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Electroactive Poly(2-chloroaniline) Film Prepared by Electrochemical Polymerization in Organic Solvents without Protic Acid

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It is revealed that the electroactive polymer film is obtained by the electrochemical polymerization of 2-chloroaniline in organic solvents such as 1,2-dichloroethane etc. without protic acid. The film exhibits the reversible electrochromic behavior with the color change from pale yellow to green to blue in the potential range of 0 V-+1.0 V vs. Ag/AgCl.

Ring-substituted aniline is useful to modify the ring with functional substituents easily after or before polymerization. The resulting polymer is expected to realize some advantages such as conductivity, solubility for many solvents, electrochromic characteristics with multiple color changes, photoresponse and other functions. The preparation of electroactive polymer film of ring-substituted aniline has been reported by means of the electrochemical polymerization in acidic aqueous solution with H_2SO_4.1-4) There are, however, few papers about the electroactive poly(aniline derivative) prepared in organic solvents without protic acid by electrochemical polymerization.5) The electroactive poly(aniline) without substituent electropolymerized in organic solvents has been already reported, but these electrolyte solutions contain protic acid such as CF_3COOH6) and HBF_4.7) Here we report on the preparation of electroactive poly(2-chloroaniline) films by the electrochemical polymerization in organic solvents such as 1,2-dichloroethane, chloroform etc. without protic acid. And, the electrochemical characteristics of this film are evaluated with the electrochromic behavior.

2-Chloroaniline was used after distillation under reduced-pressure. Other chemicals and solvents were reagent grade and used after purification by a general method. 2-Chloroaniline (0.05 M) was solved in 1,2-dichloroethane, dichloromethane or chloroform with tetra-n-butylammonium perchlorate (TBAP, 0.1 M) as the supporting electrolyte. This solution was poured into the home-made electrolytic cell (10 cm^3). The working, counter and reference electrodes consisted of a indium-tin-oxide (ITO) glass electrode (3.0 cm^2), platinum plate electrode (1 cm^2) and an Ag/AgCl in saturated KCl with a Luggin capillary probe, respectively. Electrochemical polymerization and analyses were carried out with potentiostat/galvanostat (TOHO Technical Research: 2020) and function generator (Hokuto Denko: HB-111). The signal obtained was recorded on a conventional X-Y recorder. The measurements were carried out at 25 °C after the nitrogen gas was sufficiently bubbled into the solutions.

Electrochemical polymerization of 2-chloroaniline was carried out by the cycling of potential-sweep electrolysis between -0.35 V and +1.8 V at 100 mV s^{-1}. The cyclic voltammograms recorded during electrochemical polymerization were shown in Fig. 1. 1, 2-Dichloroethane gave the uniform film compared to chloroform and dichloromethane for electrolysis. The color of the surface of ITO electrode changed from colorless to pale

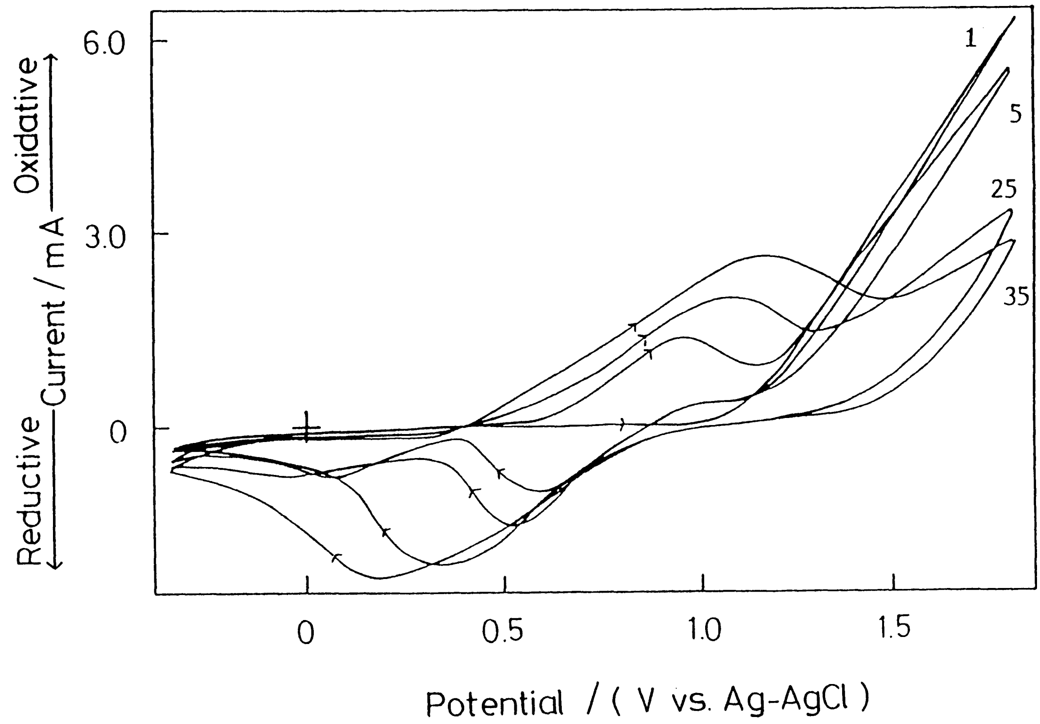

Fig. 1. Cyclic voltammograms of electrochemical polymerization of 0.05 M 2-chloroaniline in 1,2-dichloroethane. Scan rate:100 mV s^{-1}. Numerical figures indicate the number of potential cycle.

red by the oxidation of 2-chloroaniline monomer. As the number of cycling increased, the film was formed on the electrode and the color of the electrode surface turned to blue. The color changes (red↔green↔blue) on the electrode were observed at the polymerization process. In the cyclic voltammogram at the electrochemical polymerization process, oxidative and reductive peaks were found at +0.95 V and +0.52 V, respectively. This redox couple probably corresponded to the electrochemical reaction of the prepared poly(2-chloroaniline) itself. Oxidative and reductive peak potentials were shifted to higher and lower potential side, respectively, as cycling the potential-sweep. These shifts most likely reflect a large IR drop of the film on the electrode. The IR drop is concerned with the increase of film resistance, the decrease of counter ion migration and so on.

Figure 2 showed the electrochemical response of the poly(2-chloroaniline) film in 0.1 M $LiClO_4$-2.0 M H_2SO_4 aqueous solution without 2-chloroaniline. Figure 3 showed UV-Vis spectra of the poly(2-chloroaniline) film at various potentials in the same acidic aqueous solution. The changes of spectrum indicate that the polymer film exhibits electrochromic characteristics. This included the clear and reversible color changes (pale yellow↔green↔blue) by cycling the potential between 0 V and +1.0 V. These color changes are similar to those observed for poly(aniline) electropolymerized in acidic aqueous solution.8) The similar electrochromic behavior was also observed in 0.1 M TBAP/1, 2-dichloroethane solution or 2.0 M H_2SO_4 aqueous solution without $LiClO_4$, but not in 0.1 M $LiClO_4$ aqueous solution without protic acid. However, the film was gradually soluble in 1,2-dichloroethane solution when the potential-sweep was cycled to evaluate the electrochromic characteristics in the solution without monomer. The important finding is in the result that the film is not soluble by standing it in the 1, 2-dichloroethane but is soluble only at the reductive process. Work is under way to analyze the difference in the solubility for this film between oxidative state and reductive state. The surface of the polymer film obtained was seemed to be rough compared to that prepared in H_2SO_4 aqueous solution. These are probably attributed to the difference in the morphology of the resulting films obtained by different preparation methods. The polymer with solubility in suitable solvent is favorable to analyze the structure and to prepare the uniform film easily. In this point of view, the present polymer film is believed to develop some utility for many aspects such as display device,

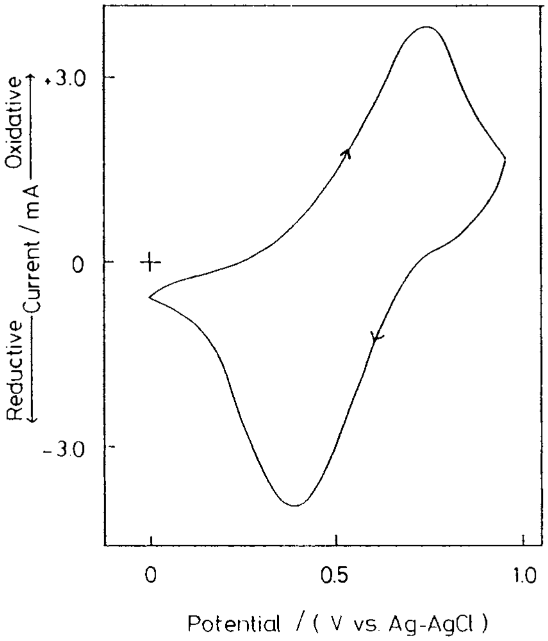

Fig. 2. Electrochemical response for poly(2-chloroaniline) in 0.1 M $LiClO_4$-2.0 M H_2SO_4 aqueous solution. Scan rate:100 mV s^{-1}.

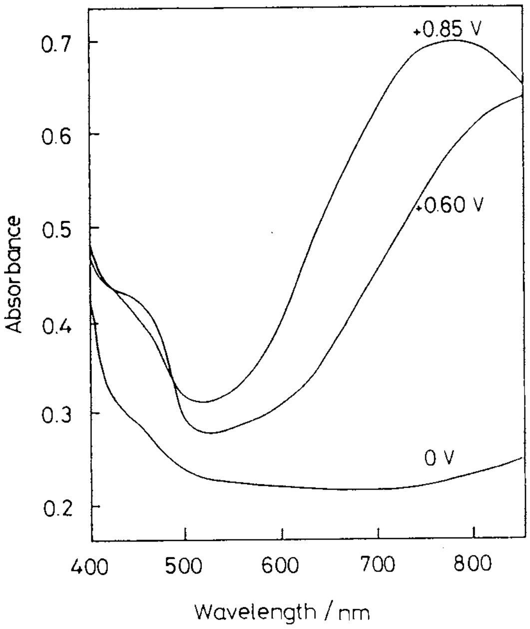

Fig. 3. Absorption spectra of poly(2-chloroaniline) filmed on ITO electrode in 0.1 M $LiClO_4$-2.0 M H_2SO_4 aqueous solution at different applied potentials.

polymer battery and so on. We also achieve to prepare several electroactive and soluble poly(aniline derivative)s with different substituent in organic solvent without protic acid. Further investigation is now in progress, and will be reported in the near future.

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