# PHYSICAL CHEMISTRY 2014

12th International Conference
on Fundamental and Applied Aspects of
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# ENHANCED MICROWAVE SYNTHESIS OF POLYANILINE NANOMATERIALS

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## ABSTRACT

Energy- and time-efficient enhanced microwave syntheses (EMS) of polyaniline (PANI) have been carried out. The GPC results showed that the molecular weight of the microwave-generated materials depends on the applied microwave power. FTIR spectroscopies confirmed the formation of PANI. The presence of a mixed morphology with the prevalence of nanofibers with different aspect ratios is confirmed through SEM. The conductivity of the samples (ca. 3-3.5 S $cm^{-1}$) is found to be relatively independent on the microwave power levels. The fact that the molecular weight depends on the power means that this approach can be fine-tuned to optimize conditions for a specific material using different power levels.

## INTRODUCTION

Polyaniline (PANI) is one of the most extensively studied electrically conducting polymers. The specific characteristics make PANI applicable in various fields such as gas sensors, biosensors, actuators, anticorrosive coatings, electronic devices etc. A novel method of synthesis of PANI using a microwave assisted approach under controlled temperature (EMS) has been recently introduced [1,2].

## EXPERIMENTAL

PANI was prepared by aniline oxidation with potassium iodate ($KIO_3$) or ammonium persulphate (APS). To an aqueous solution of 1.25 M

hydrochloric acid (12 mL) was added $KIO_3$ (0.432 g) or APS (0.4606 g). 0.480 mL of aniline was added to this solution. For conventional synthesis (CS) the solution was stirred for 10 min. We used for comparison purposes the previously obtained results for CS PANI sample synthesized after 5 h of stirring (giving the same yield as 10 min MW synthesized PANI ) [1]. The reaction mixture was filtered and washed thoroughly with distilled water and acetone to eliminate low molecular weight oligomers and other impurities. The retentates were dried in a vacuum oven at 40 °C overnight. MW irradiation was performed in a single mode focused CEM reactor (Model Discover, CEM Co., Matthew, NC) operating at 2.45 GHz with ability to control output power. Each microwave (MW) synthesis was carried out for 10 minutes. The PANI MW synthesis using different oxidizing agent was performed in the power range from 3 to 70 W. Three samples for each microwave power (3, 10, 40, and 70 W) were prepared. All experiments were done under the same conditions by keeping constant irradiation power, temperature and initial reaction mixture volume. The temperature of (24±1) °C and mixing rate of 400 RPM are maintained in all experiments. Molecular weights were determined with Gel Permeation Chromatography (GPC) using a 300 × 7.5 mm Polypore column (Polymer Laboratories, UK). The PANI samples were dissolved in 5 mL of NMP to a 3 mg $mL^{-1}$ concentration. The eluent was NMP, and the flow rate was 0.3 mL $min^{-1}$. The molecular structure of PANI samples was investigated by FTIR. Scanning electron microscopy (SEM) carried out using a Philips XL30S Field Emission Gun with a SiLi (Lithium drifted) EDS detector with Super Ultra Thin Window. Electrical conductivity of compressed pellets of the PANI samples was measured using a Jandal Multi Height Four-Point Probe with DC current source, at ambient temperature.

## RESULTS AND DISCUSSION

The yields of enhanced microwave and chemically synthesized PANI using $KIO_3$ and APS as oxidants, as a function of applied power, are all in the range 65-70% while the classical synthesis (CS) method took 5 h to achieve the same yield [1,2]. It is interesting that the percent yield differs only slightly for various microwave power levels. This may imply that the reaction was finished before the samples were taken out (10 min after the beginning of the reaction). At the same time, the yields of the samples obtained without the microwave power (CS synthesis) are only around 25% with stirring after 10 min, in agreement with previously published yields for PANI [1,2]. The final polymer molecular weights ($M_w$) depend significantly on the microwave irradiation power. The molecular weight using $KIO_3$ as the oxidizing agent increased from ca. 3900 g $mol^{-1}$ (3 W) up to 18 300 g

$mol^{-1}$ (70 W). If micro heating was a major effect, molecular weight would decrease with the increasing power level (higher temperature) in analogy with the CS syntheses [3]. On the other hand, the $M_w$ values for the samples obtained using APS were consistently higher, with a range from ca. 7400 g $mol^{-1}$ (3 W) to 22 700 g $mol^{-1}$ (70 W). The molecular weight for CS PANI was ca. 26 200 g $mol^{-1}$ using $KIO_3$ and slightly higher (30 400 g $mol^{-1}$) using APS, in agreement with previously published results [4].

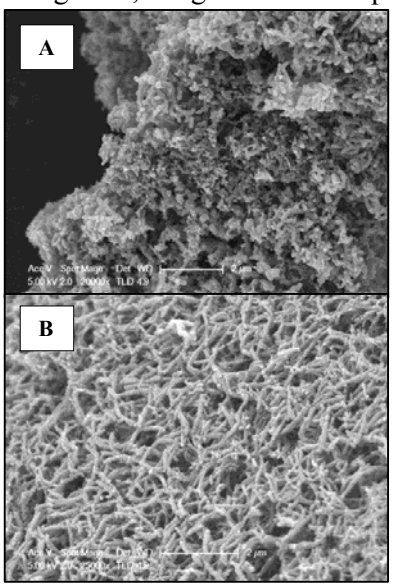


**Figure 1.** SEM micrographs of the EMS synthesized PANI using APS (A) and $KIO_3$ (B) at 70 W.

SEM micrographs of PANI samples synthesized in MW using APS and $KIO_3$ as an oxidizing agents are shown in Figure 1. All micrographs reveal a mixed nanofibrillar structures with different aspect-ratios. This means that the morphology depends to some extent on the microwave power. Despite their similarities, the morphologies of the samples prepared using APS and $KIO_3$ differ upon closer inspection [2]. Overall, the PANI samples synthesized using $KIO_3$ at higher power levels (Figure 1B) compared with the ones obtained with APS (Figure 1A) exhibit a compact and better defined, fiber-like morphology characterized with a higher aspect ratio. It has been shown that morphology depends on the nucleation and growth process and that nucleation and growth mechanisms of PANI depend on the anion type [1]. The EMS samples exhibit mainly fibrilar or rod-like morphologies, regardless of MW power applied during the synthesis, although the quality (aspect-ratio) and the morphological homogeneity of materials do depend on the applied power and the anion type.

FTIR spectroscopies confirmed the formation of PANI structure in both CS and MW synthesized samples. The intense bands and shoulders around 1560 $cm^{-1}$ and 1450-1470 $cm^{-1}$ originate from C-C stretching in the quinonoid and benzenoid rings, around 1290 $cm^{-1}$ from C−N stretching of the secondary aromatic amine, around 1240 $cm^{-1}$ is related to the protonated C−N group. The intense and very broad band which appears at around 1080-1100 $cm^{-1}$ is assigned to electronic bands that are usually considered to be a measure of the delocalization of electrons in the PANI structure. The bands at around 800 $cm^{-1}$ originate from C-H out-of-plane bending in 1,4-disubstituted ring

structures (*para*-coupling), indicating the presence of the head-to-tail coupling during the polymerization.The electrical conductivity (EC) values for MW PANIs do not change significantly with the microwave power. At the same time MW PANI samples showed a higher conductivity (ca. 3-3.5 $Scm^{-1}$) compared with CS PANI samples (~ 0.5 $Scm^{-1}$) after the reaction was completed. Comparison of these data with the molecular weight data implies that the molecular weight has no significant influence on the macroscopic electrical conductivity in the series produced at different microwave power levels, although there is a small increasing trend in conductivity values with increasing molecular weight. This is in agreement with the theoretically predicted weak dependence of electronic properties on chain length.

## CONCLUSION

EMS of PANI was investigated, with microwave power levels varied, while the reaction system was kept at constant temperature of 24 ± 1°C. GPC results showed that molecular weight depended on applied power. On the basis of SEM images, the presence of a mixed morphology with the predominance of nanofibrilar morphology was confirmed, while FTIR techniques confirmed that the microwave-generated materials structurally consist of PANI. At the same time these samples revealed a higher conductivity compared with conventionally obtained material. According to these results, it can be concluded that the microwave-enhanced approach can be used to optimize reaction conditions for obtaining PANI nanofibers with different molecular weight by varying microwave power.

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