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Title: Development of a Conductive Coating with Polyaniline

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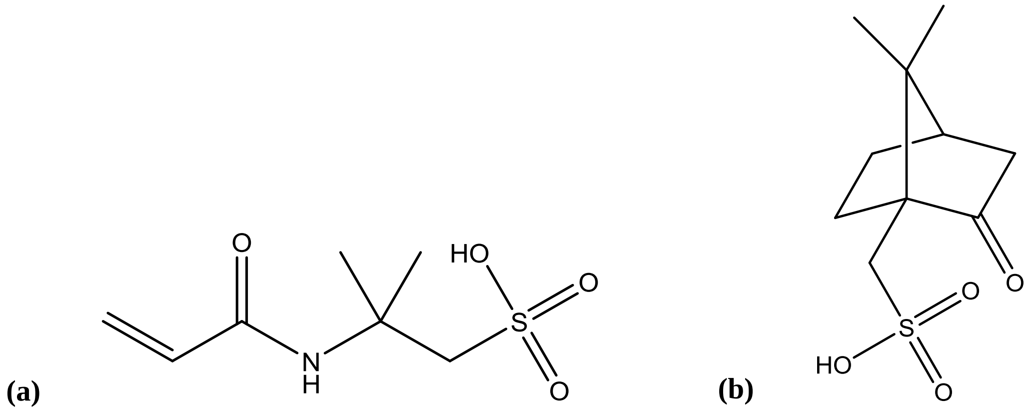
1. Introduction

Polyaniline (PANI) is considered as one of the most promising electrically conducting polymers due to its low density, good environmental stability, moderate conductivity and inexpensive polymerization.[1, 2] Commonly, polyaniline exits in three oxidation states: the fully reduced leucoemeraldine base (LEB), the half-oxidized emeraldine base (EB), and the fully oxidized pernagraniline base (PNB).[2] Among all forms, only the half, oxidized EB is electrically conductive when it is doped or protonated to the salt form.[2] There are two routes to introduce counter ions into the polymer chain. The first method is to perform polymerization of aniline oxidation with ammonium peroxydisulfate in acidic solutions.[3] PANI synthesized this way is protonated in parts.[3] The second method is to simply protonate the already prepared EB with an acid either by mechanically blending with a solid acid or by immersing it in the solution of an acid.[3] This is the only way to achieve uniform protonation.[3] Polyaniline's poor solubility has been limiting it to maximize its performance, especially with higher molecular weight polymer. It is not soluble in conventional organic solvents but in solutions such as N-methyl-2-pyrrolidinone (NMP), which permits gelations to occur.[3, 4] Another debatable issue is the effectiveness of different sizes dopants. Smaller size dopants will be able to attack the protonation sites more easily since the polymer backbone is bent at a 120 angle.[5] On the other hand, larger size dopants can force the polymer backbone to rearrange.[6]

The goal of this project is to make a conductive coating with polyaniline and a resin consisting of mostly acrylates monomers. Recent theory has suggested that there is a possibility to attain very high conductivities (~10^6S/cm) polyaniline for defect free higher molecular weight.[2] To maximize the conductivity of polyaniline, the molecular weight of EB, the solvent and dopants used during the doping process are all critical. To find the ultimate combination of protonating acid, solvent and molecular weight of EB, four organic acids (Fig. 1): 2-Acrylamido-2-methylpropane sulfonic acid (AMPSA), Camphorsulfonic acid (CSA), Dodecylbenzene sulfonic acid (DBS), Citric acid (CA), three volatile solvents: Water, methanol and tertrahydrofuran (THF) and five different molecular weights of EB: M_w ~5,000, M_w ~10,000, M_w ~20,000, M_w ~50,000, M_w ~100,000 were chosen.



(a) **(b)**

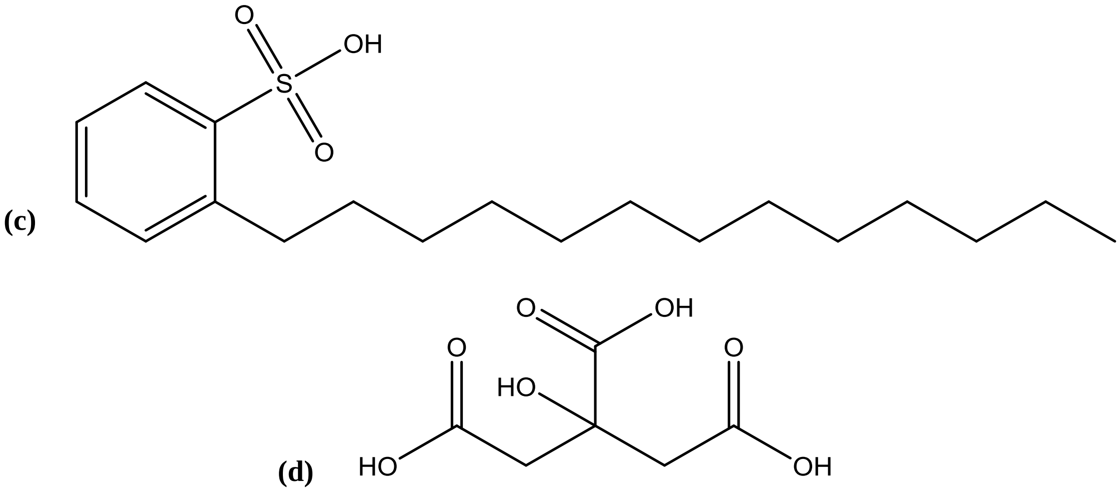


Figure 1. (a) 2-Acrylamido-2-methylpropane sulfonic acid (AMPSA), (b) Camphorsulfonic acid (CSA), (c) Dodecylbenzene sulfonic acid (DBS), (d) Citric acid (CA).

2. Experimental

2.1. Chemicals

Different molecular weights of polyanilines and protonic acids were purchased from Sigma Aldrich to perform the experiment. The resin was obtained from Objet Geometried GMBH Germany.

2.1. Dopant, Solvent, Molecular Weight Study

Approximately 700mg of EB were soaked in 10mL 0.2M acid solutions. The polymers were doped for 72 hrs. The doping solutions in the samples were later evaporated for 24 hrs using a VWR 1430 D vacuum oven at 45 ºC with pressure 25 Hg. Each study is conducted with different variables.

PANI	Amount of PANI (g)	Solvent
EB	1.23	Water
EB	0.79	Methanol
EB	0.71	1THF:1Methanol

Table 1. Solvent Study Samples. Acid: AMPSA. EB M_w~*10,000.*

PANI	Amount of PANI (g)	Acid
EB	0.79	AMPSA
EB	0.70	CSA
EB	0.44	Citric Acid
EB	0.44	DBS

Table 2. Dopant Study Samples. Solvent: Methanol. EB M_w~*100,000.*

PANI	M_w of PANI	Amount of PANI (g)
EB	5,000	0.55
EB	10,000	0.59
EB	20,000	0.57
EB	50,000	0.52
EB	100,000	0.52

Table 3. Molecular Weight Study Samples. Acid: Citric Acid. Solvent: Methanol

2.4. X-Ray Diffraction

A Siemens D5000 X-ray Diffractometer was used to collect XRD spectra. The scanning range was from 10-40 2theta with step size of 0.05 degrees.

2.5. UV-Vis Spectroscopy

UV-vis spectra were ran on 2wt.% polymer resin films. Doped EB powders were blended to a gram of resin with a slight amount of methanol to achieve uniform dissociation. The polymer resin is cured in a UV oven on quartz substrates. A Cary 5000 Scan UV-vis-NIR spectrophotometer was used to collect UV-vis spectra. The scanning range was from 350-1600 nm. The spectral measurement was conducted at room temperature.

2.5. FTIR

FTIR data were measured with KBr pallets on a Bruker Vertex 80v Infrared Spectrometer. The spectra were measured with transmittance with 200 scans. KBr pallets were made with Carver Laboratory Press Hydraulic Unit Model #3925 with 30 mm diameter dies at 30000 metric tons. 1g of KBr powder was mixed with 0.05g of samples.

2.6. 3D Modeling

3D structures of the dopants were examined using Avagadro. The width, depth, and molecular size were determined by the software. The width, defined as the longest distance between two atoms in the plane, the depth defined as the longest distance between two atoms in a plane perpendicular to the width; and the molecular size, defined as the longest distance between any two atoms in the entire molecule.

2.7. SEM

FEI Strata DB235 FIB/SEM was used.

3. **Results and Discussion**

3.1. Dopants and Solvents Study

XRD were taken to indicate the change in crystallinity. It has been known that undoped and doped EB have different crystalline contents. Emeraldine salt is partly crystalline, while emeraldine base is essentially amorphous.[5] The diffraction pattern of the undoped EB shows one broad peak at around 20º indicating an amorphous structure.[5] When it is doped, an additional new peak appears at 25º, indicating some degree of crystal has been formed. [5] The graphite like diffraction peak at 25º is a characteristic of the extent of pi conjugation in PANI. [6] Essentially, the shaper the peak at 25º the more crystalline the emeraldine salt is since the benzenoid and quinonoid units are more orderly arranged without any unfavorable clustering of quinonoid units.[6] As the XRD spectra show (Fig. 2a), methanol is a better solvent compare to water and THF. This is due to water’s Hansen solubility parameter and EB’s insolubility in THF, acetonitrile and 80% aqueous acetic acid.[4] A good solvent is necessary because it results greater polymer-solvent interactions and favors a more fully expanded-coil conformation to maximize the efficiency of the protonation process. A poor solvent will result stronger polymer-polymer interactions between different segments of the same chain and favor the compact-coil conformation, which can inhibit the dopant to successfully attack the protonation site of the polymer.[7] In a more polar and H-bonding solvent, the polymer chain-solvent interaction and solvation of the positive and/or negative ions will also increase. Both these effects will promote coil-like to expanded-coil conformational changes.[7]

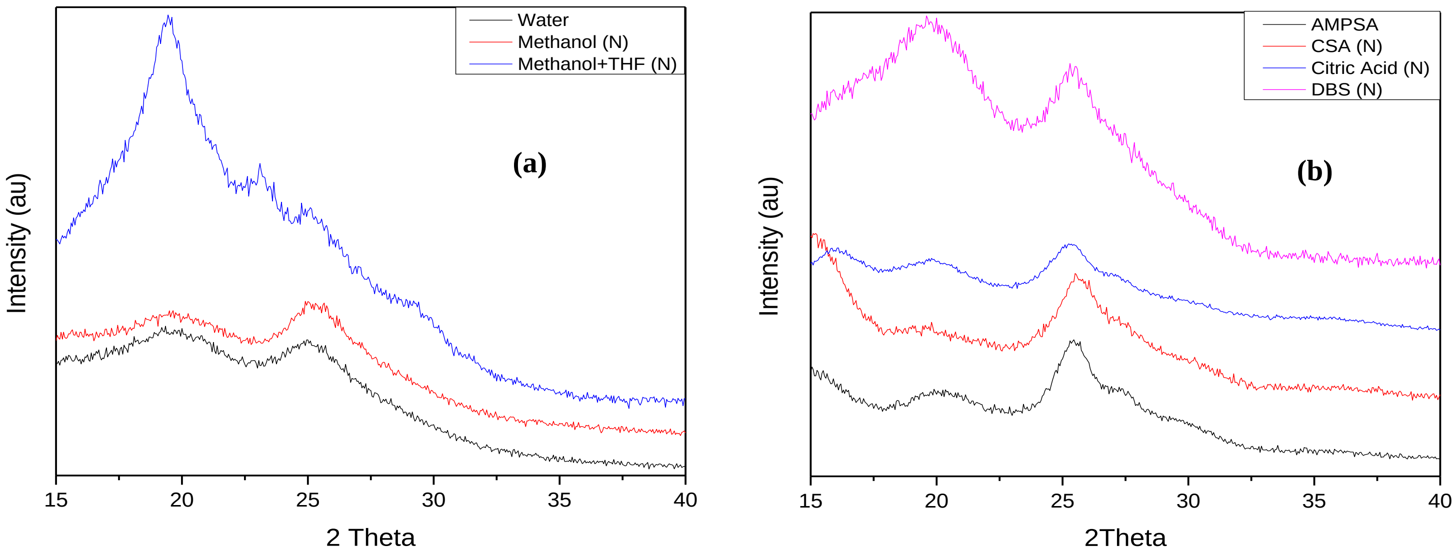


Figure 2. X-ray diffraction pattern of (a) solvent study and (b) dopant study.

Dopant species act like plasticizer to promote the movement of the PANI molecular chains and to allow crystalline regularity.[8] It has been concluded that dopants and oxidants of smaller molecular size lead to higher crystallinity.[5] Smaller dopants can enter the PANI lattice, whereas bulk dopants may distort or even destroy the lattice and reduce crystallinity.[8] However, others also argue that large sized dopants ions demand greater rearrangement of bonds along the polymer backbone, leading to better crystallinity.[6]

Acid/ Dopant	Width (Å)	Depth (Å)	Molecular Size (Å)
CSA	5.772	3.533	9.335
AMPSA	3.803	4.326	9.900
Citric Acid	4.964	4.280	7.796
DBS	7.014	3.087	21.095

Table 4. Molecular Size of Dopants

Hypothetically, citric acid would act as the best dopant due to its multiple protonation sites and its small molecular size. However, it is not the case. XRD data has indicated AMPSA and CSA doped EB yielded higher crystallinity (Fig 2b). This is because PANI doped with citric acid is not as soluble as the ones doped with sulfonic acids, which have often been used to increase the solubility and processibility of PANI.[3] Once the polymer is doped, electrostatic repulsion between similarly charged units of the chain may also occur, especially when the distance between a charged unit on the chain and its counter ion is increased. [7] Increase in charge density of the polymer chain promotes expanded coil conformation. Yet, adding excessive acids will change it back to compact-coil conformation. [7] This is caused by an increase of ionic strength of the solution brought about by the additional acid. The effects of the additional anions around the positively charged segments on the polymer will tend to screen the adjacent positive charges on the polymer chain from each other, resulting in smaller repulsion which in turn promotes expanded coil to compact-coil conformational changes.[7]

FTIR spectra (Fig. 3a) are used to trace the band characteristic of the conducting protonated form at 1238 cm^{-1} (interpreted as the $C\text{-}N^{+\cdot}$ stretching vibration in the polaron structure).[9] Other main bands are located at 3380 cm^{-1} (NH_2, symmetrical $N\text{-}H^+$ stretch, and non-H-bonded N-H), 3300 cm^{-1} (H-bonded N-H), 3035 cm^{-1} (C=C-H stretch), 1595 cm^{-1} (C=C ring stretch, imine quinoid), 1505 cm^{-1} (C=C ring stretch, amine benzenoid), 1306 cm^{-1} (aromatic amine C-N stretch), 1140 cm^{-1} (were the aromatic C-H in plane bending modes are usually observed is assigned to a vibration mode of the $–NH^{+\cdot}=$ structure, which is formed during protonation), and 830 cm^{-1} (C-H ring bend).[3]

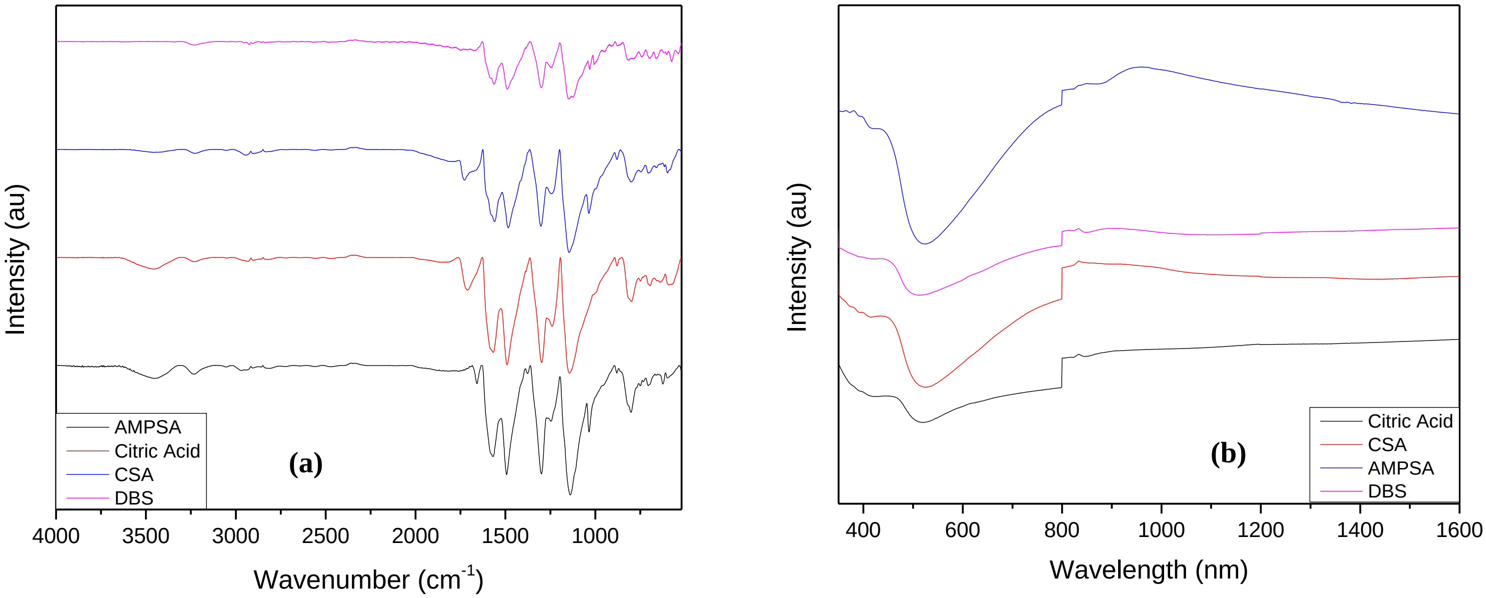


Figure 3. (a) FTIR spectra and (b) UV-vis spectra of dopant study. The drop at 800 nm is due to the detector change.

The change in conformation of the polymer can be observed in the UV-vis spectra (Fig 3b). The free carrier tail starting around 600 nm indicates that the coil-like conformation has been converted to the expanded coil-like conformation.[10] A larger free carrier tail, meaning a more expanded coil-like conformation, should give rise to a higher crystalline peak at 25° in the XRD profile. AMPSA and CSA have significantly larger magnitudes of free carrier tail, which corresponds to their sharper peaks at 25°. Even though DBS has a sharp peak at 25°, the free carrier tail is not as significant. This is because DBS not only have some degree of crystallinity; it also has a considerable amount of amorphous content, implying that both coiled and expanded coil-like conformations exist.

3.2. Molecular Weight Study

Solubility of EB decreases with increasing molecular weight, yet high molecular weight have advantages, such as higher conductivity and ultimate tensile strength.[11] From the XRD pattern (Fig. 5), it is evident that doped EB with higher molecular weight are more crystalline. The peak at 25° gets sharper as the molecular weight increases. It is assumed that increasing the molecular weight and presumably chain length, will lead to longer order pi conjugation and greater chain entanglement, allowing the polymer chains to align more easily after processing than they would if they were shorter.[12]

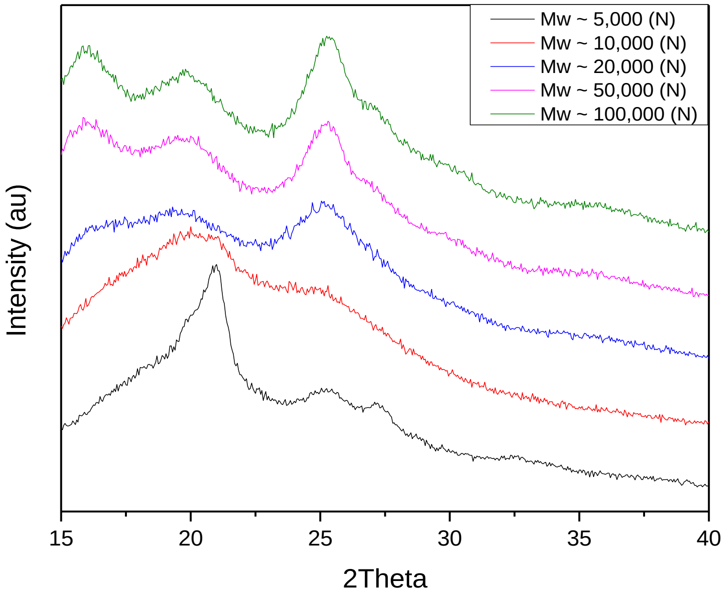
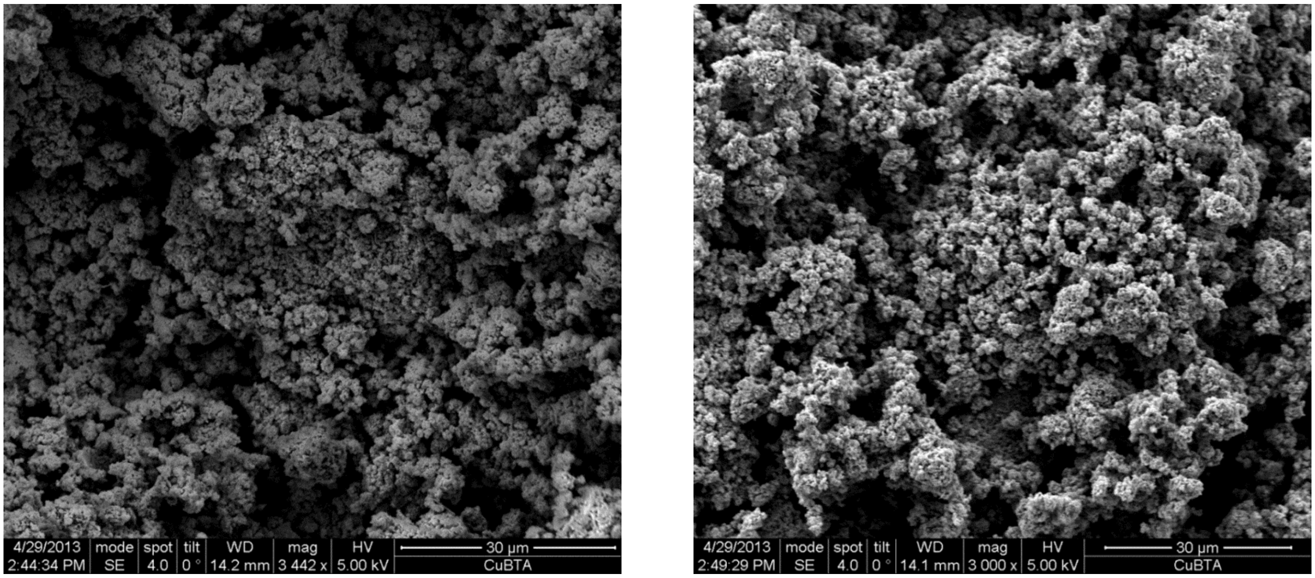


Figure 4. X-ray diffraction pattern of molecular weight study

3.3. SEM

PANI exists in different morphologies: particles, wires, fibers and tubes. pH of the synthesis process can control the resulting morphology of PANI. PANI used in this experiment is in the particle form as the SEM images show (Fig. 5). Doped PANI has a continuous surface and larger grains whereas the undoped PANI of smaller grains separated by "honeycombs".[8]



(a) **(b)**

Figure 5. SEM image of (a) undoped EB and (b) doped EB

4. Conclusion

Methanol is a better solvent compare to water and THF. It results stronger polymer-solvent interaction and favors the expanded coil conformation, which allows dopants to attack the protonation sites more easily. EB doped with AMPSA and CSA are more crystalline due to dopants' smaller molecular size and sulfonic acid's enhancement on EB solubility. Higher molecular weight doped EB does show an increase in crystallinity and possibly conductivity considering its longer pi conjugation and orderly arranged benzenoid and quinonoid units.

5. Future Work

In order to draw conclusions between crystallinity and conductivity, conductivity of more resin films are yet to be measured. Conductivities of 2 wt.% polymer resin films has been tested and only AMPSA doped EB (M_w ~100,000) showed a conductivity of 6E10^{-5} S/cm. Conductivities of resin films with increasing polymer content still needs be measured.

6. References

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