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Synthesis of Nano-Structured Polyaniline by Direct Emulsion Polymerization

M.H. Haghanifar[1], M. Pishvaei[1,*], S. Pourmahdian, A.S. Pakdel

[1] *Department of Resin and additives, Institute for Color Science and Technology, Tehran, Iran*
[2] *Department of Polymer Engineering and Color Technology, AmirKabir University of Technology, Tehran, Iran*

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A direct emulsion process was performed for the synthesis of an emeraldine salt of polyaniline (PANI) using a novel surfactant, namely cetyl dimethyl ammonium phenyl chloride (CDAPhCl). HCl was used as dopant and potassium persulfate (KPS)was used as an oxidizing agent. Variation of polymer yield was recorded using conventional gravimetric method and resulting polymer salt was analyzed by FTIR. Average particle size and latex morphology was studied using dynamic light scattering (DLS) and scanning electron microscopy (SEM).Furthermore, the influence of the reaction time followed by polymer yield on the conductivity of resulted PANI salt was investigated. SEM images showed a nanostructured polyaniline and conductivity of the polyaninle film found to be 1.65 S cm^{-1}.

Keywords: Emulsion Polymerization, Polyaniline, Conductivity, Polymer Yield.

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1. INTRODUCTION

The chemistry of polyaniline (PANI) allows us to benefit from a vast verity of synthesis routes and processing methods. The synthesis of PANI can be classified as electrochemical and chemical oxidative polymerizations. There are several oxidizing agents [1] such as $K_2Cr_2O_7$, $FeCl_3$, $KMnO_4$ and KPS which was employed in this study.

Homopolymerization of aniline has been carried out using emulsion and microemulsion techniques. Inverse emulsion method has only been employed for the synthesis of PANI composites and blends so far [2].

In this study, a direct emulsion method was performedfor the synthesis of PANI salts with Hydrochloric acid(HCl), an aqueous solution as the dispersing medium and aniline as the dispersed phase. The oxidant employed here is KPS. Electrical properties of the resulting polymer were then investigated.

2. EXPERIMENTAL

Aniline (Merck) was distilled under reducedpressure to remove any impurities. All other chemicals were analytical grade reagents and were used as procured.

In a typical experiment, 1 g of cetyl dimethyl ammonium phenyl chloride(CDAPhCl) was dissolved in 30 ml of water and the resulting solutionadded to a three necked round bottome glass flask containing 3 ml of aniline. 1.8 g of KPS dissolved in 10 ml of acid solution (HCl 3 molar), added dropwisely to the reactor. The reaction mixture turns green within 15–20 min, indicating the onset of polymerization. The reaction was allowed to proceed at room temperature for 24 hoursunder continuous stirring. The reaction mixture was then poured into 100 ml acetone and kept in the same condition for one hour to precipitate the PANI–HCl salt. Precipitated salt was then filtered, washed with methanol, acetone and water two times.

3. RESULTS AND DISCUSSION

3.1 Gravimetric analysis

The samples taken from the reactor were placed into the pre-weighted filter papers.The filter paper was then dried in avacuum oven at 65^c for eight hours. Each measurement was repeated 3 times. Final yield was more than 90%which was relatively higher than many other emulsion routes[3-6].

3.2 FT-IR analysis

Figure 1 shows FTIR spectra of dried PANI salt. A broad band at 3435.83 cm^{-1} assigned to the N–H stretching vibration. Bands at 2920 and 2451.86 cm^{-1} are assigned to asymmetric and symmetric aliphatic C–H stretching vibrations. Stretching of quinonoid and benzenoid form is observed at 1564.04 and 1483.64 cm^{-1}. The C–N stretching band of an aromatic amine appears at 1296.66 cm^{-1}. The bands at 1128.66 and 796.74 cm^{-1}can be attributed to the in-plane and out-of-plane C-H bending modes, respectively. On redoping the base with 3 M HCl, the bands are observed at 700 cm^{-1}, demonstrating that the salt is regenerated [7, 8].

3.3 DLS analysis

Before analysis, diluted sample of the end product from the reactor we dispersed in the water. The particle size distribution of PANI is measured by dynamic light scattering method with instrument of Master sizer 2000 (Fig. 2). The mean average size (d(0.5) = 65nm) confirms the nano-sized particles.

3.4 SEM analysis

The surfactant was removed from the samples before the SEM analysis, so assembly of the polymer particles took place. When the surfactant is removed PANI nanoparticles can arrange regularly to form a sharp-edged granular morphology because of their small-size effect of

*pishvaei@icrc.ac.ir

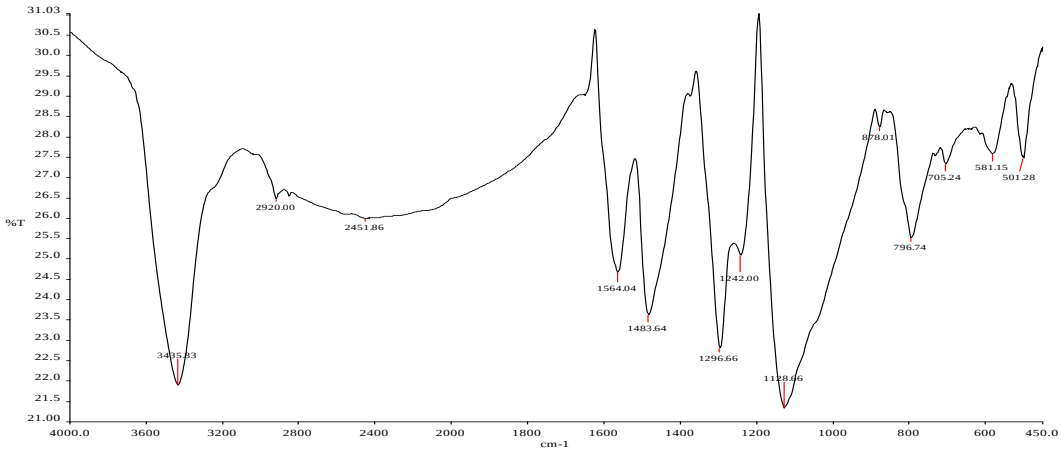

Fig. 1 – FT-IR sepectra of the dried PANI salt

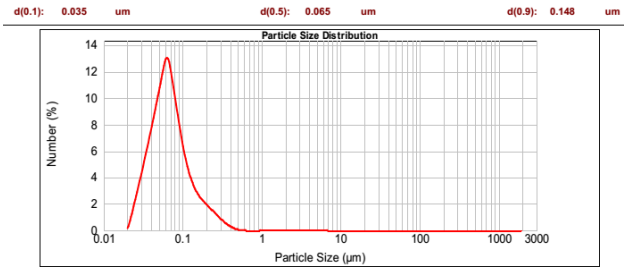

Fig. 2 – Particle size distribution of PANI.

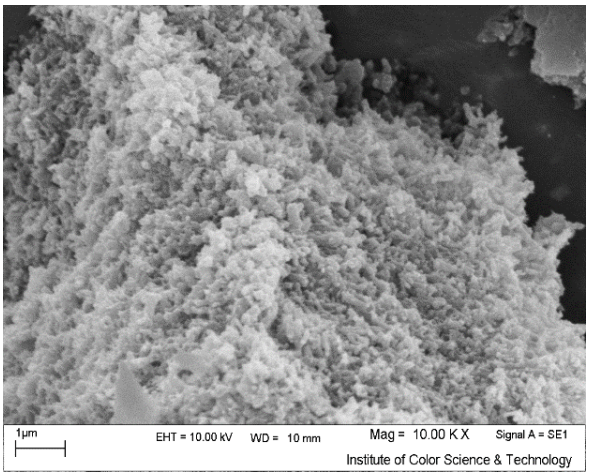

Fig. 3 – SEM image of PANI salt.

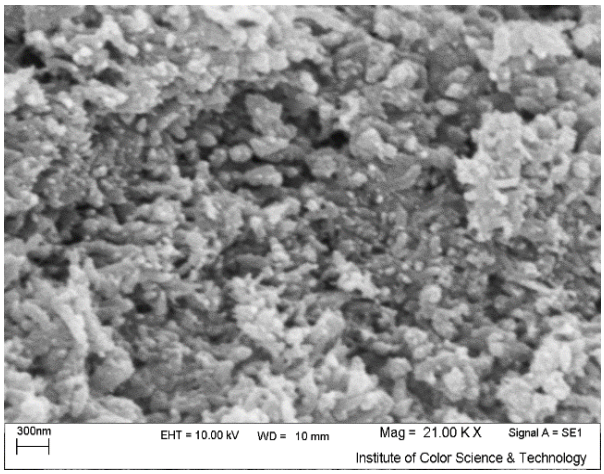

Fig. 4 – SEM images of PANI salt powder.

Table **1** – PANI conductivity versus yield

Time (hr)	Yield (%)	Conductivity (S/cm)
3	23.7	0.13
5	45.1	0.40
7	50.4	0.79
10	73.4	0.92
12	78.7	1.22
24	90.4	1.65
48	91.2	1.66

nanoparticle. The SEM images (Fig 3, 4) show a range size of PANI particles of about 50-200 nanometers.

3.5 Conductivity measurements

The electrical conductivity of the casted films prepared by these methods was determined using the standard four-probe method. A thin layer film of PANI-HCl salt dissolved in xylene at room temperature was casted. The electrical conductivity of PANI-HCl film was 1.65 (S / Cm) which was similar to the HCl doped PANI prepared by common polymerization in aqueous solution and was higher than similar works due to homogeneity of the particles [9-11].

Table 1 summarizes the time of reaction followed by polymer yield and conductivity of each sample. The longer time of reaction, resulted in the higher conductivity. For the reaction time more than 24 hours, one can see that the conductivity is almost constant Therefore, the reported conductivity of PANI film is related to the sample reaction time of 24 hours.

4. CONCLUSION

In this study, a novel surfactant (CDAPhCl) was used for direct aqueous emulsion polymerization of PANI and the yield of the end product was relatively higher than many other routes. DLS results and SEM images proved a nano-structured polymer which is formed.

Furthermore, a relatively high electrical conductivity of PANI compared to other emulsion methods was obtained.

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