

Micro-Chemical Structure of Polyaniline Synthesized by Self-Stabilized Dispersion Polymerization

Hyun Namgoong¹, Dong Jin Woo, and Suck-Hyun Lee*

Department of Molecular Science and Technology, Ajou University, Suwon 443-749, Korea

¹Kolon Central Research Park, Mabukri, Guseongseup, Youngin City 449-797, Korea

Received July 2, 2007; Revised August 27, 2007

Abstract: A variety of NMR techniques were applied to the micro-chemical structural characterization of polyanilines prepared via an efficient synthetic method in a self-stabilized dispersion medium in which the polymerization was conducted in a heterogeneous organic/aqueous biphasic system without any stabilizers. Here, the monomer and growing polymer chain were shown to function simultaneously as a stabilizer, imparting compatibility for the dispersion of the organic phase, and as a form of flexible template in an aqueous reaction medium. Polymerizations predicated on this concept generated polyanilines with a low defect content: solution state ¹³C-NMR and solid ¹³C DD/CP/MAS spectroscopy indicated that the synthesized HCPANi and its soluble derivative, HCPANi-*t*-BOC, evidenced distinctly different NMR spectra with fewer side peaks, as compared to conventionally prepared PANis, and the complete structural assignments of the observed NMR peaks could be determined via the combination of both 1D and 2D techniques. Ortho-linked defects in HCPANi were estimated to be as low as 7%, as shown by a comparison of the integration of the carbonyl carbon resonance peaks.

Keywords: polyaniline, self-stabilized dispersion polymerization, NMR characterizations, chemical microstructure.

Introduction

Polyanilines (PANis) have been known for more than 100 years and reported as existing in ill-defined forms like “aniline black”, “emeraldine”, and “nigraniline”. The major breakthrough to achieve characterization of the various forms of PANis must be the discovery of electrical conductivity for its emeraldine salt form leading to an explosion of studies since the mid 1980s.¹ MacDiarmid *et al.* undertook systematic studies on PANis and reported a series of PANis having the structure formula which is now generally accepted as shown below.^{2,3} It consists of alternating oxidized imine and reduced amine repeat units. The average oxidation state, ($1-y$) can be varied from 1 to zero to give three principal forms of PANis usually distinguished: the fully oxidized ($y=0$), “perrigraniline”, half oxidized ($y=0.5$), “emeraldine” and fully reduced ($y=1$), “leucoemeraldine” polymer. Even though enormous progress in their synthesis and spectroscopic characterization has been observed in the last two decades, the exact structure determination is still challenging because of its poor solubility in conventional solvents and structural irregularity in conventional PANis. In fact, observed complex PANi structure defies representation by its repeat struc-

ture, particularly where side branching or crosslinking affect much to the overall polymer structure-property relation like electrical conductivity. Recently we have not only discovered an efficient synthetic method⁴ to prepare highly conducting PANis with structural regularity but also succeeded in obtaining a large enough solubility in common NMR solvents to investigate its chemical structures by incorporating an acid- and thermo-labile *tert*-butoxycarbonyl (*t*-BOC) group into the PANi backbone.⁵ By this discovery we were motivated to undertake the micro-structural characterizations of PANis by NMR.

Only a few studies have been devoted to the NMR investigations, solution state ¹³C-NMR and solid ¹³C DD/CP/MAS spectroscopy to characterize PANis structurally⁶ and the available resolution was too limited to allow the identification of the postulated structures therefore defects in the structure could not be identified with certainty. To our knowledge, in no case any complete structural analysis has been given for PANi. In this paper, we present results concerning ¹H- and ¹³C-NMR analyses using distortionless enhancement by polarization transfer (DEPT) and various 2-D techniques of the newly produced PANi in our laboratory and compared them with those of the conventionally prepared PANi. The first section describes briefly an innovative method of PANi preparation using a concept of self-

*Corresponding Author. E-mail: hyja@ajou.ac.kr

stabilized dispersion polymerization (SSDP).⁴ The most commercially successful method of producing processible forms of conducting polymers has been the aqueous dispersion route through the chemical oxidation of the monomer. In this dispersion polymerization polymer particles are formed from an initially homogeneous reaction mixture by polymerization and stabilized against coagulation in the presence of steric stabilizers such as poly(vinyl alcohol), poly(ethylene oxide), poly(*N*-vinyl pyrrolidone), poly(styrene sulfonate), dodecylbenzene sulfonate and dextran sulfonate. Early work on production of PANi is summarized in Ref.1. Our SSDP is carried out in a heterogeneous organic/aqueous biphasic system without any stabilizers and the monomers and growing polymer chains play a major role in stabilizing adequate dispersions of an organic phase in an aqueous reaction medium. Throughout this paper the polymer prepared by this SSDP will be referred to as HCPANi and the conventionally prepared one by MacDiarmid method as CPANi. The second section deals with solution state ¹³C-NMR and solid ¹³C DD/CP/MAS spectroscopy. We report details of chemical microstructure of PANi from the DEPT, HMBC, HETCOSY and DQF-COSY NMR methods.

Experimental

Synthesis of Emeraldine Base (EB). Aniline (Merck) was used as purchased and water used for polymerization was purified by distillation in an all glass distillation unit. Aniline solution in HCl was added to chloroform/water mixture and stirred until it becomes turbid solution at 0 °C. Ammonium persulfate (APS) solution in HCl was then added dropwise, with stirring, to the cooled reaction mixture. The polymerization reactions were carried out in a 2-liter jacketed reaction vessel with an anchor stirrer paddle. The syntheses were stopped when the solution takes the characteristic green color. We were able to produce medium molecular weight PANis after a time period of reaction 6-10 h with a high yield (95-100% with respect to APS and almost 20% with respect to aniline). The reaction mixture was filtered, washed, deprotonated, and dried. For comparison, conventional PANi was synthesized at the same temperature according to the literature procedure reported by MacDiarmid *et al.*⁷ that becomes a standard synthesis.

Synthesis of PANi(*t*-BOC). PANi(*t*-BOC) was synthesized from the EB according to the procedure reported elsewhere.⁶ To a solution of PANi (4.9 g, 0.014 mol) and 13 mL (0.16 mol) of pyridine in 100 mL of *N*-methylpyrrolidinone (NMP) was added slowly di-*tert*-butyl dicarbonate (Boc₂O) (9.0 g, 0.041 mol) in 50 mL NMP at 80 °C. The mixture was stirred for 3 h under a nitrogen atmosphere. The reaction mixture was filtered and the filtrate solution was precipitated into methanol and dried to give a polymer PANi(*t*-BOC) as pale dark red powders.

Characterization. The inherent viscosity (IV) of the EB

solutions (0.1 g/100 mL in conc. H₂SO₄) was measured with a capillary Ubbelohde viscometer at 30 °C. Note that all the measurements here were made without the additives such as LiCl to prevent the aggregation of the chains because LiCl is known to induce a certain degree of doping in the polymer that has different levels of aggregation.⁸

The molecular weight of PANi(*t*-BOC) dissolved in THF was measured with a GPC (Waters 150 CV) at 50 °C. Calibration curves were obtained using polystyrene and polyvinylpyridine standards.

Solution NMR measurements were performed on a JEOL YH400 spectrometer at 400 MHz. For all the 2D spectra 512 t2 time domain and 256 increments were applied. After the 256 points zero-filling, the processing was carried out by using the sine-bell window function and automatic baseline correction.

Carbon-13 dipolar decoupling (DD)/cross polarization (CP)/magic angle spinning (MAS) NMR spectra were acquired with a Larmor frequency 100.62 MHz on a Bruker DSX 400 spectrometer with spinning rate 7.0 kHz at room temperature. The contact time is adjusted to maximize the intensity of carbon-13 spectra with 2 ms at 50 kHz under Hartman-Hahn condition. The chemical shift of ¹³C was referenced to the external TMS and adamantane sample with $\pi/2$ pulse (¹³C) = 2 μ s and $\pi/2$ pulse (¹H) = 5 π s.

Thermogravimetric analysis (TGA) was made by Model DSC 2010 and Model 2050 of TA Instruments (heating rate: 10 °C/min).

Results and Discussion

Characterization of EB and PANi(*t*-BOC) by H-NMR and TGA. Recently we have developed an efficient synthetic method for PANi preparation based upon a new concept of SSDP. Instead of using conventional homogeneous, dispersion,⁹ or interfacial polymerization,¹⁰ nano particles^{11,12} in an aqueous medium of aniline, acid, oxidant, we synthesized PANi in a heterogeneous organic/aqueous biphasic system without any additives such as stabilizers and anti-freezers. Here, the monomer and growing polymer chain act simultaneously as an interfacial agent, imparting compatibility for the dispersion of the organic phase, a kind of flexible template, in an aqueous reaction medium.

PANi(*t*-BOC) was synthesized by reacting the synthesized EB with Boc₂O in NMP/pyridine as solvent. The EB form has two amine nitrogens followed by two imine nitrogens along the chains. Interestingly, the mono-*t*-BOC-substituted products were obtained for CPANi while in case of HCPANi, two *t*-BOC groups substituted for the two amine nitrogens were mainly obtained as confirmed by comparisons of the integration of the ¹H-NMR peaks and TGA. The ¹H-NMR spectra of CPANi(*t*-BOC) showed a singlet peak at 1.5 ppm for 9H of *t*-BOC and broad double peaks at 6.8-7.2 ppm for 16H of aromatic protons in the benzoid and

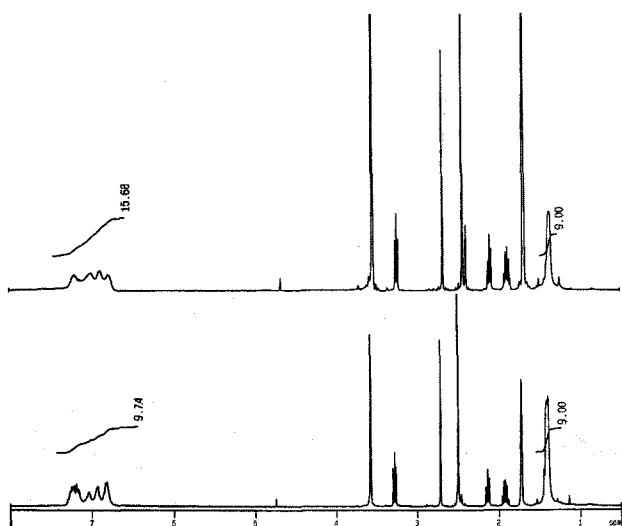


Figure 1. The ^1H -NMR spectra in THF of CPANi-*t*-BOC (top) and HCPANi-*t*-BOC (bottom) derived from CPANi synthesized by MacDiarmid method and HCPANi by SSDP, respectively.

quinoid rings as shown in Figure 1.

In case of HCPANi(*t*-BOC) the number of protons associated with the former signal of the two changed. Its ratio turned out to be 9.7H : 9H as shown in Figure 1, indicating about two *t*-BOC groups per four aromatic rings. The concentration of the repeat units substituted with two *t*-BOC groups was estimated to be more than 92%, which is consistent with the following TGA results.

Figure 2 shows comparative TGA results for PANi(*t*-BOC) prepared from the two types of the samples, HCPANi and CPANi. The results indicated that the removal of the *t*-BOC groups in CPANi occurs at about 180 °C, losing 17.2% of its weight by 250 °C while HCPANi starts to decompose at a much lower temperature around 70 °C and the decomposition processes are more complex.

The weight loss profile indicates that the cleavage in HCPANi is a two-stage process which leads to a total amount of 32.8% loss, almost two times of that reached in CPANi by 250 °C and the complete weight loss of each step by about 500 °C agrees approximately with the theoretical values, 21.6 and 35.6% of the decomposition of the two *t*-BOC groups. This different weight loss profile might be attributed to different chemical microstructure of PANi. We believe that the irregular structure comes into play in determining chemical reactivity of the amine groups with Boc_2O . The one of the amine groups in CPANi did not undergo substitution reaction due to steric hindrance caused by side reactions such as ortho-couplings. We will investigate these side reactions from the NMR analysis below.

Characterization of PANi by Solution NMR. Various solution NMR techniques were used for the structural elucidation of PANi. Compared to leucoemeraldine of the earlier known soluble PANi, the solubility in common solvents and

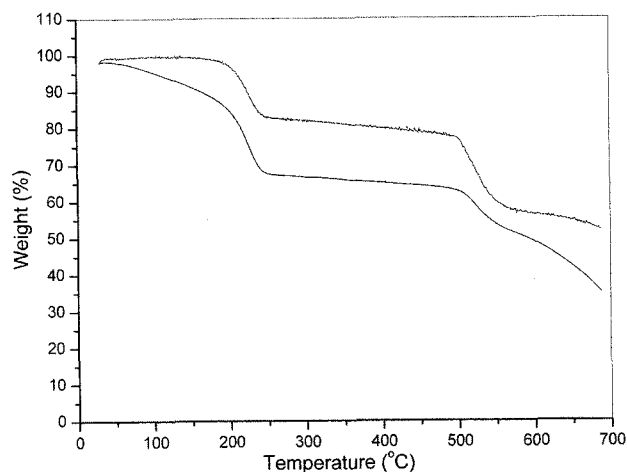


Figure 2. TGA thermograms of the CPANi-*t*-BOC (top) and HCPANi-*t*-BOC (bottom) measured under a nitrogen atmosphere, which displayed the cleavage of *t*-BOC groups.

a wealth of NMR peaks of PANi(*t*-BOC) allowed a much more detailed structural analysis. Moreover, PANi(*t*-BOC) is stable; by contrast leucoemeraldine is air sensitive and undergoes partial oxidation even with minute amounts of air. The proton-decoupled ^{13}C -NMR spectrum of HCPANi-*t*-BOC (IV=0.86) is shown in Figure 3, together with two other spectra of the samples run under similar conditions for comparison (Figure 4).

These soluble PANi derivatives are designated as HCPANi-*t*-BOC and CPANi-*t*-BOC of the present SSDP and conventional method, and Ald-PANi-*t*-BOC for PANi commercially available PANi of number average molecular weight 10,000 from Aldrich Inc., respectively. In the case of HCPANi-*t*-BOC and CPANi-*t*-BOC, the number average molecular weights were around 25,000 with polydispersity index of 5.0, respectively.

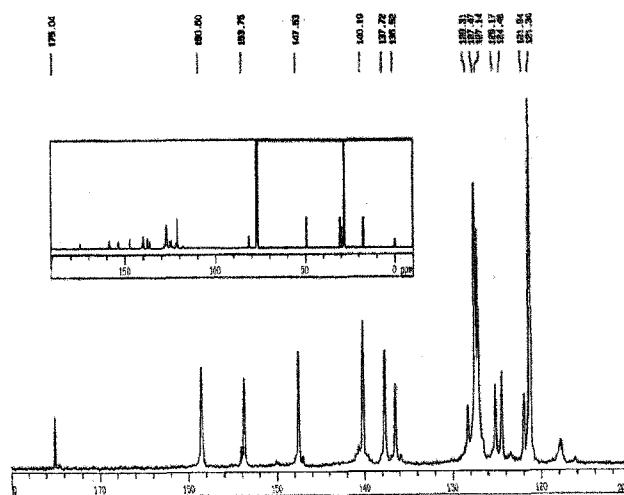


Figure 3. The ^{13}C -NMR spectra in CDCl_3 of HCPANi-*t*-BOC derived from HCPANi synthesized by SSDP. The inset is a whole spectrum.

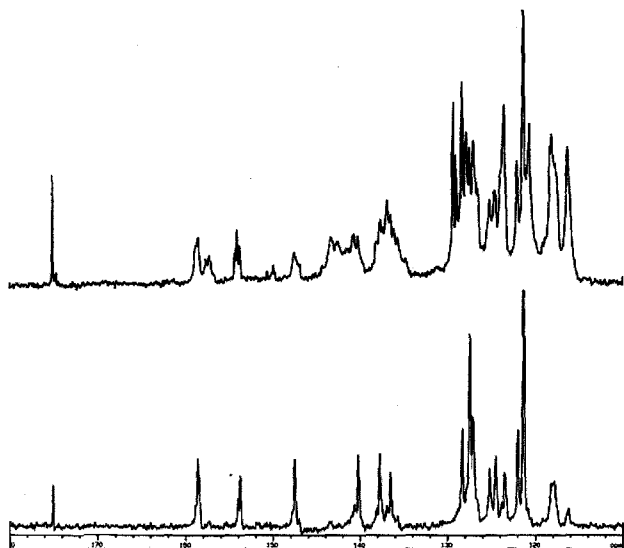
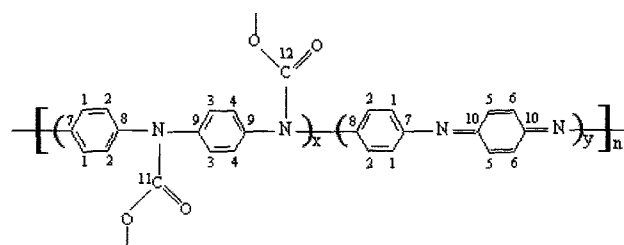


Figure 4. The ^{13}C -NMR spectra in CDCl_3 of Ald-*t*-BOC (top) and CPANi-*t*-BOC (bottom) derived from commercially available Ald-PANi ($M_w = 10,000$ from Aldrich Inc.) and CPANi synthesized by MacDiarmid method, respectively.

The most remarkable fact from the comparison of the spectra shown in Figures 3 and 4 is the reduced peak numbers and width of the aromatic carbon resonances between 110 and 160 ppm for HCPANi-*t*-BOC. There are no resonances below 110 ppm, which suggests that the meta-PANi in which aromatic rings are bonded at the meta-positions was not produced as byproducts.^{13,14} These reduced complexities enabled us to investigate its microstructure.

For the precise peak assignment the DEPT experiment was first used which is shown in Figure 5. The DEPT 90 and 135 spectra revealed that there are no signals at the chemical shift more down field than 140 ppm. Thus, the observed chemical shifts of the main peaks at about 140, 148, 154, 158 ppm are originated from the non-protonated carbons such as benzoid and quinoid and carbonyl carbons.



In order to establish the carbon-carbon connectivities of benzoid and quinoid rings the inverse detected heteronuclear multiple bonds correlation (HMBC) experiment has been carried out.

These long-range connectivities between coupled protons and carbons could exist via $^3\text{J}(\text{C},\text{H})$ and $^2\text{J}(\text{C},\text{H})$ through intervening carbon bonds. Figure 6 shows the ^1H -detected

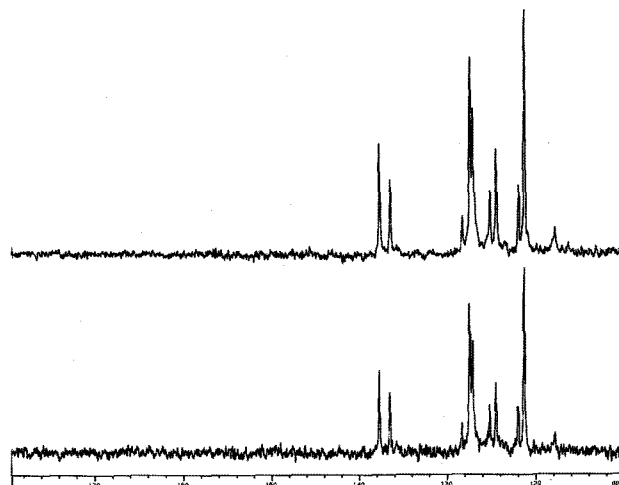


Figure 5. DEPT spectrum in CDCl_3 of HCPANi-*t*-BOC derived from HCPANi synthesized by SSDP: DEPT 135 (top) and (b) DEPT 90 (bottom).

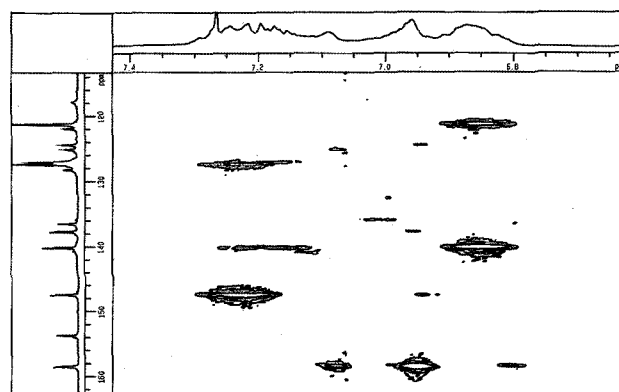


Figure 6. HMBC spectrum in CDCl_3 of HCPANi-*t*-BOC derived from HCPANi synthesized by SSDP at room temperature.

field gradient-HMBC spectrum obtained on the JEOL YH400 spectrometer. The carbon peak at 153.8 ppm shows no direct correlation with proton peaks and therefore this carbon was assigned to the carbonyl carbon (C11,12) of the *t*-BOC groups in the repeat structure. Electron withdrawing *t*-BOC groups made the quaternary carbon resonate at higher frequency.¹⁵⁻¹⁷ It can also be observed from the HMBC that the (C,H) correlation signals of quinoid quaternary carbon, C(10) at 158 ppm with 6.95 and 7.08 ppm of quinoid protons appear in the spectrum. Furthermore, the benzoid quaternary carbon, C(7) adjacent to quinoid moiety could easily be assigned on the basis of the correlation between the band at 147.0 ppm and the two proton resonances of 6.94 and 7.22 ppm. In a like manner, from the contour at the intersections of the broad line resonances around the 6.85, 7.2, 140 ppm we determined the chemical shift of the quaternary carbons (C8,9).

Having assigned the chemical shifts of the quaternary car-

bons, the HETCOSY method was used to connect the proton resonances to those of the carbons bearing them. Figure 7 shows the correlation cross peaks between the protonated ring carbons and their protons. With the aid of the proton spectrum assignment, the protonated carbons could be readily assigned. The carbon peaks C(1-4) ($\delta_c = 121.3, 127.5$ ppm) coming from the benzoid ring carbons show larger peaks than those of the quinoid due to the mobility of the aromatic ring like ring flipping; by contrast the C=N-bond of quinoid ring prevents ring rotations, thus quenching the motion of the carbon-proton inter-nuclear vector.¹⁸ This restricted motion gave rise to the smaller intensity for the quinoid carbon compared to those of the benzoid ring carbons. However, due to the double bond character of the imine linkage in quinoid moiety the inequivalence of protonated ring carbons is expected. These effects are reproduced in the observed HETCOSY spectrum with the 136.5 and 125.2 ppm, C(5,6). Figure 6 illustrates also that the unassigned central proton at 6.95 ppm of the three correlation ^1H peaks, which appeared at the carbon peak at 158 ppm in HMBC, is directly correlated with the 137.7 ppm, C(5,6). Generally the ^{14}N - ^1H coupling and the long range correlation between the carbon and proton through nitrogen nucleus are not observable because of the intrinsic quadrupolar interaction of the nitrogen nucleus with surroundings.¹⁹ Thus, the correlated proton peak at 6.95 ppm with quinoid carbon can be originated from the high symmetry of quinoid ring carbons.

To elucidate the origin of this correlated signal the DQF-COSY technique was used. We observed no cross peaks with 6.95 ppm (Figure 8). Furthermore, if the relative orientations of the quinoid ring carbons are highly symmetric as in trans quinoid conformation with syn benzoid,²⁰ a magnetically equivalent carbon is possible along the quinoid ring albeit inherent chain stiffness in the quinoid-imine system. Thus, a singlet NMR line resulted by virtue of this symmetry-related equivalence. The protonated benzoid ring carbons were also identified from the combination of the HETCOSY and DQF-COSY correlation spectra (Figures 7

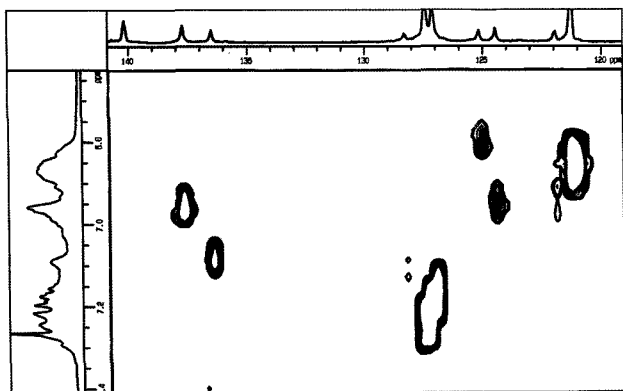


Figure 7. HETCOSY spectrum in CDCl_3 of HCPANI-*t*-BOC derived from HCPANI synthesized by SSDP at room temperature.

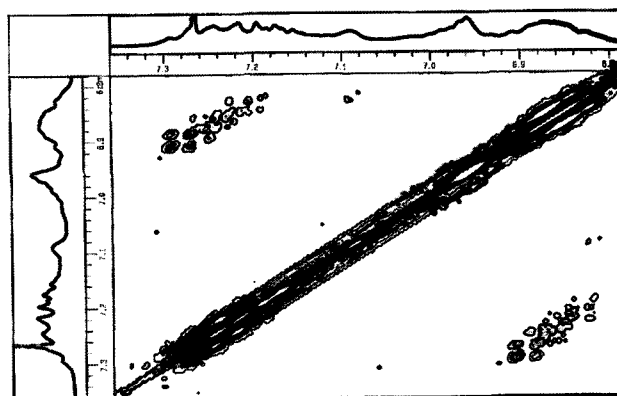
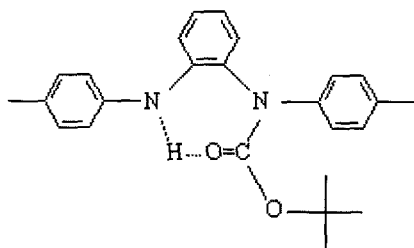


Figure 8. DQF-COSY spectrum in CDCl_3 of HCPANI-*t*-BOC derived from HCPANI synthesized by SSDP at room temperature.

and 8). The smaller peak near the carbon at 121.9 ppm and the intense NMR lines at 121.3 ppm and 127.5, 128.3 ppm were assigned to the protonated benzoid ring carbons (C1-C4).

In general the electrical conductivity is closely related to the chemical bonding and structure, especially p-overlap of conjugated aromatic ring and the observed symmetry by trans-syn structure of PANi affect the conductivity in a favorable way.^{1, 21-23} The HMBC gives the clear identification of regular repeat structure of the PANi-*t*-BOC. The bulky *t*-BOC functional groups should lie in so as para-linked with respect to the quinoid-imine ring to entail the minimum chemical shift dispersion of proton and carbon nucleus. Thus the simplicity around these chemical shifts of the observed spectrum suggests the regularly linked structure for HCPANI-*t*-BOC without branching points in contrast with those of CPANI-*t*-BOC. This explains the observed high conductivity of HCPANI. In contrast to conventional conducting polymers dominated by disorder-induced localization, this new PANi exhibited a 'true-metallic' response such that the electrical resistivity decreases as the temperature is lowered down to ~ 5 K, and the optical spectra are described by the conventional Drude model in the low energy ranges.²⁴

In order to try to evaluate some of the possible structures that might be giving rise to the minor peaks in the spectrum, we compared two spectra of HCPANI-*t*-BOC and CPANI-*t*-BOC. It should be more challenging to identify side peaks but we were encouraged to see subtle differences in the two products. What are interesting were the appearance of a minor peak at a lower field than that of the main peak at the chemical shift of carbonyl carbon, 154 ppm as well as the different intensity ratio of these two peaks: the relative ratio is roughly 7.2% for HCPANI-*t*-BOC while it's 30% for CPANI-*t*-BOC. Note that these integrations were not acquired under conditions that minimize NOE. The number of *t*-BOC groups attached to the repeat structure did not affect the chemical shift of the minor peak. As previously mentioned, HCPANI-*t*-BOC contains two *t*-BOC groups or two carbo-



Scheme I. Intramolecular hydrogen bonding.

nyl carbons in the repeat structure while CPANi-*t*-BOC contains only one but their two peak positions did not change. About the origin of this minor peak, we predict, however, that, if the polymer segments contain the following ortho-defects, a peak would appear at a more down field with different intensity ratios. As previously mentioned, the branchings arise owing to the ortho-linking and the possible Michael reductive additions of aniline.^{12,25} When the ortho-linked repeat unit exists in the chain, the relative orientations of the two rings may be controlled by intramolecular hydrogen bondings and the carbonyl carbons should be deshielded by the stereo-electronic interaction as depicted in Scheme I. Based on this reasoning we assigned this minor peak to the carbonyl carbon originated from the ortho-linked byproducts partly incorporated in the polymer. Large multiple peaks around 123.3 ppm, which are only found in CPANi-*t*-BOC support this assignment. According to Meyer *et al.*,²⁶ the resonances associated with the unsubstituted carbons of such an ortho-substituted ring occur remarkably at 123 ppm. HCPANi-*t*-BOC exhibited no discernible peak intensity at this chemical shift, indicating negligible amount of this byproduct. As would be expected on the result of this analysis, the ortho-linked defects in HCPANi were produced by as much as 7%. Even with the fact that the PANi that is dissolved reacts to produce HCPANi-*t*-BOC and is of a somewhat lower molecular MW than the material as a whole, the analysis that follows is still of interest and reveals much of the nature of PANi microstructure and the influence of polymerization conditions on molecular structure. The following solid CP/MAS spectra of as synthesized EB particles (Figure 9) supported this interpretation. To our knowledge, this is the first example of quantitative information on the byproducts of PANi. It should be also noted that the ortho-linked byproducts gave rise to most of the single substituent products in HCPANi since its concentration was estimated to be about 8% according to ¹H-NMR data (Figure 1).

The more side carbon resonances around the benzoid and quinoid protonated carbons were also observed in Figure 4, being indicative of byproducts. For example additional resonance peaks centered at 116.3 and 117.9 ppm may be due to the presence of leucoemeraldine chain defects.

Solid State Characterization of PANi-*t*-BOC and PANi. The DD/CP/MAS spectra were obtained for HCPANi and

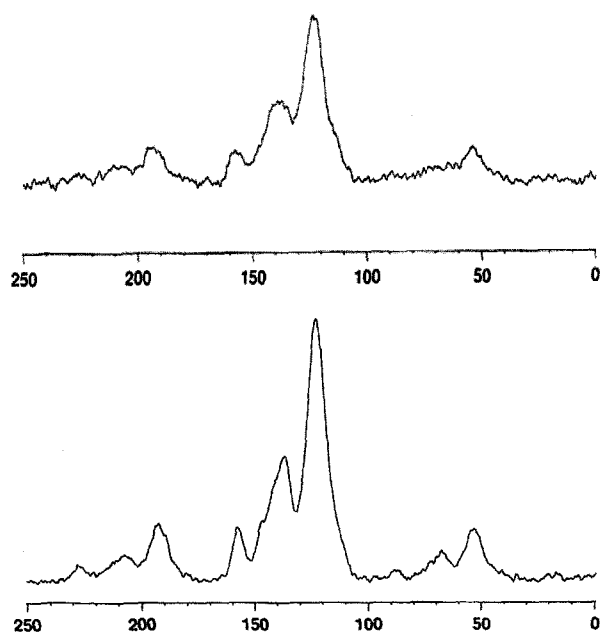


Figure 9. ¹³C DD/CP/MAS spectra of CPANi (top) and HCPANi (bottom) synthesized by MacDiarmid method and SSDP, respectively.

CPANi prepared from the EB particles and they are compared in Figure 9. The results of our solid-state NMR studies of the two PANis are consistent with several known structural features reported in the literature.^{18,27-32} Four characteristic peaks were observed at 123, 137, 141, 148 (shoulder) and 158 ppm relative to TMS. Clear peak assignment for each carbon could be made: peak at 158 ppm and a shoulder at 148 ppm (non-protonated carbons 10 and 7, respectively), peaks around 140 ppm (benzoid carbons C(8,9) at 141 ppm, and quinoid carbons C(5,6) at 137.7 ppm), peak at 123 ppm and a shoulder at 113 ppm (benzoid carbons C(1,2) and C(3,4), respectively). Compared with the spectra observed in CPANi, the spectra for HCPANi are significantly better resolved and no other small peaks or shoulders related to defect sites are appeared in the spectra. Particularly they consisted of a sharp single peak at 123 ppm, presumably a consequence of removing contributions made by carbon nuclei in side products such as ortho-byproducts.

An unexpected outcome of our studies has been the observation that the *t*-BOC substitution reaction of amine group of CPANi by Boc₂O proceeded at one of the two nitrogens in the repeat structure of the EB form. Possible causes for this notable difference of the two polymers, HCPANi and CPANi observed in the substitution reaction are probably related to the change in chain conformation.

Conventionally prepared PANi or CPANi were revealed to contain much more defects such as ortho-linked aniline rings (30%). When the conformation of a chain begins to change by such an ortho-coupling, then a cluster effect may

occur above a certain defect level such that the whole chain changes its expanded conformation into a more coil-like one. The resultant compact conformation would tend to promote one substitution of *t*-BOC only. We postulate that the substitution reaction of the amine group in the repeat structure adjacent to the amine group already substituted by *t*-BOC is hampered by the steric hindrance due to the neighboring bulky *t*-BOC group.

Conclusions

We have presented an efficient synthetic method for PANi preparation based upon a new concept of SSDP. This synthesis was carried out in a heterogeneous organic/aqueous biphasic system without any stabilizers. We have shown that polymerizations based on this concept produced PANis with a low content of defects. Solution state ^{13}C -NMR spectroscopy indicates that soluble HCPANi-*t*-BOC prepared from this HCPANi exhibits distinctly different NMR spectra with fewer small peaks, as compared to conventionally produced CPANi. By combination of both 1D ^1H - ^{13}C -NMR spectroscopy and 2D ^1H - ^{13}C -HMBC correlations the complete structural assignments of the observed NMR peaks could be made. The side peak around the main peak at 154 ppm related to the carbonyl carbon was traced to be due to the ortho-linked byproducts through the characteristic downfield shift of the resonance of carbons in the hydrogen bond-forming groups and their intensity ratio provided convincing information on the content of this defect-related products. The ^{13}C CP/MAS NMR spectra were consistent with these solution NMR data, indicating that the improvement in PANi synthesis resulted in the polymer sample to be almost entirely composed of phenylene rings connected by para-linked nitrogens. This SSDP technique can be an attractive heterogeneous route for the production and control of other conducting polymers for plastics electronics.

Acknowledgement. We acknowledge the financial support by MOCIE, M200701004, through KITECH.

References

- (1) G. G. Wallace, G. M. Spinks, L. A. P. Kane-Maguire, and P. R. Teasdale, in *Conductive Electroactive Polymers*, CRC Press, New York, 2003, pp 51. A. J. Epstein, in *Organic Electronic Materials*, R. Farchini and G. Gross, Eds., Springer, Berlin, 2001, pp 3. B. Wessling, in *Handbook of Nanostructured Materials and Nanotechnology*, H. S. Nalwa, Ed., Academic Press, San Diego, 2000, pp 501.
- (2) A. G. MacDiarmid, J. C. Chiang, M. Halpern, W. S. Huang, S. L. Mu, N. L. Somasiri, W. Wu, and S. I. Yaniger, *Mol. Cryst. Liq. Cryst.*, **121**, 173 (1985).
- (3) W. S. Huang, B. D. Humphrey, and A. G. MacDiarmid, *J. Chem. Soc. Faraday Trans. 1*, **8**, 2385 (1986).
- (4) S.-H. Lee, D. H. Lee, K. Lee, and C. W. Lee, *Adv. Funct. Mater.*, **15**, 1495 (2005).
- (5) C. Lee, Y. H. Seo, and S.-H. Lee, *Macromolecules*, **34**, 4070 (2004).
- (6) S. Kaplan, E. M. Conwell, A. F. Richter, and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **110**, 7647 (1988).
- (7) A. G. MacDiarmid, J. C. Chiang, A. F. Richter, N. L. D. Somasiri, and A. J. Epstein, in *Conducting Polymers*, L. Alcacer, Ed., D. Reidel, Dordrecht, 1987, pp 105.
- (8) A. Yasuda and T. Shimidzu, *Synth. Met.*, **61**, 239 (1993).
- (9) S. P. Armes, in *Handbook of Conducting Polymers*, T. A. Skotheim, R. L. Elsenbaumer, and J. R. Reynolds, Eds., 2nd, Marcel Dekker, New York, 1998, pp 423.
- (10) J. Hwang, S. Virji, B. H. Weiller, and R. B. Kaner, *J. Am. Chem. Soc.*, **125**, 314 (2003). J. Huang and R. B. Kaner, *J. Am. Chem. Soc.*, **126**, 851 (2004). J. Huang and R. B. Kaner, *Angew. Chem. Int. Ed.*, **43**, 5817 (2004).
- (11) J. Jang, J. Ha, and S. Kim, *Macromol. Res.*, **15**, 154 (2007).
- (12) K. Mallick, M. J. Witcomb, and M. S. Scurrell, *Gold Bulletin*, **39**, 166 (2006).
- (13) N. Spetuseris, R. E. Ward, and T. Y. Meyer, *Macromolecules*, **31**, 3158 (1998).
- (14) J. Louie and J. F. Hartwig, *Macromolecules*, **31**, 6737 (1998).
- (15) J. P. Sadighi, R. A. Singer, and S. L. Buchwald, *J. Am. Chem. Soc.*, **120**, 4960 (1998).
- (16) C. A. Fyfe, in *Solid State NMR for Chemists*, C. F. C. Press, Guelph, Ontario, 1983.
- (17) M. Mehring, *Principles of High Resolution NMR in Solids*, Springer-Verlag, Berlin, 1983.
- (18) A. Raghunathan, G. Ranbarajan, and D. C. Trivedi, *Synth. Metals*, **81**, 39 (1996).
- (19) E. O. Stejskal and J. D. Memory, *High Resolution NMR in the Solid State*, Oxford Press, New York, 1994.
- (20) A. M. Kenwright, W. J. Feast, P. Adams, A. J. Milton, A. P. Monkman, and B. J. Say, *Polymer*, **33**, 4292 (1992).
- (21) A. J. Heeger, *Rev. Mod. Phys.*, **73**, 681 (2001). A. J. Epstein, in *Organic Electronic Materials*, R. Farchini and G. Gross, Eds., Springer, Berlin, 2001, pp 3.
- (22) S. A. Ashraf, L. A. P. Kanemaguire, M. R. Majidi, S. G. Pyne, and G. G. Wallace, *Polymer*, **38**, 2627 (2003).
- (23) X. X. Zhang, J. P. Sadighi, T. W. Mackewitz, and S. L. Buchwald, *J. Am. Chem. Soc.*, **122**, 7606 (2000).
- (24) K. Lee, S. Cho, S. H. Park, A. J. Heeger, C. W. Lee, and S.-H. Lee, *Nature*, **441**, 65 (2006).
- (25) P. N. Adams, D. C. Apperley, and A. P. Monkman, *Polymer*, **34**, 328 (1993).
- (26) R. E. Ward and T. Y. Meyer, *Macromolecules*, **36**, 4368 (2003).
- (27) A. Yasuda and T. Shimidzu, *Synth. Met.*, **61**, 239 (1993).
- (28) S. K. Sahoo, R. Nagarajan, S. Roy, L. A. Samuelson, K. Kumar, and A. L. Cholli, *J. Am. Chem. Soc.*, **37**, 4130 (2004).
- (29) Y. Goddard, R. L. Void, and G. Hoatson, *Macromolecules*, **36**, 1162 (2003).
- (30) T. Young, M. P. Espe, D. Yang, and B. R. Mattes, *Macromolecules*, **35**, 5565 (2002).
- (31) R. Mathew, D. Yang, B. R. Mattes, and P. Espe, *Macromolecules*, **35**, 7575 (2002).
- (32) M. Zagorska, A. Pron, and S. Lefrant, *Handbook of Organic Conductive Molecules and Polymers*, H. S. Nalwa, Ed., Jhon Wiley & Sons, New York, 1997, Chap. 4, pp 190.