

Preparation and Characterization of Polyaniline Nanoparticles Using Various Solutions

¹H.G. Taleghani, ¹M. Aleahmad and ²H. Eisazadeh

¹Faculty of Chemical Engineering, Mazandaran University, Babolsar, Iran

²Faculty of Chemical Engineering, Babol Noshirvani University of Technology, P.O. Box 484, Babol, Iran

Abstract: Polyaniline was prepared in aqueous and aqueous/non-aqueous media by using KIO_3 as an oxidant in the presence of various solutions such as benzene, Tetrahydroforan and methanol. The polyaniline nanoparticles were characterized in terms of their Morphology, particle size, conductivity and chemical structure. The results indicate that the morphology and particle size are dependent on the type of solution. Small and spherical nanoparticles obtained using tetrahydroforan as a solution. It is interesting that the electrical conductivity of polyaniline nanoparticles increased by using ethylene glycol as solution. Also, the chemical structure of the products was determined by Fourier transform infrared spectroscopy (FTIR). The results shown that the intensity of peaks is dependent on the type of solution.

Key words: Nanoparticles • Polyaniline • Solution • Morphology • Chemical structure

INTRODUCTION

During the last decade there has been widespread interest in conducting polymers. Polyaniline (PAN) is one of the most useful conducting polymers due to its ease of synthesis and environmental stability. It also has a wide range of electrical properties which can be easily controlled by changing its oxidation and protonation states [1, 2]. However, there are still many unresolved problems concerning the structures and properties of PAN because of the complexities in molecular structure, due to synthesis conditions [3, 4]. Improvement of polyaniline properties can be achieved either by forming composites and nanocomposites of aniline, or blends with commercially available polymers or inorganic materials which offer better mechanical and optical properties, stability and processability [5-8].

Polyaniline has attracted considerable attention because of its unique electrical, optical and electrooptical properties and its numerous potential applications [9]. One of the key problems related to the potential applications of polyaniline is its processability. Processability is an important requirement in conducting polymers for their possible commercial use.

Since most of the conducting polymers are not processable, much of the efforts made in this field have been directed towards circumventing this problem. To solve this problem, various approaches have been tried, including addition of side groups to the polymer

backbone [10], grafting of polymers to a non-conducting polymer [11], direct polymerization of intractable polymers into the final desired shape, making a composite of blend of conducting polymers [12, 13] and copolymerization [14].

Extensive research has been directed toward the improvement of the processability of polyaniline by copolymerization with substituted aniline [15,16] or doping polyaniline with stable functionalized protonic acid [17, 18]. Conducting polymers have various application such as rechargeable batteries [19], electromagnetic interference (EMI) shielding [20], antistatic coatings [21], gas sensors [22], optical devices [23], removal of heavy metal from water and waste water [24-26], etc.

During the last decade, nanostructured (nanoparticles/-rods/-wires) conducting polyaniline with unusual physical and chemical properties have attracted great research interests. Much research has been conducted on the nanostructure of polyaniline (PAN) because it exhibits enhanced performance in applications where a high surface contact area is needed between the nanostructures and its environment. Recently, various strategies including template synthesis, interfacial polymerization, self-assembly and stepwise electrochemical deposition have been developed for the preparation of polyaniline nanostructures [27-31]. Although various methods of preparing PAN nanostructures have been reported, new simple and economical methods are still being explored.

Table 1: Preparation conditions and type of solution on the conductivity and conversion of monomer to polymer

Type of Solution	Type of oxidant	Concentration of oxidant (g/L)	Particle size (nm)	Conversion of monomer to polymer (%)	Electrical conductivity (S/cm)
water	KIO ₃	10	65	87	19.6×10 ⁻²
water/ethylene glycol (50/50 % v/v)	KIO ₃	10	198	83	87.2×10 ⁻²
water/tetrahydroforan (50/50 % v/v)	KIO ₃	10	89	78	2.1×10 ⁻³
water /methanol (50/50 % v/v)	KIO ₃	10	---	76	4.32×10 ⁻²
water /benzene (50/50 % v/v)	KIO ₃	10	83	78	8.2×10 ⁻³

In this study polyaniline nanoparticles were prepared using various solutions. The products, were characterized with FTIR, SEM and electrical conductivity measurement.

MATERIALS AND METHODS

Instrumentation: A magnetic mixer model MK20, digital scale model FR 200, scanning electron microscope (SEM) model XL30 and fourier transform infrared (FTIR) spectrometer model shimadzu 4100 were employed. The four point probe method was used to measure the volume resistivity of conducting polymer films.

Reagents and Standard Solutions: Materials used in this work were: Aniline monomer, sulfuric acid, Tetrahydroforan, methanol, benzene and potassium iodate from Merck. All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Aniline monomer was purified by simple distillation.

Polyaniline Preparation: The reaction was carried out in aqueous and aqueous/non-aqueous media at room temperature for 5 hours. The conditions for polymer formation are listed in Table 1.

In a typical experiment 1 mL aniline monomer was added to stirred aqueous solution of 100 mL 1 M sulfuric acid containing 1g of KIO₃. After 5 hours polymer was filtered, washed several times with deionized water and then dried in room temperature.

RESULTS AND DISCUSSION

The surface morphology of polymers was studied, using scanning electron microscope. As shown in Figures 1-5, the size and homogeneity of particles are dependent on the type of solution. As can be seen in Figures 4 and 5, the type of solution strongly influences the particle size and homogeneity of particles, because the solutions affect the rate of polymer formation.

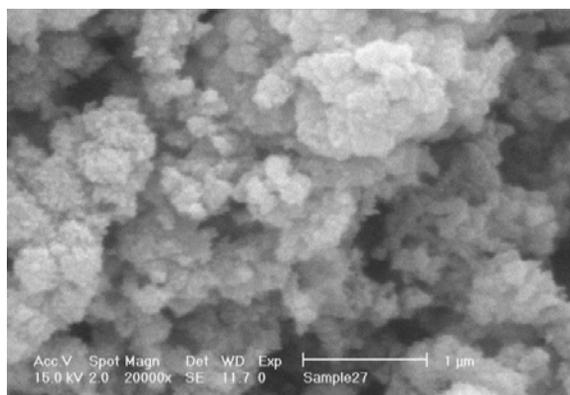


Fig. 1: Scanning electron micrograph of PAN in aqueous media. Reaction conditions: (KIO₃=10 g/L, aniline monomer 10.75×10⁻² mol/L, volume of solution 100 mL, reaction time 5 hours at room temperature)

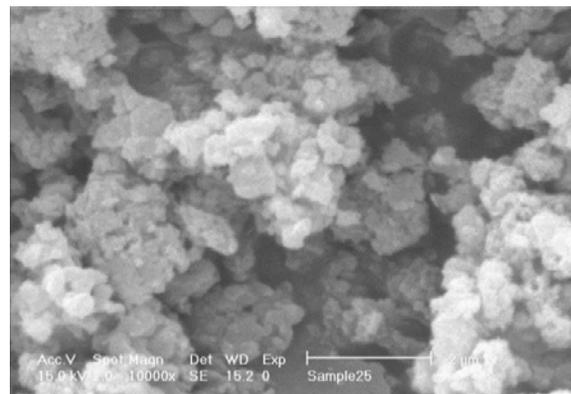


Fig. 2: Scanning electron micrograph of PAN in aqueous/non-aqueous (water/ethylene glycol) media. Reaction conditions: (KIO₃=10 g/L, aniline monomer 10.75×10⁻² mol/L, volume of solution 100 mL (50/50 % v/v), reaction time 5 hours at room temperature)

As can be seen in Figure 3, small and spherical nanoparticles obtained using tetrahydroforan as a solution.

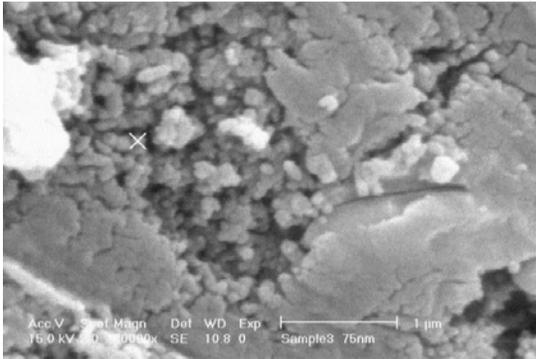


Fig. 3: Scanning electron micrograph of PAN in aqueous/non-aqueous (water/tetrahydrofuran) media. Reaction conditions: ($\text{KIO}_3=10$ g/L, aniline monomer 10.75×10^{-2} mol/L, volume of solution 100 mL (50/50 % v/v), reaction time 5 hours at room temperature).

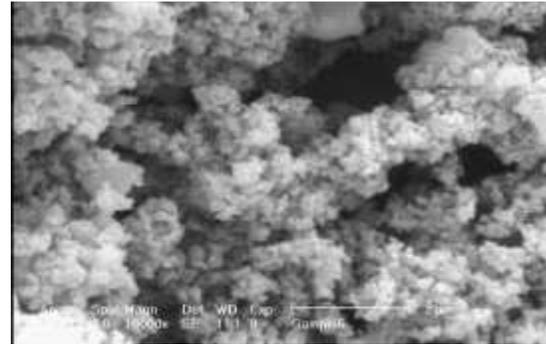


Fig. 5: Scanning electron micrograph of PAN in aqueous/non-aqueous (water/benzene) media. Reaction conditions: ($\text{KIO}_3=10$ g/L, aniline monomer 10.75×10^{-2} mol/L, volume of solution 100 mL (50/50 % v/v), reaction time 5 hours at room temperature).

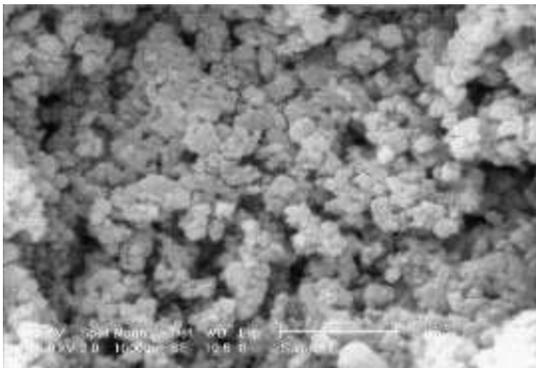


Fig. 4: Scanning electron micrograph of PAN in aqueous/non-aqueous (water/methanol) media. Reaction conditions: ($\text{KIO}_3=10$ g/L, aniline monomer 10.75×10^{-2} mol/L, volume of solution 100 mL (50/50 % v/v), reaction time 5 hours at room temperature).

The electrical conductivity of various composites produced under different reaction conditions was measured on pressed pellets of the composite powders. The electrical conductivity of compressed pellets was measured using four point probe method. The results are shown in Table 1.

As shown in table the type of solution influence the conversion of monomer to polymer, electrical conductivity and particle size, because the polarity of solution affect the rate of polymerization and electrical conductivity of product. By comparison between ethylene glycol and benzene solutions, electrical conductivity increases using ethylene glycol as solution.

The chemical structure of obtained product was determined by FTIR spectrum. The FTIR spectroscopy has provided valuable information regarding the formation of polyaniline. FTIR analysis has been done to identify the characteristic peaks of product.

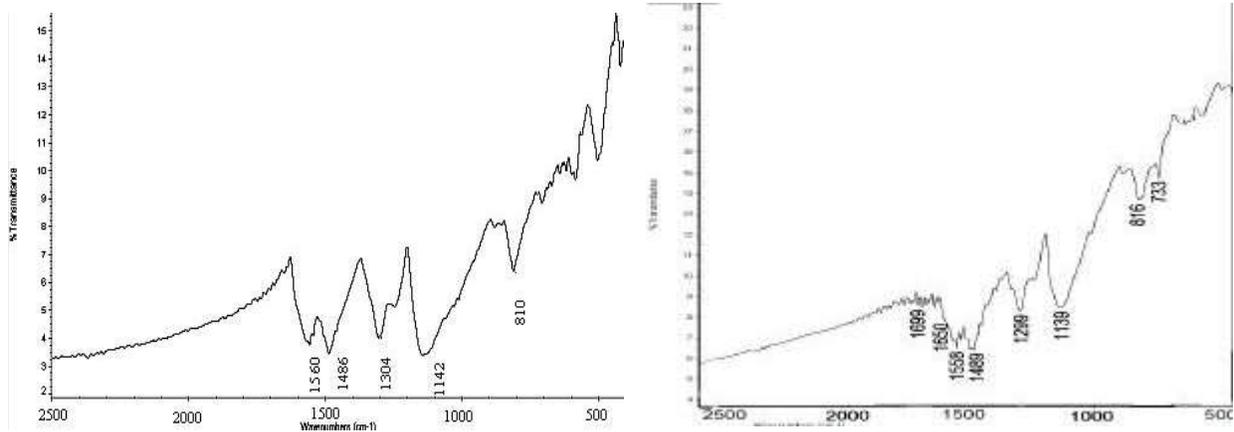


Fig. 6: FTIR spectra of pure PAN in a) aqueous media b) aqueous/ nonaqueous media

FTIR spectra in the 2500-400 cm^{-1} region, for PAN is shown in Figure 6. As can be seen figure (6a) polyaniline shows the presence of characteristic absorption bands at 1560 cm^{-1} (C=C stretching vibration of the quinoid ring), 1486 cm^{-1} (stretching vibration of C=C of the benzenoid ring), 1304 cm^{-1} (C-N stretching vibration), 1142 cm^{-1} (C-H in-plane deformation), 810 cm^{-1} (C-H out-of-plane deformation).

CONCLUSIONS

In this work the characteristics of PAN such as morphology, electrical conductivity, chemical structure and yield of monomer to polymer were investigated using various solutions. It was found that, the type of solution has a considerable effect on the conductivity and morphology of resulting product, which is probably due to polarity of solution. As it can be seen in the micrographs, particle size decreases and homogeneity increases when the polarity of solution decreases. Nano-spherical particles obtained when, tetrahydrofuran used as solution. Also electrical conductivity increased by using ethylene glycol as solution.

REFERENCES

1. Huang, W.S., B.D. Humphrey and A.G. MacDiarmid, 1986. Polyaniline, a novel conducting polymer, Morphology and chemistry of its oxidation and reduction in aqueous electrolytes. *J. Chem. Soc.*, 82(1): 2385-2400.
2. Chiang, J.C. and A.G. MacDiarmid, 1986. Polyaniline: Protonic Acid Doping of the Emeraldine Form to the Metallic Regime. *Synth. Met.*, 13(1): 193-198.
3. Yin, W., J. Li, Y. Li, J. Wu and T. Gu, 2001. Conducting composite film based on polypyrrole and crosslinked cellulose. *J. Appl. Polym. Sci.*, 80(9): 1368-1373.
4. Machado, J.M., F.E. Karasz and R.W. Lenz, 1988. Electrically conducting polymer blends. *Polymer*, 29(8): 1412-1418.
5. Paoli, M.A.D.E., R.J. Waltman, A.F. Diaz and J. Bargon, 1984. Conductive composite from poly (vinyl chloride) and polypyrrole. *J. Chem. Soc. Chem. Commun.*, 15: 1015-1016.
6. Lindsey, S.E. and G.B. Street, 1984/85. Conductive composites from poly (vinyl alcohol) and polypyrrole. *Synth. Met.*, 10(1): 67-69.
7. Cassignol, C., M. Cavarero, A. Boudet and A. Ricard, 1999. Microstructure-conductivity relationship in conducting polypyrrole/epoxy composites. *Polymer*, 40(5): 1139-1143.
8. Bhat, N.V., A.P. Gadre and V.A. Bambole, 2001. Structural, mechanical and electrical properties of electropolymerized polypyrrole composite films, *J. Appl. Polym. Sci.*, 80(13): 2511-2516.
9. Salanek, W.R., I. Lundstrom, W.S. Huang and A.G. MacDiarmid, 1986. A two-dimensional surfacestate diagram for polyaniline. *Synth. Met.*, 13(44): 291-297.
10. Pandey, S.S., S. Annapoorani and B.D. Malhotra, 1993. synthesis and characterization of poly (aniline-co-o-anisidine). *Macromolecules*, 26(1): 3190-3193.
11. Andreatta, A., A.J. Heeger and P. Smith, 1990. Electrically conductive poly blend fibers of polyaniline and poly-(p-phenylene terephthalamide). *Polym Commun.*, 31(7): 275-295.
12. Nazzari, A.I. and G.B. Street, 1985. Pyrrole-styrene graft copolymers. *J. Chem. Soc. Chem. Commun.*, pp: 375-376
13. Aldissi, M., 1984. Polyacetylene Block Copolymers. *Synth. Met.*, 13(11): 87-100
14. Nalwa, H.S., 1990. Ferroelectric Polymers: Chemistry. *J. Phys. D: Appl. Phys.*, 23(1): 745-748.
15. Wang, S., F. Wang and X. Ge, 1986. Polymerization of substituted aniline and characterization of polymer obtained. *Synth. Met.*, 16(1): 99-104.
16. Nguyen, M.T., P. Kasai, J.L. Miller and A.F. Diaz, 1994. Synthesis and Properties of Novel Water-Soluble Conducting Polyaniline Copolymers. *Macromolecules*, 27(1): 3625-3631.
17. Cao, Y., P. Smith and A.J. Heeger, 1992. Counter-ion induced processibility of conducting polyaniline and of conducting polyblends. *Synth. Met.*, 48(1): 91-97.
18. Andreatta, A. and P. Smith, 1993. Processing of conductive polyaniline-UHMW polyethylene blends from solutions in non-polar solvents. *Synth. Met.*, 55(2-3): 1017-1022.
19. Li, N., J.Y. Lee and L.H. Ong, 1992. A polyaniline and Nafion® composite film as a rechargeable battery. *J. Appl. Electrochem.*, 22(6): 512-516.
20. Epstein, A.J. and A.G. MacDiarmid, 1995. Polyanilines: From solitons to polymer metal, from chemical curiosity to technology. *Synth. Met.*, 69(1-3): 179-182.
21. Ohtani, A., M. Abe, M. Ezoe, T. Doi, T. Miyata and A. Miyake, 1993. Synthesis and properties of high-molecular-weight soluble polyaniline and its application to the 4MB-capacity barium ferrite floppy disk's antistatic coating. *Synth. Met.*, 57(11): 3696-3701.

22. Matsuguchi, M., J. Io, G. Sugiyama and Y. Sakai, 2002. Effect of NH₃ gas on the electrical conductivity of polyaniline blend films. *Synth. Met.*, 128(1): 15-19.
23. Falcao, E.H. and W.M. De Azevedo, 2002. Polyaniline-polyvinyl alcohol composite as an optical recording material. *Synth. Met.*, 128(2): 149-154.
24. Eisazadeh, H., 2007. Removal of Chromium From Waste Water Using Polyaniline. *J. Appl. Polym. Sci.*, 104(1): 1964-1967.
25. Eisazadeh, H., 2008. Removal of Arsenic in Water Using Polypyrrole and its Composites, *W. Appl. Sci. J.*, 3(1): 10-13.
26. Eisazadeh, H., 2007. Removal of Mercury From Water Using Polypyrrole and its Composites, *Chin. J. Polym. Sci.*, 25(4): 393-397.
27. Huang, J., Virji S, Weiller BH, Kaner RB, 2004. Nanostructured polyaniline sensors. *Chem. Eur. J.*, 10(6): 1314-1319.
28. Huang, J. and R.B. Kaner, 2004. Nanofiber formation in the chemical polymerization of aniline: A mechanistic study. *Angew Chem., Int. Ed.*, 43(43): 5817-5821.
29. Dong, H., S. Prasad, V. Nyame and W. Jone, 2004. Sub-micrometer conducting polyaniline tubes prepared from polymer fiber templates. *Chem Mater*, 16(3): 371-373.
30. Ma, Y., J. Zhang, G. Zhang and H. He, 2004. Polyaniline nanowires on Si surfaces fabricated with DNA templates. *J. Am. Chem. Soc.*, 126(22): 7097-7101.
31. Huang, J. and R. Kaner, 2004. A general chemical route to polyaniline nanowires. *J. Am. Chem. Soc.*, 126(3): 851-855.