

Electrochemically Oxidative Polymerization of Aniline in Aromatic Copolyamide Matrix

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SYNOPSIS

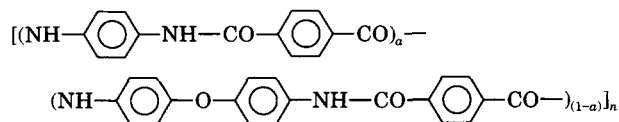
Composite films from polyaniline (PAn) and a copolyamide, poly(*p*-phenylene terephthalamide/diphenylether terephthalamide) (PPDTA), have been obtained by the electrochemical polymerization of aniline on a PPDTA/Pt (or Ni, stainless steel) working electrode in water or a mixed-solvent electrolyte solution. This PAn/PPDTA composite has higher mechanical properties than does the PPDTA matrix and the electrical conductivity close to pure PAn. The electrochemical polymerization of aniline can be carried out only in the electrolyte solution with $\text{pH} < 2$. The PAn/PPDTA film is electroactive material and very stable in air. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

It was discovered 130 years ago that the product of the anodic oxidation of aniline in aqueous sulfuric acid solution at a platinum electrode is a dark green precipitate.¹ Subsequent investigations indicated that the precipitate is polyaniline.² Polyaniline (PAn) with high conductivity has been studied only for slightly more than 20 years.³⁻⁹ Currently, it is arousing considerable interest as a novel stable conducting polymer⁴⁻⁹ and has interesting properties as materials for rechargeable batteries⁵ electrochromic display devices,¹⁰ etc.

It is known that PAn can be obtained by the chemical oxidative method and the electrochemical oxidative polymerization method.^{11,12} Even though PAn has the properties of high conductivity, stability in air, and low specific gravity, the difficulty of processibility restricts its application.

Copolyamide poly(*p*-phenylene terephthalamide/diphenylether terephthalamide) (PPDTA) is one of the lyotropic liquid crystal polymer:



which was obtained by modification of poly(*p*-phenylene terephthalamide)¹³ and has excellent mechanical properties and processibility. We think that a new material with high conductivity and higher mechanical properties can be obtained if PAn is composited with PPDTA.

In this paper, the electrochemical polymerization of aniline in the PPDTA matrix to form conducting composite PAn/PPDTA, cyclic voltammographs, SEM, and IR spectrum are reported.

EXPERIMENTAL

Starting Material

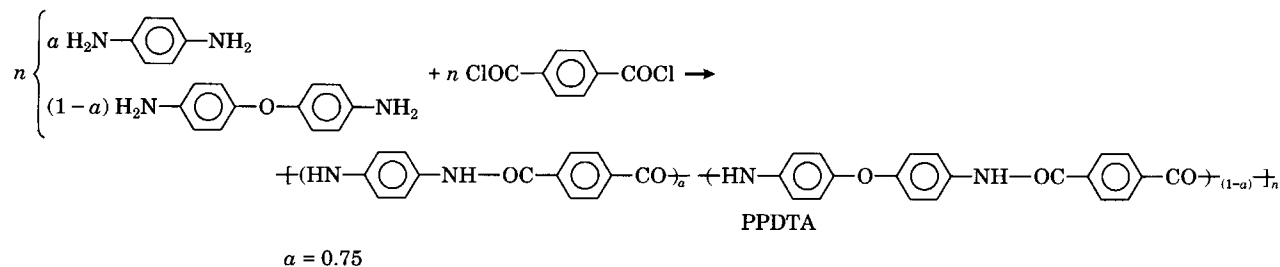
N-Methyl-pyrrolidone (NMP) of chemical pure (C.P.) grade was purified by vacuum distillation: b.p. 95°C/20 mmHg, then dried by 4A molecular sieves. *p*-Phenylene diamine (PPD) of C.P. grade was pu-

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rified by vacuum distillation: b.p. 150°C/15 mmHg. 4,4'-Diaminodiphenyl ether (DDE) was C.P. grade without further purification. *p*-Phthaloyl chloride, of C.P. grade, was the commercial product of Jiang-

Xi Agriculture Drugs Co. Aniline of C.P. grade was redistilled: b.p. 183–185°C.

Preparation of Copolyamide PPDTA



This preparation was carried out following the literature.¹³

Preparation of PPDTA/Pt (or Ni, Stainless Steel) Working Electrode

PPDTA was dissolved in concentrated H₂SO₄ (98%) to form a 6–10 wt % solution that was spread on a glass plate by a polished edge of another glass plate, then dipped into a water bath for the diffusion of H₂SO₄. A smooth, transparent matrix film that has good mechanical properties and thickness of about 20 μm was obtained. Then, the Pt slice was tightly wrapped by the matrix film to form a PPDTA/Pt working electrode.

Polyaniline Composited with PPDTA film

A PPDTA-coated Pt working electrode, a bare Pt slice counter electrode, supporting electrolyte (H₂SO₄, TsONA, Na₂SO₄; mixed electrolyte), 0.3–0.5 mol aniline, and solvents (water or acetonitrile/ethylene glycol/water mixed solvent of volume ratio 1 : 1 : 1.5) were set in a one-compartment cell. The pH value of the solution was adjusted from 2 to 12, and constant current (1, 1.5, 2.0, 3.0, 10 mA/cm²) was applied to the working electrode immersed in the electrolyte solution for 3 min for preswelling. After 20–120 min of electrochemical polymerization, the PPDTA coating on the working electrode was peeled off the Pt slice. A free-standing conducting PAN/PPDTA composite film was obtained.

Characterization of the PAN/PPDTA Composite Film

The electrical conductivity was measured using the conventional four-point probe method. Mechanical properties were determined by the stress-strain

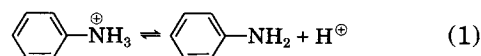
technique using an Instron Model 1122 machine at room temperature with a strain rate of 50 mm/min. Scanning electron micrographs were obtained on a Hitachi model S-530 microscope at an accelerating voltage of 25 kV. Infrared spectra were taken from a KBr pellet via a Specord 751R IR spectrometer. Instrumentation for the cyclic voltammetric experiments consisted of an HDV-7 Model constant potentiometer, XFD-8A Model ultrafrequency generator, and an LZ-3-104 X-Y recorder.

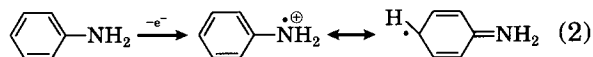
RESULTS AND DISCUSSION

Relation between the Concentration of PPDTA in H₂SO₄ to Form the Matrix Film and the Electrooxidative Reaction

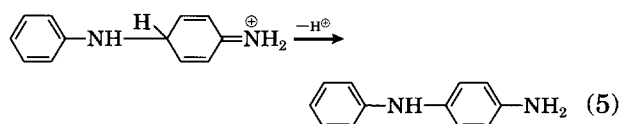
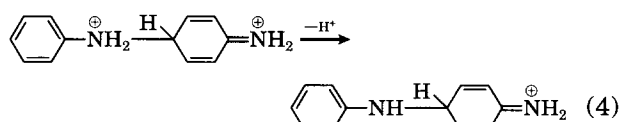
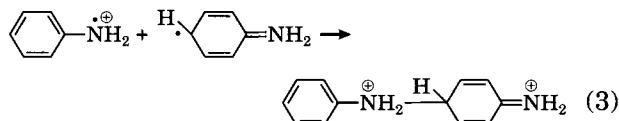
H₂SO₄ was diffused when the PPDTA/H₂SO₄ spread film on the glass plate was dipped in water. There were many small holes on the PPDTA film after the H₂SO₄ was diffused out to form a working electrode. Then, the Pt slice was wrapped by the PPDTA film. The necessary condition of the electrochemical polymerization of aniline is that the aniline molecules should pass through the small holes of the PPDTA film to the surface of Pt electrode, then polymerize at the Pt surface and grow through the PPDTA layer to the interface of PPDTA/electrolyte solution.

Experimental results showed that the aniline molecules could not pass through the matrix film when the concentration of PPDTA in H₂SO₄ is over 10%. Therefore, the electrochemical polymerization could not be carried out. That means that the oxidation reaction (2) of following equations cannot proceed¹⁴:





Then, the following polymerization reactions cannot proceed.



The electrochemical polymerization could proceed in the situation of the spread film made only at the concentration of PPDTA lower than 6 wt % in H₂SO₄ solution, and, finally, the PAN/PPDTA conductive composite film was obtained.

Electrical Conductivity of the PAN/PPDTA Composite Film

The electrical conductivity of the PAN/PPDTA composite films are influenced by many factors:

(1) Material of the Electrode

The electrical conductivity of the PAN/PPDTA film was almost the same when PPDTA/Pt and PPDTA/stainless-steel working electrodes were used (Table I), but the PPDTA/Ni working electrode did not work well, because there were many bubbles generated in the beginning of the electrochemical oxidative reaction.

Table I Effect of the Materials of the Electrode to the Electrical Conductivity of PAN/PPDTA Composite Film

Working Electrode	Electrical Conductivity (s/cm)
PPDTA/Ni	2.90
PPDTA/stainless steel	3.80
PPDTA/Pt	5.00

Current density: 2 mA/cm²; time: 60 min.

Table II Effect of Current Density to the Electrical Conductivity of PAN/PPDTA Composite Film

Current Density (mA/cm ²)	Electrical Conductivity (s/cm)
1.0	1.52
1.5	2.30
2.0	3.80
3.0	5.55
10.0	1.86

pH 2; time: 20 min; working electrode: PPDTA/Pt.

(2) Effect of the Current Density

The conductivity of the PAN/PPDTA film increased with the current density below 3 mA/cm². Polyaniline was oxidized when the current density was greater than 3 mA/cm²; then, the conductivity decreased (Table II).

(3) Effect of the pH Value of the Electrolyte Solution

The electrooxidative polymerization of aniline is very slow when the pH of the electrolyte solution is larger than 7. Some brown-red soluble substance was produced, and the brown-red matrix film as insulator was prepared.

Green-colored PAN was produced with 3 < pH < 7, a part of the PAN was composited with the PPDTA film with a conductivity of 10⁻⁴S/cm, and a large amount of the PAN was precipitated. Aniline was polymerized easily in the matrix film with pH < 2 and the conductivity of the composite film was around 10 s/cm.

(4) Effect of the Electrolyte

Mixed electrolytes are better than a single electrolyte (Tables III and IV).

Table III The Effect of Supporting Electrolyte to the Electrical Conductivity of PAN/PPDTA Wet Films

Supporting Electrolyte	Electrical Conductivity (s/cm)
H ₂ SO ₄	2.30
Na ₂ SO ₄ —H ₂ SO ₄	4.70
TsONa—H ₂ SO ₄	8.60

pH 2; time = 30 min; concentration of supporting electrolyte: 0.25M.

Table IV The Effect of Supporting Electrolyte to the Electrical Conductivity of PAN/PPDTA Dry Films

Supporting Electrolyte	Electrical Conductivity (s/cm)
Na ₂ SO ₄ —H ₂ SO ₄	1.27
TsONa—H ₂ SO ₄	1.88 × 10 ⁻¹
NaClO ₄ —H ₂ SO ₄	1.29
Et ₄ NClO ₄ —H ₂ SO ₄	7.20 × 10 ⁻²

Table V Stability of the Electrical Conductivity of PAN/PPDTA Composite Films in Air

Sample No.	Electrical Conductivity (s/cm)		
	New Film	After 30 Days	After 120 Days
1	6.43	4.90	6.5 × 10 ⁻¹
2	3.8 × 10 ⁻¹	1.3 × 10 ⁻¹	8.8 × 10 ⁻²
3	7.4	7.4	2.2 × 10 ⁻¹
4	1.02	9.0 × 10 ⁻¹	5.4 × 10 ⁻²
5	1.29	1.03	1.52 × 10 ⁻¹

(5) Stability of the Electrical Conductivity of the PAN/PPDTA Composite

The electrical conductivity remained unaltered when the composite film stood in air for 30 days. It had one order of magnitude lowering after 120 days in air (Table V).

Mechanical Properties of PAN/PPDTA Composite Film

The tensile strengths of the composite films that were made in the TsONa, Na₂SO₄, and NaClO₄ so-

lution with pH 2 are higher than or identical with the PPDTA matrix film, but the elongations at break are all lower than those of the matrix film (Table VI).

Electroactivity of PAN/PPDTA Film

Aniline polymerized on the PPDTA/Pt working electrode gave a similar cyclic voltammogram as on the bare Pt electrode. The only difference is 0.1 V of the oxidative voltage higher than using Pt electrode (Fig. 1).

IR Spectra of PAN/PPDTA and PPDTA

In comparison of the IR spectra of the PPDTA matrix film with the PAN/PPDTA composite film, a new peak appeared at 1175 cm⁻¹ of the PAN/PPDTA film, which is the S=O stretch vibration of TsO— (Fig. 2). For preparation of the composite film, TsONa was used as the supporting electrolyte and acetonitrile/ethylene glycol/water (1 : 1 : 1.5) were used as solvent.

Morphology of PAN/PPDTA

The SEM pictures of PAN/PPDTA composite films show that the composited PAN are small particles and the size of PAN particles on the surface facing the solvent are bigger than those on the surface facing the Pt electrode (Fig. 3).

CONCLUSIONS

1. A copolyamide poly(*p*-phenylene/*p*-diaminodiphenyl ether terephthalamide) (PPDTA) was obtained by the copolycondensation of *p*-phenylene diamine and 4,4'-diaminodi-

Table VI Mechanical Properties of PAN/PPDTA Film

Sample No.	Tensile Strength (N/mm ²)		Elongation at Break (%)	
	Matrix Film	PAN/PPDTA Film	Matrix Film	PAN/PPDTA Film
M-1	92.7	103.4	11.2	4.7
M-2	92.7	92.6	11.2	2.0
M-3	92.7	106.4	11.2	9.1
M-4	92.7	96.2	11.2	9.5
M-5	92.7	99.4	11.2	4.3

Supporting electrolyte: M-1, M-2, M-3: TsONa—H₂SO₄; M-4: Na₂SO₄—H₂SO₄; M-5: NaClO₄—H₂SO₄; pH: M-1 = 1; M-2, M-3, M-4, and M-5 = 2. Dry film.

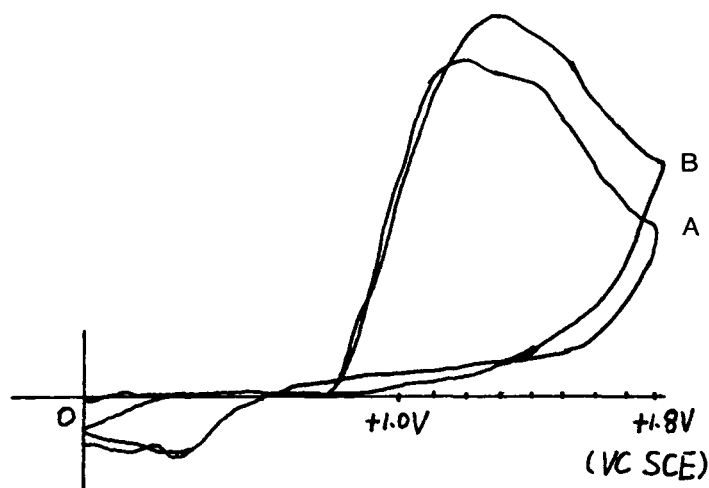


Figure 1 Cyclic voltammogram of the electrochemical polymerization of aniline. A: Pt electrode; B: PPDTA/Pt electrode; supporting electrolyte: TsONa—H₂SO₄, 0.25 M; scanning speed: 50 mv/s.

- phenyl ether with terephthaloyl chloride. Aniline was electrooxidatively polymerized on a PPDTA film-wrapped Pt working electrode to form a PAn/PPDTA composite film.
- The electrical conductivity of the PAn/PPDTA film is in the same order of magnitude as that of pure PAn: 10 s/cm. PAn/PPDTA is very stable in air.
 - The tensile strength of the PAn/PPDTA composite film is higher than that of the PPDTA matrix film. But the elongation at break is lower than that of PPDTA.
 - PAn/PPDTA composite film is an electroactive material.
 - PAn in PAn/PPDTA composite is in the form of small particles.

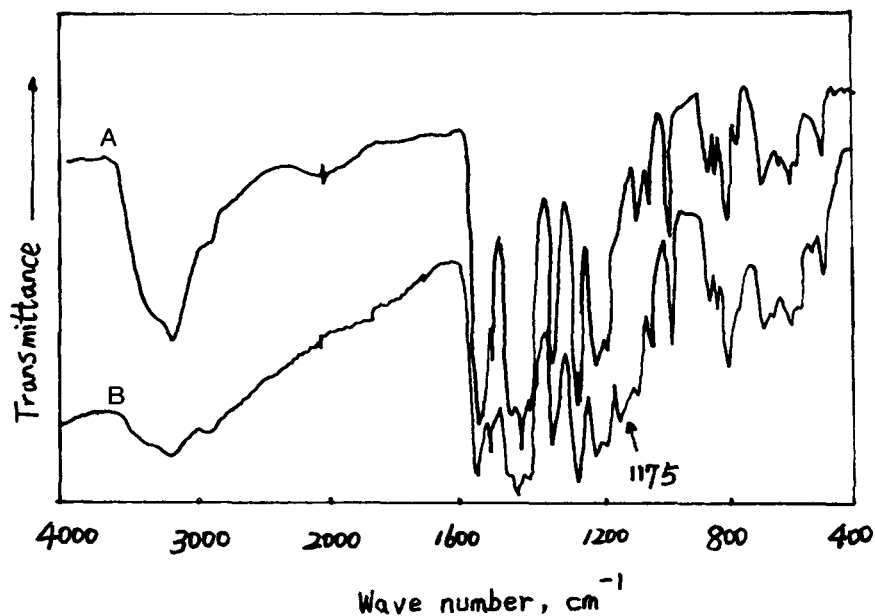


Figure 2 IR spectra of PPDTA and PAn/PPDTA film. A: PPDTA matrix film; B: PAn/PPDTA composite film; supporting electrolyte: TsONa—H₂SO₄.

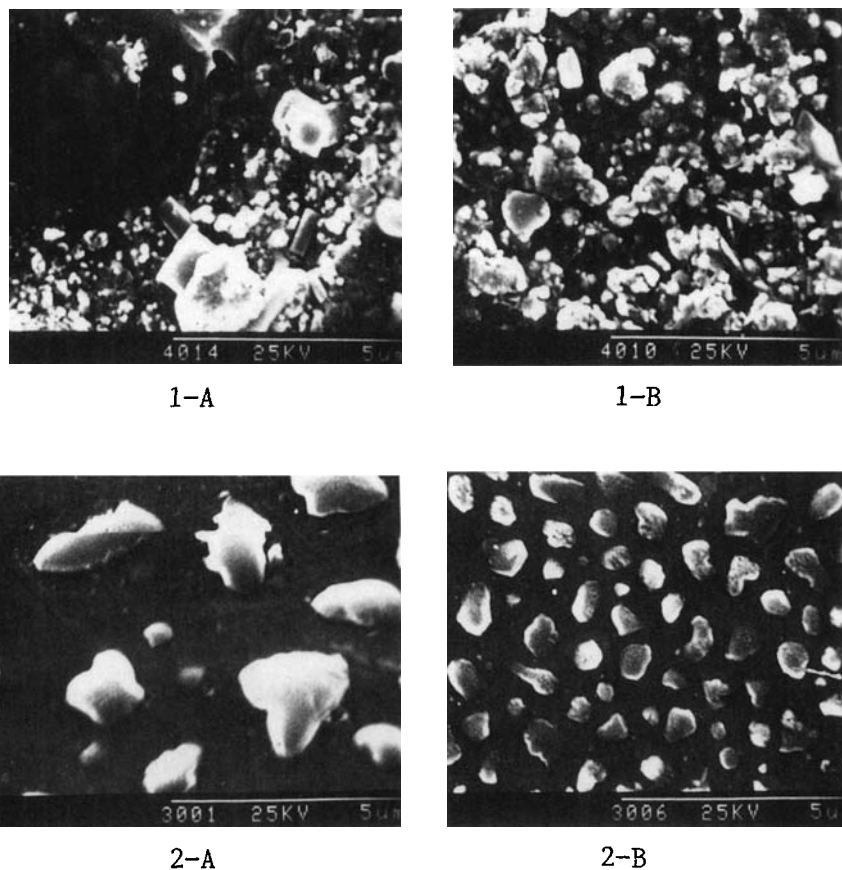


Figure 3 SEM pictures of PAN/PPDTA film.

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REFERENCES

1. H. Letheby, *J. Chem. Soc.*, **224**, 161 (1862).
2. (a) J. J. Coguillion, *Comp. Rend.*, **82**, 228 (1876). (b) F. Goppelroeder, *Comp. Rend.*, **82**, 331 (1876).
3. R. DeSurville, M. Jozefowicz, J. Perichon, and R. Buvet, *Electrochem. Acta*, **13**, 1451 (1968).
4. A. F. Diaz and J. A. Logon, *J. Electroanal. Chem.*, **111**, 111 (1980).
5. A. G. MacDiarmid, J. C. Chiang, M. Halpern, et al., *Mol. Cryst. Liq. Cryst.*, **121**, 173 (1985).
6. J. P. Travers, J. Chrobozek, et al., *Mol. Cryst. Liq. Cryst.*, **121**, 195 (1985).
7. R. J. Cushman, P. M. Macmanus, and S. C. Yang, *J. Electroanal. Chem.*, **219**, 335 (1986).
8. J. C. Chiang and A. G. MacDiarmid, *Synth. Met.*, **13**, 193 (1986).
9. M. Angelopoulos, A. Ray, A. G. MacDiarmid, and A. J. Epstein, *Synth. Met.*, **21**, 21 (1987).
10. S. Wawzonek and T. W. McIntyre, *J. Electrochem. Soc.*, **114**, 1025, 1350 (1967).
11. S. J. Wang and F. S. Wang, *Gao Fen Zi Xue Bao*, **2**, 120 (1988).
12. M. Abe, A. Ohter, Y. Umemoto, et al., *J. Chem. Soc. Chem. Commun.*, **22**, 1736 (1989).
13. J. S. Bao and X. J. Yang, *Synth. Fiber Ind.*, **4**, 1 (1981).
14. E. M. Genies and C. Tsintaus, *J. Electroanal. Chem.*, **195**, 109 (1985).

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