blend, consisting of 5 and 6 membered rings however, little attention has been paid toward its exact structure [21-24].

A few other reports on the copolymerization of PPy and PANI with certain limitations are also available (*vide supra*) [21-24, 26], but its structure is not properly discussed. D. K. Moon *et al*. [22] has copolymerized pyrrole (Py) and aniline (Ani) and concluded that conductivity of the resulted species declined contrary to their individual homo polymers [27]. They had used different comonomers ratios of Py and Ani (1:9 . . . 9:1) and found that the properties of co-polymer shifted to PPy at 9:1, 8:2, 7:3, and 6:4 ratio. Whereas, shift were observed towards PANI at 1:9, 2:8, 3:7, 4:6, 5:5 molar ratios. Overall, their work was just a confirmation of the copolymerization, not the structure determination. Stejskal *et al*. [20] and Lim *et al*. [27] reported a copolymer of Poly(Ani-*co*-Py), and found a nonlinear trend in the conductivities of Poly(Ani-*co*-Py) samples, which were synthesized using HCl as dopants. They attributed the decrease in conductivity of the copolymer, with increase in Py, to the shortening effect of PANI chain through the copolymerization or heterodiads formation of Ani with Py rather than to forming Ani blocks. M. J. Antony *et al*. [28] did not observe any nonlinear behavior in their synthesized random copolymer therefore, rejected the heterodiad formation (Lim and Stejskal work) [20, 21, 27]. They described the unusual nonlinear conductivity behaviors in the copolymers materials to variation in the morphology, and difference in the three-dimensional solid-state ordering. Y. Zhu *et al*. [29] has successfully synthesized hollow Poly(Ani-*co*-Py)-Fe_3O_4 nanospheres via the oxidative polymerization of Ani and Py in the presence of a magnetic fluid. Their copolymer had interesting electromagnetic and super paramagnetic properties. Moreover, increase in conductivity were found with Fe_3O_4 contents. Among all these reports K. Moon *et al*. has proposed the molecular structure of Poly(Ani-*co*-Py) as shown in Fig 1a. However, they were unsuccessful to support their structure from spectroscopic and other related analytical techniques. Taking into account these considerations (ambiguities), we set to synthesize a copolymer from Ani and Py in the presence of APS. The objectives of the current work is to: (I) confirm the copolymerization (II) determine decrease or increase in conductivity on copolymerization (III) validate the structure of the copolymer (if formed) through experimental and theoretical studies. DFT methods at B3LYP/6-31G (d) level of theory [30, 31] is employed which gives fruitful results especially in the field of COPs [9, 12, 26, 32-35].

METHODOLOGY

2.1. Experimental. Poly(Ani-*co*-Py) was synthesized from double distilled Ani and Py of analytical grade (Aldrich Sigma) by a well-known common oxidative polymerization method [36] at ambient temperature. We also attempted inverse emulsion (chemical) [27, 37] and electrochemical polymerization techniques but, found that chemical oxidative polymerization is much superior [38, 39]. APS (analytical grade) and HCl(aq) (37% pure) were used as oxidizing agent and supporting electrolyte, respectively. In a typical procedure, 10 mL (0.1 M) of $\mathrm{Ani}_{(aq)}$ and 10 mL (0.1 M) of $\mathrm{Py}_{(aq)}$ solutions were mixed with stirring. After 20 minutes, 10 mL of HCl (0.1 M) solution (catalyst) were added and then after another hour, 10 mL of APS (0.1 M) were added. The reaction mixture was left to stir for 24 hours. The mixture was filtered and washed with distilled water and then with acetone. The bluish-black precipitate was dried in an oven at 60 $\overset{o}{C}$ for two hours. In another optimization, the ratios of Ani, Py and HCl were kept constant however; different concentration of APS such as 0.5, 1, 1.5 and 2 M were employed. A Shimadzu UV-Vis 1700 spectrophotometer was used to record the UV-Vis spectra. The sample was dissolved in NMP and the spectra were recorded in spectral region ranging from 200 to 800 nm. Elemental analysis was performed in Pakistan Council of Scientific and Industrial Research (PCSIR) Laboratory Peshawar, Pakistan, using Elementar CHNS-0 elemental analyzer Germany. IR spectra were measured as KBr pellets, using Perkin Elmer spectrophotometer series 400 IR, in the region from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. The spectra were collected in ATR mode with 10 numbers of scans for all samples. The experimental band gap of the powder sample of Poly(Ani-*co*-Py) was measured in the range of 200 to 1000 nm, using Perkin Elmer spectrophotometer Lambda-1050.

2.2. Computational methods. All DFT calculations were carried out on GAUSSIAN 09 [33] and the results were visualized through Gabedit [40] and GaussView [41]. DFT and time depended DFT (TD-DFT) calculations were performed to determine the approximate structure of Poly(Ani-*co*-Py) and its conductivity. We have shown in our previous reports that oligomers up to five or six repeating units can accurately represent the polymeric characteristics [9-12]. Geometries of type **a**, **b**, **c** and **d** (Fig 1) of Poly(Ani-*co*-Py) were considered for calculations. Optimizations of these oligomers were confirmed from frequency calculation. Some of the calculated properties such as ionization potential (I.P), electron affinity (E.A), HOMO, LUMO, and band gap of all these three types (see Fig 1) of Poly(Ani-*co*-Py) were simulated. I.R spectra were simulated and scaled with a common scaling factor of 0.9613. The UV-vis spectra and natural bond orbitals (NBO), Mulliken charge analyses were simulated at TD-DFT-B3LYP/6-31G (d) and DFT-B3LYP/6-31G (d) level of theories, respectively. All calculations were performed in the gas phase, except UV-vis spectra which is simulated in $CHCl_3$ medium, using polarized continuum model (PCM).

RESULTS AND DISCUSSION

Synthesis of PANI and PPy. There are three different fundamental oxidation states of PANI; Leucoemeraldine (LB), Emeraldine Base (EB), and Pernigraniline Base (PNB). The EB form of PANI can be converted into a conducting state upon protonation, emeraldine salt (ES). Synthesis of all these states by chemical oxidative polymerization method is shown in the Figure 2a. Neutral PANIs have the general formula [(-B-NH-B-NH-)y(-B-N=Q=N-)1-y]x, where B and Q represent benzenoid and quinoid units, respectively. In this formula, y is the oxidation number and can be varied from 1, 0.5 and 0; from reduced to the fully oxidized one. PANI was synthesized with a common oxidative polymerization technique, although various reports are available on its chemical synthesis [36, 42-45]. Similarly, PPy typical polymerization mechanism is depicted in Figure 2b. These both homo-polymers are synthesized, compared with the well-known reported work for the validation of our experimental procedure. We found an excellent correlation among our and reported work [36, 42-45].

Synthesis of Poly(Ani-*co*-Py). Before the synthesis of copolymer, we synthesized homo-polymers; PANI and PPy according to the literature methods [36, 42-45]. The characteristics of the homopolymers were correlated with the reported work which validated our protocol. Experimental results and discussion in the subsequent discussions is limited to the copolymer. The synthesized Poly(Ani-*co*-Py) color is compared with their homopolymers analogues. Synthesized PANI is soluble in N-methyl-2-pyrrolidone (NMP), and blue in color (EB form). On the other hand, PPy is partially soluble in NMP (see Fig 3) but completely soluble in m-cresol and dark black in color. Copolymer, Poly(Ani-*co*-Py) is completely soluble in NMP and has black color with light orange filtrate (see Figure 3), where these three polymers are given along with their corresponding filtrates.

Elemental Analysis. Elemental analysis of Poly(Ani-*co*-Py) is listed in Table 1, percentages of C, H and N are 66.75, 5.25 and 23.87, respectively. A comparison of the theoretical and observed values demonstrates that hydrogen and oxygen are in more percentage than expectation, which may be attributed to moisture or incomplete combustion. The C/N ratio of the sample is close to 3. Given the close resemblance of structures **a-d** and the associated uncertainties in the experimental results, it is pointed out that the elemental analysis would not play a significant role in the identification of structure.

Mass Spectral Analyses. The mass spectrum provides vital information in assigning the structure of a compound. The structures **a-d** (shown in Figure 1) can be distinguished from the fragmentation pattern. The HR-ESI-MS spectrum of poly(Ani-*co*-Py) is shown in Figure 4. The spectra indicate that the peak at highest m/z for Poly(Ani-*co*-Py) product is 467.3, which is one unit lower than the theoretically calculated molecular mass (m/z 468 for type **c** and **d**) of a 3:3 oligomer of aniline and pyrrole (3:3 :: ANI:Py). For a 3:3 oligomer, the molecular mass should be an even number (Nitrogen rule). Therefore, the peak at ca. m/z = 467.3 is assigned to the M-1 fragment of 3:3 oligomer of ANI and Py (molecular formula $C_{30}H_{24}N_6$). A prominent peak at M-1 in the mass spectrum is common for the molecules containing acidic protons. The structures **a** and **b** have two hydrogens more than the structure **c** and **d**, and therefore, expected to have the highest m/z at 470. The lack of peak at m/z 470 probably eliminates the possibility of structures **a** and **b**. The structures **c** and **d** are the oxidized forms of **b** (dehydrogenation). Therefore, mass fragmentation pattern has been evaluated to determine the position of oxidation in order to differentiate between **c** and **d**. The mass spectrum of Poly(Ani-*co*-Py) consisted of several peaks, as shown in Figure 4. The mass fragmentation patterns of type **c** and **d** are shown in Figure 5. Structures **c** and **d** are expected to differ in the fragmentation of pyrrole part of the oligomer. Type **c** is expected to have a peak at m/z 440 whereas the type **d** is expected to have a peak at m/z 439. Analysis of the spectra indicate that the peaks are present at m/z 439 and 440 therefore, no conclusive remarks can be made from the analysis of these peaks. However, type **c** is expected to have a peak at m/z 339 compared to 337 or 338 (depending on the position of hydrogen loss for M-1 ion) for type **d**. Indeed, a peak at m/z 339 is observed in the spectrogram whereas no peaks were observed at m/z 337 and 338. The peak at m/z 339 is very helpful in deciding the position of oxidation. For any other position of oxidation, a peak at m/z 339 is not logical. The connectivity of three aniline rings can be rationalized by peaks at m/z 92 (Ph-NH), 183 (Ph-NH-Ph-NH) and 259 (Ph-NH-Ph-NH-Ph-). We believe that the M-1 peak was observed due to loss of proton from the NH next to pyrrole fragment because the fragment (Ph-NH-Ph-NH-Ph-NH) could not be located. So, this spectrogram and elemental analysis suggest that the sample has an oligomeric structure, consisting of 3ANI and 3Py rings. The mass spectral analysis suggests that the structure is probably **c**.

Optimized Geometric Structure. Geometries optimization of structures "**a**", "**b**", "**c**" and "**d**" of Poly(Ani-*co*-Py) were carried out at DFT method with B3LYP/6-31G (d) level of theory. The optimized geometric structures of types **a**, **b**, **c** and **d** of Poly(Ani-*co*-Py) are shown in Fig 6. Since the mass spectrum analysis suggest that the structure of the oligomer is more likely "**c**". The optimized geometry of type **c** is not planar but bent at one end. We discussed earlier that a planer structure of polymers provides an easy pathway for the movement of delocalized π-electron along its backbone. The oligomer in type "c" is not completely planar; therefore, delocalization of the π-electrons over the polymer backbone would be reduced. It would be expected to have less conductivity compared to homo polymers of aniline or pyrrole. These observations are consistent with the reported literature; Poly(Ani-*co*-Py) bears low conductivity contrast to their individual homo polymers [19, 20, 28]. We have also analyzed the geometries of type **d**. The optimized geometry of **d** is also bent. Both structures **c** and **d** are less bent compared to structure **b**. The structure **b** is bent much from planarity and it leads to very low conductivity (vide infra). Moreover, the structure **b** is also not supported by mass spectral analysis while type **a** has linear geometric structure.

UV-vis Spectral Characteristics. The experimental UV-vis spectrum of Poly(Ani-*co*-Py) is shown in Figure 7, whereas the simulated ones (type **a**, **b**, **c** and **d**) are depicted in Figure 8. The experimental UV-vis spectrum of Poly(Ani-*co*-Py) show uniforms absorption throughout the whole visible region and gives a broad peak in the UV region ca. 520 nm. Our experimental UV-vis spectrum are also in close agreement with recently reported work [21-24]. This single maximum absorption band peak is due to the transition of valance electron to the conduction band. This absorption band peak is correlated with the λ_{max} of type **a**, **b**, **c** and **d** which are listed in Table 3.

The TD-DFT simulated UV-vis spectrum of type **c** shows two peaks ca at of 574 (λ_{max}) and 337 nm. The simulated UV-vis spectrum of type **d** also shows two absorption transitions at 631 and 321nm. The maximum absorption peak (631 nm) is due to $\pi \rightarrow \pi^*$. Although the experimental UV-vis spectrum show a single broad peak in the region of 500-600 nm (specifically at 520 nm) but the diffuse nature of the peaks shows close resemblance to type **c**, where peak of low oscillator strength (574 nm, λ_{max}) is simulated. It may be argued that two peaks may be present but their low molar absorptivity might have resulted in the overall appearance of a single peak. The types **a** and **b** give maximum excitation energies at 387 and 3342 nm, respectively. Excitations energies of the type **a**, **b**, **c** and **d** of Poly(Ani-*co*-Py) along with their oscillator strengths and transitions states are shown in Table 3.

The observed 520 nm (λ_{max}) of the UV-vis spectrum can be easily correlated with the first allowed optical electronic excitation of type **c**, ca. at 574 nm, containing disturbed conjugation with spiral symmetry (*vide infra*). The experimental UV-vis spectra has nice correlation with that of type **c**, besides of having 50 nm difference. On the basis of this similar assignments and band peak position, we can easily conclude that the structure of the synthesized sample is just like type **c** (6Poly(Ani-*co*-Py), not **a, b** and **d**. Besides time dependent simulation, molecular orbital simulation and their different excitation transitions correlate nicely between the experiment and theory (especially in our case, see "Electronic Properties" section below).

Electronic Properties. Electronic properties such as HOMO, LUMO, IP, EA, and band gap of type **a**, **b,** **c** and **d** of Poly(Ani-*co*-Py) are simulated at B3LYP/6-31G (d) level of theory. Negative of HOMO and LUMO are taken as IP and EA, respectively using Koopman's theorem. Contours of HOMO and LUMO are depicted in Figure 9. The experimental band gap (indirect band gap) was measured from the synthesized powder of Poly(Ani-co-Py), which is 2.40 eV and is given in Figure 10. The experimental band gap is also correlated to the calculated band gaps of type **a**, **b, c** and **d** of Poly(Ani-*co*-Py), (see Table 4).

Electronic properties are simulated to account for the conductivity of Poly(Ani-*co*-Py), compared to homo polymers. The conductivity issue is extensively explained in the introduction, where J. Stejskal *et al*. reported a low conducting nature of the resulted copolymer [Poly(Ani-*co*-Py)]. The simulated band gaps are correlated with the experimental band gap, obtained from the powder sample of Poly(Ani-*co*-Py). The estimated band gaps of type **a**, **b, c** and **d** are listed in Table 4 which has 3.67, 4.10, 2.09 and 2.30 eV band gap, respectively. The band gap for type **c** can be correlated to the observed band gap of 2.40 eV. Although, this value is close to the simulated type **d**, but the UV-vis spectral analysis cannot be ignored as well (*vide supra*). The I.P and E.A of type **c** are 4.63 and 2.54 eV, which give rise to band gap of 2.09 eV. We have also evaluated the electronic nature of type **a** and **b**, but these structures are not supported by mass spectral analysis. Type **b** is less conducting than type **c** and **d**. Type **a** provides a relatively easy way for the delocalization of π-electron, whereas in **b,** this electronic cloud density is concentrated at one side.

Vibrational Spectral Characteristics of Poly(Ani-*co*-Py). Simulated IR spectra of type **a**, **b**, **c** and **d** of Poly(Ani-*co*-Py) are given in Figure 11, whereas a comparison of the observed and simulated type **c** is shown in Fig 12. The experimental IR spectrum of Poly(Ani-*co*-Py) reveals peaks ca. at 3296, 3052, 2934, 2364-2327, 1491, 1247, 1180, 1091, 981, 840, and 755 cm^{-1}. On the other hand, the simulated IR spectra of type **a**, **b**, **c** and **d** consist of 19 prominent band peaks. The experimental and calculated scaled IR peaks (type **a**, **b**, **c** and **d**) of Poly(Ani-*co*-Py), along with their approximate assignments are listed in Table 5. The simulated and observed NH stretching has little difference, as the theoretical data is for an isolated oligomer in the vacuum state while the experimental is that of condensed phase. Two NH bands are simulated for the type **a**, **b**, **c** and **d** whereas only one broad peak is observed experimentally which probably encompasses both peaks. The band peak due to N-H stretching of Py ring is simulated at ca. 3512 (type **a**), 3516 (type **b**), 3517 cm^{-1} (type **c**) and 3521 cm^{-1} (type **d**) in 6Poly(Ani-*co*-Py). The observed peak at ca. 3296 cm^{-1} is also because of N-H stretching of the aromatic ammines. This peak (3296 cm^{-1}) has 176, 134, 189 and 168 cm^{-1} differences to that of the type **a**, **b**, **c** and **d**, respectively. The peaks at ca. 2934-2852 cm^{-1} in the experimental IR spectrum have C-H stretching vibrations of the aromatic ANI rings. The functional group region of the infrared spectrum is not very helpful in differentiating among different types (**a-d**), more particularly between type **c** and **d**, mainly because of the presence of the similar functional groups. The fingerprint region is more helpful in assigning the structure of the oligomer. The most prominent and broad band peak in the observed spectrum of Poly(Ani-*co*-Py) is at ca. 1491 cm^{-1} which may be attributed to C=C and C-N stretching of both the Py and ANI rings. Band peak at ca. 1247 cm^{-1} of the experimental IR spectrum is a combination of C=C, C-N stretching and C-H wagging. This band peak has good correlation with the calculated 1293 cm^{-1} of type "**c**" compared to 1313 cm^{-1} for type "**d**" (see Table 5). The observed band peak at 1180 cm^{-1} has theoretical counterpart peak in type "**c**" at ca. at 1218 cm^{-1}, and it shows better correlation with the experiment. The observed peak at 1180 cm^{-1} is assigned to C-N stretching and N-H, C-H wagging. Although the peak for type **d** appears at 1177 cm^{-1} but it is lower than the experimental peaks.

The simulated values are, on the average, higher than the experimental values. Another observed peak at ca. 1090 cm^{-1} is assigned to the in-plane bending vibration of C-H and N-H bond. The next prominent experimental band peak in the finger print region is situated at 840 cm^{-1} on the basis of similar assignment (C-H and NH out of plane bending) it has good correlation with the calculated 846 cm^{-1} for type "**c**" than 908 cm^{-1} for type **d**. (see Table 5). The last observable peak of the chemically synthesized Poly(Ani-*co*-Py) is at 754 cm^{-1} which is attributed to out of plane of C-H and N-H bond of the Py rings. This band peak is also in close agreement with the simulated ones for type **c** (756 cm^{-1}) than type **d** (752 cm^{-1}). Moreover, not only the peaks in the simulated spectrum of type **c** show better correlation with the experimental IR spectrum, but also the shape of the peaks in the fingerprint region correlate nicely (particularly the peaks around 1200 cm^{-1}). Comparative discussion of the data of Table 5 gives more inclination towards type **c** compared to type **d**. This is consistent with the above characterization.

X-ray diffraction analysis. The X-ray diffraction pattern of the PANI, PPy, and Poly(Ani-*co*-Py) are given in Figure 13a-c, while a comparative (smoothed) XRD plot of all these species given in Fig 13d. It is widely explored in the literature that both PANI and PPy has amorphous nature [46, 47]. PANI gives a broad peak at 2θ of 25.30 which corresponds to (110) plane of PANI as can be clearly seen from Fig 13a. Furthermore, this broad peak indicates the amorphous nature of PANI with little amount of crystallinity [47]. On the other hand XRD spectra of PPy powders (Fig 13b) confirm its complete amorphous nature, without any sharp peak and broad peak ca at $2\theta = 25^{\circ}$ [46]. The broad peaks are characteristic of amorphous PPy and are due to the scattering from PPy chains at the inter-planar spacing.

XRD spectra of Poly(Ani-*co*-Py) has also a broad peak (see Fig 13c) which is located at $2\theta = 25^{\circ}$. Poly(Ani-*co*-Py) has much broader peak compared to their counterpart PANI and PPy oligomers. So, comparative analysis of the XRD spectra led us to conclude that Poly(Ani-*co*-Py) has high amorphous nature (lower crystallinity) which would be responsible for lower conducting nature as well.

Thermo gravimetric Analysis. The thermal stability of Poly(Ani-*co*-Py) was studied through thermo gravimetric analysis (shown in Figure 14) where 8 mg sample was used. The maximum weight loss was observed from 500-650 °C in which 42.5 % of sample were lost. For convenience, the weight loss of the sample is divided into three steps, weight loss occurs from 0 to 100 °C, this weight loss is about 8.75 % which is due to the loss of water of hydration. This number is consisted with % value of the elemental analysis. In the second step, weight loss occurs from 100 to 200 °C corresponding to the presence of trace amount of oligomers (both of ANI and Py) and may be some doped ion of the supporting electrolyte. From 200 to 300 °C, 10 % weight of the sample is lost whereas it is about 12.5 % at a temperature range of 300 to 400 °C. The weight loss further increases from 400 to 500 °C which is 26.25 % of the total sample. In the third step which start from 500 up to 650 °C, where continuous loss of mass occurred and stopped at 650 °C, at which the copolymer is completely dissociated. The TGA analysis led us to conclude that our copolymer has good stability up to 650 °C.

Morphological study. The scanning electron micrograph (SEM) of Poly(Ani-*co*-Py) at two different megapixels (2,000 and 10,000) is depicted in Figure 15. Our SEM results of Poly(Ani-*co*-Py) are in line with the recently reported work of J. Stejskal, P. Xu, J. Wilson, and co-workers [21-24, 46]. The different particle size can be distinguished into three categories, very big, average, and small as shown in Table S1 and Figure S1. The particle size was measured with nano-measure software. The 0.5 µm particles (first category), average size of all particles are of 0.27 µm, and small ones are about 0.05 µm. SEM analysis confirm the copolymer formation of Poly(Ani-*co*-Py) with granular morphology/flaky structures, completely different form that of its counterpart PANI (fibrillar morphology) [24] and PPy (convoluted tubules, dendrites, or fibrillar) [48]. The results of SEM image also favor the formation of Poly(Ani-*co*-Py) with closely packing.

CONCLUSIONS

We have determined the structure of an oligomer (copolymer) of aniline and pyrrole [Poly(Ani-co-Py)], through a combination of theoretical and experimental techniques. Molecular formula of Poly(Ani-co-Py) is determined by elemental analysis and mass spectrometry. The molecular mass 468 corresponds to a co-polymer, containing three aniline and three pyrrole units. The sequence of monomeric units in the oligomer is determined by mass spectral analysis and then confirmed by a comparison of theoretical and experimental spectroscopic properties. IR spectra reveal reasonable conclusive information about type c of 6Poly(Ani-co-Py). UV-vis spectral analysis strongly supports the type "**c**" as the approximate structure of the resulted oligomer. Moreover, the spiral nature of the 6Poly(Ani-co-Py) (type "**c**") can be account for its low conductivity. Estimated energy of the contours of HOMO and LUMO of type "**c**" is also supportive to low conducting nature of Poly(Ani-co-Py.

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