CHEMISTRY LETTERS, pp. 2229-2232 1994.

Novel Preparation of Polyaniline Film from Poly(anthranilic acid) as a Precursor

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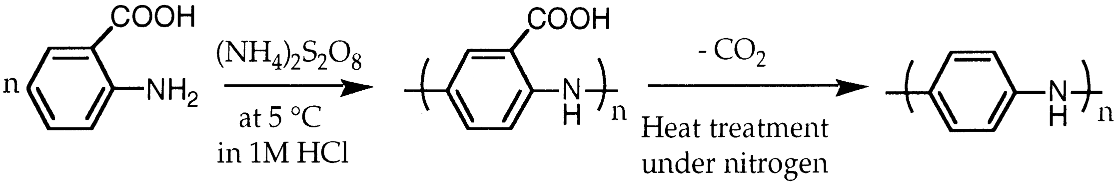
Poly(anthranilic acid), prepared by oxidative polymerization of anthranilic acid with ammonium peroxodisulfate, is soluble in N-methyl-2-pyrrolidone. The casting of the resulting solution forms a smooth film of poly(anthranilic acid). Heat treatment of the poly(anthranilic acid) film at about 240 °C produces a polyaniline film accompanying the elimination of carbon dioxide, which can provide a new method of preparation of a polyaniline film from the precursor.

Polyaniline is a promising materials for developping electronic devices.[1-4] The applications, however, have been limited because of its poor processability,[5] which is true for most conducting polymers. The substitution was reported to improve the solubility of conducting polymers in an organic solvent.[6-8] However, the substitution usually decreases the electroconductivity of the polymer film. On the other hand, processable precursor polymers are often used for the preparation of conducting polymer films, such as polyphenylenevinylene, polyparaphenylene, etc. The film of polyparaphenylene, for example, was prepared by heat treatment under argon at 310–340 °C of the precursor film of the acylated polymer, which was derived from 1,4-poly(cis-5,6-bis(trimethylsiloxy)-1,3-cyclohexadiene) by conversion of the trimethylsiloxy ether groups to more facile leaving groups such as esters via the corresponding hydoxy groups.[9] To our knowledge, however, there is no report on the cast film of substituted polyanilines as a precursor of the polyaniline film. Here we report the novel preparation of the polyaniline film by heat treatment of the cast film of poly(anthranilic acid) as a precursor polymer as shown in Scheme 1.



Scheme 1. Proposed process for preparation of polyaniline film.

Poly(anthranilic acid) was synthesized by oxidation of anthranilic acid with ammonium peroxodisulfate ($(NH_4)_2S_2O_8$) in a hydrochloric acid (HCl) aqueous solution.[10] The typical reaction procedure is as follows: An acidic solution of $(NH_4)_2S_2O_8$ (20 g(80 mmol) in 200 cm^3 of 1 mol dm^{-3} HCl) was added dropwise in 15 min under vigorous stirring into an acidic solution of anthranilic acid (11 g(80 mmol) in 200 cm^3 of 1 mol dm^{-3} HCl) at ca. 5 °C. The stirring of the reaction mixtures was continued at ca. 5 °C for 48 h in an ice bath. The resulting precipitates were separated by filtration, washed with a 1 mol dm^{-3} hydrochloric acid solution and then distilled water, and dried under vacuum overnight. The obtained product was dissolved in a 1 mol dm^{-3} aqueous solution of sodium hydroxide, and the reprecipitation was proceeded with a 1 mol dm^{-3} hydrochloric acid solution. The isolated yield was 9.0%.

The structure was identified by comparing the infrared (IR) spectra, C1s X-ray photoelectron spectroscopy (XPS) spectra and thermogravimetric analysis (TGA) curves with those reported.[10)] Poly(anthranilic acid) is soluble in a 1 mol dm^{-3} aqueous solution of sodium hydroxide (> 300 mg cm^{-3}) and N-methyl-2-pyrrolidone (NMP) (ca. 300 mg cm^{-3}).

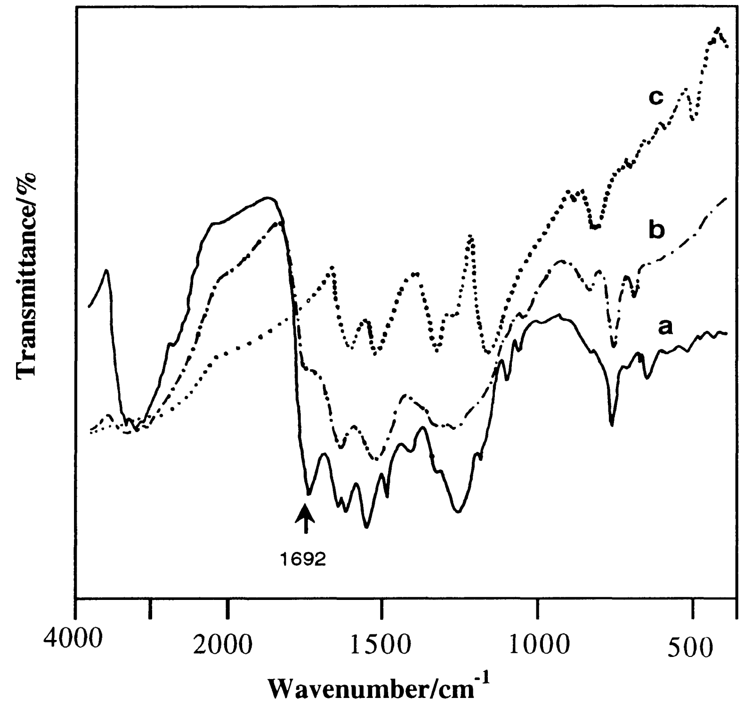


Fig. 1. FT-IR spectra of poly(anthranilic acid) (a) before and (b) after heat treatment at 300 °C under nitrogen, and (c) polyaniline prepared by using ammonium peroxodisulfate.

The film of poly(anthranilc acid) was prepared by casting from a 2 mol dm^{-3} solution of N-methyl-2-pyrrolidone (NMP). The poly(anthranilic acid) film shows anisotropic morphologies at the both plan and profile sides based on the observation of scanning electron microscopy (SEM).

Heat treatments of the poly(anthranilic acid) were performed at 300 °C under nitrogen. The structural changes were traced by IR spectra. The change of IR spectrum, shown in Fig. 1, suggests that the poly(anthranilic acid) changes to polyaniline at around 300 °C. Thus, the absorption peak at 1692 cm^{-1}(due to $\nu_{C=O}$) dramatically decreases, while the absorption peaks at 1600 and 1490 cm^{-1}(due to $\nu_{C=N}$ and $\nu_{C\text{-}N}$ stretching vibrations of the polyaniline, respectively) become clear. Although the peak at 1692 cm^{-1} does not completely dissapear by this heat treatment, it could be concluded that most of the carboxyl groups are decomposed. The C1s spectra of XPS, shown in Fig. 2, also indicate the disappearence of the carboxyl group at 287.6 eV after the heat treatment, although other peaks due to C-C, C-H and C=N, C-N remain. These observations suggest that the heat treatment results in the removal of carbon dioxide from the poly(anthranilic acid) and the formation of polyaniline.

In order to clarify this suggestion, the thermogravimetric analysis (TGA) was carrid out at 10 °C min^{-1} under an inert gas. The sample weight decreased by 2.8% till 100 °C, in which the superficial water is desorbed,[11)] with a subsequent continuous loss of approximately 0.5%/10 °C from 130 °C to 180 °C, 1.5%/10 °C from 180 °C to 303 °C, and then 1.0%/10 °C from 303 °C to 400 °C as continued heating, respectively. The total weight loss was 9.1, 24,5 and 34.5% at 200, 300 and 400 °C, respectively. If only the carbon dioxide is eliminated from all hydroxycarbonyl groups of poly(anthranilic acid) with the heat treatment, the weight loss can be calculated as 23.7% (cf. Scheme 1). It is estimated on the basis of the TGA curve that the maximun elimination of carbon dioxide could be at ca. 300 °C. The investigations of gaseous products in the thermal decomposition were performed by the gas chromatography correlated with mass spectroscopy(GC-MS). The results are illustrated in Fig. 3, which shows that the main gaseous product is carbon dioxide and that the maxinum elimination of the carbon dioxide occurs at around 235 °C. The GC-MS spectra also reveals that the eliminated gas involves a small amount of water and hydrogen chloride besides a large amount of carbon dioxide, and that the eliminated water molecules can be classified into two groups, i.e., free water and lattice water. The observation of the latter water from ca. 200 °C is consistent with that previously reported.[11] Any compounds like aniline due to decomposition of main chain were not detected by the GC-MS in the heat treatment till 320 °C. Based on these results, it is considered that the precursor polymer converts to polyaniline by elimination of carbon dioxide without decomposition of the main chain at around 240 °C.

Aromatic carboxylic acid is usually considered difficult to lose carbon dioxide from the hydroxycarbonyl group. However, the thermal decarboxylation occurs more easily for the sodium salts than for the corresponding free acids. On the other hand, some acids such as β,γ-unsaturated acids may lose carbon dioxide through a cyclic process in which the intramolecular hydrogen bonding plays an important role.[12] The above results could suggest that in the present case the precursor polymer may have a self-doped structure (cf. Scheme 2), like cyclohexyl compound,[10] which makes the elimination of carbon dioxide easy.

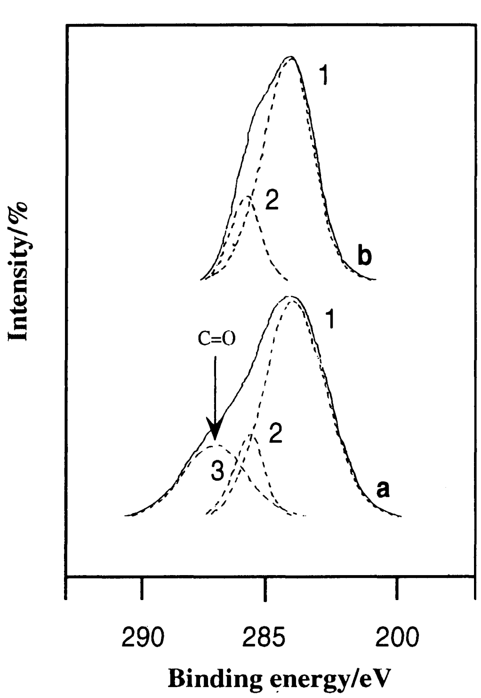


Fig. 2. XPS C1s spectra of poly(anthranilic acid), (a) before and (b) heat treatment at 400 °C under nitrogen.

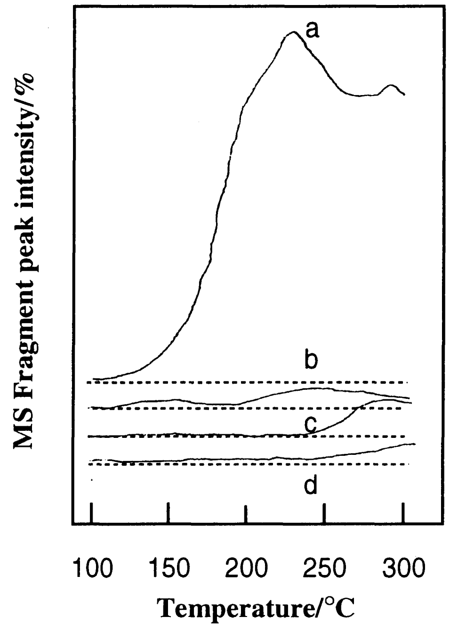
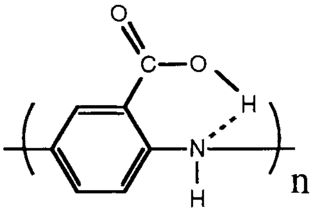


Fig. 3. GC-MS spectra of poly(anthranilic acid) in vacuum, (a) M/Z=44(CO_2), (b) 18(H_2O), (c) 36(HCl) and (d)62(H_2CO_3).



Scheme 2. Proposed self-doped structure of the precursor.

The SEM observation of the polymer films , in which the poly(anthranilic acid) film converts to the polyaniline film(1,5-3.9 μm) by heatment at 240 °C for 1h under dynamic vacuum, indicated that there is no change in the smoothness of the film plane compared with the precursor film. The polyaniline film, thus prepared, showed more compact and smooth morphology than that produced by an electrochemical method.

In conclusion, poly(anthranilic acid), prepared by oxidative polymerization of anthranilic acid with ammonium peroxodisulfate, reveals high solubility in an aqueous solution of sodium hydroxide or N-methyl-2-pyrrolidone(NMP). The casting of the NMP solution forms a smooth film of poly(anthranilic acid). Heat treatment of the poly(anthranilic acid) film at ca. 240 °C produces polyaniline film accompanying the elimination of carbon dioxide, which can provide a new method of preparation of polyaniline film from the precursor film.

The authors wish to thank Prof. Y. Yoshida, Department of Applied Chemistry, Faculty of Engineering, Toyo University and Mr. H. Sakasita, Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo for XPS and GC-MS meaurements, respectively. One of authors (H. Y.) acknowledges Iwatani Foundation for granting a Fellowship.

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(Received August 15 , 1994)