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Electrosynthesis of soluble polyaniline in acetic acid

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Summary

Aniline has been electropolymerized in acetic acid at a controlled potential of 1.1 V (vs. SCE). The polymer obtained from this system was undoped-like and soluble in many organic solvents such as acetic acid, N-methyl-2-pyrrolidone (NMP), acetonitrile, tetrahydrofuran, methanol, alcohol and acetone. Its electrochemical behavior and structure have been examined by cyclic voltammetry and UV-visible and FT-infrared spectroscopies. The experimental results indicated the polymer has a short and branched structure.

Introduction

Polyaniline (PANI) is one of the important classes of conjugated polymers due to its interesting electrochemical and optical properties and environmental stability (1-4). PANI can be obtained by chemical or electrochemical polymerization of aniline in aqueous or non-aqueous media. Electrochemical polymerization of aniline and its derivatives was usually carried out in low pH acidic aqueous solutions (e. g. HCl or H_2SO_4 aqueous solution) (5-6). Recently, some investigations focused on the electropolymerization of aniline in organic solvents such as acetonitrile or dichloroethane using $LiClO_4$ or organic ammonium salts as supporting electrolyte to improve the electric conductivity of the solvents (7-8). However, the conducting polymers obtained from these media were often insoluble in common organic solvents due to the shiftiness of their backbones (9) and cross-linking during polymerization (10). Soluble polyaniline compounds usually obtained by chemical polymerization (11-13), and the polymer can be dissolved in some organic solvents or water by the method of post-treatment of the polymer such as undoping treatment (11), attaching alkyl-side chain on the backbones (12), or introducing a sulfuric acid functional group in the benzene ring (13).

In this paper, we report a new method of direct electrosynthesis of soluble polyaniline in an organic solvent of pure acetic acid without supporting electrolyte. The PANI product without post-treatment was soluble in many organic solvents such as acetic acid, N-methyl-2-pyrrolidone (NMP), acetonitrile (AC), methanol, alcohol, acetone.

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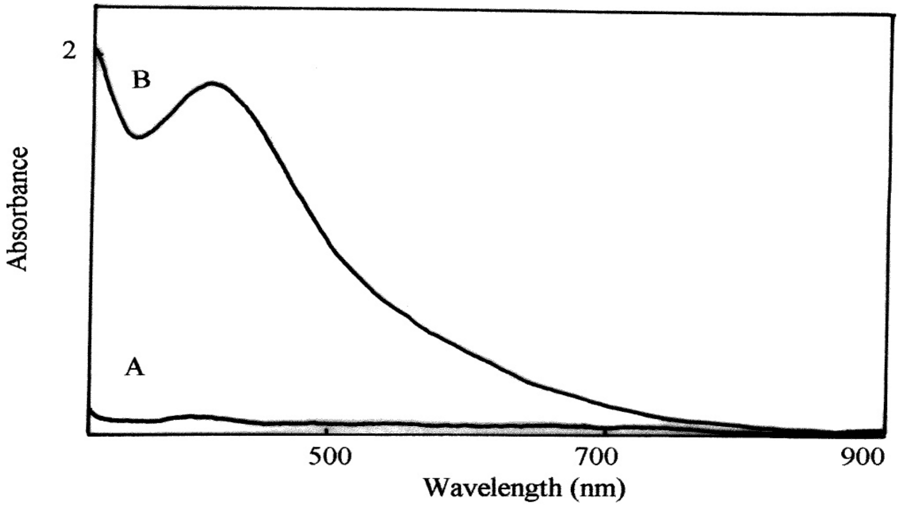

Figure 1 UV/Visible specrtra of the reaction solution.
A: before initiation of the reaction B: after 6 hr of the reaction

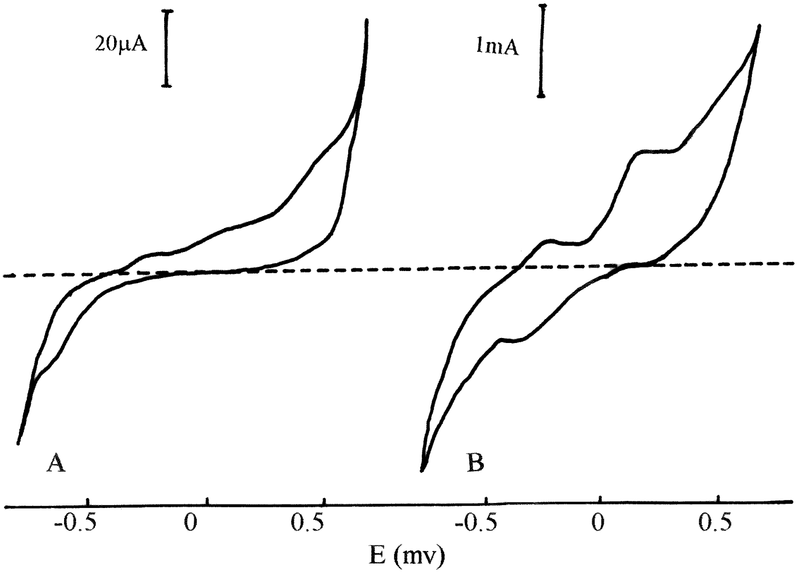

Figure 2 Cycle voltammograms (CV) of the reaction solution at potential scan rate 100 mv/s. A: at the beginning of the reaction B: after 6 hr of the reaction

Experimental

Instrumentation and chemicals

Analytical grade aniline (Nanjing chem. fact. China) was distilled under reduced pressure. Acetic acid (Nanjing chem. fact. China) was analytical grade pure and used as received. An EG&G potentiosat model 273 under computer control was employed for electropolymerization and cyclic voltammetric study. Conductivity of pressed pallet of polyaniline product was measured by four probe *d. c.* technique. UV-visible spectra were taken out on an UV-240 spectrometer. Infrared spectra was recorded on an IFS-66V FT-IR spectrometer with KBr pallets. The molar messes of products were measured in tetrahydrofuran (THF) by a GPC model 244 of Waters company at 17.2 °C and using polystyrene as standards.

Electrochemical polymerization

Polyaniline was prepared by electrolysis 5 M aniline in acetic acid at a controlled potential 1.1 V (vs. SCE) for 6 hrs. The experiment was carried out in a three-electrode cell and under a dry argon atmosphere. Working and counter electrodes were both Ni plates and each had a surface area of 5 cm^2. KCl saturated calomel electrode (SCE) was used as reference electrode. Polyaniline powders were obtained by distilling the product solution under reduced pressure at 80 °C, and then dried under vacuum at 60 °C for 24 hr.

Results and discussion

Polymerization of aniline started immediately on the surface of working electrode as 1.1 V potential was applied. The product was soluble in the solvent, and the solution discolored into dark brown gradually with the reaction continuing. Ni electrodes exhibited a well electrochemical stability during polymerization. The UV-visible spectra of the solutions got from the reaction system were shown in Fig.1. It is clear from this picture that the aniline monomer in acetic acid solution has low absorption and no obvious band is appeared. After a reaction time of 6 hr, the overall absorption of the solution increased markedly, and a new band appeared at 415 nm. This behavior similar to that of undoped state water-soluble polyaniline in base (pH 8~12) sodium phosphate buffer solution (14). This is possibly due to pure acetic acid has very low proton content.

Fig. 2 illustrates the cyclic voltammograms (CV) of the reaction solution at a potential scan rate of 100 mV/s. At the beginning of the electrosynthesis, the CV current density is very weak (in the order of microampere), and the curve displays relatively flat and smooth. After a reaction time of 6 hr, the current density increased markedly up to the order of milliampere. Two oxidation waves appeared obviously at 0.13 V and -0.21 V respectively, and a reduction wave appeared at -0.26 V. In comparison with them, the reduction response around 0.2 V is quite smooth and obscure. The overall voltammetric feature of Fig. 2B is quite similar to that of thin polyaniline film electrosynthesized in non-aqueous solution such as acetonitrile (7).

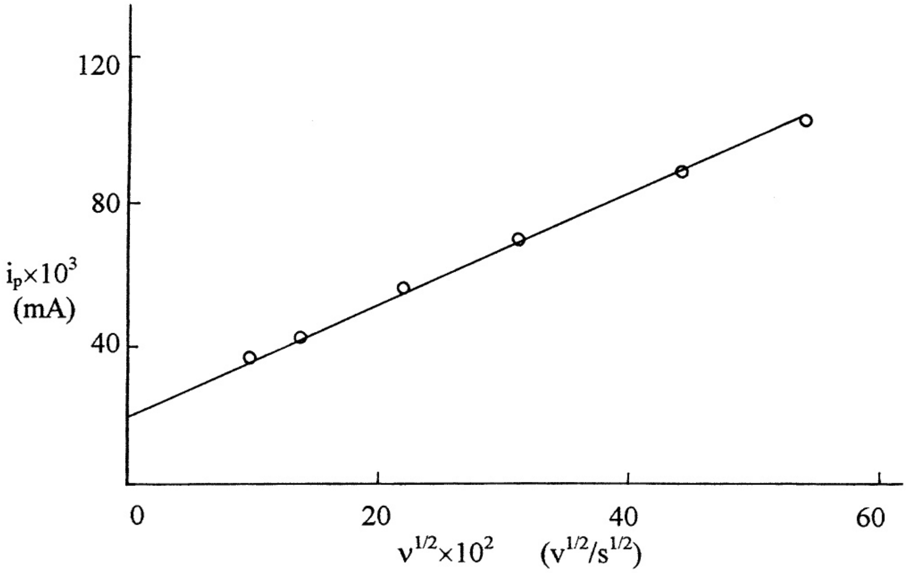

Figure 3 Plot of the i_p of the polyaniline Vs $\nu^{1/2}$.

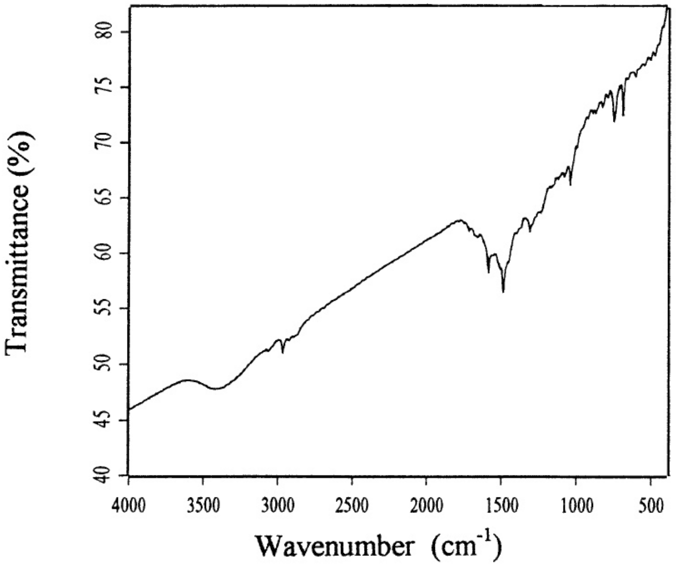

Figure 4 FT-IR spectra of the polyaniline product.

To us interesting that during the whole experiment, the PANI product was dissolved completely in the solvent and the solution is quite homogenous even the concentration of the polymer is high. At the same time the electrodes kept brightly, and no product deposited on them even after a reaction time of 6 hr. It is well known that the CV peak current (i_p) of electroactive molecules (EM) in solution is proportional to the square root of potential scan speed ($\nu^{1/2}$) at 25 °C. Fig. 3 shows the plot of the i_p of the PANI (the oxidation peak at 1.3 V) versus $\nu^{1/2}$ in acetic acid. According to this plot, the i_p is varied linearly with the $\nu^{1/2}$ within the experimental region, indicated that the electrochemistry of PANI product in acetic acid was diffusion control and soluble PANI was directly formed during the experiment.

FT-IR spectrum of the polyaniline product is shown in Fig. 4. A large descending baseline appears in the spectral region of 1750-4000 cm^{-1}, indicating the free-electron conduction in conducting polymers (15). The broad band at about 3360 cm^{-1} corresponds to the stretching of the N-H bond, those at 2900-3060 cm^{-1} are attributed to the stretching vibration of C-H bond, and the peaks at 1600 cm^{-1} and 1500 cm^{-1} are due to the stretching vibration of C-C of benzene. The band at 1300-1240 cm^{-1} is assigned to the stretching vibration of C-N. All these spectra characters similar to those of PANI film formed by electropolymerization of aniline in acidic buffer solutions (16). However, relatively strong peaks at 756 cm^{-1} and 695 cm^{-1} which can be assigned to 1,3-coupling and 1,2,3-coupling of aromatic ring respectively (17) indicated that the PANI has a graft or branched chain structure. The number average molar masses of PANI were measured in THF by GPC to be lower than 2000 g/mol.

The conductivity of pressed pallet of polyaniline product is measured in the order of $6x10^{-8}$ S cm^{-1}, which closes to that of traditional undoped PANI (18). After treating with aqueous acid such as HCl, the PANI product become insoluble in acetic acid and many other organic solvents, and its conductivity markedly increased up to the order of $2x10^{-2}$ S cm^{-1} like doped polyaniline. These phenomena indicated that undoped-like polyaniline formed during the electropolymerization of aniline in acetic acid solution. The PANI product could also be dissolved in many organic solvents other than acetic acid such as NMP, acetone, tetrahydrofuran, alcohol, methanol and acetonitrile.

Conclusion

Undoped-like polyaniline with low molar mass and graft chain structure has been electrosynthesized in acetic acid. It is soluble in general organic solvents such as NMP, acetone, acetonitrile and alcohol.

Acknowledgments

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