

Low potential of starburst six-arylamino compounds generating conducting polymers

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Abstract *N,N',N''*-tris [4-(phenylamino)-phenyl]-1,3,5-Benzenetriamine, composed of six arylamines with a starburst type, was oxidized electrochemically to yield an electrically conducting polymer film. The polymerization potential was lower than those of aniline and its derivatives. The lower shift was explained in terms of the redox interaction between the cation radical and the other arylamines through phenyl groups. The linear relation of the oxidation potential with the inverse of the number of redox sites was valid even for the starburst compounds.

Keywords Polyaniline · Polymerization · Voltammetry · Interaction energy · Intervalence states

Introduction

The polymerization of aniline derivatives starts from the oxidation of the arylamine to yield radical cation followed by radical–radical coupling [1–3]. The dimers in turn are oxidized and then are coupled or added to the monomer autocatalytically [4–6] to generate intermediate oligomers, which have been identified with electrospray mass spectrometry [7]. The autocatalysis [8, 9] is ascribed to the lower oxidation potential of oligomers than the monomer [5, 6].

Optical transition energy [10–12] and oxidation potentials [13–15] of conducting oligomers are known to be shifted with an increase in the chain length. This behavior can be quantitatively expressed in terms of a linear relation of the oxidation potential with the inverse of the length [14, 15]. The relation has been interpreted computationally with the quantum chemical approach [16, 17] and the thermodynamic approach with the redox interaction [18]. Since the potential shift is caused by the interaction of redox sites [19] rather than the length of oligomers, the relationship ought to hold even for geometrically complicated molecules. We previously synthesized the six-arylamino compound with a starburst type, which exhibited strong redox interaction [20]. This paper deals with the electrochemical polymerization of three- and six-arylamino species, as is shown in Fig. 1, in the light of the relation of the oxidation potential of forming films and the number of the redox sites.

Experimental

Ferrocene (Wako, Osaka, Japan) was purified by sublimation before use. *p*-Aminodiphenylamine (Wako), phloroglucinol (Wako), iodine (Kanto, Tokyo, Japan), and *p*-anisidine (Wako) were used as received. Tetra-*n*-Butylammonium perchlorate and tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) were used for supporting electrolyte as received. Acetonitrile and dichloromethane were of analytical grade (Kanto).

1,3,5-tris(*p*-Methoxy phenylamino) benzene (MPB) was synthesized from phloroglucinol with methoxy aniline and iodine according to literature [22]. The purification was carried out by washing with methanol (yield 65%). 1,3,5-tris-[(4-*N*-Phenylaminophenyl)amino]benzene (PAB) was

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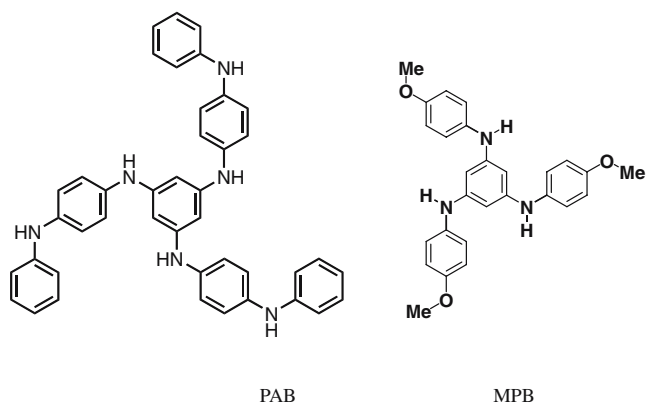


Fig. 1 Molecular structure of PAB and MPB

synthesized from phloroglucinol with *N*-phenyl-1,4-benzene diamine and iodine according to literature [21]. The purification was carried out by washing with methanol and the compound was recrystallized from acetonitrile (yield 79%).

Platinum disks 1.6 mm in diameter (BAS, Tokyo, Japan) and the GC disk 1 mm in diameter were used as a working electrode for voltammetry. The electrode surface was polished with 0.05 μm alumina before each run. The auxiliary electrode was a platinum coil. The reference electrode was an $\text{Ag}|\text{Ag}^+$ electrode (0.01 M Ag^+), of which potential was 0.35 V shifted positively from an $\text{Ag}|\text{AgCl}$ electrode. An AD/DA converter (PCI-3521, Interface, Hiroshima, Japan) was used as a function generator and a recorder connected to the potentiostat HECS-318C (Fuso, Kawasaki, Japan). Nitrogen gas was bubbled from the one-compartment cell before each electrochemical run.

Potential-controlled absorption spectra were obtained at the platinum 150 mesh electrode in the thin-layer quartz cell with a light path length of 0.5 mm. The spectra were obtained with V-570 UV/vis/NIR spectrophotometer (JASCO Hachioji, Japan) at 25 $^{\circ}\text{C}$.

Results and discussion

Figure 2 shows cyclic voltammograms of 0.2 mM PAB in acetonitrile solution containing 0.1 M TBABF₄ at iterative potential scans. The voltammogram at the first scan had two anodic peaks at 0.38 and 0.64 V and corresponding cathodic peaks at 0.21 and 0.54 V. The subsequent potential cycles made the redox waves merge to yield a broad wave. The peak current increased progressively with the cycling, indicating the accumulation of electroactive precipitate on the electrode. The negative potential shift at the iterative scan suggests the formation of oligomers or polymers on the electrode [14, 18].

The film-deposited electrode after 24 potential scans in the PAB solution was transferred into 0.2 M TBABF₄ solution

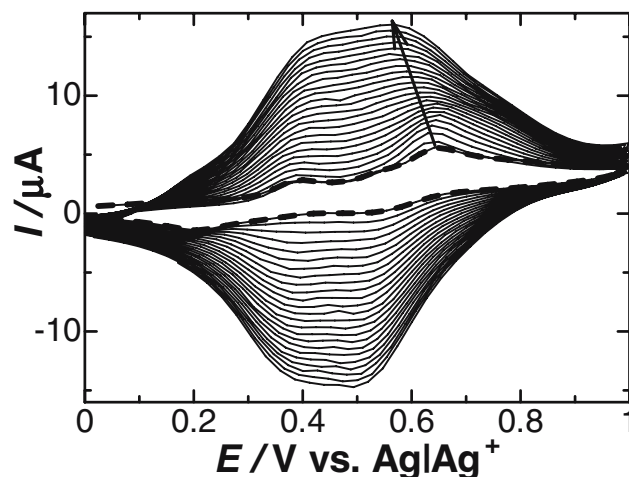


Fig. 2 Cyclic voltammograms of 0.2 mM PAB at the GC electrode 0.1 mm in diameter in acetonitrile including 0.2 M TBABF₄ at the scan rate, 0.10 V s^{-1} . The current increased with the iterative scan from the first cycle (*dashed curve*)

without PAB. The voltammogram showed the broad anodic and cathodic wave at roughly 0.5 V vs $\text{Ag}|\text{Ag}^+$ [22, 23], as is shown in Fig. 3. The peak potential was close to that of polyaniline in acetonitrile solution by the $\text{Ag}|\text{Ag}^+$ reference electrode. The voltammograms did not vary with iterative scans in the blank solution. The current increased linearly with the number of the scan performed in the PAB solution (inset of Fig. 3). When the number of the scan was over 20 and when the positive reverse potential was over 0.65 V, the electrode surface turned to a dark green color, as shown in Fig. 4. The color of the film did not change for a few months in air. The anodic and cathodic background-corrected peak currents were proportional to the scan rate for $0.01 < \nu <$

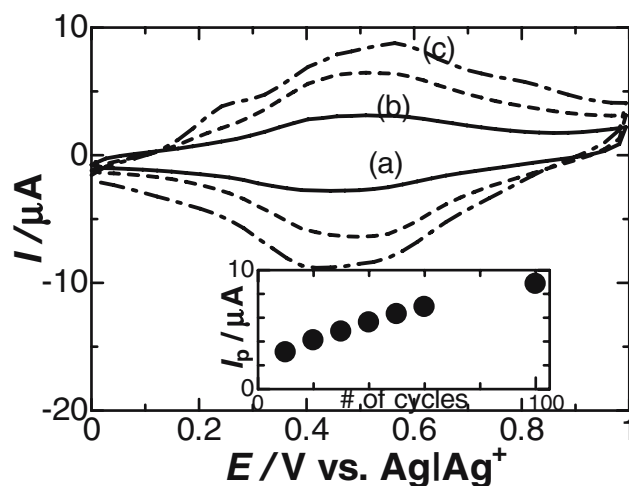


Fig. 3 Cyclic voltammograms of the film-coated electrode in the 0.2 M TBABF₄ solution. The film was deposited by 10 (a), 50 (b), and 100 (c) potential cycles in the potential domain from 0.0 to 1.0 V at 0.1 V s^{-1} in the acetonitrile solution including 0.2 mM PAB + 0.2 M TBABF₄. The *inset* is the variation of the peak current, I_p , with the number of scans

Fig. 4 Photographs of electro-polymerized film of PAB (a) and the bare Pt electrode 1.6 mm in diameter (b), obtained by the optical microscope



0.15 V s⁻¹, and hence they are for surface process-related voltammetric waves.

The Fourier transform infrared spectral bands of the deposit were close to those of PAB. Thus, the deposit can be regarded as a polymer composed on PAB. Spectroelectrochemical measurements were made in the PAB solution at the bare Pt mesh and in the blank solution at the deposited electrode. When the first oxidation potential (0.0 < E < 0.5 V)

was applied to the PAB solution, the band at 304 nm decreased gradually and the band at 416 nm grew, as is shown in Fig. 5a. These variations were reversible for the reduction. Applying the second oxidation potential (0.5 < E < 1.0 V) generated a broad band ranging from 500 to 1,000 nm. When the potential was stepped back to 0.5 V, the band at 416 nm still remained. Thus, the redox reaction at the potential 0.5 < E < 1.0 V is irreversible, and may take part in the formation of the deposit. On the other hand, the spectra of the deposit (Fig. 5b) were similar to those of PAB. The broad band at 800 nm may be ascribed to the intervalence states formed by the cation radical and the closest neighboring arylamines [20].

The film polymerized by 30 times potential scan exhibited the electric charge of 1.23 mC cm⁻² evaluated from the voltammetric area in the blank solution. Because PAB has a six-electron oxidation reaction [20], the charge density is expressed by $q = 6FwSd/W_M$, where w is the thickness of the film, d is the density, S is the area, and W_M is the molar weight (625 g mol⁻¹). If the density of the film is similar to that of polyaniline (1.46 g cm⁻³) [24], the film

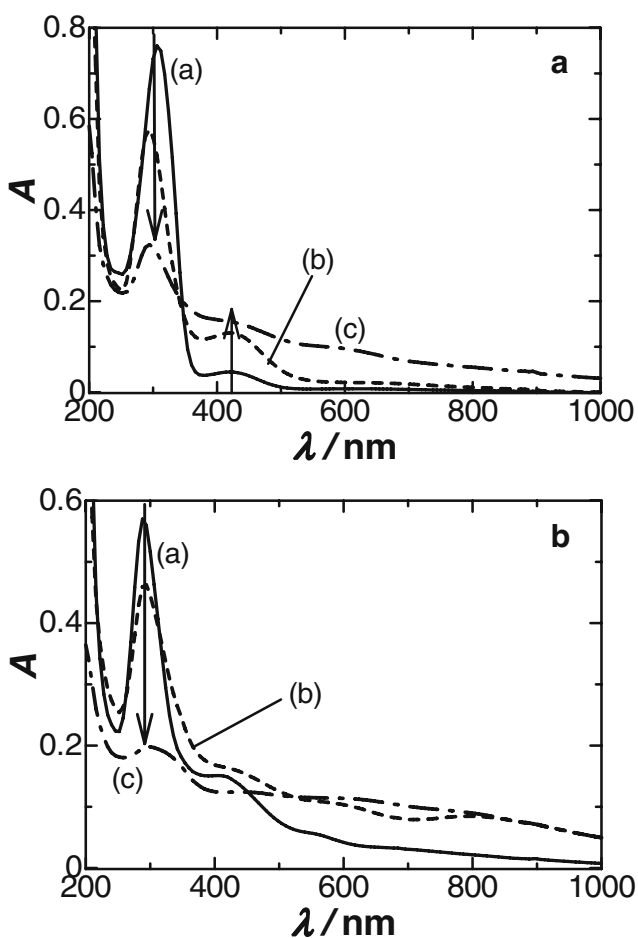


Fig. 5 UV-vis spectra of 0.2 mM PAB a and the deposit in acetonitrile containing 0.1 M TBABF₄ b at potentials of 0.0 (a), 0.5 (b), and 1.0 V (c)

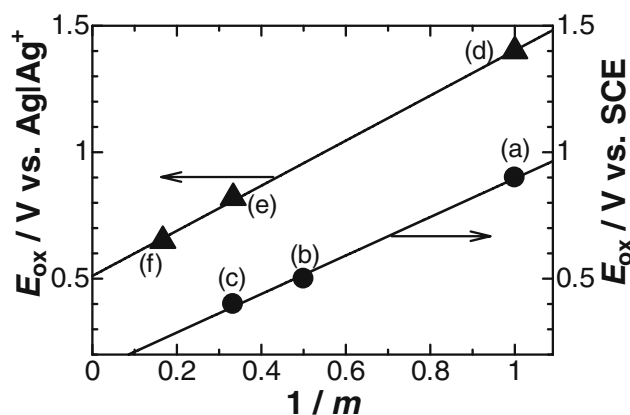


Fig. 6 Plots of the polymerization potentials of a aniline, b MeO-Ph-NH-Ph-NH₂, and c MeO-Ph-N-Ph-N-Ph-NH₂ in 1 M aqueous H₂SO₄ solution [22] against the inverse of the number (m) of nitrogen atoms, and those of d aniline, e MPB, and f PAB in acetonitrile solution including 0.2 M TBABF₄ against the inverse of m . Attention should be paid to the difference in reference electrodes

has the thickness of 0.5 μm . The resistance of the film was measured by putting a copper foil on the film after the film was dried in vacuum in 1 day. The conductivity of the film was $1 \times 10^{-4} \text{ S cm}^{-1}$.

We plotted the oxidation potentials of PAB and aniline in acetonitrile solution against the inverse of the number, m , of the redox sites per monomer in Fig. 6, where $m=6$ and 1 for the former and the latter, respectively. As an intermediate species ($m=3$), we determined the anodic potential of the second voltammetric wave of MPB (Fig. 1). The plot of the three species fell on a straight line, of which slope is 0.89 V. This value can be converted into the interaction energy, 86 kJ mol^{-1} , by multiplying F [18]. The linear variation for starburst conducting species may be reported for the first time, to our knowledge. As a control experiment, the anodic voltammetric potentials of methoxy-capped oligoanilines for $m=2$ and 3 in aqueous 1 M H_2SO_4 solution [25] are plotted against $1/m$ in Fig. 6. It is meaningful to compare the two kinds of slopes in Fig. 6, but it is meaningless to compare the potential values of Fig. 6a–c with those of Fig. 6d–f. The points fell on a line of which slope was 0.76 V. This value is close to that for the starburst compounds. The interaction energy, 86 kJ mol^{-1} , corresponds to the sum of three *para*-interactions of N and N^+ through the phenyl group (28 kJ mol^{-1} per *para*-interaction [25]). Three redox sites of the six may participate in the polymerization.

Conclusion

PAB composed of six arylamines with a starburst type was oxidized electrochemically to yield electrically conducting polymer film. The polymer showed the redox potential similar to polyaniline film in acetonitrile. The oxidation potential was much less than that of aniline because of the

stabilization of cation radicals with the other arylamines through phenyl groups. The linear relation of the oxidation potential with $1/m$ was valid even for the starburst compounds.

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