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Oligomer-immobilizing ability of an electrodeposited aramid resin film in the electrooxidation of aniline derivatives and the functions of the resulting films

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Abstract An aramid resin, poly(*p*-phenylene terephthalamide) (PPTA), was electrodeposited on an indium-tin oxide electrode as a mechanically stable film from a dimethyl sulfoxide solution. Two aniline derivatives, *o*-phenylenediamine and *o*-aminophenol, were electrooxidized from H₂SO₄ aqueous solutions using the PPTA film-coated electrode. The PPTA film was permeable to the aniline derivatives, and the derivatives were electrooxidized on the electrode surface. When the derivatives were electrooxidized, the film immobilized the corresponding oligomer species as well as the polymers plain (*o*-phenylenediamine) (PoPD) and poly(*o*-aminophenol) (PoAP), and the deposited amount of the polymers was increased by the PPTA film. The immobilized amount of PoAP was greater than that of PoPD because of the 1,4-substituted structure of PoAP. In the PPTA film, both PoPD and PoAP were electronically stabilized, and they became durable against oxidative degradation.

Key words Aramid resin · Aniline derivative · Electrooxidation · Oligomer · Polyanilines

Introduction

A popular conductive polymer, polyaniline, is an attractive material because of its useful functions. Poly-

aniline is easily prepared by electrooxidation of aniline in acidic solutions. To obtain new functional polyanilines, we have been electrooxidizing some aniline derivatives in acidic solutions, and several polyanilines were obtained [1]. The electrooxidation leaves oligomer species in the polymerizing solution, and the species are barely attached to the electrode substrate. In particular, during the electrooxidation of *o*-phenylenediamine and *o*-aminophenol, the oligomer species colored the polymerizing solution red and brown, respectively, as soon as the anodic current flowed. If the oligomer species were concentrated near the electrode surface, the polymerization efficiency would be enhanced.

An aramid resin, poly(*p*-phenylene terephthalamide) (PPTA), is widely accepted as a material for various structural applications because it is mechanically strong and heat stable. The stable PPTA film is obtainable by the electrolysis of the dimethyl sulfoxide (DMSO) solution containing PPTA [2]. It has already been confirmed that the PPTA film is permeable to dissolved species, and the species can be electrooxidized on the electrode surface [3, 4]. Therefore, the PPTA film is attractive for our objective because of its affinity to the oligomer species. In this paper, we describe (1) that the PPTA film immobilizes the oligomer species during the electrooxidation of *o*-phenylenediamine and *o*-aminophenol and (2) that both poly(*o*-phenylenediamine) (PoPD) and poly(*o*-aminophenol) (PoAP) in the PPTA film are electronically stabilized, and the durability against oxidative deterioration is enhanced.

Experimental

The *o*-aminophenol (Wako Jun-yaku Kogyo) was reagent grade and was used after distilling under reduced pressure. The *o*-phenylenediamine (Wako Jun-yaku Kogyo) was used after recrystallization from ethanol. Other chemicals were of reagent grade and used as received without further purification. Water was purified with an Auto-Still WG-22 system (Yamato) and used within a few hours. Aqueous electrolyte solutions were prepared from the distilled water.

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A conventional three-electrode system was employed for the oxidative electropolymerization of *o*-aminophenol and *o*-phenylenediamine and for electrochemical measurements. The test electrode was a transparent indiumtin oxide (ITO) coated glass plate 0.8 cm wide and 5 cm long. The ITO plate was cut off from a large ITO glass plate with 1 mm thickness supplied by Nippon Sheet Glass. The surface electric resistance was $30 \Omega \text{ cm}^{-2}$. Prior to use, the ITO plate electrode was cleaned in water with ultrasonic wave. A silver/silver chloride electrode (Ag/AgCl) was used as the reference electrode and a Pt plate having an electrode area of about 8 cm^{-2} as the counter electrode. The Ag/AgCl electrode was connected to the cell by a salt bridge filled with a saturated KCl solution. The solution level in the calomel compartment was kept lower than the level in the working cell, so that contamination by chloride ions was prevented.

Electrolyses were carried out using a potentiostat/galvanostat (model HA-301, Hokuto Denko) with a potential scanner (model HB-104, Hokuto Denko). Cyclic voltammograms were recorded by an *x-y* recorder (model RW-21, Rikadenki). The desired temperature of the electrolysis cell was maintained with a Yamato BL-22 water bath.

The absorption spectra of PPTA films were measured with a Shimadzu UV-2200 spectrophotometer.

Results and discussion

Voltammetric behavior during the electrooxidation of *o*-aminophenol and the redox activity of the resulting film

A PoAP film was electrodeposited on an ITO electrode in a 0.1 M *o*-aminophenol, 0.1 M H_2SO_4 aqueous solution. Typical cyclic voltammograms (CVs) observed during cycling in the electrodeposition solution are shown in Fig. 1. In the first positive sweep, irreversible anodic current appears from about 0.7 V. The current is due to the oxidation of *o*-aminophenol to the radical cation and to the dication [5]. As soon as the current flowed in the first positive sweep, brown oligomer species appeared on the electrode surface. The species continued to diffuse to the solution bulk with the potential cycle, and finally the solution became dark brown. After the first sweep, two redox current peaks are observed at about 0.15 V and 0.30 V. The former peaks originate from the redox reaction of PoAP, and the latter peaks are ascribable to the redox reaction of the oligomer species of *o*-aminophenol [6].

Figure 2 presents the CV showing the redox activity of the PoAP film in a 0.1 M H_2SO_4 aqueous solution. The redox current peaks of PoAP are evident, while those of the oligomer species are not observed. This implies that the oligomer species are not immobilized in the PoAP film.

The CVs for a PPTA film-coated ITO electrode in the same solution as described in Fig. 1 are shown in Fig. 3. Note that no brown oligomer species appeared during the electrooxidation, and the PPTA film became brown. There is no doubt that the oligomer species are immobilized into the PPTA film.

Figure 4 indicates the CV of the PPTA film immobilizing the oligomer species of *o*-aminophenol as well as

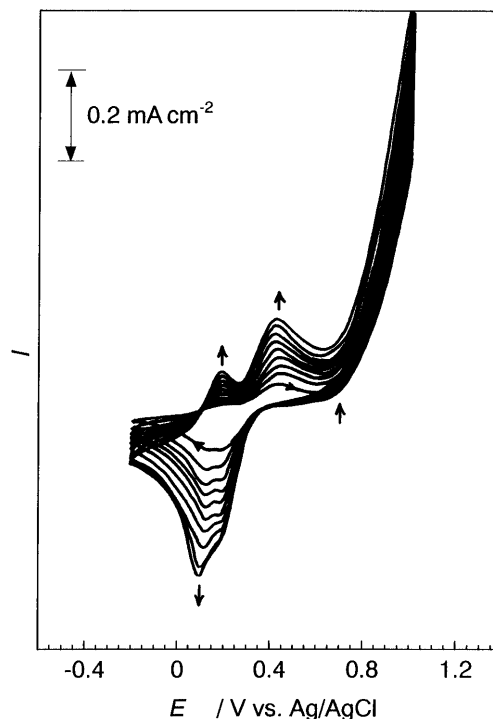


Fig. 1 Cyclic voltammograms (CVs) at 100 mV s^{-1} for electrodeposition of a poly(*o*-aminophenol) (PoAP) film on an ITO electrode from 0.1 M *o*-aminophenol in 0.1 M H_2SO_4 aqueous solution

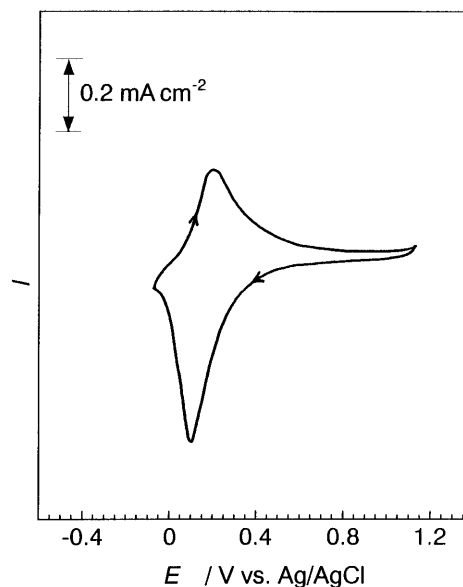


Fig. 2 CV showing the redox activity of the PoAP film electrodeposited on the ITO electrode at 100 mV s^{-1} in a 0.1 M H_2SO_4 aqueous solution

PoAP. The anodic current peak of the oligomer species is evident at about 0.5 V. In the absorption spectrum of the PPTA film, the absorption band of the immobilized oligomer species overlaps with the absorption band of PoAP at about 450 nm.

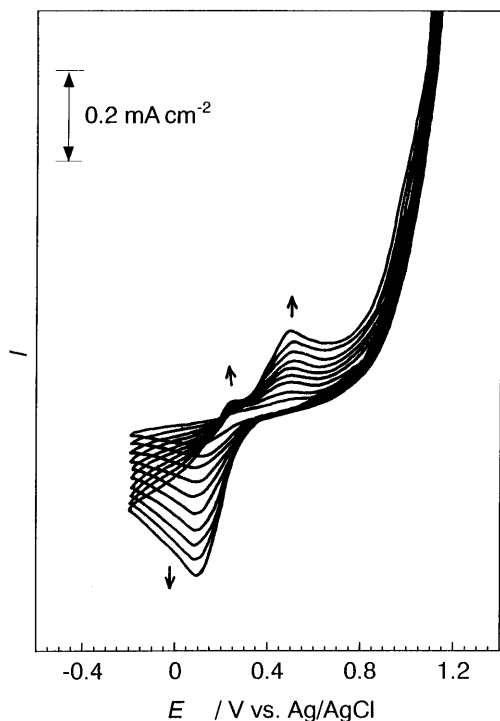


Fig. 3 CVs at 100 mV s^{-1} for the electrooxidation of *o*-aminophenol on a poly(*p*-phenylene terephthalamide) (PPTA) film-coated ITO electrode from 0.1 M *o*-aminophenol in 0.1 M H_2SO_4 aqueous solution

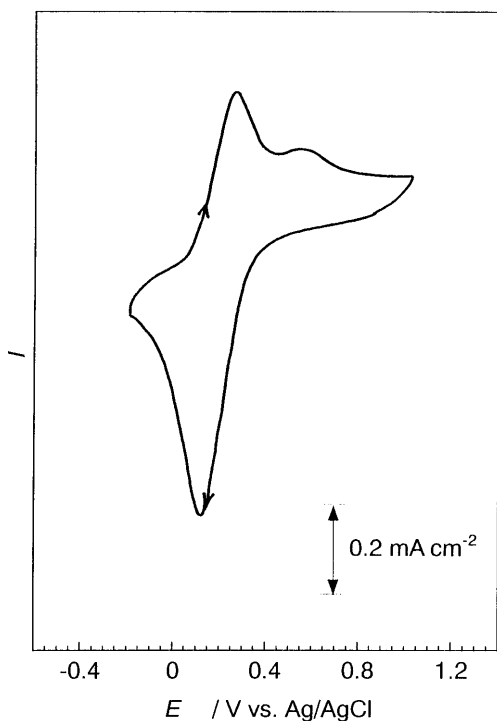


Fig. 4 CV showing the redox activity of PoAP and the oligomer species of *o*-aminophenol in the PPTA film at 100 mV s^{-1} in a 0.1 M H_2SO_4 aqueous solution

Voltammetric behavior during the electrooxidation of *o*-phenylenediamine and the redox activity of the resulting film

Typical CVs for the ITO electrode in a 0.1 M H_2SO_4 aqueous solution containing 0.1 M *o*-phenylenediamine are shown in Fig. 5. In the first positive sweep, the irreversible anodic current from about 0.5 V is due to the oxidation of *o*-phenylenediamine to the radical cation and to the dication [7]. Red oligomer species appeared on the electrode surface immediately after the first positive sweep. The species continued to diffuse to the solution bulk with the potential cycle, and finally the solution became red.

Figure 6 illustrates the CV showing the redox activity of the PoPD film in a 0.1 M H_2SO_4 aqueous solution. The redox current peaks of PoPD are evident, while those of the oligomer species are not observed, implying that the oligomer species are not immobilized in the PoPD film.

The CVs for a PPTA film-coated ITO electrode in the same solution as described in Fig. 5 are shown in Fig. 7. No red oligomer species appeared in the solution during the electrooxidation, and the PPTA film became red. Both cathodic and anodic current peaks of the oligomer species are evident at 0.10 and 0.45 V , respectively. Although the peaks imply that the oligomer species are immobilized into the PPTA film, the immobilization is weak as can readily be seen in the CV of the resulting PPTA film (Fig. 8). Only a little anodic current is observed at 0.45 V . The oligomer species are largely removed from the PPTA film by rinsing with water. In addition, the absorption band was not clearly observed

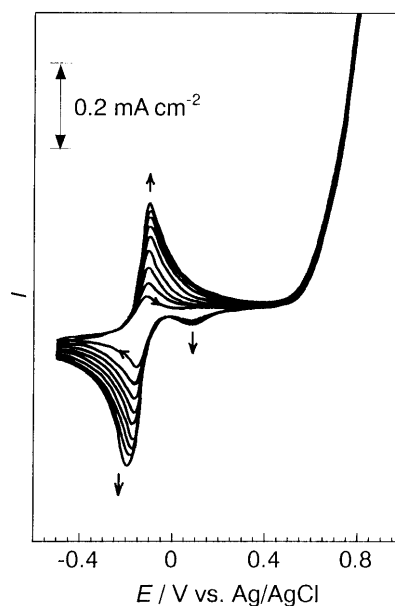


Fig. 5 CVs at 100 mV s^{-1} for electrodeposition of a poly(*o*-phenylenediamine) (PoPD) film on an ITO electrode from 0.1 M *o*-phenylenediamine in 0.1 M H_2SO_4 aqueous solution

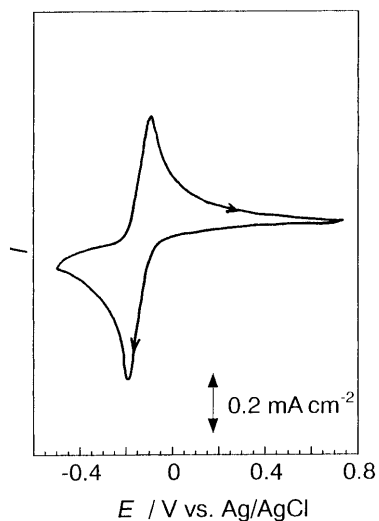


Fig. 6 CV showing the redox activity of the PoPD film electrodeposited on the ITO electrode at 100 mV s^{-1} in $0.1 \text{ M H}_2\text{SO}_4$ aqueous solution

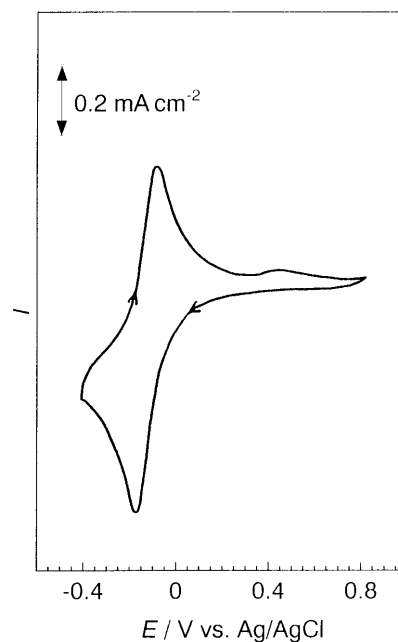


Fig. 8 CV showing the redox activity of PoPD and the oligomer species of *o*-phenylenediamine in the PPTA film at 100 mV s^{-1} in $0.1 \text{ M H}_2\text{SO}_4$ aqueous solution

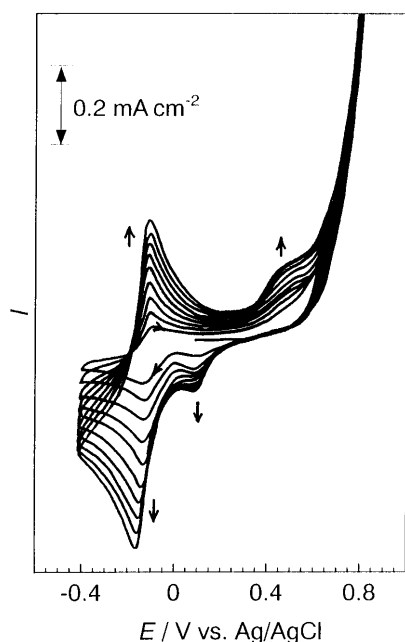


Fig. 7 CVs at 100 mV s^{-1} for the electrooxidation of *o*-phenylenediamine on the PPTA film-coated ITO electrode from 0.1 M o -phenylenediamine in $0.1 \text{ M H}_2\text{SO}_4$ aqueous solution

in the absorption spectrum of the resulting film because the band overlapped with the band of PoPD.

Enhancement of the electropolymerization efficiency by the PPTA film

Two molecular structures for PoAP are proposed based on the IR spectra: one is a ladder structure [8] and the other is a 1,4-substituted structure [9]. Barbero and

co-workers [5] reported that the rate constant of the cyclization reaction was much lower than that of the head-to-tail coupling reaction in the electropolymerization reaction of *o*-aminophenol [5]. For direct evidence about the structure, we measured the $^1\text{H NMR}$ spectrum of the oligomer species in $\text{DMSO-}d_6$. Although the spectrum was somewhat complicated, the singlet signals of $-\text{OH}$ were observed with strong intensity. Besides, the complicated multiplet signals of the rings supported the 1,4-substituted structure rather than the ladder structure. As a result, the polymer chain of PoAP mainly has the 1,4-substituted structure.

A ladder [10] and 1,4-substituted [7] structures are proposed for PoPD. Using in situ resonance Raman spectroscopy [11] and UV-vis subtractive reflectance spectroscopy [12], Lin and co-workers recently elucidated that the PoPD polymeric backbone mainly has the ladder structure.

As previously described, the electrodeposited PPTA film on the ITO electrode immobilizes the oligomer species in any case. Besides, the film is expected to immobilize the polymers not deposited on the naked ITO electrode. The immobilization must enhance the electropolymerization efficiency. To examine this, *o*-aminophenol and *o*-phenylenediamine were electrooxidized in $0.1 \text{ M H}_2\text{SO}_4$ solutions at constant current using the naked and PPTA film-coated ITO electrodes (constant current density = 1 mA cm^{-2} , monomer concentration = 50 mM , electrolytic time = 5 min). The redox charge of the deposited polymer is listed in Table 1. The charge was determined by graphical integration of the corresponding CV. In both cases, the electropolymerization efficiency is enhanced by the

Table 1 Redox charge (mC cm^{-2}) of the electrodeposited polymer^a

Polymer	PPTA film-coated ITO electrode	Naked ITO electrode
PoAP	0.720	0.275
PoPD	0.350	0.245

^a Electrodeposition conditions: monomer concentration, 50 mM; electrolyte, 0.1 M H_2SO_4 aqueous solution; current density, 1 mA cm^{-2} ; electrolytic time, 5 min

PPTA film. The charge of the PoAP deposited on the PPTA film-coated ITO electrode is 2.6 times greater than that on the naked ITO electrode. The charge of the PoPD deposited on the film-coated electrode is 1.4 times greater than that on the naked electrode. The difference in the multiple is probably due to the molecular structures. As previously described, PoAP is mainly the 1,4-substituted structure and PoPD is the ladder structure. The polaron species on the polymer chains resonate more in the ladder structure than in the 1,4-substituted structure, and the delocalization of the positive charge occurs more frequently in the former than the latter. Therefore, the polaron species of the 1,4-substituted structure are more easily coordinated by the lone pair electrons of the amino groups on the polymeric backbone of PPTA. Besides, PoAP with the 1,4-substituted structure is subject to be tangled with the polymer chain of PPTA.

Electronic stabilization of PoAP and PoPD by PPTA

Both PoAP and PoPD have more useful functions than polyaniline. For example, PoAP is the only polyaniline with ring-substituted hydroxyl groups. Zhang and co-workers [13] have suggested that PoAP can capture metal ions because of the simultaneous presence of hydroxyl and amino groups on the polymeric backbone whose lone pair electrons are available to coordinate with the metal ions. PoPD acts as an electrocatalyst for O_2 reduction [14]. Unfortunately, however, the polymers decompose by oxidative deterioration. Figure 9 shows the change of the redox charge of the polymers when they are polarized at 0.8 V. The redox charge of both PoAP and PoPD drastically decreases with the elapse of the polarization time. The decrease was significantly suppressed by the PPTA film.

The suppression of the deterioration is probably caused by the electronic stabilization with the lone pair electrons of the amino groups on the polymeric backbone of PPTA (Fig. 10). The maximum absorption wavelengths of PoAP and PoPD in the PPTA film were about 60 nm longer than those of PoAP and PoPD without the PPTA film. The lone pair electrons of the amino groups of PPTA coordinate the polaron species on the polymer chains, and the deterioration is suppressed. The suppression is expected to be an advantage for their practical use.

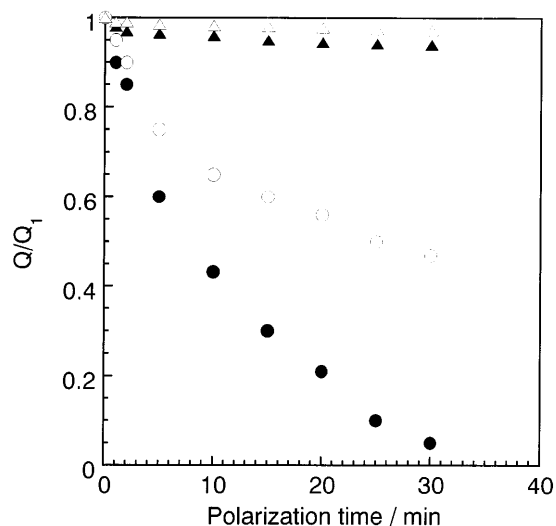


Fig. 9 Relationship between the polarization time at 0.8 V and the redox charge of PoAP and PoPD: ○ PoAP, ● PoPD, △ PoAP in the PPTA film, and ▲ PoPD in the PPTA film

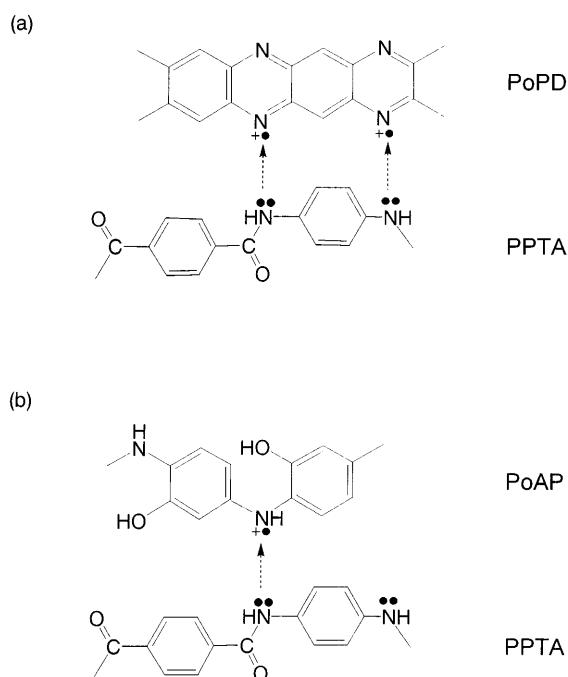


Fig. 10 Schematic depiction of the electronic stabilization of polaron species of PoPD (a) and PoAP (b) polymer chains by coordination with PPTA

Conclusions

1. The PPTA film electrodeposited on the ITO electrode immobilized not only the corresponding polymer but also the oligomer species, when *o*-aminophenol or *o*-phenylenediamine was electrooxidized in a 0.1 M H_2SO_4 aqueous solution using the film-coated electrode. The immobilization was voltammetrically confirmed.

2. PPTA electronically stabilized the PoAP or PoPD in the film and suppressed the oxidative deterioration of PoAP or PoPD.

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