Experiment 11

CONDUCTING POLYMER - POLYANILINE

Objective

The purpose of this experiment is to synthesize conducting polymer, polyaniline (PANI), by chemical oxidative and electrochemical polymerization, and to study conductive and electrochromic properties of polyaniline.

Lab Techniques

- Setting up the electrolytic cell.
- Operating DC power supply and multimeter.

Introduction

I. Conducting polymers

Conducting polymers are novel polymers that conduct electricity in contrast to normal insulating polymers. One type of conducting polymers contains a long chain of conjugated double bonds (i.e., alternating double and single bonds), allowing delocalization of π electrons over a long distance, which is important for electric conduction. Fig. 11-1 lists structures of several common conducting polymers.

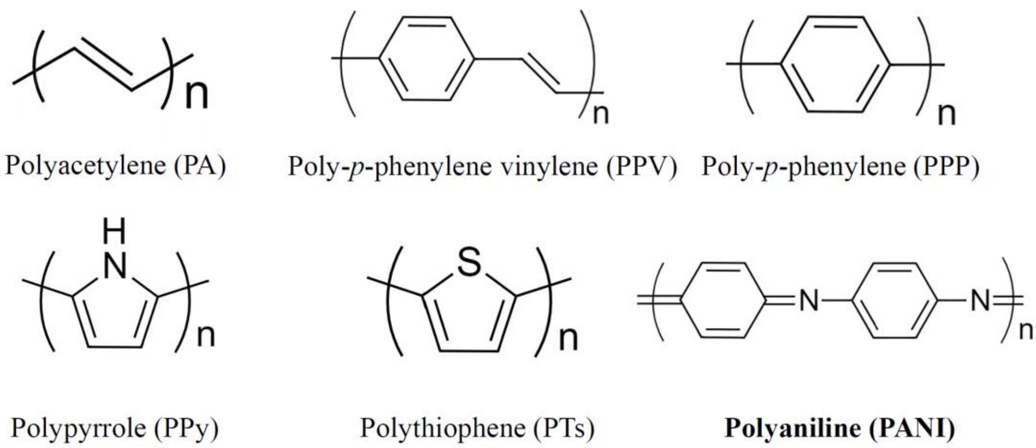


Figure 11-1 Common conducting polymers and their structures

II. Conductivity of polyaniline

Polyaniline is a polymer synthesized from the monomer aniline. Depending on the degree of oxidation, a polyaniline chain may contain two structural units A and

B as illustrated in Fig. 11-2. In unit A, two benzene rings are connected by an amine linkage (with sp^3-N) to give the reduced form. In unit B, benzene and quinoid rings are connected by an imine linkage (with sp^2-N) to give the oxidized form. Polyanilines can be classified as three different forms according to the ratio of the structural units A and B as listed in Table 11-1. These three forms are white leucoemeraldine (denoted as LE; exists as A form only), purple pernigraniline (denoted as PNB; exists as B form only), and green/blue emeraldine base (denoted as EB; exists as a mixture of A and B).

The band gaps of these polyanilines are similar to that of semiconductors. Like semiconductors, appropriate doping of polyaniline may reduce the band gap can increase its electric conductivity. When EB is exposed to acidic conditions, its imine nitrogen can be protonated (acid doping) to give the green emeraldine salt (denoted as ES) as shown in Fig. 11-3. The protonated imines and conjugated double bonds can form a series of radial cation-containing resonance structures (Fig. 11-4). Movement of radicals along the polymer chain accounts for the electric conductivity of polyanilines.

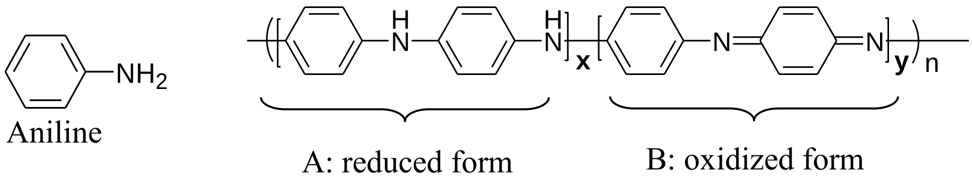


Figure 11-2 Aniline monomer and two structural units of polyaniline

Table 11-1 Three forms of polyanilines and their properties

Polymer	Degree of oxidation	Color	Property
Leucoemeraldine (LE)	y = 0 (All reduced form)	Colorless/white	No conductivity (E_g: 3~4 eV)
Emeraldine base (EB)	x > 0, y > 0 (With reduced and oxidized form)	Green/blue	No conductivity (E_g: 3~4 eV)
Pernigraniline (PNB)	x = 0 (All oxidized form)	Purple	No conductivity (E_g: 1.5~2.5 eV)

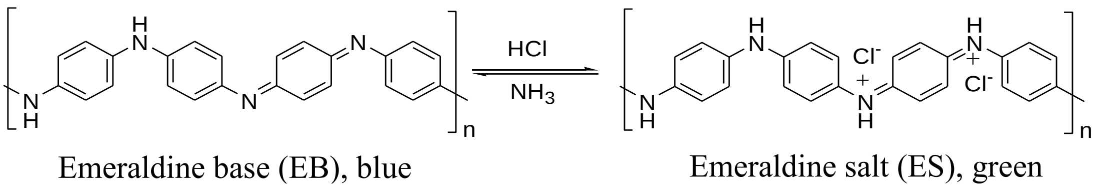


Figure 11-3 Protonated emeraldine base

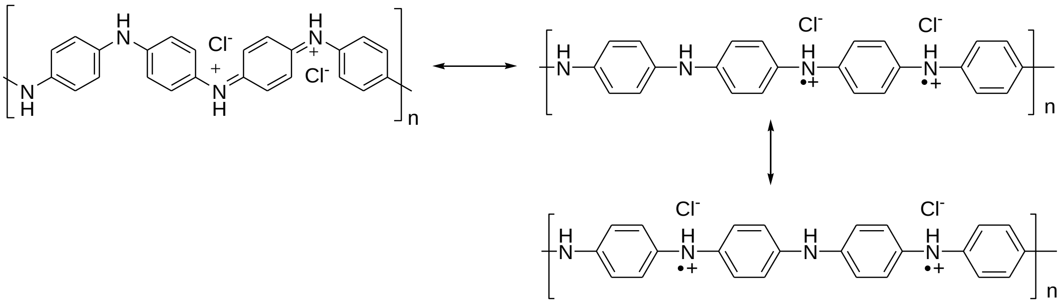


Figure 11-4 Resonance structures of polyaniline radical cations

III. Synthesis of polyaniline

In this experiment, chemical oxidative and electrochemical polymerizations are used to synthesize PANI. ES form of PANI is prepared to test its electric conductivity. The electrochromism of PANI is also examined.

1. Chemical oxidative polymerization

In the chemical method, aniline is oxidized by ammonium persulfate, $(NH_4)_2S_2O_8$, to initiate the polymerization to give the ES form of PANI. The ES form is insoluble in aqueous solution and can be obtained by filtration. The reaction is given by Fig. 11-5. The best yield of the reaction is achieved by using a molar ratio of ammonium persulfate to aniline of 1.25.

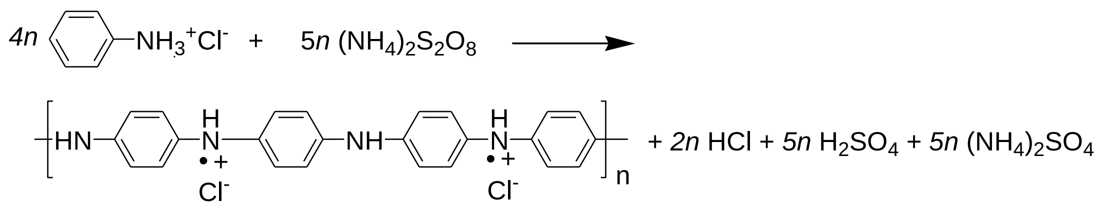


Figure 11-5 Oxidative polymerization of aniline by ammonium persulfate

2. Electrochemical polymerization

The electrochemical polymerization is similar to electroplating. Aniline hydrochloric acid is used as the electrolyte. Indium tin oxide (ITO) coated conducting glass is used as the anode, which is connected to the positive pole of DC power supply. Aniline is oxidized on the anode to form radical cations, which are polymerized to give an insoluble polyaniline film coated on ITO glass.

Apparatus

Multimeter, DC power supply & connecting wires, connecting wire with two alligator clips, 30 mL beaker (3), 50 mL beaker (3), binder clip (2), timer, conducting glass

(ITO glass), microslide (2), filter paper strip (2 cm x 4 cm), copper wire (2), LED lamp, tweezers, transparent tape, hair drier, ruler, and petri dish (shared).

Chemicals

0.4 M aniline hydrochloride, $C_6H_5NH_2 \cdot HCl$

0.5 M ammonium persulfate, $(NH_4)_2S_2O_8$

0.5 M aniline hemisulfate, $C_6H_5NH_2 \cdot 1/2H_2SO_4$

95% ethanol, C_2H_5OH

20% sodium chloride, NaCl

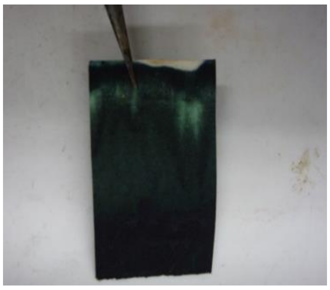
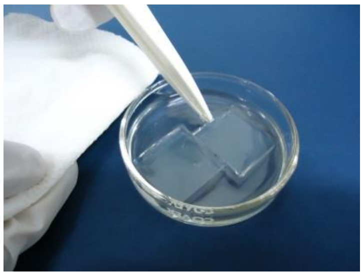
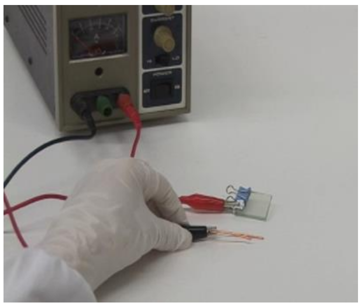
pH 2.5 hydrochloric acid solution, HCl(aq)

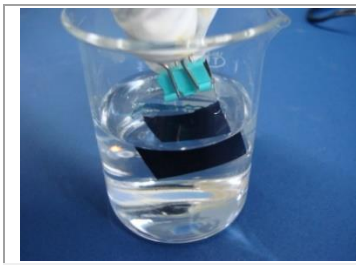
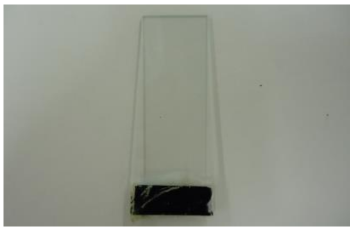
Procedure

★ Demo video: http://www.youtube.com/user/ntuchemistrylab

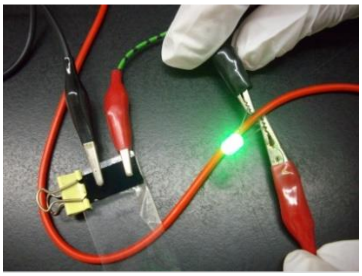
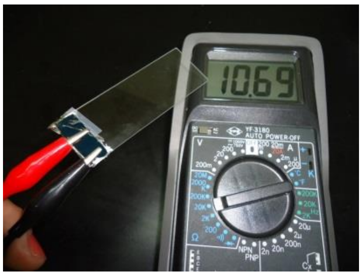
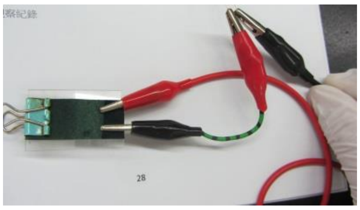
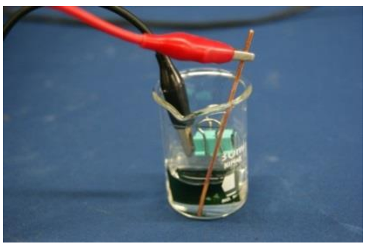
★ The reactants are toxic and may be absorbed from skin. Put the latex gloves on.

	Procedure	Illustration
I. Chemical synthesis of PANI		
1.	Preparation of reagents: (1) Use a binder clip to hold a filter paper strip and place into a 30 mL beaker. (2) Measure 5 mL aniline hydrochloride and 5 mL ammonium persulfate solutions; pour them into beaker; stir the solution thoroughly with a glass rod.	
2.	Synthesis of ES: Allow the polymer to grow on filter paper. Observe and record the color change of the solution.	

3.	Completion of the polymerization reaction: After 5 minutes of polymerization, the solution becomes sticky and jelly like. Take the filter paper out and examine the extent of polymerization and coating; record the color of polyaniline.	
4.	Washing and drying of the polymer: Dip the PANI-coated filter paper into a pH 2.5 HCl solution, followed by DI water for washing. Blow the filter paper dry with a hair drier; fixed the filter paper on a microslide glass; and save it for the conductivity test. Note 1: Use two 50 mL beakers to hold 20 mL of pH 2.5 hydrochloric acid and DI water respectively for repeated washing. Note 2: Do not pick up the filter paper with bare hands to avoid touching the chemicals that may be corrosive.	 
II. Electrochemical synthesis		
5.	Cleaning ITO glass: (1) Pour 10 mL of 95% ethanol into a petri dish. (2) Immerse ITO glass into ethanol for cleaning; pick it up with tweezers and rinse it with DI water. Wipe it dry with clean paper towels. Note: Use tweezers to hold ITO glass to avoid contamination.	
6.	Connection to DC power supply (Fig. 11-6 (a)): (1) Hold the ITO glass with a binder clip and connect it to the positive end (red) of the power supply to serve as the anode. (2) Connect a copper wire to the negative end (black) of the power supply to serve as the cathode. Make sure the connections are correct.	

7.	Setting up the electrolytic cell: (1) Take 5~7 mL of $C_6H_5NH_3HSO_4$(aq) to a 30 mL beaker. Place the two electrodes into the solution. (2) Use a microslide to separate the two electrodes to avoid a short circuit. Note 1: You may place the beaker into an empty 100 mL beaker to avoid spilling over. Note 2: Keep binder clip from touching the solution to avoid contamination.	
8.	Electro-oxidative polymerization: Turn the power supply on and set the voltage at 3 V. Press OUTPUT button to start electrolysis for 3 min. Observe the color change of the reaction. Note: Reset all the adjusting knobs to zero before turning the power on.	
9.	Cleaning and drying of polymer: Dip ITO glass into a pH 2.5 HCl solution and then rinse it with DI water. Blow PANI dry with a hair dryer.	
10.	Preparation of PANI-coated tape (Fig. 11-6 (b)): Paste a strip of transparent tape onto the PANI-coated ITO glass; press the tape with fingers back and forth, allowing PANI to stick on the tape. Peel off the tape and fix it onto a microslide for conductivity test. Note: Do not use finger nail to press the tape to avoid cracks on PANI that affecting conductivity.	 

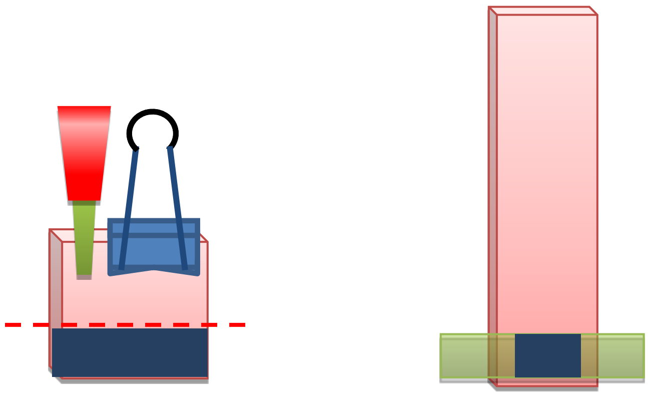
III. Conductivity test of polyaniline

11.	LED emission test: (1) Use alligator clips to connect the DC power supply, PANI-coated tape, and LED lamp. (2) Turn on the power supply and adjust the voltage to observe the emission of LED. Record the voltage.	
12.	Resistance test: Use alligator clips to connect the PANI-coated tape to a multimeter. Record the distance between the two clips and the resistance. Note 1: In each resistance measurement, clip with alligator clips at constant depth and spacing (about 1 cm). Note 2: Connection of the multimeter • Connect the anode (black) to the “COM” slot. • Connect the cathode (red) to the “Ω” slot. • Switch the function mode to maximum “Ω”; reduce it to the optimal range for testing.	 
13.	Conductivity test of the PANI-coated paper: Attach the strip of filter paper coated with PANI to a microslide. Repeat steps 11 and 12 to test it with the LED for conductivity, and the multimeter for resistance.	
IV. Electrochromic property of PANI		
14.	Preparation of the electrolyte: Measure 5 mL of 20% NaCl to a 30 mL beaker.	
15.	Electrochemical reduction of PANI: (1) Use alligator clips to connect the ITO glass to the negative end (black), and a Cu wire to the positive end (red) of a power supply. (2) Place the two electrodes into 20% NaCl solution. Apply 0.5~1.0 V of voltage to reduce PANI. Observe and record the color change of	

	PANI on the ITO glass.	
V. Waste disposal and cleanup		
16.	(1) Recycle ITO glass, microslides, and copper wires. Dispose the chemical wastes in appropriate waste containers. (2) Wash binder/alligator clips with DI water and wipe them dry to avoid rusting by chemicals. (3) Turn off the multimeter and DC power supply. Return the connecting wires.	

References

1. http://www.chemedu.ch.ntu.edu.tw/lecture/nobel.htm.
2. B. C. Sherman, W. B. Euler, and R. R. Force, *J. Chem. Educ.*, **1994**, *71*, A94.
3. R. Blair, H. Shepherd, T. Faltens, P. C. Haussmann, R. B. Kaner, S. H. Tolbert, J. Huang, S. Virji, and B. H. Weiller, *J. Chem. Educ.*, **2008**, *85*, 1102.
4. H. Goto, H. Yoneyama, F. Togashi, R. Ohta, A. Tsujimoto, E. Kita, and K. Ohshima, *J. Chem. Educ.* **2008,** *85*, 1067.



(a) (b)

Figure 11-6 (a) ITO glass and PANI; (b) Fix PANI tape onto microslide