Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Online publication date: 10 February 2002

To cite this Article Sahoo, Sangrama K. , Nagarajan, Ramaswamy , Chakraborty, Shuva , Samuelson, Lynne A. , Kumar, Jayant and Cholli, Ashok L.(2002) 'VARIATION IN THE STRUCTURE OF CONDUCTING POLYANILINE WITH AND WITHOUT THE PRESENCE OF TEMPLATE DURING ENZYMATIC POLYMERIZATION: A SOLID-STATE NMR STUDY', Journal of Macromolecular Science, Part A, 39: 10, 1223 — 1240
To link to this Article: DOI: 10.1081/MA-120014848
URL: http://dx.doi.org/10.1081/MA-120014848

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JOURNAL OF MACROMOLECULAR SCIENCE
Part A—Pure and Applied Chemistry
Vol. A39, No. 10, pp. 1223–1240, 2002

VARIATION IN THE STRUCTURE OF CONDUCTING POLYANILINE WITH AND WITHOUT THE PRESENCE OF TEMPLATE DURING ENZYMATIC POLYMERIZATION: A SOLID-STATE NMR STUDY

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ABSTRACT

Polyanilines (PANI) were synthesized from peroxidase-catalyzed polymerization of aniline with and without the presence of a template in the aqueous buffer solution of pH 4.3. The template used was poly (vinylphosphonic acid) (PVP). Solid-state ^{13}C and ^{15}N CP/MAS NMR techniques were applied to characterize the structure of polyaniline in its self-doped conducting, dedoped base, and redoped conducting form of PANI. The charge distribution along the polymer backbone in the protonated form of the polyaniline is also discussed. The structural features exhibited by a template assisted enzymatically synthesized PANI is the result of linear 1,4-coupling of aniline moiety while the PANI synthesized in the absence of template contains both 1,2- and 1,4-coupled products. Solid-state NMR studies on the enzymatically-synthesized polyaniline with the aid of template (PANI-PVP) confirmed the formation of a linear

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DOI: 10.1081/MA-120014848
1060-1325 (Print); 1520-5738 (Online)

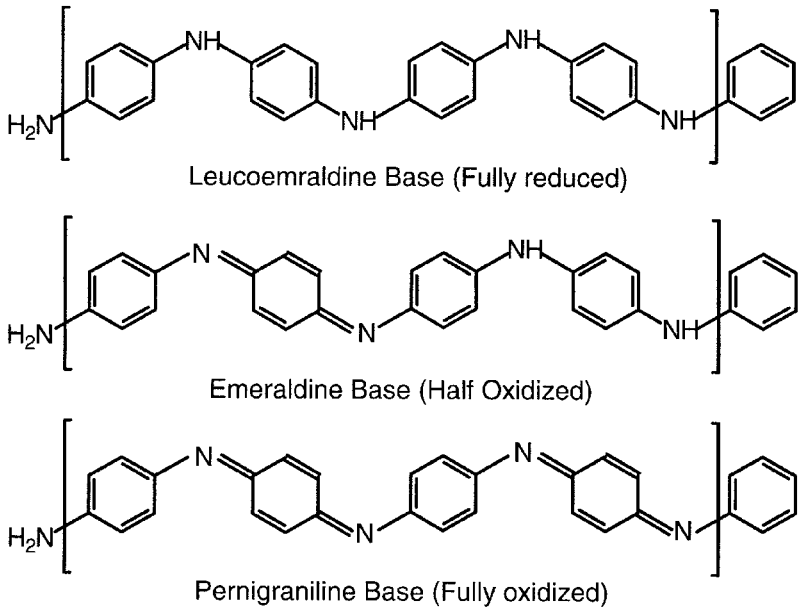
polymer chain containing alternate benzenoid-quinoid repeat units. The dedoped form is in the emeraldine base state of the polyaniline. The structural features in the spectra of the PANI synthesized without a template are quite different. Solid-state NMR data suggest that the PANI synthesized without aid of the template contains structures having C-C and C-N-C coupled products indicating the presence of branching in the polymer chain.

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

INTRODUCTION

Polyaniline, a phenylene based conducting polymer with a chemically flexible -NH- group has received a considerable amount of attention due to its unique electrochemical and optical properties.[1] Polyaniline has been synthesized by oxidizing aniline, either through chemically,[2] electrochemically,[3] or by enzymatic polymerization in aqueous acidic media,[4] the latter being an environmental benign approach. Our recent efforts are in the development of novel, environmentally friendly, enzymatic methods for the synthesis of water-soluble conducting polyaniline in the presence of macromolecular polyelectrolyte templates.[5–8] Horseradish peroxidase (HRP), a single-chain β-type hemoprotein is used as an enzyme for the polymerization of aniline. However, the local structure of the repeat units in polyaniline changes considerably with the synthesis conditions and the post-synthesis treatments.[9] The enzymatic polymerization of aniline typically results very low conductivity. In contrast, the use of a macromolecular polyelectrolyte template such as sulfonated polystyrene (SPS) or poly-(vinylphosphonic acid) (PVP) produces a linear conducting polymer in an aqueous pH 4.3 buffer medium with higher conductivity.[4] In the latter approach, preferential electrostatic alignment of aniline monomer onto an anionic polyelectrolyte template occurs in order to provide charge compensation, which also provides a low pH environment and hence promotes linear growth of polyaniline chain.[4,5] Therefore the structure of polyaniline depends on the nature of reaction medium as well as dopant.[1]

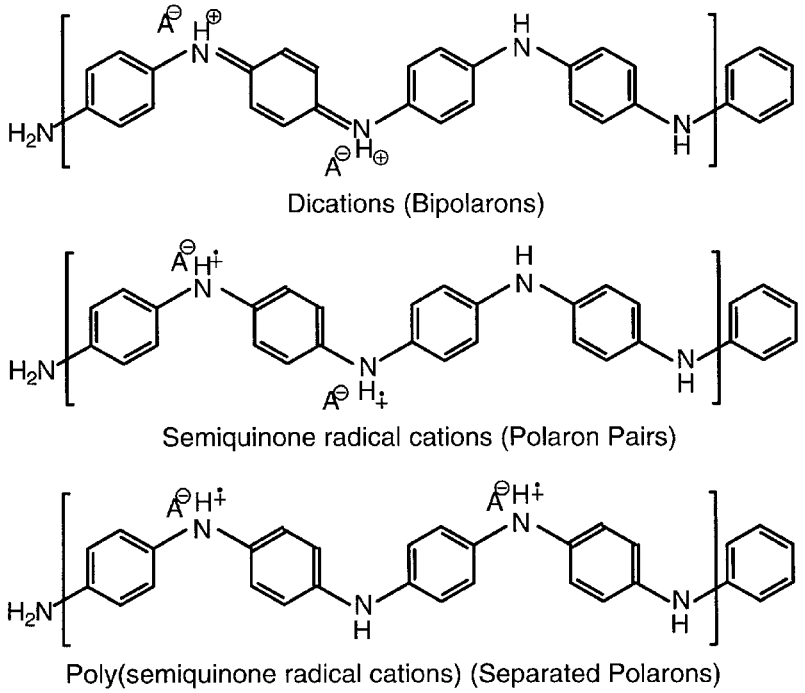
The structure properties of polyaniline, and hence its electronic and optical properties can be altered either by the nature and concentration of dopant (degree of protonation) or the oxidation state of the polymer.[10,11] Polyaniline exists in several oxidation states (e.g., Leucoemeraldine (fully reduced), Emeraldine (half oxidized), Pernigraniline (fully oxidized), etc.) with varying conductivity in the range of 10^{-11}–10^{2} S cm^{-1} depending on the degree of protonation. Some of the postulated structures of polyaniline in different oxidation states in the base form are shown in Sch. 1. Protonation of the base form (structures in Sch. 1) leads to the salt form of polyaniline with



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

an increase in conductivity, depending on the ratio of reduced to oxidized units. Higher conductivity is achieved from the protonation of emeraldine base form of polyaniline, which contains an equal number of reduced and oxidized units. In general, the doping of the polyaniline by strong acids leads to dications (localized bipolarons) due to the preferential protonation of imine nitrogen centered on the quinoid rings. The bipolarons may then inter convert into localized semiquinone radical cations (polaron pairs) or delocalized poly(semiquinone radical cations) (separated polarons) suggesting multiple structures of polyaniline in the conducting form (Sch. 2). Although these structures are widely accepted for conducting polyaniline, there are many variations in the compositions of various structures in the polymer obtained by different synthesis routes. The focus of the present work is to investigate the influence of polyelectrolyte template on the molecular structure during the enzymatic synthesis of polyaniline.

High-resolution solid-state NMR is a useful method in investigating the structural and dynamic aspects of chemically and electrochemically synthesized polyaniline in the base (insulating) as well as in the conducting form.[10–12] The solid-state ^{13}C and ^{15}N NMR studies of various forms of polyaniline synthesized chemically and electrochemically provided a wealth of information on the molecular structure, conduction mechanism, and dynamics of polymer chains in solid-state.[10–14] However, there is a limited literature information on the structural and dynamic aspects of enzymatically



Scheme 2. Various forms of polyaniline (PANI) in conducting form.

synthesized polyaniline by solid-state NMR spectroscopy.[9] Both ^{13}C and ^{15}N CP/MAS NMR techniques are used to elucidate the structural variation of PANI.

EXPERIMENTAL

Enzymatic Synthesis of Polyaniline

HRP catalyzed polymerization of aniline was carried out at room temperature with and without the presence of a PVP polyelectrolyte template. The pH of the reaction mixture was kept at 4.3 throughout the reaction. The detailed synthesis procedure was described elsewhere.[9] The color of the template-assisted polyaniline was green, while the latter was brown in color. The dedoping and redoping of PANI sample was carried out by treating with NH_4OH and HCl, respectively.[9] The conductivity was measured using a Cascade Microtech four-point probe, which displays a very low conductivity ($<10^{-8}$ S cm^{-1}) for polyaniline synthesized without template and 10^{-2} S cm^{-1} for polyaniline synthesized with template (PANI-PVP complex).

Solid-State NMR Measurements

Solid-state ^{13}C NMR experiments were carried out on a Bruker DMX 7.05 Tesla widebore magnet system equipped with a 4 mm triple resonance broadband probehead. 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 kHz. The typical parameters for ^{13}C CP/MAS NMR experiments were as follows: spin-lock field of 70 kHz, a 35 ms acquisition time, a 3 s recycle time, contact time of 2 ms and sweep width of 31 kHz. The total number of free induction decays (FIDs) co-added per spectrum was 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 176.03 ppm with respect to tetramethylsilane (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 15,000 to 40,000 FIDs which were co-added to get reasonable signal-to-noise ratio. The spectra were externally referenced to the ^{15}N signal of solid ammonium sulfate at 0.0 ppm.

Cross polarization time constants (T_{CH}) were determined from variable contact time experiments, and rotating frame proton spin-lattice relaxation times ($T_{1\rho}(H)$) were determined by holding the proton magnetization in a spin-lock field for a variable delay prior to cross polarization. The CP contact time was varied from 10 μs to 10 ms for these measurements. 8000 transients were coadded for each experiment.

RESULTS AND DISCUSSION

^{13}C NMR measurements on template-guided enzymatically synthesized PANI: The solid-state ^{13}C CP/MAS NMR spectra of polyaniline synthesized in the presence of PVP template are shown in Fig. 1. Figures 1a and b show the solid-state ^{13}C CP/MAS NMR spectra of polyaniline synthesized in the presence of PVP template, PANI-PVP complex in its self-doped conducting form and dedoped base form, respectively. The ^{13}C CP/MAS NMR spectrum of self-doped PANI-PVP complex (Spectrum **a**) shows a broad resonance (width at half height $\sim$20 ppm) centered about 128.6 ppm for all aromatic ring carbons. The resonance at 30.0 ppm in the aliphatic region is due to the presence of PVP polyelectrolyte template. The broadening in the aromatic spectral region of the conducting polyaniline is attributed to both

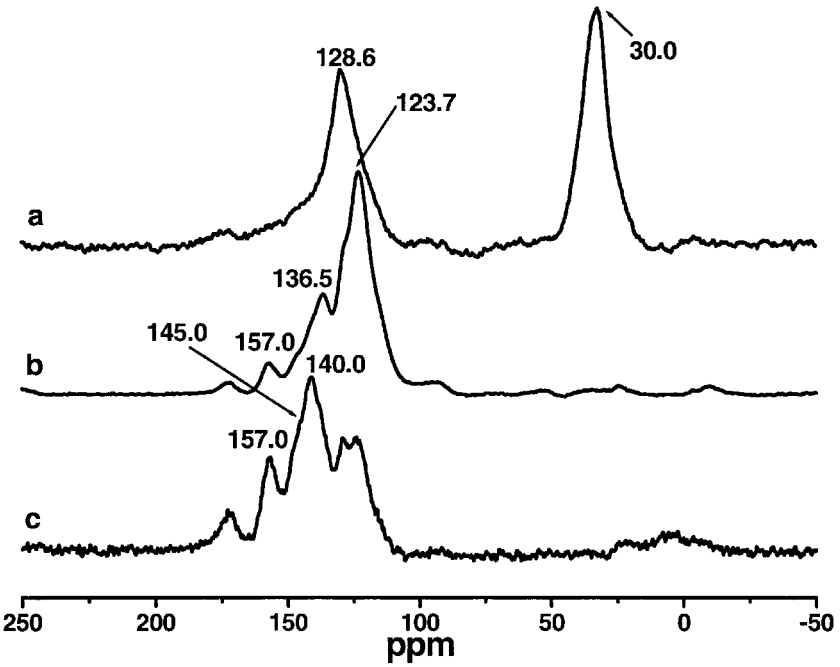


Figure 1. Solid-state ^{13}C NMR Spectra of enzymatically synthesized PANI with PVP template: (a) ^{13}C CP/MAS NMR spectrum of self-doped conducting form of PANI-PVP complex; (b) ^{13}C CP/MAS NMR spectrum of dedoped base form of PANI; (c) ^{13}C CP/MAS NMR spectrum of the sample in b with dipolar dephasing delay of 50 μs.

site heterogeneity and a distribution of isotropic chemical shifts due to the superposition of different structures as shown in Sch 2.[10,11] It may also have homogeneous line broadening due to electron-nuclear interactions. The solid-state ^{13}C spin-echo experiment on these polymers[15] shows a significant amount of line broadening suggesting the presence of electron-nuclear interactions. Inhomogeneous line broadening is removed in the spectrum by the spin-echo experiment. However, the line widths of the broad aromatic resonance in the spectrum of PANI-PVP complex (20 ppm) (Fig. 1a) are narrower compared to chemically and electrochemically synthesized PANI, which is ca. 50 ppm.[10,12] Low conductivity (10^{-2} S cm^{-1}) and narrower line widths may be related to the extent of self-doping by the PVP template, variation of charges and structural defects.

The dedoping of PANI-PVP complex results in the base form of polyaniline and the resultant solid-state ^{13}C NMR spectrum is shown in Fig. 1b. The dipolar dephasing ^{13}C CP/MAS NMR spectrum (technique is normally used to suppress the signals of the protonated carbons or those having strong dipolar coupling) with a dephasing delay of 50 μs is shown in Fig. 1c. The most significant spectral feature in Fig. 1b is the complete removal of macro-

molecular polyelectrolyte template PVP from the PANI-PVP complex during the dedoping process. This suggests that it is possible to remove the template from the enzymatically synthesized PANI-PVP complex after its role in directing the linear polyaniline chain growth. Thus the polyelectrolyte template has an electrostatic interaction with the polymer chain in the conducting form of polyaniline. The spectral feature of the resonances representing the polyaniline that is detached from the PVP is in the base form (Spectrum **b**) and agrees with the reported data on chemically and electrochemically synthesized PANI in the base form.[10–14] The ^{13}C CP/MAS NMR spectrum in Fig. 1b shows three well-resolved resonances at 123.7, 136.5 and 157.0 ppm. The resonance due to CH carbons of the benzenoid unit in the base form appears at 123.7 ppm, which is ~ 5 ppm up-field shift with respect to the doped PANI sample. This shift may be due to the localized charges on the neighboring nitrogen atoms or due to the delocalized charges in the aromatic rings.[16] The peak at 128.5 ppm is observed as a shoulder to the 123 ppm resonance peak in the base form PANI-PVP spectrum (Fig. 1b) and may be due to the residual charge domains, which failed to neutralize during the dedoping by NH_4OH. Figure 1c shows the modified ^{13}C CP/MAS NMR spectrum obtained in which protonated carbon (=CH-) resonances are partially suppressed and resonances due to non-protonated aromatic carbons (>C=) dominate the spectrum. The strong resonance peak at 140.5 and a shoulder at 145 ppm are distinct and clearly observed after the suppression of the peaks due to the protonated aromatic carbons at 115, 123.5, 128.5 and 136.5 ppm. The chemical shifts of all these resonances agree with the earlier reported data of Kaplan et al.[10] for chemically synthesized PANI. The NMR spectral analysis suggests the presence of alternate benzenoid-quinoid repeat units in the base form of template-assisted enzymatically synthesized PANI resembling the emeraldine base form of PANI.

A series of spectra obtained after different cross-polarization contact time for the dedoped PANI-PVP sample are presented in Fig. 2A. The spectra with short contact times (Fig. 2A) show resonances due to protonated carbons only. As the contact time increases in the cross-polarization experiment the resonances due to non-protonated aromatic carbons were also enhanced. The growth and decay of spin locked proton magnetization of different resonances in the dedoped form of PANI was measured by detecting ^{13}C cross-polarized NMR signals and the plots of peak amplitude vs. cross-polarization contact times are presented in Fig. 2B. These data reflects the cross polarization dynamics of the various resonances and it is possible to quantify the relaxation parameters such as T_{CH} and $T_{1\rho}$ (H). The values of these parameters as well as peak assignments are given in Table 1. The value of T_{CH} reflects the carbon-proton second moment, which is proportional to the C-H average distance and ^1H-^1H dipolar fluctuations modulated by molecular motions.[17] In the present work, the T_{CH} values can be divided into two categories, short T_{CH} for protonated ring carbons and long T_{CH} for

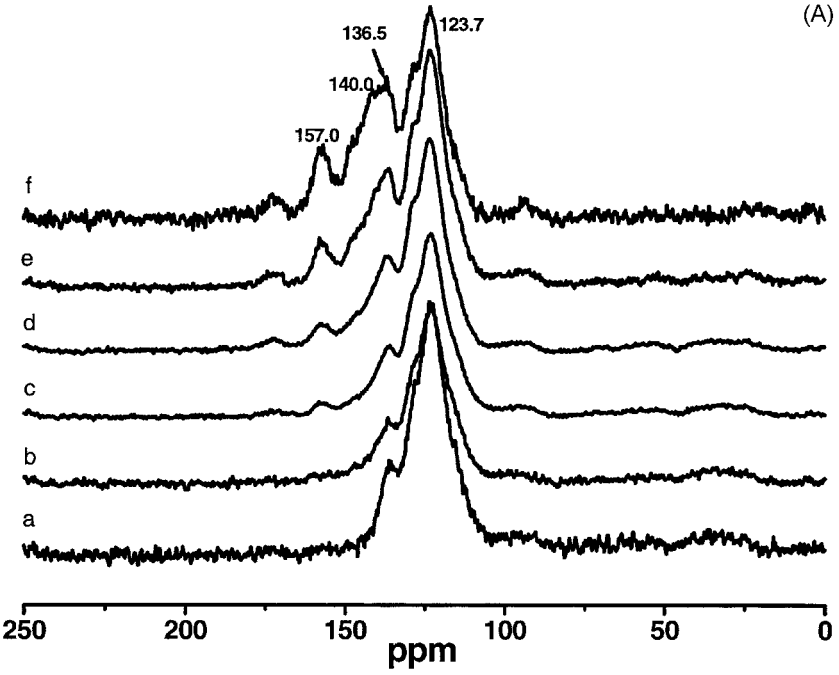


Figure 2. (A) Stacked Plot of solid-state ^{13}C CP/MAS NMR spectra of base form of PANI synthesized with PVP template at various contact time: (a) 10 μs; (b) 100 μs; (c) 500 μs; (d) 1 ms; (e) 5 ms; (f) 10 ms. (B) Plot showing the dynamics of cross polarization of various aromatic resonances of the sample in a.

non-protonated ring carbons. These relaxation data are in agreement with the assignments of various resonances and its comparison to chemically synthesized PANI. The rotating frame proton relaxation values of various resonances varied from 6 to 12 ms. In comparison, the self-doped PANI sample shows a very short T_{CH} value (20 μs) compared to dedoped PANI sample. Low T_{CH} value in the self-doped form represents restricted molecular motion of the PANI chain and may be due to the presence of macromolecular polyelectrolyte template hence its interaction with PANI chain reduces the mobility of the polyaniline moiety.

^{13}C NMR measurements of enzymatically synthesized PANI without the presence of template: The solid-state ^{13}C CP/MAS spectra of polyaniline synthesized without a template in its as-synthesized, dedoped and redoped form are shown in Fig. 3. The as-synthesized protonated form of PANI shows similar ^{13}C NMR spectral features as compared to PANI-PVP complex. ^{13}C CP/MAS NMR spectrum shows a broad peak in the aromatic region ca. 129.0 ppm. The shape of the resonances indicates the overlapping of two components: a relatively narrow resonance at 129 ppm overlapped by a broad one (Fig. 3a). The broad resonance may be due to the delocalization

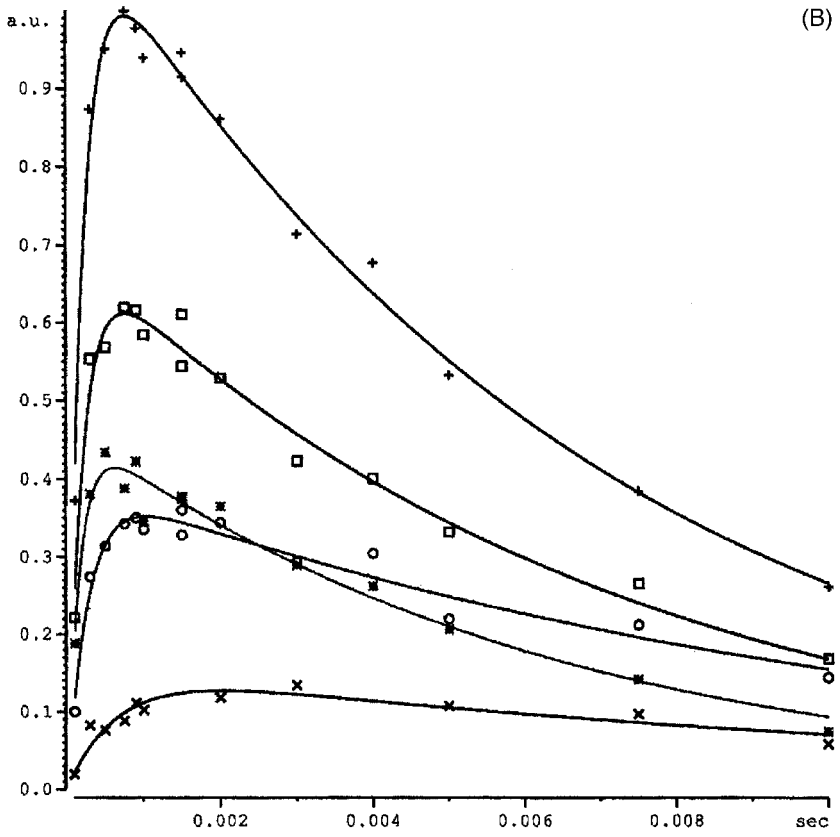
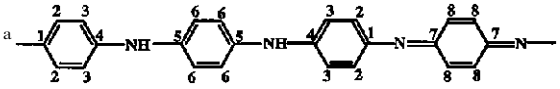


Figure 2. Continued.

Table 1. Chemical Shifts and T_{CH} and $T_{1\rho}$ (H) Values of Dedoped PANI Sample

Chemical Shift (in ppm)	Carbon Number[a]	T_{CH} (in μs)	$T_{1(\rho)}$ (in ms)
Base Form of Polyaniline			
114	6	168	6.2
123	2,3	207	6.8
136	8	274	10.6
140, 145	1,4,5	641	12.5
157	7	697	10.4
Conducting Form of Polyaniline			
129	–	20	11.5

a 

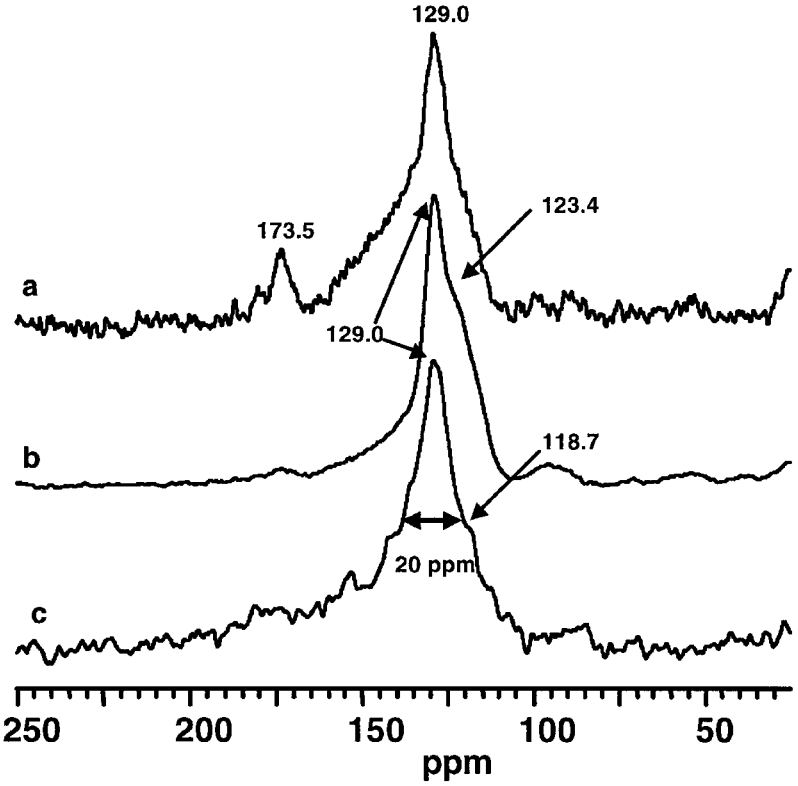


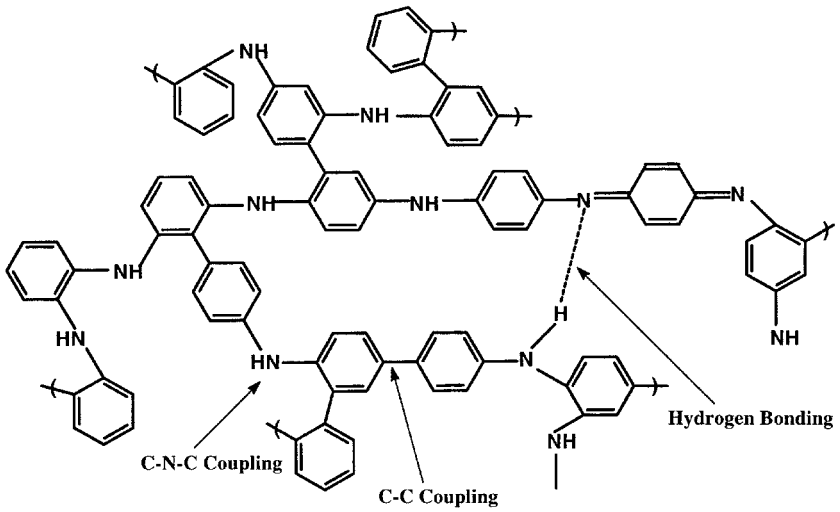
Figure 3. Solid-state ^{13}C CP/MAS NMR Spectra of enzymatically synthesized PANI without the presence of template (a) as-synthesized doped form of PANI; (b) dedoped base form of PANI; (c) redoped form of PANI. (* denotes spinning side band).

of charges on the nitrogen to the aromatic ring as observed in the conducting PANI. This observation agrees with the postulate that in the protonated form of polyaniline, the positive charge resides mainly on nitrogen and some portion of the charge delocalizes onto the C_6H_4 rings.[16] However, poor signal-to-noise ration in the spectrum (Fig. 3a) compared to its dedoped spectrum (Fig. 3b) shows that most of the magnetization in the doped sample is lost due to the presence of paramagnetic centers. The relative integral area for the doped and dedoped PANI is 0.2:1.0. This indicates the loss of ^{13}C magnetization in the doped state of enzymatically synthesized PANI without template is greater than the chemically synthesized PANI.[11] These results suggest that the bipolaronic contribution in the doped state is significantly lower relative to the conducting PANI sample.[15] The observable ^{13}C magnetization in the conducting form is from the bipolaronic states as the signals in the vicinity of radical center (polaronic sites) vanishes due to various paramagnetically induced relaxation processes. The presence of down-field

resonance peak at 173.5 ppm is not clear in the PANI system (Fig. 3a). It may be due to oxidation of the PANI chain ends to form N=O, which shifts the neighboring non-protonated aromatic carbon resonance to down-field. The ^{13}C CP/MAS NMR spectrum of PANI prepared without the presence of template shows striking structural differences (Fig. 3) when compared to Fig. 1 for template assisted PANI.

The base (dedoped) form of PANI shows unusual ^{13}C NMR spectral features (Fig. 3b) compared to data shown in Fig. 1. Treating the PANI sample with NH_4OH resulted in the removal of charges from the aromatic rings, showing reduced line broadening in the down-field region (135–170 ppm). The peak at 129 ppm in as-synthesized form (Fig. 3a) did not shift up-field as a result of dedoping. However, unlike emeraldine base form where the number of benzenoid and quinoid rings is the same, in this sample, the quinoid resonances are not detected indicating the structural variations. The appearance of 123.4 ppm peak for CH type aromatic resonances is possible only if these aromatic rings are next to the quinoid type structures. Even though quinoid resonances were not observed in the natural abundant ^{13}C NMR spectrum (Fig. 3b). However their presence was observed in labeled ^{15}N NMR spectrum (discussed below). The other non-protonated carbons of the PANI sample show a broad distribution of chemical shifts in the region of 125–160 ppm mostly due to the branched products as a result of both C-C and C-N-C couplings.[18]

A structural model of branched PANI is proposed along with a predicted ^{13}C NMR spectrum (using commercially available NMR software (ACD Labs.)) is presented in Sch. 3 and Fig. 4, respectively. No line



Scheme 3. Model for branched Polyaniline structure showing C-C and C-N-C coupling at 1,2- and 1,4-positions as well as possible hydrogen bonding.

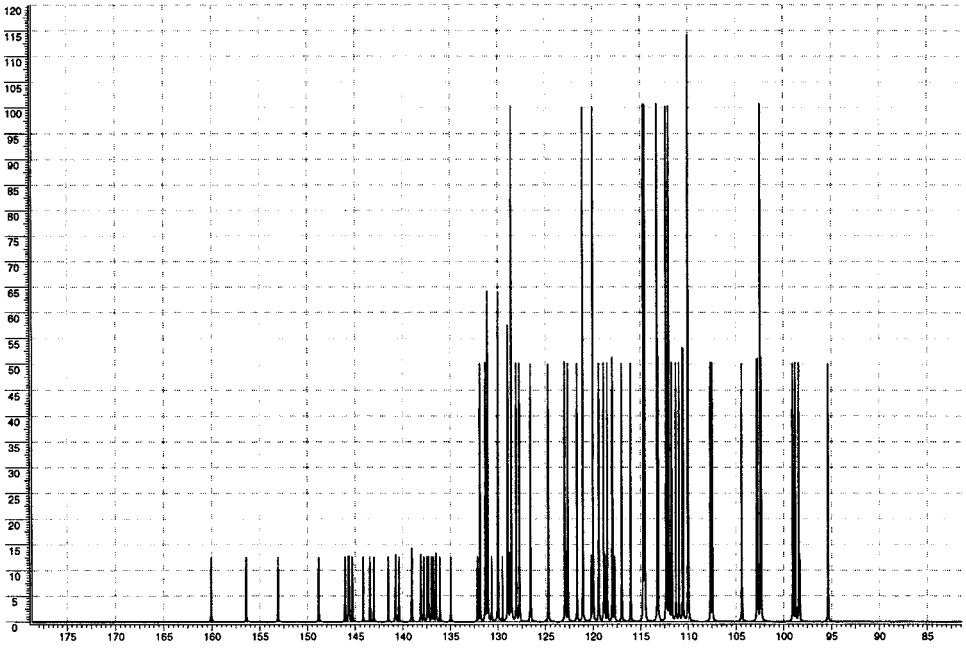


Figure 4. Predicted ^{13}C NMR spectrum of model compound as described in Sch. 3 using ACD software.

broadening was used in the synthetic spectrum presented in Fig. 4 to show the possible variation of chemical shifts arising from structural heterogeneities. In Fig. 4, due to the dominance of branched products most of the intense resonances are in the 110–130 ppm range. The non-protonated aromatic carbons are in many different environments showing a heterogeneous chemical shift distribution resulting a broad distribution of peaks down-field to 125 ppm. These features matched with the experimental data (^{13}C CP/MAS NMR spectrum in Fig. 3b) on the enzymatically synthesized PANI without a template. The dominant branched structures contribute to the broad distribution of chemical shifts for the non-protonated aromatic carbons and hence no well defined peaks in the ^{13}C CP/MAS NMR spectrum (Fig. 3b). Thus, the ^{13}C NMR observation in the branched form of PANI without a template suggests the presence of branching in the polymer. This is also supported by conductivity measurements on the as-synthesized PANI ($\sigma < 10^{-8}$ S cm^{-1}). The spectral features of PANI redoped with HCl (Fig. 3c) shows a similar ^{13}C NMR spectral feature as of as-synthesized PANI (Fig. 3a). However, after redoping, the down-field tail is relatively less intense and the peak at 173.5 ppm is absent. The intensity decrease for the 123 ppm resonance suggests the preferential doping on the residual benzenoid-quinoid repeat units. The chemical shifts of other resonances were remained the same even after doping.

^{15}N measurements on template-guided enzymatically synthesized PANI: The Solid-state ^{15}N CP/MAS NMR spectra of PANI-PVP complex in its self-doped, dedoped, and redoped forms are presented in Fig. 5. A broad resonance in the 0–200 ppm range is mostly due to uncharged amine and charged (protonated) imine nitrogens of the PANI-PVP complex (Sch 2). The broad chemical shift heterogeneities are mostly due to the delocalization of charges along the polyaniline backbone, and the nitrogen-anion distribution due to variation in the proximity of counter ions of the polyelectrolyte template.[19] The heterogeneity of the charges on the nitrogen atom in the PANI backbone is mostly due to the contributions from various structures that are present in the conducting form.[11] The strong peak at 140 ppm indicates the presence of positively charged imine nitrogens, which proves the

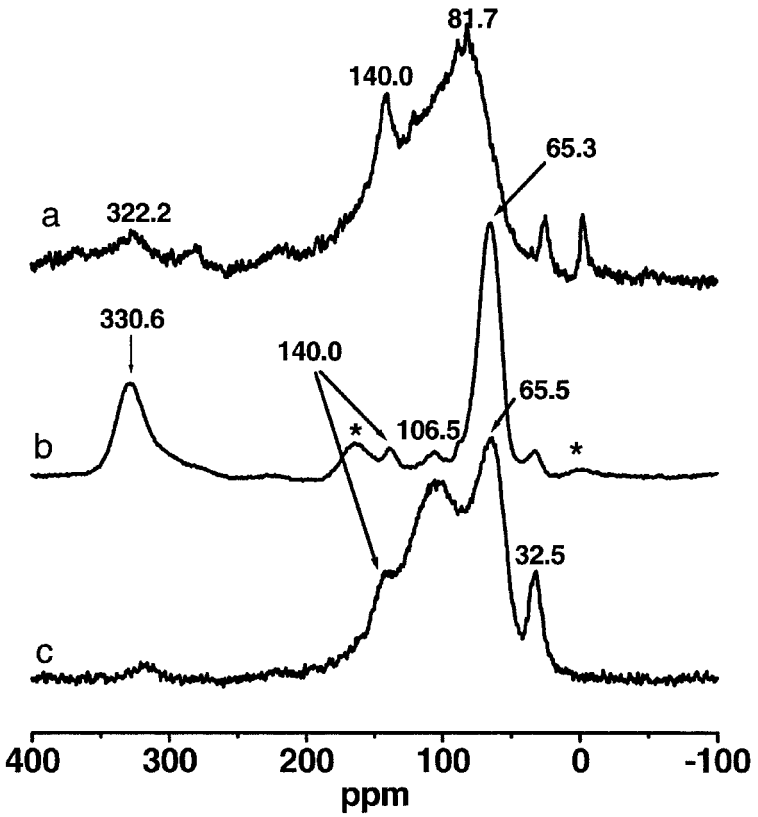


Figure 5. Solid-state ^{15}N CP/MAS NMR Spectra of enzymatically synthesized PANI with the PVP template: (a) self-doped conducting form of PANI-PVP complex; (b) dedoped base form of PANI; (c) redoped conducting form of PANI.

existence of bipolaronic charge carriers in this sample. Upon dedoping, the spectrum narrowed (Fig. 5b) and the prominent changes are seen in the imine nitrogen region. The dedoping resulted in the deprotonation and hence the down-field shifts of the imine peak from 140 ppm to 330 ppm due to the unprotonated imine nitrogen. The removal of charge from the PANI backbone also resulted in the up-field shift of the amine nitrogen resonance to 65 ppm. Similarly, the protonated anilinium ion end group complexed with the template, which appeared at 24.5 ppm in the doped PANI-PVP complex (Fig. 5a), shifted ~ 8 ppm down-field to 33 ppm after deprotonation. The redoping of the dedoped PANI-PVP sample by HCl resulted in the broadening of the resonances (Fig. 5c). As a result of protonation, the imine nitrogen peaks shifted up-field and appeared around 100–140 ppm. The peak at 65 ppm is the intense resonance peak in the redoped form. The data shows that during redoping, the imine nitrogens are preferentially protonated to form bipolarons and the polaronic contribution may be relatively less compared to as-synthesized PANI-PVP complex. The strong peak at 100 ppm (Fig. 5c) suggests that the charges are not as much localized as in the as-synthesized self-doped PANI-PVP complex. This is mostly due to the small size of the counter ion Cl^- compared to macromolecular polyelectrolyte template that is present in the sample of Fig. 5a. The small counter ion is more mobile than the bulky template, thus minimizing the nitrogen-anion distance distribution.

^{15}N NMR measurements of enzymatically synthesized PANI without the presence of template: The solid-state ^{15}N CP/MAS spectra of polyaniline synthesized without a template and its dedoped and redoped forms are shown in Fig. 6. The ^{15}N NMR spectrum of the as-synthesized PANI sample shows three resolved resonances in the amine and protonated imine chemical shift range (40–150 ppm). The resonance at 72.5 ppm is due to the unprotonated amine nitrogens (-NH-) in the PANI backbone. The other resonances appear relatively down-field to the peak at 72.5 ppm are mostly due to the protonation of imine nitrogens. Two well-resolved peaks at ~ 104 and 146 ppm can be assigned to the partially charged and fully charged nitrogen species.[11] However, the intensity of these resonances is less compared to the PANI-PVP complex and may be due to the relatively smaller concentration of imine nitrogens in the PANI backbone. Another interesting feature of the spectrum in Fig. 6a is the chemical shift for the imine protons appears at ca. 275 ppm where as it is ca. 330 ppm in the template assisted PANI. The appearance of a broad resonance at the 275 ppm, which can be assigned to imine nitrogens (Ph = N-Ph) hydrogen bonded with the amine nitrogens (Ph-NH-PH) in the branched structures of the PANI chain. This assignment is based on the ^{15}N NMR studies of model compound azophenine.[20] After dedoping of the PANI sample, the ^{15}N NMR spectral features resembled to the dedoped PANI-PVP sample in the amine region, and showed a less intense resonance in the imine region. The relative area of amine to imine

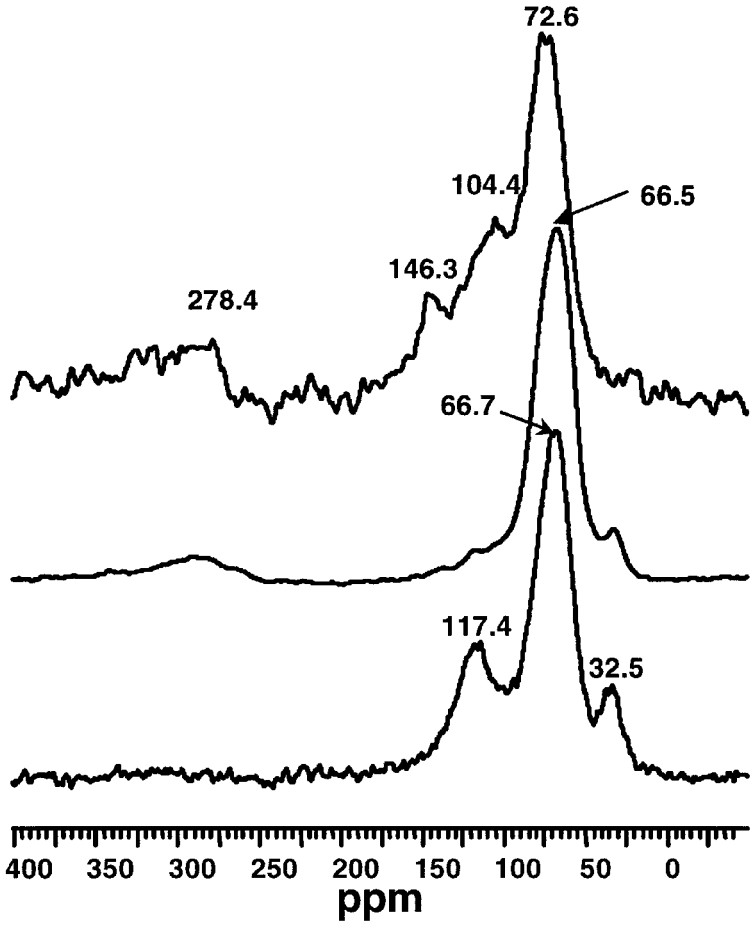


Figure 6. Solid-state ^{15}N CP/MAS NMR Spectra of enzymatically synthesized PANI without the presence of template (a) as-synthesized doped form of PANI; (b) dedoped base form of PANI; (c) redoped form of PANI.

nitrogens in Fig. 6b indicates that the polymer is dominated by -NH- species and only a few imine nitrogens (i.e., quinoid rings) are present. It is postulated that the polyaniline that contains an equal number of benzenoid and quinoid repeat units exhibits highest conductivity.[10] Thus, the PANI sample synthesized without a template shows less conductivity due to the absence of an equal number of quinoid repeat units in the PANI backbone. After dedoping the up-field peak that appeared at 72 ppm in doped state shifted further up-field to 66 ppm indicating complete removal of charges from the PANI backbone. After dedoping, the imine nitrogens appeared in the same

position as in the doped base form suggesting that the intramolecular hydrogen bonding is also present in the dedoped form. The ^{15}N Spectra obtained before and after dedoping showed an increase in the signal-to-noise ratio of the PANI sample suggesting that doping induced localized paramagnetic centers in the PANI backbone. Comparing the results of the conducting PANI sample[9b] with the present work on PANI synthesized without aid of a template indicates the loss of magnetization in the doped state compared to the dedoped state is greater for the latter sample. This may be due to the absence of a linear PANI backbone, forbidding the hopping or tunneling of electrons, which is necessary for conductivity. These dispersed radicals cause relaxation of NMR resonances resulting in the loss of magnetization in both ^{13}C and ^{15}N NMR spectra. Unfortunately, for a fully doped PANI with HCl at pH 1.0 we were unable to see any magnetization in the ^{15}N NMR spectrum. This may be due to the presence of large amount of fixed paramagnetic centers, which wipes out the entire magnetization. To confirm this, the redoped sample was further treated with a pH 4.0 buffer to reduce the paramagnetic centers from the PANI backbone by partial dedoping. The ^{15}N CP/MAS spectrum obtained after redoping at pH 4.0 is presented in Fig. 6c. This spectrum shows the preferential protonation of the imine nitrogens, which is observed from the disappearance of imine nitrogen peak at 275 ppm and the appearance of a well-resolved peak at 117 ppm due to protonated imine nitrogens. The resonance position of the amine nitrogens (-NH-) remained the same after redoping and resembled the results obtained from the redoping of the PANI-PVP complex. The analysis of the spectral features of the various forms of PANI synthesized without a template shows that the ^{15}N magnetization in the doped state represents only a fraction of PANI that contain benzenoid-quinoid repeat units.

CONCLUSION

Detailed solid-state ^{13}C and ^{15}N NMR characterization of polyaniline, enzymatically synthesized with and without a template, revealed the variation in the structural features of PANI chain with varying synthetic conditions. We have shown that solid-state NMR is a sensitive technique in detecting the changes in the various forms of the PANI backbone. Comparative study revealed that PANI obtained without the use of a template during enzymatic polymerization catalyzed by HRP produced a branched product in which the dominant coupling mechanism is either C-C or C-N-C at the 1,2- and 1,4-positions. The required benzenoid-quinoid repeat units of the conducting PANI are minor constituents of the total polymer. The spectral features in the conducting PANI-PVP sample are distinct compared to that of PANI synthesized without a template. The fewer benzenoid-quinoid repeat units in the PANI synthesized without a template is clear from the ^{15}N NMR spec-

trum of the dedoped sample. Moreover, the spectral features of the imine nitrogen species showed intramolecular hydrogen bonding with the neighboring benzenoid amine nitrogens.

ACKNOWLEDGMENTS

The authors thank the National Science Foundation for the research grant (Grant # DMR-9986644). SC thanks for the summer support in part by the U.S. Army Research and Engineering Apprentice Program through the Academy of Applied Sciences, Concord, NH.

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