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ENZYMATICALLY SYNTHESIZED POLYANILINE IN THE PRESENCE OF A TEMPLATE POLY(VINYLPHOSPHONIC ACID): A SOLID STATE NMR STUDY

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

Template guided enzymatic synthesis of conducting polyaniline (PANI) is a one-step reaction and more importantly, it is an environmentally friendly process. Understanding of the reaction and coupling mechanism at the molecular level is of paramount significance to improve its processability and conductivity. Solid-state NMR techniques are useful to investigate molecular structures of enzymatically synthesized polyaniline (PANI). The PANI sample in three different forms i.e., (a) as-synthesized, self-doped conducting form; (b) dedoped, base form and; (c) redoped, conducting form, are investigated by solid-state ^{13}C and ^{15}N CP/MAS NMR techniques. Solid-state NMR data analysis shows that the structural features of enzymatically synthesized PANI are similar to that of chemically synthesized PANI. The solid-state ^{13}C CP/MAS NMR spectrum of the base form of PANI confirmed that benzenoid-quinoid repeating units are present in the backbone of the PANI polymer

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chain. The poly(vinylphosphonic acid) (PVP) template provides charge compensation during the chain growth of linear polyaniline. After the completion of template-guided synthesis of PANI, it is now possible that the PVP template can be completely removed from the complex by dedoping with aqueous NH_4OH. The detached PANI from the PANI-PVP complex can then be redoped to conducting form without the presence of the template. The conductivity of the PANI and PANI-PVP complex are of the same order of magnitude. The solid-state ^{15}N CP/MAS NMR chemical shifts are sensitive to charge distribution on the nitrogens in the backbone. The solid-state ^{15}N CP/MAS NMR spectrum of the base form of the enzymatically derived PANI sample showed the clear signature for benzenoid-quinoid repeating units in the polymer backbone.

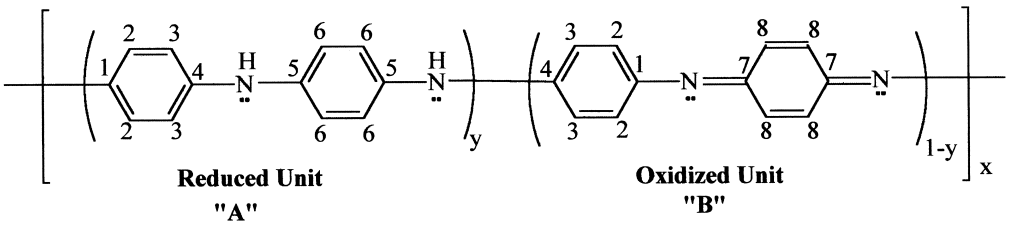
Key Words: Polyaniline; Template; Enzymatic polymerization; Conducting polymer; Solid state ^{13}C and ^{15}N CP/MAS NMR

INTRODUCTION

Polyaniline (PANI), a conducting polymer, has attracted considerable attention in the last few decades for its environmental stability and promising electrical and optical properties [1]. The uniqueness of this material is based on the fact that its physicochemical properties and conductivity can be varied by varying the oxidation state and/or the degree of protonation [2]. Polyaniline can be synthesized either chemically or electrochemically in strong acid media [3-5]. However, the harsh synthesis environment and poor solubility of the polymer in common solvents limits its wide commercial applications. Recently, a novel, environmentally friendly enzymatic approach has been developed to synthesize water-soluble conducting polyaniline in the presence of various macromolecular polyelectrolyte templates [6-8]. The enzyme being used for the synthesis is horseradish peroxidase (HRP) [9]. This approach is based on preferential electrostatic alignment of aniline monomers onto an anionic polyelectrolyte template in order to provide charge compensation and promote a linear polyaniline chain growth. The resulting PANI-polyelectrolyte complex is water-soluble, and thus has much improved processability compared to its chemically synthesized analogs. Recently, we have reported the enzymatic synthesis of conducting polyaniline that is dispersed in polyelectrolyte template such as sulfonated polystyrene (SPS) or poly(vinylphosphonic acid) (PVP) under aqueous conditions [10, 11]. As the structure and properties of polyaniline varies significantly with different synthetic conditions and post-synthesis treatments, it is necessary to understand its structure for improving its processability and conductivity. Although considerable progress has been made in the field of enzymatic polymerization, the structure of various polyaniline-polyelectrolyte complexes has yet to be studied in detail. Liu *et al*. [8] first reported solution NMR and other analytical studies of initial interaction of various template molecules with the monomer molecules. Attempts have been made to

understand the effectiveness of various templates prior to the synthesis. Very limited information is available on the mechanistic studies of enzymatic synthesis of PANI. To date, most of the structural characterizations of polyaniline are restricted to chemically synthesized materials [12-14].

In general, enzymatically synthesized polyaniline is in the protonated form, which can be converted to the unprotonated base form by treatment with aqueous NH_4OH or any other suitable base. The unprotonated base form of polyaniline consists of reduced base units, "A" and oxidized base units, "B" as repeat units, where the oxidation state of the polymer increases with decreasing values of y ($0 \leq y \leq 1$) (Figure 1) [15]. The three extreme possibilities for value of y are 0, 0.5 and 1, corresponding to fully oxidized polyaniline (pernigraniline), the half oxidized polyaniline (emeraldine), and fully reduced polyaniline (leucoemeraldine), respectively. Protonation of the base form of PANI gives the conducting form whose conductivity depends on the ratio of reduced and oxidized units as well as on the extent of protonation. The highest conductivity is observed in the case of the emeraldine salt, which has a y value of 0.5. The protonated form of the polyaniline may exist in various forms as shown in Figure 2 (II-V) [15]. The preferential protonation of the imine nitrogen of the base form (Figure 2-I) gives rise to a structure containing localized bipolarons centered on the quinoid rings (Figure 2-II). Internal redox reactions resulted in the formation of semiquinone radical cations (polarons) (Figure 2-III). The conducting form is believed to be a delocalized poly(semiquinone radical cations) having polaron conduction band, with most of the positive charge residing on the nitrogen atoms (Figure 2-IV). Although the formation of structure (Figure 2-V) is not favored in highly acidic conditions, the existence cannot be completely ruled out in different synthetic environments. It was proposed that, at higher pH and with $y > 0.5$, the protonated amine fraction increases relative to the semiquinone fraction [16]. The overlap-



y = 1 Leucoemeraldine base

y = 0.5 Emeraldine base

y = 0 Pernigraniline base

Figure 1. Various oxidation states of the base form of polyaniline (PANI).

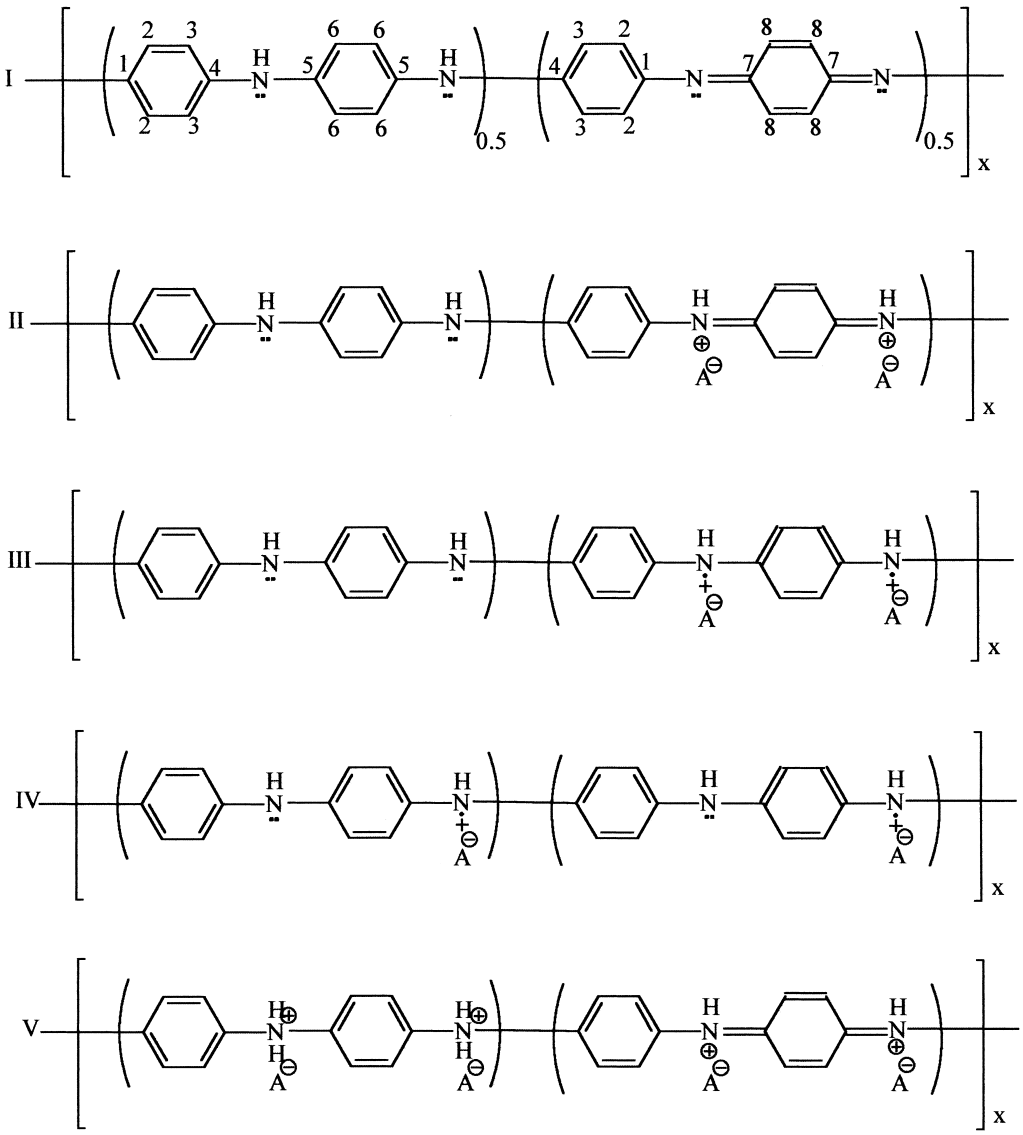


Figure 2. Possible structures of polyaniline in base and conducting form.

ping of these structurally distinct moieties in the protonated form of polyaniline makes the structural characterization of this material a challenging task. With the presence of a polyelectrolyte template, the structural analysis becomes even more complicated, especially by ^{13}C NMR, if the template polymer contains an aromatic moiety such as with sulfonated polystyrene (SPS). The ^{13}C NMR resonance peaks due to SPS overlaps in the spectral region of PANI. This overlapping of resonances can be avoided if there is a suitable non-aromatic polyelectrolyte template. Our recent work shows that poly(vinylphosphonic acid) (PVP), which does

not have aromatic functionality, appears to be a suitable template for the synthesis of conducting polyaniline having either higher or similar levels of conductivity (~10^{-2} S/cm) as the PANI-SPS system [10, 11]. Thus, in this paper we undertake a detailed solid state NMR study of PVP template assisted enzymatic synthesis of PANI in its (a) as-synthesized, self-doped conducting form; (b) dedoped, base form; and (c) redoped, conducting form. Solid-state ^{13}C and ^{15}N CP/MAS NMR are used for the study of these enzymatically synthesized PANI materials. The preliminary solid-state NMR results of the enzymatically synthesized molecular complex of PANI-PVP are presented and compared with chemically synthesized PANI. We also report here on the physical separation of PANI polymer chains from PVP in the PANI-PVP complex.

EXPERIMENTAL

Enzymatically Synthesized PANI

Horseradish peroxidase (HRP, EC 1.11.1.7) type II, 150-200 units/mg solid, was purchased from Sigma Chemical Co., St. Louis, MO. Poly(vinylphosphonic acid) was obtained from PolySciences, Inc. and used as received. Aniline monomer (purity 99.5%) and hydrogen peroxide (30 wt%) were purchased from Aldrich Chemicals Inc., Milwaukee, WI, and were used as received. Polymerization was carried out enzymatically at room temperature according to the following procedure. For the synthesis of PANI-PVP, 500 ml of phosphate buffer was used. To 10 mM solution of PVP (540 mg in 500 ml phosphate buffer), 10 mM aniline (455.6 μL), and 25 mg of HRP were added with constant stirring. The pH of the solution was constantly monitored and adjusted to pH 4.3. Reaction was initiated by the addition of 510.5 μL of 30% H_2O_2 (20 addition of 25.5 μL at 5 minute intervals) with constant stirring. The mixture containing dark-green PANI-PVP precipitate was filtered through 1 micron polycarbonate filters and washed with acidified acetone several time to remove unreacted monomer/branched products along with enzyme. The precipitate was then dried in a vacuum oven at 60°C for 24 hours. The dedoping was carried out with aqueous NH_4OH. The emeraldine salt form of PANI-PVP complex was stirred in NH_4OH for 6 hours and filtered and washed thoroughly before drying in a vacuum oven overnight. Redoping was done by stirring the base form with 1N HCl for 6 hours at room temperature, and filtering and washing with water before vacuum drying. The above procedure was also employed to synthesize the ^{15}N-enriched sample and reproducibility of the synthesis was checked by conductivity and ^{13}C NMR measurements.

Chemically Synthesized Polyaniline

The emeraldine base form of chemically synthesized polyaniline was obtained from Aldrich Chemicals Inc., Milwaukee, WI and used as received for the NMR measurement.

Conductivity Measurements

These measurements were carried out on as-synthesized, base and redoped conducting forms of PANI-PVP pressed pellets using a Cascade Microtech four-point probe connected to a current source and electrometer [17]. The conductivity values reported are the average of 5-6 readings at different regions and sides of the disk.

Solid-State NMR Measurements

Solid-state ^{13}C and ^{15}N measurements were recorded on a 300 MHz Bruker DMX wide-bore spectrometer operating at 75.47 and 30.4 MHz for ^{13}C and ^{15}N nuclei, respectively. Zirconium oxide (ZrO_2) 4 mm (o.d.) rotors were used with Kel-F caps for all the measurements. The NMR measurements were carried out at room temperature. Cross-polarization with magic angle spinning (CP/MAS) and dipolar decoupling (DD) techniques were used to study these materials. A one-time magic angle adjustment was accomplished by maximizing the spinning side band intensities of ^{79}Br NMR signal of KBr sample. All spectra were recorded using a rotor spinning speed of 10 and 5 kHz for ^{13}C and ^{15}N NMR, respectively. The typical parameters for ^{13}C CP/MAS NMR experiments were as follows: a pulse width of 3.6 μs, a recycle time 3 s, contact time of 2 ms and sweep width of 31 kHz. The total number of free induction decays (FIDs) co-added per spectrum ranged from 10,000 to 20,000. All the FIDs were processed by exponential apodization function with a line broadening of 30-40 Hz. All the ^{13}C CP/MAS NMR spectra were externally referenced to glycine by assigning the carbonyl signal at 176.3 ppm with respect to tetramethyl silane (TMS). For ^{15}N CP/MAS NMR, a pulse width of 4.8 μs, a recycle time 4 s, contact time of 5 ms and sweep width of 31 kHz were used along with 30,000 to 40,000 FIDs which were co-added to get better signal-to-noise ratio. The spectra were externally referenced to the ^{15}N signal of solid ammonium sulfate at 0.0 ppm.

RESULTS AND DISCUSSION

The solid-state ^{13}C CP/MAS NMR spectra of enzymatically synthesized self-doped PANI-PVP (3a), its base form (3b) and redoped form (3c) are presented in Figure 3. The measured conductivity of the self-doped PANI sample whose solid-state ^{13}C CP/MAS NMR spectrum is shown in Figure 3a, was 5×10^{-2} S/cm. Two broad resonance peaks are observed for self-doped PANI-PVP sample, one in the aliphatic and the other in the aromatic region (Figure 3a). The broad aliphatic peak in 10.0-50.0 ppm region is due to -CH and -CH_2 carbons of the PVP template. In the aromatic region, a broad single resonance peak for self-doped PANI sample is observed. The spectral feature in the aromatic region is similar to that of the chemically synthesized PANI sample [12]. The broad reso-

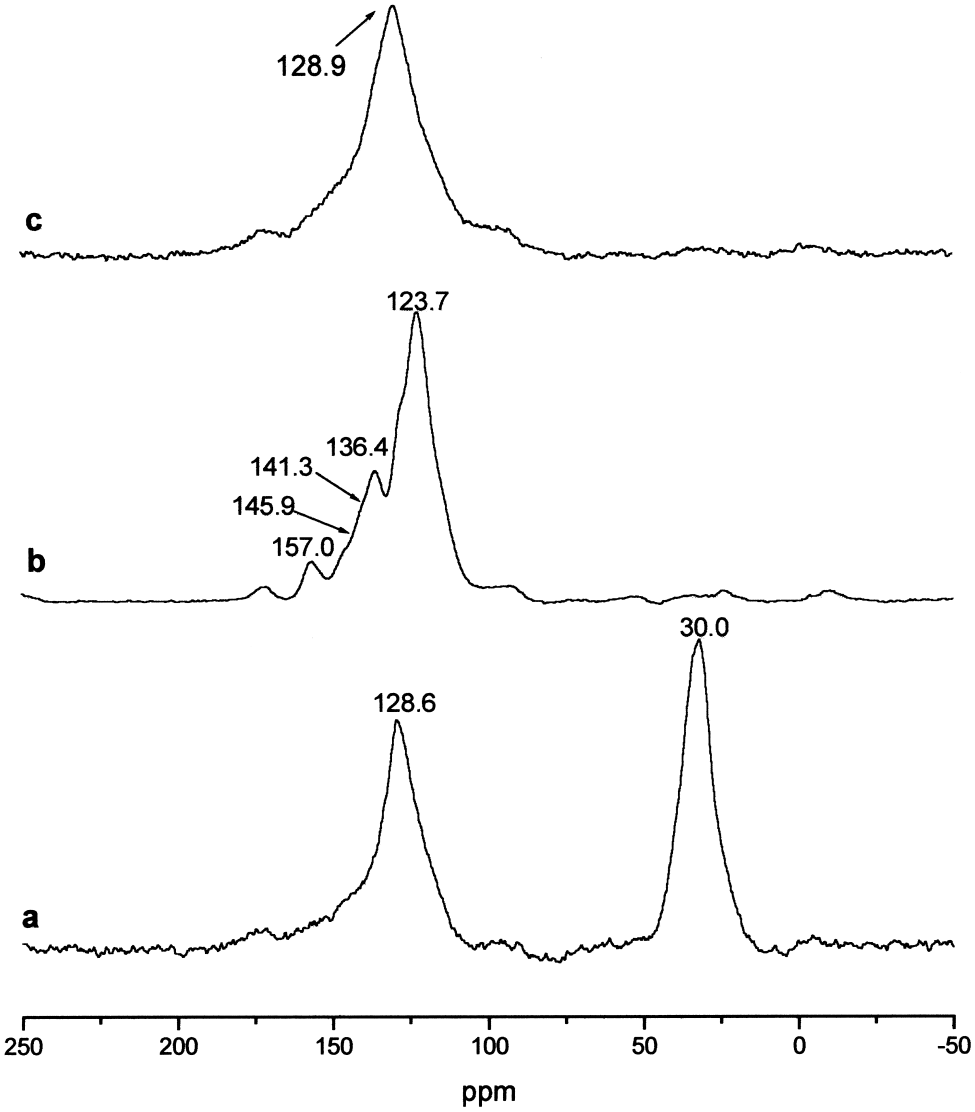


Figure 3. ^{13}C CP/MAS NMR spectra of enzymatically synthesized polyaniline (PANI): (a) Self-doped conducting form of PANI-PVP complex; (b) dedoped base form of PANI; (c) redoped conducting form of PANI (ssb = spinning side band).

nance peak at 128.6 ppm is due to the protonated carbons of the PANI sample (Figure 2 (II-V)) and the excessive line broadening is as a result of overlapping resonances arising from various bipolaron and polaron states of polyaniline. The resonance for non-protonated carbons appears as an unresolved shoulder to the protonated carbon peak at 140.0-180.0 ppm. The major contributions to the resonance peak of the self-doped PANI in Figure 3a can be attributed to (i) the influence of paramagnetic centers (see Structures III and IV in Figure 2) on the neigh-

boring carbons in PANI and (ii) the local charge density variation along the polymer backbone [12, 18-20]. According to Espe *et al*., the primary contribution to the resonance peak of conducting PANI is from amorphous carbons that are at least 50 Å away from the paramagnetic centers [20]. The line width of the ^{13}C resonance peak of self-doped PANI in the PANI-PVP complex sample is ca. 20.0 ppm whereas it is ca. 60.0 ppm for the chemically synthesized HCl-doped conducting PANI [12]. The narrower line width in the NMR spectrum for the enzymatically synthesized PANI sample, compared to chemically synthesized conducting PANI, can be attributed to: (a) a narrower chemical shift distribution due to high concentration of localized charged domains; (b) a low level of dopant concentration; (c) morphological changes as a result of the PANI-PVP complex resulting in molecular motions and phenyl ring flipping that may differ with chemically synthesized PANI.

The base form of enzymatically synthesized PANI in the presence of PVP was obtained by dedoping the conducting form sample using aqueous NH_4OH. The solid-state ^{13}C CP/MAS NMR spectrum of the base form of the PANI sample is presented in Figure 3b (see Figure 2-I for its structure). The spectral features in 3b are significantly different compared to its conducting form (Figure 3a). Figure 3b shows only resonances for polyaniline in the base form. The resonances for the PVP template are not observed in this spectrum. This suggests that polyaniline is no longer complexed with the template and it is detached from the PVP template in the base form. The detached PVP dissolves in water whereas PANI is insoluble. Therefore, no trace of PVP is observed in the solid-state ^{13}C CP/MAS NMR spectrum in Figure 3b. These results suggest that it is possible to separate the template from the enzymatically synthesized PANI-PVP complex after its role in promoting the linear chain growth. This is important, since it was believed earlier that it might not be possible to separate the template from the polyaniline. With this procedure, it may now be possible to enhance the conductivity of template-detached PANI by redoping. The separation of PANI from its template, PVP, is further confirmed by ^1H NMR data of the filtrate. The ^1H NMR spectrum shows the spectral feature of PVP (spectrum not shown).

In Figure 3b, the strong resonance peak at 123.7 ppm is assigned to protonated carbon of the benzenoid ring (C2, C3) while the protonated carbon resonance of the quinoid ring appears at 136.4 ppm (C8) (Figure 2-I). Other features of the spectrum are the appearance of shoulders at 141.3 and 145.9 ppm. These resonances are assigned to non-protonated carbons of the benzenoid ring (C4, C5, C1). The resonance at 157.0 ppm is due to non-protonated carbons of the quinoid ring (C7). The chemical shifts assignment for various resonance peaks of the base form of enzymatically synthesized PANI are summarized in Table 1. The above assignments are based on the earlier work reported by Kaplan *et al.* [12] for chemically synthesized PANI. This indicates that the enzymatically synthesized PANI contains bezenoid-quinoid repeating units in its backbone. The spectrum in Figure 4 is the ^{13}C CP/MAS NMR spectrum of the chemically synthesized emeraldine base that is a para-directed linear polymer chain. Both spectra in Figure 3b and 4

Table 1. ^{13}C CP/MAS NMR Chemical Shifts of Base Form of Enzymatically and Chemically Synthesized PANI

	Emeraldine Base Chemical Shift (in ppm*)	
Carbon No.	Enzymatically Synthesized	Chemically Synthesized
1	145.9	145.4
2,3	123.7	123.5
4	141.3	141.4
5	141.3	141.4
6	117.2	115.8
7	157.0	157.0
8	136.4	137.4

*Error of estimate = ± 0.5.

are identical in chemical shifts (Table 1), which confirm the para-directed enzymatic polymerization of aniline to form PANI in the presence of PVP template. Although all the peaks assigned for the chemically synthesized emeraldine base form are present in the spectrum of enzymatically synthesized PANI, some additional features are worth mentioning. The presence of a shoulder peak at 128.6 ppm in the ^{13}C NMR spectrum of the base form of enzymatically synthesized PANI suggests that this sample may contain some fraction of charged species like bipolarons shown in Structures II and V in Figure 2. The presence of a resonance peak at ca. 128 ppm is also observed in the base form of the chemically synthesized PANI (Figure 4). Solid-state ^{13}C NMR analysis of chemically synthesized and enzymatically synthesized PANI samples suggest that the dedoping process is incomplete and that some of the bipolaron states might have remained as residues in the base form. These observations are consistent with the earlier work reported by Kababya *et al.* [21].

The solid-state ^{13}C CP/MAS NMR spectrum of the redoped PANI sample after removal of PVP is shown in Figure 3c. The spectrum of enzymatically synthesized conducting PANI reproduces all the spectral features of the conducting PANI-PVP complex in 3a, except for the line width of the resonance of PANI. The line width of the redoped PANI sample is comparatively larger than the as-synthesized conducting PANI sample (Figure 3a and c). The larger line width may be a result of template removal from the complex during dedoping. The heterogeneities in the various chemical shift environments due to a change in morphologies of the redoped PANI sample may contribute to the line broadening. The measured conductivity of the doped PANI sample of Figure 3c was 7×10^{-2} S/cm. The origin of weak resonances at 95.0 and 172.0 ppm in Figure 3 not clearly understood at the present time and these resonances were not reported in the earlier studies [12, 20].

Solid-state ^{15}N CP/MAS NMR is a useful technique to study PANI samples since it is sensitive to monitor the chemical environments of charged and uncharged nitrogens in the polymer backbone. The chemical shift dispersion in

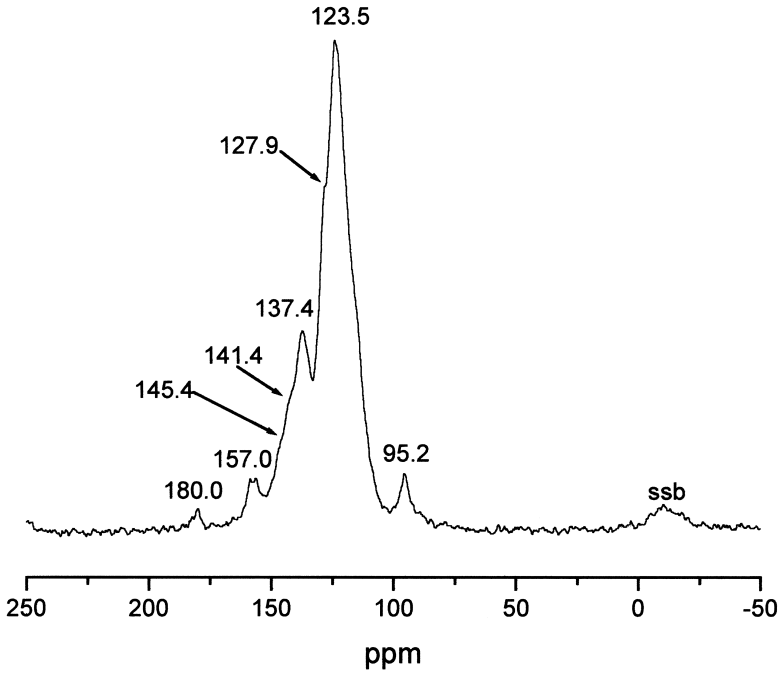


Figure 4. ^{13}C CP/MAS NMR spectrum of chemically synthesized PANI.

^{15}N NMR is large compared to ^{13}C NMR and it compliments the understanding of structural changes that may occur as a result of enzymatic synthesis. For example, the chemical shift difference between the resonances arising from benzenoid and quinoid structures is ca. 270 ppm where as the chemical shift difference between these structures is only ca. 10-20 ppm in the ^{13}C NMR. In addition, it is possible to distinguish the extent of charge distribution on various nitrogen species in PANI.

The solid-state ^{15}N CP/MAS NMR spectra of 100% ^{15}N-enriched of the enzymatically synthesized PANI-PVP complex and its dedoped base form are presented in Figure 5. The solid-state ^{15}N NMR spectrum of self-doped conducting sample (Figure 5a) shows interesting features compared to the spectrum of chemically synthesized polyaniline [20]. A broad peak in the 0-200 ppm region consisting of resonances at 24.5, 82.0 and 140.0 ppm are observed and assigned to amine and protonated imine nitrogens present in the conducting form of the PANI-PVP complex. The resonance peak at 82.0 ppm is due to amine -NH whereas protonated imine (Structure II in Figure 2) having positive charge on nitrogen appears at 140.0 ppm [22]. The broad nature of resonance peaks in 5a is a result of the chemical shift heterogeneities due to the delocalization of charges on the PANI backbone resulting in various resonance structures shown in Figure 2 (II-V). The nitrogens in the vicinity of radical cations (Structure III and IV in Figure 2) are not observed due to broadening caused by the paramagnetic electrons [12]. Excessive

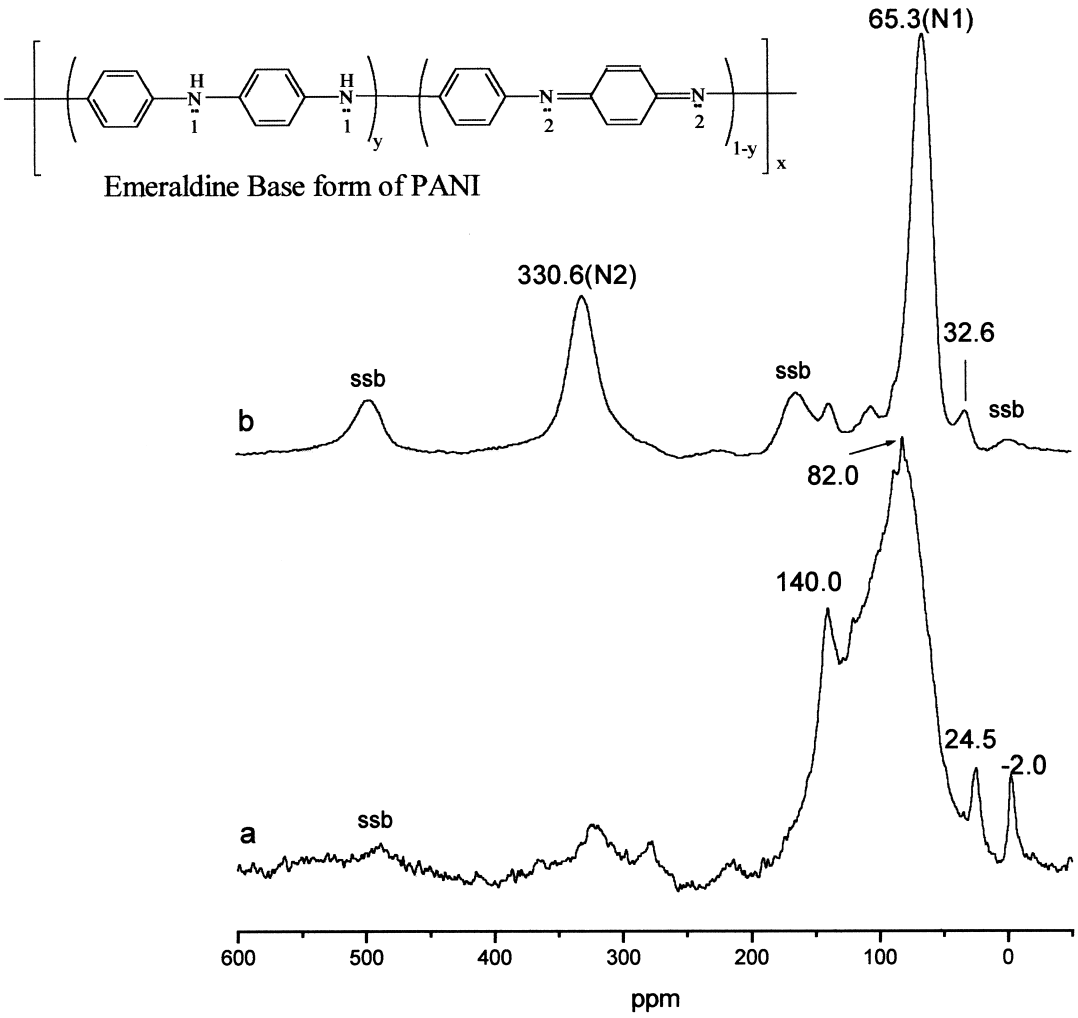


Figure 5. ^{15}N CP/MAS NMR spectra of enzymatically synthesized polyaniline (PANI): (a) self-doped conducting form; (b) dedoped base form (ssb = spinning side band).

line broadening of the ^{15}N resonance peaks as a result of higher conductivities in the chemically synthesized PANI was also observed by Wehrle *et al*. [23]. The two peaks at 82.0 and 140.0 have been assigned ppm to partially charged and fully charged nitrogen species (Espe *et al.* [20]) whereas uncharged amine nitrogen is assigned to the resonance peak at 67.0 ppm. The resonance peak for the uncharged amine nitrogen at 67 ppm in the chemically synthesized PANI is very strong [20]. Unlike in chemically synthesized PANI [20], the resonance peak at 82 ppm in Figure 5a is predominant and broad suggesting that the amine nitrogens in Structures III and IV of Figure 2, which are in the vicinity of paramagnetic species, charged nitrogen radicals. The chemical shifts of the amine nitrogens are

highly dependent on the extent of charges on the nitrogen radicals thus giving a distribution of chemical shifts for amine nitrogens. This suggests that the chemical shifts of the amine nitrogens are dependent on the extent of charge delocalization along the backbone. The ^{15}N NMR data presented for enzymatically synthesized PANI are similar to those of Wehrle *et al*. [23] for chemically synthesized conducting PANI. The resonance at 140.0 ppm may be due to nitrogens with highly localized charges (Structure II of Figure 2).

The upfield resonance at 24.5 ppm is assigned to the presence of anilinium ion end group ($–NH_3^+$) while the resonance peak at –2.0 ppm is assigned to the contributions of $-NH_2^+$ species of Structure V in Figure 2 [24]. In addition, broad downfield peaks between 250.0-400.0 ppm observed in the ^{15}N NMR might be due to the presence of uncharged imine nitrogen species. ^{15}N CP/MAS NMR data analysis suggests that there are few domains that are not protonated in the conducting form. The presence of the end group $-NH_2$ species may be assigned to either the formation of low molecular weight species or branched products.

The dedoping of PANI resulted in the appearance of two major peaks (Figure 5b). The resonance peak at 65.3 ppm is due to benzenoid -NH nitrogens whereas quinoid =N- nitrogens appear in the downfield (330.6 ppm) region. The spectral features in Figure 5b are identical to those of chemically synthesized PANI. This comparison strongly suggests that the enzymatically prepared PANI has the same structural units as in chemically synthesized PANI consisting of bezenoid and quinoid structures as shown in Figure 2-I. The peak at 32.6 ppm is mainly due to the end group $-NH_2$ species and is moved downfield by 8 ppm compared to its conducting form. The peak at –2.0 ppm in 5a is not observed in the base form due to the deprotonation of the amine nitrogen.

CONCLUSIONS

For the first time, it has been demonstrated using solid-state NMR techniques that the structural features of the conducting and base forms of PANI prepared from the template assisted enzymatic synthesis are similar to those of chemically synthesized PANI. The ^{13}C and ^{15}N CP/MAS NMR data clearly distinguishes charged and uncharged domains present in the various forms of PANI. Solid-state NMR results suggest that it is possible to separate the template from the polymer by dedoping the PANI-PVP complex with an aqueous NH_4OH solution.

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