J. Myanmar Acad. Arts Sci. 2018 **Vol. XVI. No.2**

EFFECTS OF MONOMER ON THE ELECTRICALLY CONDUCTIVE POLYMER

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Abstract

The effects of monomers on the electrically conductive polymer films were studied. In the preparation of conductive film, pyrrole (Py) and formyl pyrrole (FPy) were used as the source of monomers. Trifluoroacetic acid (TFA) and chloroform were utilized as a catalyst and solvent. One of the synthesis parameters, mole fractions of FPy against Py, was systematically varied from 0.1, 0.3, 0.5, 0.7 to 0.9 respectively. Then, the effects of monomers on the electrical properties of obtained conductive polymer films were studied. The formation of film was characterized and confirmed by ultraviolet-visible(UV-vis), X-rays diffraction (XRD) and Fourier transform infrared spectrometry(FTIR). Frequency dependent electrical conductivity of the prepare film is increased with the increasing mole fraction of FPy.

Keywords: conductive polymer, pyrrole, formylpyrrole, molar fraction

Introduction

Electrically conductive polymers with conjugated double bonds have been attracting in much attention of advanced materials due to their wide range of electrical conductivity. Such conductivities of polymers can be achieved with various doping levels while maintaining mechanical flexibility and high thermal stability. Among them, polypyrrole (PPy) is commonly used since it can easily be prepared pyrrole monomer in various organic solvents and in an aqueous media by chemical and electrochemical polymerization methods. In these preparation, polymerization condition and introducing additives into the reaction mixture could influence the properties of resultant conductive PPy [1-3]. Besides, using single monomerby chemical polymerization method usually used to obtain polymer powders which have limitations to fabricate the desired shape and size of electrodes [4-6]. Salmon *et al.,* reported chemical polymerization of pyrrole for forming PPy films in

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the presence of sulfuric acid in ethanol [7]. But, the resultant films were fragile and unstable in their polymer properties. Consequently, very few investigations were examined for single component PPy films prepared by chemical methods. Later, Yusuke *et al.,* successfully synthesized conductive copolymer films by using two monomers, pyrrole (Py) and formylpyrrole (FPy),which could construct conjugated structure between them showing methine group [8]. Recently, Sirilak*et al.,* modified the work of Yusuke by using surfactant and dopant, sodium dodecylsulfate (SDS) and poly (styrenesulfonate) (PSS)[9]. However, the final product could be obtained only polymer particles when emulsion polymerization method was used. On the other hand, they observed that electrical conductivity increased with the increasing surfactant concentration of SDS. Yusuke *et al.,* studied the effect of acidic catalysts in the polymerization and compare the conductivity of the resultant films. In addition to the different types of carboxylic acids, other important parameter, the amount of monomers, will be the critical role for the copolymer films. In the present work, depending of the formation of films, the effect of monomers in the copolymerization was studied by varying the mole fraction of FPyagainstPyin order to compare the conductive properties of the resultant films.

Materials and Method

Firstly two monomers solution containing (200 mg, 3 mmol) of Py and (286 mg, 3 mmol) of FPy were mixedand dissolved in 2 mL of chloroform ($CHCl_3$). They were stirred at room temperature for30 min. Then,13 mmol of trifluoroacetic acid (TFA) in2 mLof $CHCl_3$were added to the monomer solution. As a result, the color of the solvent immediately changed from transparent brown to yellowish red. Then, the mixed solution was spin-coated onto 9 cm diameter of the Petri dish at 20 rpm by using a homemade spin coater. The polymerization was carried out for 2 h at room temperature, and finally a film was formed in a Petri dish. The obtained film was a metallic greenish black and insoluble in several solvents. When the polymerization was performed using TFA in $CHCl_3$, the mole fraction of FPy was varied from 0.1 to 0.9. Total monomer content in each feed solution was 6 mmol in 2 mL of $CHCl_3$ in the presence of 13 mmol of TFA system. The synthesis route of polymer films was depicted in Fig.1. It was found out that when only one monomer Py was used, the color of the monomer Py solution changed from transparent color to a brownish black film when TFA was added and thus a fragile film was obtained without a metallic greenish black color. In contrast, the color of the solution changed from transparent brown to yellowish red and then the formation of the shiny greenish black film was observed when both monomers were mixed. Fig.2 shows the formation of polymer film in the Petri dish. For the measurement of electrical conductivity, chemical doping was performed on the films. Each film was washed with excess water and acetone and then dry 24 h in the desiccator. After that, a small amount of I_2 was put for 24 hin a closed vessel for chemical doping. Then, the electrical conductivity of the doped film was measured by LCR meter.

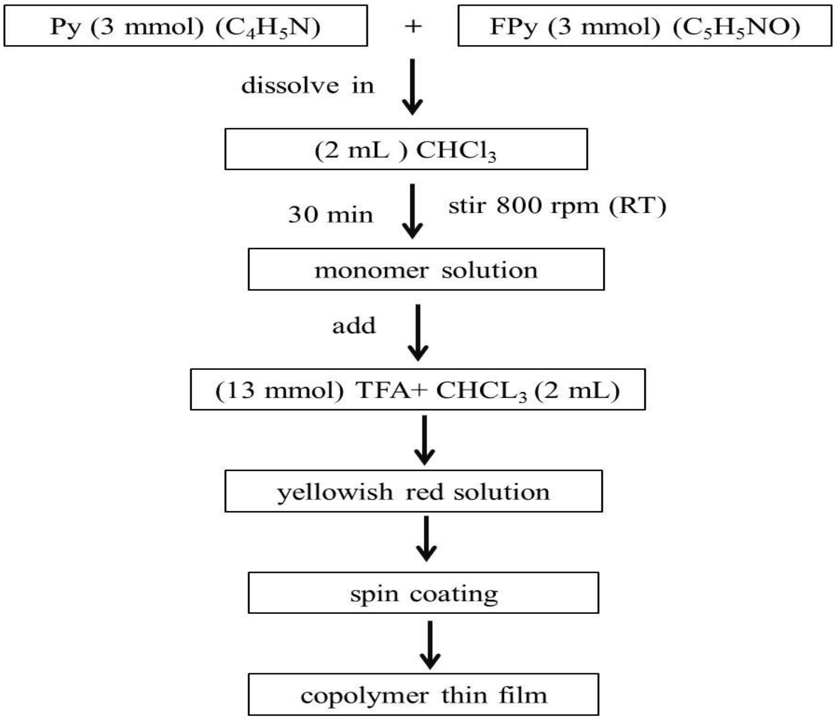

Figure 1. Preparation route of copolymer film

Figure 2. Conductive polymer film

Characterization Techniques

The functional groups of prepared films were investigated by FT-IR NICOLET iS5 spectrophotometer by using the iD7 ATR mode within the wave number from 4000 cm^{-1} to 650 cm^{-1}. The chemical doping of films were analyzed by FTIR 8400 Shimadzu spectrophotometer by using a KBr pallet method in the MIR radiation with the wave number from 4000 cm^{-1} to 400 cm^{-1} range with a resolution of 4.0 cm^{-1}. RIGAKU Miniflux 600 using CuK_{α} radiation (40 kV, 40 mA) over a 2θ range from 10º to 70º on a powder type X-ray diffractometer equipped with a diffracted-beam graphite monochromator was used to examine the crystal structure of copolymer film. The electrical properties were measured by GW Instek LCR-8110G meter.

Results and Discussion

XRD spectra shown in Fig.3were the copolymer film before and after Iodine (I_2) doping. No diffraction peaks could be detected except only for the broad peak around at the diffraction angle 23.3º which is corresponding to amorphous polymer. Since the crystallinity is much better after I_2 doping, the intensity is higher than the sample before I_2 doping.

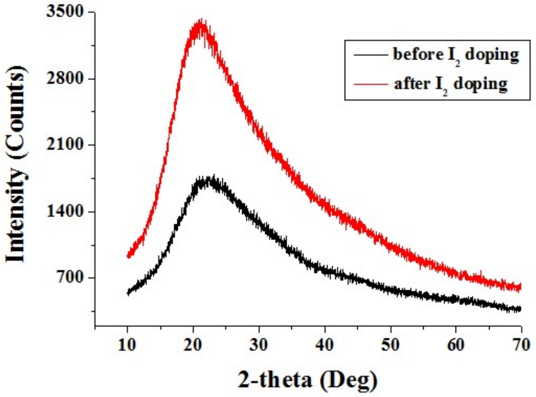

Figure 3. XRD spectra of conductive polymer film before (black) and after (red) I_2 doping

UV-vis spectrum of resultant copolymer film is shown in Fig.4. It was noted that characteristic absorption band of the π-π* transition of polypyrrole is appeared at around 492 nm. This fact indicated that the FPy group was incorporated into the chemical structure of the conjugated polymer chains. Since Py and FPy had no absorption band at about 500 nm, this could be assigned with π-π* transition of the C=C double bond, which was formed by the copolymerization. In addition, weaker and broader band was appeared at about 700 nm. This strongly implied that the bipolaron state of polypyrrole was present in the films. This indicated that such strong acid (TFA) strongly interacted with pyrrole segments to form bipolaron state.Fig.4 shows UV-Visible spectrum of Py-FPy copolymer film using by acid catalyst (TFA).

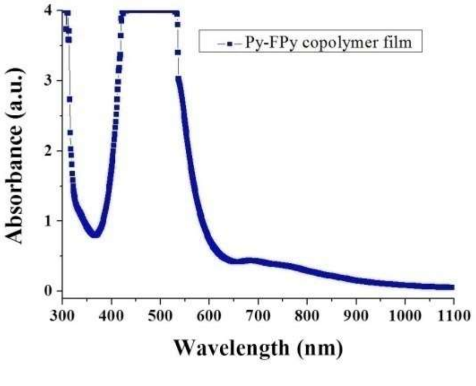

Figure 4. UV-Visible spectrum of Py-FPy copolymer film using by acid catalyst (TFA)

Fig.5shows FT-IR spectra of the copolymers prepared ateach mole fraction of FPy. As indicated by (a), N-H stretching vibrations of two types (3380 and 3260 cm^{-1}) were present in the film. The peaks (b) of saturated C-H stretching at 2935 and 2866 cm^{-1} became very weak when the mole fraction was higher than 0.5. This indicated that the conjugated structure was increased in the polymer backbone, when the mole fraction of FPy increased. In peaks (c) and (d) for C=C double bond stretching of the pyrrole ring at1626 and 1538 $cm^{-1}$and C=N stretching at 1490 cm^{-1}, these were attributed to the formation of conjugated structure in the copolymer. It was noted that the broad peak (e) observed at 1258 $cm^{-1}$was assigned to -C=CH- stretching from the methine group. Additionally, the peak (f) of C-H out-of-plane deformation vibration from the methine group and peak (g) of the aromatic C-H out-of-plane deformation vibration appeared at 1008 and 836 cm^{-1}, respectively.

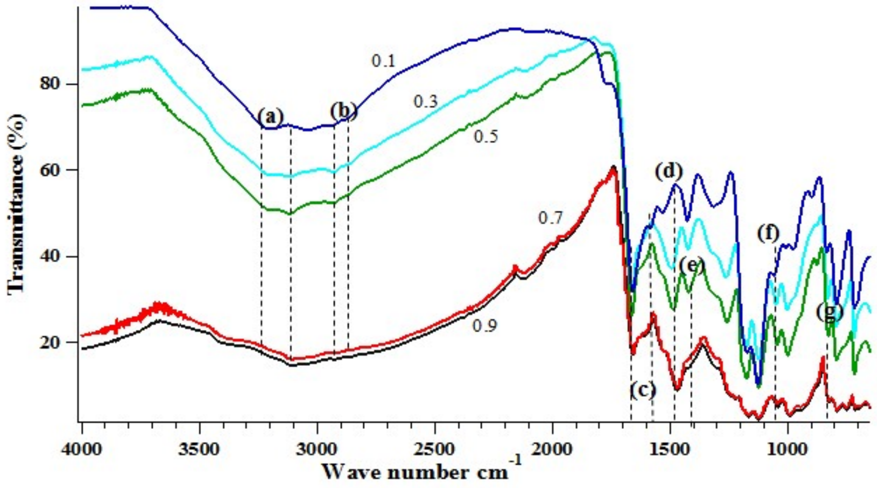

Figure 5. FT-IR spectra of polymer films prepared by various mole fractions of FPy against Py

The doping process was confirmed by FT-IR measurement. Fig.6shows FT-IR spectra of polymer films before and after I_2doping. The peak at 3117$cm^{-1}$was aromatic C-H stretching. The peaks of C=N stretching at 1494-1402 cm^{-1}were attributed to the formation of the conjugated structure in the film. The peak observed at 1263$cm^{-1}$was assigned to -C=CH- stretching from methine group of the copolymer. The peak at 1201cm^{-1}can be related to

C-N stretching of aminegroup. The peak of C=N appeared at 1134cm^{-1} The peak at 1055cm^{-1}canbe attributed to C-H in plane deformation.The peak of the aromatic C-H out-of-plane deformation vibration appeared at 1008-800 cm^{-1}, respectively. The two additional peaks occurred at 547 and 486 cm^{-1}were due to the presence of iodine in the analyzed sample. Figure 6 shows FT-IR spectra of conductive polymer film before (black) and after (red) I_2 doping.

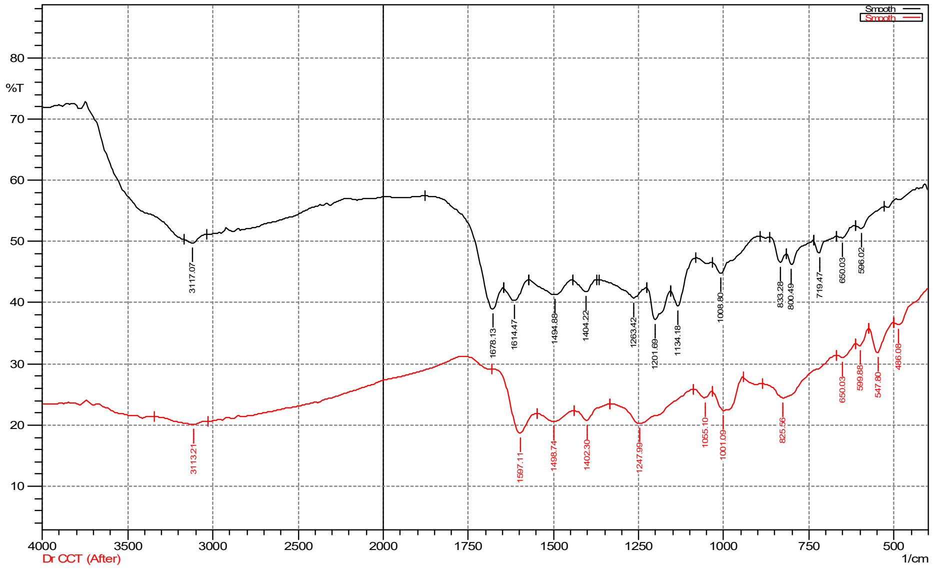

Figure 6. FT-IR spectra of conductive polymer film before (black) and after (red) I_2 doping

The dielectric properties of conductive filmswere studied by using the LCR meter. The diameter of the sample size is9.5 mmin a circular shape for each film. The parameters including capacitance and dielectric loss in the frequency range 0.1 Hz-1MHz are measured. Dielectric constant (κ) was calculated by using the formula:

$$\kappa = \frac{Cd}{\varepsilon_0 A} \qquad (1)$$

Where, κ *is* dielectric constant of the medium, *C is* the capacitance, *d* is the thickness of the sample, and Ais the cross sectional area of the sample and ε_0

is the permittivity of vacuum ($8.854\times10^{-12}\mathrm{Fm}^{-1}$). Then dissipation factor (tan δ)is determined by the formula:

$$\tan\ \delta = \frac{D}{\kappa} \qquad (2)$$

Where D is the dielectric loss obtained from LCR measurement. Finally, the AC conductivity (σ_{ac}) was determined by using the relationship:

$$\sigma_{ac} = 2\pi f\ \tan\delta\ \ \varepsilon_0\kappa \qquad (3)$$

Where, f is the frequency of applied field.

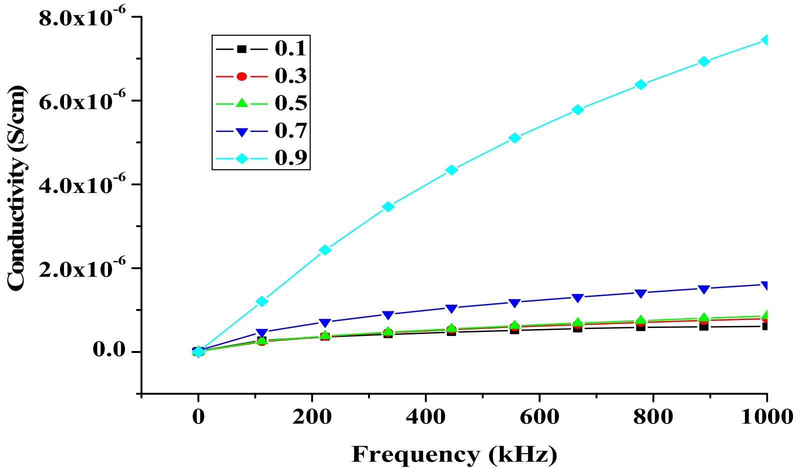

Figure 7. The electrical conductivity of I_2 doped copolymer films dependence on frequency for various mole fractions.

AC conductivity dependence on frequency was studied in the frequency range of 0.1 Hz -1000 kHz. As shown in Fig.7, the ac conductivity of the films increased with an increasing amount of FPy for all films. Among the films, the film prepared the mole fraction 0.9 FPy amount has the highest conductivity. On the other hand, mole fraction 0.7 FPy has the second highest conductivity. In addition, the films prepared the mole fraction 0.1, 0.3 and 0.5 has lower conductive properties than the others. Thus, it is remarkable that the mole fractions was the important parameters for the enhancing the conductivities of the polymer films. Therefore, it can be concluded that polymer films can enhance the conductivity with an increasing amount of mole fraction of FPy against Py. Fig.8 shows theaverage electrical conductivity of films prepared by various amount of FPy. It can be clearly see that the values abruptly increased when the mole fraction is larger than 0.7 and becomes the highest for 0.9 mole fraction. As a result, monomers are one of the critical parameters for determining the electrical properties of polymer films.

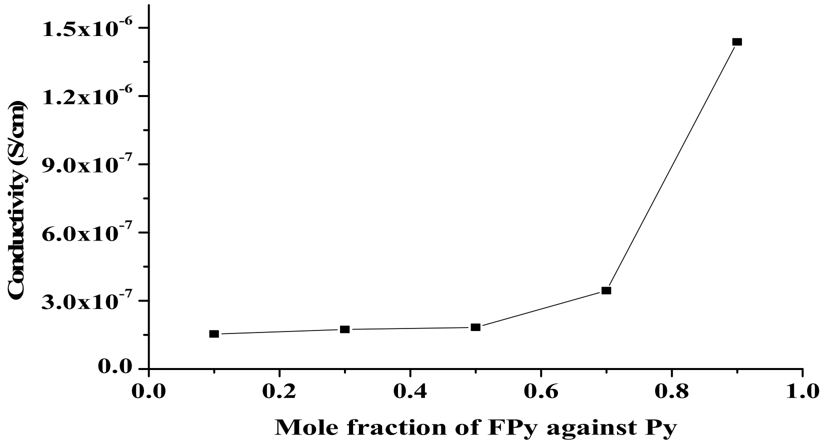

Figure 8. Average electrical conductivity of I_2 doped P(Py-co-FPy) films prepared by various mole fractions of FPy against Py.

Conclusion

The conductive polymer films have been successfully prepared by chemical polymerization method. The characterizations of formation and electrical properties are performed for different mole fractions of FPyand Py. The π-π* transition of polypyrrole in UV-vis spectrum at around 492 nm evident that the formation of polymer and indicates that the FPy group is incorporated into the chemical structure of the conjugated polymer chains. The broaden peaks around 23° in XRD spectral and stretching vibrations in FT-IR spectra show the characteristic of polymer and effect of I_2onthe film formation. In the observation of electrical properties, it is found that ac conductivity of the film is significantly increased at mole fraction of 0.9. The interesting results would be anticipated for use in several applications as a new conductive polymeric material.

Acknowledgements

I would like to acknowledge to Professor Dr Khin Khin Win, Head of Department of Physics, University of Yangon, for giving me the chance to participate in this event. My thanks go to Professor Dr Soe Soe Nwe for her encouragement of this work. I do specially thank you to my Supervisor, Dr Ye Chan, Professor and Head of URC, for his guidance of my work. I am also indebted to my Co-supervisor, Dr Cho Cho Thet, Lecturer, Universities' Research Centre, who gives me valuable comments and suggestions to this work and for a large number of excellent discussions.

References

1. H. D. Tran, K. Shin, w. G. Hong, J. M. D'Arcy, R. W. Kojima, B. H. Weiller and R. B. Kaner, "A Template- Free Route to Polypyrrole Nanofibers," Macromolecular Rapid Communications, Vol. 28. No. 24, 2007, pp. 2289- 2293.
2. K. S. Jang, H. Lee and B. Moon, "Synthesis and Characterization of Water Soluble Polypyrrole Doped with Functional Dopants," Synthetic Metals, Vol. 143. No. 3, 2004, pp. 289-294.
3 K. Ishizu, H. Tanaka and R. Saito, "Microsphere Synthesis of Polypyrrole by Oxidation Polymerization," *Polymer*, Vol. 37. No. 5, 1996, pp. 863-867.
4. M. Omastová, M. Trchová, J. Kovářová and J. Stejskal, "Synthesis and Structural Study of Polypyrroles Prepared in the Presence of Surfactants," Synthetic Metals, Vol 138. No. 3, 2003, pp. 447-455.
5 M. Salmon, K. K. Kanazawa, A. F. Diaz and M. Krounbi, "A Chemical Route to Pyrrole Polymer Films," Journal of Polymer Science: Polymer Letters Edition, Vol. 20. No. 3, 1982, pp. 187-193.
6. R. E. Myers, "Chemical Oxidative Polymerization as a Synthetic Route to Electrically Conducting Polypyrroles," Journal of Electronic Materials, Vol. 15. No. 2, 1986, pp. 61-69.
7. Sirilak Arunsawad, Kawee Srikulkit and Sarintorn Limpanart "Effect of surfactant on conductivity of Poly(pyrrole-*co*-formylpyrrole) via Emulsion Polymerization" Journal of Metals, Materials and Minerals, Vol.24 No.2 pp.29-34, 2014.
8. Y. Kudoh, "Properties of Polypyrrole Prepared by Chemical Polymerization Using Aqueous Solution Containing $Fe_2(SO_4)_3$ and Anionic Surfactant," Synthetic Metals, Vol. 79. No. 1, 1996, pp. 17-22.
9. Yusuke Hoshina, Takaomi Kobayashi "Effect of Acidic Catalyst on Properties of Novel Conductive Copolymer Films Made of Pyrrole and Formyl Pyrrole" Engineering, 2012, 4, 139-145.