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ELECTROCHEMICAL POLYMERIZATION OF BENZENE BY USE OF ALUMINUM CHLORIDE AND COPPER(I) CHLORIDE

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ABSTRACT

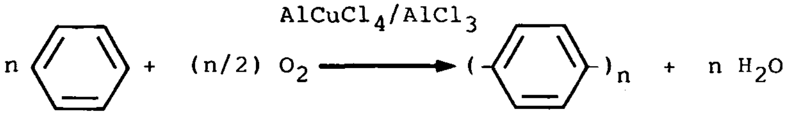
Electrochemical polymerization of benzene has been carried out in a one-compartment cell using indium-tin oxide conducting glass as a working electrode and Pt mesh as a counterelectrode by the use of a composite electrolyte of aluminum chloride and copper(I) chloride in nitrobenzene. On applying a constant voltage at +1.8 V vs SCE, a brown and flexible polyparaphenylene (PPP) film was smoothly obtained on the ITO anode surface. The electrical conductivity of the film as grown was 1.9×10^{-5} S/cm. Aluminum and chlorine atoms were detected in the film from XPS studies, so the film might contain $AlCl_4^-$ (and Cl^-) as a dopant. Scanning electron micrographs of the growing side surface of the film prepared at a constant potential of +1.8 V vs SCE showed a fibrillar morphology. The fibril diameter (∿100 nm) was similar to that of a polyaniline film. The PPP film exhibited a spin concentration of 1.0 ×

10^{19} spins/g, which corresponds to 800 phenylene units per spin. The *g*-value and the peak-to-peak linewidth were 2.0045 and 7 G, respectively.

INTRODUCTION

Electrochemical polymerization of aromatic hydrocarbons such as benzene [1, 2], toluene [3], naphthalene [4, 5], and anthracene [6] has been proposed as a way to obtain conducting polymer films. The surfaces of polyparaphenylene (PPP) films prepared by several methods were quite smooth and very compact [7, 8] or highly porous [8].

In this work a PPP film, which had a fibrillar morphology, was prepared electrochemically by using a composite electrolyte of aluminum chloride and copper(I) chloride in nitrobenzene. The method used in our work was an electrochemical modification of the chemical polymerization of benzene as described in Eq. (1) [9]:



The electron spin resonance (ESR) spectra of the PPP film were measured at various temperatures. Identification of the radical species and estimation of a spin concentration of the PPP film will be described.

EXPERIMENTAL

Preparation of the electrolytic solution was performed as follows. Copper(I) chloride (4.95 g, 0.050 mol), aluminum chloride (13.3 g, 0.10 mol), benzene (9 cm^3, 0.1 mol), and nitrobenzene (91 cm^3) were placed in a flask and the mixture was heated at 40°C for 2 h under argon with stirring. The electrochemical polymerization of benzene was carried out with the solution in a three-electrode cell using indium-tin oxide (ITO) conducting glass as a working electrode and platinum mesh as a counterelectrode. Potential values quoted in this paper are given on the saturated calomel electrode (SCE) scale. Benzene was polymerized at a constant voltage of + 1.8 V vs SCE by the use of copper(I) chloride and aluminum chloride as a composite electrolyte or aluminum chloride as an electrolyte. The electrochemical polymerization procedure was reported in detail in a previous paper [10].

ESR measurements were performed at temperatures of 20–500°C and microwave power of 0.01–100 mW on a JEOL FE-3XG spectrometer equipped with a JEOL ES-PRIT23 data analysis system. The PPP film obtained was washed successively with aqueous hydrochloric acid solution (2 mol/dm^3), distilled water, and acetone, and then it was dried *in vacuo* at 80°C for 12 h before ESR measurements. Five milligrams of ground PPP were used for ESR measurements. 1,1-Diphenyl-2-picrylhydrazyl (DPPH) was used as the standard for the determination of spin concentration.

RESULTS AND DISCUSSION

On applying a constant voltage of +1.8 V vs SCE, a brown and flexible film was obtained on the ITO anode surface. Figure 1 shows scanning electron micrographs (SEM) of the growing side surface of the PPP films prepared by using a composite electrolyte of aluminum chloride and copper(I) chloride (a) or aluminum chloride (b). The fibrillar diameter (∿100 nm) shown in Fig. 1(a) was similar to that of a polyaniline film grown electrochemically [11]. No fibrillar morphology was observed for the film prepared in the absence of copper(I) chloride (Fig. 1b).

The electrical conductivity of the as-grown PPP film was 1.9×10^{-5} S/cm, which was measured by using a two-probe technique at room temperature under atmospheric pressure. The conductivity of the film increased to 9.5×10^{-4} S/cm after doping it electrochemically with Li$^+$ at

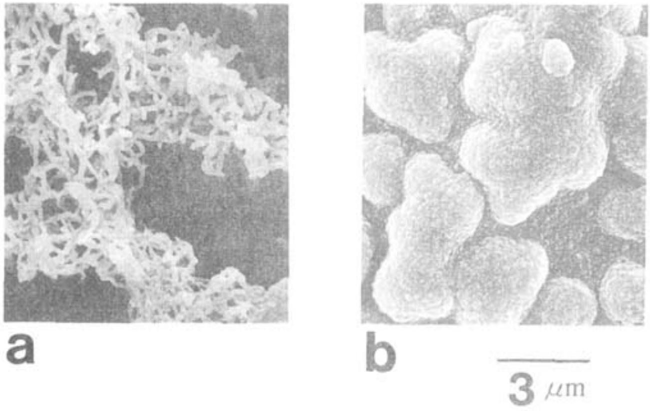


FIG. 1. SEM photographs of the growing side surfaces of PPP films prepared at +1.8 V vs SCE by the use of aluminum chloride and copper(I) chloride as a composite electrolyte (a) or aluminum chloride as an electrolyte (b).

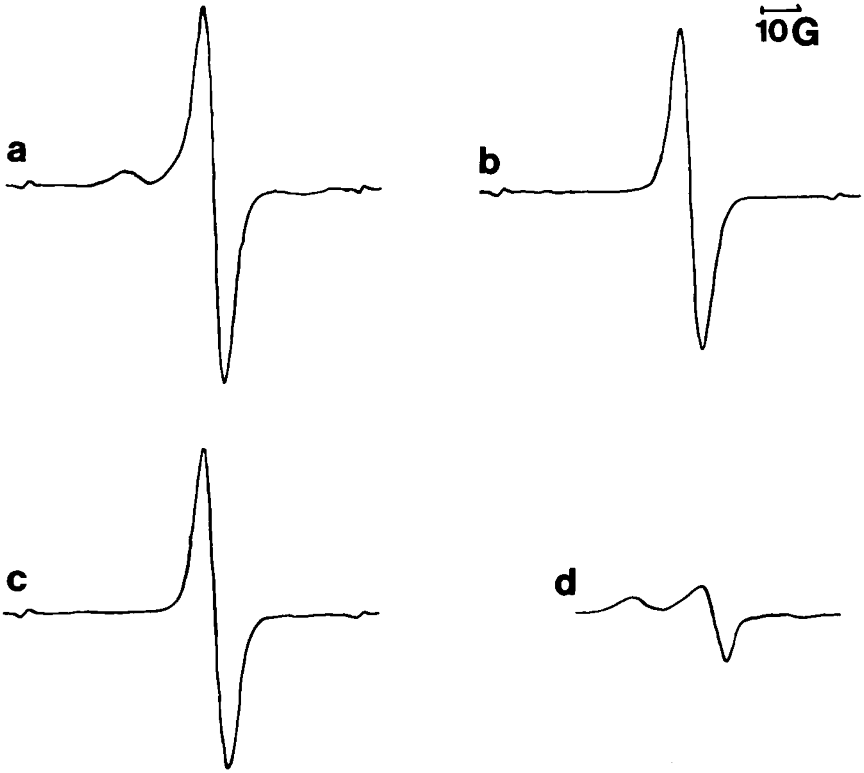


FIG. 2. ESR spectra of PPP film prepared at +1.8 V vs SCE by the use of aluminum chloride and copper(I) chloride as a composite electrolyte at prescribed temperatures: 20°C (a), 250°C (b), and 20°C (c). The spectra were measured in the order a, b, and c. The difference spectrum (d) was the difference in the spectra obtained at 20°C (a) and 250°C (b).

a constant voltage of −3.0 V vs SCE in a solution of propylene carbonate containing 0.5 mol/dm^3 of lithium tetrafluoroborate. The conductivities of the PPP films prepared at constant voltages of +2.0, +3.0, and +5.0 V vs SCE were also around 10^{-3} S/cm after doping in a manner similar to that described above. The dopants in the as-grown film might be $AlCl_4^-$ and/or Cl^-, since aluminum and chlorine atoms were detected in the film from XPS studies. The conductivity of our material on doping was roughly equal to those of other PPP films prepared by using $AlCl_3$ as an electrolyte [1, 12].

Figure 2 shows the ESR spectra of the PPP obtained. The signal is much different from that of a PPP powder chemically synthesized by using an $AlCl_3$–$CuCl_2$ system (the Kovacic method) [13]. The *g*-value and the peak-to-peak linewidth of the PPP obtained were 2.0045 and 7 G, respectively. The *g*-value of our material was larger than that (∿2.003) of an electrochemically generated PPP film obtained previously [7] or the PPP powder obtained by the Kovacic method [13]. The apparently large *g*-value might be mainly attributable to the interaction between the carbon radicals and the oxygen atoms of the hydroxyl function in the vicinity of the radicals, and partly to the shoulder of the peak having a *g*-value above 2.0051. The shoulder of the peak disappeared on heating to 250°C (Fig. 2b), and it did not emerge again on cooling to 20°C (Fig. 2c). The radical species responsible for the shoulder of the peak were identified as peroxide radicals based on the shape of the difference spectrum (Fig. 2d) and the disappearance temperature mentioned above, which corresponded to that of peroxide radicals. The peroxide radicals might be produced by contaminated oxygen during the electrochemical polymerization, even though the reaction was carried out under argon, or by oxygen in the air during post treatment of the PPP obtained. In the ESR study at various levels of microwave power, the intensity of the main peak and the shoulder of the peak changed independently, so the two peaks should be ascribed to different radical species. The PPP film exhibited a spin concentration of 1.0×10^{19} spins/g, which corresponds to 800 phenylene units per spin.

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