

Preparation and Characterizations of Phenylenediamine Nanofibers

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ABSTRACT: Phenylenediamine-oxalic acid nanofibers were chemically synthesized by chemical oxidative polymerization in the presence of ammonium persulfate as oxidant. In this paper we report a simple method to develop Phenylenediamine (PDA) doped with oxalic acid (OA) having nanofibers morphology. The morphology of synthesized Phenylenediamine doped with oxalic acid nanofibers were analyzed by SEM, UV-Vis. As the concentration of oxalic acid increases conductivity goes on increasing.

Keywords: nanofibers, conducting polymer, organic acid dopant, Phenylenediamine, spectroscopy.

INTRODUCTION

In recent years, electrically conducting and intrinsically colored polymers are widely used in diverse applications. [1]. Polyaniline is one of the most studied conducting polymers due to its chemical stability and relative high conductivity [2]. Polymers based on aniline derivatives have also been extensively investigated [3]. The polymer of aniline and its derivatives is one of the most widely researched electrically conductive polymers because of their easy preparation, high stability, good electrical conductivity, and high gas-separation ability. Among them, poly (Phenylenediamine) homopolymer is reported to be a highly aromatic polymer containing 2,3-diaminophenazine or quinoraline repeating unit and exhibiting high thermostability [4].

Homopolymerization of three isomers of *o*-, *m*-, *p*-Phenylenediamine (amino aniline) by a simple and easy oxidative polymerization yields a ladder like polymer containing a phenazine ring that may be a new rigid rod and heat-resistant polymer.

It is believed that the investigations of polymers synthesized from aromatic diamine are more attractive since they exhibit more novel multifunctionality than PANI. Phenylenediamine

are a class of ANI derivatives having an extra -NH₂ group in the *o*-, *m*-, or *p*- position., *o*-PDA is the most frequently studied number.

Here we report a facile chemical route to high-quality Phenylenediamine nanofibers. The nanofibers have nearly uniform diameters. The synthesis is based on the well known chemical oxidative polymerization of PDA with ammonium peroxydisulfate as the oxidant.

This article reports the effect of the molar ratio of oxalic acid to phenylenediamine on the morphology of the resulting phenylenediamine-oxalic acid, which shows nanofibers.

CHARACTERIZATIONS

The UV-Vis spectra of the polymer solution in Dimethyl Formamide (DMF) were recorded by using UV-1800 Shimadzu automatic recording double beam spectrophotometer in the range of 200-1100 nm. Room temperature conductivity of the samples was measured by four probe method. SEM was analyzed from VNIT, Nagpur by JEOL 6380-A instrument. The samples were precoated with Pt before scanning.

Experimental

Materials: Phenylenediamine (PDA), Ammonium persulfate (APS), oxalic acid (OA) used as received. All chemicals were of analytical grade.

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Polymerization: 0.2M PDA and specific molar concentrations of oxalic acid were mixed with stirring at room temperature for 30 min. The stirring was then stopped, 50ml aqueous solution of 0.2M APS was added and the reaction was left for 12 hrs. The resulting PDA precipitate was washed with deionized water, methanol and ether several times. Finally the product was dried in vacuum at 80 °C temperature for 24 hrs.

RESULT AND DISCUSSION

UV-Vis absorption of PDA-OA

UV-Visible spectroscopy is a powerful tool for the study of protonation effect (and hence the formation of different oxidation states of the polymer) as well as for the elucidation of the interactions between the solvent, the dopant and the polymer chains.

Fig. 1 shows the UV-Vis absorption spectra of PDA doped with different concentrations of oxalic acid in DMF as a solvent.

The spectra reveal the presence of two absorption bands, one in the visible region and the other in the UV region in the polymers. The band in the UV region corresponds to $\Pi-\Pi^*$ transition and the band in the visible region corresponds to the inter-ring charge transfer associated with excitation from benzenoid to quinoid moieties

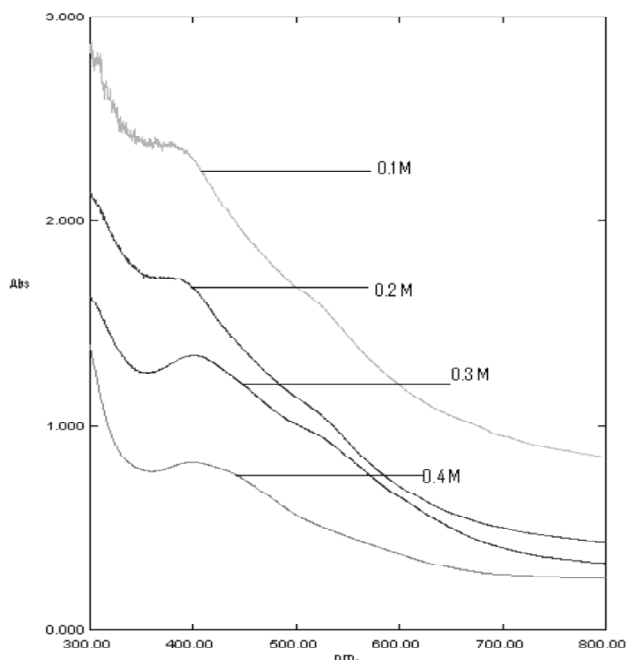


Figure 1: UV-Vis spectra of PDA Doped with 0.1M to 0.4M Concentration of Oxalic Acid

[5,6]. 0.1M and 0.2M OA shows the absorption peak in the UV region but as the concentration increases this UV peak is shifted to higher wavelength which shows red Shift.

Conductivity Study : The PDA to OA mole ratio and reaction time effects on the room temperature conductivity of PDA-OA are summarized in Table 1. Conductivity increased significantly from 3.17×10^{-8} to 1.76×10^{-7} S/cm as the concentration of dopant (oxalic acid) increases i.e. 0.1M to 0.4.

As the concentration of oxalic acid increases conductivity goes on increasing. This increase in conductivity with increase in temperature is the characteristic of “thermal activated behavior” [7]. The increase in conductivity could be due to increase of efficiency of charge transfer between the polymer chains and the dopant with increase in temperature [8].

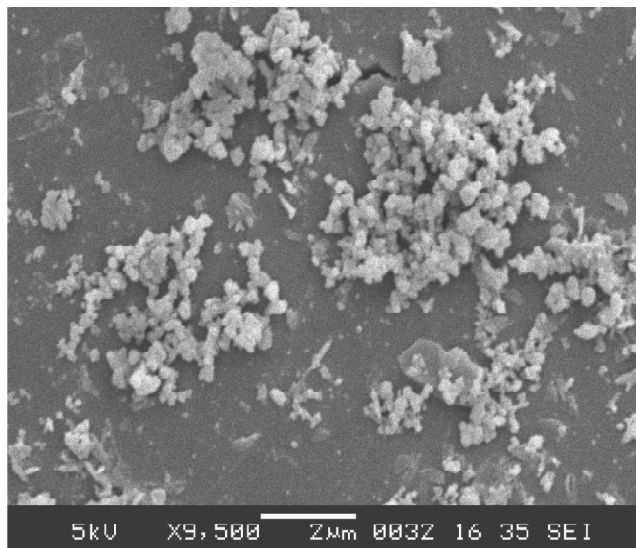
Table 1
Room Temperature and High Temperature Conductivity of PDA Doped with Oxalic Acid

Oxalic acid Concentration	Conductivity S/Cm	
	25 °C	125 °C
0.1M	3.17×10^{-8}	5.28×10^{-8}
0.2 M	4.56×10^{-8}	6.32×10^{-8}
0.3 M	1.53×10^{-7}	2.30×10^{-7}
0.4 M	1.76×10^{-7}	3.56×10^{-7}

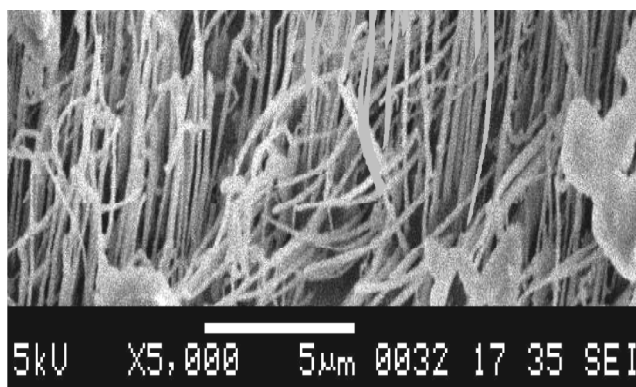
It is also possible that the thermal curing affects the chain alignment of the polymer, which leads to the increase of conjugation length and that brings about the increase of conductivity. There also had to be molecular rearrangement on heating, which made the molecular conformation favorable for electron delocalization [9].

Morphologies of PDA with lower and higher concentration of Oxalic acid

Low concentration of OA content led to the formation of small diameter micelles. But high concentration of OA content caused micelles to react and join together along the direction of the polymer chain in the polymerization process. The micelles act as the template in the self-assembly of PDA doped with oxalic acid to form microspheres or nanotube structures. [10, 11, 12, 13, 14].



(a)



(b)

Figure 2a: SEM Image of 0.1M(OA) Concentration (b) SEM Image of 0.4M(OA) Concentration

CONCLUSION

The effect of concentration of dopant (OA) on the morphology, UV–Vis absorption, and conductivity property of Phenylenediamine was investigated. The morphology of Phenylenediamine changed

from nanospheres to nanotubes by increasing the concentration of OA molar ratio in the copolymerization reaction. Different nanostructures and larger conductivity have been achieved in this work.

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References

- [1] C. L. Curtis, *Adv. Mater.*, 1994, 6, 688; A.G. MacDiarmid, *Synth. Met.*, **1997**, 84, 27.
- [2] (a) Q. Pei, G. Yu, C. Zhang, Y. yang and A. G. Heeger, *Science*, 1995, 269, 1086; (b) A.G. MacDiarmid and J.A. Epstein, *Synth. Met.*, 1994, 65, 103; (c) A.G. MacDiarmid, J.C. Chiang and A.F. Richter, *Synth. Met.*, 1987, 18, 285; (d) Y. Cao, P. Smith and A. J. Heeger. *Synth. Met.*, **1992**, 48, 91.
- [3] T. Sulimenko, J. Stejskal and J. Prokes, *J. Colloid Interface Sci.*, **2001**, 236, 328.
- [4] A. H. Premasiri and W. B. Euler, *Macromol. Chem. Phys.*, 1995, 196, 3655; *F. Cataldo, Eur. Polym. J.*, **1996**, 32, 43.
- [5] D. Machines and B. L. Fimt, *Synth. Met.* 25, **1998**, 235.
- [6] S. K. Dhawan, D. C. Trivedi and S. I. Vasu, *Electrochemistry* 5, **1989**, 208.
- [7] F. Zuo, M. Angelopoulos, A. G. MacDiarmid and A. J. Epstein, *Phys. Rev. B* 36, **1987**, 3475.
- [8] A. Kobayashi, H. Ishikawa, K. Amano and M. Satoh, *J. Appl. Phys.* 74, **1993**, 296.
- [9] M. G. Han and S. S. Im, *Polymer* 41, **2000**, 3253.
- [10] L. Zhang, Y. Long, Z. Chen, M. Wan, *Adv. Funct. Mater.* 14, **2004**, 693.
- [11] Y. Sahin, K. Pekmez, A. Yildiz, *Synth. Met.* 129, **2002**, 107.
- [12] C. H. Yang, Y. K. Chih, H. E. Cheng, C. H. Chen, *Polymer* 46, **2005**, 10688.
- [13] M. Adachi, T. Harada, M. Harada, *Langmuir* 16, **2000**, 2376.
- [14] B. J. Kim, S. G. Oh, M. G. Han, S. S. In, *Langmuir* 16, **2000**, 5841.

