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Communications

Highly Cross-Linked, Self-Doped Polyaniline Exhibiting Unprecedented Hardness

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Inherently conducting polymers have had a profound impact on a wide range of emerging technologies from polymer-based electronics¹ to microrobotics.² However, the use of these materials in mechanically and thermally demanding environments has been limited due to the low molecular weight³ and the volatility of dopants⁴ produced with conventional synthetic methods. To date, attempts to address these issues through cross-linking⁵ have not been successful in yielding enhanced mechanical properties while maintaining good conductivity. This is likely due to the incompatibility of the volume reduction accompanying cross-linking and the presence of counterions. Here we demonstrate a new strategy utilizing a chemically modified conducting polymer [poly(anilineboronic acid), PABA] that forms an-

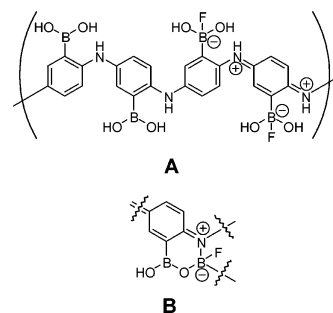


Figure 1. Emeraldine salt form of PABA (A), self-doped in the presence of fluoride. Proposed cross-link (B), resulting from an interchain dehydration reaction between a boronic acid-imine and a boronic acid moiety, hence, maintaining a self-doped state.

ionic cross-link sites. In so doing, a self-doped, cross-linked conducting polymer is formed, possessing extreme hardness while maintaining conductivity. This eliminates the need to create composites or other modification procedures that compromise the desirable electronic properties of the polymer.

PABA exhibits unique self-doping properties through the formation of four-coordinate boronate species in the presence of fluoride.⁶ The presence of boronic acid groups along the conjugated backbone of polyaniline (Figure 1A) also offers many possibilities for chemical modification and reactivity. For example, aryl boronic acid chemistry is rich with examples of the formation of boron chelates.⁷ Two cases closely related to the system described herein include fluorine-containing salicaldimine-boron complexes⁸ and the

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dimer of 2-aminophenylboronic acid formed in aprotic solvents and in the solid state.⁹ These compounds exist as six-member heterocyclic complexes containing a boron-imine dative bond and are air stable.

In our approach we exploit similar chemistry resulting from the intermolecular reaction between boronic acid groups and imines in PABA containing fluoride to produce cross-links with an analogous structure involving four-coordinate boron (Figure 1B), to produce a self-doped, cross-linked polyaniline. The key advantage of such a structure is that the cross-link site can also act as a dopant site. In turn, this structure can accommodate the volume shrinkage associated with cross-linking while maintaining the anionic dopant required for conductivity.¹⁰ This results in a cross-linked conducting polymer that should exhibit enhanced hardness and thermal stability.

Self-doped PABA was synthesized chemically as described previously.¹¹ For conductivity and microhardness measurements,¹² pellets of air-dried PABA were pressed at 10,000 psi for 5 min. To facilitate cross-linking, pellets were heated at 100 °C in *vacuo* for 24 h.

Vickers microhardness measurements for air-dried and heat-treated PABA pellets were 0.3 and 0.5 GPa, respectively. These values are dramatically higher than polyaniline (<0.03 GPa) and those reported for other bulk polymers and approach values achieved with composites.¹² The increase in hardness of the heat-treated PABA is a result of increased cross-linking facilitated by heating and removal of water (a product of the cross-linking reaction) under vacuum. The hardness measurements represent a lower limit since the material likely yields due to the breakdown of intergranular cross-links prior to the plastic flow of polymer chains. The conductivity of the heat-treated PABA pellet was 0.09 S cm⁻¹, similar to the conductivity of sulfonated (self-doped) polyaniline.¹³ However, the conductivity of HCl-doped polyaniline dropped approximately 2 orders of magnitude (8–0.19 S cm⁻¹) upon heat treatment. This is consistent with reports of the loss of the HCl dopant at these temperatures.¹⁴ The fact that PABA loses only about a third of its conductivity after heat treatment further supports the creation of an anionic cross-link site involving four-coordinate boron (Figure 1B).

Infrared attenuated total reflectance spectra (Figure 2) of air-dried and heat-treated PABA pellets reveal changes consistent with increased cross-linking while maintaining the basic polyaniline structure (detailed peak assignments of polyaniline and PABA are given in the Supporting Information). The spectrum of the heat-treated pellet shows a decrease in B–OH bending modes and an additional peak

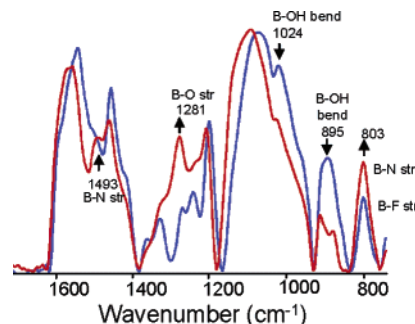


Figure 2. Fourier transform infrared attenuated total reflectance absorption spectra of PABA pellet (blue line) air-dried and (red line) heat-treated.

at 1493 cm⁻¹ assigned to a B–N stretching mode.^{15,16} Also, there is an increase in the intensity of 1281 and 803 cm⁻¹ vibrations assigned to B–O and the B–N stretching mode of a dative bond.^{15,16} While B–F and B–N stretching modes overlap at 803 cm⁻¹, the increase in intensity can only be associated with an increase in the formation of B–N dative bonds. All of the spectral observations are consistent with increased cross-linking involving the formation of boronic acid anhydride and boron-nitrogen dative bonds (Figure 1B). Furthermore, the relatively unchanged ratio of vibrations at 1597 and 1462 cm⁻¹ indicates that the ratio of quinoid to benzenoid structures in the film remains the same after heat treatment; hence, the polymer remains in an oxidized state.

Magic-angle spinning (MAS) ¹¹B NMR is an ideal method for quantifying the coordination environment of boron.^{17,18} At sufficiently high magnetic fields (i.e., ≥ 11.7 T) the signals corresponding to three- and four-coordinate boron are generally resolved and yield relative populations by direct peak integration. While the application of MAS NMR to conducting samples is rare due to the potential for sample heating during rapid spinning and probe damage from the requisite high radio frequency fields, no anomalous effects were observed in the present case. In the ¹¹B NMR spectrum (Figure 3A) obtained for heat-treated PABA, the three-coordinate boron gives rise to the broad signal centered at 16.5 ppm, and the four-coordinate boron produces a sharper peak at 1.5 ppm.

A two-dimensional multiple-quantum (MQ) MAS¹⁹ experiment reveals that two four-coordinate boron sites are present in the sample (Figure 3B), one of which (6.6 ppm) is partly obscured by the quadrupole-broadened three-coordinate boron signal in the MAS spectrum. While the precise identities of the four-coordinate boron species are unclear, the chemical shifts are consistent with the local atomic connectivities indicated in Figure 1 (see Supporting Information for details). Fitting the one-dimensional MAS spectral intensities using the site information from the two-dimensional MQMAS experiment reveals that 21 ± 2% of the boron in the sample is four-coordinate. Since such sites

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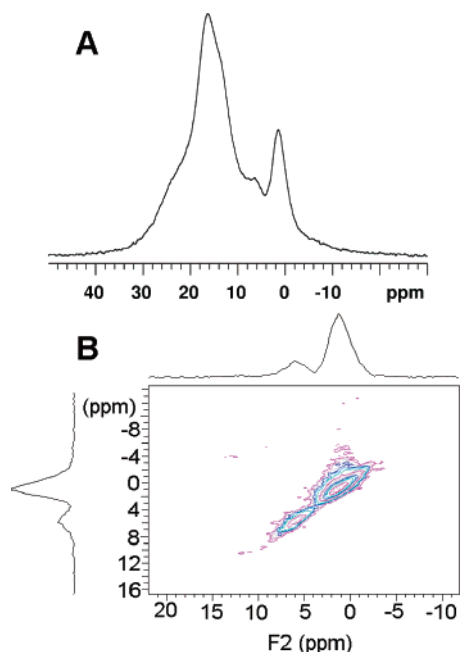


Figure 3. ^{11}B NMR spectra of heat-treated PABA pellet obtained at 192.4 MHz (14.1 T). (A) One-dimensional MAS experiment. (B) Two-dimensional sheared MQMAS experiment optimized to preferentially excite four-coordinate boron sites (displayed region).

can act as a dopant (Figure 1B), the NMR results suggest that the heat-treated polymer is doped to that level, which is sufficient to account for the measured conductivities based on other forms of self-doped polyaniline.¹³

In summary, we report a new strategy for the generation of a cross-linked, self-doped conducting polymer. By having a negatively charged cross-link site that can simultaneously

act as a dopant, this approach circumvents major obstacles encountered using traditional methods of cross-linking. Furthermore, no fillers or other nonconducting cross-linking agents are required that will ultimately reduce conductivity. We demonstrate this method by self-cross-linking PABA, which results in the creation of four-coordinate boron through the formation of a dative boron-imine bond. Under unoptimized conditions, the percentage of four-coordinate boron and in turn the level of doping is estimated to be 21%. In addition to retaining a significant degree of conductivity, the cross-linked PABA exhibits unprecedented hardness, surpassing more common “hard” polymers. Optimization of the synthesis and processing conditions in conjunction with the novel use of ^{11}B NMR is expected to provide further elucidation of the unique role of boron in the structure of the polymer as well as inter- and intragranular effects on hardness and conductivity. These results have the potential to significantly broaden the range of applications and environments in which conducting polymers are used.

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Supporting Information Available: Supporting experimental data and details of PABA synthesis (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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