



Synthesis of nano-sized polyindole via emulsion polymerization and doping



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ABSTRACT

The nano-sized PIn were successfully synthesized via emulsion polymerization at room temperature. Effects of oxidizing agent type (APS and FeCl_3) and various emulsion systems using different surfactants and concentrations were studied. Three surfactant types namely cationic cetyltrimethylammonium bromide (CTAB), anionic sodium dodecylsulfate (SDS), and non-ionic polysorbate 80 (TW80) were utilized. PIn with higher electrical conductivity was obtained by using FeCl_3 because it was of a lower oxidizing capacity leading to lower over-oxidation. The emulsion system of SDS provided the smallest particle in nanometer size of 60.3 ± 10.8 nm in diameter and higher electrical conductivity than CTAB and TW80 because the anionic surfactant was an efficient dopant. Thermal stability of PIn in various conditions was also investigated, PIn/APS manifested the highest thermal stability as it produced a higher char yield than the PIn synthesized with the other conditions. Higher electrical conductivity of PIn was improved by doping with HClO_4 at different doping mole ratios. At the doping mole ratio of 25:1, the electrical conductivity of PIn increased by 4–5 orders of magnitude comparing to PIn before doping. In this work, the highest electrical conductivity of PIn was $14.56 \pm 2.39 \text{ Scm}^{-1}$ which has never been reported previously.

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1. Introduction

Conductive polymers have been of interest after the discovery of Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa by Chemistry Nobel Prize award in the 2000s [1]. A conductive polymer has a conjugation structure between sigma bond and π -bond along the polymer main chain. This material is able to conduct electricity and generates charge carriers through a doping process as electrons or holes can be delocalized along the polymer chain. A hole is a positive charge where an electron is missing too naive. When a hole is filled by an electron which jumps from a neighboring atom, a new hole is created and so on, allowing the charge to move a long distance. In the doped state, the charge compensation between a conductive polymer and a dopant or counter ion is formed by the electrostatic force. The material presents many extraordinary properties over the conventional polymer because it is capable of variations in mass, color, and conductivity by doping/de-doping process. In case of the strong acid dopants (H_2SO_4 , HClO_4 , HCl , and HNO_3), Permpool and Sirivat reported that perchloric acid (HClO_4) could produce higher

electrical conductivity of PDPI when compared with that H_2SO_4 and HNO_3 since the strong acid promoted more holes in the polymer backbone resulting in more charge carriers available and consequently high electrical conductivity [2]. Thus, a dopant type has been known to be an important ingredient to control the electrical conductivity of conductive polymers [3].

Polyindole (PIn) is one of conductive polymers containing the benzene ring linked with the pyrrolic ring. Although PIn contains the heterocyclic of nitrogen atom like polypyrrole (PPy) and polyaniline (PAni), its electrical conductivity is less by two orders of magnitude than those of the two polymers [4]. However, the outstanding properties of PIn are excellent thermal stability, high redox activity, and stability as well as slow degradation rate [5,6]. Consequently, PIn and its derivatives have been of interest for using in various applications such as battery [7], sensor [8], corrosion protection [9], and drug delivery [10].

PIn can be easily synthesized at room temperature by various chemical approaches: emulsion polymerization; interfacial polymerization [11,12] and electrochemical polymerization [13]. The coupling position of indole radical cations is widely known to be at 2, 3 position in which nitrogen atom and benzene ring do not involve in the polymerization as confirmed by FT-IR [12,14,15]. For chemical synthesis, indole monomers are oxidized by the oxidizing

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agents such as ammonium persulfate [16] and ferric chloride [17]. Generally, PIn in the doped state is a dark green precipitate having the electrical conductivity $\sim 10^{-3}$ – 10^{-1} S cm $^{-1}$ [11]. Urkmez et al. (2013) prepared pure PIn via chemical synthesis in chloroform, the synthesized polymer showed good thermal stability with the degradation temperature of 610 °C, the glass transition temperature (T_g) at 65 °C, and the dopant removal appeared at 150 °C. The electrical conductivity of PIn was 2.21×10^{-3} S cm $^{-1}$ [18]. Gupta et al. (2010) synthesized PIn with two strategies, the interfacial polymerization and the two miscible solvents polymerization technique. The particle shapes were different; the hollow spherical shape was obtained by the first strategy and rod-like shape by the second strategy [10]. Giribabu et al. (2013) synthesized PIn nanowires by oxidative polymerization using ammonium persulfate as the oxidant. XRD pattern showed various sharp peaks supporting a crystalline structure of the nanorod PIn [19]. Handore et al. (2014) studied the effect of oxidant types (K₂S₂O₈ and CuCl₂) on electrical conductivity of PIn. The electrical conductivity of PIn strongly depended on the oxidant types; the electrical conductivity of K₂S₂O₈ was less than CuCl₂ by one order of magnitude. PIn formed the micro-scaled clusters with a weak attraction [20].

Emulsion polymerization is facile, convenient, economic and environmentally friendly for polymer synthesis by using surfactant to control particle size, shape and an electrical conductivity. Surfactant behaves in a dual function: template and dopant. In the role of template, the polymerization reaction takes place in the micro or nano-reactor of surfactant micelles. In the role of dopant, surfactant can incorporate into the polymer backbone by ionic complex formation [21]. However, surfactants can form micelles when their concentration is greater than their critical micelle concentration (CMC) leading to the control over morphology and particle size [22]. Generally, an emulsion system can produce a polymer particle size in the range of 50 – 1000 nm [23]. Common surfactants such as cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), (polyoxyethylene (20) sorbitan monooleate) or Tween 80 are typically used to prepared conductive polymers by means of emulsion polymerization [24].

In this work, a systematical study was devoted to the synthesis of PIn by emulsion polymerization in aqueous solution at room temperature under the effects of surfactant type and concentration utilizing an anionic surfactant SDS, a cationic surfactant CTAB, and a non-ionic surfactant Tween 80. The effect of oxidizing agent type (APS and FeCl₃) was investigated, where the over-oxidation of PIn was verified by FT-IR and XPS, on electrical conductivity of PIn. The element composition and chemical structure of the obtained PIn were examined by FT-IR, XRD, and XPS. To improve the electrical conductivity of PIn, the doping process with HClO₄ at different doping mole ratios of HClO₄ to indole was carried out. Morphology and particle size of PIn in various synthesis conditions were identified by FE-SEM.

2. Experimental

2.1. Materials

Indole powder (monomer), ferric chloride (FeCl₃), tween 80 (TW80) and CTAB, were purchased from Sigma Aldrich. Ammonium persulfate (APS) ((NH₄)₂S₂O₈) was purchased from Merck. SDS was purchased from OmiPur. Hydrochloric acid (HCl) (37%v/v) was purchased from RCI Labscan. Ethanol for dissolving of indole monomers was purchased from HAYMAN. For dedoping and doping processes, ammonium hydroxide (NH₄OH) (30%v/v; Panreac) was employed to dedope the PIn powder at room temperature while perchloric acid (HClO₄) (70%v/v; Panreac) was used as a doping agent. Distilled water was used as solvent for all

reagents. All reagents were of analytical reagent grades. The reagents were used without distillation.

2.2. Polyindole synthesis

Each surfactant calculated in gram by the indole to surfactant mole ratio was dissolved in 0.1 M of HCl (180 ml) then continuously stirred by magnetic stirrer at room temperature to prepare a homogeneous surfactant solution. Surfactant concentration was studied as a function of indole to surfactant mole ratios: 1:0.05, 1:0.1, 1:0.15, 1:0.2 and 1:0.4 The surfactant solution was gradually added with a powder of oxidizing agents (FeCl₃ or APS), followed by continuous stirring to obtain a homogenous solution for 30 min. Subsequently, indole solution (indole \sim 3 g dissolved in 10 ml of ethanol) used as a monomer solution was gradually added into the mixture solution and finally the solution became to be a dark green color. Molar ratio of oxidizing agent to indole monomer was fixed at 2.57, according to Saleh and co-worker [25]. After that, the reaction was continuously stirred for 24 h. The precipitate was rinsed with 1 M of HCl (200 ml) and then was collected by gravitational filtration, washed by distilled water several times before drying in oven at 70 °C overnight to obtain a PIn powder. Generally, PIn color was green, however, it depended upon the synthesis condition. The dried PIn precipitate was grounded and always kept in a desiccator overnight before further use. The proposed mechanism pathway for PIn synthesis is shown in Scheme 1(a)-(b). PIn synthesized by using FeCl₃ and APS as an oxidizing agent is represented by PIn/FeCl₃ and PIn/APS, sequentially. The PIn synthesized in the systems of SDS, CTAB, and TW80 is labeled as PIn-SDS, PIn-CTAB, and PIn-TW80, respectively. PIn without surfactant was also synthesized under the similar condition.

2.3. De-doping/doping process

PIn/FeCl₃ powder was treated with 5 M of NH₄OH under N_{indole}/N_{NH₄OH} mole ratio of 1:10 for 24 h to produce the de-doped PIn/FeCl₃ (dePIn/FeCl₃). The dePIn/FeCl₃ precipitate was filtered, washed with distilled water until it was in a neutral state, and dried at 70 °C overnight. The dePIn/FeCl₃ powder appeared in a pale green color. After that, the dePIn/FeCl₃ powder was stirred in 2.5 M of HClO₄ at the N_{HClO₄}/N_{indole} mole ratios of 1:1, 5:1, 10:1, 25:1, 50:1 and 75:1 for 24 h. The doped PIn/FeCl₃ (dPIn/FeCl₃) was filtered by using a cellulose acetate filter paper, dried at 70 °C overnight, and kept in a desiccator before testing. PIn/FeCl₃ color after the doping returned to dark a green color or a black color depending on the doping mole ratio. Finally, the appropriate doping mole ratio was applied to study the doping of PIn synthesized under the surfactant systems.

2.4. Characterization

The critical micelle concentration (CMC) of each surfactant (SDS, CTAB, and TW80) was determined by measuring surface tension using a tensiometer (Kruss/Easydyne tensiometer, K20) with the Wilhelmy plate mode at 25 °C. The surfactants were dissolved in a 0.1 M of HCl solution used as a solvent for the PIn synthesis.

The functional group analysis of all conditions was identified by a Fourier transformed infrared spectrometer, FT-IR (Thermo Nicolet, Nexus 670). All FT-IR spectra were recorded in the wavenumber range of 400–4000 cm $^{-1}$, 64 scans, and with a resolution of 4 cm $^{-1}$. The PIn samples were mixed with KBr powder (the background material) then compressed by a hydraulic press machine.

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