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SYNTHESIS AND CHARACTERIZATION OF POLYANILINE NANOFIBRES BY RAPID LIQUID-LIQUID INTERFACIAL POLYMERIZATION METHOD

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Abstract. Inherently conducting polymer polyaniline (Pani) has been synthesized by a novel interfacial polymerization technique using trichloroethane as organic media. Ammonium peroxydisulphate was used as an oxidizing agent dissolved in aqueous media. The synthesized polymer was subjected to the physico-chemical characterization by UV-Vis and FT-IR Spectroscopy and Scanning Electron Microscopy. From the SEM Micrographs it was observed that interfacial polymerization offers the fibrillar type of morphology having 200 nm sized fibers. Thermal properties of the synthesized polyaniline nanofibres were evaluated by thermogravimetric analysis. Conductivity of the polymer was measured by four-probe conductivity measurement technique and found to be ~ 0.1 S/cm.

Keywords: polyaniline, interfacial polymerization, nanofibers, spectroscopy, conductivity.

1. Introduction

In the few past decades inherently conducting polymer (ICP) polyaniline (Pani) has been paid considerable attention because of its high electrical conductivity [1], thermal stability [2], ease of preparation, and good environmental stability [3]. This polymer was found to be the most promising candidate for technological applications [4, 5] especially in light-weight batteries and sensors [6, 7]. However, the great potential of this compound is masked by serious disadvantages such as its insolubility in common organic solvents, infusibility, and hence non-processability [8]. Conducting form of polyaniline (emeraldine salt) powder synthesized in aqueous HCl solution is insoluble in most of the common organic solvents including 1-methyl 2-pyrrolidone (NMP). Due to strong interchain interactions these compounds are not soluble and do not melt, thus they can be neither solutions nor thermally processed. Implementation of practical applications has been facilitated by the

improvement of the processability of the conducting polymers. For these reasons in the past few years significant research efforts have been directed towards the synthesis of processable forms of electroactive polymers and their nanocomposites [9-11]. Among these areas of progress, the approach of chemical synthesis method and the use of functional dopants in the polymer matrix as an inherent part of the doping is more attractive, as it eliminates the use of volatile dopants. Recently, new types of protonic acids have been used, such as polyacids and functionalized acids, to dope chemically synthesized polyaniline in order to improve the selected properties, in particular, solubility, processability, and electrical conductivity [12, 13]. Conventional polyaniline synthesis is known to produce particulate products with irregular shapes. Therefore, many methods have been developed to make nanostructures of polyaniline (with diameters smaller than 100 nm) by introducing "structural directing agents" during the chemical polymerizing reaction. A great variety of such agents have been reported in the literature, including surfactants [14-17], liquid crystals [18], polyelectrolytes [19], nanowire seeds [20], aniline oligomers [21], and relatively complex and bulky organic dopants [22-26]. It is believed that such functional molecules can either directly act as templates (*e.g.*, polyelectrolytes) or promote the self-assembly of ordered "soft templates" (*e.g.* micelles, emulsions) that guide the formation of polyaniline nanostructures.

2. Experimental

All chemicals were of analytical reagent (AR) grade and used as received. In a typical polymerization process the appropriate amount (0.553 M) of the monomer (aniline) was dissolved in the organic solvent (trichloroethane) to form the organic phase. The aqueous phase consists of the oxidizing agent (ammonium persulphate) (0.554 M) dissolved in double distilled water together with HCl (1.33 M) as a protonic acid. The monomer to oxidizing

agent ratio was kept 1:1. After complete addition of the oxidizing agent (aqueous phase) to the reaction mixture (organic phase) slowly, the two phases are formed and the polymerization is observed to be initiated at the boundary or at the junction of the two phases. Fig. 1 shows different steps involved during the polymerization process. After completion of the reaction the polymer was separated and washed with distilled water until the filtrate was colorless. Finally, the polymer was dried in an oven at 343 K for 12 h. The yield of the polymer was found to be ~ 82 %.

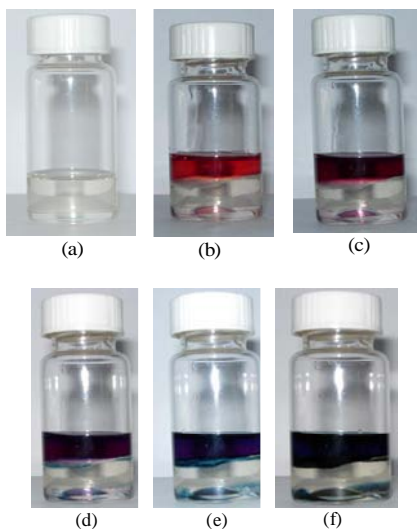


Fig. 1. Various steps involved during the interfacial polymerization process

The UV-Visible spectrum of the polymer solution in *m*-cresol was recorded using Hitachi-U3210 spectrophotometer in the range of 300–900 nm. The FT-IR spectrum was taken on a Perkin-Elmer-Spectrum 2000 spectro-photometer between 400–4000 cm^{-1} . The sample was prepared in the pellet form using a spectroscopic grade KBr powder. Morphological studies were performed with the help of a Philips XL-30 Scanning Electron Microscope. Thermogram of the polymer sample was recorded using Mettler-Toledo 851 thermogravimetric analyzer in the presence of N_2 atmosphere from RT to 1173 K at a heating rate of 10 K/ min. Electrical conductivity was measured by the four-probe technique. Dry powdered sample was made into pellet using a steel die of 1.5 cm diameter in a hydraulic press under the pressure of 7 tons.

3. Results and Discussion

Electronic absorption of conducting polymers is useful in investigating the oxidation and doping state of the polymer backbone. The optical absorption spectra of the polyaniline doped with HCl is presented in Fig. 2. In *m*-cresol, polyaniline exhibits two sharp peaks at 300 nm and 420 nm and shoulders at 600 and 820 nm. The peak at

300 nm corresponds to the π - π^* transition of the benzenoid rings, while the peak at 420 nm is very sharp and intense, which can be attributed to the localized polarons which are characteristic of the protonated polyaniline. The shoulders at 600 nm and 820 nm are assigned to the insulating pernigraniline phase and conducting emeraldine salt phase of the polymer, respectively [27].

The spectral features observed in Fig. 2 reveals that the polymer is composed of different oxidation states (conducting and insulating phase) of the polymer.

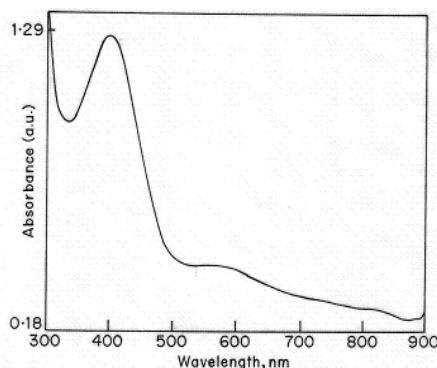


Fig. 2. UV-Vis spectra of polyaniline recorded using *m*-cresol as a solvent

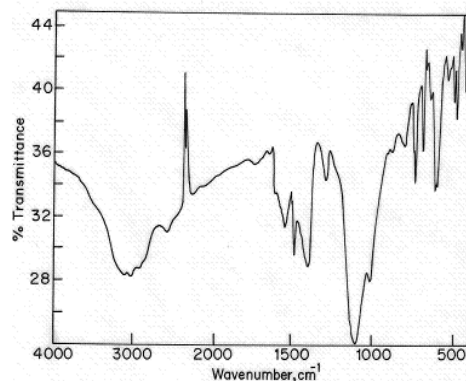


Fig. 3. FT-IR Spectrum of polyaniline synthesized by interfacial polymerization technique

Fig. 3 represents the FT-IR spectra of the polyaniline synthesized by interfacial polymerization technique and the peak positions related to the corresponding chemical bonds are listed in Table 1. The presence of the two bands in the vicinity of 1500 cm^{-1} and 1600 cm^{-1} are assigned to the nonsymmetrical C_6 ring stretching modes. The higher frequency vibration at 1600 cm^{-1} has a major contribution from the quinoid rings while the lower frequency mode at 1500 cm^{-1} depicts the presence of benzenoid ring units. The presence of these two bands clearly shows that the polymer is composed of amine and imine units. Furthermore, this supports our UV-Vis characterization, discussed earlier, where different phases are observed in the spectrum. The presence of other characteristic bands confirms the presence of conducting emeraldine salt phase in the polymer.

Table 1

Characteristic frequencies of HCl doped polyaniline

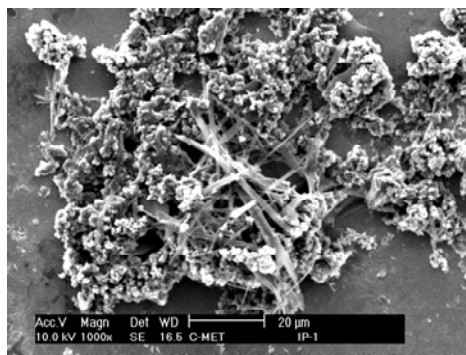
Wave-number, cm^{-1}	Band characteristics
804.17	Paradisubstituted aromatic rings indicating polymer formation
614.00	C–H out of plane bending vibration
1112.12	C–H in plane bending vibration
1295.85	Aromatic C–N stretching indicating secondary aromatic amine group
1494.93	C–N stretching of benzenoid rings
1605.52	C–N stretching of quinoid rings
3031.46	The aromatic C–H stretching

Fig. 4 shows the micrographs of polyaniline doped with HCl at different magnifications. The morphology of the polymer synthesized by interfacial polymerization methods offers very interesting morphological features. At the lower magnifications of 1000 and 2000x (Figs. 4a and b) it is observed that the polymer is composed of different-sized fibrillar type structure. At higher magnification of 4000x, (Fig. 4c) the clarity of the morphology is found to be further enhanced and it is observed that the fibers are of different size. The size of the fibers is ranging from 450 nm to 200 nm for broad and small fibers respectively.

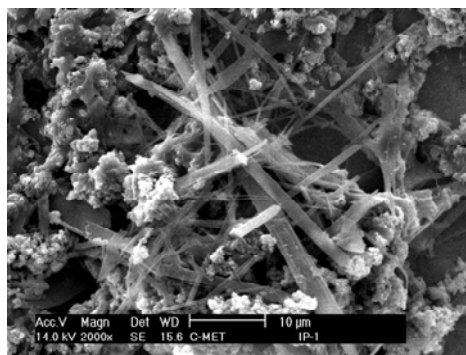
The formation of the fibers offered by the interfacial polymerization process is due to the controlled availability of the monomer at the junction of the organic and aqueous phase during the polymerization. It is expected that a very limited amount of monomer molecules present in the organic phase is interacting with the oxidizing agent present in the aqueous phase. Since the as-made polyaniline product is synthesized in its hydrophilic emeraldine salt form it diffuses away from the reactive interface into the water layer. This makes more reaction sites available at the interface and allows avoiding further overgrowth. In this way, the nanofibers formed at the interface are collected in the water layer without severe secondary overgrowth.

After complete addition of the oxidizing agent formation of the boundary between the two different phases takes place. The density of the water is less than that of the organic solvent trichloroethane thereby forming the upper phase in the reaction media. At the boundary the oxidizing agent reacts with the monomer molecule and initiates polymerization which proceeds till complete polymerization of the monomer present in the non-aqueous media.

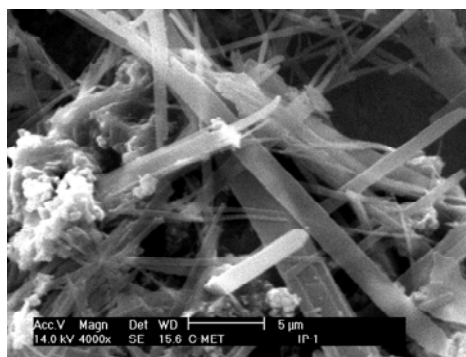
On the contrary, during the bulk polymerization process all the monomer molecules present in the reaction media interact with the oxidizing agent and the reaction initiates at all monomer sites and proceeds further. The initially formed granular polyaniline further reacts with the monomers present in the reaction flask and the size of the granules increases to form a sponge like structure in the end.



(a)



(b)



(c)

Fig. 4. Scanning electron micrographs of polyaniline at the magnifications of 1000x (a), 2000x (b) and 4000x (c)

Uniform distribution of the fibers with similar size and shape requires control over various parameters involved during the synthesis. The efforts to optimize these parameters in order to get polyaniline fibers with uniform size and shape are in progress in our laboratory.

Fig. 5 displays the thermal profile (TG/SDTA) of the polyaniline synthesized by interfacial method. From the figure it is observed that the polymer exhibits a three-step decomposition pattern similar to that of unsubstituted polyaniline synthesized by bulk polymerization process. The first step in the decomposition pattern from RT–373 K is obviously due to the removal of free water molecules/moisture present in the polymer matrix. The second step loss starting from 393 to 573 K is mainly due to the loss of

the dopant ion from the polymer chains (thermal dedoping), whereas the third step loss starting from 623 K onwards is accounted for the degradation and decomposition of the skeletal polymer backbone after the elimination of the dopant ion [27]. The first derivative plot also reveals the similar weight loss pattern.

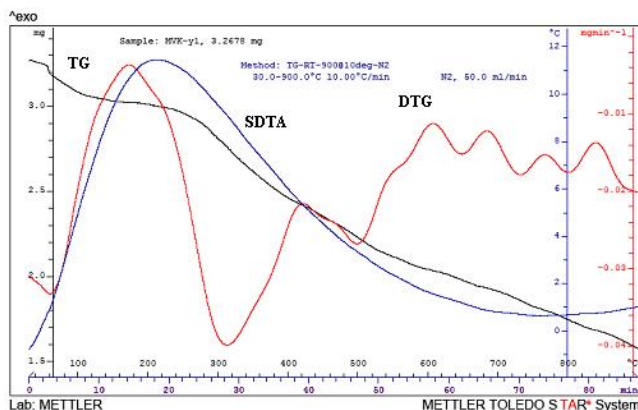


Fig. 5. Thermogram of polyaniline synthesized by interfacial polymerization method

The room temperature solid state conductivity of the polymer was measured on pressed pellets having a diameter of 1.5 cm using the four-probe conductivity measurement techniques. The conductivity of HCl doped polyaniline is found to be 0.1 S/cm, which is higher than that of synthesized by bulk polymerization process.

4. Conclusions

Nanofibers of conducting polyaniline were synthesized by interfacial polymerization method using ammonium persulphate as an oxidizing agent. The presence of conducting emeraldine salt phase of the polymer was confirmed by the UV-Visible and FT-IR spectroscopic measurements. The SEM analysis showed fibers with different size ranging between 400–200 nm in size. Thermogravimetric analysis shows the three-step decomposition pattern similar to the polyaniline synthesized by bulk polymerization method. The conductivity of the polymer was measured by four-probe conductivity technique and found to be 0.1 S/cm.

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References

- [1] Li W. and Wan M.: *Synth. Met.*, 1998, **92**, 121.
- [2] Jing X., Wang X., Geng Y. *et al.*: *Synth. Met.*, 1995, **69**, 265.
- [3] Genies E., Boyle A., Lapkowski M. and Tsintavis C.: *Synth. Met.*, 1990, **36**, 139.

- [4] Pouget J., Jozefowicz M., Epstein A. *et al.*: *Macromolecules*, 1991, **24**, 779.
- [5] MacDiarmid A. and Epstein A.: *Synth. Met.*, 1994, **65**, 103.
- [6] Ogura K., Saino T., Nakayama M. and Shiigi H.: *J. Mater. Chem.*, 1997, **7**, 2363.
- [7] Kulkarni M. and Viswanath A.: *Sensors & Actuators B: Chem.*, 2005, **107**, 2791.
- [8] Skotheim T. [in:] Dekker M. (Ed.), *Handbook of Conducting Polymers*, v. 2. Marcel Dekker, New York 1986.
- [9] Angelopoulos M., Ray A., MacDiarmid A. and Epstein A.: *Synth. Met.*, 1987, **21**, 21.
- [10] Chen S. and Lee H.: *Macromolecules*, 1993, **26**, 3254.
- [11] Soundararajah Q., Karunaratne B. and Rajapakse R.: *Mater. Chem. Phys.*, 2009, **113**, 850.
- [12] Cao Y., Smith P. and Heeger A.: *Synth. Met.*, 1993, **57**, 3514.
- [13] Santos Jr., Motheo A., Malmonge J. *et al.*: *Synth. Met.*, 1995, **69**, 141.
- [14] Zhang X. and Manohar S.: *Chem. Commun.*, 2004, **20**, 2360.
- [15] Yu L., Lee J., Shin K. *et al.*: *J. Appl. Polym. Sci.*, 2003, **88**, 1550.
- [16] Michaelson J. and McEvoy A.: *Chem. Commun.*, 1994, **1**, 79.
- [17] Li G. and Zhang Z.: *Macromolecules*, 2004, **37**, 2683.
- [18] Huang L., Wang Z., Wang H. *et al.*: *J. Mater. Chem.*, 2002, **12**, 388.
- [19] Liu J. and Yang S.: *Chem. Commun.*, 1991, **21**, 1529.
- [20] Zhang X., Goux W. and Manohar S.: *J. Am. Chem. Soc.*, 2004, **126**, 4502.
- [21] Li W. and Wang H.: *J. Am. Chem. Soc.*, 2004, **126**, 2278.
- [22] Qiu H., Wan M., Matthews B. and Dai L.: *Macromolecules*, 2001, **34**, 675.
- [23] Wei Z. and Wan M.: *J. Appl. Polym. Sci.*, 2003, **87**, 1297.
- [24] Wei Z., Zhang Z. and Wan M.: *Langmuir*, 2002, **18**, 917.
- [25] Wan M.: [in:] Nalwa H. (Ed.), *Encyclopedia of Nanoscience and Nanotechnology*, V. 2. Am. Sci. Publ., Los Angeles 2004.
- [26] Qiu H. and Wan M.: *J. Polym. Sci. A*, 2001, **39**, 3485.
- [27] Kulkarni M. and Viswanath A.: *J. Macromol. Sci. A*, 2004, **41**, 1173.

СИНТЕЗ І ДОСЛІДЖЕННЯ ПОЛІАНІЛІНОВИХ ВОЛОКОН ОТРИМАНИХ ШВИДКИМ МІЖФАЗНИМ РІДИННО-РІДИНИМ ПОЛІМЕРИЗАЦІЙНИМ МЕТОДОМ

Анотація. Сучасним методом міжфазної полімеризації з використанням трихлоретану як органічного середовища синтезовано інтенсивно провідний полімер поліаніліну (ПАНІ). Як окисник використано водний розчин пероксидисульфату амонію. Синтезований полімер охарактеризовано з використанням методу спектрофотометричного аналізу, Фур'є спектроскопією та скануючою електронною мікроскопією. Знайдено, що міжфазна полімеризація приводить до морфології фібрилярного типу з розміром волокон 200 нм. Оцінювання термічних властивостей синтезованих нановолокон поліаніліну проведено з використанням термогравіметричного аналізу. Провідність полімеру вимірювалася за допомогою методики чотирьох-електродної провідності і становила ~ 0,1 См/см.

Ключові слова: поліанілін, міжфазна полімеризація, нановолокна, спектроскопія, провідність.