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Synthesis and conductive properties of a novel azobenzene-based conjugated polymer

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ABSTRACT

The conjugated polymer with an azobenzene backbone can be synthesized by diazotization and coupling using the common raw such as *m*-phenylenediamine, *p*-phenylenediamine, *o*-phenylenediamine and *o*-aminophenol. The products obtained by the different synthesis conditions are very different. For example, the solubility and the conductivity are very different with a different greater proportion of the product $NaNO_2$. The conductivity of synthetic polymers were studied after doping, the results show that the conductivity of synthetic polymers can be improved by controlling the doping ratio of $NaNO_2$ and the draw ratio dopant. As the result, poly(azo-*o*-phenylenediamine), and poly(azo-*o*-aminophenol) are relatively more worthy of further study in the four different types of polymers, because the two materials are semi-solid state, the future research will be focused on solidification the materials. The novel material will be a cheap and popularize material and be used widely.

1. Introduction

Since the 1970s, *trans*-polyacetylene was found to have conductivity [1–3], a variety of new conductive polymer continue to be synthesized [4–9]. From 2000, polymer solar cells became heated research, new types of polymer after adjusting the band constantly have been synthesized, and the studying of polyfluorene and the derivatives of polydibenzothiophene is a heated study on polymer solar cell materials [10–12]. Conductive polymers are commonly used in electronic devices, such as battery electrodes, electrolytic capacitors, electronic sensors, and organic shine diode. Conductive polymer can also be installed in the "molecular wire" nano scale electronic device.

There are two directions of the development of materials, the one is to improve material performance, the another one is to reduce the cost of the material. Here a kind of novel and cheap conductive polymer are discussed based on azo benzene conjugated structure.

Azo benzene conductive polymers were first synthesized in the 1980s [13,14], but only few studies focused it. Azo film was reported to be used for the electrode of OLED (organic light-emitting diodes) [15]. Some studies pointed out that it has photoconductivity in the wavelength range of 300–550 nm [16]. In recent years, there were two main using about azobenzene conductive polymers. The one is photoswitching molecules, photoswitched selectively from an extended *trans* to a more compact *cis* conformation by using light of wavelength 365 nm, whereas the reverse *cis*-to-*trans* isomerization is induced by light of wavelength 420 nm [17,18]. The other is nonlinear optics material that is based on azobenzene self-assembled monolayers (SAMs) [19–27]. The azobenzene conductive polymers above are the polymer with azo bond in azo bond in the middle, ends with a long chain. The main chain that is composed of azobenzene groups totally was seldom researched. Ma et al. conducted some studies of azo film using molecular modeling technology [28–31], the structure and the electronic energy levels were analyzed, and they found that the introduction of multiple keys has a huge effect on the electronic structure and morphology of the material. Durgaryan et al. synthesized the azo bond of the main chain and the benzene ring of alternating conjugated polymer by using undoped-phenylenediamine and *p*-phenylenediamine as the raw material, and studied its conductivity by using doping. It is found that the conductivity was about 10^{-6} S cm^{-1} in case of un-doping, after the doping, it can be achieved 10^{-1} S cm^{-1}. It is proved that azobenzene polymer is a good polymer semiconductor material [32–34].

The structure of conjugated polymer which is formed by alternating copolymer of benzene ring and azo double bonds, is

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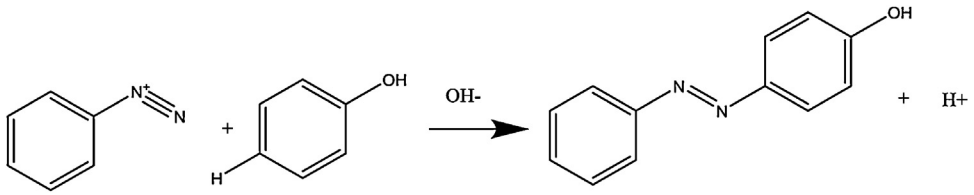

Fig. 1. AZO coupling.

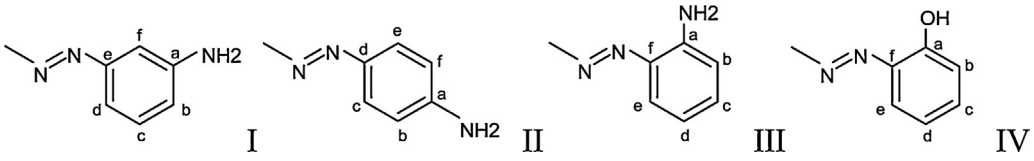

Fig. 2. The structure of diazonium salts.

similar to the poly(*p*-phenylenevinylene), except that the azo bond substituted carbon double bond. Benzene azo bond conjugated polymer main chain has a two-step synthetic route: diazotizing the amino benzene diazonium salt in an acidic (alkaline some cases), and benzene diazonium coupling conditions, the process is simple and does not require special equipment and catalysts. In this paper we describe preparation of azopolymers by using *m*-phenylenediamine, *p*-phenylenediamine, *o*-phenylenediamine and *o*-aminophenol as precursor (precursor) and research the conductivity by dosing.

2. Experiments

2.1. Materials

m-Phenylenediamine, *p*-phenylenediamine, *o*-phenylenediamine and *o*-aminophenol was bought from China Shanghai Sinopharm, AR grade and purified by recrystallization. Other substances were AR grade reagent without further purification.

Mechanical stirrer, low temperature thermostat bath, type 2XZ-1 rotary vane vacuum pumps, RTS-8-type four-probe tester, KW-8A intelligent spin coater, Hitachi S-3700N variable pressure versatile analytical scanning electron microscope, Thermofisher Nicolet IS5 FT-IR spectrometer, Bruker DRX-400 NMR spectrometer, Shimadzu UV–vis 2550 spectrophotometer.

2.2. Preparation

The synthesis of polymer using *m*-phenylenediamine, *p*-phenylenediamine and *o*-phenylenediamine as a raw material. 5.4 g (0.05 mol) *m*-phenylenediamine (*p*-phenylenediamine, *m*-phenylenediamine) was added in the flask at 0 °C, nitrite was weighted according to the different experimental conditions, and then the mixture was dissolved with 50 mL water. Hydrochloric acid which was slightly excessive than nitrite was slowly added dropwise to control pH value of 5. Then warmed to 25 °C, stirred for 48 h to complete the polymerization. The reaction product was filtered, washed until neutral and dried. The dried product was dissolved in DMF, filtered and the filtrate was collected, then the product was dried in vacuo under 80 °C.

The synthesis of polymer using *o*-aminophenol as raw material. 5.4 g (0.05 mol) *o*-aminophenol, 40 mL water, 8 mL of concentrated hydrochloric acid (0.09 mol) were added in the three-necked flask at constant temperature, and stir until the *o*-aminophenol is dissolved completely. 3.45 g (0.05 mol) sodium nitrite solved in 20 mL water was slowly added dropwise and stirred for 0.5 h. Preparation of 2 mol L^{-1} NaOH solution. 50 mL of the diazonium salt product was dissolved in the NaOH solution, and reacted for 48 h. The reaction product was dried in vacuo at 80 °C, and dried product was dissolved in ethanol, insoluble product was filtered off. The filtrate was dried then dissolved in ethanol, collected by filtration, dried.

2.3. Dosing by iodine

The product polymer was dissolved in chloroform, and formulated the solution of 0.05 mol L^{-1} statistics by structural units. I_2 was dissolved in chloroform to prepare a liquor of 0.05 mol L^{-1}. Based on different doping ratio, the iodine solution and the polymer solution

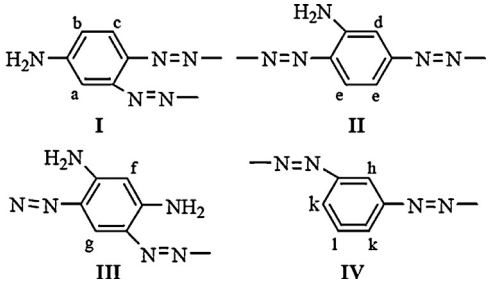

Fig. 3. The structures of poly(*m*-phenylenediamine).

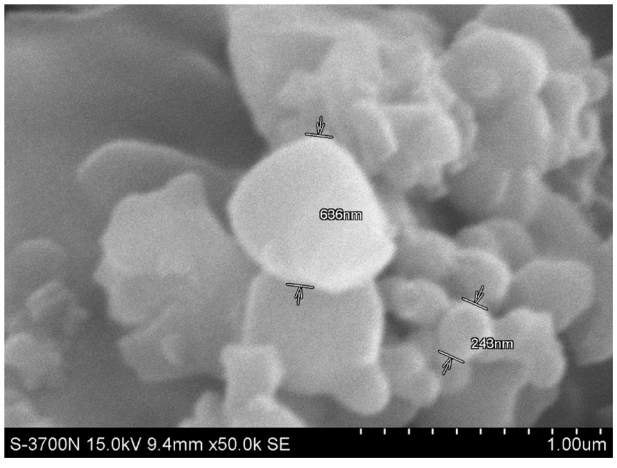

Fig. 4. The SEM diagram of poly(azo-*m*-phenylenediamine).