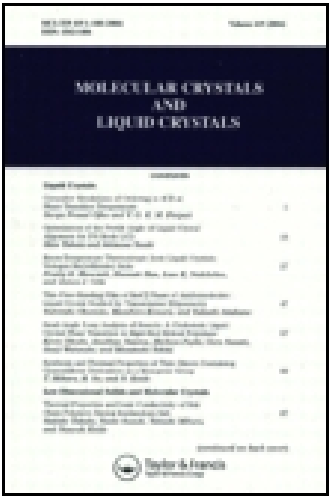

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Synthesis and Characterization of Water Soluble Conducting Poly (3-Amino-4-Methoxybenzenesulfonic Acid)

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Synthesis and Characterization of Water Soluble Conducting Poly (3-Amino-4-Methoxybenzenesulfonic Acid)

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The preparation of conducting water soluble sulfonated polyaniline, poly (3-amino-4-methoxybenzenesulfonic acid), has been investigated. Poly (3-amino-4-methoxybenzenesulfonic acid) has been polymerized via chemical oxidation. Using a dialysis membrane, separation and purification of high molecular weight polymer from low molecular oligomers were carried out successfully. UV-Visible spectroscopy, cyclic voltammetry and four-point-probe conductivity measurements of polymer were recorded. The prepared polymer was conducting and fully water soluble. The conductivity of polymer was about 0.0430–0.75 S/cm and it were found that reaction temperature, monomer and oxidant concentration had dramatic effect on conductivity of poly(3-amino-4-methoxybenzenesulfonic acid).

Keywords: 3-amino-4-methoxybenzenesulfonic acid; conducting polymers; PMAS; water soluble polymer

INTRODUCTION

Inherently conducting polymers such as polyaniline and their derivatives have attracted many attentions due to their electrical and optical properties. The polymers have been used for various applications including batteries [1], anti-corrosive coatings [2], electromagnetic shielding [3], rechargeable polymeric batteries [4], polymer photovoltaics [5] and polymer actuators [6,7]. Most industrial application of

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conducting polymers are limited due to its low mechanical properties. They also suffer by poor solution and melt proceessibility.

The use of appropriate dopants, for example, dodecylbenzene sulfonic acid or camphor sulfonic acid, can render the polyaniline salt soluble in some organic solvents such as N-methylpyrrolidone (NMP) or m-cresol [8,9]. Alternatively the introduction of alkyl (alkyl group on N substituent) [10,11], alkoxy substituents [12,13], or formation of graft polymerization polymers [14] renders polyaniline soluble in solvents such as tetrahydrofuran. Such materials are then amenable to subsequent processing.

A common approach used to improve polyaniline solubility in water is the introduction of sulfonic acid groups onto the polymer backbone. This can be achieved by treating the polymer with fuming sulfuric acid after polymerization or by polymerizing/copolymerizing substituted aniline derivatives. Introduction of the sulfonate group does have a dramatic effect on the polymerization process. The strong electron-with-drawing effect of the $-SO_3H$ lowers the electron density on the amino groups, making it difficult to obtain polyaniline sulfonic acid (PASA) with high molecular weight and high conductivity. In order to solve this problem a methoxy electron-donating group was substituted onto the aniline ring to produce 3-amino-4-methoxybenzene-sulfonic acid.

EXPERIMENTAL

3-amino-4-methoxybenzenesulfonic acid (MAS) was prepared through the reaction of dissolved O-Anisidine in sulfuric acid and fuming sulfuric acid. The temperature range and stirring rate of reaction were 75–85°C and 100 rounds per minutes (rpm) respectively. The reaction carried out in 20 Minutes. Before polymerization of MAS it purified by acid base crystallization.

The 25 mL of 0.7 M Aqueous MAS solution was prepared. And solution pH was adjusted to 4.2 using 0.5 M NH_4OH solution. Then 25 mL of 1 M Ammonium peroxydisulfate (as oxidant) was added drop wise to MAS solution while temperature was kept lower than 20°C. The solution was then stirred at temperature range lower than 20°C under stirring rate of 100 rpm for a period of 24 hours. The polymer solution purified with 12 KDa MWCO Sigma dialysis membrane. Dialyzing was performed in 1 L water 3 times each for 12 hours. Free-standing films of PMAS were prepared by casting the solution onto a glass slide.

Sulfuric acid, fuming sulfuric acid, O-Anisidine, Ammonium hydroxide and Ammonium peroxydisulfate were purchased from MERK Company.

INSTRUMENTATION

UV-Visible spectra were recorded by shimdzu UV-1601 UV-Visible spectrophotometer. Cyclic voltammetry (CV) studies were carried out using by model 101 cyclic voltammeter (Sahand Pardazan, Tabriz, Iran) with conventional three-electrode electrochemical cell a glassy carbon working electrode in combination with platinum mesh and Ag/AgCl (3 M NaCl) auxiliary and reference electrode, respectively. four-point-probe conductivity measurements were performed on dried films.

RESULTS AND DISCUSSION

The UV-Visible spectra of aqueous PMAS (0.1 g/L) exhibits two absorption bands at 474 nm and around 330 nm (Fig. 1). The peak at 330 nm may be recognized as π-π^* transitions and the peak at 474 nm is assigned to a polaron bond.

Cyclic voltammogram (i vs. E) was recorded. The first response (A/A′) is due to the oxidation of leucoemeraldine form of MAS to emeraldine form. The response (B/B′) may be attributed to the oxidation of emeraldine to pernigeraniline form of full oxidized PMAS (Fig. 2). The

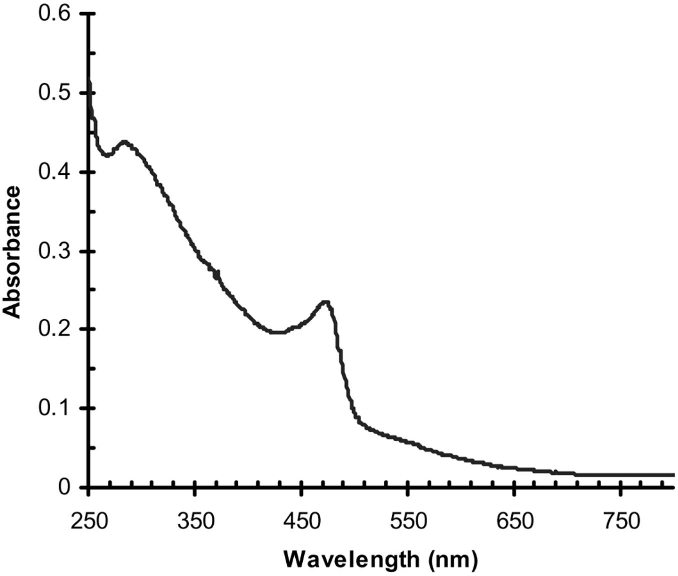

FIGURE 1 UV-Visible spectrum of pure PMAS (0.1 g/L).

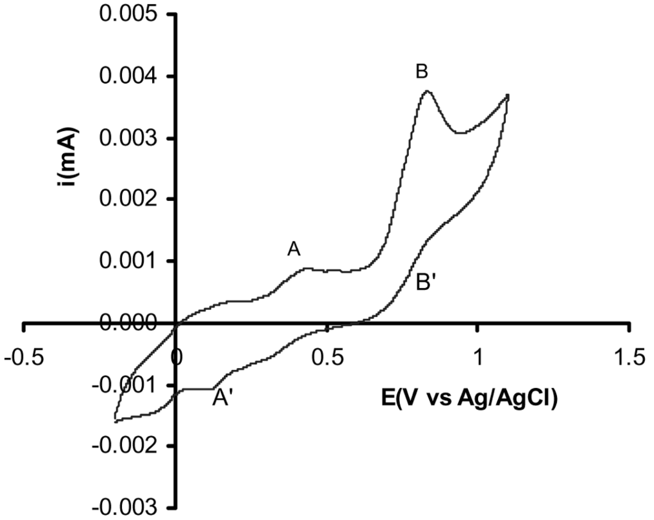

FIGURE 2 Cyclic voltammogram obtained for PMAS 0.5 g/L at a glassy carbon electrode in scan rate of 20 mV/s between −0.2 and 1.1 V potentials.

solution process ability studies showed that PMAS solution process ability improved and it is fully water soluble (Table 1).

The study of electrical conductivity with four-point-probe conductivity measurements at room temperature determined that the conductivity of polymer is about 0.0430–0.75 S/cm and it was found that experimental conditions such as temperature, monomer and oxidant concentration (Fig. 3) and dialyzed time (Fig. 4) had dramatic effect on conductivity of PMAS. By evaluation of adhesion, it was found that PMAS polymer has not high adhesion on glass and metallic surfaces.

TABLE 1 Improved PMAS Solution Process Ability (The Maximum Mass of PMAS Which Dissolves in 100 g of a Given Solvent)

Solvent	Solubility
N-methyl-pyrrolidone	>5
Dimethylformamide	2.5
1,2-dichloroethane	0
Butyl acetate	0.05
Chloroform	0
Acetone	0
Water	>30

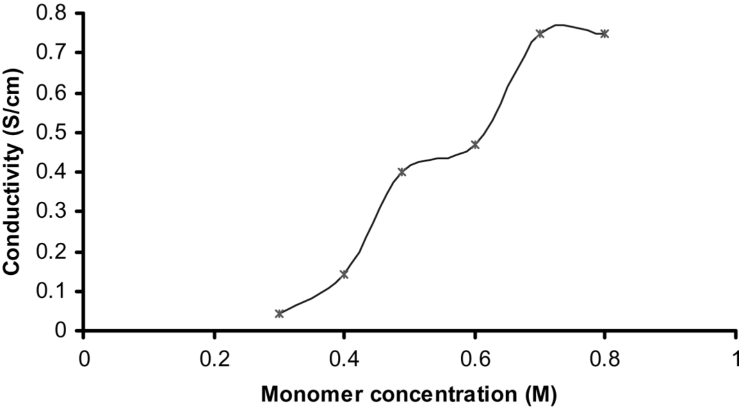

FIGURE 3 Effect of monomer concentration on conductivity of PMAS in a low temperature (below 10°C) and the oxidant/monomer molar ratio of 1.

CONCLUSIONS

Water soluble conductive sulfonated polyaniline can be produced by chemically oxidation of 3-amino-4-methoxybenzenesulfonic acid by using ammonium peroxydisulfate. The prepared polymer was conducting, electro active and fully water soluble. The study of electrical conductivity determined that the conductivity of polymer is about 0.0430–0.75 S/cm and experimental conditions such as temperature, monomer

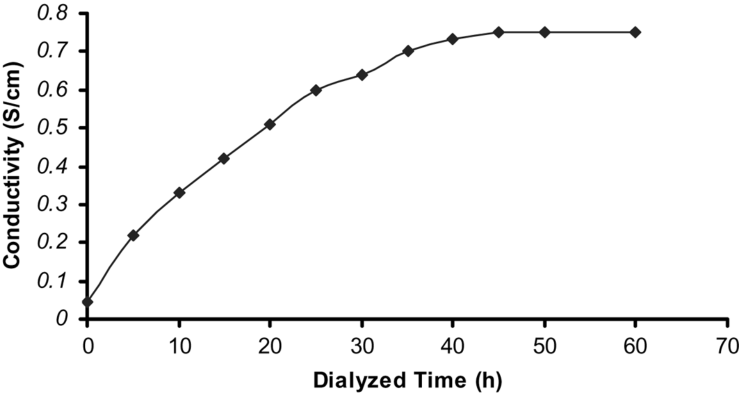

FIGURE 4 Effect of dialyzed time on conductivity of PMAS using a high concentration of monomer (0.7 M) in a low temperature (below 10°C) and the oxidant/monomer molar ratio of 1.

and oxidant concentration had dramatic effect on properties of PMAS. The higher conductivity (~0.75 S/cm) were obtained using a high concentration of monomer (0.7 M) in a low temperature (below 10°C) and the oxidant/monomer molar ratio of 1.

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