

A Switchable Self-Doped Polyaniline: Interconversion between Self-Doped and Non-Self-Doped Forms

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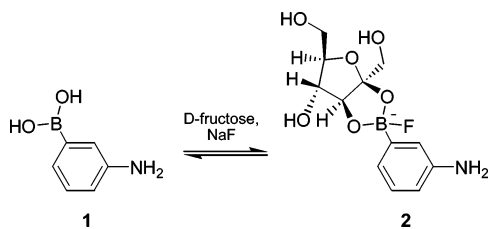
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Polyaniline, one of the most promising intrinsically conducting polymers, has received considerable attention in recent years due to its straightforward polymerization, chemical stability, relatively high conductivity, and potential applications in electronic devices, batteries, and sensors. A major breakthrough in the field was the discovery of self-doped polyaniline due to its desirable properties.¹ For example, the self-doped form of polyaniline has several advantages, including better solubility^{2,3} as well as redox activity⁴ and conductivity^{1–3a} over a wider pH range. However, there are a number of tradeoffs, including reduced mechanical stability (especially in the presence of good solvents) and decreased conductivity due to steric effects.⁵ Ideally, it should be possible to switch between self-doped and non-self-doped states so that the properties of the polymer can be manipulated to achieve desired properties during synthesis, processing, and finally use of the polymer.

Herein we report a novel approach to the creation of a substituted polyaniline whose self-doped state can be controlled via complexation between boronic acid groups along the backbone with D-fructose in the presence of fluoride. For the first time, this allows the formation of a water-soluble, self-doped, conducting polymer under the polymerization conditions. In turn, this facilitates the synthesis of polyaniline over a wider pH range. This has important implications toward synthesis (yield, molecular weight), processing (controlled precipitation), and implementation (extended pH range).

The complexation of saccharides with aromatic boronic acids is pH dependent and can result in a neutral or anionic ester, depending on solution conditions.⁶ Addition of fluoride can be used to enhance the complexation of saccharides under less basic conditions and facilitates the formation of an anionic ester.⁷ Under neutral pH conditions in the presence of excess D-fructose (10 M) and 1 equiv of fluoride, ¹¹B NMR⁸ indicates that the monomer (**1**) is converted to a boronate ester (**2**),⁹ which can in turn form the basis of a self-doped polyaniline.



Oxidative polymerization of **2** was carried out under ambient conditions with the addition of ammonium persulfate, resulting in a water soluble,¹⁰ self-doped polymer (vide infra). Poly(**2**) was precipitated by reducing the fluoride concentration via dilution. Following filtering and rinsing with water, the precipitate could be redissolved in an aqueous solution containing the original D-fructose and fluoride concentrations.

The UV–vis spectra of the soluble form of poly(**2**) (in the presence of D-fructose and fluoride) as well as thin films of the

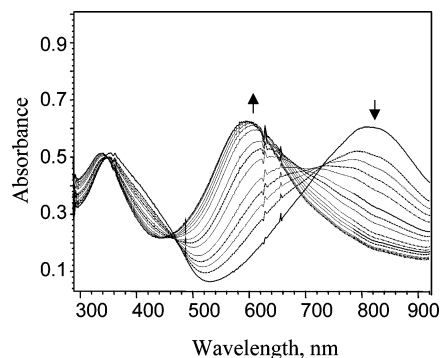


Figure 1. UV–vis spectral changes of a poly(**2**) thin film as a function of time upon exposure to pH 7.4 phosphate-buffered saline over the course of an hour.

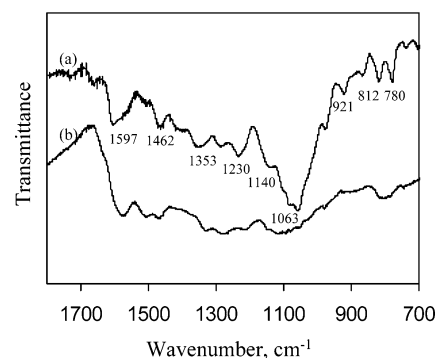


Figure 2. IR spectra of (a) poly(**2**) and (b) poly(**1**).

precipitated form of poly(**2**) are similar to those of the emeraldine salt form of unsubstituted polyaniline, exhibiting absorption bands near 350 and 820 nm due to the π – π^* and bipolaron band transitions, respectively.¹¹ The existence of these bands in pure water suggests that poly(**2**) exists in a self-doped state.

Poly(**2**) was converted to poly(**1**) by the removal of D-fructose from the polymer in phosphate-buffered saline solution. The conversion to the non-self-doped state and subsequently to the emeraldine base form of the polymer is characterized by the appearance of an absorption band at 600 nm and the disappearance of the peak at 820 nm, as shown in Figure 1. The switching behavior is reversible by exposing the base form of poly(**1**) to the original concentrations of D-fructose and fluoride either in phosphate-buffered saline or pure water.

Switching between the self-doped and non-self-doped state is further supported by IR spectra and elemental analysis. The IR spectra of poly(**2**) and poly(**1**) are shown in Figure 2. Characteristic IR bands attributed to the poly(**2**) form occur at 1597, 1462, 1353, 1230, 1140, 921, 812, and 780 cm^{-1} . The ratio of the relative intensities of quinoid to benzenoid ring modes (I_{1597}/I_{1462}) clearly shows that the percentage of imine units is higher than that

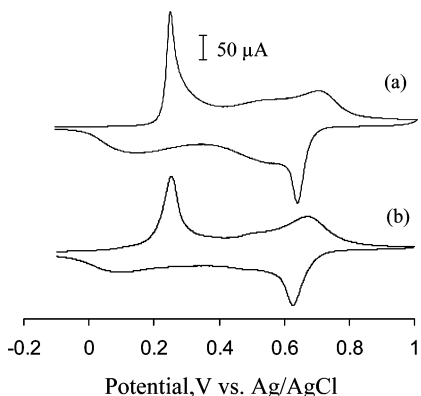


Figure 3. Cyclic voltammograms of (a) an electrochemically deposited film and (b) a film cast from precipitate of poly(**1**) on glassy carbon in 0.5 M HCl at a scan rate of 100 mV s⁻¹.

of amine units, and the polymer is therefore in its conductive self-doped form. The band at 1063 cm⁻¹ is attributed to C–O stretching and bending modes in the D-fructose moiety. Following conversion to poly(**1**), the spectra exhibit reduced intensity for all bands, which is consistent with the emeraldine base form of polyaniline and is due to charge carrier motion connected with lower conductivity of the polymer. The disappearance of the 1063 cm⁻¹ band further supports the conclusion that D-fructose is removed from the polymer to form poly(**1**) in a non-self-doped state.

Elemental analysis of the two forms of the polymer is consistent with the UV–vis and IR results. Atomic ratios of the poly(**2**) confirmed the presence of somewhat more than 1 equiv of D-fructose bound to the boronic acid group on the backbone (C:N:O, theoretical 12:1:6 and experimental 16:1:11). In the case of poly(**1**), the atomic ratios (C:N:O, theoretical 6:1:2 and experimental 6:1:2) are similar to those of the uncomplexed monomer, indicating that D-fructose is no longer present in the polymer and that it is therefore in a non-self-doped state.

Thin films of poly(**2**) that had been converted to poly(**1**) exhibit electrochemical behavior similar to that of films of poly(**1**) deposited electrochemically under acidic conditions in the presence of fluoride alone¹² (see Figure 3). In addition, the redox behavior is similar to that observed for unsubstituted polyaniline, which shows two sets of redox peaks at ~0.18 and 0.74 V,¹³ suggesting facile conversion between oxidation states. Consequently, it appears that polymerization under the conditions reported herein has no detrimental influence on the electronic properties of the polymer.

Since poly(**2**) is soluble under the reported polymerization conditions, it was not expected to suffer from effective termination of polymerization resulting from precipitation and in turn the limited molecular weight observed for polyaniline.¹⁴ Gel permeation chromatography of poly(**1**) and poly(**2**) in *N*-methylpyrrolidone¹⁵ was performed to determine the molecular weight of the polymers produced. Poly(**1**) and poly(**2**) exhibited single chromatographic peaks with weight-average molecular weights of 2.2 and 1.9 million, respectively, and polydispersities of approximately 1.2 in both cases.

In conclusion, a novel substituted polyaniline has been synthesized with the unique ability to switch between a self-doped and a non-self-doped state. In its self-doped state, the polymer is soluble under the polymerization conditions and can be easily and reversibly converted into the insoluble non-self-doped form. The ability to take advantage of the properties of both states of the polymer allows unprecedented control over the polymer during synthesis, processing, and utilization.

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Supporting Information Available: Supporting experimental data (including ¹¹B NMR, and GPC) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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