fraction of free ions is small in this system. The negative slopes observed on plotting $\bar{k}_p$ versus $[I]^{-1/2}$ indicate that free ions are less reactive than ion pairs. Moreover, the fit of the data to the equations derived on the basis of a negligible reactivity of the hydrated ion pairs shows that these species do not contribute to propagation. Thus the effect of water present in the reaction medium is to remove a large fraction of the ion pairs from the propagation reaction by hydration.

Preliminary studies by us on the Raman spectra of anhydrous and hydrated samples of tetraethylammonium benzoate in the solid state support these conclusions to the extent that two types of carboxylate ion pairs can be observed for the hydrated sample and only one for the anhydrous. On exposure of the latter sample to moist air, its spectrum develops a second peak. Further work in this field is in progress.

Experimental Section

The synthesis and purification of α-methyl-α-*n*-propyl-β-propiolactone were previously described. The initiator, tetraethylammonium benzoate, was obtained from Eastman Chemical Co. and recrystallized from a solution in THF containing 5% DMSO. The crystals were dried for 20 h under vacuum at 10^{-5} mmHg, at room temperature, and then sealed under vacuum. The tube was opened in a drybox. THF was of high-performance liquid chromatography grade. It was refluxed over KOH and then over $LiAlH_4$ and siphoned with a double-tipped needle into an apparatus for distillation containing $LiAlH_4$ and distilled in dry argon and collected in a storage bottle with a Teflon stopcock, ground glass joints, and two rubber septum stoppers.

Kinetics and Measurements. A standard solution of the tetraethylammonium benzoate initiator was prepared in a drybox in a volumetric flask stoppered with a rubber septum. The reactor was also stoppered with a rubber septum and kept under argon, and calculated quantities of the standard tetraethylammonium benzoate solution and THF were added with syringes. Monomer was added with a syringe with stirring while the reactor was maintained at a constant temperature. Samples were removed with a syringe and injected into a THF–methanol solution to terminate the polymerization. The clear solution so obtained was analyzed in an infrared spectrometer for monomer conversion as previously described.[2]

Registry No. H_2O, 7732-18-5; $Et_4N^+Ph_4B^-$, 12099-10-4; α-methyl-α-propyl-β-propiolactone, 16230-68-5; α-methyl-α-propyl-β-propiolactone (homopolymer), 25188-77-6; α-methyl-α-propyl-β-propiolactone (SRU), 25265-42-3.

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Preparation of Thin Polymeric Films on Electrode Surfaces by Electropolymerization of *o*-Aminophenol

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ABSTRACT: Polymerization of *o*-aminophenol in acidic aqueous solutions was achieved electrochemically at basal-plane pyrolytic graphite and In–Sn oxide conducting glass electrodes by application of anodic potentials. The polymer poly(*o*-aminophenol) (PAP), which was prepared as a thin (0.2–0.5 μm) coating film on electrode surfaces, was electroactive in aqueous solutions and protic nonaqueous solutions and was semiconducting (conductivity 4.0×10^{-7} S cm^{-1} at 298 K). The characterization of the PAP film by IR spectroscopy, electrochemical and electrical methods, thermal gravimetric analysis, etc. suggested that the PAP is a ladder polymer with phenoxazine rings as electroactive sites.

Introduction

For the last several years electropolymerization of various aromatic compounds has been developed in our laboratory with the goal of obtaining thin polymer films and polymer film-modified electrodes for specific applications, such as electron-transfer catalyst (or mediator), sensors, and electrochromic materials and new conducting (or semiconducting or insulating) polymers.[1-22] This technique has been extensively applied to a great number of organic monomers by many investigators. In the case of the electropolymerization,[23] the polymerization reaction occurs at and/or in the vicinity of electrode surface and in some cases the resulting, insoluble polymers deposit on electrode surfaces as thin (typically ca. 100 Å–10^{-3} cm) organic layers, and consequently "polymer-coated electrodes" can be obtained in situ.

Recently, we[13] have reported the in situ preparation of the electrodes coated with conducting, electroactive, thin, ladder poly(*o*-phenylenediamine) (abbreviated as PPD (I)) films with phenazine rings by electropolymerization of the

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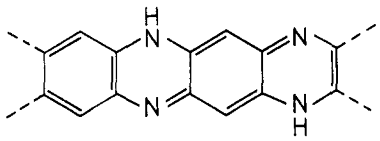
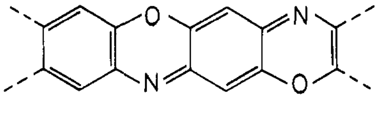


(I)

corresponding monomer and their functions and properties. This is a first example of the in situ electrochemical preparation of double-stranded or ladder polymer film-coated electrodes. Some interesting properties (e.g., electron-transfer catalysis (mediation), electrochemical diode properties, and electrochromic properties) of the PPD film-coated electrodes have been realized.[2,5,13,24-28] Along this line of investigation, we have extended the electrochemical preparation of ladder polymer film-coated electrodes to other aromatic compounds which possess the 1,2-disubstituted benzene structure similar to that of *o*-phenylenediamine. New ladder polymer film-coated electrodes, which might be prepared by an in situ electrochemical preparation, can be expected to be useful as "composite electrode materials".[29]

In the present work, we examine the possibility of preparing the ladder polymer films on electrode surfaces as polymer coatings by anodic electrochemical polymerization of *o*-aminophenol. Previously it has been suggested that a chemical polymerization of *o*-aminophenol by using Fe chelate complexes as catalysts under an atmosphere of oxygen leads to the formation of the ladder polymer with the structure like polyphenoxazine (II).[30] The ladder (or double-stranded) polymers similar to II have also been prepared by polycondensation of 4,6-diaminoresorcinol dihydrochloride with 2,5-dihydroxy-*p*-benzoquinone (or 2,5-diacetoxy-*p*-benzoquinone) and of 2,5-dichloro-*p*-phenylenediamine with 2,5-dihydroxy-*p*-benzoquionone.[31,32] In view of the usefulness of polymer film-coated electrodes electrochemically prepared, our aim is to investigate whether or not the ladder polymer like II can be prepared by electropolymerization as thin film coatings on electrode surfaces.



(II)

Experimental Section

Materials. *o*-Aminophenol (Kanto Kagaku Co., Ltd., Tokyo) of reagent grade was purified 3 times by ordinary recrystallization from water and was dried by heating under reduced pressure. Phenoxazine was reagent grade and was used without further purification. The supporting electrolytic solutions were 0.5 M Na_2SO_4 (or 0.2 M $NaClO_4$) adjusted to the desired pH's with H_2SO_4 (or $HClO_4$), NaOH, and/or the commonly used buffer solutions. Aqueous solutions were prepared from doubly distilled water. Basal-plane pyrolytic graphite (BPG) (Union Carbide Co.) and In-Sn oxide conducting glass (ITO) (Matsuzaki Shinku Co. Ltd., surface resistance is ca. 10 $\Omega/\square$) were used as working electrodes. Unless otherwise noted, the areas of BPG and ITO electrodes used were 0.19 and 0.25 cm^2, respectively. A platinum wire was used as a counter electrode. Other chemicals were reagent grade and were used as received.

Preparation of Poly(*o*-aminophenol) Film. Poly(*o*-aminophenol) (abbreviated as PAP in this paper) films were prepared on BPG and ITO electrodes by a potential-sweep electrolysis by using a standard three-electrode, two-compartment electrochemical cell. The electrode potential was cycled between −0.4 and 1.0 V versus a sodium chloride saturated calomel electrode (usually abbreviated as SSCE) at 50 mV s^{-1} in a 0.5 M Na_2SO_4 solution (pH 1.0) containing 50 mM *o*-aminophenol. The film thickness could be controlled by the amount of charge passed during the electropolymerization (as mentioned below). The PAP film-coated electrodes thus prepared were then thoroughly rinsed with distilled water and used for further electrochemical measurements. The samples for the measurement of the IR absorption spectra and the elemental analysis were prepared as follows: The PAP films of ca. 0.5 μm were prepared on large ITO electrodes (area, ca. 10 cm^2), and then they were stripped from the electrode by using a microspatula (stainless steel) with caution so as not to scrape the electrode surface. The samples thus obtained were thoroughly washed with 0.5 M Na_2SO_4 solution (pH 1.0) and then distilled water and dried in vacuo.

Characterization Techniques. The electrochemical measurements of the PAP films were carried out according to the procedure described previously.[2,3,6] The amounts (Γ) of the electroactive site in the PAP films were estimated in units of moles per centimeter squared by measuring the area of cyclic voltammograms (for the oxidation-reduction reaction of PAP film) obtained at slow potential scan rates (1-5 mV s^{-1}) in 0.2 M $NaClO_4$ aqueous solution (adjusted to pH 1.0 with $HClO_4$) and/or by measuring the charge required in a potential-step experiment to quantitatively oxidize or reduce the electroactive site in the films. The Γ values estimated by the two procedures were the same within experimental error. The molar concentration (in units of mol cm^{-3}) of the electroactive site was calculated from the Γ thus obtained using the measured thickness of the PAP films.

The film thickness of the PAP films deposited on electrode surfaces was measured with a Surfcom 550A (Surface Texture Measuring Instrument, Tokyo Seimitsu Co.) without stripping the films from the electrode surface.

Scanning electron micrographs of the films were obtained on a JEOL JSM-T100 scanning electron microscopy (SEM) at an accelerating voltage of 25 kV. In this case, the films deposited on electrodes were sputter-coated with ca. 100 Å of gold.

The IR absorption spectra of the PAP films (as KBr pellets) were obtained by using a FT/IR-3 Fourier-transform infrared spectrometer (Japan Spectroscopic Co.). The UV-visible absorption spectral measurements were conducted with a 320H Hitachi spectrophotometer.

The electrical conductivities of the films in dry state (after drying them thoroughly in vacuo) were measured with a two-point probe technique[33] at ambient temperature by means of dc power supply (Metronix Corp., Model 5126) and dc microvolt ammeter (Toa Electronic Ltd., Model PM-18R).

All electrochemical experiments were run under a nitrogen atmosphere at laboratory temperature (25 ± 1 °C). Potentials were measured and are quoted with respect to SSCE.

Results and Discussion

Electrooxidative Polymerization of *o*-Aminophenol. Typical cyclic voltammograms of *o*-aminophenol at BPG electrode in an aqueous solution containing 0.5 M Na_2SO_4 and 50 mM *o*-aminophenol are shown in Figure 1A, where the electrode potential was continuously swept at a rate of 50 mV s^{-1} between −0.4 and 1.0 V versus SSCE. *o*-Aminophenol electrooxidizes irreversibly and the oxidation of the monomer appears as the broad peaks in the potential region of ca. 0.5-1.0 V versus SSCE. After the first reverse scan, the cathodic and anodic currents were observed in the potential region between ca. −0.2 and 0.2 V versus SSCE. The current response increased continuously with successive potential scans, indicating the buildup of the electroactive polymeric products (PAP) on the electrode surface. As the potential scan was continued, the electrode was covered with a brownish orange, thin film. Almost the same cyclic voltammetric behaviors as those shown in Figure 1A were also observed with ITO electrodes.

The reversible redox response of the PAP film deposited on the electrode surface was observed at ca. 0.0 V versus SSCE, when after the electrolysis the electrode was thoroughly washed with distilled water and then transferred into a 0.2 M $NaClO_4$ aqueous solution (pH 1.0) containing no *o*-aminophenol (Figure 1B). The amount

Table I
IR Absorption Spectra of PAP Film, *o*-Aminophenol, and Phenoxazine (Fundamental Vibrations)

compound	vibration mode ν(C—H)[a]/ cm^{-1}	ν(C=C)[a]/ cm^{-1}	γ(C—H)[b]/ cm^{-1}	ν(N—H)[c]/ cm^{-1}	ν(C—N)[d]/ cm^{-1}	ν(C=N)[e]/ cm^{-1}	ν(C—O—C)[f]/ cm^{-1}	ν(C—O)[g]/ cm^{-1}	ν(C=O)[h]/ cm^{-1}
PAP film	3060	1590, 1580, 1500, 1430	935, 850, 760	3420	1310, 1250	1645	1235, 1050		1670
o-aminophenol	3000	1605, 1570, 1500, 1460	930, 850, 750	3420, 3340	1340, 1280			1400, 1215	
phenoxazine	3060	1600, 1590, 1500, 1430	925, 830, 745	3420	1300, 1250		1230, 1050		

[a] Stretching vibration of the C—C and C—H bonds of benzene nuclei. [b] Out-of-plane bending vibration of the C—H bonds of benzene nuclei. [c] Stretching vibration of the N—H bonds. [d] Stretching vibration of the C—N bonds. [e] Stretching vibration of the C=N bonds. [f] Stretching vibration of the C—O—C bonds. [g] Stretching vibration of the C—O bonds of phenolic compounds, overlapped with the in-phase bending vibration of the O—H bonds. [h] Stretching vibration of the C=O bonds.

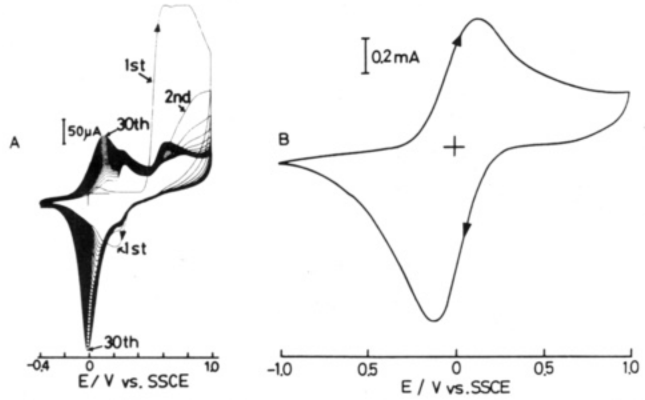


Figure 1. (A) Cyclic voltammograms for *o*-aminophenol recorded continuously at a BPG electrode in 0.5 M Na_2SO_4 aqueous solution (pH 1.0) containing 50 mM *o*-aminophenol. The electrode potential was swept repeatedly between −0.4 and 1.0 V versus SSCE at a scan rate of 50 mV s^{-1}. (B) Cyclic voltammogram obtained when after the potential sweep (30 times) as in A the electrode was washed with water and transferred to a 0.2 M $NaClO_4$ aqueous solution (pH 1.0): scan rate; 100 mV s^{-1}; film thickness, 0.2 μm.

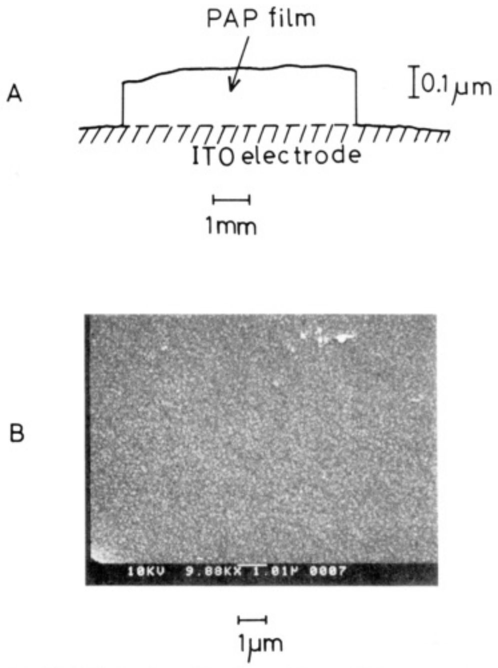


Figure 2. (A) Typical sectional profile and (B) scanning electron micrograph of the PAP film prepared on an ITO electrode (the amount of charge passed, 1 C cm^{-2}).

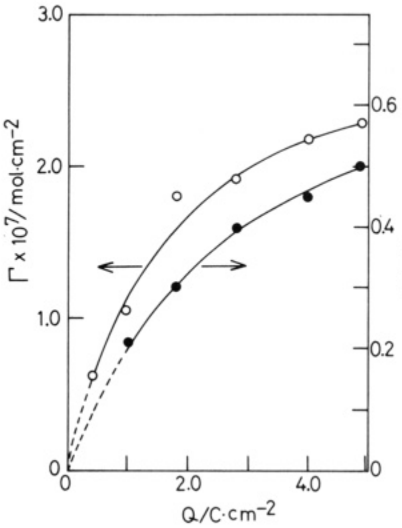


Figure 3. Plots of the film thickness (l) and the surface concentration (Γ) of an electroactive site in the film versus the charge (Q) passed during the potential-sweep electrolysis.

of charge involved in both oxidation and reduction processes was almost equal. The cyclic voltammogram has a so-called diffusion tail and the shape is unsymmetric, as expected for a simple, reversible, redox reaction of a solution-phase reactant that diffuses to the electrode surface.[33]

Morphology and Thickness Control of PAP Film. The vertical sectional profile of the PAP film produced on the ITO electrode shows that it is continuous and has a fairly smooth surface and that the thickness is almost uniform over the whole film (Figure 2A). Further, from the scanning electron micrograph of PAP film surface (Figure 2B), we can also see that the film displays nonspecific amorphous surface features. Its morphology appears to be granular rather than fibrous. The size of the nodules is on the order of ca. 0.1 μm. The whole feature of the film surface is very similar to those of poly(2,6-dimethylphenol) films[16,17] prepared by electropolymerization of 2,6-dimethylphenol in basic nonaqueous solutions. The PAP films were insoluble in the commonly used organic solvents except for dimethyl sulfoxide. They were soluble in H_2SO_4, HNO_3, and NaOH solutions but insoluble in HCl, $HClO_4$, and NH_4OH solutions and H_2O.

Figure 3 shows plots of film thickness (l) and surface concentration of electroactive sites (Γ) versus the amount (Q) of charge passed to prepare PAP films. l increased with increasing Q as in the relation between Γ and Q. As a result, the volume concentrations of electroactive sites in the PAP films with different thicknesses, being estimated as Γ/l from Γ and l at a given Q, were found to be almost constant ($(5.0 \pm 0.5) \times 10^{-3}$ mol cm^{-3}), irrespective of l. This indicates the uniform distribution of electroactive sites in the films of different l's. The data in Figure 3 also indicate that PAP film thickness can be arbitrarily controlled by the charge passed during the electrolysis.

IR Absorption Spectra of PAP Film. The IR absorption spectrum of a KBr pellet of the PAP film (oxidized form) is shown in Figure 4, together with the spectra of *o*-aminophenol and phenoxazine. These spectral data

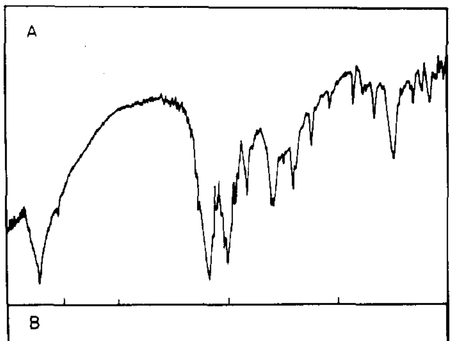


Figure 4. IR absorption spectra of (A) PAP film (oxidized form), (B) *o*-aminophenol, and (C) phenoxazine. The PAP film was prepared on BPG electrode as in Figure 1.

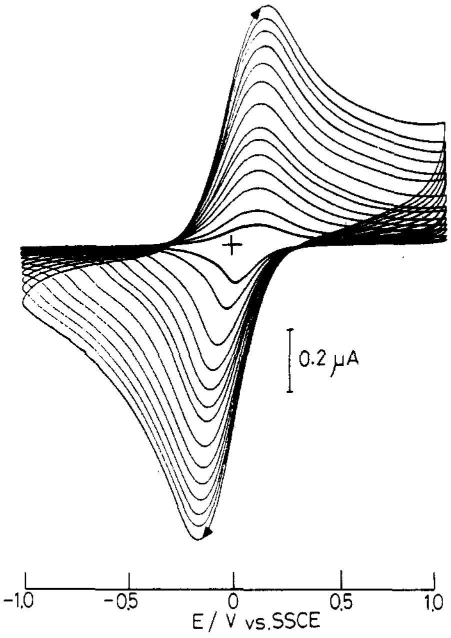
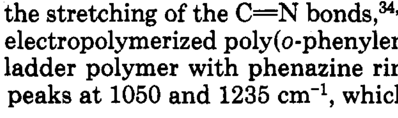


Figure 5. Typical cyclic voltammograms for the oxidation–reduction reaction of PAP film deposited on BPG electrode in 0.2 M $NaClO_4$ aqueous solution (pH 1.0) at various potential scan rates: film thickness, 0.4 μm; volume concentration of electroactive site in the film, 4.9×10^{-3} mol cm^{-3}; potential scan rates, (from bottom) 5, 10, 20, 30, 40, 50, 60, 80, 100, 120, 140, 160, 180, and 200 mV s^{-1}.

are summarized in Table I. The absorption peaks at ca. 3000 and 1430–1605 cm^{-1}, which are common to the PAP film, *o*-aminophenol, and phenoxazine, are characteristics of the stretching vibration modes of the C—H and C=C bonds, respectively, of the aromatic nuclei.[34,35] The absorption peaks due to the N—H stretching vibrations[35] of the imino groups of the PAP film and phenoxazine were observed at 3420 cm^{-1}, while two absorption peaks corresponding to the N—H stretching vibrations of the amino groups of *o*-aminophenol were, as expected,[34] observed at 3340 and 3420 cm^{-1}. The presence of the relatively strong absorption peak around 3420 cm^{-1} may suggest that the PAP does not possess the completely ring-closed structure such as II (i.e., it is partially ring opened, e.g., III) and/or that the degree of the polymerization of PAP is relatively low.[40] The absorption peaks ascribable to the stretching vibrations of C—N bonds were observed at 1250 and 1310 cm^{-1}.[34,35] Similar peaks were also observed for *o*-aminophenol and phenoxazine. The peak at 1645 cm^{-1} is ascribable to the stretching of the C=N bonds,[34,35] as in the case of the electropolymerized poly(*o*-phenylenediamine) which is a ladder polymer with phenazine rings.[13] The absorption peaks at 1050 and 1235 cm^{-1}, which are characteristics of the C—O—C stretching vibration,[34,35] were observed for the PAP film and phenoxazine, but not for *o*-aminophenol. For *o*-aminophenol, the absorption peaks due to the C—O stretching vibration which is overlapped with the in-phase bending vibration of the O—H bond were observed at 1215 and 1400 cm^{-1}.[34] Several absorption peaks, which arise from the C—H out-of-plane bending modes,[34,35] were observed for all the samples examined. For the PAP film, the peaks at 760, 850, and 935 cm^{-1} can be considered to correspond to 1,2-disubstituted, 1,2,4-trisubstituted, and/or 1,2,4,5-tetrasubstituted benzene structures.[34,35] The absorption patterns corresponding to these substituted benzene structures are actually indistinguishable. All of these structures seem possible for the PAP. Finally, from the fact that the absorption peak which is considered to correspond to the stretching vibration of the C=O bonds of aromatic keto groups was, though as a weak peak, observed at 1670 cm^{-1} (it has been usually observed around 1690 cm^{-1} as a strong peak),[34,35] the partially hydrolyzed structure of III[40] and a structure such as IV, which is considered to be polymerized via C—N=C bonds, are also conceivable.



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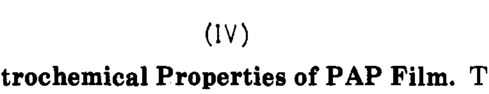


(IV)

Electrochemical Properties of PAP Film. The dependence of the cyclic voltammograms of the PAP film deposited on a BPG electrode upon potential scan rate (v) was examined in 0.2 M $NaClO_4$ aqueous solution (pH 1.0). A typical result of such experiments is shown in Figure 5. The relations between anodic (or cathodic) peak currents (i_p^a or i_p^c) and v are also shown in Figure 6. Both i_p^a and i_p^c were found to scale linearly with $v^{1/2}$ in the range of v from ca. 30 to 200 mV s^{-1}, indicating that the charge-transport process within the film (the thickness, 0.4 μm) is diffusion-controlled.[6,14,38] In this case, the different

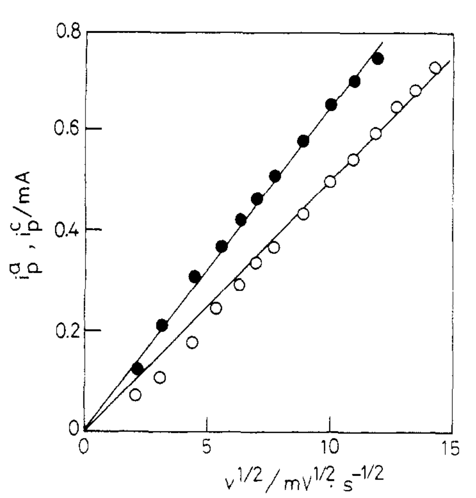


Figure 6. Anodic and cathodic peak currents (i_p^a and i_p^c) as a function of potential scan rate (v) for the cyclic voltammograms in Figure 5: (●) cathodic peak currents (i_p^c); (○) anodic peak currents (i_p^a).

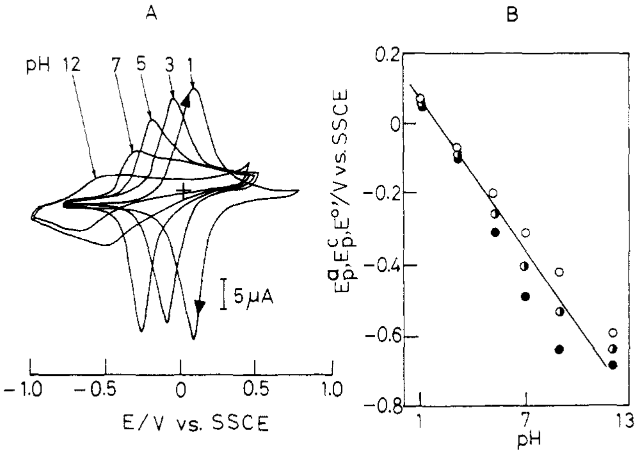
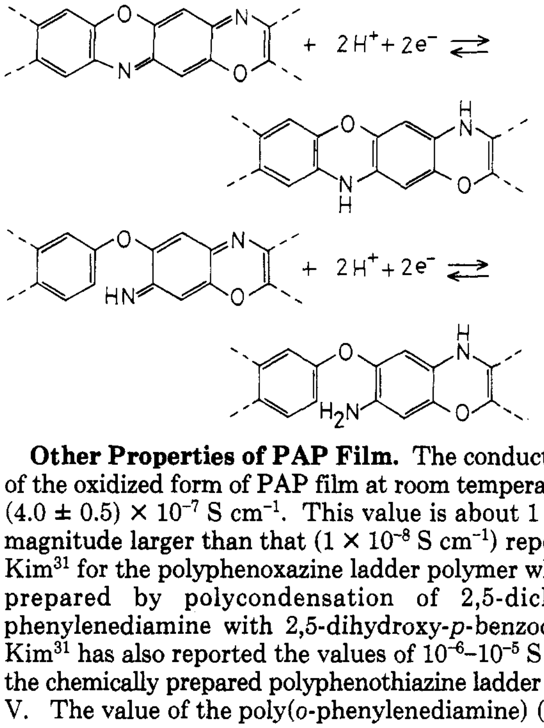


Figure 7. (A) Cyclic voltammograms of PAP film deposited on BPG electrode in aqueous solutions of various pH's: scan rate, 2 mV s^{-1}; film thickness, 0.2 μm; volume concentration of electroactive site, 5.0 × 10^{-3} mol cm^{-3}. (B) pH dependences of the cathodic and anodic peak potentials (E_p^c and E_p^a) and formal redox potential ($E^{\circ\prime}$) for the oxidation–reduction reaction of PAP film. The data were taken from (A): (○) E_p^a; (●) E_p^c; (◑) $E^{\circ\prime}$.

slopes reflect the different charge-transport rates for the anodic and cathodic processes. By potential-step chronoamperometry and chronocoulometry, the apparent diffusion coefficients for the diffusion-like charge-transport process of the Fickian type were estimated to be (3.6 ± 0.4) × 10^{-10} and (5.5 ± 0.3) × 10^{-10} $cm^2\ s^{-1}$ for the anodic and cathodic processes, respectively. These values are about 2 orders of magnitude smaller than those obtained for the ladder polymer poly(*o*-phenylenediamine) film.[13] The details will be reported elsewhere.[36]

Figure 7A shows the cyclic voltammograms of the PAP film deposited on a BPG electrode in aqueous solutions of various pH's. The voltammetric response is reversible at all the pH's examined. However, as pH was increased, (i) the waves shifted to the negative direction of potential, (ii) the anodic and cathodic peak currents decreased, and (iii) the potential separation between the anodic and cathodic peak potentials (E_p^a or E_p^c) increased. The pH dependence of the voltammograms is shown in a quantitative manner in Figure 7B, where the values of E_p^a, E_p^c, and the formal oxidation–reduction potential ($E^{\circ\prime}$) (estimated as $(E_p^a + E_p^c)/2$) are plotted against pH. The $E^{\circ\prime}$ versus pH plot is almost linear in an acidic region and its slope is about −65 mV/pH, indicating that protons and electrons take part in the electrode reaction of the PAP film in a 1/1 ratio (the theoretical slope for a H^+/e^- (1/1) reaction is −60 mV/pH at 25 °C).[38] In this case, the linear plot of E_p^a versus pH gave the slope of −60 mV/pH in the wide pH range of 1 to 13. In contrast, the pH dependence of E_p^c seems complicated. That a proton addition–elimination reaction is involved in the overall electrode reaction (i.e., the heterogeneous electron-transfer process at the electrode/PAP film interface and the homogeneous charge-transport process within the PAP film) can be considered as the reason for the complicated pH dependence of E_p^c and the decrease of peak currents with increasing pH. A similar behavior has recently been also observed for other electroactive electropolymerized films (e.g., polyaniline,[1] poly(1-pyrenamine),[10] and poly(*o*-phenylenediamine)[37] films).

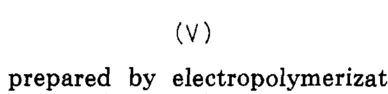
The PAP film was also found to be electroactive in nonaqueous solutions containing protons but electroinactive in nonaqueous solutions containing no protons. A typical example of such experimental results is shown in Figure 8. The data in Figures 7 and 8 indicate that protons are essential for the electrode reaction of the PAP film in both aqueous and nonaqueous solutions. Based on the above-mentioned results, the electrode reactions of the PAP film with structures II and III may be expressed as



(1)

(2)

Other Properties of PAP Film. The conductivity (σ) of the oxidized form of PAP film at room temperature was (4.0 ± 0.5) × 10^{-7} S cm^{-1}. This value is about 1 order of magnitude larger than that (1 × 10^{-8} S cm^{-1}) reported by Kim[31] for the polyphenoxazine ladder polymer which was prepared by polycondensation of 2,5-dichloro-*p*-phenylenediamine with 2,5-dihydroxy-*p*-benzoquinone. Kim[31] has also reported the values of 10^{-6}–10^{-5} S cm^{-1} for the chemically prepared polyphenothiazine ladder polymer V. The value of the poly(*o*-phenylenediamine) (PPD, I),



(V)

which was prepared by electropolymerization of *o*-phenylenediamine and has a ladder polymer structure with phenazine rings, has recently been estimated to be 2 × 10^{-4} S cm^{-1}.[15] The σ values of these heteroaromatic ladder polymers are in the following order: poly(*o*-phenylenediamine) (I) > polyphenothiazine (V) > polyphenoxazine (II, III). This is worthy of note, especially in elucidating the correlation between the structures of heteroaromatic ladder polymers and their conductivities. However, a reasonable explanation for this result is difficult, because we have no evidence that these polymers possess com-

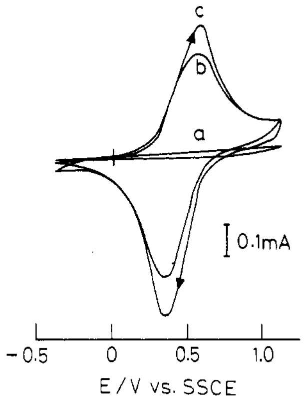


Figure 8. Typical cyclic voltammetric responses of PAP film in acetonitrile solutions containing (a) 0.1 M tetrabutylammonium perchlorate (TBAP), (b) 0.1 M TBAP + 0.1 M CH_3SO_3H, and (c) 0.1 M TBAP + 0.5 M CH_3SO_3H: scan rate, 100 mV s^{-1}; film thickness, 0.6 μm.

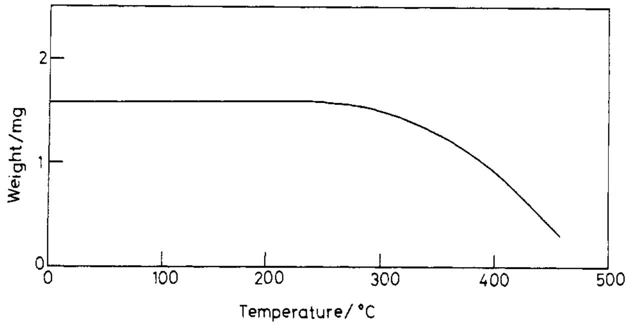


Figure 9. Thermal gravimetric analysis curve of PAP film in air.

pletely ring-closed ladder structures. For the electropolymerized poly(*o*-phenylenediamine) and poly(*o*-aminophenol) films, the partially ring-opened structures are confirmed in the present and previous studies.[13]

The color of the oxidized form of the PAP film is brown (λ_{max} = 440 nm) and the reduced form is almost colorless. The PAP film-coated ITO electrode displayed the reversible electrochromic response: A reversible color change of the film between brown and colorless was observed when the electrode potential was cycled between 0.7 and −0.7 V versus SSCE. Electrochromic properties of the PAP film and kinetic examination of the electrochromic process will be reported in detail in a separate paper.[36]

Based on the thermal gravimetric analysis of PAP film (Figure 9), this film was found to start a slow loss of weight around 300 °C in analogy with the chemically prepared ladder polyphenoxazine.[32] A loss in weight was at most 3% at 300 °C.

Conclusions

The preparation of the ladder polymer (PAP) with phenoxazine rings by electrooxidative polymerization of *o*-aminophenol has been reported for the first time. The polymer can be obtained as uniform coating film on electrode surfaces. The films are very adhesive[39] to electrode surfaces, electroactive, and semiconducting. The PAP film-coated electrodes prepared could be expected as useful "composite electrode materials" as in the case of recently reported other electropolymerized film-coated electrodes.[29]

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Registry No. *o*-Aminophenol (homopolymer), 25668-01-3.

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(39) Yank tested with Scotch tape.

(40) The elemental analysis of the PAP film (oxidized form) indicated that the molar ratios of C, H, and N are 6.0, 3.8, and 0.76, respectively. It seems likely that this result does not necessarily support III as a possible structure of PAP, but taking into account that imino groups (=NH) of III are partially hydrolyzed to produce aromatic keto groups,[41] one can speculate some reasonable structures the molar ratios of C, H, and N of which are in fair agreement with those calculated based on the elemental analysis data.

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New Aspect of Cationic Ring-Opening Polymerization of Seven-Membered Spiroorthocarbonates: Synthesis and Polymerization of Substituted 1,6,8,13-Tetraoxaspiro[6.6]tridecanes

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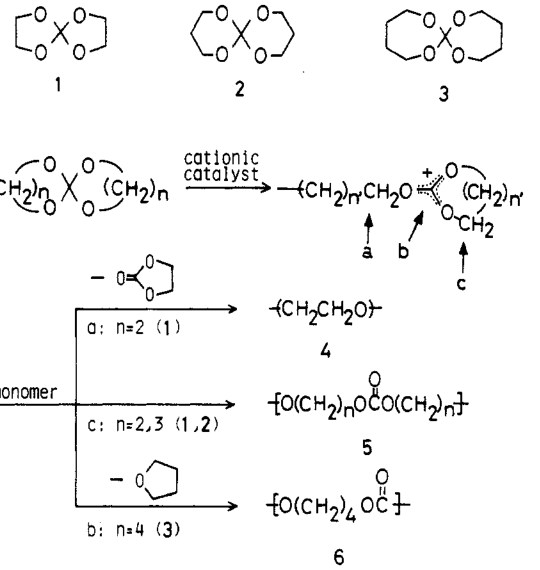
ABSTRACT: Two new spirocyclic monomers, spiroorthocarbonates (SOCs, 7 and 8) having spiro[6.6]tridecane skeletons, were synthesized and their polymerization behavior was studied under cationic conditions. By cationic ring-opening polymerization, SOCs 7 and 8 afforded clearly structure-different polymers, polycarbonate 9 and poly(ether–carbonate) 12, respectively, depending on the structure of SOC, but independent of solvent (chlorobenzene, ethylene dichloride, nitrobenzene), catalyst (BF_3OEt_2, $Ph_3C^+BF_4^-$, $PhCH_2\overline{S^+CH_2CH_2CH_2CH_2}$ SbF_6^-), and temperature (from room temperature to 120 and 150 °C). On the basis of the difference of the structures between the SOCs, the results suggested two distinguishable polymerization courses controlled presumably by the electrophilicity of the reaction site of the propagating cationic species or the leaving ability of the eliminated moiety.

Introduction

Spiroorthocarbonate (SOC) is a useful monomer which shows expansion in volume on polymerization[1-5] and its application to new materials has recently become important. In 1973, Sakai et al. first studied the cationic ring-opening polymerization of three types of SOCs (**1**, **2**, and **3**) catalyzed by boron trifluoride etherate.[6] From the structure of the products, they proposed three modes of ring-opening polymerization of the SOCs in terms of the attacking sites of monomer toward cationic propagating species, as shown in Scheme I. SOC **2** having two six-membered rings effectively gives poly(ether–carbonate) alternative copolymer **5** (n = 3), while SOC **1** having two five-membered rings mainly affords polyether **4** [poly(ethylene oxide)] with a loss of ethylene carbonate. As for SOC **3**, polycarbonate **6** is obtained with complete elimination of tetrahydrofuran. From the viewpoint of material science, it is rather difficult to use SOCs other than **2** for expanding materials, if Sakai's polymerization map (Scheme I) is always operative.

Bailey et al.[7] and we[8-11] have already studied syntheses and cationic ring-opening polymerization of various derivatives of **2**, suggesting their utility as new monomers,[1-5] promising no shrinkage. During the course of the study, we have also prepared **3** and reexamined its reactivity, and have noticed higher sensitivity of **3** than **2** toward cationic species. Since low cationic polymerizability of SOC **2** has caused an emerging problem in designing the materials, it is of great significance in material science if a monomer can be obtained that not only retains the same skeleton as **3** but also undertakes cationic ring-opening polymerization without any elimination of tetrahydrofuran derivative. In this situation we have continued detailed investigations on the synthesis and the polymerization behavior of derivatives of **3**, so as to obtain the basis of the molecular designing of the better SOC monomers. Thus, from the results of the polymerizations of two SOC monomers bearing fused-ring systems based on the structure **3** (i.e., SOCs **7** and **8**), we have obtained important mechanistic information of the polymerization of SOCs. This paper reports these results.

Scheme I



Experimental Section

Both ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer operating in the pulsed FT modes, using tetramethylsilane (TMS) as internal standard in deuteriochloroform at 27 °C, unless otherwise stated. FT-IR specta were obtained with a JASCO FT/IR-3 at 25 °C. Mass spectra were taken at 25 °C with a Hitachi M-80 spectrometer equipped with a data processing system at an ionizing potential of 70 eV. Molecular weight and its distribution (MWD; $\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) on a Toyo Soda HPLC CCP & 8000 system with a data processor, equipped with three polystyrene gel columns (TSK gel, G2000H, G2500H, and G3000H), using tetrahydrofuran as an eluent, flow rate 1.0

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