

ISSN: (Print) (Online) Journal homepage: <https://www.tandfonline.com/loi/gmcl20>

Synthesis and characterization of poly(pyrrole-co-aniline) copolymer using atmospheric pressure plasma polymerization

Eun Young Jung, Choon-Sang Park, Hyo Jun Jang, Gyu Tae Bae, Bhum Jae Shin & Heung-Sik Tae

To cite this article: Eun Young Jung, Choon-Sang Park, Hyo Jun Jang, Gyu Tae Bae, Bhum Jae Shin & Heung-Sik Tae (2022) Synthesis and characterization of poly(pyrrole-co-aniline) copolymer using atmospheric pressure plasma polymerization, *Molecular Crystals and Liquid Crystals*, 733:1, 103–113, DOI: [10.1080/15421406.2021.1972205](https://doi.org/10.1080/15421406.2021.1972205)

To link to this article: <https://doi.org/10.1080/15421406.2021.1972205>



Published online: 20 Sep 2021.



Submit your article to this journal [↗](#)



Article views: 90



View related articles [↗](#)



View Crossmark data [↗](#)



Synthesis and characterization of poly(pyrrole-co-aniline) copolymer using atmospheric pressure plasma polymerization

Eun Young Jung^{a†}, Choon-Sang Park^{b†}, Hyo Jun Jang^a, Gyu Tae Bae^a,
Bhum Jae Shin^c, and Heung-Sik Tae^{a,d}

^aSchool of Electronic and Electrical Engineering, College of IT Engineering, Kyungpook National University, Daegu, South Korea; ^bDepartment of Electrical and Computer Engineering, College of Engineering, Kansas State University, Manhattan, Kansas, USA; ^cDepartment of Electronics Engineering, Sejong University, Seoul, South Korea; ^dSchool of Electronics Engineering, College of IT Engineering, Kyungpook National University, Daegu, South Korea

ABSTRACT

This paper investigates the characteristics of poly(pyrrole-co-aniline) copolymer (PYPAN) films deposited by using an atmospheric pressure plasma (APP) polymerization relative to various concentrations of aniline and pyrrole monomers. The surface morphology and structure properties of PYPAN films are observed to strongly depend on the pyrrole concentration (%), which is confirmed by Field emission-scanning electron microscopy (FE-SEM), Fourier transforms-infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and time of flight-secondary ion mass spectrometry (ToF-SIMS). In particular, it is observed that the PYPAN film grown at an optimal pyrrole concentration condition (that is, aniline 25% and pyrrole 75%) shows a lower electrical resistance and higher deposition rate.

KEYWORDS

Aniline; atmospheric pressure plasma (APP) polymerization; conducting polymer; poly(pyrrole-co-aniline) copolymer; pyrrole

1. Introduction

The flexible optoelectronic devices, including organic light emitting diodes, sensors, organic photovoltaics, touch panels, energy storage devices, organic transistors, and photodetectors have recently attracted great attention due to the flexibility and light weight for integrating with wearable devices [1–3]. For a realization of flexible devices with strong stretchability, it is necessary to develop a new polymeric material for the conductive electrode in various flexible devices. As conductive electrodes, these flexible devices have mainly used the various materials such as an indium tin oxide, aluminum-doped zinc oxide, fluorine-doped tin oxide, graphene, and conducting polymers (CPs) [3]. The CPs are extensively applied to conductive electrodes for various flexible devices due to their good electrical, electrochemical and optical properties [4]. Many researches have been mainly reported on the synthesis of CPs for copolymerization using conventional chemical or electrochemical method in order to

CONTACT Heung-Sik Tae  hstae@ee.knu.ac.kr  School of Electronics Engineering, College of IT Engineering, Kyungpook National University, Daegu 41566, South Korea.

[†]These authors contributed equally to this work.

enhance the electrical conductivity, thermal stability, and mechanical flexibility of CPs [5]. Most of these conventional methods have limitations and disadvantages such as process complexity, toxicity, high cost, thermal heating process, and environmental problems. In order to overcome these disadvantages, the atmospheric pressure plasma (APP) polymerization method appears to be a promising alternative for depositing the copolymer film because the APP method has various merits such as a simple of equipment, ease synthesis, low cost, and thermal heating free process [6,7]. However, there have been no attempts on the copolymerization of CPs in the case of atmospheric pressure plasma (APP). Accordingly, this study carried out the synthesis of copolymerization by using an APP polymerization method with solution of aniline and pyrrole monomer. In this work, we systematically investigated the structural and electrical properties of poly(pyrrole-co-aniline) copolymer (PYPAN) films with respect to various concentrations of aniline and pyrrole monomer. The properties of PYPAN film are examined in detail by using field emission scanning electron microscopy (FE-SEM), Fourier transforms infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and time of flight-secondary ion mass spectrometry (ToF-SIMS). In order to monitor the suitability of conductive layer for flexible electronic devices, the electrical resistance of PYPAN films is measured after ex-situ doping with iodine (I_2) by two probe methods.

2. Experiment

The aniline (Sigma-Aldrich) and pyrrole (Sigma-Aldrich) monomers were mixed together in a flask. The total amount of the mixed solution was fixed at 40 ml, whereas the concentration of the mixed solution was varied by increasing the amount of pyrrole monomer. To efficiently dissolve the solution, the mixed solutions were stirred at an angular velocity of 500 rpm for 1-h without agglomeration. The mixed solution was used to deposit the PYPAN film by using APP polymerization method as a function of various concentrations of aniline and pyrrole monomer. The cleaning of substrate was performed by using an ultrasonic bath in an acetone, ethanol, and de-ionized water for 20 min for each one after drying. Then, the mixed solution was coated on glass substrates by APP polymerization method. The equipment for a novel APP polymerization system was reported in detail in a previous publication by C.-S. Park et.al. [6,7]. Argon gas was used as a plasma discharge gas at a flow rate of 2000 standard cubic centimeters per minute (sccm). The mixed solution of aniline and pyrrole was vaporized using a glass bubbler, which was supplied by argon gas with a flow rate of 200 sccm. The sinusoidal power with a peak value of 23 kV and a frequency of 26 kHz was applied to produce a plasma for depositing the PYPAN films on the glass substrate for 0.5-h. The detailed deposition conditions of PYPAN film were given in Table 1.

The surface morphology and cross-sectional images of the fabricated PYPAN films were examined by the field emission-scanning electron microscope (FE-SEM; Hitachi SU8220) with accelerating voltage and current of 5 kV and 10 mA, respectively. Before FE-SEM analysis, the samples for the PYPAN films were coated with platinum material before being loaded into the chamber. In order to identify the crystalline phase of the PYPAN films, the crystalline phases of PYPAN films were determined by a Fourier

Table 1. Deposition conditions of poly(pyrrole-co-aniline) copolymer (PYPAN) films deposited by atmospheric pressure plasma (APP) polymerization method with respect to the various pyrrole concentration.

Monomer solution	Liquid monomer (pyrrole + aniline), 40 ml					
Mixing conditions		Case I	Case II	Case III	Case IV	Case V
	Aniline (%)	100	75	50	25	0
	Pyrrole (%)	0	25	50	75	100
Vapor pressure				200 sccm		
Ar gas pressure				2000 sccm		
Voltage				23 kV		
Frequency				26 kHz		
Deposition time				0.5 h		
Bluff-body height				15 mm		
Deposition temperature				R. T.		

transformation infrared spectroscopy (FT-IR; Vertex 70, Bruker) at the Korea Basic Science Institute (KBSI; Daegu). The FT-IR spectra were measured by averaging 128 scans at a wavenumber resolution of 0.6 cm^{-1} in the range from 600 to 4000 cm^{-1} under the attenuated total reflection (ATR) mode. An X-ray photoelectron spectroscopy (XPS; ESCALAB 250XI, Thermo Fisher Scientific) was used to investigate the surface chemical compositions and atomic concentration of PYPAN film. In the XPS measurement, the voltage and current of the monochromatic Al $K\alpha$ X-ray source (energy = 1486.7 eV) were 15 kV and 20 mA , respectively. The measurement area was $500\text{ }\mu\text{m} \times 500\text{ }\mu\text{m}$ and the pressure was maintained below 10^{-8} Pa . The C 1 s spectrum (285.0 eV) was used to calibrate the energy scale. The element compositions of the deposited PYPAN film were identified from XPS survey scans and quantified with Thermo Avantage software (v.5.977) using a Shirley background. For high-resolution spectra, the constant analyzer energy modes were used at 200 eV for the survey scan and 50 eV pass energy for the high-resolution spectra, respectively. During the measurement of the PYPAN film, an additional electron gun was used to adjust the charge compensation for maintaining surface neutralization. To fit the curve for the high-resolution C 1 s , N 1 s and O 1 s peaks, the deconvolution of C 1 s and N 1 s peaks was analyzed by the Thermo Avantage software. The peaks were deconvoluted using Gaussian-Lorentzian peak shapes (constrained between 80 and 100% Gaussian) and the full-width at half maximum (FWHM) of each line shape was constrained between 2.0 and 3.0 eV . The surface structure and composition of PYPAN films were examined by the time of flight-secondary ion mass spectrometry (ToF-SIMS; ION-TOF GmbH, Germany) with a bismuth primary-ion (Bi^{3+}) gun source. The pressure of ToF-SIMS chamber was maintained below $1 \times 10^{-9}\text{ Torr}$. The negative-ion and positive-ion mass spectra of a $500\text{ }\mu\text{m} \times 500\text{ }\mu\text{m}$ area were acquired at a Bi^{3+} primary-ion beam of 0.5 pA current accelerated at 30 keV .

Also, in order to check the suitability of conductive layer for flexible electronic devices, the electrical resistance of PYPAN films was measured at the room temperature condition using two probe methods after ex-situ doping with iodine (I_2). The electrical resistance was obtained at the room temperature condition using an electrometer (FLUKE 179). For ex-situ I_2 doping, the deposited PYPAN film had been placed in a sealed glass container containing 2 g of solid I_2 crystals (Sigma-Aldrich Co., USA, 99.99%) for 30 min [8].

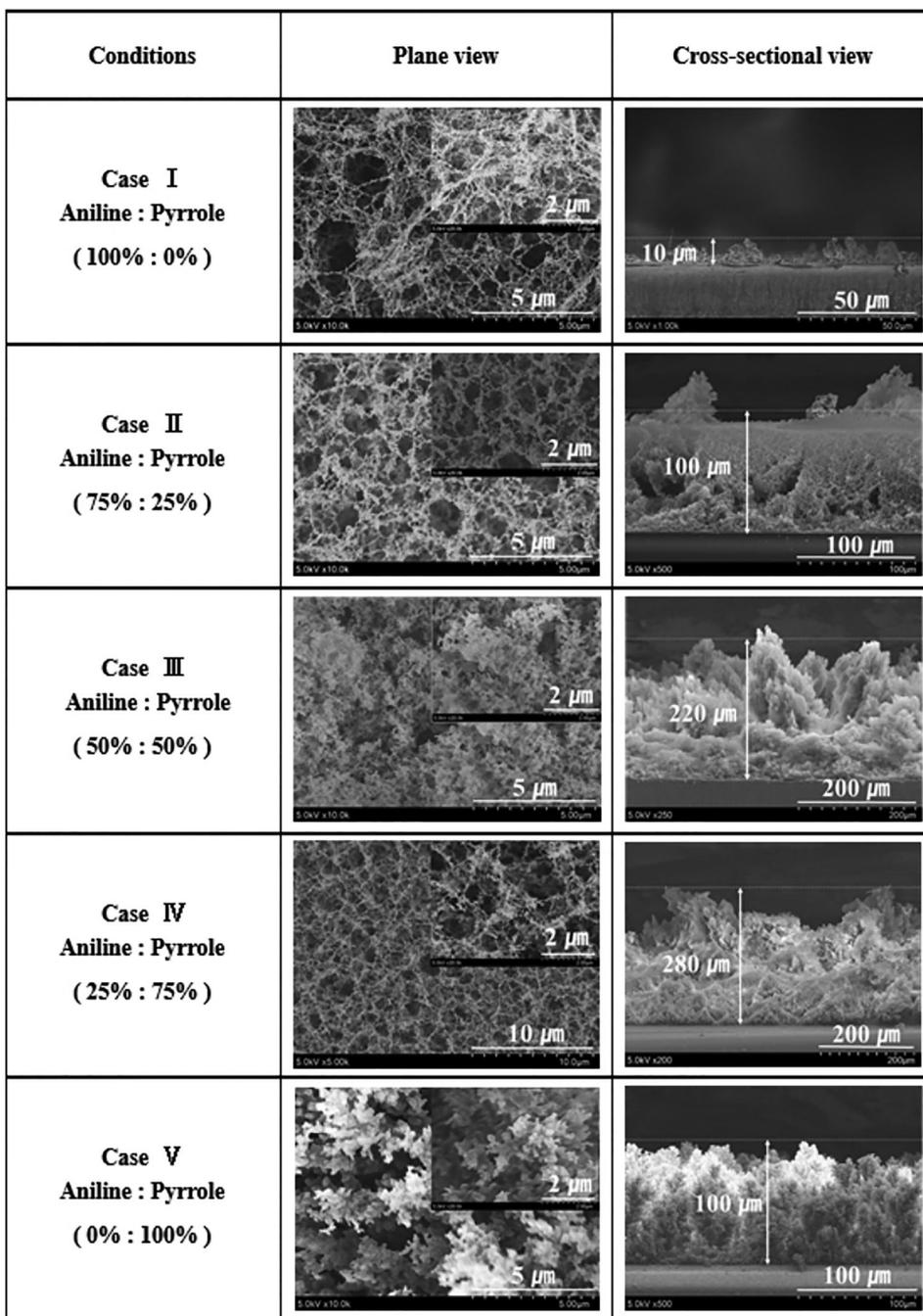


Figure 1. Plane and cross-sectional scanning electron microscopy (SEM) images for poly(pyrrole-co-aniline) (PYPAN) copolymer film deposited on glass substrate by using the new atmospheric pressure plasma (APP) polymerization method with increasing the pyrrole concentration.

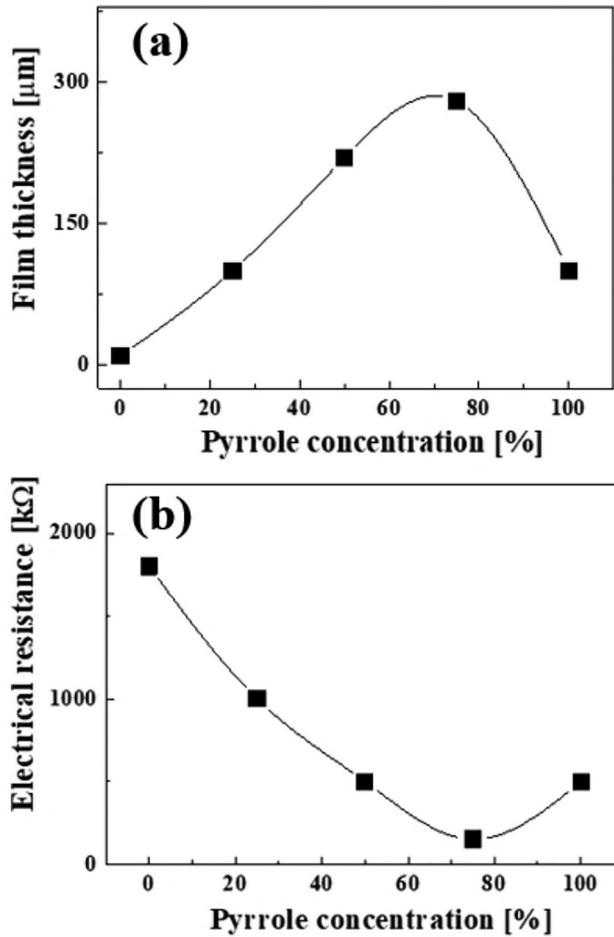


Figure 2. (a) Film thickness and (b) electrical resistance of PYPAN films deposited by using the APP polymerization method with increasing the pyrrole concentration.

3. Result and discussion

Figure 1 show the plane and cross-sectional images by the field emission-scanning electron microscope (FE-SEM) of PYPAN films deposited on glass substrate under the aniline and pyrrole monomer conditions with various concentrations. As shown in Fig. 1, for homo-polymer of PANI, the film illustrated spherical nanoparticles and nanofibers with irregularly cross-linked networks [8]. Plus, for homo-polymer of PPy, the film shows spherical nanoparticle. Furthermore, the particle size of PANI film was observed to be smaller than that of PPy. Whereas, when increasing the pyrrole concentration, the PYPAN films was composed of nanofibers with irregularly cross-linked networks and spherical nanoparticles [9,10]. In this case, the particle size of PYPAN films was observed to be larger than that of pure PANI with increasing the pyrrole concentration. The increase of particle size is presumably due to the fact that the PYPAN films can further form hydrogen bonds as well as π - π interactions with an increase in the concentration of pyrrole monomer [11–13]. Thus, the PYPAN films had a homogeneous and

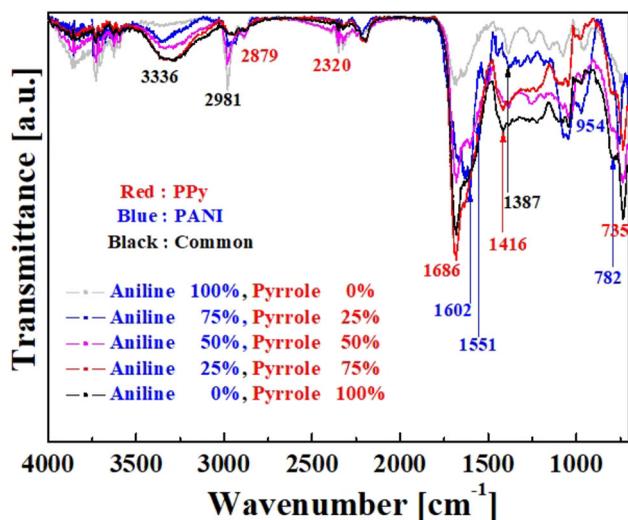


Figure 3. Fourier transformation infrared spectroscopy (FTIR) spectra of PYPAN films deposited on glass substrate by using the APP polymerization method with increasing the pyrrole concentration.

high cross-linked morphology with increasing the pyrrole concentration, as shown in Fig. 1.

Figure 2a and b shows the variations in the film thickness and electrical resistance for PYPAN films deposited by APP polymerization method relative to pyrrole concentration (%), respectively. The film thicknesses of PYPAN film were measured through the cross-sectional FE-SEM images of Fig. 1. At pyrrole concentration of 0%, namely, pure PANI case, the film thickness was about 10 μm , and at pyrrole concentration of 100%, namely, PPy case, the film thickness was 100 μm . As shown in Fig. 2a, the film thickness of PANPY films was observed to be increased when increasing the pyrrole concentration. In particular, the maximum film thickness of 280 μm for the PYPAN film was obtained at a pyrrole concentration of 75%. Thus, the rapid incorporation of two different kinds of fragments of monomers would cause this increase of π - π interactions, thereby resulting in the higher deposition rate of PYPAN film during APP polymerization [13–15].

Figure 2b shows the electrical resistance of PYPAN films deposited on the substrates of interdigitated electrodes (IDEs) as a function of pyrrole concentration (%). The iodine doping was carried out ex-situ in order to enhance the electrically conductive properties of the PYPAN film. The changes in the electrical resistances of deposited PYPAN films including the homopolymer PANI and PPy were indicated in Fig. 2b. The electrical resistances of homopolymer of PANI and PPy were about 1800 and 500 $\text{k}\Omega$, respectively. The homopolymer of PANI have a higher electrical resistance than the PPy, meaning that the electrical contact was weak between the nanoparticles and nanofibers due to small nanoparticles with nanofiber networks, as shown in Fig. 2 [13]. When the content of pyrrole achieved a certain amount, the electrical resistance of PYPAN film could reach the same order of magnitude to the homopolymers of PPy.

Table 2. Absorption peaks of Fourier transformation infrared spectroscopy (FTIR) for crystalline phases of PYPAN films deposited on the glass substrate by APP polymerization method with increasing the pyrrole concentration.

PANI peak	782 cm ⁻¹	C-H out-of-plane deformation
	1551 cm ⁻¹	C=C stretching vibrations of benzenoid ring
	1602 cm ⁻¹	C=N stretching vibrations of quinoid ring
PPy peak	735 cm ⁻¹	C-H out of plane bending
	1416 cm ⁻¹	C-N stretching vibrations
	1686 cm ⁻¹	C-C and C=C stretching vibrations
	2320 cm ⁻¹ , 2879 cm ⁻¹	C-H stretching vibration
Common peak	1387 cm ⁻¹	C-H in-plane vibration of benzene ring
	2981 cm ⁻¹	C-H stretching
	3336 cm ⁻¹	N-H stretching

The electrical resistance of the deposited PYPAN film was remarkably decreased with increasing the pyrrole concentration, when compared to the pure PANI film. The improvement of the electrical conductivity of the PYPAN film is attributed to the formation of a conductive path between the nanoparticles and nanofibers induced by the long conjugated π -bonds and dense nanoparticles, as shown in Fig. 2 [11–13]. From these results, the change of electrical resistance was in good correlation with the morphology of PANPY film [10]. Also, the optimum condition of PYPAN film was established with lower electrical resistance (150 k Ω) at a pyrrole concentration of 75%.

Figure 3 shows the Fourier transformation infrared spectroscopy (FT-IR) spectra ranging from 700 to 4000 cm⁻¹ of PYPAN films deposited on the glass substrates by using an APP polymerization method with respect to various concentrations of aniline and pyrrole monomers. For PANI, the peaks at 1550 and 1602 cm⁻¹ are attributed to benzenoid (C=C) and quinoid (C=N) ring stretching vibrations, respectively. The band at 782 cm⁻¹ is ascribed to the C-H out-of-plane deformation [5,16]. For PPy, the band at 735 cm⁻¹ correspond to C-H out of plane and the bands at 1416 and 1686 cm⁻¹ are ascribed to the C-N stretching vibrations and C-C/C=C stretching vibrations, respectively. Besides, the peaks at 2320 and 2879 cm⁻¹ are due to C-H stretch [17–19]. For the common peak of PANPY film, the assigned N-H vibration at 3363 cm⁻¹ is attributed to the C-H stretch and the bands at 1387 and 2981 cm⁻¹ are ascribed to the C-H in-plane vibration benzene ring and C-H stretching, respectively [5,16–19]. The FTIR peak assignments of PYPAN film deposited by APP polymerization method were given in Table 2. In FTIR spectra, two phases originating from both PANI and PPy were clearly observed in the crystalline phase of the PYPAN film. With an increase of pyrrole concentration, the pyrrole chain peaks and peak intensities of π -conjugated bonds (1551 and 1602 cm⁻¹) were increased, respectively [10]. This increase of π -conjugated bonds is expected to enhance π - π stacking of inter-molecular polymer chain, resulting in good carrier mobility and improved electrical conductivity [11,12].

Figure 4 shows the high-resolution spectra with deconvolution peaks of PYPAN film grown at optimal pyrrole concentration condition (pyrrole 75% and aniline 25%) by APP polymerization method. As shown in Fig. 4 and Table 3, the XPS elemental composition of PYPAN film grown at optimum condition (pyrrole 75% and aniline 25%) consists of carbon, nitrogen, and oxygen. The atomic concentrations of carbon, nitrogen, and oxygen were 74.7, 15.3, and 10.0%, respectively. The contents of C 1s spectrum at 284.5, 285.6, 286.6, 288.0, 289.3, and 290.9 eV were confirmed to be

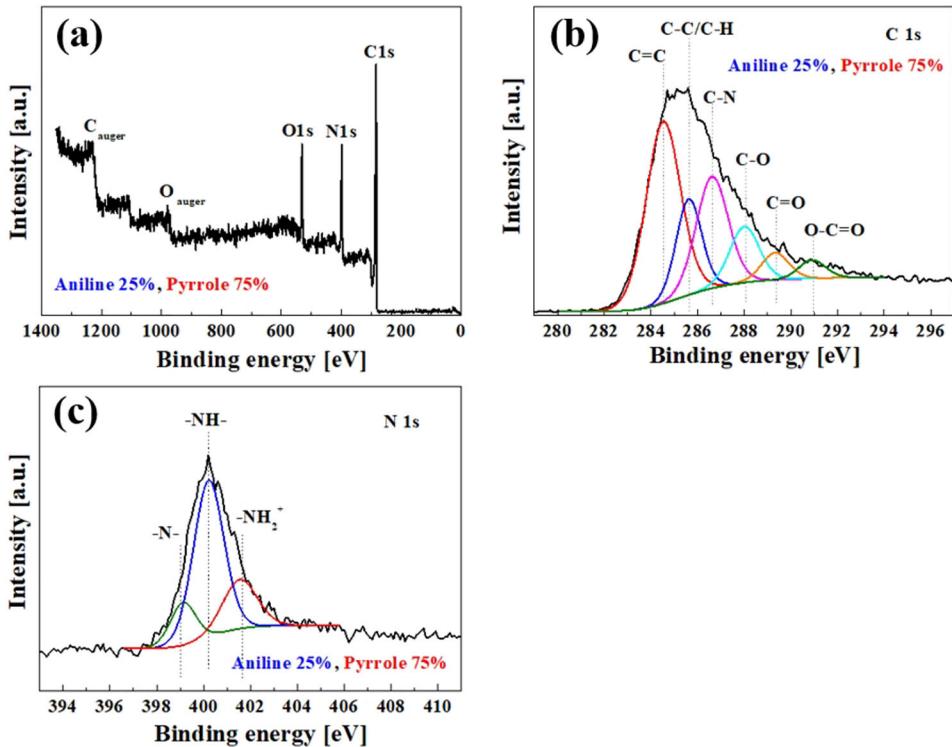


Figure 4. High-resolution spectra with deconvolution peaks of PYPAN film grown at optimal pyrrole concentration condition (pyrrole 75% and aniline 25%) by APP polymerization method.

Table 3. The elemental composition of X-ray photoelectron spectroscopy (XPS) spectra of PYPAN film deposited on the glass substrate by APP polymerization method with optimal condition (pyrrole 75% and aniline 25%).

Conditions	C 1s (atomic %)	O 1s (atomic %)	N 1s (atomic %)
Pyrrole 75%, aniline 25%	74.7	10.0	15.3

Table 4. Peak assignment (BE, eV) and envelope composition (% total = 100) of C 1s and N 1s spectra for chemical structure of PYPAN film deposited on the glass substrate by APP polymerization method with optimal condition (pyrrole 75% and aniline 25%).

Conditions	C 1s (%)						N 1s (%)		
	284.5 eV C=C	285.6 eV C-C/C-H	286.6 eV C-N	288.0 eV C-O	289.3 eV C=O	290.9 eV O-C=O	398.8 eV -N-	399.9 eV -NH-	401.2 eV -NH ₂ ⁺
Pyrrole 75% aniline 25%	41.4	16.1	23.5	10.9	4.9	3.2	14.6	63.2	22.2

corresponding to C=C, C-C/C-H, C-N, C-O, C=O, and O=C-O, respectively [20,21]. Also, the contents of N 1s spectrum have three peaks centered at 398.8, 399.9, and 401.2 eV, which correspond to the quinoid imine (-N-), benzenoid amine (-NH-) structure, and protonated amine (-NH₂⁺) [8,20,21]. For C 1s and N 1s peaks, the assignments of the fitted component and envelop compositions were summarized in Table 4. The high electrical conductivity of PYPAN film is deeply related to the proton acid

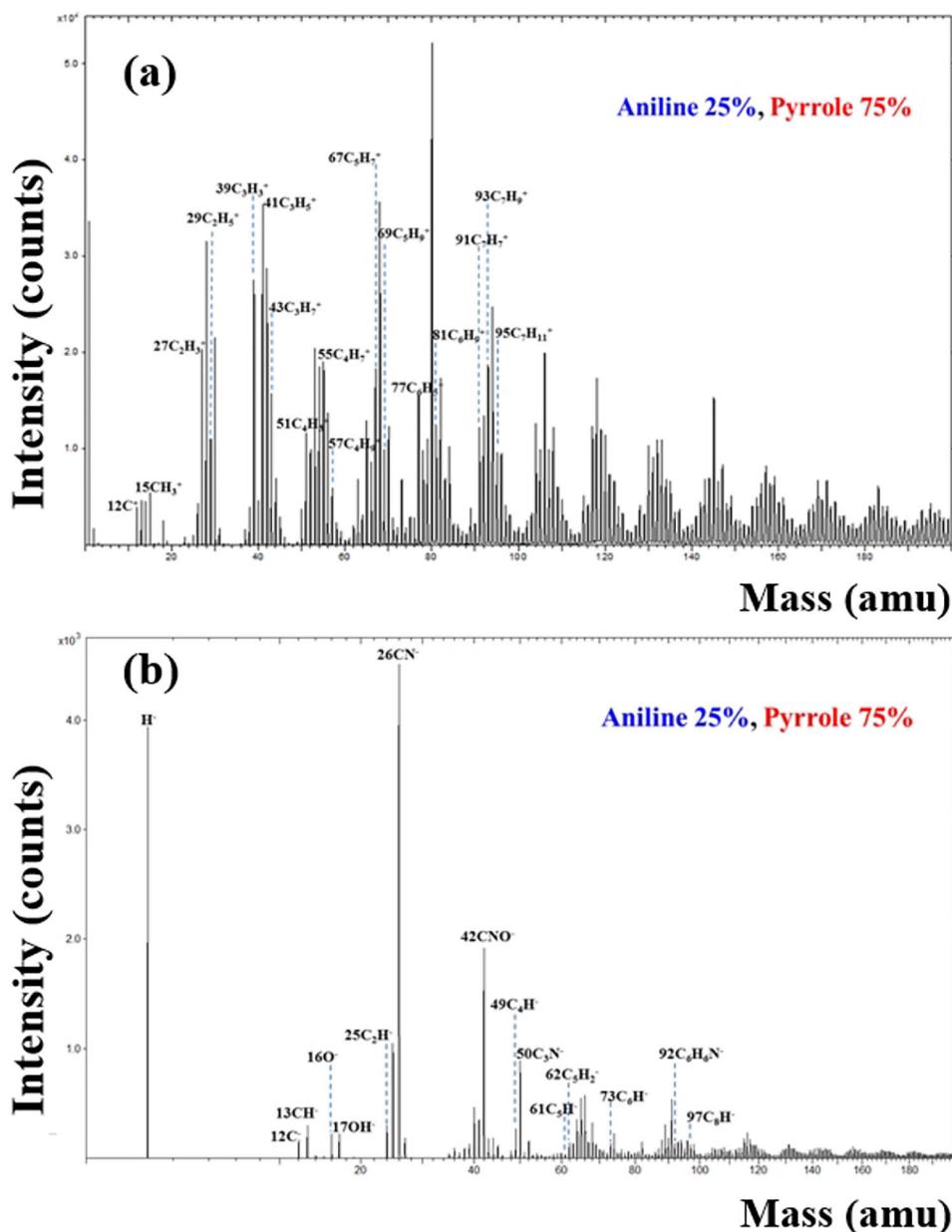


Figure 5. (a) Positive-ion and (b) negative-ion static mass spectra ranging from 0 to 200 amu of time of flight-secondary ion mass spectrometry (ToF-SIMS) for PYPAN film grown at optimal pyrrole concentration condition (pyrrole 75% and aniline 25%) by APP polymerization method.

preferred to the N of quinone ring. When the aniline was directly connected with the pyrrole, the H^+ of protonation aniline formed quasi-hydrogen bonding with N of adjacent pyrrole resulting from the strong electronegativity of N [10]. When these Ns were protonated, the proton charge was delocalized in the vicinity of aromatic ring. The resultant conjugated system, that is, PYPAN film, was formed, thereby resulting in high electrical conductivity [11–13].

To identify the polymer structure of PYPAN film grown at an optimal pyrrole concentration condition (pyrrole 75% and aniline 25%), the PYPAN film was measured in both the positive and negative ion modes using ToF-SIMS analysis. Figure 5 shows the positive-ion (a) and negative-ion (b) static mass spectra ranging from 0 to 200 amu for the PYPAN film. As shown in the positive-ion spectra of Fig. 5a, some characteristic peaks of PYPAN film were detected as follows: the ions at 39, 41, 43, 51, 55, 57, and 77 amu were assigned to $C_2H_5^+$, $C_3H_3^+$, $C_3H_5^+$, $C_3H_7^+$, $C_4H_3^+$, $C_4H_9^+$, and $C_6H_5^+$, respectively. These positive-ion fragments were attributed to the PANI and PPy polymer chains. As shown in the negative-ion spectra of Fig. 5b, the peaks at $m/z=26$, 42, and 50 amu were assigned to CN^- , CNO^- , and C_3N^- , respectively. These negative-ion fragments were also originated from the PANI and PPy polymer backbone [8,20,21]. The ToF-SIMS spectra illustrated that several fragmentation peaks originating from both PANI and PPy were clearly observed in the PYPAN film.

5. Conclusions

This article investigated the characteristics of PYPAN film deposited at room temperature by using the APP polymerization method with various concentrations of aniline and pyrrole monomers. In the deposited PYPAN film, a larger nanoparticle and nanofiber with irregularly cross-linked networks was observed, confirmed by the FE-SEM images. The electrical resistance of PYPAN films was decreased with an increase of pyrrole concentration. The characteristic peaks of PANI and PPy polymer chains were observed in the PYPAN film, as confirmed by FT-IR, XPS, and ToF-SIMS. These results confirmed that the deposited PYPAN films had an enhanced electrical property, *i.e.*, lower electrical resistance than pure PANI. Furthermore, our case studies illustrated that there was an optimal pyrrole concentration condition for obtaining the PYPAN film applicable to the flexible electronic devices: that is, the PYPAN films with a high thickness of 280 μm and low electrical resistance of 150 $k\Omega$ were successfully grown at an optimal pyrrole concentration condition (75%).

Funding

This research work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MOE) (No. 2018R1D1A1B07046640) and Korea government (MOE) (No. 2016R1D1A1B03933162).

References

- [1] J. Wu *et al.*, *RSC Adv.* **8** (11), 5721 (2018). doi:10.1039/C8RA00023A
- [2] S. Y. Ahn *et al.*, *Adv. Opt. Mater.* **5** (3), 1600512 (2017). doi:10.1002/adom.201600512
- [3] Y. Ma, and L. Zhi, *Small Methods* **3** (1), 1800199 (2019). doi:10.1002/smt.201800199
- [4] A. S. Hammad *et al.*, *IOP Conf. Ser: Mater. Sci. Eng.* **290**, 012001 (2018). doi:10.1088/1757-899X/290/1/012001
- [5] A. K. Sharma *et al.*, *Aml.* **6** (5), 414 (2015). doi:10.5185/amlett.2015.5690
- [6] C. S. Park *et al.*, *Materials* **9** (39), 1 (2016).
- [7] C. S. Park *et al.*, *Materials* **9**, 812 (2016).

- [8] C.-S. Park *et al.*, *Materials* **10**, 1272 (2017).
- [9] S. Palaniappan, S. B. Sydulu, and P. Srinivas, *J. Appl. Polym. Sci.* **115** (3), 1695 (2010). doi:[10.1002/app.31208](https://doi.org/10.1002/app.31208)
- [10] X. Ou, and X. Xu, *RSC Adv.* **6** (17), 13780 (2016). doi:[10.1039/C5RA26469C](https://doi.org/10.1039/C5RA26469C)
- [11] S. Wang *et al.*, *J. Mater. Chem. C.* **8** (2), 528 (2020). doi:[10.1039/C9TC06300E](https://doi.org/10.1039/C9TC06300E)
- [12] N. Su, *Nanoscale Res Lett* **10** (1), 997 (2015). 301.
- [13] H. Karami, S. Jafari, and F. Goli, *Int Int. J. Electrochem. Sci.* **11**, 3056 (2016). doi:[10.20964/110403056](https://doi.org/10.20964/110403056)
- [14] S.-H. Cho *et al.*, *Surf. Coat. Technol.* **174-175**, 1111 (2003). doi:[10.1016/S0257-8972\(03\)00596-6](https://doi.org/10.1016/S0257-8972(03)00596-6)
- [15] V. Chan *et al.*, *IJNT.* **14** (12), 1045 (2017). doi:[10.1504/IJNT.2017.087781](https://doi.org/10.1504/IJNT.2017.087781)
- [16] C. J. Mathai *et al.*, *J. Phys. D: Appl. Phys.* **35** (17), 2206 (2002). doi:[10.1088/0022-3727/35/17/318](https://doi.org/10.1088/0022-3727/35/17/318)
- [17] Z. Ahmad *et al.*, *Macromol. Res.* **24** (7), 596 (2016). doi:[10.1007/s13233-016-4081-x](https://doi.org/10.1007/s13233-016-4081-x)
- [18] M. M. Kamal, and A. H. Bhuiyan, *AMR.* **741**, 59 (2013). doi:[10.4028/www.scientific.net/AMR.741.59](https://doi.org/10.4028/www.scientific.net/AMR.741.59)
- [19] V. Ponnswamy, P. Jayamurugan, and S. Deivanayaki, *J. Optoelectr. Adv. Mater.* **12** (2), 315 (2010).
- [20] S. Elmas *et al.*, *RSC Adv.* **6** (74), 70691 (2016). doi:[10.1039/C6RA12886F](https://doi.org/10.1039/C6RA12886F)
- [21] M. M. Mahat *et al.*, *J. Mater. Chem. C.* **3** (27), 7180 (2015). doi:[10.1039/C5TC01038A](https://doi.org/10.1039/C5TC01038A)