



STRUCTURAL & PHYSICAL PROPERTIES OF SOME CONDUCTING POLYMERS SYNTHESIZED BY HYDROTHERMAL METHOD

A. N. Ingole^a, D. B. Patil^{a*}, S. R. Thakare^a

^aDept. of chemistry, Govt. Institute of Science, R.T. Road, Civil Lines,
Nagpur – 440001 (MS) India.

Corresponding Author Email: avinashingolechem@gmail.com

Abstract:

Conducting polymers are of great importance for a wide variety of applications due to their low cost processing and flexibility for optoelectronic devices. These materials are useful for sensor applications because of their electronic properties which are sensitive for specific target analytics due to molecular interactions. The present investigation aims to study the effect and use of benzoic acid for the design of anisotropic structure of well known conducting polymer Pani. The Pani was synthesised by hydrothermal method in presence of benzoic acid as a dopant as well as a template.

Introduction:

Conducting polymers are unique photonic and electronic functional materials owing to their high π -conjugated length, unusual conducting mechanism and reversible redox doping or dedoping process. Conducting polymers show various promising applications, such as in transistors [1], sensors [2], memories [3], actuators [4], super capacitors [5] and lithium ionic batteries [6]. In the past decade, conducting polymers nanostructures have become a rapidly growing field of research because they display new properties related to their nanoscale size and have greatly improved the performance of devices [7]. Conducting polymer nanostructures can be synthesized by several approaches such as well-controlled solution synthesis [8], soft-template methods [9], hard-template methods [10] and electro-spinning technology [11].

In hydrothermal method, Components are subjected to the action of water at temperatures generally near above the critical temperature of water ($\sim 370^\circ\text{C}$) in closed bombs and under the corresponding high pressures developed by such solutions. Usually hydrothermal growth means growth of molecular species in an aqueous solution at ambient or near ambient conditions. Hydrothermal synthesis involves water as a catalyst and occasionally as a component of solid phases in the synthesis at elevated

temperature ($>100^{\circ}\text{C}$) and pressure. Water is one of the most important solvent present in nature in abundant amount and has remarkable properties as a reaction medium under hydrothermal conditions.

One of the biggest advantages of using water is an environmental benefit and cheaper than other solvents and it can act as a catalyst for the formation of desired materials by tuning the temperature and pressure. It is nontoxic, non flammable, non carcinogenic, non mutagenic and thermodynamically stable. Another advantage is that water is very volatile, so it can be removed from the product very easily. Hydrothermal solvents have different properties at above the temperature 100°C and pressure 1 atm., especially at critical point as shown in (fig-1).

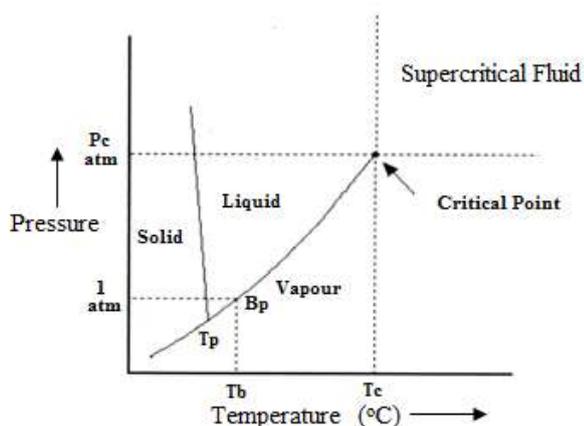


Fig-1: Critical point of water and super critical region

In recent years, the low carbon economy of sustainable and renewable resources has become a great challenge due to climate change and the decreasing availability of fossil fuels. It is now essential to develop new, low cost and environmentally friendly energy conversion and storage systems. Conducting polymers having good electrochemical activity [12], such as polyaniline, polypyrrole and polythiophene are important electrode materials for pseudo capacitors and rechargeable lithium batteries [13]. Owing to its relatively easy preparation, good environmental stability and high degree of conductivity, the synthesis of electrically conducting polymers such as polypyrrole (PPy), polyaniline (Pani) and polythiophene (PTh) has



received considerable attention in recent years. In particular, because of its uniqueness in conducting polymers for its non redox doping property which is based on a simple acid-protonation reaction, the synthesis of nanostructural Pani like fibers, tubes, dots, spheres, etc. has attracted much interest. For example, polyelectrolyte coated microspheres, sulfonated polystyrene, porous alumina membranes [15] and thin glass tubes such as micelles, surfactants and liquid crystals have been reported in the preparation of nanostructural Pani. Other methods like ultrasonic irradiation assisted polymerization [17], inverse microemulsion polymerization [18], aqueous or organic interfacial polymerization [19], mechanochemical polymerization [20], self assembly process synthesis [21], electrosynthesis [22] have also been employed in order to obtain nano microstructural Pani. Furthermore, the synthesis of Pani with controllable morphologies was also the target of chemists. By simply decreasing the molar ratio of dopant to monomer, Zhang *et al* synthesized salicylic acid doped Pani with the morphology changing from one dimensional nanotubes to three dimensional hollow microspheres [16]. Under hydrothermal conditions in different concentrations of the doping acid, Shi *et al* synthesized pani with mesostructures varying from fibers to plates and spheres [23].

Conducting polymer nanostructures have unique properties arising from their nanoscale size and shows improved performance in technological applications [24], High electrical conductivity [25], Large specific surface area [26], Short path length for transportation of ions, Improved cycle life due to better accommodation of the strain caused electrochemical reaction [27]. H. Huang *et al* synthesized Pani nanotubes successfully, using hydrothermal method via in situ polymerisation [28]. Conducting polymer nanostructures also shows mixed conductive mechanism of electronic and ionic conductivity which lowers interfacial impedance between electrodes and electrolyte, light weight and large ratio of specific discharge. Wan *et al* reported its universality, controllability and self assembly mechanism by changing



the polymeric chain length, polymerization method, a dopant structure and reaction conditions [29]. Researchers synthesized a variety of micro-nanotubes [30], nanofibers, nanotube junctions [31] and hollow microspheres [32] by the template free method. Zheng *et al* reported an anisotropic polyaniline plates decorated with self-aligned nanofiber arrays were synthesized under the hydrothermal conditions. Lu *et al* obtained polypyrrole nanotubes by using ferric chloride and methyl orange as the template [33]. In this paper, Synthesis of nanopolyaniline (Pani) using benzoic acid as a template as well as a dopant is reported.

Experimental:

Materials and Methods:

Aniline (99.5 %) and Ferric chloride (99.5 %) were procured from E. Merck. Aniline was distilled before use. All supplementary chemicals (Benzoic acid, Hydrochloric acid, Ethanol) were of AR grade and solutions were prepared with double distilled water. Transmission electron microscopy (TEM) analysis was done from IIT, Mumbai, India.

Synthesis of Polyaniline Nanostructures:

In this synthesis, 1.5 mol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 ml hydrochloric acid aqueous solution (pH=5) containing 0.075 mol of benzoic acid with stirring for 45 min, then 1.5 mol of aniline monomer was added and stirred for another 10 min. Then reaction mixture was poured in a 100 ml Teflon inner container and diluted with double distilled water and it was sealed with plumbing pliers and finally transferred into the preheated oven. The autoclave temperature was maintained at 115°C for 12 h. After completion of reaction, autoclave was taken out and allowed to cool at room temperature. The resulting solution was centrifuged and the solid precipitate was washed with distilled water and ethanol thoroughly to remove excess ions and monomers. The final product was dried in oven at 42°C for 10 h. To understand the effect of the experimental condition on the morphologies of Pani nanotubes, parallel experiments were carried out

by changing pH value of the solution, reactant molar ratio and hydrothermal temperature [28].



Fig-2: Autoclave used for Hydrothermal Synthesis

Results and discussion:

TEM images revealed morphologies of Pani. As shown in Fig-3, the TEM image indicates that the product is a complex of nanofibers and high yielding microscale plates. The plates which are seen in the figure are decorated with isometric and quasi-paralleling nano fiber arrays developed during the polymerization reaction. It is observed that, the two unravel fine self assembled structures of the microscale plates. One typical fine structure is a ladder like structure, in which the ladder like layer is constituted of isometric and paralleling nanofibers grown along the surface of the Pani substrate. Another structure characterized as grid like morphology has similar features as those of the ladder like plates but just differs in the aligned direction of some different ladder like layers. The two fiber arrays with distinct orientations in the grid like structure are not located in the same plane because the crossed region of every two fibers has obviously deeper contrast than that of a single fiber. Therefore, it is reasonable to infer that the two distinct fiber arrays are developed on the different surfaces of Pani plate and tend to be perpendicular to each other. The similar features between the aligned Pani fiber arrays and grid like Pani plates such as the paralleling arrangement of fibers

and equal distance between fibers indicate that similar mechanism of fiber self assembly has featured in the formation of these two kinds of textured plates during aniline polymerization in presence of benzoic acid as a template.

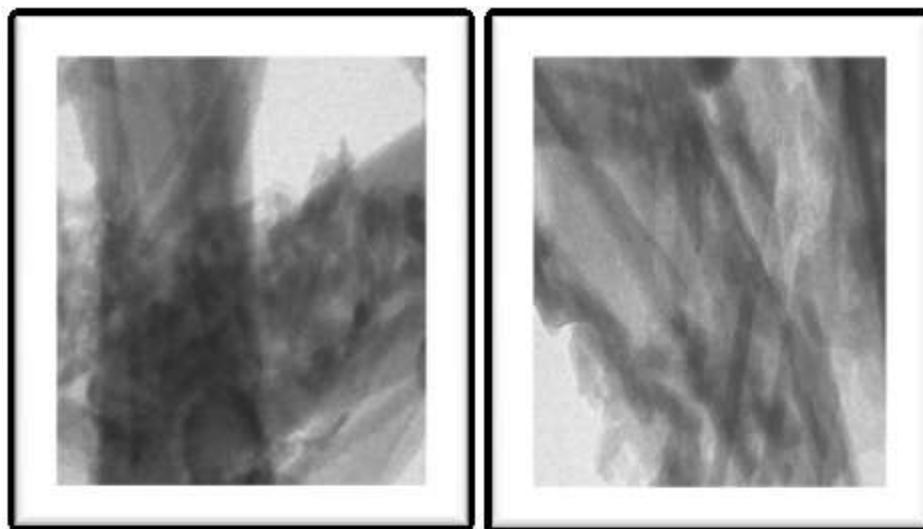


Fig-3: TEM images of polyaniline nanostructures.

The possible formation mechanism of the self assembled Pani structures is schematically illustrated in Fig-4. The self assembling growth of fibers is started from the electrostatic absorption of fiber seeds around the surface which is determined by the chemical structure of Pani. As is commonly known, Pani can be easily doped with protonic acid in hydrothermal conditions. The HCl doped Pani is analogical to a polyelectrolyte in the solution and should be positively charged with the counter benzoate anions being ionized into the surrounding solution. In general, the nitrogen atoms in the as prepared HCl doped Pani are capable of being positively charged up to a high proportion of 40%. So, the positive charged doped sites are more active in absorbing the counter ions (Benzoate ions) from the environmental solution and then forming electrostatic dipoles, as shown in Fig-4. At the same time, the oligomer radical cations fiber seeds, positively charged in the solution would be re-adsorbed via the electrostatic interaction provided by dipoles. If there are enough monomers, the oligomer radical cations could trigger polymerization and finally developed into fibers, as shown in Fig-4. It is assume that,

the crystalline nature of the benzoic acid may be important to get such anisotropic structure of Pani.

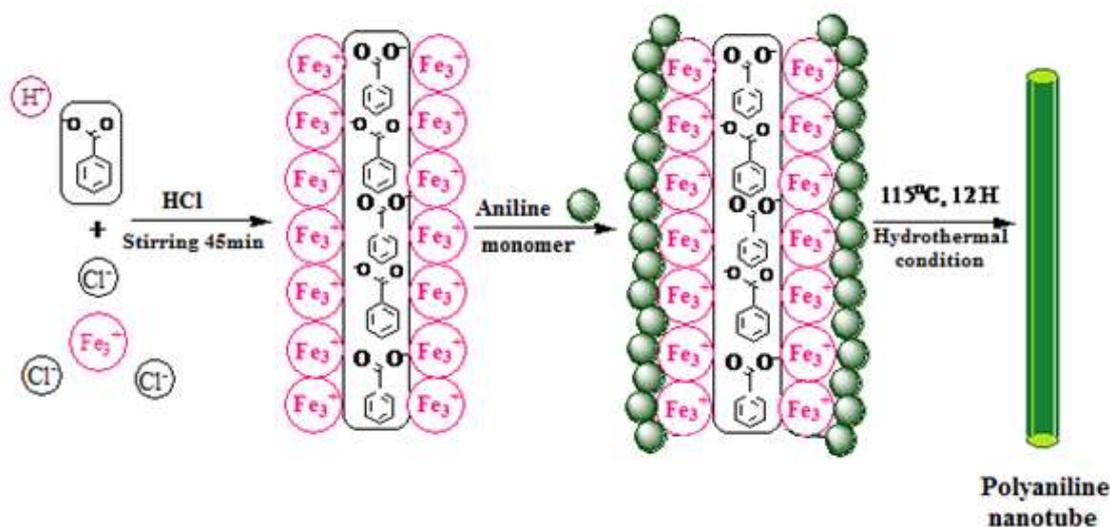


Fig-4: Hydrothermal synthesis of Polyaniline

Conclusion:

Rapidly decreasing availability of fossil fuel requires society to move in an accelerating speed towards the use of sustainable and renewable resources. Super capacitor and lithium batteries are two important devices for energy storage and release. Conducting polymers are electronic functional materials with their high π -conjugated length, unusual conducting mechanism and reversible redox process. The design and bulky fabrication of fine nanostructures of conducting polymers and composites is the key to success in designing required high energy and high power devices. This review is strongly suggests the use of Hydrothermal method for synthesis of conducting polymers as a simple, universal and controlled approach to fabricate novel conducting polymer nanostructures and composites. The use of an organic acid (benzoic acid) plays a dual role such as a dopant and a template to design such anisotropic structure.

Acknowledgement:

The author is thankful to Dr. M. T. Bharambe, Director, Govt. Institute of Science, Nagpur and Authorities of Nanotechnology laboratory, Shri. Shivaji Science college, Nagpur, India for providing the necessary research facilities.



References:

- Aleshin, A.N., (2006) *Adv. Mater.* 18, 17-27.
- Virji, S., Huang, J.X., Kaner, R.B., and Weiller, B.H., (2004) *Nano Lett.*, 4, 491-496.
- Tseng, R.J., Huang, J.X., Ouyang, J., Kaner, R.B., and Yang, Y., (2005) *Nano Lett.* 5, 1077-1080.
- Baker, C.O., Shedd, B., Innis, P.C., Whitten, P.G., Spinks, G.M., Wallace, G.G., and Kaner, R. B., (2008) *Adv. Mater.* 20, 155-158.
- Wang, Y.G., Li, H.Q., and Xia, Y.Y., (2006) *Adv. Mater.* 18, 2619-2623.
- Oyama, N., Tatsuma, T., Sato, T., and Sotomura, T., (1995) *Nature* 373, 598-600.
- Long, Y.Z., Duvail, J.L., Li, M.M., Gu, C.Z., Liu, Z.W., and Ringer, S.P., (2010). *Nanoscale Res. Lett.* 5, 237-242.
- Huang, J.X., and Kaner, R.B., (2004). *Angew. Chem. Int. Edit.* 43, 5817-5821.
- Wan, M.X., (2008). *Adv. Mater.* 20, 2926-2932.
- Pan, L.J., Pu, L., Shi, Y., Song, S.Y., Xu, Z., Zhang, R., and Zheng, Y.D., (2007). *Adv. Mater.* 19, 461-464.
- Yu, J.H., Fridrikh, S.V., and Rutledge, G.C., (2004). *Adv. Mater.* 16, 1562-1566.
- Smela, E., Inganas, O., and Lundstrom, I., (1995) *Science* 268, 1735-1738.
- Novak, P., Muller, K., Santhanam, K.S.V., and Haas, O., (1997) *Chem. Rev.* 97, 207-281.
- Song S., Pan L., Li Y., Shi Y., Pu L., Zhang R., and Zheng Y., (2008). *Chin. J. Chem. Phys.* 21, 187-192.
- Shi X. Y., Briseno A. L., Sanedrin R. J., and Zhou F. M., (2003). *Macromolecules*, 36, 4093.
- Zhang L. J. and Wan M. X., (2003). *Adv. Funct. Mater.* 13, 815.



- Lu X. F., Mao H., Chao D. M., Zhang W. J., and Wei Y., (2006). *Macromol.Chem.Phys.* 207, 2142.
- Marie E., Rothe R., Antonietti M. and Landfester K., (2003). *Macromolecule*, 36, 3967.
- Huang J. X. and Kaner R. B., (2004). *J. Am. Chem. Soc.*126, 851.
- Huang J. X., Moore J. A., Acquaye J. H. and Kaner R. B., (2005) *Macromolecules* 38, 317.
- Huang K., Zhang Y. J., Long Y. Z., Yuan J. H., Han D. X., Wang Z. J., Niu L. and Chen Z. J., (2006). *Chem. Eur. J.*12, 5314.
- Tian S. J., Wang J. J., Jonas U. and Knoll W., (2005). *Chem. Mater.* 17, 5726.
- Pan L. J., Pu L., Shi Y., Sun T., Zhang R. and Zheng Y. D., (2006). *Adv.Funct.Mater.*16, 1279.
- Zhang, F.L., Nyberg, T., and Inganas, O., (2002). *Nano Lett.* 2, 1373-1377.
- Wu, C.G., and Bein, T., (1994) *Science* 264, 1757-1759.
- Penner, R.M., and Martin, C.R., (1987). *J. Electrochem. Soc.* 134, C504-C504.
- Pei, Q.B., Inganas, O., (1992). *J. Phys. Chem.* 96, 10507-10514.
- Huang, H., Feng, X., and Zhu, J., (2008). *Nanotechnology* 19,145607.
- Wan, M.X., (2009). *Macromol. Rapid Commun.* 30, 963-975.
- Zhang, Z.M., Wan, M.X., and Wei, Y., (2006). *Adv. Funct. Mater.* 16, 1100-1104.
- Wei, Z.X., Zhang, L.J., Yu, M., Yang, Y.S., and Wan, M.X., (2003). *Adv. Mater.* 15, 1382-1385.
- Zhu, Y., Hu, D., Wan, M.X., Jiang, L., and Wei, Y., (2007). *Adv. Mater.* 19, 2092-2096.
- Dai, T.Y., and Lu, Y., (2007). *Macromol. Rapid Commun.* 28, 629-633.
- Pan P., Qiu H., Dou C., Li Y., Pu L. , Xu J. and Shi Y., (2010). *Int. J. Mol. Sci.* 11, 2636-2657.