Particle Size Reduction of Polyaniline Assisted by Anionic Emulsifier of Sodium Dodecyl Sulphate (SDS) Through Emulsion Polymerization

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Abstract. Reduction of particle size of Polyaniline (PANI) evaluated after anionic surfactant assisted polymerization reaction was observed during synthesis. The use of Sodium Dodecyl Sulfate (SDS) during the reaction has reduced the particle size of PANI to the smallest 212 nm from original size 713 nm obtained from a synthesis of SDS free. The single compound of SDS has specific fingerprint at wavenumbers of 1247 and 1216 cm\(^{-1}\) indicating an asymmetric stretching, vibration and a symmetric stretching vibration of SO\(_2\) molecule at 1080 cm\(^{-1}\). After SDS assisted polymerization reaction completely, the fingerprint specifically appears in the range of 950 - 1000 cm\(^{-1}\) wavenumber for SO\(_2\) molecule peaks. It indicates that there was SO\(_2\) molecule bonded into PANI molecule. It was obtained that the higher SO\(_2\) content in PANI of a high SDS concentration shows a wider of spectra and higher absorbency. In addition, there was no pH effect during the polymerization reaction under various SDS concentrations. It is concluded that the particles of PANI were reduced with the addition of SDS during polymerization reaction. The smallest average particle size obtained through the emulsion polymerization technique containing 0.67 % SDS was 212 nm.

Keywords: Conductive polymer, anionic surfactant, emulsion polymerization, particle size formation, sodium dodecyl sulfate

1. Introduction

Particle size in polymer synthesis is being an attractive area to be explored [1,2,3]. Generally, there are some polymerization techniques to control the particle size during the polymerization. A few to mention are solution polymerization [4], emulsion [5], suspension [6], dispersion [7] and precipitation polymerization techniques [8]. Those kinds of techniques are able to control the particle size of the polymer during synthesis. In addition, batch process [9], continuous or semi-continuous processes [10,11] also can control the particle size during the polymerization reaction.

The particle size of the polymer molecules is formed from chain length of monomer which grows through a propagation stage of polymerization reaction [5]. The technique of polymerization apart of allowing control of the particle size, the homogeneity of the particle size distribution is not exceptional [4-8]. The latter was obtained by introducing the anionic dispersion in the reaction which produces a
narrow molecular weight distribution with a uniform size of the polymer particle [1]. Meanwhile, heterogeneous polymerization like emulsion polymerization generated in aqueous medium has been the best polymerization technique to obtain a polymer with a wide range of particle size distribution [2]. The potential applications of polymer which require control of the particle size are spread out in some areas like biomedicine [12], coating and paint industry [13], biopolymer synthesis [14], electronic devices [15] and other applications that require the differences particle size of the polymer.

In this paper, we report some results associated with particle size reduction during the synthesis of polyaniline (PANI) through the emulsion polymerization reaction by a semi-continuous method. Sodium dodecyl sulfate (SDS) was selected as an anionic surfactant that introduced during the reaction. For a certain application of PANI, smaller particle size with high uniformity of particle size distribution is required [22]. To fulfill this inquiry, it needs a suitable technique and polymerization method. Feeding of anionic surfactant during the polymerization process being one of the alternative solutions in order to obtain the smaller particle size of PANI [22,23]. Hence, the role of anionic surfactant to the particle formation of PANI is discussed in this paper. The particle size was measured using Particle Size Analyzer (PSA) Malvern ZS Nano series. Other supporting characterizations are required in order to obtain a complete result through a series of measurements like chemical molecule functional group by Fourier Transform Infra-Red (FTIR), Spectrophotometer Thermo and the pH value by pH Meter.

2. Methods
Aniline and ammonium persulfate of 99.95 % purity together with pro analysis hydrochloric acid (HCl) of 37% concentration were used for the synthesis of PANI. The HCl was diluted in demineralized water (DW) to form 1.5 M acid solution. The emulsion polymerization reaction was carried out in a glass apparatus using a round bottom flask with four necks for 7 hours under a continuous agitation speed of 300 rpm through the semi-continuous method. There were two different solutions which placed in two different dropping funnel containing aniline monomer dissolved in HCl 1.5 M and initiator solution made of ammonium persulfate dissolved in HCl 1.5 M. Those two chemical agents were dropped constantly by managing the flow rate of approximately 3.5 ml/minute. The aniline monomer solution was prepared from 75 ml aniline and 650 ml HCL 1.5 M. Meanwhile the initiator solution was prepared from 75 grams of APS and 650 ml HCL 1.5 M. Anionic surfactant of sodium dodecyl sulphate (SDS) type with four different concentrations was set respectively 0.25%, 0.67%, 1.00 and 2.00% and successively used as additives during each polymerization reaction. Sampling point was taken every 5 minutes for particle size measurement by Particle Size Analyzer (PSA) Malvern ZS Nano series. The synthesized PANI was characterized by Thermo Scientific Nicolet iS5 Fourier Transform infrared (FTIR) spectrophotometer.

3. Results and Discussion
As described in the foregoing section, the polyaniline has been successfully synthesized through emulsion polymerization technique. All monomer conversion was measured by FTIR Spectrophotometer indicated complete reaction to form polymer molecules as polyaniline. As a continuation of previous studies, the use of sodium dodecyl sulphate (SDS) became the focus of observation. The observation began with collecting the FT-IR spectrum using the Thermo Scientific Nicolet iS5 Fourier Transform infrared spectrophotometer. Figure 1 shows the difference plotted in transmission (%) and wavenumber (cm⁻¹) between the spectrum of a single solid SDS substance and a 2% SDS solution in water. This spectrum will explain whether the polymerization reaction is carried out in aqueous media. This confirms that a 2% SDS solution in water has a specific fingerprint at 3235-3380 cm⁻¹ as a molecule containing hydroxyl groups of water.

In a previous report, it was clearly revealed that the aniline monomer had specific fingerprints at 3472 and 3394 cm⁻¹. The peak will disappear when the amine group forms the base of polyaniline emeraldine (PANI-EB) specifically at 3223 cm⁻¹ [24]. The polymerization reaction process has shown a complete reaction when all aniline monomers are converted to polyaniline [11,16,24]. Anionic
surfactant seeds use Sodium Dodecyl Sulphate (SDS) with various concentrations in the aniline polymerization reaction process described in Figure 2.

Where the PANI-EB is formed containing each SDS concentration of 0.25, 0.67, 1.00 and 2.00% respectively. The number of SDS produces a different transmittance intensity than PANI-EB, which is higher than SDS content will get a higher transmittance of polymer molecules, especially at 950-1100 cm\(^{-1}\) which shows the S = O stretching vibration. In other words, higher SDS concentrations will produce polyaniline which contains higher SO\(_2\) molecules that are attached between polyaniline molecules. This supports the observations reported by Yu-Chun et al., described the characteristics of composite PANI/graphene peaks with and without SDS content inside [25]. Similar results were also conveyed by J.A. Raj and all who conveyed that the two bands at 1030 and 1000 cm\(^{-1}\) became visible due to SO\(_3^-\) molecular stretching which showed the presence of anionic surfactant molecules in polyaniline [26].

![Figure 1. FTIR Spectrum of SDS solid and 2 % SDS containing solution in water](image1)

![Figure 2. FTIR Spectrum of PANI EB containing several of SDS Solution](image2)
Another supporting characteristic for observing the formation of polyaniline is a change in pH value during the reaction. Determination of the final pH value was carried out using pH meter series Metrohm 827 with double-digit precision. Through measurement, the pH value of a solution can determine whether SDS has the same effect as the polymerization reaction without the surfactant content. Referring to Figure 3, the value of the solution is 1.10 and slowly increases to 1.13, 1.15, 1.17 starts at around 125 minutes from the stable condition to find 1.20 after the 180-minute reaction. The final propagation stage is indicated when all molecular chains have been formed constantly. The termination stage is achieved in about 300 minutes of reaction time where the final pH value is 1.30. There is no significant effect that can be observed from the involvement of SDS in the PANI polymerization reaction. One of the donor acid values comes from the reaction of the media in 1.5 M HCl solution. The pH value of the total reaction solution starts from a value of about 1.10 to 1.30 after 420 minutes of reaction and is applied to various solutions containing various concentrations of SDS. Observation of the pH value of the reaction solution has been explored by Slamet et al which shows the pH profile of aniline polymerization reaction in acidic media and neutral media for 480 minutes [17]. Based on the report, it was concluded that the pH value of acidic media occurred in 0.80-1.20. Meanwhile, Stejskal et al have reported similar results with regard to the pH value of polyaniline which explained that the pH value of the polymerization process of aniline monomers depends on the reaction medium in which aniline has different phases from the oxidation number at different pH [27-29].

![Image of pH changing during the polymerization reaction](image-url)

**Figure 3.** Graph of pH changing during the polymerization reaction

One of the most important parameter to ensure the polymerization reaction was carried out through the correct path is particle size of polymer [30]. It can indicate that the stages of the molecular chain extend to form a stable polymer molecule. According to observation result was reported by Slamet et al, the final average particle size of polyaniline without using any kind of surfactants in the range 30-40 μm [17]. Another report demonstrated that the final particle size of polyaniline was synthesized through chemical oxidative polymerization was ~ 54.72 μm [16]. The following data was collected starts from Table.1, Figure 4 and Figure 5 present a series result of particle size evaluation to polyaniline containing various concentrations of SDS solution. Referring to the observation result, the average particle size of polyaniline was reacted without surfactant content was ~713 nm, on the other hand, there was a significantly different result when involving the surfactant during the polymerization reaction. The average particle size of polyaniline decreased to ~350 nm when there was 0.25% surfactant content inside then it decreased again being smaller to ~212 nm when additional of SDS was 0.67%. It explained the observation result was reported by Sajjadi, et al [30] and Pierre, et al [31,32] who had evaluated the effect of an anionic surfactant of Sodium Dodecyl Sulphate (SDS) to particle size distribution of polymer particle in emulsion polymerization. The presence of SDS was able to reduce the particle size of the polymer particle. They informed that SDS is the best emulsifier for emulsion polymerization technique since can produce fine particle polymer. SDS also was an effective stabilizer because as an anionic surfactant, it’s molecule contained surface charge density which caused an apparently larger surface area when the SDS was presence [1,30,31,32]. The similar result also has been delivered by Jeevananda,
In the report was exhibited the presence of SDS to synthesize polyaniline nanostructures. The report mentioned that the average diameter of the polymer particle was 30-35 nm [22].

| Concentration of SDS | Average Particle Size Polyaniline |
|----------------------|----------------------------------|
| 0.00 %               | 713 nm                           |
| 0.25 %               | 350 nm                           |
| 0.67 %               | 212 nm                           |
| 1.00 %               | 255 nm                           |
| 2.00 %               | 295 nm                           |

Figure 4. Average Particle Size Formation of PANI with and without Surfactant Presence

In the classical theory of emulsion polymerization, the particle of the polymer grows within three stages [1,5,7]. When the reaction of polymerization is carried out by emulsifier-free, the particle will grow randomly without any backbone for particle developing, but on the other hand, when the emulsifier especially anionic emulsifier was presence, the propagation stage to develop the polymer chain will extend regularly in the micelle as a polymer backbone to form a stable particle. It is because the emulsifier molecule which adsorbed on the monomer droplets during the polymerization reaction is out weighted than the amount of emulsifier molecule in the aqueous phase. These phenomena will produce a stable and fine particle of the polymer [1,5,7]. The appropriate amount of emulsifier is used in emulsion polymerization is in the critical micelle concentration (CMC) or above the CMC value to build a stable home base for propagation stage of the polymer molecule. The CMC value of SDS is 8.2 mM at 25°C [30]. When the presence of SDS is below the CMC value, all the emulsifier molecules will be adsorbed on the monomer droplet, this causes the emulsifier will not contribute to particle formation of the polymer [30,31]. The particle polymer is obtained under additional of the emulsifier at the CMC value or above the CMC value will play a role in the particle size growing of polymer. In this research, the amount of SDS was used above the CMC value which demonstrated smaller final particle size with smaller and narrow particle distribution compare with the polymer emulsifier-free which has a broad particle size distribution (Figure 5). The average particle size of polyaniline slightly increased when used 1.00% and 2.00% to ~255 nm and ~295 nm respectively. It can be explained by the aggregation theory of emulsifier. When the amount of emulsifier is sufficient to adsorb on monomer droplet, the excess of emulsifier will tend to build an aggregation. When the emulsifier began to aggregate, the final particle polymer increased [1,5,7,30,31,32].
This work has provided supporting evidence to confirm the previous report regarding particle size evaluation on polymerization reaction process especially the effect of sodium dodecyl sulphate (SDS) as an anionic emulsifier which has an important role in emulsion polymerization reaction, specifically for polymerization process reaction to synthesize polyaniline as a conductive polymer.

4. Conclusion
This result has demonstrated that anionic surfactant type of sodium dodecyl sulphate (SDS) was able to produce smaller particle size and narrow particle size distribution of polyaniline which synthesized through emulsion polymerization technique. Decreasing of polymer particle size is in line with increasing the amount of SDS presence. The average particle size reached ~212 nm with 0.67% of SDS content. It almost more than three times decreased compare with the average particle size was ~713 nm when SDS was absence.

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Figure 5. Particle Size Distribution of PANI with several SDS solutions
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