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# Synthesis and characteristics of a semi-interpenetrating polymer network based on chitosan/polyaniline under different pH conditions

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## Abstract

The chitosan/polyaniline (PANi) semi-interpenetrating network polymers (semi-IPN)s were prepared under different pH conditions. Changes of structural properties were investigated using Fourier transform infrared (FT-IR) spectroscopy, Solid-state $^{13}C$ NMR and wide angle X-ray diffraction (WAXD). The spectroscopic studies revealed that the PANi had converted to its pH-switched, emeraldine salt (ES) form when prepared from solutions of pH<1. The surface conductivity of the semi-IPN was dependent on the chitosan/PANi weight ratio and on the pH.



**Key words:** chitosan, polyaniline, conductivity, pH condition, semi-IPN

## Introduction

Conductive electroactive polymers (CEPs) and polyelectrolyte hydrogels are both fascinating materials that have been much investigated for use in smart structures[1,2]. The stimuli-responsive nature of hydrogels has been utilized in controlled drug delivery systems, "soft" actuators and separation membranes[3,4]. These hydrogels can be made to respond to a wide variety of stimuli, including temperature[5], pH[6], solvent composition[7] and electrical stimuli[8]. The major limitation of hydrogel devices in smart systems is the slow response time, which is attributed to the slow diffusion of activating species (solvent, $H^+$ ions *etc*.) and water into and out of the hydrogel matrix. Improved response time (seconds) has recently been demonstrated for micro-gels[9], but this approach is not always feasible.

CEPs are commonly utilized as electroactive materials, where a response is stimulated by application of an electrochemical potential. Among the most numerous applications of CEPs are their use in rechargeable batteries[10], corrosion protection of metals[11], gas separation membranes[12] and as a molecular sensor[13]. Response times can be relatively fast (msec) for CEP devices, but the magnitude of response can be somewhat smaller than hydrogels. In the case of artificial muscles, for example, swelling strains in excess of 100% is possible with hydrogels while CEPs produce

strains typically smaller than 10%.

There have been a limited number of reports showing that CEP / hydrogel composite or blend systems can be synthesized and that the composites retain properties of both materials. Hydrogel-like properties can be produced in CEP thin films by the use of polyeletrolytes as dopants (eg. for polypyrrole[14]). Larger hydrogel structures containing CEP phase have also been prepared by adding CEP colloids to the hydrogel solution prior to crosslinking[15] and by electropolymerisation of the CEP throughout the hydrogel matrix[16].

In the present study, we investigate a new route for the formation of CEP/hydrogel blend systems with the aim of producing a chitosan / polyaniline interpenetrating polymer network (IPN). The IPN is so desired so as to maximize the molecular interactions between the two polymers. Ultimately, we aim to prepare an electronically conductive network (polyaniline) that may be stimulated electrochemically to alter its surrounding electrolyte composition (eg. pH) and so induce large scale phase changes in the neighboring chitosan network. The molecular distances involved should shorten the time for the hydrogel response.

Polyaniline (PANi) has been chosen for this study for both its solution processability and its unique pH switching behaviour. PANi undergoes two distinct redox processes as

well as pH switching between unprotonated and protonated states (Figure 1)[1]. The starting material for redox reactions involving PANi is usually the emeraldine salt (ES) as this is the only conductive form of PANi. Oxidation or reduction of the ES produces the pernigraniline base (PGB) and the leucoemeraldine base (LEB, respectively. Both the leucoemeraldine salt and pernigraniline salts are only stable at pH below 1 or 0[1] so that they do not occur in common electrolytes. Of interest in the present study is the fact that reduction of the ES (stable at pH < 4) to the LEB could induce a further decrease in the local pH (Fig.1). This local pH change may then trigger a response from neighboring hydrogel polymer.

Chitosan has been chosen as the hydrogel phase in the present study because of its high swellability at low pH and its general usefulness in biomedical applications. Chitosan, a high molecular weight carbohydrate polymer, is manufactured from chitin,[17,18] which owes it cationic nature to the free amino groups left by the partial removal of the acetyl groups of the chitin. Chitosan appears to be more useful for biomedical applications and in the dehydration of aqueous solutions than does chitin, because it has both hydroxyl and amino groups that can be easily modified.[19,20] Chitosan has many useful features, such as hydrophilicity, biocompatibility and anti-bacterial properties.[21] Recent studies have shown that chitosan IPN structures with

polyvinylalcohol show strong swelling in acidic media due to the protonation of the amino groups. Thus, the chitosan is a suitable candidate for swelling induced by the reduction of PANi ES.

The aim of the present study was to develop synthesis methods for preparing chitosan / PANi-ES IPNs. The pH switching properties of the PANi within the IPN structure has been determined so as to determine the nature (oxidation state and degree of protonation) of the PANi.

## Experimental

### Materials

The chitosan with an average molecular weight of $2.0 \times 10^5$ and a 76 % degree of deacetylation was obtained from Jakwang Co., Korea. Glutaraldehyde (25 wt% solution in water) (GA) was purchased from Yakuri Chem. Co., Japan. Acetic acid and methanol were supplied by Duksan Pure Chem. Co. Ltd. Japan. PANi EB with an average molecular weight of $6.5 \times 10^4$ (undoped form, minimum assay 99.5%), HCl and NMP (1-methyl-2-pyrrolidone) were purchased from Aldrich Chem. Co., USA.

### Doping of PANi EB powder

PANi EB powder was doped by immersion in dopant solution - aqueous HCl solution (pH < 1), for 24 h, followed by drying under dynamic vacuum at room temperature.[22]

**Preparation of semi-IPN hydrogels**

The chitosan was dissolved completely in 2 wt% acetic acid (the solid content in solution was 2 wt%) for 24 h while the PANi-EB was dissolved in NMP (0.5 wt%). Chitosan/PANi mixed solutions were obtained by mechanical stirring for 24 h. The mixed solutions were poured into petri dishes and dried in a vacuum oven at 50$^{o}$C for 48 h. The dried blend films were used as it or were crosslinked to form semi-IPNs. Crosslinking of a sample was carried out by immersing the film in glutaraldehyde solution (methanol : glutaraldehyde (6 wt% of chitosan) in deionized water = 1 : 1) at room temperature. The residual NMP in the film and residual material was further washed by methanol solution (methanol : deionized water = 1 : 1), and dried under vacuum for more than 24 h.

An attempt was also made to prepare PANi-ES blends and IPNs with chitosan. The same procedure as above was used with the exception that in each solution the pH was adjusted to less than 1 using HCl. Thus, the PANi-EB solution in NMP was adjusted to

pH<1 as were the solutions of chitosan in acetic acid and glutaraldehyde in methanol/water. The PANi-ES/chitosan blend was formed by casting the mixed solution and drying under vacuum. The PANI-ES/chitosan semi-IPN was formed by crosslinking the blend film in glutaraldehyde solution and again drying under vacuum. and adjusted to an acidity of pH < 1 using aqueous HCl solution. The detailed composition and designations of the chitosan/PANi blends and semi-IPNs are listed in Table 1.

**Characterization**

Fourier-transform infrared spectra (FT-IR) of the samples were obtained using a Nicolet Model Magna IR 550 spectrometer for which the samples were palletized with KBr powder. Solid–state $^{13}C$ NMR spectra were obtained by using a Varian Unityinova 300 spectrometer, with a solids accessory. Experimental conditions were: $^{13}C$ (300 MHz frequency); zircon cell (length: 2 cm; internal diameter: 5 mm). WAXD (wide angle X-ray diffraction) scans for samples were obtained using a D/MAX RINT 2000 model diffractometer. Nickel-filtered copper radiation ($K_\alpha$) was incident on the sample, which was scanned at the rate of 1°/min in the reflection mode over a range of 2θ from 5-50°. The surface conductivities of chitosan/PANi semi-IPN films were measured using a

custom built d.c. linear four-point probe apparatus with a CMT-SR1000N sheet resistance measurement system. Under these conditions the surface conductivity σ can be calculated using equation (1):[23]

$$\sigma = \left[ \left( \frac{\pi}{\ln 2} \right) t \left( \frac{V}{I} \right) \right]^{-1} \qquad (1)$$

where, $t$ is the film thickness, $V$ is the voltage drop across the inner two probes and $I$ is the current driven through the sample.

## Results and Discussion

The FT-IR spectra of PANi EB, doped PANi ES, CP-31 semi-IPN prepared from solutions adjusted and unadjusted to pH < 1 conditions are shown in Figure 2. The prominent absorption peaks at 1589 $cm^{-1}$ and 1500 $cm^{-1}$ are due to the quinoid and benzenoid unit stretching modes of EB (curve (a)) and the relative intensity of these two bands gives an indication of the oxidation state of EB. The band at 1164 $cm^{-1}$ is from the quinoid unit stretching mode of EB and the vibrations at 1240 $cm^{-1}$ and 1303 $cm^{-1}$ are the C–N stretch from the benzenoid unit stretching mode of EB. The band at 829 $cm^{-1}$ in the spectrum from EB is from the C–H bending mode of the benzenoid unit. The FT-IR spectrum of the CP-31 semi-IPN with PANi EB (curve (d)) is similar to the spectrum from the neat EB form of PANi (curve (a)). The new absorption peaks of

curve (c) and (d) are related to the chitosan in the semi-IPNs.

The doped PANi ES (curve (b)) causes a slight shift of all bands and changes in band intensities. The characteristic peaks of doped PANi appear as a composite, which are 1558, 1484, 1289, 1241, 1117 and 802 $cm^{-1}$, respectively. Also, the band at 1117 $cm^{-1}$ is due to the quinoid unit doped PANi. The FT-IR spectrum of the PANi doped by aqueous HCl solution (curve (b)) is similar to those reported previously for doped PANi[24] as well as being very similar to the FT-IR spectrum from the CP-31 semi-IPN adjusted to pH <1 (curve (c)). The FTIR spectra indicate that chitosan / PANi blends can be prepared in both the PANi-ES and the PANi-EB protonation states by appropriate control of the pH of the preparation solutions.

Figure 3 shows the FT-IR spectra of cross-linked chitosan and both a blend and a crosslinked semi-IPN of CP-31 both prepared from solutions adjusted to pH <1. Characteristic peaks of cross-linked chitosan (curve (a)) are located at: 3500~3450 $cm^{-1}$, the stretching peaks of the $–NH_2$ and the hydroxyl group, and 1637 $cm^{-1}$ and 1313 $cm^{-1}$ for amide I and amide III, respectively. A peak at 1637 $cm^{-1}$ is attributable to the amide I band caused by the remaining acetamide group in chitosan. When comparing the crosslinked CP-31 semi-IPN (curve (c)) with the non-crosslinked CP-31 blend (curve (b)), a new peak appears at 1654 $cm^{-1}$ due to imine bonds (C=N) formed by a

crosslinking reaction between amino groups in chitosan and aldehyde groups in glutaraldehyde.[25] The Schiff's reaction of glutaraldehyde with primary amine groups to produce covalent glutaraldehyde crosslinking has been studied under many different circumstances in order to discover the presence of free amine organic functions in simple or complex inorganic and organic compounds.[20,26]

The $^{13}C$ NMR spectrum of the PANi EB powder and doped PANi ES powder are shown in Figure 4. Also, Table 2 shows the assignments for the CP-31 blend containing PANi ES and PANi EB, as well as the neat PANi EB and doped PANi ES. The spectrum from PANi EB (Fig. 4 curve (a)) has peaks near 124 ppm from the protonated benzenoid unit, peaks near 144 ppm from nonprotonated benzenoid unit, a peak at 137 ppm the protonated carbons of the quinoid unit, and a peak at 159 ppm from the imine carbon (unprotonated quinoid unit). The doped PANi ES (Fig.4 curve (b)) causes a slight shift of all peaks. The acidic doping of PANi ES and CP-31 blend containing PANi ES is shown by the increase in the intensity of the peak from the imine carbons (159 ppm) with a concomitant increase and shift in the peak from the protonated carbons of the quinoid unit (138 ppm).[27] Consistent with the FT-IR data, the NMR spectra show that the chemical nature of the PANi in the IPN is identical to the neat PANi ES and PANi EB.

Usually, PANi EB consists of amine (-NH-) and imine (=N-) sites in equal proportions. The imine sites are protonated by HCl acid to the bipolaron (dication salt) form. Although theoretical calculations have predicted that the bipolaron state is energetically more favored than the polaron, it is widely agreed that polarons are the charge carrier responsible for the high conductivity in PANi. It has been proposed that the presence of columbic interactions, dielectric screening and local disorder in the PANi lattice act to stabilize the delocalized polaron state. On the other hand, this undergoes a further rearrangement to form the delocalized polaron lattice, which is a polysemiquinone radical-cation salt. It has also been shown that bipolaron states do exist in PANi, but they are few in number and are not associated with the conducting regions of the polymer.[1]

Table 3 shows the assignments for chitosan, CP-31 blend containing PANi ES and CP-31 semi-IPN containing PANi ES, respectively. The $^{13}C$ NMR pattern of cross-linked chitosan in semi-IPN is less well resolved than for that of its raw form. The signals observed on the spectra at 25 and 173 ppm, were attributed to the signals of –C=O and $–CH_3$, respectively. Moreover the C-1 signal is broad, the C-3 and C-5 signals overlap and form a shoulder at the bottom of the C-4 signal. The C-2 and C-6 signals are also less well resolved and it appears that the C-2 signal decreases. For crosslinked

chitosan, the C-1, C-3, C-5 and C-6 peaks are enlarged and have decreased overlap with the neighboring C-2 and C-4 peaks. Glutaraldehyde grafting produces new alkyl groups that cause the appearance of a new broad peak. Thus, additional signals appear at 141 ppm. These bands are related to the appearance of new bonds between amine functions and aldehyde groups.[28] Crosslinked chitosan is produced via the Schiff's base reaction of amino groups in chitosan and aldehyde groups in glutaraldehyde. [29]

WAXD patterns of PANi EB, PANi ES, and for CP-31 semi-IPN with PANi ES and PANi EB are shown in Figure 5. For PANi EB, there is only one broad, amorphous single peak at 2θ=20°, which may be ascribed to periodicity parallel to the polymer chain.[30] After doping with HCl, PANi became more crystalline. Its WAXD pattern shows peaks with an increased intensity, as reflected in the presence of several diffraction peaks at 2θ = 9°, 22°, 26°, and 31°, which indicate a more crystalline structure. It was reported that emeraldine salt (PANi-HCl) was partially crystalline, while emeraldine base (undoped PANi) was essentially an amorphous polymer.[22] The disappearance of the two WAXD peaks for semi-IPN proves that in those cases the PANi was completely imbedded in the chitosan matrix and lacks the long range periodicity necessary for X-ray diffraction.

WAXD patterns of chitosan/PANi semi-IPNs of various contents are shown in figure

6. The X-ray diffractograms of the semi-IPN showed distinct crystalline peaks corresponding to chitosan and PANi. This was indicated by the presence of a broad peak at 12.8°, in agreement with the characteristic diffractogram of the original chitosan.[26] The wide peak appearing at approximately 20° was assigned to overlapped chitosan and PANi, and the peak became sharp with an increasing content of PANi in the semi-IPN. The crystallinity decreases with an increasing amount of crosslinked chitosan, by glutaraldehyde in the solid gel formed in semi-IPN.

Table 1 shows the surface conductivity of the PANi EB, chitosan/PANi blends with PANi ES and PANi EB and semi-IPNs containing PANi ES. The values of surface conductivity of the chitosan/PANi samples are all within the range $10^{-7}$ to $10^{-4}$ Scm $^{-1}$, which is much higher than of the neat PANi EB. Even the blend of chitosan and PANi-EB shows a higher conductivity ($3.9 \times 10^{-7}$ S/cm) than the neat EB ($10^{-10}$ S/cm). This higher conductivity of the blend may be due to doping of acetic acid in chitosan. The value of conductivity of the chitosan film is about $10^{-9}$ Scm$^{-1}$.[31] And, the treatment of chitosan film by doping of acidic solution gave better conductivity.[32]

The conductivity of the semi-IPN samples increased as the weight content of PANi increased with the CP-21 semi-IPN having the highest surface conductivity ($10^{-4}$ S/cm). By comparison this conductivity is an order of magnitude higher than previously

reported for polypyrrole/hydrogel composites made by adding polypyrrole to the gel solution prior to crosslinking[15]. When the semi-IPN was compared with the blend form, the lower conductivity value found for the crosslinked semi-IPN may be attributed to two distinct causes. The first one is related to the lower HCl diffusivity inside the more compact crosslinked network structure of the material, which may have resulted in it being only partially doped. The other possible cause is related to the different morphology assumed by the polymer.[33]

Conducting polymers, such as PANi, can be useful for applications as a sensor, with a conductivity range from $10^{-7}$ to $10^{3}$ S/m. The combination of chemical properties with the electrical properties of the chitosan/PANi semi-IPN system could lead one to expect the development of new sensor. The electrical signals measured could be current flow, change in capacitance or change in resistance. The field of biosensors has proven particularly interesting in this regard because conducting polymer systems have been shown to be capable of *in situ* control of antibody-antigen interactions, making them reversible under selected conditions. [1]

## Conclusions

The effects of pH conditions on chitosan/PANi semi-IPNs on changed chemical and

conductivity properties were investigated. The semi-IPNs based on PANi and crosslinked chitosan have been strongly dependent on the synthesis conditions, such as the pH. The FT-IR and NMR studies have also revealed the structure of the semi-IPNs adjusted to aqueous HCl solution (pH < 1) product was similar to that observed for the doped PANi (emeraldine salt form). For the HCl treated samples, the WAXD pattern shows more crystalline than for the untreated samples. The conductivity of the semi-IPNs increases with an increase in the PANi contents (adjusted to pH < 1) and formed a blend structure. The observed increase in the electrical conductivity caused by interaction of the components also reflects the charge transfer, which is associated with the acidic doping of PANi. As a result, PANi EB can be switched by protonic acidic solution (i.e. adjusted to aqueous HCl solution (pH < 1)), leading to a conductive form - the emeraldine salt form. Therefore, the present chitosan/PANi semi-IPN system could be useful for micro-electronics applications such as biosensors, chemical sensors and molecular sensors.

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Table 1 Conductivities of PANi EB and the chitosan/PANi sample.

| Sample | Weight ratio [Chitosan/PANi] | at pH < 1[b] | Conductivities (S/cm) |
|---|---|---|---|
| PANi EB[a] | · | × | ca. $10^{-10}$ |
| CP-21 semi-IPN | 2 : 1 | ○ | $1.0 \times 10^{-4}$ |
| CP-31 semi-IPN | 3 : 1 | ○ | $2.9 \times 10^{-5}$ |
| CP-41 semi-IPN | 4 : 1 | ○ | $2.1 \times 10^{-6}$ |
| CP-31 blend | 3 : 1 | ○ | $3.4 \times 10^{-5}$ |
| CP-31 blend | 3 : 1 | × | $3.9 \times 10^{-7}$ |

[a] from reference #15

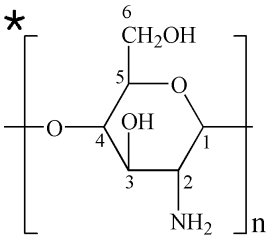
[b] ○ = adjusted to pH < 1; × = unadjusted to pH < 1

Table 2 The observed solid-state $^{13}C$ NMR chemical shifts and peak assignments of EB PANi, ES PANi, and chitosan/PANi semi-IPNs.

| Assignment (polyaniline) | PANi EB (ppm) | PANi ES | CP-31 semi-IPN (PANi EB) | CP-31 semi-IPN (PANi ES) |
|---|---|---|---|---|
| C-6, C-2, C-3 | 124 | 126 | 125 | 126 |
| C-1, C-4, C-5 | 144 | 144 | 143 | 142 |
| C-7 | 159 | · | 158 | · |
| C-8 | 137 | 132 | 136 | 131 |

Table 3 The observed solid-state $^{13}C$ NMR chemical shifts and peak assignments of chitosan, CP-31 blend (PANi ES) and CP-31 semi-IPN (PANi ES).

| Assignment (chitosan)* | Chitosan (ppm) | CP-31 blend (PANi ES) | CP-31 semi-IPN (PANi ES) |
|---|---|---|---|
| C-1 | 105 | 102 | 104 |
| C-2 | 58 | 57 | · |
| C-3, C-5 | 75 | 76 | 72 |
| C-4 | 79 | 79 | · |
| C-6 | 63 | 62 | 61 |
| imine bond (-N=CH-) | · | · | 141 |



Chitosan

## Figure captions

Figure 1. The protonation and redox reactions between the various forms of polyaniline. ($H^+A^-$ is acidic solution)

Figure 2. FT-IR spectra of (a) PANi EB, (b) PANi ES doped with HCl, (c) CP-31 semi-IPN adjusted to pH <1 (PANi ES) and (d) CP-31 semi-IPN unadjusted to pH <1 (PANi EB).

Figure 3. FT-IR spectra of (a) chitosan, (b) CP-31 blend adjusted to pH <1 and (c) CP-31 semi-IPN adjusted to pH <1.

Figure 4. Solid-state 13C NMR spectrum and structure of (a) PANi EB and (b) PANi doped with HCl.

Figure 5. WAXD patterns of (a) PANi EB, (b) PANi doped with HCl, (c) CP-31 semi-IPN with PANi ES and (d) CP-31 semi-IPN with PANi EB.

Figure 6. WAXD patterns of (a) CP-21 semi-IPN adjusted to pH <1, (b) CP-31 semi-IPN adjusted to pH <1 and (c) CP-41 semi-IPN adjusted to pH <1.

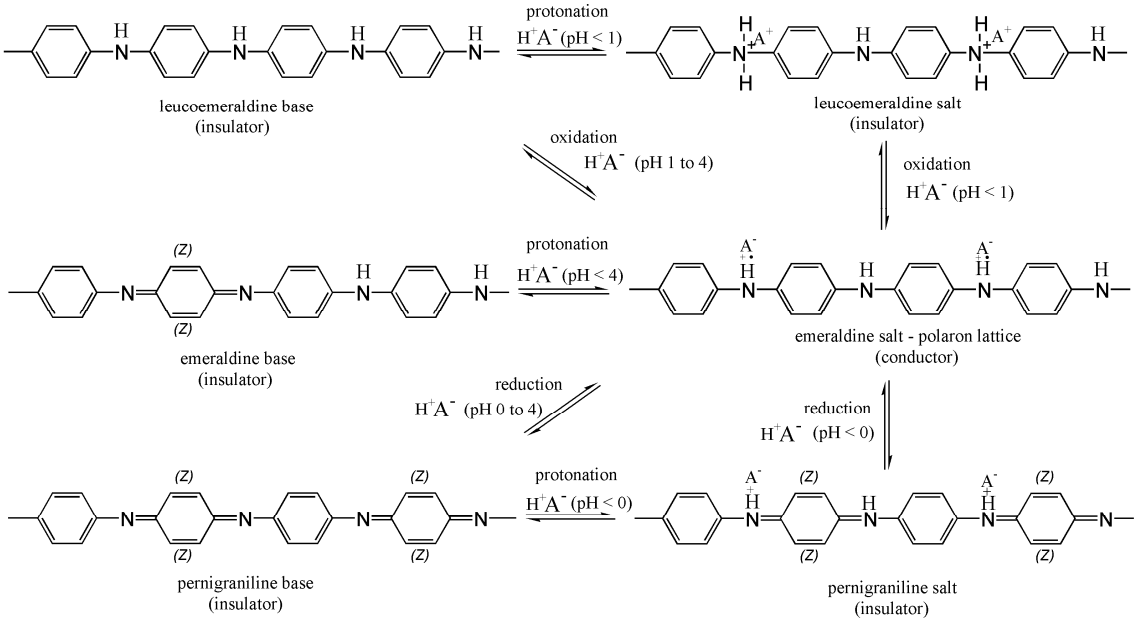

protonation
H+A- (pH < 1)
leucoemeraldine base
(insulator)
leucoemeraldine salt
(insulator)
oxidation
H+A- (pH 1 to 4)
oxidation
H+A- (pH < 1)
protonation
H+A- (pH < 4)
emeraldine base
(insulator)
emeraldine salt - polaron lattice
(conductor)
reduction
H+A- (pH 0 to 4)
reduction
H+A- (pH < 0)
protonation
H+A- (pH < 0)
pernigraniline base
(insulator)
pernigraniline salt
(insulator)

Figure 1

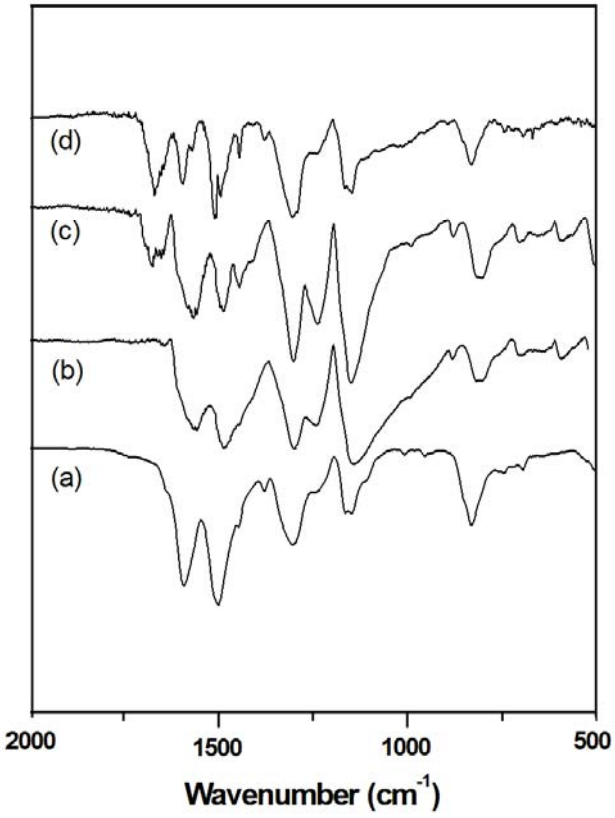



Figure 2

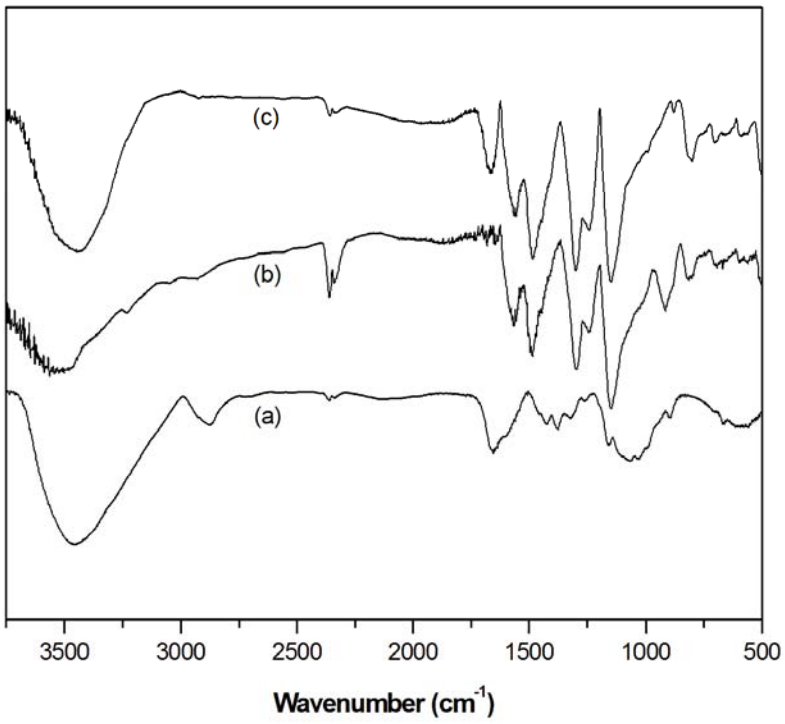



Figure 3

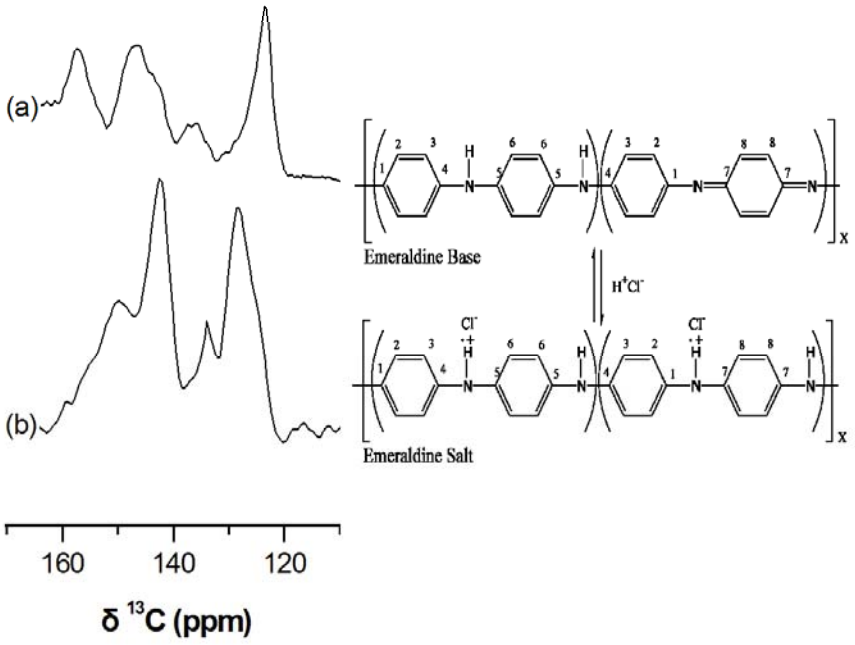

(a)
(b)
Emeraldine Base
H+Cl-
Emeraldine Salt
Cl-
160
140
120
δ 13C (ppm)

Figure 4

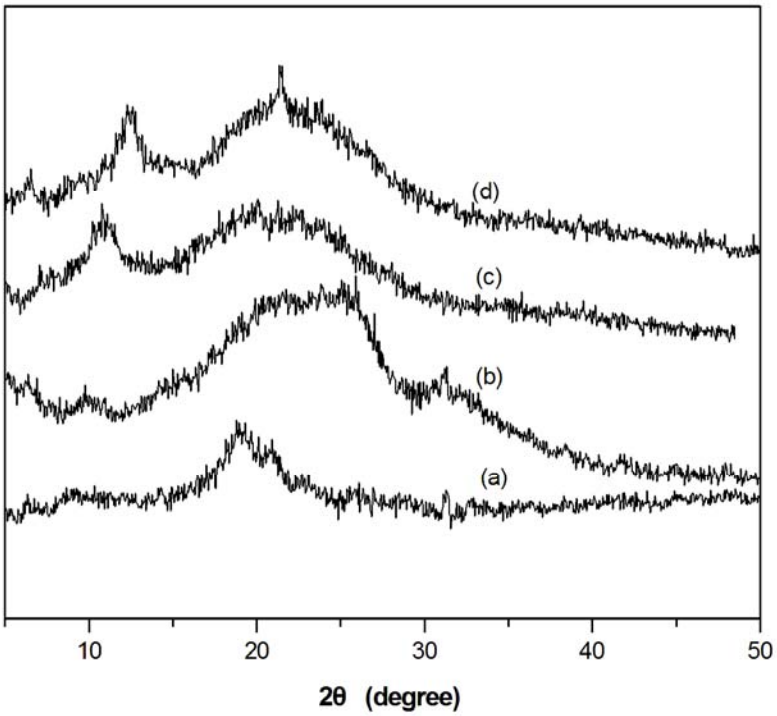



Figure 5

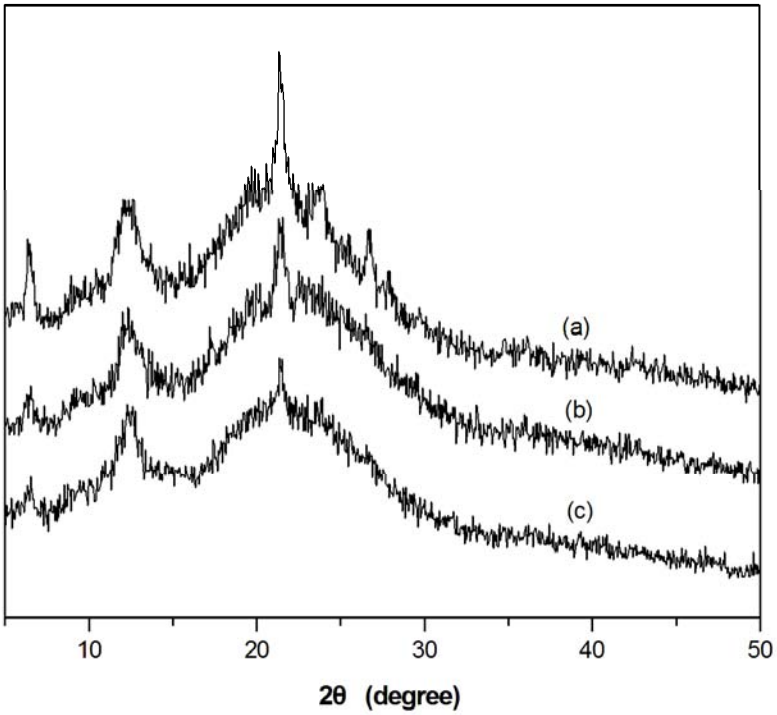



Figure 6