

Synthesis of Polypyrrole Nanofibers by Ultrasonic Waves

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ABSTRACT: Nanofibers of polypyrrole have been synthesized by sonochemical method in the presence of a structure directing agent, i.e. dodecyl benzene sulphonic acid (DBSA). The length of the fibers is seen to increase significantly from ~ 13 nm to greater than ~ 1700 nm, while the diameter is ~ 13 – 17 nm, respectively. The reaction was carried out under ambient conditions by varying the concentration of pyrrole (0.001–0.1M), ammonium persulphate (0.0075–0.02M), and DBSA (0.05–0.2M). However, the formation of fibers is observed at a specific ratio of 1 : 0.5 : 5. The UV–vis spectra exhibit a sharp peak at a wavelength of ~ 490 nm corresponding to the polaron band

indicating the formation of polypyrrole. The X-ray diffractogram shows a broad peak in the 2θ range of $\sim 10^\circ$ – 30° and two sharp peaks at $\sim 31^\circ$ and 32° confirming the formation of polypyrrole. The morphological analysis of the sample have been carried out by transmission as well as scanning electron microscopy which reveals the formation of extraordinary long fibers having the length extending to more than ~ 1700 nm. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2872–2875, 2008

Key words: DBSA; sonication; nanofibers; structure directing agent

INTRODUCTION

It is well known that the properties of the material depend not only on their chemical structures but also on their morphologies, e.g. nanoscale materials possess unique properties on account of their finite size and have wide ranging applications in a variety of areas.¹ Thus, the synthesis of nanoscale materials has become a thrust area of research. Therefore, attempts have been made to prepare polypyrrole (PPy) in nanosize. Few reports are available on the synthesis of polypyrrole nanoparticles, e.g. polypyrrole nanofibers synthesized by electrochemical polymerization using a scanning microneedle electrode or a microporous membrane as a template.^{2,3} One of the alternative methods to synthesize polypyrrole in nanoregime is the use of sulphonic acids⁴ as they can play two way role, i.e. dopant as well as surfactant.⁵ Earlier also, these surfactants have been utilized to prepare water soluble polypyrrole or polyaniline⁶ by template synthesis. However, they bear several disadvantages such as formation of irregular or nonuniform particles, poor processibility, low yield etc. To overcome these limitations, one has to search for new methods of synthesis.

In the present article, we report the synthesis of polypyrrole nanofibers using ultrasonic waves. The method of synthesis involves shorter reaction time and ambient temperature conditions. It is mainly focussed on the morphology of polypyrrole thus obtained.

EXPERIMENTAL

All chemicals used were of A. R. grade (Qualigens, India). Monomer pyrrole was doubly distilled prior to use. Dodecyl benzene sulphonic acid (DBSA) (Fluka) and ammonium persulphate (APS) were used as received.

Micellar solutions containing pyrrole (0.001, 0.01, and 0.1M) and DBSA (0.05M) were kept for slow stirring at room temperature for a period of 2 h. The addition of DBSA was carried out after complete dissolution of pyrrole in 75 mL of distilled water. Other set of solution consisted of APS (0.005M) which was stirred separately for 1 h. The APS solution was added drop wise to the micellar solution with the help of a soxhlet funnel followed by sonication for a period of 2 h in an ultrasonic bath (IMECO VC-500W). The temperature was maintained to 27°C. After the addition of APS, the solution underwent various color transitions i.e. colorless to pale yellow to brown to light green. After 2 h sonication, the intensity of the green color increased thereby, indicating the formation of polypyrrole.

During sonication the formation of radicals of monomer molecules is facilitated through the cavitation events and polymerization progresses through

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the subsequent oxidation reactions. Growth in one dimension is favored as the DBSA acts as a soft template directing the growth in one direction especially, when the concentrations are kept to a low.

Characterization

The UV-vis spectra were recorded on a Shimadzu 1650 spectrophotometer over a wavelength range of 200–1100 nm with a slit width of 2 mm.

The X-ray diffractogram of the polypyrrole nanofibers was taken on a Rigaku Miniflex Diffractometer with Cu K α radiation ($\lambda = 1.540 \text{ \AA}$) between 2θ values of 10° – 70° at a speed of 2° per min.

The scanning and the transmission electron micrographs were viewed under CM 102 XL scanning electron microscope and a Philips CM 200 transmission electron microscope.

RESULTS AND DISCUSSION

As ultrasonic waves are known to assist the formation of nanoparticles, in the present work, attempts were made to synthesize polypyrrole nanofibers. For this, DBSA was used as a structure directing agent and APS as the oxidizing agent.

The primary set of experiments involved the synthesis of polypyrrole using three different monomer concentrations as 0.001, 0.01, and 0.1M. The concentration of DBSA and APS were taken as 0.05 and 0.005M, respectively. The color of the reaction mixture when noted after complete addition of APS appeared to be reddish brown in color which continued to be so after 24 h when kept undisturbed. On the other hand, on subjecting the reaction mixtures to sonication (ultrasonic waves) the color of the solution was seen to change gradually. Sharp differences could be observed in the UV-vis spectra with respect to monomer concentration as well as sonication time.

Figure 1 shows the UV-vis spectra of polypyrrole nanosols obtained in presence of varying monomer concentrations after 2 h of sonication. A comparison of the spectra reveals the presence of a peak at $\sim 490 \text{ nm}$ in case of nanosol formed at 0.01M monomer concentration which can be attributed to the polaron band of polymer and the nanosol is observed to be homogeneous with dark green color. Similar peak is observed at a monomer concentration of 0.1M but the sharpness is relatively less, though the overall absorbance is higher due to higher monomer concentration and precipitation is observed at this particular concentration.

On the other hand, absence of peak at $\sim 490 \text{ nm}$ indicates that polymerization does not seem to occur in the solution containing 0.001M pyrrole monomer (Fig. 1, curve a).

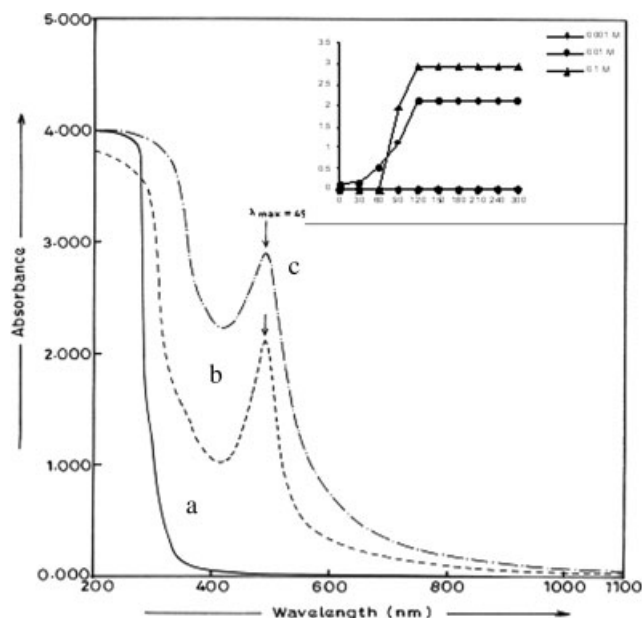


Figure 1 UV-vis spectra of polypyrrole nanofibers synthesized at different concentrations of monomer (a) 0.001M, (b) 0.01M, (c) 0.1M. Inset: A plot of sonication time vs. absorbance at λ_{max} .

Further, the curves of absorbance vs. sonication time (inset of Fig. 1) shows that in case of the nanosol prepared using 0.001M as monomer concentration the absorbance increases gradually and saturation is observed after $\sim 150 \text{ min}$ whereas, at 0.1M concentration measurable absorbance is observed only after $\sim 50 \text{ min}$ which increases rapidly with a subsequent saturation after $\sim 120 \text{ min}$. From these results, it could be concluded that 0.01M monomer concentration is optimum, yielding expected product.

Similarly, experiments were performed to optimize the DBSA as well as APS concentration. In case of DBSA, the concentration was varied between 0.05 and 0.2M and it was observed that proper sol was formed in presence of 0.05M DBSA concentration, while at higher concentrations partial reaction occurred together with precipitation. The optical spectra showed sharp peak at 0.05M concentration. Accordingly, experiments were carried out by varying the APS concentration and from the results it was found that the concentration of 0.005M yielded homogeneous sol with no precipitation.

These results were further supplemented by TEM, SEM, and XRD analysis. Figure 2 shows the TEM micrographs of the nanosol (optimum concentrations—0.01M pyrrole, 0.05M DBSA, and 0.05M APS) recorded at different time intervals, (a) nanosol formed after complete addition of the oxidizing agent, (b) after 2 h sonication, and (c) after aging the sample for 8 days. Figure 2(a) shows the presence of particles (size $\sim 13 \text{ nm}$) as well as fibers (diameter

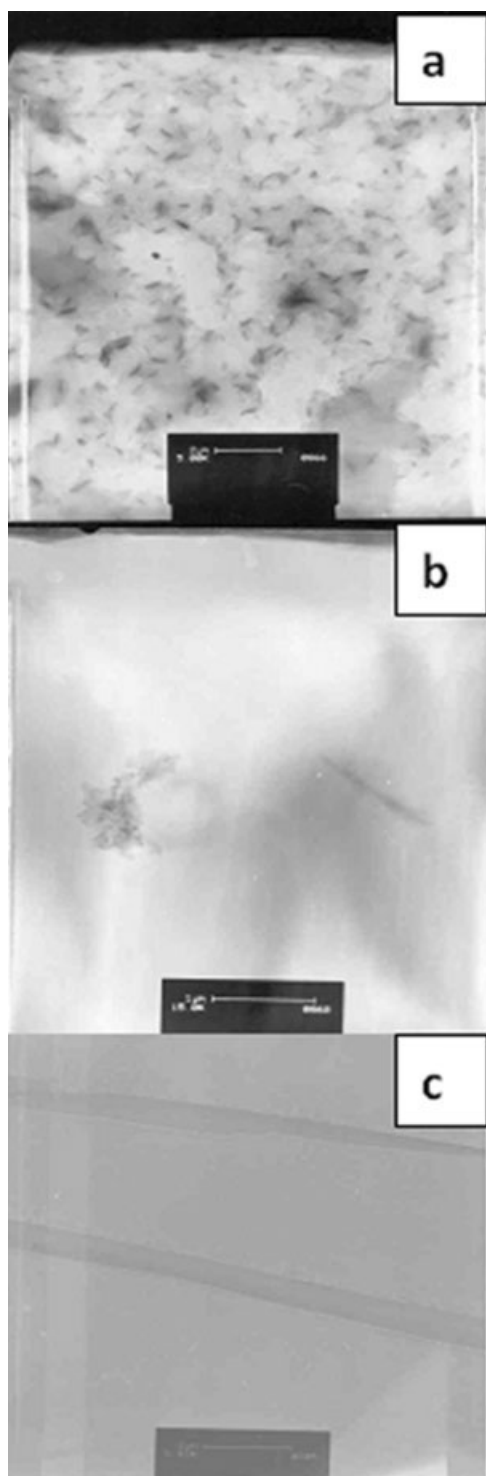


Figure 2 Transmission electron micrographs of polypyrrole nanofibers (a) before sonication, (b) after 2 h of sonication, and (c) after 8 days of aging.

~ 13 nm and length ~ 21 nm) indicating that the fiber formation is initiated before sonication. After sonication, as the reaction progresses the size of the fibers is seen to increase with the length extending up to ~ 35 nm and diameter ~ 17 nm. On aging the nanosol up to 8 days, the length of the fiber was

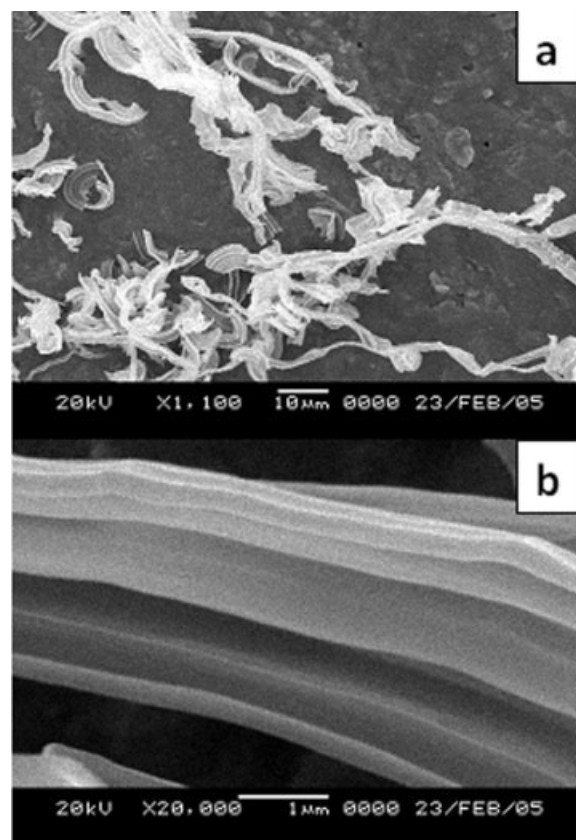


Figure 3 Scanning electron micrographs of polypyrrole nanofibers at two different magnifications (a) $100\times$ and (b) $20000\times$.

found to increase further to ~ 1536 nm, however, the diameter of the nanofibers did not seem to change indicating growth only in longitudinal direction. The same sample when observed after a period of ~ 60 days under transmission electron microscope, the fibers could not be visualized to their full-length. Therefore, the sample was analyzed under SEM where the length is seen to extend beyond ~ 1700 nm (Fig. 3). The X-ray diffractogram

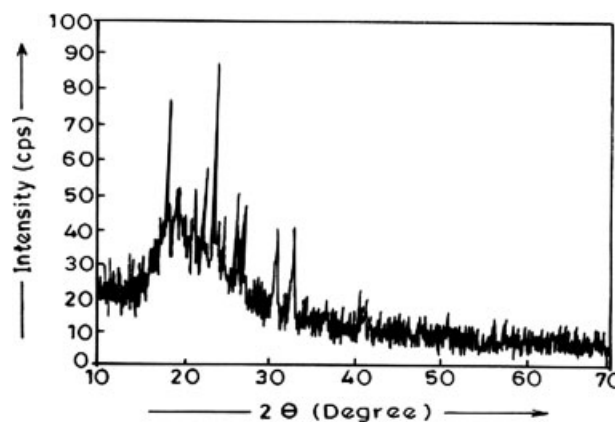


Figure 4 X-ray diffractogram of polypyrrole nanofibers.

(Fig. 4) of the sample (8 days) exhibits a broad peak in the range of $\sim 10^{\circ}$ – 30° and two sharp peaks at 2θ values of $\sim 31^{\circ}$ and 32° confirming the formation of polypyrrole. However, no differences were observed in the XRD pattern taken at varying time intervals.

CONCLUSION

Polypyrrole nanofibers were successfully prepared at room temperature using ultrasonic technique. The dimensions of the nanofibers especially the length is observed to increase with the time of sonication as well as aging.

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