Journal of Metals, Materials and Minerals, Vol.24 No.2 pp.29-34, 2014

Effect of surfactant on conductivity of Poly(pyrrole-*co*-formyl pyrrole) via Emulsion Polymerization

Sirilak ARUNSAWAD[1], Kawee SRIKULKIT[2] and Sarintorn LIMPANART[3*]

[1]*Program in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*
[2] *Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*
[3]*Metallurgy and Materials Science Research Institute, Chulalongkorn University, Bangkok 10330, Thailand*

Abstract

Poly(pyrrole-co-formyl pyrrole), P(Py-co-FPy), were synthesized via emulsion polymerization using sodium dodecylsulfate (SDS) and poly(styrenesulfonate) (PSS) as surfactants and trifluoroacetic acid (TFA) as a catalyst. Amounts of surfactant were vary as mole ratio of surfactant:monomer (0.25, 0.5 and 1.0). The synthesis copolymers were characterized by FTIR, SEM, particle size analyzer and four point probes. As a result of FT-IR spectra proved that the synthesized copolymers are associated with the structure of the P(Py-*co*-FPy). Spherical particles were detected by SEM and particles diameter is in range of 60-600 nm depending on type and amounts of surfactant. The electrical conductivity is in the range of 1.74x 10^{-5} to 2.21 x 10^{-3} S/cm. The P(Py-co-FPy) nanoparticles doped with PSS are higher conductivity than doped with PSS.

DOI : 10.14456/jmmm.2014.1

Introduction

Polypyrrole (PPy), electrically conducting polymer, has high electrical conductivity and thermal stability.(1) PPy is easily synthesized by a chemical or electrochemical polymerization. PPy obtained by electrochemical process presents in black coating film covering an electrode. On the other hand, PPy synthesized by a chemical process is available in black powder. Advantages of chemical process include large amount synthesis possible and no requirement of special instruments. PPy is suitable for preparation of conductive composites due to its conductive characteristic which is the functional property of electrodes and electronic device.(2) However, its limitation is associated with the poor processability and insolubility in common solvents due to the rigid-rod structure combined with strong intermolecular or intramolecular interactions.(3)

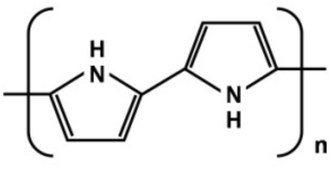

Figure 1. The chemical structure of PPy

Fortunately, these drawbacks can be solved by alternative synthesis of copolymers.(5) Yusuki Hoshina et al.(5) had successfully synthesized the novel conductive poly(pyrrole-*co*-formyl pyrrole), P(Py -co-FPy), films by straightforward chemical copolymerization containing of pyrrole (Py) and 2-formyl pyrrole (FPy) monomers. The synthesized polymer exhibits conjugated structures in the polymer chain, deriving from a methine group of FPy monomer. As a result, an ease of processability is possible.(6)

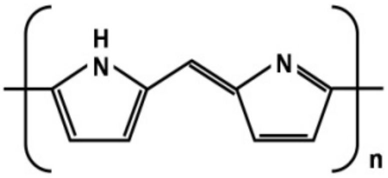

Figure 2. The chemical structure of P(Py-*co*-FPy)

However, an electrical conductivity of P(Py-co FPy) film was lower than PPy. In 2000, Emulsion polymerization has been reported as an effective method for synthesis P(Py-*co*-FPy) nanoparticles.(7) Some research groups have prepared nano-sized conductive polymers using microemulsion polymerization. For example, Reung-U-Rai et al.(1) reported that

---

*Corresponding author E-mail : sarintorn.c@chula.ac.th spherical PPy nanoparticles of 60-90 nm in diameter have been achieved. Víctor and coworkers(8) also studied the synthesis of PPy nanoparticles with narrow size distribution by oil-in-water microemulsions stabilized with low concentration of sodium decylsulfate (SDS) as surfactant. Furthermore, Feng-Hao Hsu et al.(9) studied the effect of electrolyte poly(styrenesulfonate) (PSS) on the conductivity and morphology of PPy/graphene composites. As a result, they found that the conductivities of PPy/graphene composites synthesized with the weight ratio of poly(styrenesulfonate)/pyrrole monomer at 0.5 are about five times of magnitude higher than that of composites without poly(styrenesulfonate). These results are perhaps thanks to the part of cationic electrolyte served as a dopant.

Therefore, in this present work, we have paid attention at preparing the P(Py-*co*-FPy) nanoparticles by emulsion polymerization techniques using SDS and PSS as a surfactant, which also acts as dopant and trifluoroacetic acid (TFA) as catalyst according to modified method from the report of Yusuki Hoshina et al. An influence of SDS and PSS concentration on particle size, morphology and conductivity of P(Py-*co*-FPy) nanoparticles has been studied.

Materials and Experimantal Procedures

Materials

The Pyrrole-2-carboxaldehyde (2-formyl pyrrole, FPy, Aldrich) and 98% Pyrrole (Py, Aldrich) were source of monomers. The acid catalyst was trifluoroacetic acid (99%TFA, SIAL). Chloroform and acetone were purchased from Sigma-Aldrich and the surfactants or dopants including sodium dedecylsulfate (SDS, Sigma) and sodium poly(styrenesulfonate) (PSS, Sigma, $M_w \cong 70,000$) were used as received.

Preparation of P(Py-co-FPy) by solution polymerization

Py (0.215 g, 3 mmole) and FPy (0.291 g, 3 mmole) were dissolved and stirred in 2 ml of chloroform in a 20 ml beaker. Then, the solution of TFA (1.005 ml, 13 mmole) in $CHCl_3$ (2 ml) was added to the monomers solution. As a result, the color of solution changed immediately from transparent brown to yellowish red. After the polymerization was carried out for about 30 minutes at room temperature, the resultant powders were washed with water and acetone for several times, dried at 60°C for 24 hrs, ground down and kept in desiccator.

Preparation of P(Py-co-FPy) by emulsion Polymerization

The 0.02 mole of Py (1.3875 ml) and 0.02 mole of FPy (1.9038 g) dissolved in 2 ml chloroform in a vial (10 ml) were slowly added dropwise into its respective surfactant in 100 ml of deionized water inside a beaker and continuously stirred for 30 minutes. Here, surfactant: monomer mole ratios were 0.25:1.0, 0.5:1.0 and 1.0:1.0. Then, the acid catalyst, TFA (6.63 ml, 0.0866 mole) was added into the solution. After the polymerization was carried out for about 24 hrs, at room temperature, the resultants powders were washed with water and acetone for several times. Finally, The P(Py-*co*-FPy) precipitate was vacuum filtered, dried at 60°C for 24 hrs, ground down and kept in desiccator.

Measurements

Chemical structure and morphology of P(Py-*co*-FPy) nanoparticles were investigated by FT-IR, SEM and particle size analyzer. FT-IR spectrometer (Perkin Elmer, Spectrum One) in transmittance mode, Transmission spectra were obtained by forming a thin KBr-P(Py-*co*-FPy) pellet. The resolution of the spectral measurements was 4 cm^{-1} for each spectrum. To evaluate the particle size distribution, a laser diffraction particle size analyzer (Malvern Instruments Ltd, Zetasizer Nano ZS) was also used on the aqueous dispersion solutions after remove acid catalyst. The polymer morphology was observed by scanning electron microscope (SEM, Philips XL30CP Model). For electrical conductivity, about 0.1g of dried P(Py-*co*-FPy) nanoparticles was compressed as pellets of 13 mm diameter and 1 mm thickness with a hydraulic pressure at 3,000 psi. and the thickness of the pellets were measured by digital thickness gauge meter (Model: DTM-25). Conductivity was measured using a typical four-point machine (Jandel model:RM-3) according to four point probe standard of sheet resistance measurement (ASTM Standard D4496) at room temperature over the surface of the pellets without doping in I_2 atmosphere.

Results and Discussion

P(Py-*co*-FPy) nanoparticle were prepared by emulsion polymerization adopted from the method of Yusuki Hoshina et al.(5) Two surfactants, SDS and PSS were used for P(Py-*co*-FPy) polymer synthesis. Mole ratio of Py and FPy was fixed on 1:1 and used TFA as catalyst as reported in Yusuki Hoshina et al. The black powders of P(Py-*co*-FPy) were obtained(6)

Morphology

Figure 3 and 4 show SEM images of the P(Py-*co*-FPy) particles prepared by solution and emulsion polymerization, respectively. As seen, P(Py-*co*-FPy) powder preparing via solution polymerization without surfactants presented an irregular shape in hard aggregate form, with about 1-2 micron sizes. On the other hand, P(Py-*co*-FPy) nanoparticles prepared via emulsion polymerization using both SDS and PSS as a surfactant at various concentrations, exhibits spherical morphology with 60-600 nm in average diameter. Moreover, the average size of the P(Py-*co*-FPy) nanoparticles prepared by SDS system was smaller than those of PSS system except at surfactant and monomer ratio of 0.25:1. At low surfactant and monomer ratio (0.25:1), the surfactant concentration was below the critical micelle concentration (CMC). Therefore, the monomers were present in large droplet form, leading to the large particle size of P(Py-*co*-FPy).

The average particle sizes measured by a Zetasizer were found in range of 99 – 780 nm as shown in Table 1. However, P(Py-*co*-FPy) nanoparticles tended to form an aggregation judged by actual particle sizes (Zetasizer) are much larger than the particle sizes observed from SEM.(1,10)

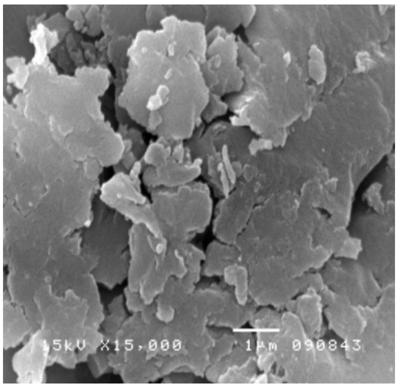

Figure 3. SEM image of the P(Py-*co*-FPy) powders synthesized by solution polymerization

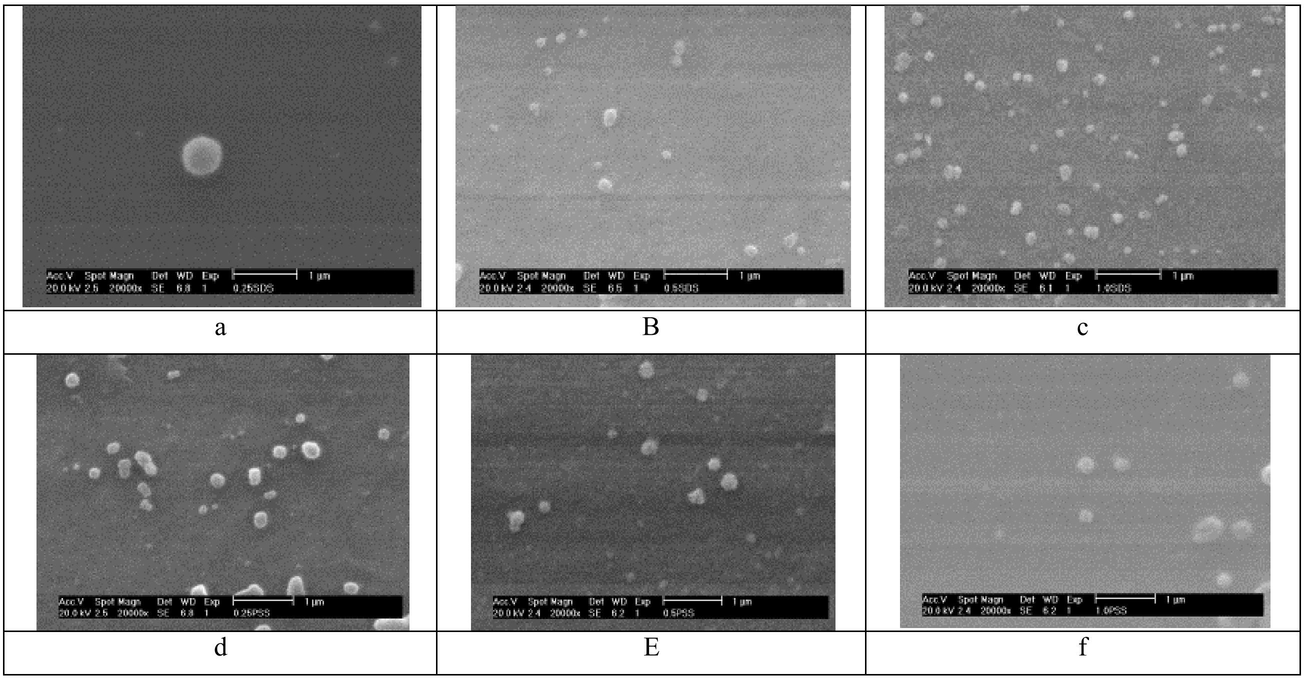
a
B
c
d
E
f

Figure 4 . SEM images of P(Py-*co*-FPy) nanoparticles synthesized with mole ratio of SDS: monomer of *(a)* 0.25:1.0, *(b)* 0.5:1.0, *(c)* 1.0:1.0, and with mole ratio of PSS: monomer of *(d)* 0.25:1.0, *(e)* 0.5:1.0, and *(f)*1.0:1.0.

FT-IR analysis

Figure 5 shows FT-IR spectra of P(Py-*co*-FPy) nanoparticles. The FTIR spectra of P(Py-*co*-FPy) nanoparticles prepared with various concentrations of SDS and PSS and FTIR spectrum of P(Py-*co*-FPy) prepared by solution polymerization show almost identical fingerprint similar to the work of Yusuki Hoshina et al.(5,6) The characteristic absorption bands are found at 3,406 and 3,227 cm^{-1} corresponding to N−H vibrations of pyrrole ring, and C−H stretching vibrations at 2,936 and 2,853 cm^{-1} responsible for the SDS alkyl chain. For these peaks appear weakly and decreasingly as the PSS concentration increases, relating to an increase in the number of conjugated double bonds.(5) Peaks at 1,688 and 1,535 cm^{-1} responsible for pyrrole C=C double bond stretching. In addition, the absorption band at 1,488 cm^{-1} is attributed to C=N stretching. Also, the broad peak observed at 1,253 cm^{-1} is assigned to –C=CH−stretching from the methine group. Additionally, the peak of C−H out-of-plane deformation vibration from the methine group and peak of the aromatic C−H out-of-plane deformation vibration appeared at 1,003 and 830 cm^{-1}, respectively. The peak of the S=O stretching vibration of SO_3^- expected to be found at 1,183 cm^{-1} could not be clearly observed due to overlapping with the pyrrole ring vibration at 1,003cm^{-1}.(1,11)

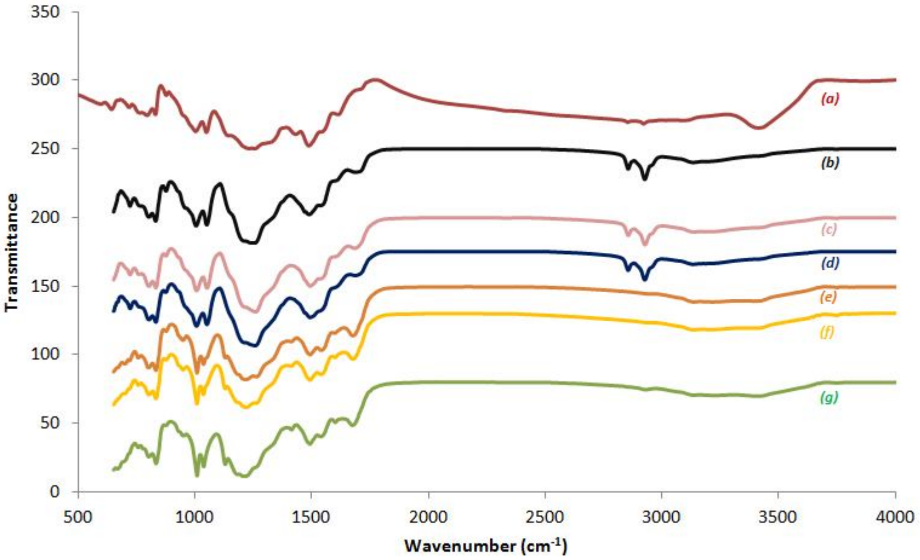

Figure 5. Typical FT-IR spectra of the P(Py-*co*-FPy) nanoparticles synthesized *(a)* without surfactant and with mole ratio of SDS: monomer of *(b)* 0.25:1.0, *(c)* 0.5:1.0, *(d)* 1.0:1.0, and with mole ratio of PSS: monomer of *(e)* 0.25:1.0, *(f)* 0.5:1.0 and *(g)*1.0:1.0.

Conductivity

The average conductivities are summarized in Table 1. The conductivities of the P(Py-*co*-FPy)'s obtained from the solution polymerization is also lower than those synthesized in the emulsion polymerization. The obtained P(Py-*co*-FPy) nanoparticles had electrical conductivity of 1.74×10^{-5} to 2.21×10^{-3} S/cm when using various concentrations of SDS and PSS. It has been determined that the conductivity of doped conducting polymers depends on the doping level and it can be assumed here that the relatively higher conductivity of the P(Py-*co*-FPy) synthesized in the emulsion system may come from the effects of a longer conjugation length and the ordered arrangement of the macromolecule chains.(7) Furthermore, the four-point machine cannot detect the data of P(Py-*co*-FPy) obtained from solution polymerization due to the fact that the sheet resistance of material is beyond the capability performance of testing machine. In emulsion polymerization, the surfactant played a dual function; dopant and surfactant. In case of surfactant, the surfactant created a micro-reactor vessel via micelle formation.(1) In case of dopant, the surfactant was incorporated into the polymer backbones with ionic complex formation.(10) However, when using PSS as dopant, the electrical conductivity is higher than SDS and the electrical conductivity increased with the increasing surfactant concentration. These results are perhaps because the part of PSS can be attracted closely to the copolymer when compared to SDS, enhancing the conductivity of synthesized P(Py-*co*-FPy).(9)

Table 1. Particle size distribution and conductivity of P(Py-*co*-FPy) synthesized with or without each surfactant (solution polymerization)

Specimen Name	Surfactant type	Mole ratio	Conductivity (S/cm)	Particle Size Average (nm)	Particle Distribution Index (PDI)
P(Py-*co*-FPy)	-	-	N/A	N/A	N/A
0.25:1.00	SDS	0.25	(1.74±0.03) x 10^{-5}	775.0± 5.1	0.510±0.020
0.50:1.00		0.50	(6.58±0.01) x 10^{-5}	99.2±0.3	0.117±0.002
1.00:1.00		1.00	(8.13±0.13) x 10^{-5}	178.7±1.4	0.161±0.003
0.25:1.00	PSS	0.25	(1.99±0.09) x 10^{-4}	291.5±3.3	0.244±0.008
0.50:1.00		0.50	(1.24±0.05) x 10^{-3}	336.4±2.2	0.261±0.010
1.00:1.00		1.00	(2.21±0.01) x 10^{-3}	289.2±2.9	0.252±0.001

Conclusions

In this work, higher-conductivity P(Py-*co*-FPy) nanopaticles with well-dispersion in water has been successfully synthesized by emulsion polymerization of Py and FPy monomers using various concentration of SDS and PSS as a surfactant which also acts as dopant and TFA as acid catalyst. The morphology of the synthesized P(Py-*co*-FPy) is spherical with 60-600 nm in average diameter, and the electrical conductivity is in the range of 1.74x 10^{-5} to 2.21 x 10^{-3} S/cm. FT-IR spectra proved that the synthesized copolymers are associated with the structure of the P(Py-*co*-FPy) and the surfactant was incorporated into the polymer backbone with ionic complex formation as the dopant. For compared to SDS, the nanoparticles doped with PSS show much higher conductivity. The increasing extent of the p-conjugation along the polymer backbone and the order arrangement of the macromolecule chains enhance an electrical conductive of P(Py-*co*-FPy).

Acknowledgements

This research was funded by the Ratchadapisek Sompoch Endowment Fund (2013), Chulalongkorn University (CU-56-803-FC), equipments and laboratory facilities were supported by the Program of Petrochemistry and Polymer Science, Chulalongkorn University and Metallurgy and Materials Science Research Institute, Chulalongkorn University.

References

1. Reung-U-Rai, A., Prom-jun, A., Prissanaroon-Ouajaiand, W. and Ouajai, S. (2008). Synthesis of Highly Conductive Polypyrrole Nanoparticles via Microemulsion Polymerization. *J. Met. Mater. Miner.* **18(2)** : 27-31.

2. Gangopadhyay, R. and De, A. (2000). Conducting polymer nanocomposites : a brief overview. *Chem. Mater.* **12(3)** : 608-622.

3. Simmons, M.R., Chaloner, P.A., Armes, S.P., Greaves, S.J. and Watts, J.F. (1998). Synthesis and Characterization of Colloidal Polypyrrole Particles Using Reactive Polymeric Stabilizers. *Langmuir.* **14(3)** : 611-618.

4. Elschner, A., Kirchmeyer, S., Lövenich, W., Merker, U. and Reuter, K. (2010). *PEDOT : Principles and Applications of an Intrinsically Conductive Polymer.* 113-166

5. Hoshina, Y. and T. Kobayashi. (2012). Electrically conductive films made of pyrrole-formyl pyrrole by straightforward chemical copolymerization. *Ind. Eng. Chem. Res.* **51(17)** : 5961-5966.

6. Tagaya, M., Hoshina, Y., Ogawa, N., Takeguchi, M. and Kobayashi, T. (2013). Nanostructural analysis of self-standing pyrrole/2-formylpyrrole copolymer films. *Micron.* **46** : 22-26.

7. Yan, F., Xue, G. and Zhou, M. (2000). Preparation of electrically conducting polypyrrole in oil/water microemulsion. *J. Appl. Polym. Sci.* **77(1)** : 135-140.

8. Ovando-Medina, V.M., Peralta, R.D., Mendizábal, E., Martínez-Gutiérrez, H., Lara-Ceniceros, T.E. and Ledezma-Rodríguez, R. (2011). Synthesis of polypyrrole nanoparticles by oil-in-water microemulsion polymerization with narrow size distribution. *J. Poly. Sci.* **289(7)** : 759-765.

9. Feng-Hao, H. and Tzong-Ming, W. (2012). In situ synthesis and characterization of conductive polypyrrole/graphene composites with improved solubility and conductivity. *Synthetic Metals.* **162(7)** : 682-687.

10. Hoshina, Y., Zaragoza-Contreras, E.A., Farnood, R., Kobayashi, T. (2012). Nanosized polypyrrole affected by surfactant agitation for emulsion polymerization. *Polym, Bull.* **68(6)** : 1689-1705.

11. Hazarika, J. and Kumar, A. (2013). Controllable synthesis and characterization of polypyrrole nanoparticles in sodium dodecylsulphate (SDS) micellar solutions. *Syn. Met.* **175** : 155-162.

12. Tzong-Ming, W., Hsiang-Ling, C. and Yen-Wen, L. (2009). Synthesis and characterization of conductive polypyrrole/multi-walled carbon nanotubes composites with improved solubility and conductivity. *Compos. Sci. Technol.* **69(5)** : 639-644.