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# Synthesis and Properties of Self-doped Polyaniline with Polycationic Templates via Biocatalysis

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*The enzyme horseradish peroxidase (HRP) was used to polymerize acid-functionalized anilines to make self-doped polymer in the presence of a polycationic template. Anionic templates such as sulfonated polystyrene (SPS) could not function as a suitable template for the polymerization of acid-functionalized aniline derivatives. Several types of polyelectrolytes were used as templates to observe the structural effects and doping behavior of polyaniline/template complexes. The synthesis is straightforward and the conditions are mild in that the polymerization of conducting polyanilines may be carried out in buffered solutions as high as pH 6, with a stoichiometric amount of hydrogen peroxide and catalytic amount of enzyme. The conductivity of these enzymatically synthesized self-doped polymers was relatively high without additional doping due to the self-doping of the acid moieties. The conductivity did not decrease dramatically at pH 3 as is the usual case of unsubstituted HCl-doped polyaniline and maintained good conductivity even at pH 6. The measured conductivity at pH 4 ~ pH 6 is around  $10^{-4}$  S/cm to  $10^{-6}$  S/cm.*

**Keywords** enzyme, conducting polyaniline, doping, polyelectrolytes

## Introduction

Conjugated polymers can be oxidized or reduced by electrochemical and chemical methods followed by an insertion of dopant counterions to achieve electrical conductivity. During the doping/dedoping process, the rate of doping is governed by diffusion of counterions. In order to improve the rates of doping/dedoping and the solubility of polymers, researchers have tried to prepare self-doped polymers. Among these studies, polyaniline has attracted great attention because of its electronic, electrochemical, and optical properties, and especially because of its good environmental stability (1, 2) However, the poor solubility of polyaniline and harsh chemical synthetic procedures have limited its use in commercial applications. Attempts to improve the processability of polyaniline has been the modification of the polymer with various N-substitution,

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(3–7) or the post treatment of polymer with fuming sulfuric acid, i.e., sulfonation methods (8–10). Partial substitution of the phenyl ring with a  $-\text{SO}_3\text{H}$  group on the parent polyaniline does not substantially sacrifice conductivity and is of interest because of increased solubility in aqueous media and improved environmental stability due to its strong electron withdrawing properties. However, polyaniline, having  $-\text{SO}_3\text{H}$  at each phenyl ring, has poor conductivity because of bulkiness of the sulfonic acid groups and disruption of the conjugation in the backbone (11). Several types of functional groups such as  $\text{B}(\text{OH})_2$  (12, 13) and  $\text{CO}_2\text{H}$  (14) have also been introduced onto the backbone of polyaniline to generate self-doped and water-soluble polyanilines. Boronic acid-functionalized polyaniline is especially interesting because the complexation of saccharides with aromatic boronic acid is pH dependent. However, the chemical synthesis of a carboxylated polyaniline has not been successful to date because of the poor solubility of a monomer in acidic media. Thus carboxylated oligoaniline having poor conductivity is generated by sodium peroxodisulphate (14).

Biocatalytic synthesis of conducting polyaniline has received great attention in recent years since enzyme-catalyzed process can offer environmentally benign reaction conditions, a higher degree of control over the kinetics of the reaction, and a higher yield of product (15, 16). Horseradish peroxidase (HRP) is known to catalyze the oxidation of a wide range of compounds such as amines and phenols in the presence of hydrogen peroxide (17). A major drawback of enzymatic oxidation of anilines and phenols from aqueous solutions, however, is poor solubility of products resulting in the formation of only low molecular weight polymers (18). To improve processability, linearity of polymers, and molecular weight of polymers, a variety of modified enzymatic polymerization reactions have been investigated. These include solvent mixture, (19, 20) water-soluble monomers, (21, 22) micelles, (23) reverse micelles, (24, 25) reactions at the air-water interface (26) and polyanions (27, 28). In particular, the recent development of polyanionic template-assisted polymerization of aniline at pH 4.3 by our group has shown that a para-linked, linear, and especially conductive polyaniline with good solubility in water may be generated (27–30). Since the pKa of aniline is 4.63, enzymatic polymerization is performed in acidic media of pH 4.3 such that aniline will have a positive charge by a protonation of the primary amine and bioactivity can be prolonged. This increase in a protonation promotes both electrostatic interaction of the aniline monomer to the negatively charged polyelectrolyte template, sulfonated polystyrene (SPS), and head-to-tail coupling of the monomers during the reaction.

This paper discusses the enzymatic template synthesis of self-doped polyaniline in the presence of cationic templates using a carboxylated aniline monomer and a polycationic template. The conditions and mechanisms of polymerization of acid-functionalized aniline in the presence of a polycationic template do not follow that of typical polymerization of aniline. For example, immediate generation of the polaron transition in the UV-Vis absorption is observed with this system at pH above 4.3. This is also believed to be the first report of synthesis of a carboxylated polyaniline with good yield and electrical conductivity. The detailed synthesis and characterization of this facile, inexpensive, environmentally benign and water soluble self-doped conducting polyaniline are presented.

## Experimental

### Materials

Horseradish peroxidase (EC 1.11.1.7) (200U s/mg) was purchased from Sigma Chemical Co., St. Louis, MO, with RZ > 2.2. A stock solution of 10 mg/ml of enzyme in pH 6.0,

0.05 M phosphate buffer was prepared. 3-amino-4-methoxybenzoic acid (CA) (FW: 167.16; 98 +%), poly(sodium 4-styrenesulfonate) (MW of 70,000 and 1,000,000), poly(ethylene oxide) (PEO) (MW 10,000), poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethylamino)propyl]urea] (62 wt%) (MW < 10,000), poly(diallyldimethyl ammonium chloride) (20 wt%) (MW 100,000 ~ 200,000), poly(acrylamide-co-diallyldimethyl ammonium chloride) (10 wt%) (MW 1,000,000 ~ 2,300,000), N,N-dimethylethanolamine (99%), and poly(vinylbenzyl chloride) (Mn: 55,000; Mw: 100,000) were obtained from Aldrich Chemical Co. Inc., Milwaukee, WI, and used as received.

Poly(4-vinyl-1-methylpyridinium bromide) (20 wt%) (MW 50,000) was purchased from Polysciences, Inc., Warrington, PA, and used as received. Quaternization of poly(vinylbenzyl chloride) with N,N-dimethylethanolamine was performed in DMF solution as in the literature (31). All other chemicals and solvents used were also commercially available, of analytical grade or better, and used as received.

### **Polymerization**

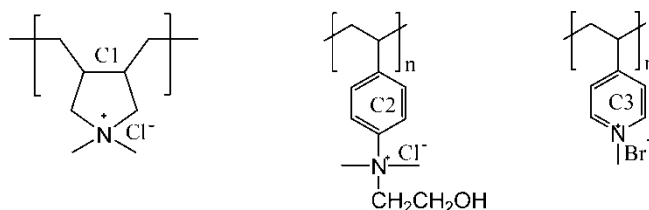
The enzymatic polymerization of CA was carried out at room temperature in 100 mL, 0.05 M sodium dihydrogenphosphate buffer solution of desired pH, which contained a 1 mM: 1 mM molar ratio of template units to aniline derivatives. Template was added first to the buffered solution, followed by addition of CA with constant stirring. To the solution, HRP stock solution containing 5 mg of enzyme was then added. The reaction was initiated by the addition of a stoichiometric amount of hydrogen peroxide under vigorous stirring. To avoid inhibition of HRP due to excess H<sub>2</sub>O<sub>2</sub>, diluted H<sub>2</sub>O<sub>2</sub> (0.3 wt%) was then added dropwise, incrementally, over 2 h. After the addition of a stoichiometric amount of H<sub>2</sub>O<sub>2</sub>, the reaction was left stirring for at least 1 h, and then the final solution was dialyzed (cutoff molecular weight of 3500) to remove any unreacted monomer, oligomer, and phosphate buffer salts to measure the conductivity of polyaniline complex at pH 5. The yields of polymerization were determined by measuring the total weight of polyaniline/template complex after precipitation in concentrated ammonium hydroxide solution, which removes unreacted monomers and water-soluble HRP, and then subtracting the weight ratio of a template polymer in the 1 : 1 complex. The precipitates were dried *in vacuo* to remove water and ammonia before measuring weight of the precipitates (9). The percentage yields of the 1 : 1 polymer complexes are 81% with C1 and 85% with C2 template (Figure 1).

### **Self-doped Polyaniline/Template Complex Characterization**

The UV-Vis spectra were recorded on a Perkin-Elmer Lambda-9 UV/Vis/near-IR spectrometer. FT-IR measurements were carried out on a Perkin-Elmer 1760X FT-IR spectrometer. FT-IR spectra were measure from precipitated polyaniline/template complex using KBr pellets. Cyclic voltammograms were recorded by using a three-electrode cell with a Pt wire as the counter electrode, a saturated calomel electrode as the reference electrode, and platinum foil (1 cm<sup>2</sup>) with a cast film of the polyaniline/template complex as the working electrode. Cyclic voltammograms were carried out at room temperature in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile with a scan rate of 100 mV/min. The conductivity of the complex was measured using the four-probe method with a Keithley 619 electrometer/multimeter (32).

## **Results and Discussion**

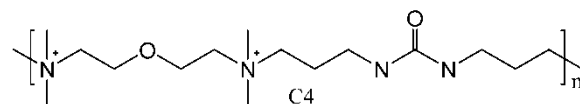
To synthesize acid-functionalized polyaniline, several types of templates were used with CA. Since the pK<sub>a</sub> of aniline derivatives is close to 4.6, the polymerization of CA was at



Poly(diallyldimethyl ammonium chloride) (C1)

Quaternized poly(vinylbenzyl chloride) (C2)

Poly(4-vinyl-1-methylpyridinium bromide) (C3)



Poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethyl amino)propyl]urea] (C4)

Poly(acrylamide-co-diallyldimethyl ammonium chloride) (C5)

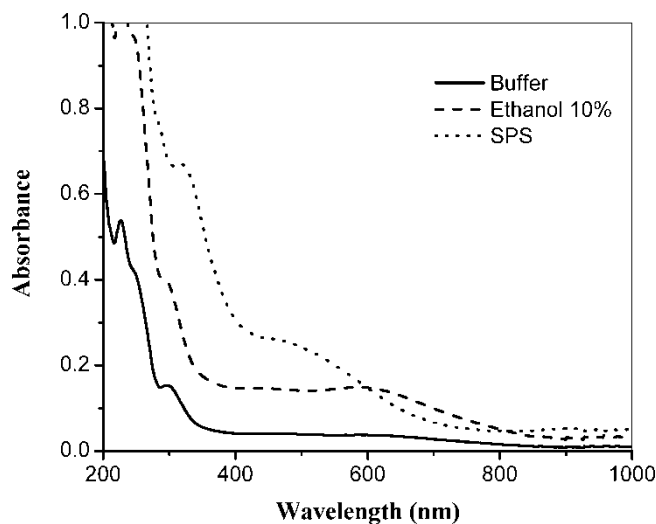


3-Amino-4-methoxybenzoic acid (CA)

**Figure 1.** Chemical structure of polycation templates and monomer.

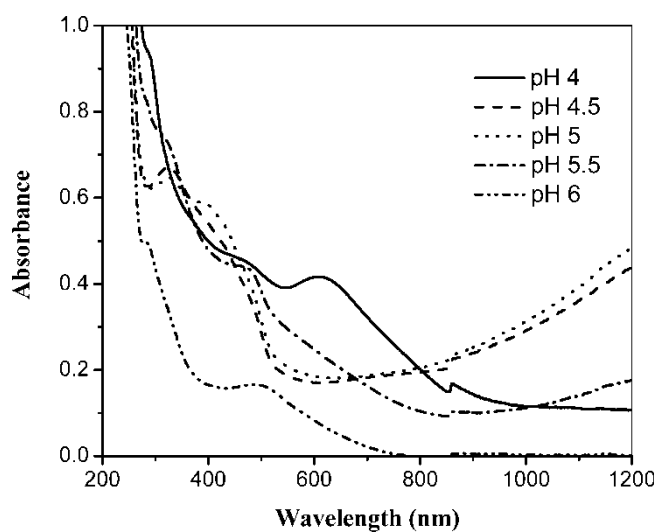
first performed at pH 4 to generate positive charge on the aniline derivative in the presence of SPS. However, only a change of color from transparent to red brown was observed in aqueous solution. This color change indicates the oxidation of the aniline derivatives and no polaron transition was detected in the UV-Vis spectra indicating the formation of the emeraldine salt form of polyaniline. Although many variables such as the concentration of buffer and monomer, pH of the aqueous media, temperature, and mole ratio between SPS and monomer have been changed, no polaron transition in the UV-Vis spectra was observed for the CA and SPS as shown in Figure 2. As mentioned previously, solubility of a monomer is critical to obtain the self-doped polymer. To increase the solubility of the CA monomer, polar organic solvent such as THF, ethanol, methanol, and DMSO was added up to 45%. However, the absorption spectrum of the reaction in these mixed solvent systems still did not show any evidence of the polaron transition in the UV-Vis spectra.

The CA monomer has a carboxyl group with a pKa close to 4.33. It has been previously shown that aniline, when below its pKa of 4.3, can be templated with the polyanion, SPS, to form conducting polyaniline (29). Conversely, it is possible to complex a monomer having a negative charge with a positively charged template under an appropriate condition. This is the alternative approach described in this paper to form a self-doped polyaniline.



**Figure 2.** UV-Vis spectra of CA and SPS; reaction time: 2 h at pH 5.

Figure 3 shows the UV-Vis spectra of poly(3-amino-4-methoxyaniline) (PCA) with poly(diallyldimethylammonium chloride) (C1) at varying pH. As shown, the PCA complex generates a strong delocalized polaron transition starting from 800 nm at pH 4.5 and pH 5 (34). However, no polaron transition appears at pH 4 because of the weak negative and positive charge interaction and poor solubility of CA in acidic media. The intensity of the polaron peak decreases as the pH of the medium increases as expected and no polaron transition appears at pH 6. At this pH, HRP only oxidizes CA and does not generate a polymer. This is verified by dialysis and by decreasing pH.



**Figure 3.** Synthesis of PCA at different pH conditions with poly(diallyldimethylammonium chloride) (C1).

Due to steric and electronic effect of the carboxylic acid group carbon-carbon (head-to-head) coupling seems to be suppressed during the polymerization (28). Therefore, the branching of CA, which severely limits the degree of conjugation in the polymer and the electrical and optical properties of the resulting polymers, is minimized in this system. It is assumed that the exciton transition at 500 nm is due primarily to low molecular weight oligoanilines (23). The reason for this oligomerization is still under investigation, but one possible reason is that as the pH increases, the negative charge repulsion between monomers and oligomers may become stronger and hinder further polymerization. Another explanation may be due to the decreased solubility by charge compensation between ionized forms of the oligoanilines and positive polycations. Although the solubility of the complex can be increased by the addition of excess polycation, the PCA/C1 (1 : 1) complex is only soluble at a pH close to 5. As the pH of the aqueous solution deviates from pH 5, the complex gradually aggregates and precipitates in strong acidic and basic media.

To study the effect of the templates on the polymerization, several types of polycation were used to synthesize PCA. As the molecular weight of the PCA increases the solubility of the PCA/template complex decreases, because of charge compensation between the polycation and the PCA. To solve this problem, quaternization of poly(vinylbenzyl chloride) with *N,N*-dimethylethanolamine, giving rise to hydroxyl groups in a quaternized polymer, was performed in DMF solution to generate poly(vinylbenzyl dimethylhydroxyethylammonium chloride) (C2) (31). Poly(4-vinyl-1-methylpyridinium bromide) (C3) was chosen as one of the templates, which has similar structure but different solubility in water when it is complexed with PCA.

Poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethylamino)propyl]urea] (C4) was chosen to investigate the effect of spacing between each positive charge. Poly(acrylamide-co-diallyldimethyl ammonium chloride) (C5) is a random copolymer. Therefore, the linear arrangement of negatively charged monomers is severely hampered by random positioning of acrylamide moieties.

The PCA/C5 shows the weakest polaron transition intensity, as expected, due to the poor templating of CA. However, C4 which has a long uncharged chain segment induces intensive polaron transition. This strong polaron transition might be due to the systematic folding of urea units into polar/nonpolar segregated units, which brings the positive charges in close proximity as the polymerization is proceeding. C2 also has strong polaron transition due to the increased solubility of the PCA/C2 complex. An interesting phenomenon is the intense polaron transition of the PCA/C3 complex. This might be due to the different yield of polymerization which was also observed by Kim et al. during the polymerization of poly(*m*-phenylene) (35). Kim et al. found that the yield of polymerization decreases dramatically as the molecular weight of a template, poly(ethylene oxide) increases, which was also observed in the polymerization of CA and SA with different sizes of surfactant micelles (36). Another reason may be attributed to the varying molecular weights of the daughter polymers formed from the different MW templates and the different conformation of the PCA/template complexes. As the molecular weight of PCA increases, the conjugation of PCA may decrease due to the bulky carboxyl and methoxy groups in the PCA backbone. C3 has a lower MW than C1 and C2, and thus, the twisting of a daughter polymer, PCA may not be as severe when PCA has a lower MW. The large decrease in the conductivity of fully sulfonated polyaniline (11) and the decrease in conductivity of the 50% sulfonated polyanilines (8–10) compared to the unsubstituted polyaniline, further support this possibility.

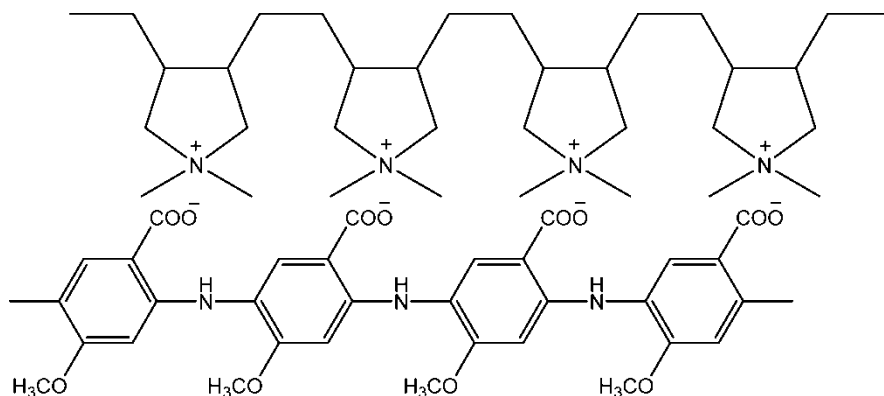
As expected, no absorption in the near IR region is observed at pH 4, except with the PCA/C2 complex, due to the poor solubility of the low MW oligomer complex. The polaron transition of the PCA/C2 complex appears, as anticipated, due to the enhanced solubility of the complex at pH 4. The increase in reaction time does not increase the intensity of the polaron transition of the PCA/template at pH 4.

The synthesis of unsubstituted polyanilines with HRP is possible only below pH 4.6. However, PCA shows strong polaron transition even at pH 6. The C1 complex shows the strongest polaron transition at pH 5 and does not show polaron transition at pH 6. An additional advantage of enzyme-catalyzed synthesis of self-doped polymer is that HRP is most active at pH 6, therefore less enzyme is required at this pH. There are several possibilities as to why the PCA shows a strong polaron transition at pH 6. The first is that even though the bulk pH is 6, the local pH environment may be lower due to the carboxylic acid group interacting with the cationic template (27). In addition, C2 and C3 have lower MWs than the other templates, which might increase the intensity of the polaron transition due to increased solubility of the complex.

The intensity of the polaron transition of the polyaniline can be easily tailored by changing the pH of media (27). However, the complexes which do not show any strong absorption in the near IR region do not form a new polaron peak when the pH of the solution decreases, which demonstrates that no polymerization occurs under these conditions (Scheme 1).

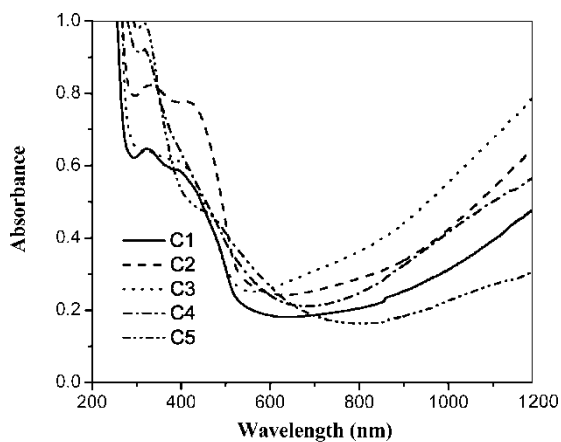
The PCA/template complexes, synthesized at pH 5 and further doped with HCl vapor for an hour, showed a consistent high electrical conductivity in the range of 0.1 ~ 0.3 S/cm. Furthermore, the complexes showed relatively good conductivity in the range of  $10^{-4} \sim 10^{-6}$  S/cm at pH 5 and 6 without any additional doping. The PCA/C5 complex, however, shows a conductivity of  $\sim 10^{-7}$  S/cm, at pH 5, probably due to poor templating. In comparison, unsubstituted polyaniline has conductivity of  $10^{-10}$  S/cm at pH 5 (37). The PCA/template complexes show almost *five* to *six* orders of magnitude higher conductivity, which indicates a self-doping mechanism with the PCA.9 (Figure 4).

To study the influence of mole ratio in the polymerization of PCA, the ratio between template and CA was changed incrementally and the results are given in Figure 5. As the mole ratio of CA increases, the intensity of the polaron peak increases up to a mole ratio of 3 : 1. The intensity of the polaron transition is significantly increased along with the

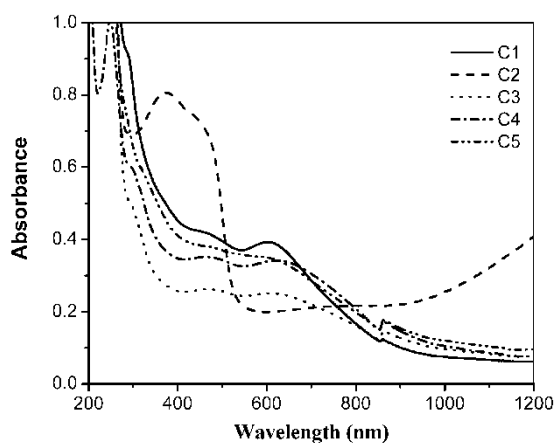


**Scheme 1.** Complex formation between ionized PCA and C1 template at high pH.

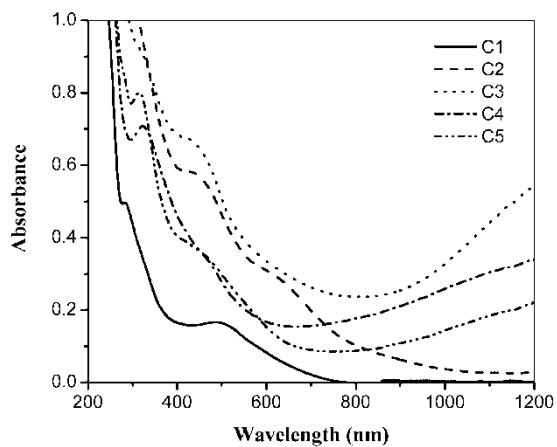




a)

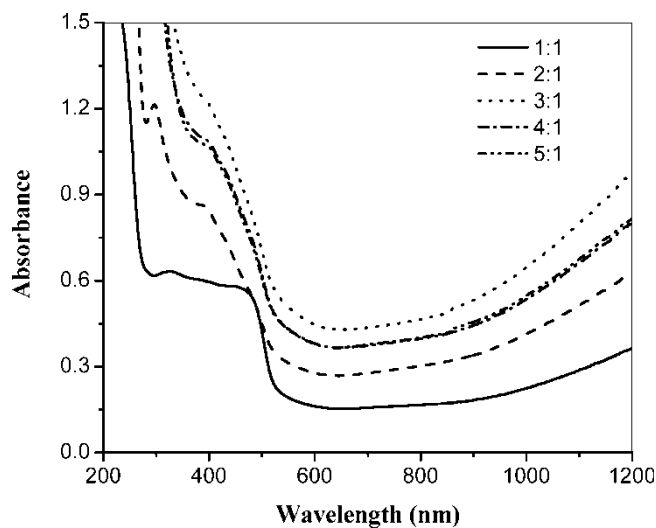


b)



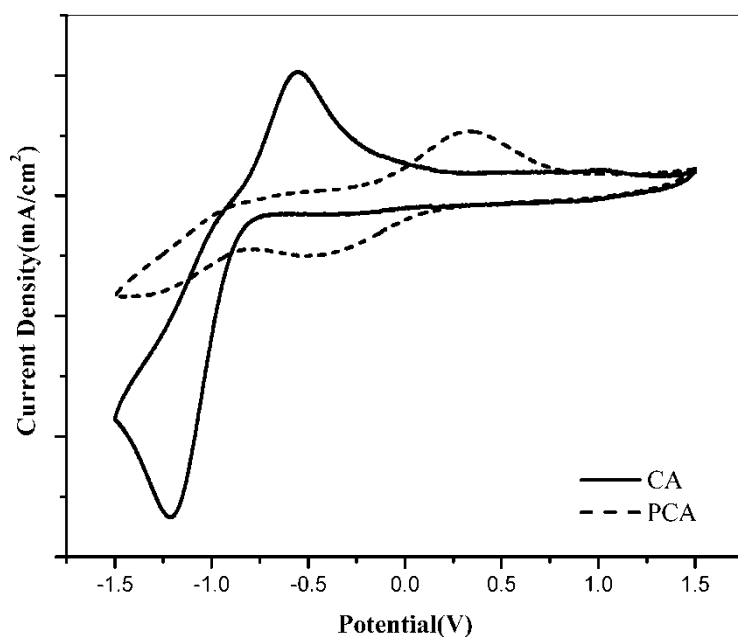
c)

**Figure 4.** UV-Vis spectra of PCA with different templates at different pH.; a) pH 5; b) pH 4; c) pH 6; reaction time 2 days.



**Figure 5.** UV-Vis spectra of CA/Cl complex at different CA concentrations.

viscosity with increasing mole ratio during the polymerization. However, as the mole ratio increases further to a value of 3:1, a decreased polaron intensity is observed, which suggests that polymerization of CA is as efficient at this higher molar ratio. This is most likely because the positive charges in the polycation are screened and compensated by the negatively charged PCA. This is easily observed and verified in dilute solution

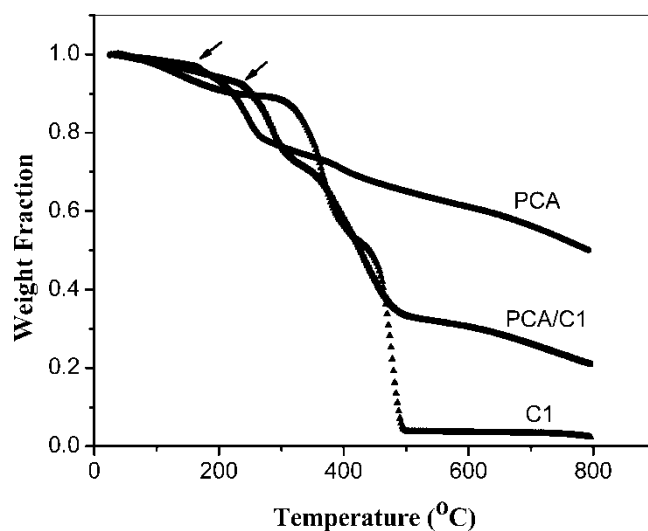


**Figure 6.** Cyclic voltammograms of monomer and PCA/Cl complex.

which allows fast diffusion of CA toward a template unit. As the mole ratio of C1 against PCA is equal to two, the intensity of the delocalized polaron transition is stronger, which might be due to the increased solubility of the PCA/C1 complex with increasing amounts of C1. However, when the mole ratio is larger than two, the intensity of the absorption decreases. Thus, it is believed that the excess numbers of charges in a template actually hinder the linear one-to-one arrangement of monomer with each repeating unit of a polycation template. As a result, the yield of polymerization and the intensity of polaron absorption in the near-IR region decrease.

The electrochemical properties of the PCA/C1 complex and CA were determined by using cyclic voltammetry. Figure 6 shows the cyclic voltammograms (cv) of a cast film of the complex against monomer, CA. One distinct reduction peak of the monomer at  $-1.25$  V appears with a  $E_{1/2}$  of  $-0.89$  V and another weak peak at  $0.31$  V appears with a  $E_{1/2}$  of  $0.633$  V. Two oxidation peaks appear at  $-0.52$  and  $0.95$  V. However, unlike the electrochemically grown and chemically synthesized polyaniline (38–40) the PCA/C1 complex has only one reduction peak at  $-0.55$  V and one oxidation peak at  $0.37$  V with  $E_{1/2} = -0.09$  V. The absence of second redox process may be related to the resistance of the complex to the oxidation to the pernigraniline state (28).

Thermogravimetric analysis, (Figure 7) showed that the decomposition of the PCA is retarded by the strong charge interaction with the C1 template. The first onset of decomposition of the self-doped PCA, shifted from  $183^{\circ}\text{C}$  to  $250^{\circ}\text{C}$  when the PCA was complexed with C1. This decomposition is believed to be due to the cleavage of the carboxyl groups. These results suggest that thermal stability of the self-doped conducting polymer can be increased via the complexation with oppositely charged templates. As the PCA alone gradually degrades with increasing temperature, the second onset of the decomposition of the PCA/C1 complex ( $365^{\circ}\text{C}$ ) is considered to be due to decomposition of C1. Considering that most of the C1 is decomposed at  $500^{\circ}\text{C}$ , the decomposition of the PCA/C1 complex above  $500^{\circ}\text{C}$  is mainly due to that of PCA.



**Figure 7.** Thermogravimetric analysis of PCA, C1 and PCA/C1 complex; ramp rate:  $20^{\circ}\text{C}$ ; The MW of a repeating unit of PCA and C1 are 167 and 162 (g/mol), respectively.

## Conclusions

Novel carboxyl group functionalized self-doped polyanilines were successfully synthesized with HRP at moderately acidic pH (pH 4 ~ 6) for the first time. The optimum pH conditions of polymerization were not lower than the pKa value of an amine but higher than the pKa value of a carboxylic acid. The intensity of the polaron transition of the polymers was dependant on the templates used. Thus, the template, having good solubility when complexed and having low molecular weight, could be used to tune the resulting polaron transition of the final complex. However, PCA/C2 generated an intense delocalized polaron transition in the near-IR region even below the pKa of a carboxyl group, which is due to the increased solubility of the PCA complex. One positive charge in a template, could on average, template up to three monomers. However, when the mole ratio was larger than 3 : 1, the positive charge in the templates was screened severely by negatively charged polymers and was not able to interact with the monomers. CV spectra showed that the self-doped PCA complex has only one redox couple whose  $E_{1/2}$  value decreased with increasing pH. TGA analysis showed the increased thermal stability of a PCA, when it is complexed with a cationic template. The PCA/C1 complex showed a conductivity of 0.3 S/cm with additional doping with hydrochloric acid.

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