Increased Electrical Conductivity of Polypyrrole Through Emulsion Polymerization Assisted Emulsifier Synthesis

Prestika Gema Sari1, Mas Ayu Elita Hafizah1, Andreas2, Azwar Manaf 1*
1 Postgraduate Program of Materials Science Study, Department of Physics Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Depok 16424, Indonesia
2 Indonesian Institute of Science, LIPI, Komplek PUSPITEK, Serpong, Banten 15314, Indonesia
azwar@ui.ac.id

Abstract. A conductive Polypyrrole (PPy) has been successfully synthesized and characterized. The PPy was prepared through oxidative chemical polymerization using ammonium peroxydisulfate (APS) as an oxidizing agent in aqueous media. The reaction is prepared without heating. Anionic and non-ionic emulsifiers, sodium dodecyl sulfate (SDS), nonylphenol (NP) ethoxylate (EO) with 10 mole EO were respectively used during polymerization to increase the electrical conductivity. The FTIR spectrum of PPy indicates a change in the absorbance peaks of pyrrole monomer at 1530 cm⁻¹ and those in the range region of 1100 - 1000 cm⁻¹. With the SDS addition, the temperature of solution increased with reaction time reached the highest 35 °C within 2 minutes reaction. The pH value of an SDS added solution was 3.3 higher than that of SDS free solution (1.8). The addition of SDS was also to change the color changing during the polymerization reaction. The final characteristic of PPy by measuring the electrical conductivity (σ) value concluded that the presence of emulsifier anionic in a polymerization reaction increased the electrical conductivity of PPy 150 times higher compared with that obtained of emulsifier free solution.

Keywords : Polypyrrole, emulsifier, emulsion polymerization, conductive polymer

1. Introduction
Polymeric materials have been interesting materials to be explored until today. As a macromolecule, the polymer is made of repeating huge small molecules which have long been used for insulation in various devices. However, in the 1970s, a new class of polymers possessing high electronic conductivity was introduced [1]. The so-called conductive polymers (CPs) have shown the capability of being doped or de-doped to gain their electrical properties. The conductive polymers were considered potential for various applications and able to meet current needs that require environmentally friendly because the CPs can be naturally degradable, and yet still superior against their inorganic predecessors like Li, Ni and Ni-Cd [2]. The CPs potentially can be low cost products having good environmental, more stable compared with other type of conductive materials like silver, gold and graphite based compounds by mixing with polymer material in electronics industry [3]. A few of CPs in its series, among them are Polypyrrole (PPy), Polythiophene (PTh) and Polyaniline.
(PANI) have been receiving great attention and being explored intensively by various researchers [3-7]. Polypyrrole (PPy) and its derivatives become one of the material that gain more attention due to its exceptionally high electrical conductivity, high flexibility in preparation, physically stable and have good mechanical property [4]. The PPy is suitable for electronic and Electrochromic devices and gas sensor applications like super-capacitors [5], and other important applications. In addition, the pyrrole monomer can easily be dissolved and oxidized in water [6]. The simplicity of the synthesis procedures and availability of the initial monomers is also attractive features of PPy synthesis [7].

Polypyrrole can be synthesized chemically or electrochemically through the oxidative polymerization process [8]. Chemical polymerization is a simple method that has been developed intensively involving some oxidant agents. In a chemical oxidative polymerization of pyrrole monomer, many oxidants have been used like ferric chloride (FeCl$_3$), ferric perchlorate, ammonium peroxysulfate (APS), etc. APS was found to be the best inferior stability of electrical conductivity [9] and water is the best solvent for chemical polymerization with respect to desirable conductivity characteristic [3]. However, PPy is also having a deficiency which is rigid and brittle in physical properties. Its insolubility in some common organic solvent limits its wide range of applications [10]. Therefore, a solution to resolve the deficiency is urgently needed. It was shown that emulsion polymerization is one of the most promising methods in improving the process ability of PPy [10,11]. The mechanical properties and surface smoothness of PPy films prepared from aqueous solutions with the addition of the non-ionic surfactants were greatly improved in comparison with those of PPy prepared from the aqueous solutions in the absence of surfactants [11]. Chemical preparation of PPy from aqueous solutions containing ferric sulfate as an oxidant and a surfactant, was reported by Omastova [11]. The addition of surfactants accelerated the polymerization.

In conducting this research, polypyrrole monomer was polymerized using ammonium persulfate (APS) as an oxidation agent through emulsion polymerization assisted by anionic and non-ionic surfactants. This was compared with a sedimentation surfactant free polymerization. Both polymerization processes were conducted through a batch polymerization at a room temperature under the agitation speed of 900 rpm for 4 hours during the polymerization reaction. Analytical grade Pyrrole monomers and ammonium persulfate (APS) were obtained from Sigma Aldrich with the purity level 99.9%. Dodecyl Sulfate (SDS) which has white flake form with 99.5% purity level was used as anionic surfactant. A selected non-ionic surfactant of Nonyphenol (NP) with 10 moles ethoxylate as a white powder with 99.7% of purity was used during polymerization reaction.

In the initial stage, the pyrrole monomers of 5% is mixture with a distilled water in a beaker glass under continuous magnetic stirring at room temperature. Meanwhile, the initiator solution of 5% of ammonium persulfate was water dissolved in another beaker glass at a room temperature. In 1 liter capacity of a reactor flask consisted of four necks the 1% of SDS solution in water was prepared under a heating treatment at 40°C for 30 minutes. A continuous agitation with a 500 rpm agitation speed was employed until all flakes of SDS dissolved completely. The SDS containing solution was then cooled naturally until the temperature reached back to a room temperature. Polymerization reaction was started by putting altogether of pyrrole monomers mixture and initiator solution into reactor flask immediately. Observation during the polymerization reaction was carried out periodically by taking up samples while the polymerization reaction in progress. Changes in the temperature of the solution, the particle sizes, viscosity and pH values, color degradation were all brought into objects of observation.
and evaluations. During the 4 hours of reaction, the black polymer particles were formed and collected using a Whatman filter paper no 40 and then successively washed 3 times with 100 ml distillate water. The Polypyrrole particles were then dried in a vacuum desiccator for 10 hours. The dried polypyrrole subject to further characterizations, including chemical molecule functional groups by Fourier Transform Infra-Red (FTIR) spectroscopy, particle size evaluation by Malvern Zetasizer Nano ZS Particle Size Analyzer (PSA) and electrical conductivity by Four Point Probe (FPP) method. The similar preparation polymerization experiment was repeated with different concentration of surfactants (1% and 2%), different type of surfactant (anionic and non-ionic surfactant) that represented by SDS and NP10EO respectively. These are to be compared with surfactant free PPy obtained through a similar polymerization reaction.

3. Results and discussion
During the polymerization reaction of pyrrole monomer, various main parameters are put as the object indicators for PPy formation. One of such parameters is the color changing which associated with the particle formation and changing in bonds of chemical molecules \[12,13\]. In the current research work, two different synthesis processes were set to be studied. There are the PPy obtained from the so-called emulsion polymerization with the presence of surfactant \[14\] and the sedimentation polymerization \[15\] with no surfactant added. The two polymerization processes have resulted a different pathway in color changing during the formation of PPy particles. The color changing of the two processes is compared in Figure 1.

\[\text{Figure 1. Visual appearance of color degradation during polymerization reaction of PPy (a) surfactant free and (b) 1 \% surfactant added solution.}\]

A color changing as shown in Figure 1 (a) was started from a yellowish transparent liquid of pyrrole monomer to form a black particle of PPy through four steps. Whereas, Figure 1 (b) clearly indicates that with the presence of surfactant, a color changing occured at the initiation reaction started with a brownish hazy liquid and then gradually changing to a strong dark brown color prior to have similar color changing to that of surfactant free solution (Figure 1 (a)). A long pathway in color changing of surfactant added solution indicated that the polymerization reaction progresses in a slower reaction rate when compared with that of surfactant free.
A chemical reaction like polymerization where the products in the form of particles, mostly accompanied by a releasing or absorbing energy. It is common that the temperature of the solution is set also as the object of observation to find out whether a chemical reaction is in progress [16-18]. The increase of solution temperature during polymerization is due to releasing of thermal energy accompanied by a breakdown of chemical bonds [19]. Figure 2 compares the temperature profile between SDS added and SDS free solutions for 240 minutes polymerization reaction. The two profiles have a somewhat similar pattern consisted of initiation, polymerization and post polymerization periods. The two profiles differ only in a temperature degree change from which the SDS containing solution has a temperature higher than that of SDS free solution during the whole period of reaction. The highest temperature of the SDS containing solution achieved 35 °C, 2 °C higher than that of surfactant free solution. This happened due to any movement of surfactant molecules released energy into the system. Such temperature profile was also obtained in the previous research works reported elsewhere [16-18]. In can be concluded that the polymerization reaction of pyrrole monomer by ammonium persulfate as the oxidation agent has no different with that of general polymerization reactions in which there is always a temperature increased due to chemical oxidation reactions. It is once again confirmed that the temperature of solution can be an important key indicator for polymerization reaction [20].

![Figure 2. Comparison of the temperature profile between SDS added and SDS free solutions for 240 minutes PPy polymerization reaction.](image)

Acidity level during polymerization reaction was also observed completely by means of real time measurement using pH meter series Metrohm 827 with double digit precision. Figure 3 compares the pH profile between SDS added and SDS free solutions for 240 minutes polymerization reaction. The two profiles differ in pH values from which the SDS containing solution has pH values higher than that of SDS free solution during the whole period of reaction. The pH of SDS added solution was 6.5 at the initial stage of the reaction which is much higher when compared with that of the SDS free solution. Obviously, the high value of SDS added solution must be due anion sulfate based (SO\(_4^{2-}\)) and cation sodium based (Na\(^+\)) of SDS molecule. Hence the pH meter measured the acidity value based on the ionic movement of SDS. The pyrrole monomer is clear and transparent liquid, slightly yellowish and have the pH value 3.9. During the polymerization reaction in SDS added solution, the increased pyrrole monomer amount of the solution along with the ionization reaction of SDS affected the pH of the solution. The pH decreased towards 3.3 after 15 minutes of reaction time and then stable by the reaction time of polymerization finished completely. On the other hand, the polymerization reaction of
an SDS free solution had no significant changing on pH value which approximately 1.8 – 2.0 during the reaction time. The pH value of SDS free solutions originally came from the polymerization reaction only without any additional impact from side products. Hwang and Pyo have shown that the pH value of PPy in a basic solution will depend on the OH exchange against deprotonation of acidic proton of pyrrole units which described by the following chemical reaction:

$$\text{PPyH}^+\text{X}^- \leftrightarrow \text{PPy} + \text{H}^+ + \text{X}^- \quad \text{(in basic pH)} [21].$$

**Figure 3.** Comparison of pH profile between 1 % SDS added and SDS free solutions for 240 minutes polymerization PPy.

The most important parameter to find out if the polymerization reaction has occurred in the right direction can be indicated by the chemical structure of forming polymeric products. The FTIR spectrum of the products could be used for the identification. A series of study have also been carried out by several researchers pertaining the chemical molecule structure properties of polypyrrole with its derivative by FTIR spectrophotometer [11, 22]. Figure 4 presents the complete FTIR spectrum for each pure single substance and the formed PPy. The spectrum of PPy in aqueous media with no surfactant added featured by the absorption band at 1433 cm\(^{-1}\) indicating a C–N stretching vibration in the pyrrole ring and a shifting of C–N vibration was observed to occur in spectrum PPy-SDS to 1435 cm\(^{-1}\). The shifting is affected by doping and different degree of doping in the two samples [11]. Refer to spectrums plotted in Figure 4, it can be seen that a shifting in absorption peaks of pyrrole monomers occurred in both PPy with SDS and no SDS additions. The peaks shifting of PPy for the two types occurred in the region ranging from 1250 to 1000 cm\(^{-1}\) associated with the breathing vibration of pyrrole ring.

The region of C–H and N–H vibrations in the range 1130 -1000 cm\(^{-1}\) is probably influenced for PPy –SO\(_4\) sample by C–O vibration of hydroxypyrrrole units formed by nuclophilic attack of water during the preparation [11]. It is then confirmed that the PPy has formed with a specific fingerprint of the FTIR spectrum due to a change in pyrrole monomer as a single substance to PPy. The absorbance at 689 cm\(^{-1}\) in pyrrole spectrum disappeared in the PPy spectrum. However, considering that the absorbance peaks were found broadened in PPy spectrum, the absorption peak of payroll still exists. The broadening might be caused by overlapping bands of sulfate anion situated in the same position in the spectrum [11]. Polypyrrole which reacted with ammonium persulfate produced shorter conjugation lengths of polymer molecule chain which could be confirmed by FTIR in which the highest numbers of carbonyl groups occurred at formed polymer. Meanwhile the PPy with SDS addition have a specific transmittance at certain wavenumber due to the sulfate groups of oxidant agent reacted with the
polymer chains to form sulfonic functional groups caused the polymer with the shorter delocalization chain length [11,23].

![Figure 4. Spectrum FTIR of PPy With and Without Presence of Surfactant.](image)

Electrical conductivity was evaluated through measurement of resistivity employing four point probe equipment. The voltage varied from -0.06 to 0.06 resulted in the V–I curve as shown in Figure 5. A V–I curve of the two samples showing an ohmic relationship indicating conducting samples. The resistivity values for the two PPy samples were calculated from each ohmic curve and subsequently determined its electrical conductivity. The electrical conductivity of the two samples is listed in Table 1. It is confirmed now that the addition of SDS during the polymerization reaction has increased significantly the electrical conductivity of PPy. The 1 % SDS addition PPy has increased the conductivity value more than 150 times higher than that of SDS free. The electrical conductivity value obtained from the current study is 0.16 S/cm when SDS free and increased to 24.46 S/cm when 1% of SDS added. This result is higher than values reported by Sirilak on the effect of SDS as anionic surfactant to a conductivity value of PPy through emulsion polymerization which was obtained in the range of 1.74x10⁻⁵ to 2.21x10⁻³ S/cm [24].

| Sample                          | Conductivity Value, \(\sigma\) |
|---------------------------------|---------------------------------|
| PPy with surfactant free        | 0.16 S/m                        |
| PPy with 1% of SDS              | 24.46 S/m                       |

![Table 1. Comparison of electrical conductivity value of SDS added and SDS free PPy.](image)
Figure 5. V-I curve relationship of (a) SDS added PPy and (b) SDS free PPy.

4. Conclusion
Conductive polypyrrole has successfully synthesized through chemical oxidative polymerization with the addition of SDS surfactant. Key parameters for PPy formation are real time of temperature and color changing together with a pH profile for 240 minutes reaction time. The reaction rate of polymerization of pyrrole with surfactant added is slower than that of surfactant free. The synthesis of polypyrrole is stable at acidic condition. The role of SDS anionic surfactant acted as a doping agent during polymerization and increased the electrical conductivity value significantly. The addition of 1\% SDS increased the electrical conductivity value to 24.46 S/m from 0.16 S/m in SDS free PPy.

Acknowledgment
The authors gratefully acknowledge the support of Postgraduate Program of Material Science Universitas Indonesia for the research facilities. We are also thankful for the financial support provided by the Directorate of Research and Community Service Universitas Indonesia under program Grants of International Publication Indexed for Final Project student 2018 (PITTA 2018) under contract no. 2237/UN2.R3.1/HKP.05.00/20018.

References
[1] G. Inzelt, Conduction polymers, A new era in Electrochemistry, no. 1. 2014.
[2] R. A. William, B. Sitorus, P. S. Kimia, U. Tanjungpura, P. S. Fisika, and U. Tanjungpura, “Sintesis Polianilina Pada Matriks Selulosa Sebagai Elektrolit Padat,” vol. 3, no. 4, 2014.
[3] R. Ansari, “Polypyrrole Conducting Electroactive Polymers: Synthesis and Stability Studies,” E-Journal Chem., vol. 3, no. 4, pp. 186–201, 2006. DOI: 10.1155/2006/860413
[4] H. K. Chitte, N. V Bhat, V. E. Walunj, and G. N. Shinde, “Synthesis of Polypyrrole Using Ferric Chloride (FeCl 3 ) as Oxidant Together with Some Dopants for Use in Gas Sensors,” vol. 2011, no. June, pp. 47–56, 2011. DOI: 10.4236/jst.2011.12007
[5] Patil, B., H., Bulakhe, R., N dan Lokhande, C., D., J. Mater Sci.: Master Electron, vol. 25, pp. 2188-2198, 2014.
[6] Qomariyah dan Susi, Nur, 2011, Pengembangan Sensor Alkohol dari Bahan Polipirol Konduktif dengan Variasi Konentrasi Dopen Flouroborat, Fakultas Matematika dan Ilmu Pengetahuan Alam, Universitas Jember, Jember, 2011.
[7] T. V Vernitskaya and O. N. Efimov, “Polypyrrole: a conducting polymer; its synthesis, properties and applications,” Russ. Chem. Rev., vol. 66, no. 5, pp. 443–457, 2002.
[8] P. Saville, “Polypyrrole Formation and Use,” no. January, 2005.
[9] J. Tabaciarová, M. Mičušik, P. Fedorko, and M. Omastová, “Study of polypyrrole aging by XPS, FTIR and conductivity measurements,” Polym. Degrad. Stab., vol. 120, pp. 392–401, 2015.
[10] S. Bilal, F. Perveen, and A. A. Shah, “Chemical synthesis of polypyrrole doped with dodecyl benzene sulfonic acid,” J. Sci. Innov. Res. 2015; vol. 4, no. 1, p. 33, 2015.
[11] M. Omastová, M. Trchová, J. Kovařová, and J. Stejskal, “Synthesis and structural study of polypyrroles prepared in the presence of surfactants,” Synth. Met., vol. 138, no. 3, pp. 447–455, 2003.
[12] A. M. Gueli, G. Bonfiglio, S. Pasquale, and S. O. Troja, “Effect of particle size on pigments colour,” Color Res. Appl., vol. 42, no. 2, pp. 236–243, 2017.
[13] L. M. Liz-Marzán, “Nanometals: Formation and color,” Mater. Today, vol. 7, no. 2, pp. 26–31, 2004.
[14] T. F. Tadros, Emulsion Science and Technology. 2009.
[15] H. Zhang and A. I. Cooper, “Compressed Fluid Sedimentation Polymerization,” Macromolecules, vol. 36, no. 14, pp. 5061–5064, 2003.
[16] Hafizah M.A.E, Bimantoro A, Andreas and Manaf A, Procedia Chemistry 19 162 – 165, 2016.
[17] Manaf A, Bimantoro A, Hafizah M A E and Andreas, IOP Conf. Ser. Mater. Sciece Eng. 223, 2017 .
[18] Manaf A, Prasutiyo Y J, Hafizah M A E, Andreas, Int. J. of mechanical and Production Engineering 5 2320-2092, 2017.
[19] Stejskal J and Gilbert R G, Pure Appl. Chem. 74 857867, 2002.
[20] G. J. Salomons, Y. S. Park, K. B. McAuley, and L. J. Schreiner, “Temperature increases associated with polymerization of irradiated PAG dosimeters,” Phys. Med. Biol., vol. 47, no. 9, pp. 1435–1448, 2002.
[21] Hwang, Ji-Hyun, dan Myoungho Pyo., Bull. Korean Chem. Soc., vol. 27 (12), pp. 2067, 2006.
[22] Y. Kudoh, Synth. Met. 79 : 17, 1996.
[23] Hossein E., World Journal of Chemistry, 2 (2): 67-74, 2007.
[24] S. K. y L. S. Arunsawad Sirilak, “Effect of surfactant on conductivity of Poly(pyrrole-co-formyl pyrrole) via Emulsion Polymerization,” J. Met. Mater. Miner., vol. 24, no. 2, pp. 29–34, 2014.