



Nanostructures obtained in the oxidative polymerization of aniline: Effects of polarons



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ABSTRACT

Effects of polarons on the single (NH₄OH) and double (NH₄OH + LiOH) dedoped nanostructured products obtained in the oxidative polymerization of aniline are investigated. These effects are probed by ¹⁵N and ¹³C solid-state NMR, FTIR, Raman and EPR spectroscopy. The morphologies were imaged using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The micrographs confirmed the presence of mixed morphologies which include granular and nanotubular products. Single dedoping with NH₄OH (SD) was not sufficient to completely remove positive charges. Subsequent dedoping with LiOH (DD) significantly removed positive charges. NMR experiments confirmed that the imine part of the structure has been more exposed to the effects of polarons. EPR data showed that the spin concentration in the DD samples was more than an order of magnitude lower than that of the SD sample. The FTIR and Raman spectra exhibit characteristic bands for polyaniline and oligoanilines.

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1. Introduction

Over the last two decades, polyaniline (PANI), an intrinsic electrically conducting polymer has attracted significant attention from the scientific community [1]. This is mainly due to its interesting chemical and physical properties, as well as its ability to provide novel advanced materials for modern technologies [2].

One of the useful and very attractive characteristics of PANI is its capability to form morphologically different structures at the micro and nanoscale [3–5]. These structures very often have different characteristics compared with the bulk macrocounterparts. Usually, chemically synthesized PANI is prepared by the oxidative polymerization of aniline using an oxidant and a dopant acid [6]. Low pH syntheses (pH < 2) favour a morphologically featureless and highly conductive polymer (standard PANI), while syntheses at higher pH (pH > 2) result in morphologically well-defined and less conductive micro and nanostructures [7–9]. Therefore, an understanding and control of the aniline oxidative polymerization process as a pathway for the formation of various PANI nanostructures is of fundamental importance for both science and technology. One of the simplest ways to make PANI nanostructures is through their self-

assembly in the “falling pH” synthesis [7,8,10–13]. In this approach the pH is allowed to freely change (decrease) during the aniline oxidative polymerization. The synthesis usually starts from neutral or mildly acidic solution (pH ≈ 7). During the aniline oxidation in the “falling pH” synthesis protons are continuously released in the reaction solution [7,8,11–13]. This increases the acidity of the reaction solution, resulting in a low pH at the end of the reaction. It has been reported that the morphology and structure of the final product depend on the pH value and the concentration of the reagents [14]. Different products are self-assembled during the falling pH profile, the final product is often heterogeneous in a structural and morphological sense [3–14]. Therefore, it is important to know the structure and physical properties of the various morphologies formed to understand the role of synthetic conditions (pH, concentration and type of reactants, temperature, etc.) in the “falling pH” synthesis. Besides this, the structural characterization of PANI is limited because of its insolubility in common organic solvents [15].

In this regard, cross-polarization with magic angle spinning (CP MAS) solid-state NMR (SSNMR), being one of the most powerful structural analytical methods, offers a promising way to investigate such complex systems [7,11,16–22]. Commonly, when applied to standard PANI, SSNMR can give very important information about the structure and conformation of the polymer backbone and the nature and distribution of charge carriers. SSNMR is a multinuclear technique, which means that various nuclei can be probed and for standard PANI the most important isotopes are ¹³C and ¹⁵N. ¹⁵N

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detected SSNMR is especially useful since it offers a much better spectral resolution in PANI spectra than ^{13}C detection [23,24]. It reveals the chemical environment of amine and imine groups, which in turn allows probing the distribution of benzenoid and quinonoid segments along the polymer backbone and, consequently, reveals conductivity properties [19].

Standard PANI obtained at low pH (doped-as-synthesized) is electrically conductive ($\sigma \sim 10^{-2}$ – 10^3 S cm^{-1}) [1]. This is due to the presence of cation radicals (polarons) which are mainly located on the nitrogen atoms and are much less delocalized into the adjacent aromatic rings. Positive charges are neutralized by negatively charged counterions such as sulphate, chloride, phosphate, etc. [1].

It has been shown that ^{13}C and ^{15}N CP MAS spectra of the doped-as-synthesized form of PANI consist of inhomogeneously broadened lines [25]. The chemical shift dispersion is due to a structural disorder resulting from disruptions in electron delocalization [25]. Besides this, it has been reported that the integrated area obtained from ^{15}N resonances for dedoped (deprotonated) PANI is around five times higher than for the doped-as-synthesized form [22]. This confirms that the most of the signal is not observed in the doped-as-synthesized PANI due to the presence of paramagnetic centers (adjacent polarons). Usually, as the degree of protonation increases, the concentration of radical polaronic centers (paramagnetics) increases which lowers the NMR signal [22]. However, at some level of protonation a bipolaronic state prevails (non-paramagnetic) which improves the signal-to-noise-ratio in the NMR spectrum. At this level of protonation, the fraction of observed ^{15}N (or ^{13}C) atoms increases compared with the state where the polaronic state dominates [22].

To get better resolution and sensitivity a PANI sample should be dedoped, i.e. treated with a base such as NH_4OH or LiOH . In this way paramagnetic polarons (spin effects) and positive charges from bipolarons (heterogeneity effects) are removed and their interference with the NMR signal is diminished.

However, we have noticed in our investigations and it has also been shown elsewhere [26], that ^{15}N CP MAS does not perform in the same way for standard PANI and for nanostructured products. This has been especially the case with the imine nitrogens that are often significantly underestimated in ^{15}N spectra of nanostructures [7] compared with data obtained by other techniques such as elemental analysis, FTIR and UV–Vis spectroscopy [7].

Therefore, the main objective of this work is to characterize in detail nanostructured polyanilines (NS PANI) obtained by the “falling pH” reaction and critically analyse effects of polarons on SSNMR spectra. This should lead to a better understanding of the applicability of the method to NS PANI, and of the structural, physical and morphological characteristics of these products.

2. Experimental section

Syntheses: 11 ml of pre-cooled 0.3 M ammonium persulfate solution was added to 11 ml of milli-Q water containing 2.2×10^{-3} mol of aniline (50% of the aniline monomers enriched to 100% ^{15}N and 50% of the aniline monomers enriched to 100% ^{13}C) which had been sonicated for 15 min. The mixture was left in the fridge at 5 °C to react for 24 h. The ammonium persulfate:aniline mole ratio was 1.5:1. The reaction mixture was then filtered, washed several times with water and seven times with methanol [12]. The residue was then added to 65 ml of 15% ammonium hydroxide solution and stirred for 48 h. The product was dried in a vacuum oven at 40 °C before characterization. A portion of this product was subjected to a second dedoping in which the sample was added to a 1% LiOH solution, and the resulting mixture was stirred for 4 h and left to stand for another 20 h. The product was

then collected, washed several times with water and dried in a vacuum oven before characterization.

FTIR spectroscopy: FTIR spectra of the samples dispersed in pressed KBr pellets were recorded in transmission mode at a resolution of 4 cm^{-1} , using a Perkin Elmer Spectrum 400 FTIR spectrophotometer.

Raman spectroscopy: Raman spectra were recorded in back-scattered geometry using a Renishaw 1000 Raman Imaging Microscope consisting of a single grating spectrograph (1200 lines/mm), a Leitz microscope with 50× objective (NA 0.75) which focused the beam to a size of 1–2 μm at the sample surface and a Thermo-Electrically cooled CCD array detector. The excitation laser was a Renishaw solid-state diode laser emitting a line in the near-infrared region at $\sim 785 \text{ nm}$ at 0.26 mW. The entrance slit width was 50 μm , resolution 6 cm^{-1} and the laser power at the surface was 26 μW . Each spectrum was recorded with 50 accumulations with an integration time of 10 s. The wavenumber accuracy was better than 0.5 cm^{-1} .

EPR spectroscopy: EPR spectra were recorded of the powder samples in Suprasil quartz tubes, using a JEOL JES-FA200 spectrometer under the same conditions: magnetic field: 336.7 mT, power: 0.250 mW, microwave frequency: 9434.285 MHz, modulation frequency: 100 kHz, modulation amplitude 0.35 mT, gain: 1; scan time: 2 min, time constant: 0.1 s. The spin concentration, N_{sample} (spins g^{-1}) was calculated using the area calculated from the second integral of the first-derivative signals using Matlab according to:

$$N_{\text{sample}} = \frac{\text{Area}_{\text{sample}}}{\text{Area}_{\text{reference}}} \times \frac{\text{mass}_{\text{reference}}}{\text{mass}_{\text{sample}}} N_{\text{reference}}$$

where the reference substance used was $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, for which $N_{\text{reference}} = 2.412 \times 10^{21}$ spins g^{-1} .

SEM characterization: The morphologies of the products were investigated using a Philips XL30S field emission scanning electron microscope (SEM). The samples for SEM were mounted on aluminium studs using adhesive graphite tape and sputter-coated with platinum. The diameters of the nanotubes were estimated by measuring 10 nanotubes from SEM images at 50,000 times magnification using Adobe Photoshop 6.0 software.

TEM characterization: A JEOL TEM-2010 transmission electron microscope (TEM) was used. The TEM sample was dispersed in water by ultrasonication, and then pipetted onto copper coated grids.

Solid state NMR: All solid-state NMR experiments were carried out on dry powder samples using a Bruker AVANCE 300 standard bore magnet system operating at 300.13 MHz proton frequency (7.05 T). Spectra were obtained by using CP MAS (Cross-Polarization Magic Angle Spinning) and SPE (Single Pulse Excitation) techniques. The experiments were carried out using a Bruker double resonance broadband probe with zirconium oxide (ZrO_2) 7 mm rotors and Kel-F caps. The magic angle was adjusted by maximizing the sidebands of the ^{79}Br signal of a KBr sample.

The typical parameters for ^{13}C NMR spectroscopy were: a 90° pulse width of 4.2 μs , a spin-lock field of 62.5 kHz, contact time of 1.5 ms, a recycle delay of 1–2 s and a spectral-width of 40 kHz. Experiments were carried out with 3000 scans at ambient temperature using samples enclosed in the rotors. The ^{13}C chemical shift scale was referenced to tetramethylsilane (TMS). Samples were rotated at $7000 \pm 1 \text{ Hz}$.

The parameters for ^{15}N CP/MAS and SPE measurements carried out at a spectrometer frequency of 30.41 MHz were as follows: a 90° pulse width of 7.3 μs , contact time of 1.5 ms, a recycle delay of 1–2 s and a spectral-width was 30.03 kHz. ^{15}N chemical shifts were measured to external $^{15}\text{NH}_4\text{Cl}$ ($\delta^{15}\text{NH}_4^+ = 17.4 \text{ ppm}$ relative to $^{15}\text{NH}_4\text{NO}_3$) but are reported relative to $^{15}\text{NH}_4\text{NO}_3$ ($\delta^{15}\text{NH}_4^+ = 0 \text{ ppm}$). The rotation frequency was $4500 \pm 1 \text{ Hz}$. To explore the effects of T_1^H time on the quantitative proton inversion-recovery relaxation

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