

# Influence of interfacial polymerization on the crystallinity, molecular weight, conductivity and redox behavior of poly(2,3-dimethyl aniline)



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## ABSTRACT

The synthesis of *crystalline* nanofibers of poly (2,3-dimethyl aniline) using interfacial polymerization is reported with dichloromethane-water and hexane-water interfaces as illustrations. Apart from the differences in the morphology, molecular weight and conductivity, there exist remarkable variations in the optical and electrical properties of the interfacially synthesized polymer in comparison with the conventional single phase method. Furthermore, the morphologies and conductivities of the polymer vary with the choice of interfaces and are attributed to the rate of polymerization as well as the solvent polarity. The origin of the crystallinity is ascribed to the reaction kinetics as well as nature of the oxidant. The electrochemical sensing of hydrogen peroxide using poly (2, 3-dimethyl aniline)-coated glassy carbon electrodes is investigated in neutral phosphate buffer solutions.

## 1. Introduction

Conducting polymers have attracted much interest during the past few decades on account of their diverse applications in various fields viz. sensors [1], supercapacitors [2], electrocatalysis [3], corrosion prevention [4], optical switching devices [5], electrochromism [6], solar cells [7], batteries [8] etc. Among various types of conducting polymers studied in this context, polypyrrole, polyaniline, polythiophene and polyindole deserve mention because of their tunable properties [9]. In particular, diverse synthetic protocols and applications of *polyaniline* (PANI) have been extensively investigated due to its satisfactory environmental stability and facile redox switching behavior [10]. However, the rigid backbone structure and steric hindrance between the molecular chains leads to unsatisfactory solubility of PANI [11]. In recent years, substituted PANI derivatives have also been extensively analyzed on account of their diverse applications [12–14]. The synthesis of substituted PANI with electron donating groups is a non-trivial exercise due to the decrease in the oxidation potential of the corresponding monomers [15]. Due to the presence of electron-donating group, the interaction between the polymer chains gets diminished which result enhanced solubility in non-aqueous solvents [15]. In the present study, 2, 3-dimethyl aniline is chosen as a typical example for demonstrating new synthetic approaches [16,17].

The liquid/liquid (L/L) interfacial polymerization consists in dissolving the monomer in a non-aqueous solvent while the desired oxidizing agent is present in the aqueous phase [18]. The typical non-aqueous solvents are hexane, dichloromethane, chloroform,

diethylether, methylene chlorides etc [19], the common oxidizing agents being ammonium persulphate [20] and ferric chloride [21]. By a judicious choice of solvents and oxidizing agents, the interfacial technique leads to interesting morphologies and eliminates the use of templates [22]. Due to the accessibility of both aqueous and organic phases, this synthetic protocol is capable of avoiding impurities or by-products e.g. oligomers, inorganic salts etc. The room temperature synthesis of PANI nanofibers using various binary solvents has been accomplished using L/L interfacial polymerization [23].

We report here, the synthesis of poly (2,3-dimethyl aniline) (PDMA) at dichloromethane-water (D-W) and hexane-water (H-W) interfaces with different oxidizing agents. Employing various spectroscopic techniques viz Fourier Transform Infrared, UV–Visible and Nuclear Magnetic Resonance in conjunction with X-ray diffraction, Matrix Assisted Laser Desorption Ionization and Scanning Electron Microscopy, the distinct advantages of the present strategy are pointed out. The crystalline nature of the PDMA samples is rationalized using the reaction kinetics at L/L interfaces. It is shown that the morphologies and conductivities of PDMA are influenced by the nature of the non-aqueous solvent.

## 2. Experimental

### 2.1. Chemicals

2, 3-dimethyl aniline (Avra Synthesis, India) was distilled at 180 °C under N<sub>2</sub> atmosphere at reduced pressure and stored in the refrigerator.

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Nitric acid, methanol, ammonium persulphate (APS), ferric chloride, dichloromethane and hexane were procured from Sigma Aldrich and employed without further purification. All the experiments were carried out using triply distilled water.

## 2.2. Synthesis of poly (2, 3-dimethyl aniline)

The monomer 2, 3- dimethyl aniline (0.4 M) was dissolved in 10 mL dichloromethane (DCM) while the aqueous solution contains 0.1 M APS and 0.1 M HNO<sub>3</sub>. In a vial, these two solutions were added sequentially and an interface is formed between the two immiscible solutions (the solubility of DCM in water is nearly 17.5 g/litre at 25 °C). The variation in color from red to brown at different time intervals indicates the occurrence of the polymerization. The solution was kept undisturbed at 30 °C for 24 h. The precipitate was collected from the interface and filtered through Whatmann 42 filter paper followed by repeatedly washing with dichloromethane and water (at the end). The sample was then dried at room temperature. An identical procedure was also adopted in the case of H-W interface wherein the monomer was dissolved in hexane, the aqueous phase consisting of APS and HNO<sub>3</sub> (identical concentration was taken for all components as indicated for D-W interface). Addition of these two solution in a vial leads to the formation of interface in this case also (the solubility of hexane in water is nearly 9.5 mg/litre at 25 °C). It is of interest to mention here that in both cases, the polymerization commences at the interface and progresses towards the aqueous phase.

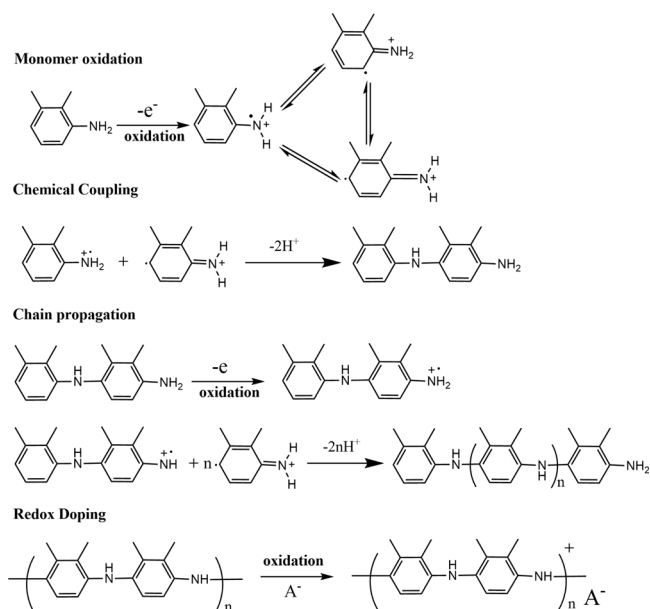
In order to compare the physicochemical properties of PDMA synthesized at the interfaces, polymerization was also carried out using the conventional aqueous phase method. In this case, 0.4 M of 2, 3-dimethyl aniline was dissolved in 30 mL water via sonication followed by the addition of 0.1 M HNO<sub>3</sub> and 0.1 M APS. After 24 h, the solution was filtered through Whatmann 42 filter paper and the precipitate was repeatedly washed with water, followed by drying at room temperature.

## 2.3. Instrumentation

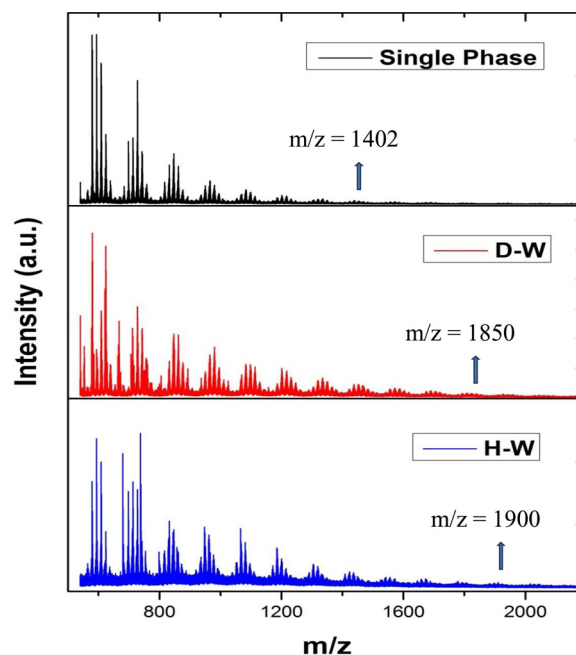
The FTIR spectra were obtained using the Jasco FTIR-4100 spectrometer (resolution = 0.9 cm<sup>-1</sup>) with KBr pellets, while the X-ray diffraction (XRD) pattern was recorded with Bruker D<sub>8</sub> System equipped with CuK<sub>α</sub> radiation (1.5405 Å). UV-Visible absorption spectra were obtained with the Ocean Optics GmbH DT-MINI-2-GS UV-Vis spectrometer. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using Bruker 400 MHz NMR Spectrometer in D<sub>6</sub>-DMSO. The scanning electron micrographs were acquired using FEI Quanta FEG 200. The Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) using the Bruker ultraflex extreme was studied for estimating the number of monomer units. The MALDI spectra were recorded using the PDMA solution (in methanol) in the presence of the matrix  $\alpha$ -cyano hydroxyl cinnamic acid. The PDMA samples were made into pellets and the conductivities were estimated by the four probe method using a multichannel potentiostat.

## 2.4. Electrochemical studies

All the electrochemical experiments were carried out in a one-compartment cell of three-electrode configuration using the PDMA-coated glassy carbon electrode (PDMA/GCE) as the working electrode, with Pt wire and saturated calomel electrode (SCE) as the counter and reference electrode respectively. The differential pulse voltammetric studies were performed using CH Instruments 660 A (CH Instruments USA) in the potential range of 0.0 to -0.8 V with pulse width = 0.05 s, pulse period = 0.5 s and amplitude = 0.05 V.



**Scheme 1.** Schematic representation depicting the oxidative polymerization of 2,3-dimethyl aniline as well as the doping mechanism.



**Fig. 1.** MALDI TOF spectra of PDMA synthesized using the single phase and interfacial (D-W and H-W) polymerization.

## 3. Results and discussion

### 3.1. Reaction mechanism

In the interfacial polymerization, 2,3-dimethyl aniline, (DMA) from the organic phase and APS from the aqueous phase, diffuse towards the interface. The initial step is the formation of radical cations from the oxidation of DMA. The coupling of two radical cations yields bi(2,3-DMA) by the elimination of two H<sup>+</sup> ions. In the propagation step, the oxidation, coupling and deprotonation steps continue to form PDMA. Subsequently, PDMA is oxidized and the counter anions (NO<sub>3</sub><sup>-</sup>) get incorporated into the polymer matrix, in order to maintain electro-neutrality. A plausible mechanism for the formation of PDMA is

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