Efficient Synthesis of Well-Defined, High Molecular Weight, and Processible Polyanilines under Mild Conditions via Palladium-Catalyzed Amination

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Polyaniline (PANI) ranks among the most potentially useful conducting organic polymers, due to its environmental stability and tunable electrical conductivity; many industrial applications have been demonstrated.[1] PANI is generally prepared by the chemical or electrochemical oxidation of aniline.[2] The polymer thus obtained may be processed in the neutral emeraldine base (EB) form, as a solution in *N*-methylpyrrolidinone (NMP);[3] the conductive salts of emeraldine with bulky organic counterions, particularly camphorsulfonate, are typically processed from *m*-cresol.[4] Because the standard syntheses of PANI give rise to a certain level of regioerrors, and produce some insoluble materials,[5] alternative methods have been designed. Most notably are the polycondensation of 1,4-phenylenediamine with a hydroquinone surrogate,[6] and the recent enzymatic oxidation of aniline in the presence of a polyanionic template.[7]

The palladium-catalyzed amination of aryl halides and triflates,[8] an increasingly important method for the synthesis of arylamines in many applications,[9] holds great promise for the construction of the PANI framework. Polymerizations based on this reaction would be regiospecific and could afford access to modified polymers with otherwise inaccessible substituent patterns. Palladium catalysis has been used to prepare a number of arylamine polymers.[10] However, no synthesis of the conductive *p*-PANI by this route has yet been reported, possibly because aryl halides bearing the N−H group in the para position are generally poor substrates for the aryl amination process. Previously, we reported a general route to controlled-length and end-functionalized oligoanilines, using the Pd/BINAP catalyst system.[11] New-generation catalysts, using bulky, electron-rich phosphinobiphenyl ligands, display far higher activity toward electron-rich substrates and allow the amination of aryl chlorides.[12] We now report the efficient synthesis of regiopure BOC-protected PANI of high molecular weight. These PANI precursors are soluble in common, low-boiling organic solvents, and are readily and quantitatively converted to the parent PANI.

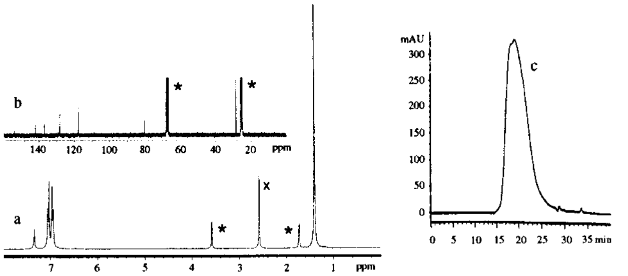
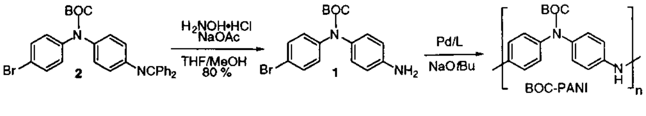


Figure 1. ^{1}H (a) and ^{13}C (b) NMR spectra in THF-d_8 (∗, solvent peaks; ×, H_2O) and GPC chromatograph in THF (c) for BOC-PANI.

Scheme 1



The simplest palladium-catalyzed synthesis of PANI would involve the polymerization of 4-bromoaniline, or the copolymerization of 1,4-dibromobenzene with 1,4-phenylenediamine. Initial studies showed that these reactions only produced low molecular weight polymers of poor solubility. In contrast, the BOC-protected monomer **1**, prepared by selective deprotection of the fully protected dimer bromide **2**[11] at the terminal amine position, underwent efficient step-growth polymerization (Scheme 1). The ab-type monomer may be prepared on large scale and purified by crystallization; no chromatography is necessary. Polymerization of **1** using a combination of $Pd_2(dba)_3$ and phosphine ligand 2-(di-*tert*-butylphosphino)biphenyl (L/Pd = 3) as the catalyst affords partially BOC-protected polyaniline (BOC-PANI). A typical polymerization was carried out in THF between 25 and 80 °C, with 1.4 equiv of the base, NaO*t*-Bu, per halide. During a reaction time of 24 h, the initially clear solution became a gel. The crude product was washed by sonication in ether, water, and methanol. The remaining solid was dissolved with sonication in THF and reprecipitated by addition of methanol. Isolated yields of the pale olive or pale gray polymers range from 80% to 96%, depending on the reaction conditions. The elemental analyses of these materials are consistent with the expected structures.

The polymers can be dissolved, with the aid of sonication, in common organic solvents such as THF and $CHCl_3$, permitting full characterization by NMR and GPC. The ^{1}H and ^{13}C NMR spectra (Figure 1a,b) for BOC-PANI in THF-d_8 were well resolved and the polymer endgroups are not discernible. The ^{1}H NMR spectrum exhibits two doublets for the aryl protons and a singlet for the BOC protons, in the ratio of 2:2:9. The N−H resonance appears as a singlet at 7.35 ppm, corresponding to one proton by integration. The ^{13}C spectrum shows resonances for a carbonyl group, four types of aromatic carbons, and the quaternary and primary carbons of the *tert*-butyl group. Analysis by ^{31}P NMR

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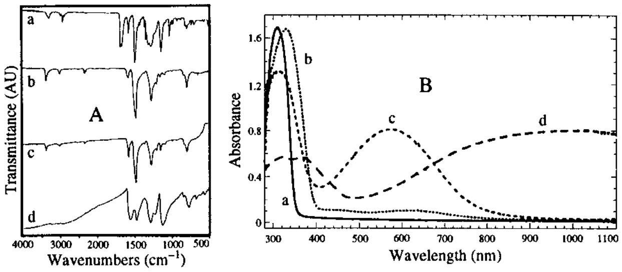
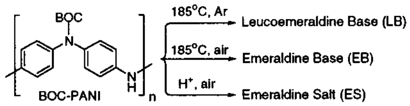


Figure 2. IR (A) and UV−vis (B) spectra of BOC-PANI (a) and its deprotection products: 185 °C, Ar (b); 185 °C, air (c); and H$^+$, air (d).

Scheme 2



showed no detectable peaks after several thousand scans, indicating that the phosphine ligand was successfully removed during workup, and incorporation of phosphine into the polymer chain is minimal.[13] The molecular weights (MW) of the polymers were determined by GPC in THF. The typical GPC trace for the polymer (Figure 1c) exhibits a monomodal distribution and the presence of minimal low molecular weight oligomers.

Factors that influence the yield, MW, and MW distribution of the polymers were examined. The polymerization was typically carried out for 24 h. Longer reaction times make no significant difference. Among several solvents used, THF normally gave a highest yield. Higher monomer concentrations gave rise to polymers with higher MW and lower PDI. At 1.0 M concentration in THF with 1.0 mol % $Pd_2(dba)_3$, BOC-PANI was obtained at 80 °C in 96% yield with a M_w of 80 400 and a M_n of 19 200. The reduction of the catalyst loading led to a surprisingly large effect on MW. A lower catalyst loading led a significant increase in both M_w and M_n, although a decrease in yield was observed. At 0.25 mol % $Pd_2(dba)_3$ with 1.0 M concentration in THF, a polymer with a M_w of 109 400 and a M_n of 34 800 was made at 80 °C in 82% yield. At lower reaction temperatures, polymers were synthesized in better yields, with higher M_w and M_n as well as lower PDI. For example, the polymerization reaction carried out at room temperature in THF using 1.0 mol % $Pd_2(dba)_3$ at 1.0 M concentration gave the best result, with a M_w of 98 300 and a M_n of 39 500 in 92% yield. These weights correspond to a PDI of 2.49 and a number-averaged degree of polymerization of over 140. Since the monomer is derived from an aniline dimer, the average chain length is greater than 280 aniline units.[14]

The BOC-protected precursor, soluble in common organic solvents and easily deprotected, is a conveniently processed form of PANI. Homogeneous thin films of the protected polymer may be readily fabricated from solutions in THF or $CHCl_3$. The colorless or pale gray films may be directly converted to the parent PANI in different electroactive forms by thermolysis or protonolysis (Scheme 2). Thermolysis of BOC-PANI films at 185 °C under an inert atmosphere affords PANI in the fully reduced LB form, whereas thermolysis in air affords the deep blue, partially oxidized EB form. This process can be completed in 6 to 8 h, depending on the thickness of the film. Alternatively, the BOC-PANI films may be directly transformed to the dark-green conductive ES form simply by immersion in acid solutions under air. Complete removal of the BOC groups takes only 15 to 30 min and the subsequent air oxidation requires several hours. These processes can be monitored by IR and UV−vis spectroscopy (Figure 2). The IR spectrum (Figure 2Aa) of the BOC-PANI film clearly exhibits both N−H (3342 cm^{-1}) and carbonyl stretches (1707 and 1686 cm^{-1}) as well as aromatic C−H (3035 cm^{-1}) and aliphatic C−H stretches (2975 and 2929 cm^{-1}). It has a simple optical spectrum (Figure 2Ba) with only the benzene $\pi-\pi^*$ transition in the UV region (310 nm). Upon thermolysis or protonolysis, no obvious morphology changes of the films were observed. The IR spectra (Figure 2Ab, 2Ac, and 2Ad), however, show the complete disappearances of the carbonyl and aliphatic C−H stretches and changes in the N−H stretches. The vibrational bands characteristic of the polymer backbone broaden and shift systematically to lower energy from BOC-PANI (Figure 2Aa: 1604 and 1510 cm^{-1}) to its deprotected ES product (Figure 2Ad: 1580 and 1494 cm^{-1}), indicating longer effective conjugation lengths. Consistent with this interpretation, the localized $\pi-\pi^*$ transition in the UV region of BOC−PANI became broader, less intense, and red-shifted, and new bands appeared in the visible region (Figure 2B). The resulting IR and UV−vis spectra are similar or identical to those of the corresponding forms of conventionally prepared PANI.[1−3] Notably, in the case of the ES produced by protonolysis, the IR spectrum shows a broad and intense band extending from about 1600 cm^{-1} into the near-IR region (Figure 2Ad). Correspondingly, a lower-energy broad absorption band beginning at ca. 500 nm and increasing in intensity up to the spectrometer's limit at 1100 nm toward the near-IR region can be observed in the UV−vis spectrum (Figure 2Bd). These spectroscopic features are characteristic of the conductive form of PANI, ES. Conductivities of ca. 1 S/cm, similar to those reported for PANI·HCl prepared by aniline oxidation,[3] have been measured for films treated with 1.0 M HCl solution in diethyl ether under air.

In conclusion, well-defined, high molecular weight BOC-protected polyanilines have been synthesized in high yield, under mild conditions, through step-growth polymerization of a bifunctional dimeric monomer via palladium-catalyzed amination chemistry. The polyaniline precursor is soluble in common organic solvents and can be conveniently fabricated into films. The BOC-PANI films can be directly converted to the parent PANI in different electroactive forms including the conductive emeraldine salt in a facile manner. This new approach expands the processibility and structural variability of polyaniline, potentially enhancing its practical utility.

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Supporting Information Available: Experimental details and characterization data, and enlarged copies of Figures 1 and 2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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