Experiment 11

CONDUCTING POLYMER — POLYANILINE

Objective

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

Lab Techniques

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

Introduction

I. Conducting polymers

Conducting polymer is a novel material that differs from the typical insulating polymers (plastics) used in everyday life. Conducting polymer is capable of conducting electricity, combining the seemingly contradictory properties of conductors and plastics. Due to its lightweight nature and excellent processability, conducting polymer is increasingly used in various applications. Currently, it has been developed into lightweight and highly adaptable plastic batteries. Additionally, conducting polymer possesses electrochromic properties, allowing it to change color and transparency reversibly under an applied electric field. Therefore, after appropriate treatment, it can be used to manufacture car windows that can switch from transparent to opaque at the push of a button, effectively blocking out intense sunlight.

Several representative conducting polymers are shown in Fig. 11-1. Analyzing the structures of these polymers, it can be concluded that their backbones all have conjugated systems. Such polymers are also called conjugated polymers. A conjugated system refers to a structure where single and double bonds alternate and repeat. This conjugated structure is the primary requirement for a polymer to conduct electricity. Due to the parallel arrangement of *p* orbitals of a series of atoms on the polymer backbone (mainly carbon atoms; nitrogen and/or other atoms in some cases) within the conjugated structure, these *p* orbitals can overlap, as shown in Fig. 11-2. The more *p* orbitals that are aligned in parallel, the greater the extent of overlap. Thus, when there are free electrons on this polymer chain and a voltage is applied across both ends of the polymer, the free electrons can move along these regions following the electromotive force.

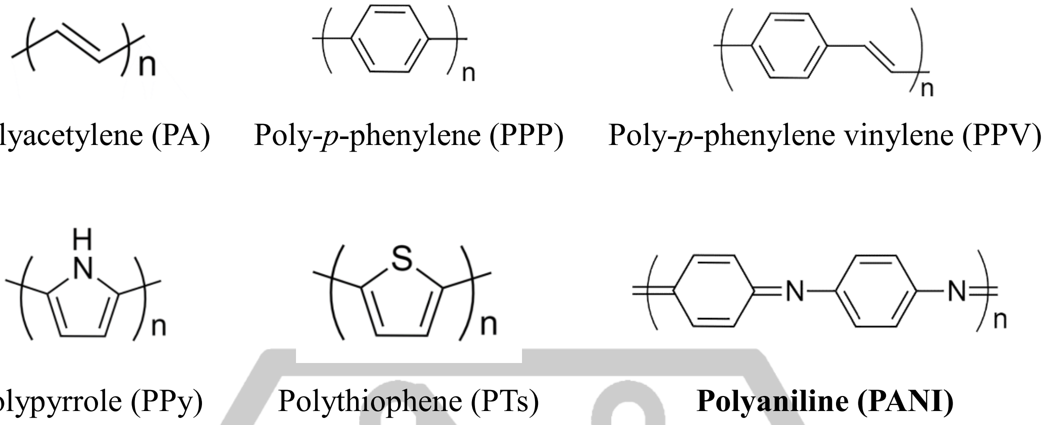


Figure 11-1 Common conducting polymers and their structures

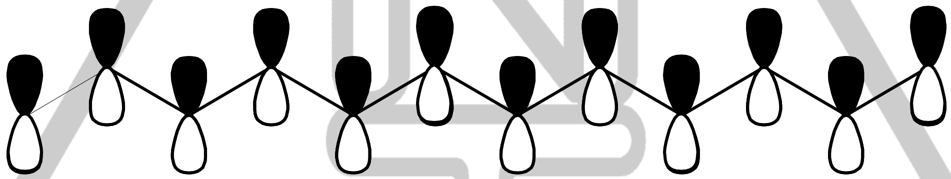


Figure 11-2 Parallel aligned *p* orbitals in the conjugated structure

II. Conductivity of polyaniline

Polyaniline is a polymer synthesized from the aniline monomers by oxidative polymerization. Depending on the degree of oxidation, a polyaniline chain may contain two structural units A and B as illustrated in Fig. 11-3. In unit A, two benzene rings are connected by an amine linkage (with sp^3-N) to give the benzene-benzene reduced form. In unit B, benzene and quinoid rings are connected by an imine linkage (with sp^2-N) to give the benzene-quinone oxidized form.

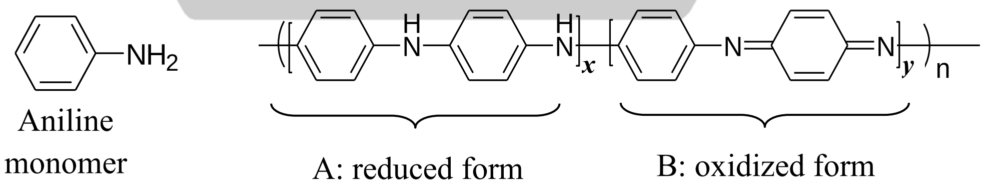


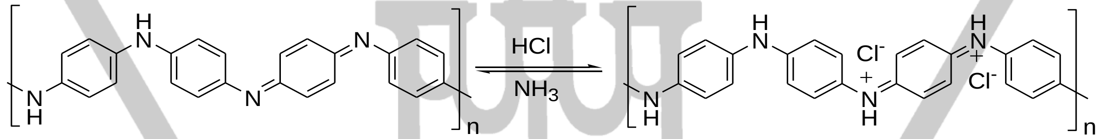
Figure 11-3 Aniline monomer and two structural units of polyaniline

Polyanilines can be classified into three different types according to the ratio of the structural units A and B as listed in Table 11-1. These three types 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 (E_g) of these polyanilines are similar to that of semiconductors. Like semiconductors, appropriate doping may reduce the band gap and increase the electric conductivity of polyaniline. 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. 11-4. The protonated imines and conjugated double bonds can form a series of radial cation-containing resonance structures (Fig. 11-5). The movement of radicals along the polymer chain accounts for the electric conductivity.

Table 11-1 Three types 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)



Emeraldine base (EB), blue   Emeraldine salt (ES), green

Figure 11-4 Protonation of emeraldine base

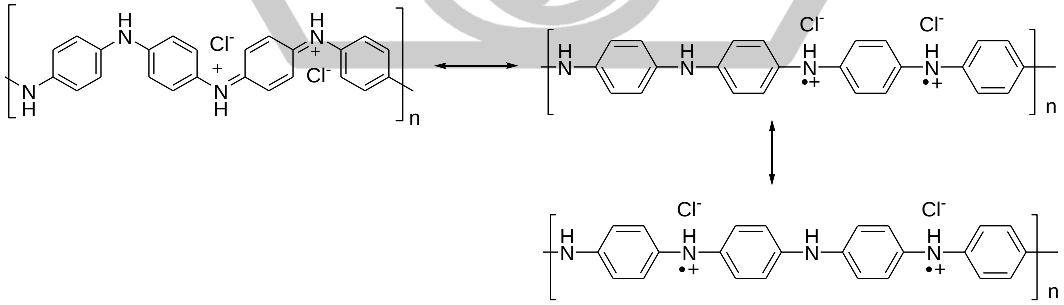


Figure 11-5 Resonance structures of polyaniline radical cations

III. Synthesis of polyaniline

In this experiment, aniline is used as the monomer to synthesize the conducting polymer polyaniline through two methods: chemical oxidative polymerization and electrochemical oxidative polymerization. The conductivity and electrochromic properties of the resulting material are measured and observed to understand the preparation methods and characteristics of this novel material.

1. Chemical oxidative polymerization

In the chemical oxidative method, aniline hydrochloride, $C_6H_5NH_2 \cdot HCl$, 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 polymerized on filter paper or obtained by filtration. The reaction is given by Fig. 11-6. The best yield of the reaction is achieved by using a molar ratio of ammonium persulfate to aniline of 1.25.

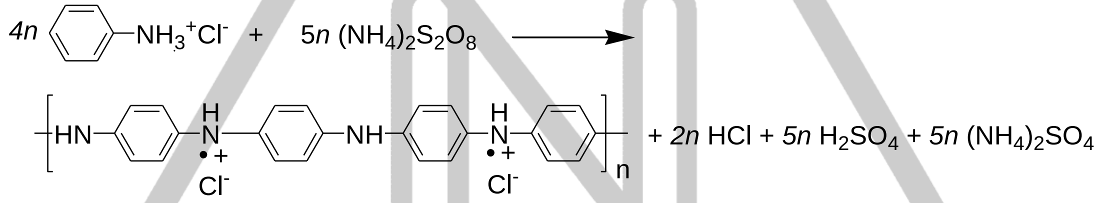


Figure 11-6 Oxidative polymerization of aniline hydrochloride by ammonium

2. Electrochemical oxidative polymerization

The electrochemical oxidative polymerization is similar to electroplating. Aniline sulfate, $(C_6H_5NH_2)_2 \cdot H_2SO_4$, is used as the electrolyte. Indium tin oxide (ITO) coated conductive glass is used as the anode, which is connected to the positive pole of the DC power supply. Aniline is oxidized on the anode to form radical cations, which are polymerized to give an insoluble polyaniline layer coated on the ITO glass.

3. Electrochromism

The ITO glass coated with polyaniline is connected to the negative pole of the DC power supply instead to perform a reduction reaction. In that case, it can be observed that the polyaniline coating appears in different colors depending on the degree of reduction. This phenomenon is named electrochromism, which means changing the color of the substance (color switching) by applying a voltage.

Apparatus

Multimeter, DC power supply & connecting wires, connecting wire with two alligator clips, 30 mL beaker (3), 50 mL beaker (2), binder clip (2), timer, conductive glass (ITO glass), microslide (2), filter paper strip (2 cm × 4 cm), copper wire (2), LED lamp, tweezers, hair drier, NBR gloves, and ruler.
Shared: petri dish and transparent tape.

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 sulfate, $(C_6H_5NH_2)_2 \cdot H_2SO_4$

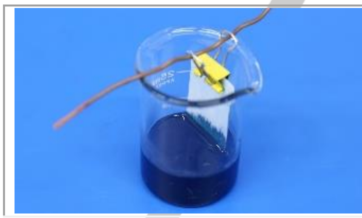
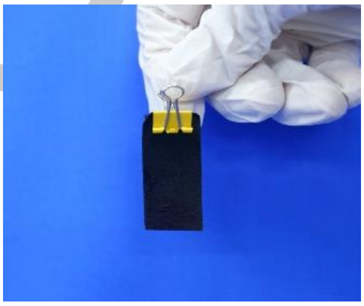
95% Ethanol, C_2H_5OH

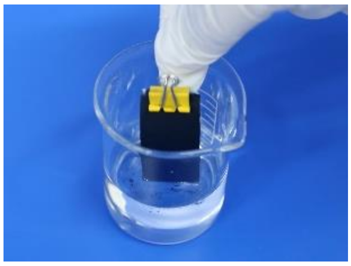
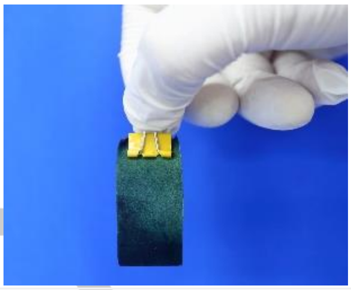
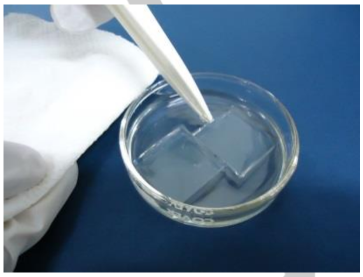
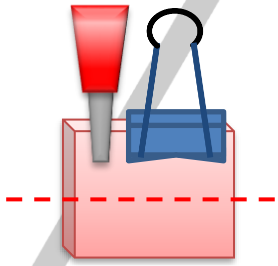
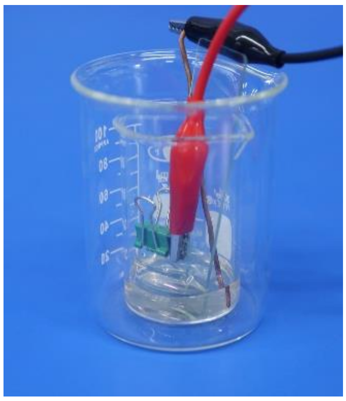
20% Sodium chloride, NaCl

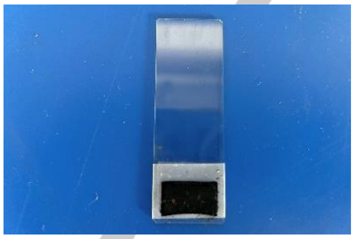
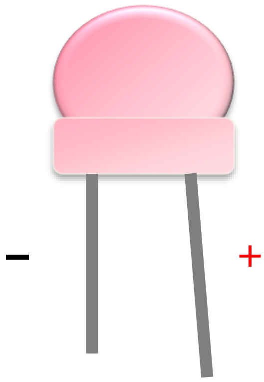
pH 2.5 Hydrochloric acid, HCl(aq)

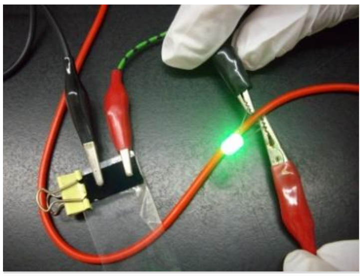
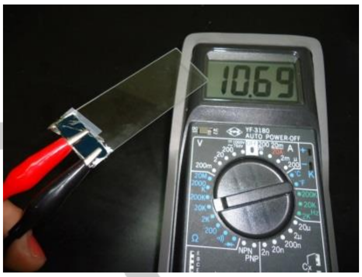
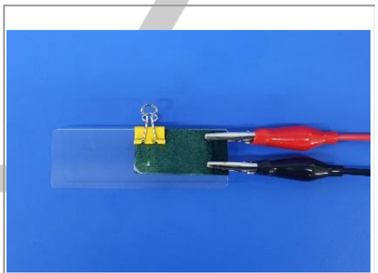
Procedure

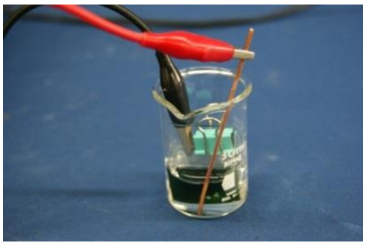
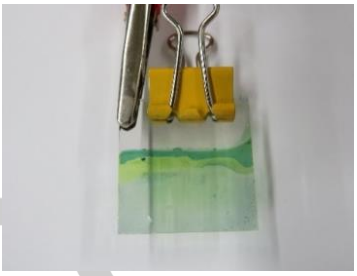
★ The reactants are toxic and may be absorbed by the skin. Put the NBR gloves on.

	Procedure	Illustration
I. Chemical oxidative synthesis of PANI		
1.	Preparation of reagents: (1) Use a binder clip to hold a filter paper strip and hang it into a 30 mL beaker. (2) Add 5 mL aniline hydrochloride and 5 mL ammonium persulfate solutions into the beaker; stir the solution thoroughly with a glass rod.	
2.	Synthesis of ES: Allow the polymer to grow on the filter paper. Observe and record the color change of the solution.	
3.	Completion of the polymerization reaction: After about 5 min. 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. Note: After the reaction, the polyaniline solution in the beaker is poured into the waste bottle first to avoid polyaniline coating on the beaker and making it difficult to clean.	

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 dryer; fix the filter paper on a microslide; 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.	 
II. Electrochemical oxidative synthesis of PANI		
5.	Cleaning ITO glass: Pour 10 mL of 95% ethanol into a petri dish. Immerse the ITO glass into ethanol for cleaning; pick it up with tweezers and rinse it with DI water. Wipe it dry with clean paper towels.	
6.	Connection to DC power supply: (1) Hold the ITO glass with a binder clip and connect it with an alligator clip to the positive pole (red) of the DC power supply to serve as the anode. (2) Connect a copper wire with another alligator clip to the negative pole (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 mL of aniline sulfate in 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: Place the beaker into an empty 100 mL beaker to avoid toppling over. Note 2: Keep the binder clip from touching the solution to avoid contamination.	

8.	Electrochemical oxidative polymerization: (1) Turn on the DC power supply, set the voltage output to 3.0 V, and then complete the connection of the positive and negative circuits. (2) Press the OUTPUT button to conduct the electrochemical reaction at this voltage for 3 min. Observe and record the color change on the ITO glass during the reaction. Note: Reset all 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. 11-7): Paste a strip of transparent tape onto the PANI-coated ITO glass; press the tape with your fingers back and forth, allowing PANI to stick on the tape. Peel off the tape and fix it onto a microslide for the conductivity test. Note: Do not use a fingernail to press the tape to avoid cracks on PANI that affect conductivity.	 
III. Conductivity of PANI		
11.	LED function test: (1) The longer pin of the LED is the positive (+) terminal. Connect it to the positive pole of the DC power supply using an alligator clip wire. The shorter pin is the negative (−) terminal; connect it to the negative pole using another clip wire. (2) Turn on the DC power supply and test whether the LED can emit normally with a voltage of about 2 V. If it doesn't work, replace the LED.	

12.	LED emission test: (1) Use alligator clip wires to connect the DC power supply, PANI-coated tape, and LED in series. (2) Turn on the power supply and adjust the voltage to observe the emission of LED. Record the minimum voltage of the emission.	
13.	Resistance measurement: Connect the tape coated with polyaniline and the multimeter using two alligator clip wires. Set the central function switch of the multimeter to the appropriate scale in the "Ω zone" and measure the resistance value. Record the multimeter's resistance measurement scale and the resistance reading with units. 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" port. • Connect the cathode (red) to the "Ω" port. • Switch the function mode to the maximum scale in the "Ω zone"; reduce it to the optimal scale for testing.	 10.69 kΩ 
14.	Conductivity test of the PANI-coated paper: Attach the strip of filter paper coated with PANI to a microslide. Repeat steps 12 and 13 to test it with the LED for conductivity, and the multimeter for resistance.	
IV. Electrochromic property of PANI		
15.	Preparation of the electrolyte: Measure 5 mL of 20% NaCl to a 30 mL beaker.	

16.	Electrochemical reduction of PANI: (1) Use alligator clips to connect the ITO glass used in step 10 to the negative pole (black), and a Cu wire to the positive pole (red) of the power supply. (2) Place the two electrodes into the 20% NaCl solution. Separate the electrodes by a microslide. Apply 0.5~1.0 V of voltage to reduce PANI. Observe and record the color change of PANI on the ITO glass. Note: The applied voltage should not be greater than 1.0 V to avoid side reaction.	 

V. Waste disposal and cleanup

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

References

1. https://teaching.ch.ntu.edu.tw/nobel/2000/
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.
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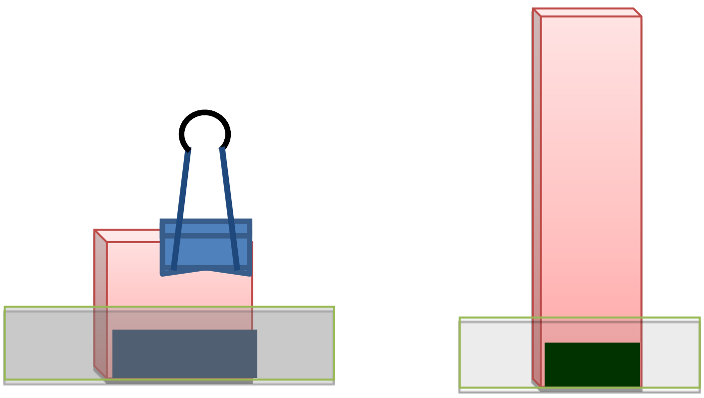

(a) (b)

Figure 11-7 (a) Use a sticky tape to adhere PANI on ITO glass.
(b) After tearing off the tape, fix the tape on a microslide with the PANI side facing outward.