

The Synthesis and Characterization of Polyaniline Nanorod: by the Method of Ethanol Solution Polymerization

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Polyaniline polymers were prepared using ethanol as solution in this paper while a kind of copolymer was formed with o-toluidine. And then the products were characterized and analyzed by the tests of infrared, electron microscopy and so on. The results shows that the products have the structure of nanorod, and the thermal stability of the copolymer proved to be worse than Polyaniline (PANI) after vulcanization process. Besides, the conductivity of the copolymer increased first and then decreased with the adding of o-toluidine, which is mainly due to the addition of polar groups methyl that affects π electron transfer speed on the molecular chain.

Keywords: Polyaniline, O-toluidine, Nanorod, Conductivity.

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1. INTRODUCTION

Since the 1906s, Intrinsically Conducting Polymers (ICPs) has been paid more attention because of their potential uses in the fields of electronic, electrochemical, electromagnetic, electrical machinery, the photoelectric effect, ER, chemistry, membranes, sensors and other aspects. However, there are still several obstacles to overcome before the practical application of ICP [1].

In the existing ICP, PANI receives wide concern for its simple synthesis, cheap monomer, chemical controllability, and good stability compared with other ICPs.

Currently, there are lots of ICP problems including PANI: low conductivity compared to metals, and being insoluble and infusible in any known solvent [2]. Yet, solubility of ICP can be improved by adding proper dopant, or modifying the starting monomers. Therefore, the conductivity of PANI can be raised as well as the processing performance can be improved by the means of choosing the appropriate dopant and its amount, controlling microstructure of the polymer during the synthesis. Another way to improve the application performance of PANI is being polymerized with other polymers which are easily obtained with own good processability and mechanical properties. Polymer composites containing PANI as conductive additive have been noticed for its good machining properties, mechanical properties and high electrical conductivity. Therefore, this material also has a wide range of applications [3].

Compared with other CIPs, polyaniline has the advantages of good thermal stability, good workability, and higher electrical conductivity. For price, aniline has greater advantage as its monomers are cheaper and more available. The synthesis of polyaniline is relatively simple and regulated, which means a bright future in application [4].

2. EXPERIMENT PART

2.1 Materials and Instruments

Ethanol(AR) was purchased from Beijing Chemical Plant; Ammonium persulfate (AR), Hydrochloric acid (AR), Aniline (AR) and O-toluidine (AR) were purchased from Beijing Yili Fine Chemicals Co., Ltd.; 81-2 Thermostat Magnetic Stirrer was from Shanghai Sile Instrument; KQ-250DE CNC Medical Ultrasonic Cleaner was from Kunshan Ultrasonic Instrument Co., Ltd.; DZF-2001B Vacuum oven was from Shanghai Shengxin Scientific Instrument Co., Ltd.; 202-1 Electric Oven was from Shanghai County Experimental Instrument Factory.

2.2 The Synthesis of Polyaniline

Appropriate amount of ethanol was added into deionized water, fully dispersed and then HCl was mixed until the pH value was under 1, strongly acidic environment. Aniline was added after that and stirred for 15 mins, then an equimolar amount of APS as aniline was joined, stirred again, placed, then polyaniline was formed.

Ethanol can reduce the hydrogen bonding between polymer molecules, as amino of polyaniline have excess hydrogen atom, which can form hydrogen bond inside or among moleculars to assemble polymer groups and gather into lamellar structure. Polymerization mechanism is shown in Fig. 1.

2.3 The Synthesis of Polyaniline-o-toluidine Copolymer

Following the synthesis of Polyaniline, we added o-toluidine and increased the amount of ethanol. Reacted for 5~6 hs, placed, filtrated, dried the residues to constant weight under 60 °C, dark green powder was obtained which referred to polyaniline-o-toluidine copolymer samples.

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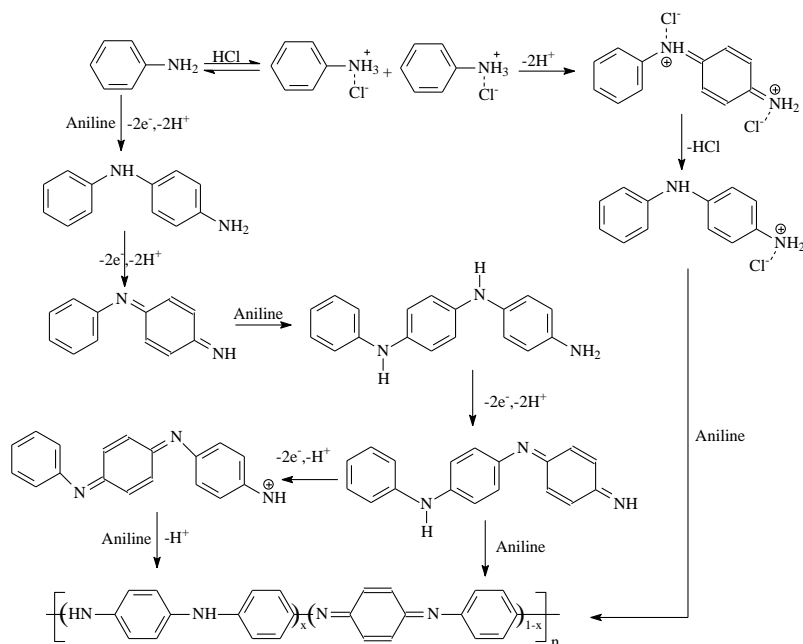


Fig. 1 – Polymerization process of aniline

3. RESULTS AND DISCUSSION

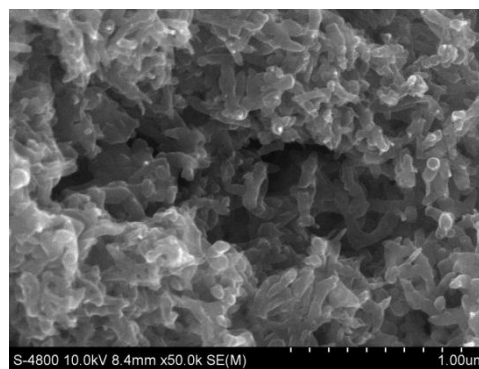
3.1 Morphology of Products

SEM of polyaniline can be seen in Fig. 1.a, which shows that the products have the structure of nanorod with diameter of 60nm and length of about 200 nm. From the SEM of aniline-*o*-toluidine copolymer

(Fig. 1.b), we can see that this structure has the same nanorod with similar diameter but shorter length compared with Fig. 1, indicating that the adding of *o*-toluidine doesn't affect the morphology of the product, but as ethanol should be used as the solvent for *o*-toluidine, more ethanol prevent the lengthening of nanorods to some extent.



a



b

Fig. 2 – SEM of prepared polyaniline (a), SEM of prepared aniline-*o*-toluidine copolymer (b)

3.2 Characterization of Synthetic Products

In Fig. 3, the curve of FTIR of prepared polyaniline and that of copolymer are compared, showing the absorption peak for skeleton structure of polyaniline at 1590 and 1495 cm^{-1} (quinone structure and benzene); absorption peak for C-N at 1305 cm^{-1} , C=N at 1140 cm^{-1} which stands for polyaniline conductive properties [5]; while the peak at 1380 cm^{-1} is the characteristic absorption peak of methyl which confirms the occurrence of copolymerization.

3.3 Vulcanization of Prepared Products

Polyaniline and its copolymers were sealed respectively into the ground joint flask and heated with dif-

ferent amounts of sulfur under the condition of 155 °C and no protective atmosphere for 24hs.

SEM of sulfide samples (sulfur content were 50% and 80%) can be seen from Fig. 4 and Fig. 5, which shows that after heating with equal quality of sulfur, the diameter distribution of polymer nanorods becomes uneven, from 50~150 nm; and local accumulation is emerged in the polymers, which perhaps results from the melting and adsorption of sulfur, as they bond polyaniline nanorods together. With the increase of sulfur content, the structure with 100 μm diameter or below disappears, which means diameter significantly increases, and accumulation phenomenon of polymers becomes more serious, which confirms the bonding role of sulfur.

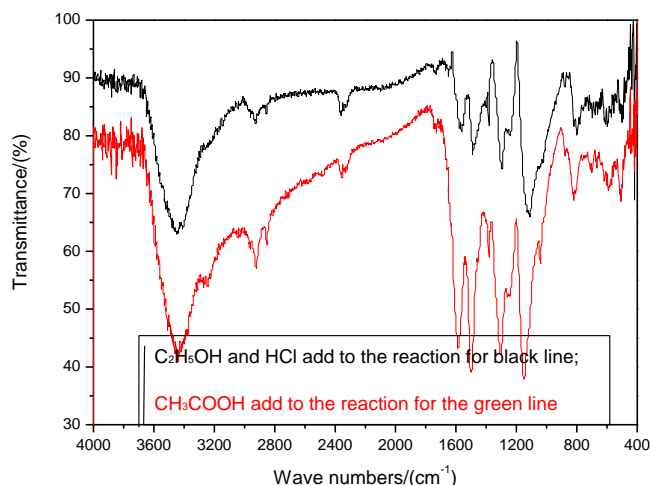


Fig. 3 – Comparison of FTIR curves for polyaniline and copolymers

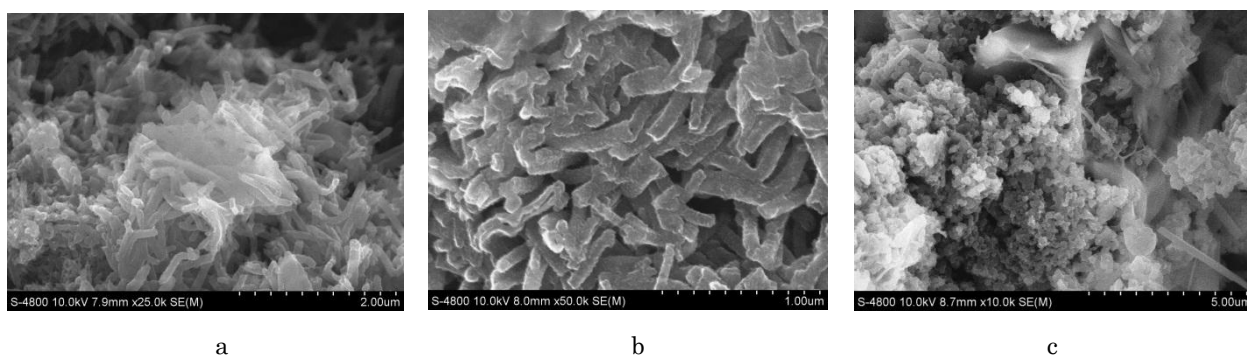


Fig. 4 – Polymers with 50% sulfur, firing at 155°C for 24hs (a), Polymers with 80% sulfur, firing at 155°C for 24hs (b), SEM of Vulcanized anilin-o-toluidine copolymers

3.4 Conductivity of Copolymer

Seen from table 1, after introducing o-toluidine, conductivity of the copolymer increases first. It's mainly because that there are many by-products during the polymerization process of aniline, which will affect the formation of π bond in the products and decrease the conductivity indirectly. And after the adding of o-toluidine, one of its active positions (an amino group on the benzene ring ortho) is occupied by methyl, which reduces the possibility of the formation of by-products. In addition, because of the steric hindrance of methyl, aniline molecules tend to polymerize head to tail, which also reduce the by-products and enhance the conductivity of products. However, the more OT adds, the lower the conductivity becomes. For more polar groups are brought into polymer chains to affect the π electron transfer rate, and then cause the conductivity to reduce [6].

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Table 1 – Conductivity of copolymer and polyaniline at room temperature

Molar ratio (An:OT)	Conductivity
1:0	0.692
1:0.5	0.734
1:1	0.581
1:1.5	0.252

4. CONCLUSION

Polyaniline with nanorod structure was prepared by using ethanol as solvent. Copolymerization of aniline and o-toluidine and its treatment shows that the thermal stability of the copolymer proves to be worse than PANI. With the adding of o-toluidine, copolymer conductivity first increased and then decreased.