Title: Conducting Polymer: Polyaniline

Author(s): Lin, Terri C.

Intended for: Report

Terri Lin
3/18/13

Conducting Polymer: Polyaniline

1. Introduction

Electronically conductive polymers composites have gained tremendous attention over the last decade due to their unique properties for various applications such as rechargeable batteries, electromagnetic shielding, sensors and electronic devices [1]. Polyaniline has been one of the most popular conducting polymer for the past fifty years [2]. It has low density, good environmental stability, moderate conductivity and is considered as one of the most promising electrically conducting polymers [1]. Polyaniline exists in three forms (Fig. 1): Leucoemeraldine, pernigraniline, and emeraldine [3]. Leucoemeraldine is the fully reduced state and is white/clear colorless [3]. Pernigraniline is the fully oxidized state with imine links instead of amine links and is blue/violet [3]. The emeraldine form of polyaniline, often referred as emeraldine base (EB), is neutral and blue.

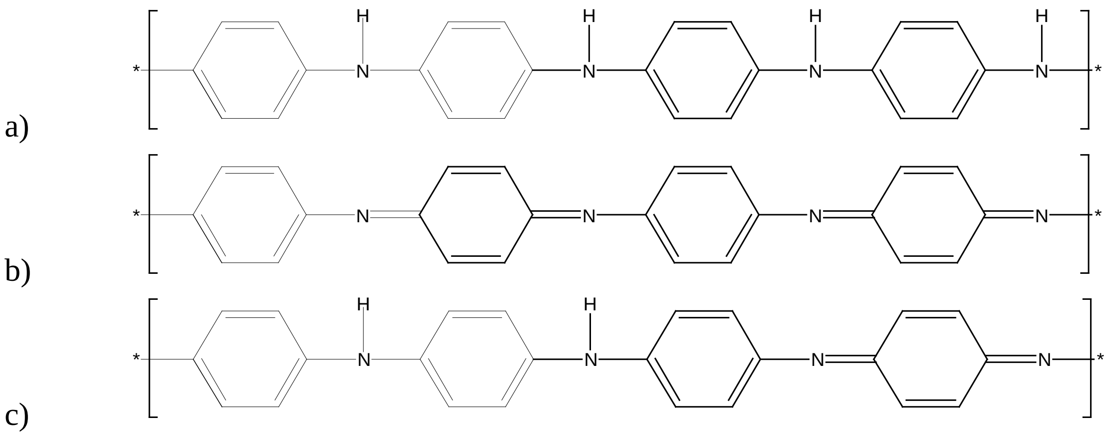


Figure 1. Three different forms of emeraldine base: (a) Leucomeraldine, (b) pernagraniline, (c) emeraldine base.

When EB is doped, it turns green and is called emeraldine salt (ES) with the imine nitrogens protonated by an acid [3]. EB delocalizes to the trapped diiminoquinone-diaminobenzene state, which is highly electrically conducting [2]. Emeraldine base is regarded as the most useful form of polyaniline due to its high stability at room temperature [2].

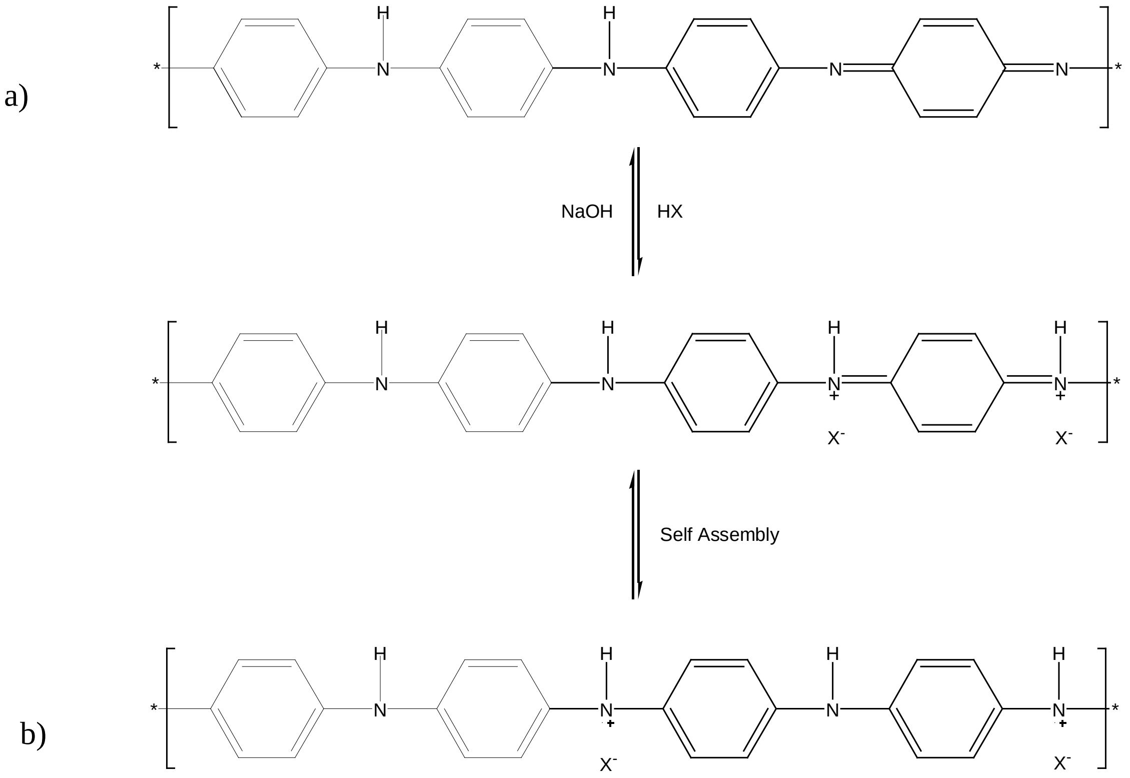
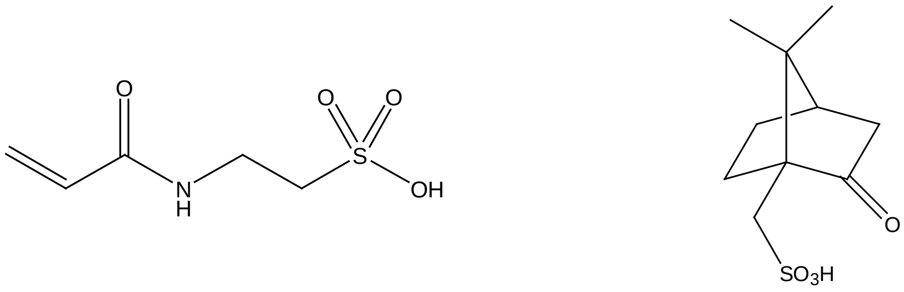


Figure 2. Doping mechanism of polyaniline emeraldine base (a) and salt (b) [4].

In this experiment, EB is doped with two different protonic acids (Fig. 3), 2-Acrylamido-2-methylpropane sulfonic acid (AMPSA) and camphorsulfonic acid (CSA), to compare the effectiveness of the dopants. The doped EB (ES) is later casted into films with a new resin to produce new polyaniline conductive composites and their conductivities are being studied.



(a) (b)

Figure 3. Structures of the dopants (protonic acids) used in the experiment: (a) 2-Acrylamido-2-methylpropane sulfonic acid (AMPSA) and (b) Camphorsulfonic acid (CSA).

2. Experimental

2.1. Chemicals

Polyaniline can be synthesized fairly easily. However, due to the time constraint, polyanilines used in this experiment were purchased from Sigma Aldrich. Three polyanilines were used: emeraldine base with M_w of ~10,000, long chain emeraldine salt (LES) with M_w of ~10231, and short chain emeraldine salt (SES) with M_w of ~9423. The ESs from Sigma Aldrich are already doped with ligno-sulfonic acid. However, doping is still performed to ensure the consistency of the doped samples. Protonic acids, 2-Acrylamido-2-methylpropane sulfonic acid (AMPSA) and camphorsulfonic acid (CSA), were also ordered from Sigma Aldrich.

2.2. Dopant Stability Study

Three solvents were chosen for doping due to their compatibility with the resin and their high volatile properties which is important during the film making process: Water, methanol and acetone. To find good doping solutions, six 0.1M acid solutions were made and monitored over time: (1) AMPSA/Water, (2) CSA/Water, (3) AMPSA/Methanol, (4) CSA/Methanol, (5) AMPSA/Acetone, (6) CSA/Acetone. UV-Vis spectra were taken right after the solutions were made and 24 hrs after to see if the solutions have remained stable.

2.3. Doping

0.1M Acid/Methanol solutions were chosen to be the doping acid solutions. The polymers were doped overnight due to polyaniline's poor solubility [5]. The reasoning is further discussed in the Results and Discussion session.

PANI	Amount of PANI (g)	Acid	Solvent	Amount of doping solution (mL)
EB	0.0251	AMPSA	Methanol	5
EB	0.0257	CSA	Methanol	5
LES	0.0252	AMPSA	Methanol	5
LES	0.0250	CSA	Methanol	5
SES	0.0255	AMPSA	Methanol	5
SES	0.0256	CSA	Methanol	5

Table 1. Doped Solutions

2.4. UV-Vis Spectroscopy

A Cary 5000 Scan UV-vis-NIR spectrophotometer was used to collect UV-vis-NIR spectra. The scanning range was from 300-800 nm for the dopant stability study and 300-2000 nm for the doping study. Diluted solutions were prepared for the spectral study using 2mm quartz cuvettes. For some samples, UV-vis-NIR spectra were collected at different concentrations to obtain the most reliable spectra. The spectral measurement was conducted at room temperature.

2.5. Films Preparation

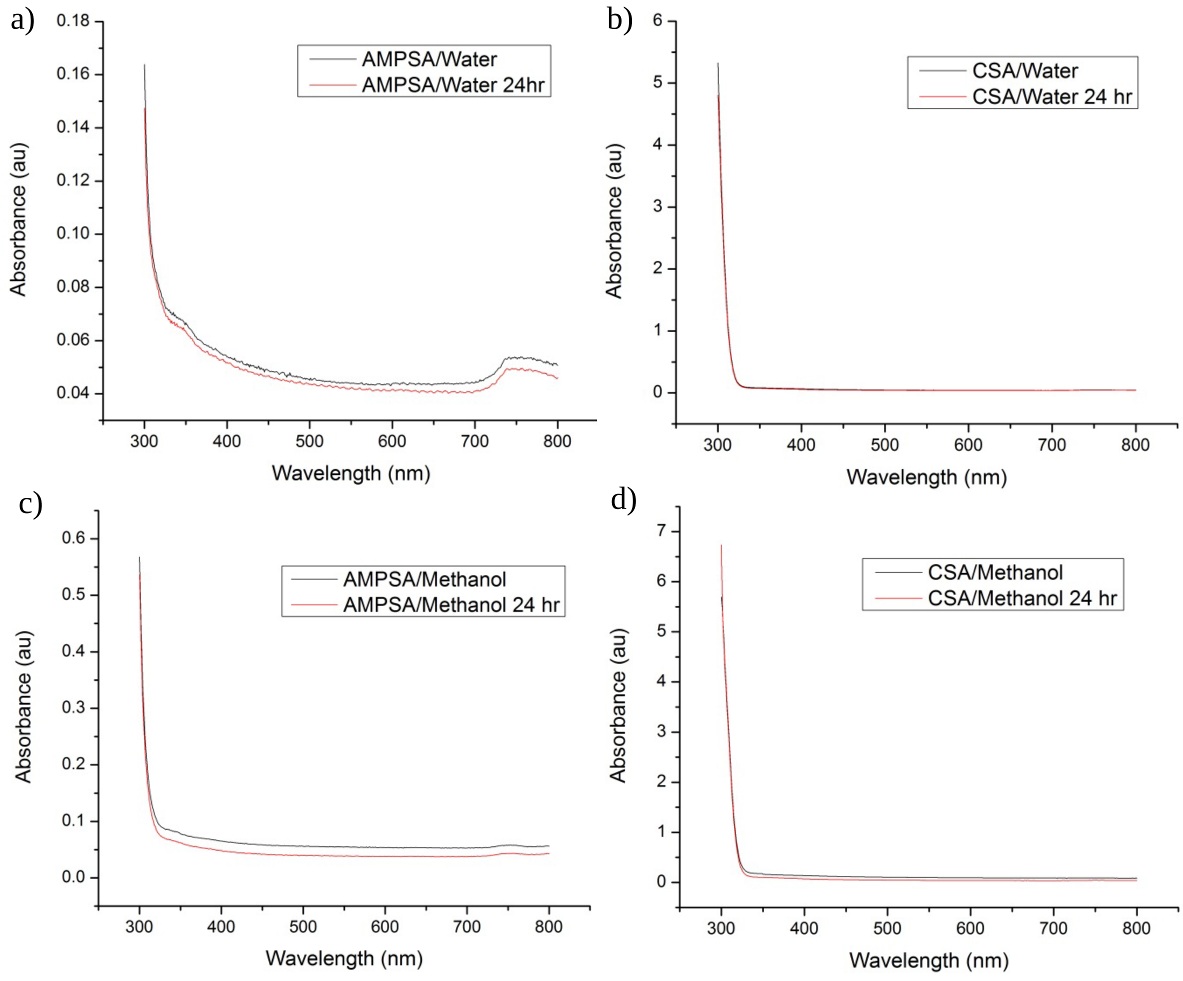
1 mL of doped EB/ LES/SES solutions were added to 1g of resin. Composition of the

resin is proprietary. Most of the methanol was evaporated in the hood for 40 hrs and the remaining was removed during the curing process. EB particles originally suspended in the methanol solutions were blended in the resin after the methanol had evaporated.

3. Results and Discussion:

3.1. Dopant stability study

Doping solutions are monitored because they have to remain stable throughout the doping process in order to maximize the efficiency. As mentioned earlier, water, methanol, and acetone were chosen as the solvents due to their high volatile nature and their compatible with the resin, which was used to make films.



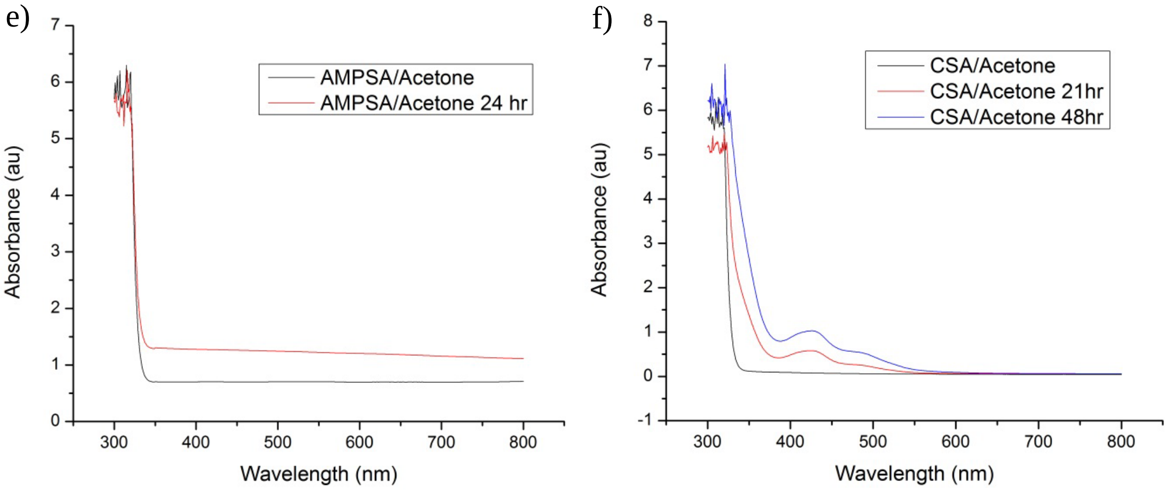


Figure 4. UV-Vis spectra of (a) AMPSA/Water, (b) CSA/Water, (c) AMPSA/Methanol, (d) CSA/Methanol, (e) AMPSA/Acetone, (f) CSA/Acetone. CSA in acetone was monitored for an extra day because significant change has been found over the first 24 hours.

Acetone is the least favorable solvent due to its reactive nature. UV-Vis spectra (Fig. 4) have indicated that CSA/Acetone has a significant change over time while the rest of the solutions have stayed constant. Acetone is unstable because there is a possibility for the ketone group to react with the sulfonic group on the acids. Besides the distinguish spectra, color change is also an indicator of unstable solutions. CSA/Acetone has changed from clear to yellow in 24 hrs and to dark brown in 48 hrs. There are a few possible mechanisms regarding the CSA/Acetone reaction. Further analyses such as NMR and IR have to be performed in order to understand the reaction better. In addition, AMPSA has poor solubility in acetone. AMPSA's solubility in acetone is 0.004M which is extremely low and inefficient for the doping process.

Compare to acetone, water and methanol are more stable. However, water does not blend well with the resin and it requires a longer time to evaporate from the resin. Methanol is therefore the ideal solvent for the doping process. Both CSA and AMPSA dissolve in methanol and have remained stable.

3.2. Doping

Color change and UV-Vis are used to confirm that the EB/LES/SES have been doped. When EB is not protonated, there are two peaks – the benzenoid (B) peak (310-340 nm) and quionoid (Q) peak (610-660 nm) corresponding to the $\pi - \pi*$ transition [6]. In organic acid solutions, EB is usually in the protonated form [6]. If EB is fully protonated, there is one polaron peak (Peak II) between 410-490 nm with a free carrier tail (Peak III) in the NIR region (Fig. 5) as the literature shows [6]. Even though the solvents used in the literature are different, the polymers are expected to behave the same way.

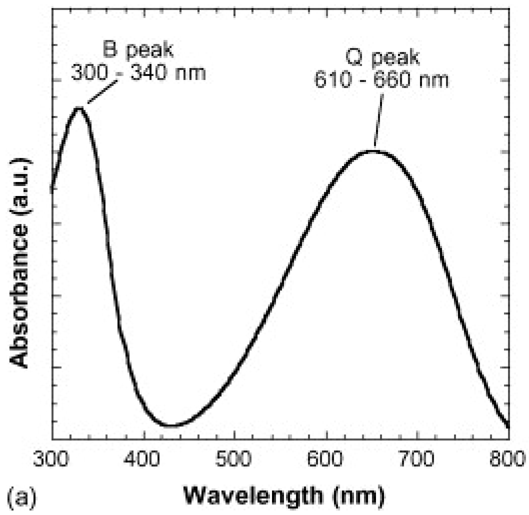


Figure 5. UV-Vis spectra of EB in N-Methyl-2-pyrrolidone (NMP) and doped PANI in 2-4 Dichlorophenylacetic Acid (DCAA) [6].

The free carrier tail, Peak III should be equivalent to the quionoid (Q) peak [6]. The H-bonding complexes between acids and EB cause the large shift on the Q peak [6]. We speculate that the bulky AMPSA and CSA molecules insert between the EB molecules and cause these EB molecules to separate and take up expanded coil conformation (Fig. 6) [6].

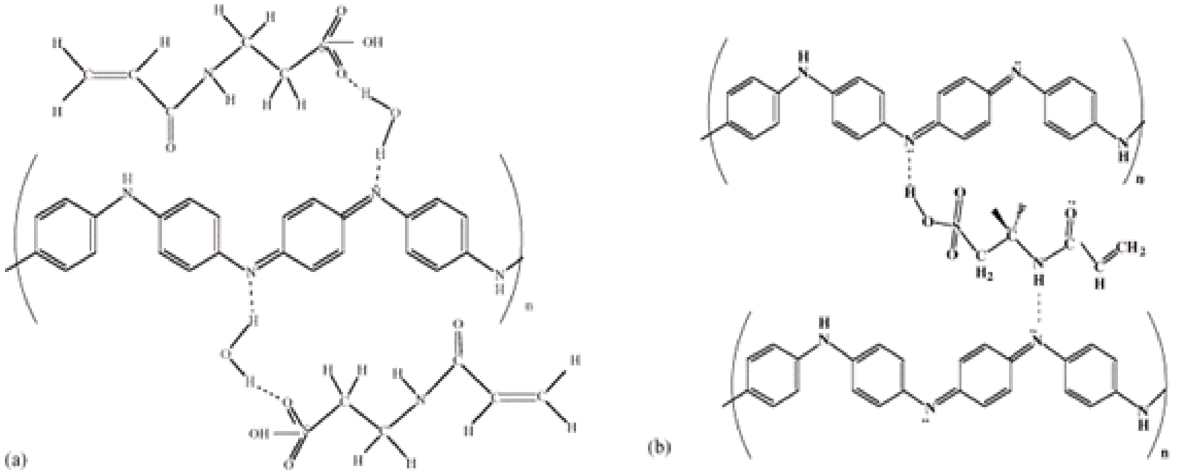


Figure 6. Possible H-bonding between EB and AMPSA molecules [6]. CSA are expected to behave the same way since it also has a sulfonic group .

The UV-Vis spectra of the doped EB solutions were hard to obtain due to methanol’s high absorbance nature (Fig. 7).

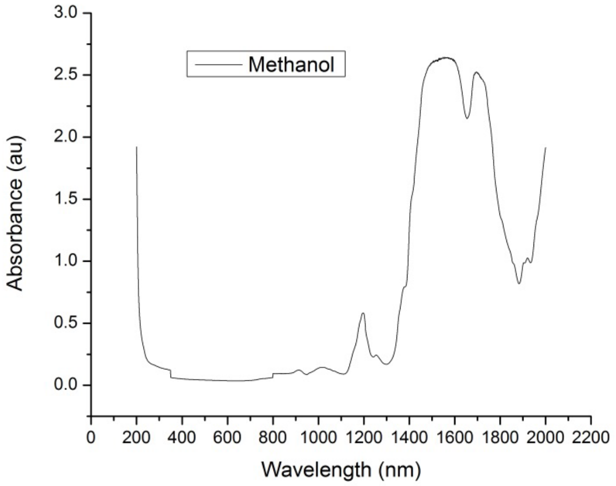
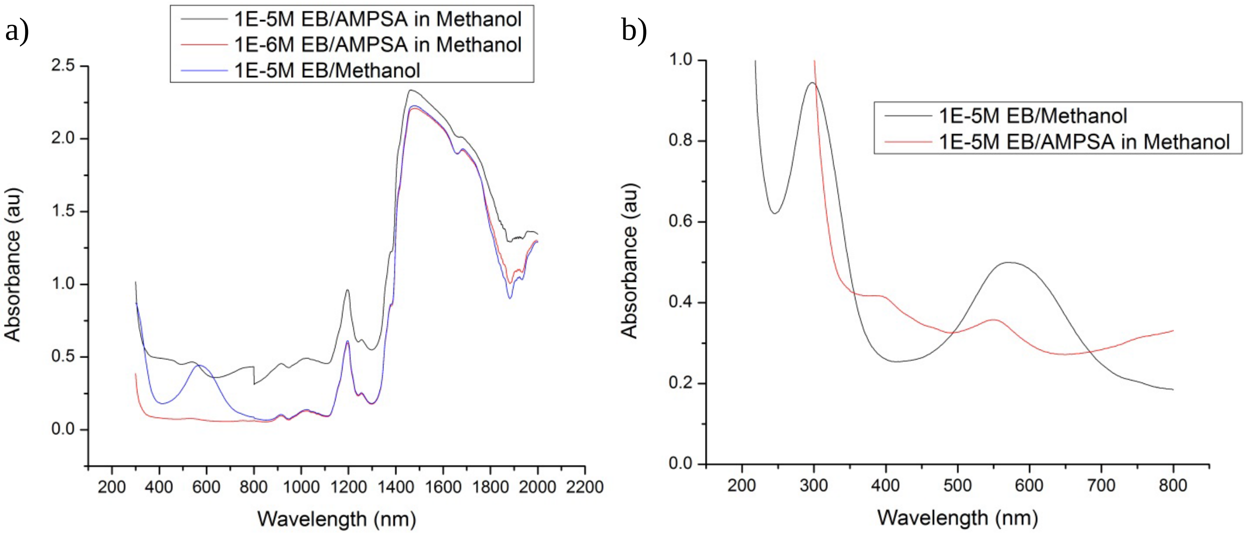


Figure 7. UV-Vis spectrum of pure methanol.

Many different parameters were tried before finding the optimal setting. The glitch at 800 nm is the detector change and at 350 nm is the source change. The dip is also visible in the 1E-5M EB/AMPSA in Methanol spectrum (Fig. 8). The glitch disappeared when the solution is run at a lower concentration but most features before 800 nm become indistinguishable. When the spectra are zoomed into 200 – 800 nm, the doped and undoped spectra are very distinctive. The benzenoid (B) peak at 300-340 nm and the quionoid (Q) peak at 610-660 nm for undoped EB showed up at the same positions as the literature. However, for AMPSA doped EB, only the polaron peak ~400 nm and the quionoid (Q) peak ~550 nm appeared. The benzenoid (B) peak and the H-bonding free carrier tail is very likely to be buried under the strong methanol peaks before 300 nm and after 900 nm. On the other hand, all peaks except the free carrier tail due to H-bonding showed up for CSA doped EB: Benzenoid (B) peak ~300 nm, polaron peak ~400 nm and the quionoid (Q) peak ~550 nm. The dramatic decrease in the intensity of the quionoid (Q) peaks also further confirms the occurrence of the protonation at the imine nitrogen sites [7].



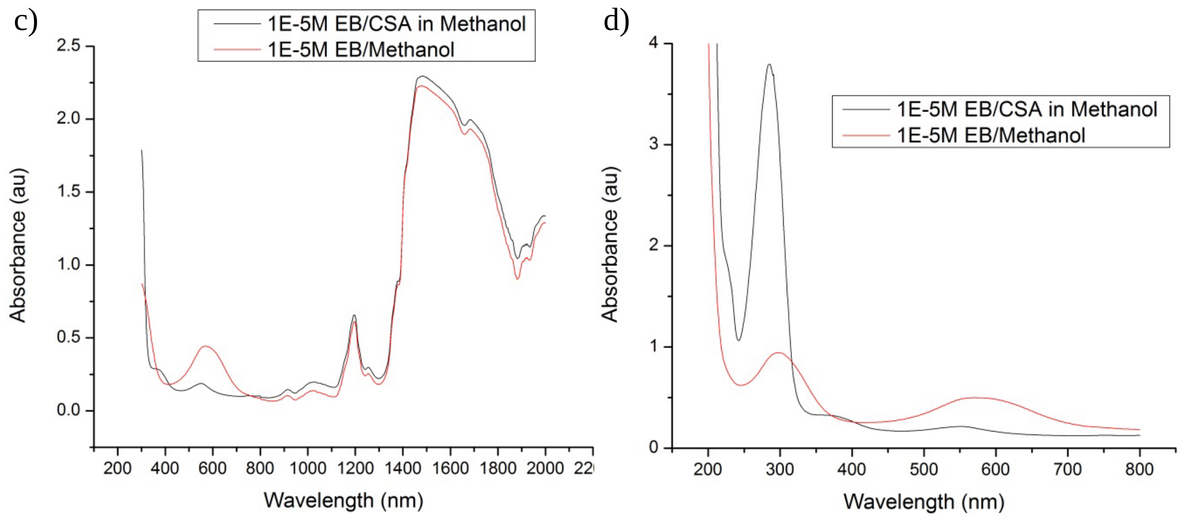


Figure 8. Experimental UV-Vis spectra: (a) EB in AMPSA/Methanol, (b) zoomed in EB in AMPSA/Methanol, (c) EB in CSA/Methanol, (d) zoomed in EB in CSA/Methanol.

LES and SES solutions showed similar results, since they are essentially the same compound. To obtain better spectra of EB and ES in the future, UV-Vis spectra will be taken on films to avoid any high solvent peaks.

3.3. Film

EB and SES/Methanol solutions blended with the resin very well whereas the LES solutions did not due to its longer chain property. The particles were settled at the bottom of the vial rather than completely blending in to the resin which could affect the conductivity measurement.

3.4. Conductivity Study

Proprietary information.

4. Conclusion:

From the UV-Vis spectra obtained, methanol is the best solvent compare to acetone and water. The polaron peaks ~400 nm and the large decrease in the quionoid (Q) peaks are indications of doped emeraldine base (EB). However, the down side of using methanol as a solvent is its high absorbance nature. The free carrier tail, which is due to H-bonding between emeraldine base (EB) and acids were buried under methanol’s high absorbance peeks beyond 900 nm.

References:

1. Jia, Q.M., et al., *Electrically conductive epoxy resin composites containing polyaniline with different morphologies.* Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing, 2007. **448**(1-2): p. 356-360.
2. Skotheim, T.A., *Hankbook of Conducting Polymers*. 1989, Marcel Dekker Inc.: New York. p. 1060.
3. Ding, Z.F., et al., *Polyaniline Morphology and Detectable Intermediate Aggregates.* Macromolecular Chemistry and Physics, 2010. **211**(6): p. 627-634.
4. Hundley, M.F., P.N. Adams, and B.R. Mattes, *The influence of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) additive concentration and stretch orientation on electronic transport in AMPSA-modified polyaniline films prepared from an acid solvent mixture.* Synthetic Metals, 2002. **129**(3): p. 291-297.
5. Dali, Y. and B.R. Mattes, *Polyaniline emeraldine base in N-methyl-2-pyrrolidinone containing secondary amine additives: B. Characterization of solutions and thin films.* Synthetic Metals, 2002. **129**(3): p. 249-260260.
6. Dali, Y., et al., *Impact of hydrogen bonds in polyaniline.AMPSA n/acid solutions.* Synthetic Metals, 2006. **156**(18-20): p. 1225-12351235.
7. Junjie, L., et al., *Synthesis and thermoelectric properties of hydrochloric acid-doped polyaniline.* Synthetic Metals, 2010. **160**(11-12): p. 1153-11581158.