

Influence of Solvent on Interfacial Polymerization of Polyaniline Nanostructure

S. J. Balamurugan, D. Sathya, S. Kalyanaraman, R. Murugesan*

Department of Physics, TDMNS College, T. Kallikulam, Tamil Nadu, India

ABSTRACT

In recent years, polyaniline (Pani) nanostructures have received much attention owing to their superior properties to the conventional bulk Pani materials. Interfacial polymerization is the latest among a variety of approaches to chemically synthesize nanostructured electronic conducting polymers. The Pani samples were prepared by using different methods like solution and inter-facial polymerization with three different organic solvent such as chloroform, benzene and toluene. The polymerisation yields and reaction condition are reported. In chloroform act as solvent in inter-facial methods, the polymerization yield, growth of polymerization and purity of polyaniline are high as compared to other solvents. So the chloroform is a best organic solvent in inter-facial method. All the Pani samples are confirmed by FTIR and UV-Visible spectral studies. The FTIR studies are also indicated the presence of chemical inter-action between polymer chain and dopant species. All the Pani samples are observed (π - π') extended conjugation at around 350-385nm; (n - π') polaronic peak around 530-570 nm and above 800 nm has a emeraldine base form in tail structure. The solubility of Pani samples is high due to high intensity of peak of UV-Visible spectra. The better processability of samples have used as active component of organic lightweight batteries, microelectronics, optical display, for anticorrosive protection, in biosensors, etc., due to its good electrical and optical properties as well as high environmental stability.

Keywords: Influence of solvent, polyaniline, interfacial polymerisation, spectral studies (UV-visible and FTIR)

I. INTRODUCTION

Organic conducting polymer like polyaniline has potential applications depending upon their synthetic techniques and the nature of the different solvent medium. Nano-structures of conducting polymers are of great significance due to their unique properties and application in nano-scale electronic and molecular devices [1, 2, 3]. The conducting polymers having the conjugated π bonds are as good as inorganic materials for the application of sensors or biosensor due to their redox reversibility with the variation of conductivity as well as colour change, ease of synthesis and sensitivity at room temperature [4]. Conducting polymers in the form of nano-fibers, nano-rods and nano-tubes are reported as the good

sensing materials due to their high surface/volume ratio [5,6,7]. Although the fabrications of these nano-materials are more complicated than that of flat film, such nano-structures can enhance the performance of gas sensors efficiently [8]. Nanostructured materials have attracted much interest because they show physical properties that are significantly different from their bulk materials [9]. Dimensionality plays an important role in determining the properties of nanomaterials and synthesis of nanostructured materials with controllable morphology, size, chemical composition, and crystal structure. Polyaniline and its derivatives are synthesized through two general routes: (a) electrochemical; and (b) chemical methods [10,11]. The common method for fabrication of polyaniline in large quantities is

based on chemical methods. In conventional chemical methods, the aniline is polymerized in water based solution in the presence of oxidant and dopant [12]. The synthesized polyaniline appears in the form of irregular granular particles. Several studies have shown that granular polyaniline particles have poor solubility and processing in common solvents such as water [13,14]. More attempts were made to improve their processing and solubility. It has been found that nanomaterials owing to their high surface area have better solubility in common solvents [15,16]. Different methods used to fabricate polyaniline nanofibers include electrospinning [17, 18], ultrasonic irradiation [19, 20], hard templates [21,22], soft template [23, 24], interfacial polymerization [25,26] and seeding polymerization [27, 28]. Among these methods, interfacial polymerization has achieved more attention due to its easiness, large-scale production-ability and environmentally gentle nature. Furthermore, it has a capability to produce high-quality polyaniline nanofibers with control of their morphology, size and diameter [29], new and powerful method for synthesis of the water-soluble conducting polyaniline.

II. EXPERIMENTAL

2.1. Materials

Aniline, ammonium perdisulphate, chloroform, benzene and toluene and sulphuric acid were purchased as research grade samples and aniline was purified by usual procedure and other chemicals were used as received without further purification process.

2.2. Synthesis

The polyaniline was prepared by *in-situ* chemical oxidative dispersion polymerization of 0.1 M aniline in 100ml of 1M sulphuric acid using 0.1 M ammonium perdisulphate (APS) as oxidant in 100 ml of 1M sulphuric acid. Then the ammonium perdisulfate solution was added into the aniline solution and was left at room temperature for 24 hours. Finally, the black green precipitate was collected and washed several times by distilled water and acetone. The pure polyaniline was then dried at ambient temperature for 24 hours.

Table 1. Polymerization yield of polyaniline samples by different methods.

Sample	Aniline	APS	Chloroform	Benzene	Toluene	Yield (g)	method
Pani-SO ₄ ²⁻	0.10M	0.10M	-	-	-	2.643	Solution
Pani-SO ₄ ²⁻	0.10M	0.10M	25ml	-	-	0.761	Inter-facial
Pani-SO ₄ ²⁻	0.10M	0.10M	-	25ml	-	1.182	Inter-facial
Pani-SO ₄ ²⁻	0.10M	0.10M	-	-	25ml	0.486	Inter-facial

Similarly the polyaniline was prepared by inter-facial method with different solvent *in-situ* chemical oxidative dispersion polymerization of 0.1 M aniline in 75 ml of 1M sulphuric acid and 25 ml of organic solvent (chloroform or benzene or toluene) using 0.1 M APS as oxidant in 100 ml of 1M sulphuric acid in a separating funnel. Then the oxidant based solution was carefully transferred to aniline based solution. After a short induction time, the reaction took place and the polyaniline was initially formed at the interface of the immiscible solutions. The green

polyaniline nanofibers increased in amount over time and filled the water based solution. After 24 hours, the black green polyaniline nanofibers were filtered and washed with distilled water and acetone. Finally the samples dried at room temperature for 24 hours. Polymerisation yield is noted.

2.3 Spectral Characterisation of polymer samples

All the polymer samples were characterized by FTIR and UV-VIS spectral studies. FTIR spectra of polymer samples in KBr pellet were recorded on computer-

controlled FTIR spectrophotometer at room temperature in 400-4000 cm^{-1} at PSN engineering college, Melathidiyur, Palayamkottai. All the polyaniline materials are dissolved in N-methyl pyrrolidone (NMP), which is highly coordination solvent. It can easily dissolve. UV-VIS spectra of the synthesized polymer samples were recorded at room temperature in NMP 390-900 nm range with UV-VIS spectrophotometer with computer software in matched 1 cm quartz cuvettes available at Department of PG chemistry and Research Centre, Adithanar Arts and Science College, Tiruchendur, Tamil Nadu.

III. RESULTS AND DISCUSSION

3.1. Polymerisation yield

The polymerization yield of polyaniline were prepared by different methods are given in table 1. In solution chemical oxidative polymerization, the yield is higher than interfacial methods of preparation of polyaniline. The solution method, polymer powder has micro size where as interfacial methods with different solvent, the polyaniline samples are very fine powder. This indicates that the interfacial methods, the polyanilines are nanolevel.

3.2 FTIR Spectral studies

The characteristics vibrational band of quinoid, benzenoid, $\text{C}=\text{N}^+$ and $\text{C}-\text{N}$ moieties and of dopant ions appear at the usually observed positions in the FTIR spectra of all the samples. The $\text{C}=\text{C}$ stretching vibration of quinoid and benzoid became stronger and the relative absorption band at 1576 and 1476 cm^{-1} shift to change in values. All the polymeric materials FTIR spectral characteristic peak data were presented in the given table2. Especially the characteristic peak of the doped polymer at 1028 cm^{-1} shifts to higher frequency and high intensity in inter-facial prepared samples. The original absorption band at 1125 cm^{-1} gradually shifts to higher frequency with the ordered extent. These results are all due to the change from ordered to disorder one. 1300 and 1006 cm^{-1} bands are

assigned to the $\text{C}-\text{N}$ stretching and $\text{C}-\text{H}$ in-plane bending vibrations, respectively. The increase of their intensities probably involved in the molecule close arrangement [30]. From the FTIR data is clearly indicated that all the polymer samples, the inter-facial prepared materials are strong binding with polymer and dopant molecules. The charge delocalization peaks of inorganic nanoparticles doped polymer is enhanced intensities. This is clearly indicated that all the inter-facial prepared samples are to increase its electrical conductivity.

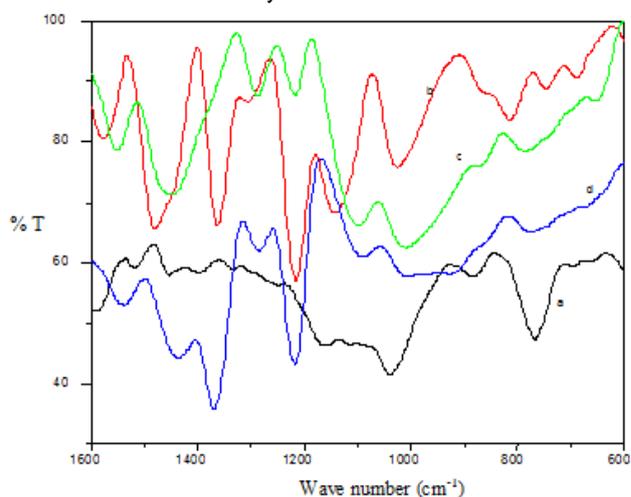


Figure 1. FTIR spectra of a) Pani- SO_4^{2-} ; b) Pani- SO_4^{2-} in chloroform (IF);c) Pani- SO_4^{2-} in benzene (IF); d) Pani- SO_4^{2-} in toluene (IF)

Table 2. Comparative FTIR Spectral data for Polyaniline prepared by different medium

Characteristic FTIR peaks	Solution method	Interfacial method			
		Pani- SO_4^{2-}	Pani- SO_4^{2-} chloroform	Pani- SO_4^{2-} benzene	Pani- SO_4^{2-} toluene
The $\text{C}=\text{C}$ stretching vibration of quinoid	1520	1579	1552	1538	
The $\text{C}=\text{C}$ stretching vibration of benzenoid	1453	1481	1452	1436	
The $\text{C}=\text{N}$	1214	1216	1222	1218	

stretching vibration in quinoid		1363	1288	1286 1369
Charge delocalization due to Dopants	-	1143	1098	1089
C-H in-plane bending vibrations	1038	1025	1009	1007
C-H out - place bending vibrations	767 884	745 814	786	775

3.3 UV-Visible Spectral Studies

All the polyaniline materials are dissolved in N-methyl pyrrolidone, which is highly coordination solvent. The inter-facial method prepared samples are more soluble than solution methods. The chloroform used inter-facial method can easily dissolve. The results are supported by UV-Visible spectra. All the polyaniline samples are observed ($\pi-\pi^*$) extended conjugation at around 350-385nm; ($n-\pi^*$) polaronic peak around 530-570 nm and above 800 nm has a emeraldine base form in tail structure. All the polyaniline samples shape of graph, intensity of peak height and intensity of positions is different. It indicates that all polymer materials have different compositions. The solubility of polyaniline in inter-facial different method is high due to high intensity of peak. Polaronic and bipolaronic peaks are higher wave length and high intensity. It indicates that polyanilines are pure and rich form oligomers in polymerization.

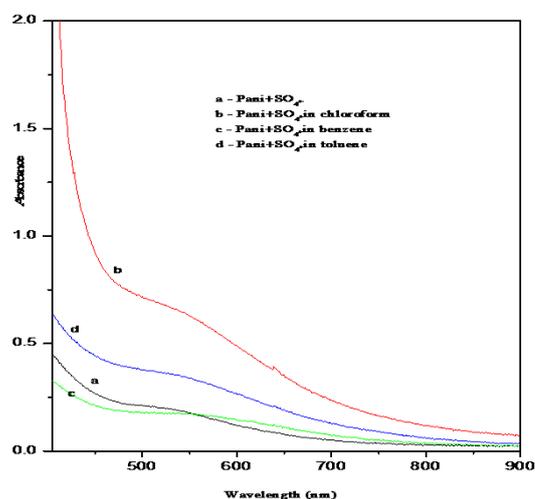


Figure 2. UV-Visible Spectra for Polyaniline materials dissolved in N-methyl pyrrolidone (NMP)

IV. CONCLUSION

The present study indicates the possibility of a formation of an environmentally stable electronically conducting polyaniline. Conducting polyaniline is prepared by using different methods like solution and inter-facial method with three different organic solvent. The polymerisation yields are increased due to the growth of polymerization is also enhanced. In chloroform act as solvent in inter-facial methods, the polymerization yield, growth of polymerization and purity of polyaniline are very high. Therefore, the chloroform is the best organic solvent in inter-facial method. All the polyaniline samples are confirmed by FTIR and UV-Visible spectral studies. The FTIR studies are also suggested the presence of chemical interaction between polymer chain and dopant species. The solubility of polyaniline materials is high due to high intensity of peak of UV-Visible spectra. The better process ability of polymer samples is used in many applications.

V. REFERENCES

- [1]. Fei Zhao, Ye Shi, Lijia Pan and Guihua Yu 2017, 'Multifunctional Nano structured Conductive Polymer Gels: Synthesis, Properties, and Applications', Accounts chemical research, 50, 1734–1743. DOI:10.1021/acs.accounts.7b00191

- [2]. Duong Nguyen Nguyen and Hyeonseok Yoon 2016, 'Recent Advances in Nanostructured Conducting Polymers: from Synthesis to Practical Applications', *Polymers*, 8, 118. DOI: 10.3390/polym8040118.
- [3]. H.J. Qiu and M. X.Wan 2001, 'Nanostructures of polyaniline doped with a Novel dopant', *Materials Physics mechanics*, 4, 125.
- [4]. Siti Amira Othman and Shahidan Radiman 2017, 'Role of Horseradish Peroxidase in Polypyrrole Conductivity', *Solid state phenomena*, 268, 370-373.
- [5]. Kenry and Chwee TeckLim 2017, 'Beyond the Current State of the Syntheses and Applications of Nanofiber Technology', *Progress in polymer science*, 70, 1-17. DOI: 10.1016/j.progpolymsci.2017.03.002
- [6]. J. Huang, S. Viriji, B.H. Weiller and R.B. Kaner 2004, 'Nanostructured polyaniline sensors', *Chemistry A European Journal*, 10, 1314. DOI: 10.1002/chem.200305211
- [7]. S. Viriji, J.Huang, R.B. Kaner and B.H. Weiller 2004, 'Polyaniline Nanofiber Gas Sensors: Examination of Response Mechanisms', *Nanoletters*, 4, 491. DOI: 10.1021/nl035122e.
- [8]. Sukumar Basu and Surajit Kumar Hazra 2017, 'Graphene–Noble Metal Nano-Composites and Applications for Hydrogen Sensors', *Journal of carbon research*, 3, 29. DOI: 10.3390/c3040029
- [9]. Ibrahim Khan, Khalid Saeed and Idrees Khan 2017, 'Nanoparticles: Properties, applications and toxicities', *Arabian journal of Chemistry*, Article in Press. DOI: 10.1016/j.arabjc.2017.05.011
- [10]. Afroz Latifi, Mohammad Imani, Mohammad Taghi Khorasani and Morteza Daliri Joupari 2013, 'Electrochemical and chemical methods for improving surface characteristics of 316L stainless steel for biomedical applications', *Surface & Coatings Technology* 221, 1–12. DOI: 10.1016/j.surfcoat.2013.01.020
- [11]. S. Bhadra, N.K. Singha, D. Khastgir, 2007, 'Electrochemical synthesis of polyaniline and its comparison with chemically synthesized polyaniline', *Journal of Applied Polymer Science*, 104, 1900. DOI: 10.1002/app.25867.
- [12]. Huanhuan Wang, Jianyi Lin and Ze Xiang Shen 2016, 'Polyaniline (PANi) based electrode materials for energy storage and conversion', *Journal of Science: Advanced Materials and Devices*, 1 (3), 225-255. DOI: 10.1016/j.jsamd.2016.08.001
- [13]. Ahmad Abdolahi, Esah Hamzah, Zaharah Ibrahim and Shahrir Hashim 2012, 'Synthesis of Uniform Polyaniline Nanofibers through Interfacial Polymerization', *Materials*, 5, 1487-1494. DOI: 10.3390/ma5081487
- [14]. P. Hany and E.M. Genies, 1989, 'Polyanilines with covalently bonded alkyl sulfonates as doping agent. Synthesis and properties', *Synthetic metals*, 31, 369. DOI: 10.1016/03796779(89)90804-7.
- [15]. Kurt Ernst Geckeler and Thathan Premkumar 2011, 'Carbon nanotubes: are they dispersed or dissolved in liquids?', *Nanoscale Research Letters*, 6, 136. DOI: 10.1186/1556-276X-6-136.
- [16]. D. Li, J. Huang and R.B. Kaner 2009, 'Polyaniline nanofibers: a unique polymer nanostructure for versatile applications', *Accounts of chemical research*, 42, 135. DOI: 10.1021/ar800080n.
- [17]. Chen Chen, Yongan Tang, Branislav Vlahovic and Fei Yan 2017, 'Electrospun Polymer Nanofibers Decorated with Noble Metal Nanoparticles for Chemical Sensing', *Nanoscale Research Letters*, 12, 451. DOI: 10.1186/s11671-017-2216-4.
- [18]. M. Lia, Y. Guob, Y. Weib, A.G. Macdiarmid and P. I. Lelkes 2006, 'Electrospinning polyaniline-contained gelatin nanofibers for tissue engineering applications', *Biomaterials*, 27, 2705. DOI: 10.1016/j.biomaterials.2005.11.037.
- [19]. Manayil Valappil Swapna and Karickal R. Haridas 2016, 'An easier method of preparation of mesoporous anatase TiO₂ nanoparticles via

- ultrasonic irradiation', *Journal of Experimental Nanoscience*, 11(7), 540. DOI:10.1080/17458080.2015.1094189.
- [20]. X. Jing, Y. Wang, D. Wu, L. She and Y. Guo 2006, 'Polyaniline nanofibers prepared with ultrasonic irradiation', *Journal of Polymer Science*, 44, 1014. DOI: 10.1002/pola.21217.
- [21]. Yadian Xie, Duygu Kocaefe, Chunying Chen and Yasar Kocaefe 2016, 'Review of Research on Template Methods in Preparation of Nanomaterials', *Journal of Nanomaterials*, Article ID 2302595. DOI: 10.1155/2016/2302595.
- [22]. C. G. Wu and T. Bein 1994, 'Conducting polyaniline filaments in a mesoporous channel host', *Science*, 264, 1757. DOI: 10.1126/science.264.5166.1757.
- [23]. Krushna J Kshirasagar, Uddhav S Markad, Abhijit Saha, Kiran Kumar K Sharma and Geeta K Sharma 2017, 'Facile Synthesis of Palladium Nanoparticle Doped Polyaniline Nanowires in Soft Templates for Catalytic Applications', *Materials Research Express*, 4 (2), 025015. DOI: 10.1088/2053-1591/aa5947.
- [24]. W. Zhong, J. Deng, Y. Yang, and W. Yang 2005, 'Synthesis of large- area three dimensional polyaniline nanowire networks using a "soft template" ', *Macromolecular Rapid Communications*, 26, 395. DOI: 10.1002/marc.200400463.
- [25]. Michiel J.T. Raaijmakers and Nieck E. Benes 2016, 'Current trends in interfacial polymerization chemistry', *Progress in Polymer Science*, 63, 86-142. DOI:10.1016/j.progpolymsci.2016.06.004.
- [26]. J. Huang and R.B. Kaner 2004, 'A General Chemical Route to Polyaniline Nanofibers', *Journal of American Chemical Society*, 126, 851. DOI: 10.1021/ja0371754.
- [27]. Soichiro Ogi, Vladimir Stepanenko, Kazunori Sugiyasu, Masayuki Takeuchi, and Frank Würthner 2015, 'Mechanism of Self-Assembly Process and Seeded Supramolecular Polymerization of Perylene Bisimide Organogelator', *Journal of the American Chemical Society*, 137 (9), 3300-3307. DOI: 10.1021/ja511952c
- [28]. X. Zhang, W.J. Goux and S.K. Manohar 2004, 'Synthesis of Polyaniline Nanofibers by "Nanofiber Seeding" ', *Journal of American Chemical Society*, 126, 4502. DOI: 10.1021/ja031867a.
- [29]. Qingkun Wen , Kai He, Chengwei Wang, Baoxiang Wang, Shoushan Yu, Chuncheng Hao and Kezheng Chen 2018, 'Clip-like polyaniline nanofibers synthesized by an insitu chemical oxidative polymerization and its strong electrorheological behavior', *Synthetic Metals* 239, 1-12. DOI: 10.1016/j.synthmet.2018.02.007.
- [30]. Kuestan A. Ibrahim 2017, 'Synthesis and characterization of polyaniline and poly(aniline-co-o-nitroaniline) using vibrational spectroscopy' *Arabian journal of Chemistry*, 10(2), s2668-s2674. DOI: 10.1016/j.arabjc.2013.10.010.