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Synthesis and characterization of anionic surfactants doped polypyrrole

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ABSTRACT

Conducting polypyrrole (PPy) was synthesized using polymerization of pyrrole monomer in aqueous containing ferric chloride as an oxidant and a surfactant at temperature below 5^{o}C. Anionic surfactants namely ethane sulfonic acid (ESA) and sodium dodecyl sulphate (NaDS) were used as dopants. The polymer were characterized by using elemental analysis (CHNS-O), Fourier Transform Infra- Red (FTIR) and Field Emission Scanning Electron Microscope (FESEM). CHNS-O and FTIR showed that surfactant were incorporated into PPy and FESEM was used to confirm the morphology of the sample.

Keywords: Polymerization, ethane sulfonic acid, sodium dodecyl sulphate

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INTRODUCTION

In recent years, intrinsic conducting polymers (ICP) have assumed a great importance in several technologies such as display devices, solar cells, gas sensor and actuators [1]. Many new conducting polymers such as polyaniline (PANi), polypyrrole (PPy) and polythiophene (PTh) were discovered. Among conducting polymers, polypyrrole is one of the most studied material. This polymer have a good electrical conductivity, environmental stability and relative ease of synthesis [2].

Polypyyrole can be prepared by electrochemical [3] or chemical oxidation of pyrrole [4] in organic solvents and in aqueous media. However, PPy is insoluble and infusible because of the rigidity of its molecular chains of π-conjugated structure [5]. To overcome these problems, using various dopants has contributed to the development of soluble PPy [6]. Organic sulfonates and aromatic acid derivatives such as dodecyl benzene sulfonic acid (DBSA), sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (DBSNa) are widely used as dopant.

According to Lee et. al [7] PPy chemically prepared and doped with bulky anion of dodecyl benzene sulfonic acid (DBSA) was soluble in m-cresol and after the addition of a co-surfactant such as camphor sulfonic acid, chloroform, dichloromethane and 1,1,2,2-tetrachloroethane. Kudoh [8] reported that chemical preparation of PPy from aqueous solution containing ferric sulphate as an oxidant and anionic surfactants such as DBSNa, sodium n-alkyl naphthalene sulfonate and sodium n-alkyl sulphate. The properties of PPy was improved when incorporated with anionic surfactant into the PPy as the dopant.

In the present work, polypyrrole was synthesized by chemical oxidation of pyrrole with $FeCl_3$ in aqueous at temperature below 5^{o}C. The effect of doping agents on structural and morphology is investigated.

MATERIALS AND METHODS

Reagents

All chemicals used were analytical grade. Pyrrole was purchased from Acros, purified and stored in a refrigerator prior to use. Ferric chloride ($FeCl_3$) (SIGMA) was used as an oxidant. Ethanesulfonic acid (ESA) and sodium dodecylsulphate (NaDS) from Acros were used as the surfactant. Methanol (Merck) and deionized water were used for the synthesis.

Synthesis of polypyrrole

The anhydrous $FeCl_3$ was dissolved in 200 mL of deionized water and then freshly purified pyrrole (3.5 mL) was added. The pyrrole/oxidant molar ratio was fixed at 1:2. The reaction was allowed to proceed for 6 hours at below 5^oC with a moderate stirring speed. The polymerization reaction was terminated by pouring the reaction mixture into an excess amount of methanol. The precipitate of PPy powder was filtered off, washed with deionized water and dried for 24 hours in an oven at 40^oC.

Synthesis of anionic surfactants doped polypyrrole

$FeCl_3$ (0.05 mol) was dissolved in 100 mL of deionized water and was mixed with 0.01 mol anionic surfactant and stirred. The freshly purified pyrrole (0.15 mol) dispersed in water was added slowly into the mixture. The polymerization conditions as for the synthesis of PPy were followed.

Characterization methods

The PPy and anionic surfactants doped PPy samples were characterized by elemental analysis using an elemental analyzer Flash 2000. The structural properties of the respective samples were studied using a Nicolet 6700 Spectrometer by ATR technique. All spectra were recorded in the range of of 2000-400cm^{-1}. The Field Emission Scanning Electron Microscope (FESEM) was used to study the surface morphology of the synthesized PPy particles.

RESULTS AND DISCUSSION

Elemental analysis

Generally, the elemental analysis gives the percentage of weight of each elements that are present in the sample. The elemental analysis can be used to estimate the extent of doping in the polymer chain. This analysis was conducted on the dried sample and the data were shown in Table 1.

The doping level of PPy-NaDs sample is higher than that of PPy-ESA. This indicated that doping level of PPy increased when doping agent with longer alkyl chain was used. The large size surfactants anions being predominantly incorporated into the PPy backbone [9].

TABLE 1. Elemental composition of PPy, PPy-ESA and PPy-NaDs particles

PPy-surfactant	C	H	N	S	Doping level
PPy	59.86	3.63	17.60		
PPy-ESA	48.31	2.99	14.23	0.58	1.77
PPy-NaDs	55.61	6.61	8.80	5.24	25.88

Morphology

Figure 1 displays the comparison of the morphology of PPy and doped PPy samples with different anionic surfactant, PPy-ESA and PPy-NaDs respectively. As shown by FESEM images in Figure 1 (a), the surface structure of PPy showed a globular porous structure like a cauliflower. In Figure 1 (b) display sphere-like while in Figure 1 (c) powder particle looks more compact. Different doping agents give the different size of particles. It was observed that the presence of the surfactant in polymerization strongly influenced the morphology of PPy samples [2].

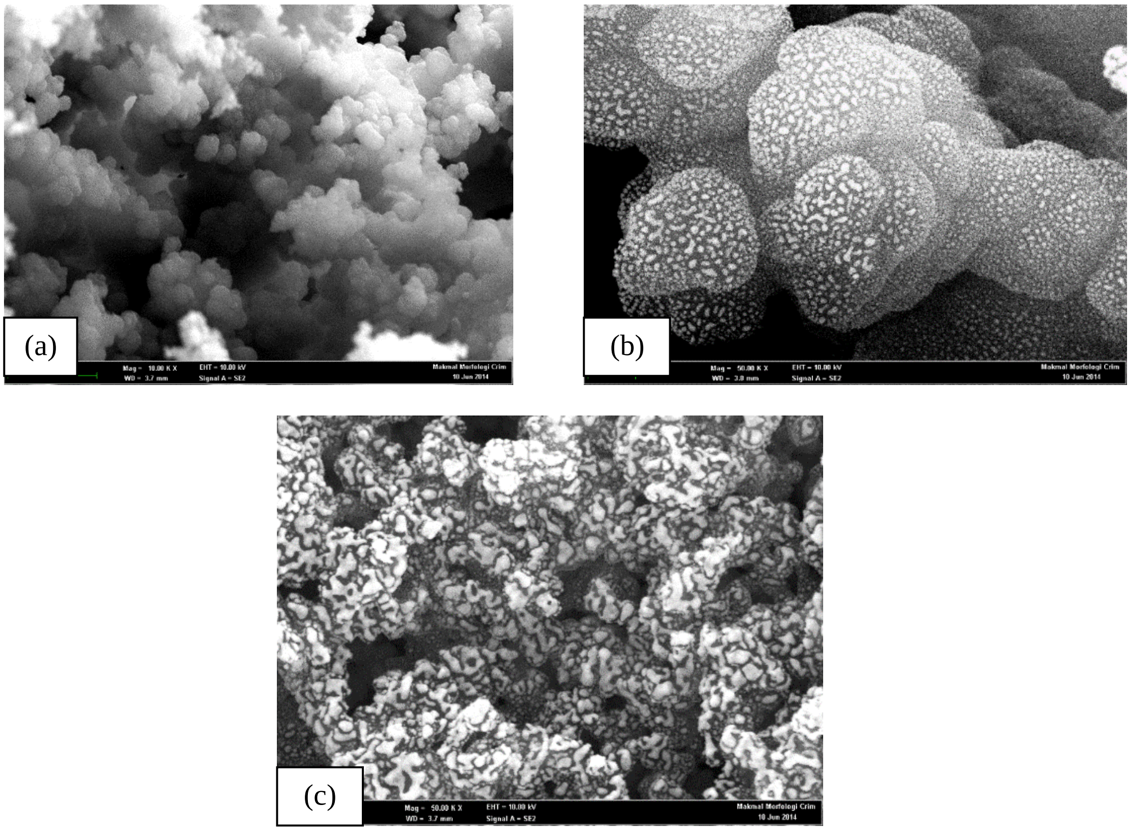

Figure 1: FESEM images of PPy (a), PPy-ESA (b) and PPy-NaDS (c)

FTIR

The infrared spectra of PPy and PPy with dopants in the region from 3500 to 500 cm^{-1} are shown in Figure 2. The bands at 2915 cm^{-1} correspond to S=O and C-H stretching modes, which indicate the presence of benzoid ring in molecule. The bands at 1530 cm^{-1} correspond to the C-C stretching vibrations in pyrrole ring. It is known that the skeletal vibrations, involving the delocalized π electrons, are affected by doping the polymer [10].

The peaks at 1449 cm^{-1} represent the C-N stretching vibration in the ring. The band from 1400 to 1290 cm^{-1} is attributed to C-H and C-N in-plane deformation vibrations of doped PPy. The broad band in the spectra of PPy and doped PPy samples, were found in the region of 1200 cm^{-1} to 1030 cm^{-1}. These peaks correspond to the breathing vibration of the pyrrole ring.

Meanwhile, in the spectra of PPy the corresponding peaks were found in the range of 1538 to 1041 cm^{-1}. The bands at 1147 and 1141 cm^{-1} in the spectrum of PPy-ESA and PPy-NaDs correspond to the S=O stretching vibration of sulfonate anion [21]. The peak at 1031 cm^{-1} is present in the spectrum of PPy sample and in the spectra of PPy-ESA and PPy-NaDs samples. It suggests that the peak corresponds to the mode of in-plane deformation vibration of N^+H_2 which is formed on the PPy chains by protonation [11].

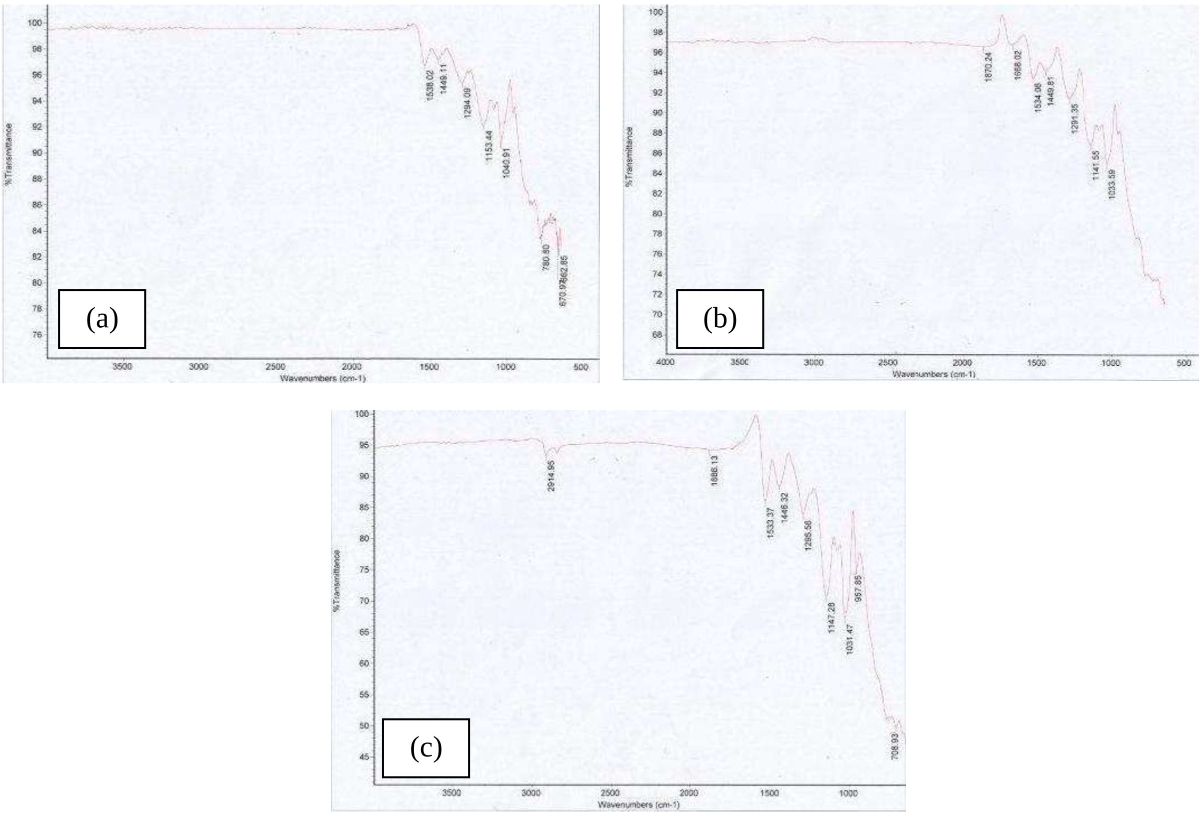

Figure 1: FTIR spectra of PPy (a), PPy-ESA (b) and PPy-NaDS (c)

CONCLUSION

In summary, PPy was synthesized by chemical polymerization using the aqueous solution containing $FeCl_3$ and doped with ESA and NaDs at lower temperature. All these materials were characterized using elemental analysis, FESEM and FTIR.

The doping level was calculated based on results of elemental analysis. Anionic surfactant has strong effect on the polypyrrole morphology and the FTIR analysis shows that surfactant was incorporated into PPy structure.

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