

Interfacial Synthesis of Long Polyindole Fibers

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ABSTRACT: Polyindole fibers upto a length of 1000 μm and $\sim 25 \mu\text{m}$ in diameter have been reproducibly synthesized by interfacial polymerization, which was performed at a stationary interface of aqueous (FeCl_3 solution)/organic (indole in dichloromethane) biphasic system. On the other hand, disturbing the aqueous/organic interface by constant stirring of solution—termed as bulk polymerization—resulted in globular (average size $\sim 2 \mu\text{m}$) polyindole. The results of Fourier transform infrared spectroscopy revealed that polymerization takes place at carbon atoms located at

positions 2 and 3 in indole monomer, and this has explained origin of different polyindole morphology obtained in interfacial and bulk polymerization. Cyclic voltammograms recorded as a function of scan rate indicated a high electroactivity of the synthesized polyindole. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 595–599, 2007

Key words: indole; interfacial polymerization; FTIR spectroscopy

INTRODUCTION

Conducting polymers, such as polyaniline, polypyrrole, polycarbazole, polyindole, etc., are an interesting class of materials for fundamental and applied researches because of their one-dimensional (1D) intrinsic properties and potential for commercial applications viz. field effect transistors, displays, rechargeable batteries, electronic nose, actuators, etc.^{1–4} One of the essential requirements for some applications, in particular, for actuators and artificial muscles, is to synthesize polymers in the form of long fibers.^{5,6} It has been observed that conducting polymer fibers have higher charge carrier mobility and are thus preferred in field effect transistors.⁷ In addition, long fibers are also needed to carry out four-probe resistivity measurements to investigate the intrinsic 1D conduction mechanism of conducting polymers.

Among various conducting polymers mentioned earlier, polyindole has comparatively been less studied. This is because polyindole, which is mainly synthesized by chemical oxidation or electropolymerization of indole monomer (C_8NH_7),^{8–12} has low polymerization efficiency. In addition, the conductivity of polyindole has been found to be low, i.e., 10^{-3} to 10^{-1} S/cm .^{8,9} It may be noted that the polyindole synthesized by chemical oxidation or electropolymerization had micron-size globular morphology. Conduc-

tivity data collected on compacted pellets of such globular polyindole would obviously represent the contribution from grain boundaries, and would not elucidate the intrinsic conductivity of the polymer. Synthesis of long polyindole fibers is, therefore, of interest for measuring the intrinsic conductivity and investigating the conduction mechanism(s) as well as for technological applications. It may be added that the biopolymer melanin is a chemical derivative of indole,^{13,14} and therefore, the availability of polyindole fibers would facilitate the experiments to understand the functioning of such biopolymers.

Recently, Huang et al.^{15,16} developed a simple interfacial polymerization method for making uniform, template-free nanofibers of polyaniline. In this method, the polymerization is initiated via self-assembly at the stationary interface of an aqueous/organic biphasic system. In this article, for the first time, we demonstrate that the interfacial polymerization method can be extended to a reproducible synthesis of long polyindole fibers (up to 1000 μm in length) performed at the stationary interface of aqueous (FeCl_3 solution)/organic (indole in dichloromethane) biphasic system. The growth mechanism of such fibers is understood in terms of electrostatic alignment of monomers at the interface and directional polymerization, subsequently, through self-assembly.

EXPERIMENTAL

The interfacial polymerization of indole was carried out in a 100-mL glass beaker. All chemicals used were analytical grade and were used as received. Indole and

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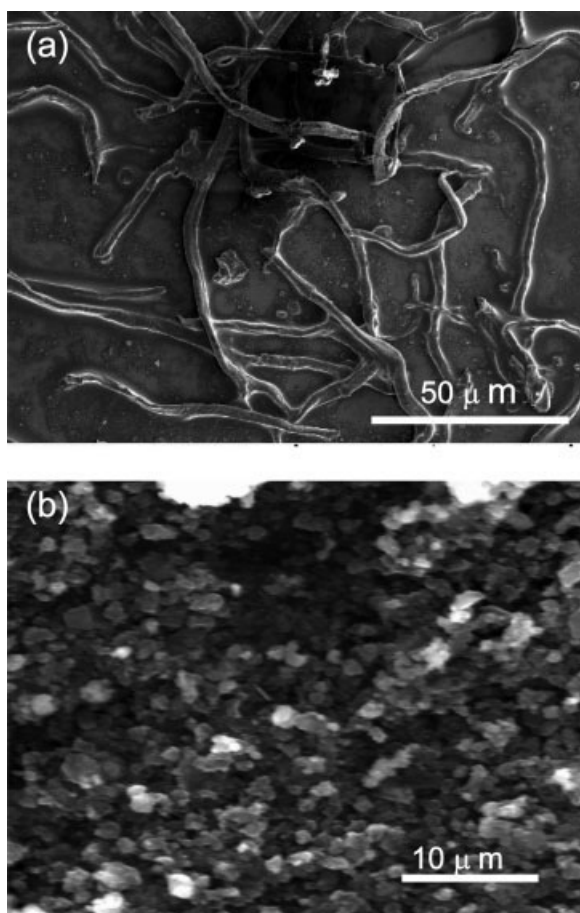


Figure 1 Scanning electron micrograph of polyindole synthesized by (a) interfacial and (b) bulk polymerization.

dichloromethane were obtained from Sisco Research Laboratory, Mumbai, India. Deionized water ($18M \Omega$) was obtained from Millipore water purification system.

Organic 1M indole solution, which was optically transparent, was prepared in dichloromethane; while 1M $FeCl_3$ solution, dark yellow in color, was prepared by dissolving anhydrous ferric chloride in deionized water. For interfacial polymerization, aqueous solution of $FeCl_3$ was poured slowly over organic solution. These two immiscible solutions form an interface, which separates aqueous (on top) and organic (at bottom) solutions. Care was exercised to maintain the interface in a stationary state. It was observed that, with passage of time, aqueous solution gradually turned green (a color of doped polyindole), indicating that the polymerization initiated at the interface propagated toward the aqueous solution. After a period of 12 h, the green precipitate was filtered and washed several times first with distilled water to remove unreacted ferric chloride and then with dichloromethane to remove indole monomers. The synthesized polymer was finally dried under vacuum.

In other sets of experiments, termed as bulk polymerization (conventional route), ferric chloride and

indole solutions were mixed in 1 : 1 volume ratio, and subjected to a constant stirring for 12 h. The polymer was obtained after washing and vacuum drying.

The morphology of the synthesized polymers was examined by scanning electron microscope (Vega MV 2300T/40, Tescan), and composition was determined by energy dispersive X-ray analysis (Oxford). Fourier transform infrared (FTIR) spectroscopy measurements of the polymer were carried out by Jasco 420 FTIR instrument using KBr as matrix. X-ray photoelectron spectra were recorded using Mg $K\alpha$ (1253.6 eV) source (XPS system attached with RIBER MBE). The binding energy scale was calibrated to Au $4f_{7/2}$ line of 84 eV. Cyclic voltammetry (CV) experiments were carried out using Autolab PG Stat 20 (Electrochemie, The Netherlands) Galvanostat/Potentiostat. For this purpose, thick films ($\sim 20 \mu m$) of synthesized polyindole was deposited on ITO-coated glass, and the cyclic voltammogram was recorded in 0.1M tetrabutyl ammonium perchlorate in dichloromethane at different scan rates using a three-neck, one compartment cell equipped with Ag/AgCl and Pt (1 cm^2) foil as reference and counter-electrode, respectively.

RESULTS AND DISCUSSION

Typical SEM images depicting the morphology of polyindole synthesized using interfacial and bulk polymerization are shown in Figure 1. It is seen that surface polymerization yielded bunches of long fibers of polyindole. The length of fibers varied between 200 and 1000 μm , while diameter varied between 5 and 25 μm . The length and diameter of these fibers can be controlled by the duration of polymerization. On the other hand, bulk polymerization yielded globules of polyindole of average size $\sim 2 \mu m$. It may be noted that globular morphology is frequently observed for other polymers as well.⁹

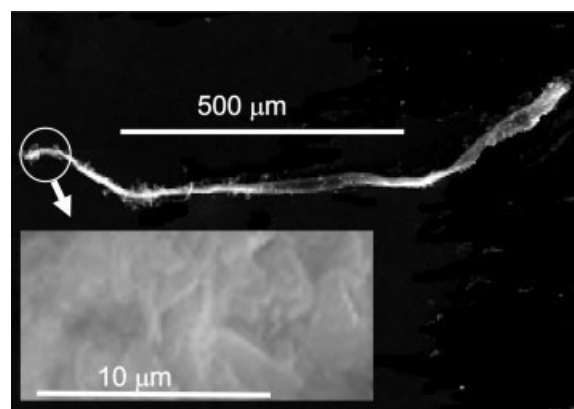


Figure 2 SEM micrograph of a mechanically separated single long fiber obtained by interfacial polymerization. The inset shows a magnified image of the fiber.

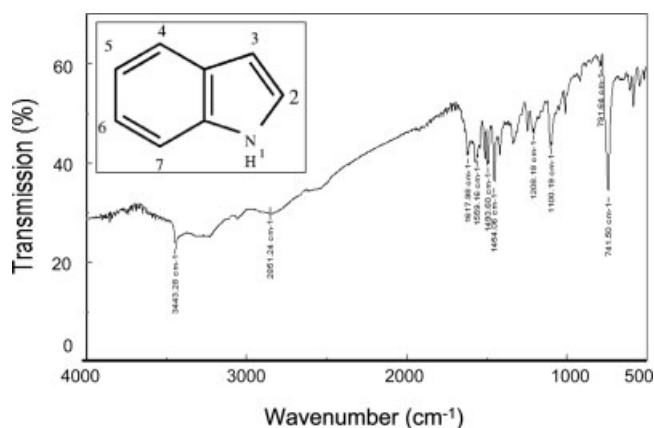


Figure 3 FTIR spectrum recorded for polyindole synthesized by bulk polymerization method. The surface polymerized indole had identical spectrum. The inset shows chemical structure of indole monomer.

The isolation of single polyindole fiber from the bunch was easily done by mechanical means under optical microscope. A SEM photograph of such an isolated fiber is shown in Figure 2. It is observed that these fibers are very soft and easily get twisted and bended. The magnified image of a portion of the fiber is shown in the inset of the Figure 2, which indicates a dense structure and absence of any regular patterns. The elemental analysis of the fiber using EDX indicated that Cl^- is the counterion in polyindole. The chlorine-doping level (x) in the formula $(\text{C}_8\text{NH}_5\text{Cl}_x)_n$ is found to be 0.25. Absence of iron indicated that FeCl_3 does not incorporate in the fiber.

A typical FTIR spectrum recorded for a polyindole is shown in Figure 3. The chemical structure of indole, consisting of a benzene and pyrrole ring, is presented in the inset of Figure 2. The major inferences drawn from the FTIR data are given as follows:

1. A strong peak at 741 cm^{-1} corresponds to the benzene ring in indole monomer. The peak located at 1454 cm^{-1} is assigned to the stretching of the benzene ring, indicating that benzene ring is not involved in the polymerization.^{17,18}
2. The strong and broad peak at 3443 cm^{-1} observed is a characteristic of the N—H bond. This band together with the band at 1559 cm^{-1} can be ascribed to be the stretching and deformation vibrations of the N—H bond, respectively.^{17,18} These results imply the presence of N—H bonds on the polyindole backbone. Thus, nitrogen species could not be the polymerization site.¹⁷
3. A band around 720 cm^{-1} —a characteristic feature of the in-phase vibration of hydrogen species located at 2 and 3 carbon positions of indole monomer—is missing in polyindole. This suggests that 2,3-position of pyrrole ring is responsi-

ble for polymerization, and this is in agreement with reported experimental¹⁷ and theoretical results.¹⁹ Very recent NMR studies have also confirmed that polymerization of indole occurs at the 2,3-position.²⁰

4. Peaks at 1617, 1493, 1208, and 1100 cm^{-1} are induced by different stretching frequencies of aromatic ring in the polymer chain.¹⁷

The EDX and FTIR results were well supported by XPS measurements. XPS spectra did not reveal the presence of iron, while chlorine was amply present. The core level C1s and N1s XPS spectra of polyindole are shown in Figure 4. The nonsymmetrical peak of C1s has been deconvoluted into two peaks: (i) 284.5 eV (C—C bond) and (ii) 286 eV (C—N bond). In indole, the relative distribution of these carbon atoms is 6 C—C (75%) and 2 C—N (25%). For polyindole, this distribution, computed from the area under the curve, is 77 and 23%, respectively. This indicates that nitrogen do not participate in polymerization. This is also supported from N1s XPS spectrum in which two nitrogen

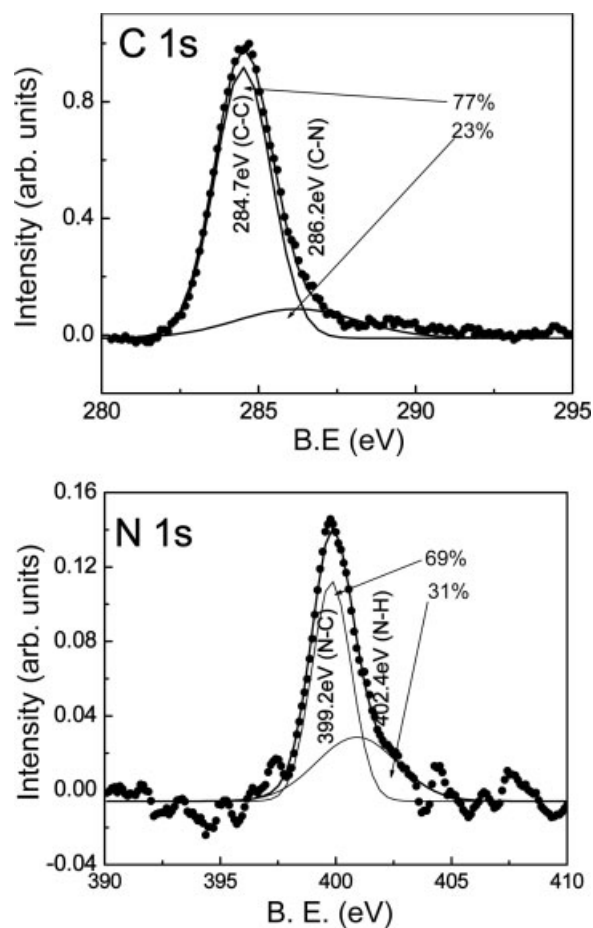


Figure 4 Core level C1s and N1s XPS spectra for synthesized polyindole.

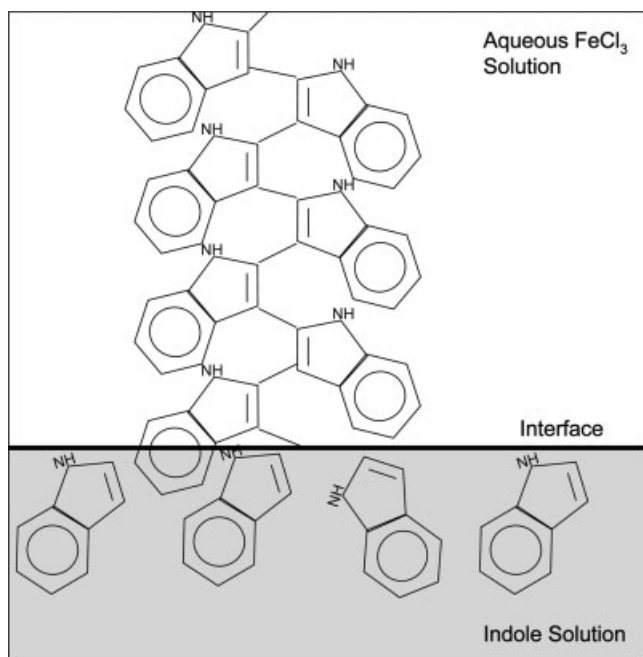


Figure 5 Schematic depicting polymerization of indole at an aqueous/organic interface.

components, i.e., 399.2 eV (N—C) and 402.08 eV (N—H), are close to the desired 2 : 1 ratio.

Now, we try to understand why long fibers are synthesized during interfacial polymerization. At the immiscible aqueous/organic interface, as schematically shown in Figure 5, indole monomer gets protonated in the presence of oxidant FeCl_3 . The electrostatic charging of indole monomers is thought to preferentially align them at the interface.²¹ Since the polymerization sites in indole are 2 and 3 carbon positions, preferentially aligned monomers would therefore undergo a directional polymerization via self-assembly, leading to long fibers of polyindole. On the other hand, by disturbing the interface, as done in bulk polymerization, the monomers no longer remain preferentially aligned, making 2 and 3 carbon positions of indole monomers equally available in all the directions, leading to a globular morphology, during polymerization.

The CV recorded for bulk- and interfacial-polymerized indoles are shown in Figure 6. The bulk-polymerized indole shows anodic (E_{pa}) and cathodic (E_{pc}) peak potentials at 0.57 and 0.51 V, respectively, which are in agreement with the literature values.^{8,9} The CV of interfacial polymerized indole, though similar to that of bulk polymerized, indicates a shift of E_{pa} (0.61 V) and E_{pc} (0.53 V) peaks to slightly higher values, which is attributed to an increase in conjugation length of polymer. It may be noted that in both the cases the value of peak potential (E_{pa} , E_{pc}) is independent of the scan rates, indicating a reversible redox reaction. However, as shown in Figure 6, cathodic (I_{pc})

and anodic (I_{pa}) peak currents increase with the scan rate (v). For a reversible reaction, i.e., $\text{O} + n\text{e} \rightleftharpoons \text{R}$, assuming semiinfinite linear diffusion, it has been shown that peak current (I_p) has following theoretical relation with v ²²

$$I_p = [(2.69 \times 10^5)n^{3/2}ACD^{1/2}]v^{1/2}$$

where I_p is the maximum anodic or cathodic peak current and is determined by base line charging current (I_c), which appears owing to a continuous potential sweep; n is the number of exchanged electrons in the redox reaction, and is related with peak potential via equation: $E_p = 28.5/n$ mV at 25°C; A is electrode area (4 cm² in the present study); C (in mol/cm³) is active site concentration; and D (in cm²/s) is the diffusion coefficient of counterions.

For bulk- and surface-polymerized indole, I_{pa} as a function of $v^{1/2}$ has been plotted in Figure 7. Linear fits indicate that data is in agreement with the above

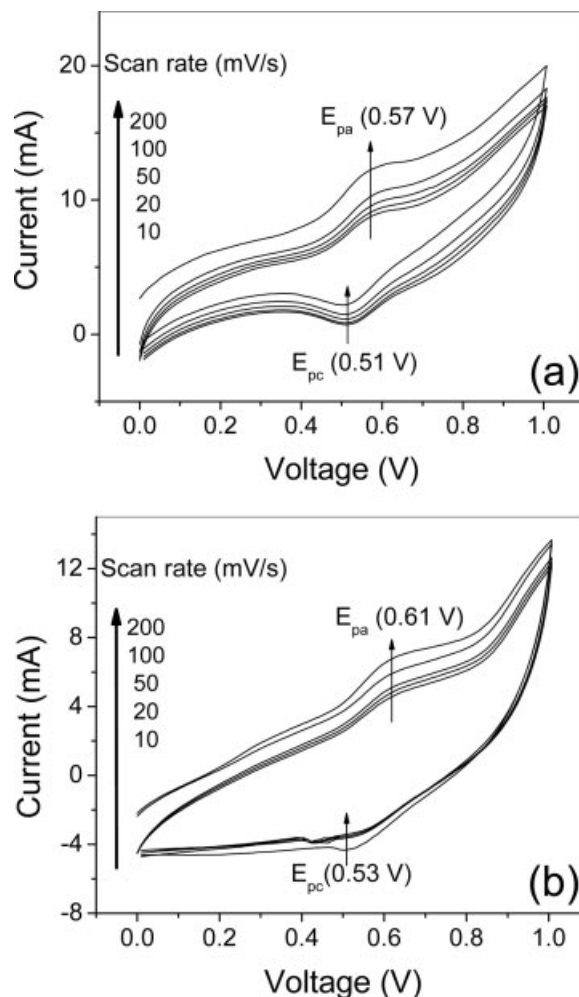


Figure 6 CV of bulk (a) and interfacial (b) route synthesized polyindole film deposited on ITO substrate recorded at different scan rates.

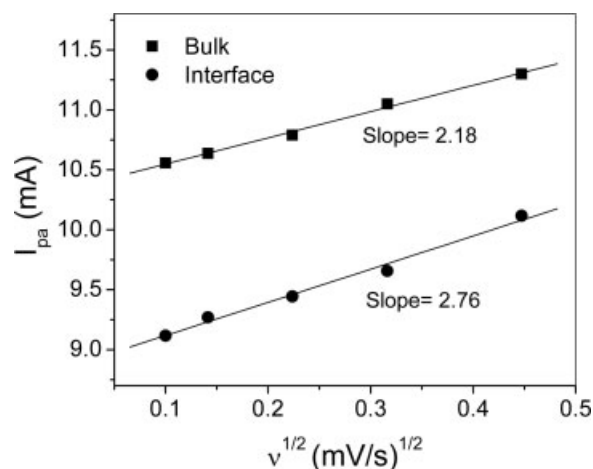


Figure 7 Variation of anodic peak current (I_{pa}) with the square root of scanning rate ($v^{1/2}$). The data show excellent linear fit.

theoretical relation. From the slopes of linear fit, the product $CD^{1/2}$ can be calculated, which provides the information on the electroactive character of the polymer. The value of product $CD^{1/2}$ calculated for the oxidation of bulk- and surface-polymerized indole is 1.5×10^{-4} and 2.1×10^{-4} mol cm⁻² s^{-1/2}, respectively. These values are about an order of magnitude higher than that reported for electrochemically polymerized indole,⁹ indicating better electroactivity of bulk- and interfacial-polymerized polymer.

We have attempted to measure the four-probe resistivity of these fibers, which was hampered by a difficulty in making proper electrical contacts. Two conventional options for making electrical contacts were explored: (i) By using silver paste: the organic substance of silver paste (methanol/acetone) was found to swell the polyindole fibers and (ii) Thermal evaporation of gold electrodes: this process also did not work as the high energetic gold atoms impinging fibers under high vacuum let its evaporation. Thus, new options for making electrical contacts on these fibers need to be explored and this work is underway.

CONCLUSIONS

We have shown that interfacial polymerization is a good method for synthesizing very long polyindole fibers (up to 1000 μ m long). The growth mechanism of fibers is believed to involve electrostatic alignment of indole monomers at the interface, and directional polymerization via self-assembly at 2 and 3 carbon positions of the indole monomer. The CV data indicated a high electroactivity of polyindole fibers.

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