Optical and Electrochemical Detection of Saccharides with Poly(aniline-*co*-3-aminobenzeneboronic acid) Prepared from Enzymatic Polymerization

PilHo Huh,[†,⊥] Seong-Cheol Kim,[†,⊥] Younghoon Kim,[†] Yanping Wang,[†] Jagdeep Singh,[†] Jayant Kumar,*[,†] Lynne A Samuelson,*[,‡] Bong-Soo Kim,[§] Nam-Ju Jo,[§] and Jang-Oo Lee*[,§]

Center for Advanced Materials, Polymer Science Program, Departments of Chemistry and Physics, University of Massachusetts, Lowell, MA 01854, U.S. Army Natick Soldier Development and Engineering Center, Natick, Massachusetts 01760, and Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea

Received April 18, 2007; Revised Manuscript Received July 16, 2007

Boronic acid-based sensors for saccharides have been developed via biocatalysis. The self-doped copolymer of poly(aniline-*co*-3-aminobenzeneboronic acid) [poly(aniline-*co*-AB)], with various mole ratios of two components, was synthesized by oxidative enzymatic polymerization using a natural biocatalyst such as horseradish peroxidase together with an anionic polyelectrolyte template (sulfonated polystyrene) under mild conditions (pH 4.5). Poly(aniline-*co*-AB), having an aniline boronic acid-to-aniline ratio of 1:2 on average, gave rise to a green doped polymer with absorption maxima at 745 nm. The potentiometric detection of saccharides using poly(aniline-*co*-AB) is presented. Characteristics of both transient and steady-state response associated with the complex formation of poly(aniline-*co*-AB) with various saccharides were monitored by UV−vis spectroscopy and cyclic voltammetry (CV). The results obtained from UV−vis spectroscopy and CV show that the sensitivity of enzymatically synthesized water-soluble poly(aniline-*co*-AB) for various saccharides was improved significantly compared to the chemically synthesized counterpart. A possible mechanism for the sensitive detection of sugar molecules by boronic acid is proposed on the basis of UV−vis and IR spectrophotometry, and four-point probe conductivity measurements.

Introduction

Saccharides are nature's conveyors of energy and are therefore essential for cell survival.[1−7] The specific recognition of organic species of important biological relevance such as saccharides by synthetic molecular receptors has been of great interest.[8−12] The importance of saccharides in both biomedical and clinical research has given impetus to the development of improved detection methods. In addition to industrial applications such as monitoring sugar concentrations in beverages, quantitative analysis of saccharides is critically linked to certain disease therapies. Biosensors such as glucose oxidase have been extensively utilized in saccharide detection and offer a reliable method to detect glucose. However, some disadvantages, such as the poor stability of the enzyme and consumption of the substrate during the detection process, represent some limitations to biosensing applications.[13]

Although less selective than enzyme-based biosensors, synthetic chemosensors offer advantages such as greater stability and reliability in a variety of conditions. Recent progress toward improved synthetic hosts has been reported based on the affinity of phenylboronic acid compounds.[14,15] Phenylboronic acid has been widely utilized for the design of chemosensors in the detection of saccharides over the past decade.[16] The first reports of the complexation of saccharides with boric and boronic acids appeared in the 1950s,[17−24] and this pioneering work has since attracted considerable attention. The covalent interactions between phenylboronic acid and the hydroxyl groups of saccharides (1,2- or 1,3- diols) lead to the formation of five- or six-membered rings[25] and allow boronic acid to be a sensitive detector for saccharides.

Conducting polymers such as polyaniline[26,30] have been the focus of considerable research interest for sensing applications because of their stability, electrical conductivity, ease of synthesis, and pH-dependent redox behavior.[27−29] The oxidation state of a conducting polymer is readily varied and hence may be used to tune the electronic properties of the polymer's backbone, thereby influencing the properties of the boronic acid moiety, that is, its complexation with saccharides. In addition, since the complexation changes the redox properties of the boronic acid-substituted materials, it is possible to monitor the binding event by measuring changes in the electrochemical potential of the polymer.

Here we describe the enzymatic synthesis of poly(aniline-*co*-3-aminobenzeneboronic acid) [poly(aniline-*co*-AB)] with horseradish peroxidase (HRP). The detailed investigation of the nature of complexation of the boronic acid in poly(aniline-*co*-AB) with saccharide molecules and the electrochemical properties of the conducting polymeric material in the presence of a saccharide such as sorbitol is presented. The possible mechanism of the detection of sugar molecules was investigated by monitoring the change in polaron intensity.

* Corresponding author. (J.K.) Fax: 978-458-9571; tel: 978-934-3687; e-mail: Jayant_kumar@uml.edu. (L.A.S.) Fax: 508-233−5527; tel: 508-233−4618; e-mail: Lynne.Samuelson@us.army.mil. (J.-O.L.) Fax: 82-51-513-7720; tel: 82-51-510-2404; e-mail: leejo@pusan.ac.kr.

† University of Massachusetts.

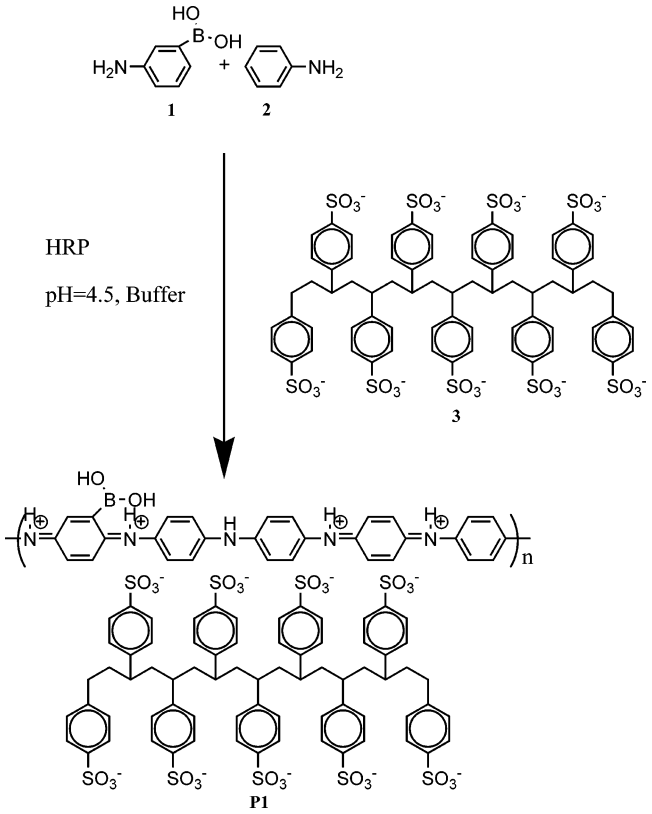
‡ U.S. Army Natick Soldier Development and Engineering Center.

§ Pusan National University.

⊥ These authors contributed equally.

10.1021/bm070421+ CCC: $37.00
Published on Web 10/06/2007

Scheme 1. Synthesis of Copolymer **P1** from AB (**1**), Aniline (**2**), and Poly (4-styrene sulfonate) (**3**) by Using a Biocatalytic Method in Phosphate Buffer Solution at pH 4.5



Experimental Section

Materials. 3-Aminophenylboronic acid hemisulfate (**1**), poly(4-styrene sulfonate) (**3**), HRP, sorbitol, glycerol, glucose, fructose, saccharose, and all other chemicals were obtained from Aldrich and were used as received. All were of analytical grade. Aniline **2** was used after distillation. A buffer was prepared containing 0.05 M potassium dihydrogen phosphate. Hydrochloric acid (0.4 M) was prepared and used to adjust the pH to the desired value.

Polymerization Reaction. Scheme 1. Synthesis of copolymer **P1** from 3-aminophenylboronic acid **1** (AB), aniline **2**, and poly(4-styrene sulfonate) **3** by using a biocatalytic method in phosphate buffer solution at pH 4.5.

Synthesis of poly(aniline-*co*-AB) was prepared according to Scheme 1 from readily available starting materials. The copolymerization of aniline and AB in the presence of an polyelectrolyte template (sulfonated polystyrene or SPS) was carried out enzymatically in 10 mL of 50 mM sodium phosphate buffer of pH 4.5 at room temperature, which contained a 30 mM:20 mM:10 mM molar ratio of template units to aniline and AB. The polyelectrolyte template, aniline, and AB were placed in a 20 mL glass vial and dissolved in the phosphate buffer. To the solution, HRP stock solution, a natural biocatalyst, containing 10 mg of enzyme was then added. The reaction was initiated by the addition of a stoichiometric amount of H_2O_2 under vigorous stirring. To avoid the inhibition of HRP due to excess H_2O_2, a stoichiometric amount of diluted H_2O_2 (0.3 wt %) was then added dropwise, incrementally, for 30 min to initiate the polymerization. The reaction was left stirring for 2 h, and then the product was precipitated by the addition of concentrated NaOH solution and then washed with an acetone/water mixture several times to remove any unreacted monomer, oligomers, uncomplexed free anionic templates, HRP, and phosphate buffer salts.

Characterization. The UV−vis−near-IR (NIR) spectra were recorded on a Perkin-Elmer Lambda-9 UV−vis−NIR spectrophotometer. The UV−vis−NIR spectra of poly(aniline-*co*-AB) in phosphate buffer were recorded at a scan rate of 240 nm/min after 1 day of addition of HRP + H_2O_2 to the reaction solution. Cyclic voltammetry (CV) was performed at room temperature using an EG&G potentiostat/galvanostat model 263. Measurements were taken in a three-electrode cell configuration by using solution casting of poly(aniline-*co*-AB) with/without saccharides as the working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. All CV experiments were conducted with a tetrabutylammonium hexafluorophosphate (TBAFP) acetonitrile solution at a scan rate of 100 mV s^{-1}. Conductivity measurements were performed on pellets using the four-point probe method with a Keithley 619 electrometer/multimeter. As seen in Scheme 2, the binding of saccharides results in a change in the conformation of polymer **P1.** Polymer **P2** was investigated for the effect of saccharides on absorption spectra by added glucose, sorbitol, mannitol, glycerol, and saccharose in different concentrations (5, 10, 50, and 100 mM). CV was investigated in various concentrations of sorbitol. To exclude the possibility that absorption changes are not due to the binding of saccharides, but rather due to changes in pH, all solutions were prepared freshly before use.

Results and Discussion

It is known that polyalcohols such as glucose reversibly bind to boronic acids. The process occurs in aqueous solution and is much less sensitive to pH, ionic strength, or temperature compared to enzyme-based reactions.

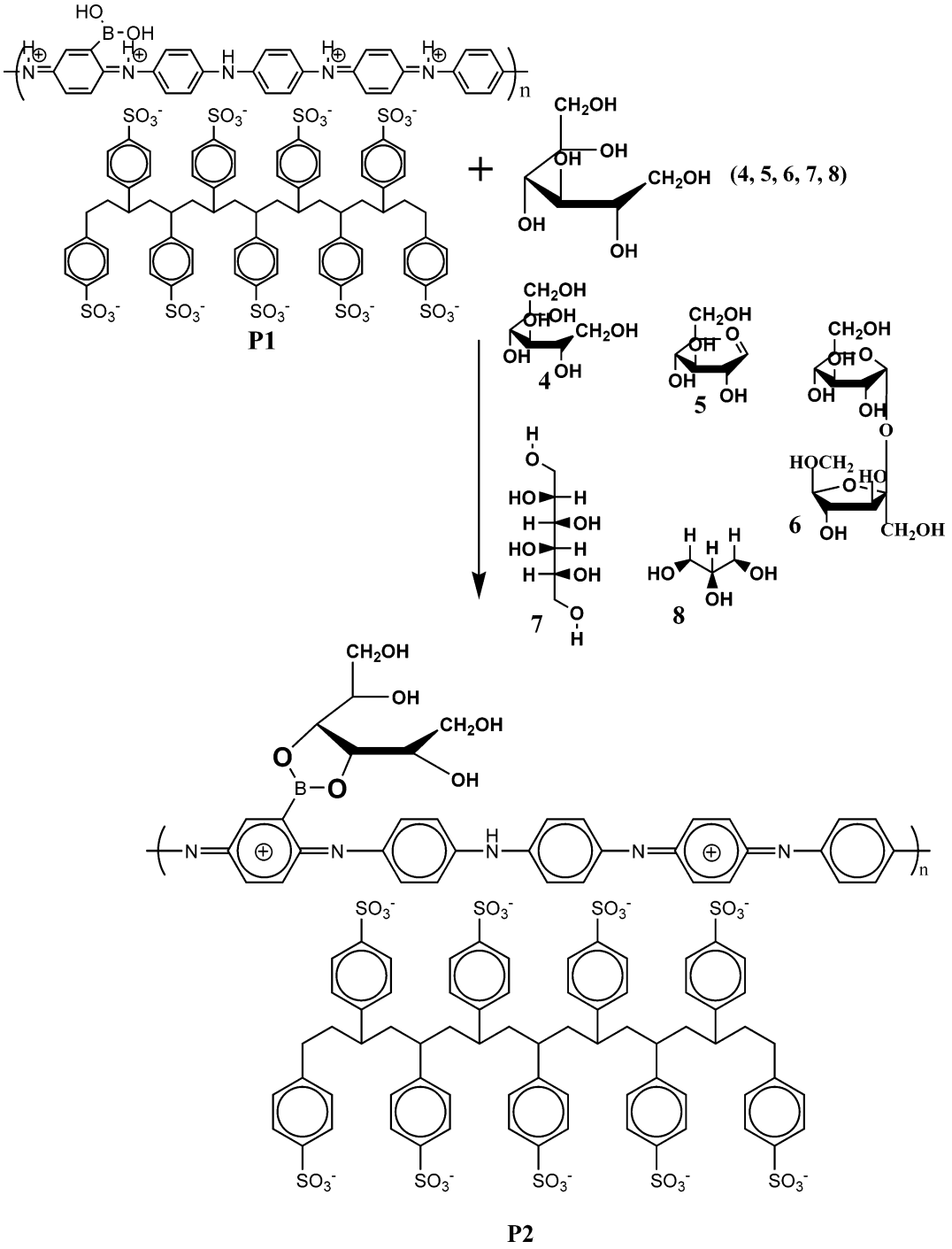
The UV absorption spectra of homopoly(AB), which was synthesized in phosphate buffer solution, are given in Figure 1. As discussed previously,[30] the synthesis of polyaniline is possible at pH below 4.6 with the aid of an anionic template. Meanwhile, the synthesis of AB does not occur at pH below 4, probably because of the poor solubility of the boronic acid monomer. Figure 1 shows the absorption spectra of poly(AB) at different pH values. Poly(AB) has the maximum intensity of a polaron peak at pH 4.5, which demonstrates that $B(OH)_2$ is the major dopant at this pH, as polyaniline is in the emeraldine base state at pH above 4.[30−34] The unsubstituted polyaniline is in the state of undoped emeraldine base because of the low concentration of HCl at pH 4.5. In this case, SPS functions only as a template solubilizing the polyaniline.[31] To maximize the intensity of the polaron peak, the copolymerization of aniline and AB was performed at this pH condition.

To verify the identity of the boron−oxygen stretching peak, Fourier transform infrared (FT-IR) spectroscopy was performed (refer to Supporting Information). Poly(AB) shows two B−O stretching peaks at approximately 1760 and 1595 cm^{-1}.[35] These two peaks shifted to approximately 1770 and 1657 cm^{-1} for poly(aniline-*co*-AB) with the addition of aniline. In addition, the B−O−H stretching band appears at 3300 cm^{-1} overlapped with the aromatic C−H stretching peak.[36]

The intensity of polaron absorption of the poly(AB) in aqueous solution reached a maximum at certain time intervals and then shifted to shorter wavelength with a shoulder at the polaron peak (see the Supporting Information). At the beginning, poly(AB) is in the doped emeraldine salt form, yielding a green color as reflected by the presence of the polaron transition at 415 and 735 nm. A dark blue solution of poly(AB) is formed at the end of the reaction, indicating that the polyaniline is somewhat dedoped over a period of time.

To study the effect of boronic acid on the doping of polyaniline, the mole ratio between aniline and AB was changed systematically from 16:1 to 0:1 at pH 4.5. The intensity of the polaron transition of self-doped poly(aniline-*co*-AB) synthesized with SPS as a function of mole ratio at pH 4.5 is given in Figure 2. **P1** self-doped by $B(OH)_2$[37−39] underwent a [$B(OH)_2$]-

Scheme 2. Poly(aniline-*co*-AB) (**P2**) upon Binding to Sorbitol in the Solution State[a]



[a] **4**: sorbitol; **5**: glucose; **6**: saccharose; **7**: mannitol; **8**: glycerol.

dependent increase of polaron peaks at 740 and 420 nm until the ratio of aniline/AB reached 2:1. However, when the mole ratio of AB is more than 33% in the polymer, the intensity of polaron peaks decreases. Therefore, the relationship between the intensity of polaron and the concentration of $B(OH)_2$ suggests that the weak dopants ($B(OH)_2$) not only function as a dopant but also function as a pendant group sterically hindering the conjugation of the polyaniline backbone. At higher mole ratios of AB, the weak dopant rather functions as a pendant group with a weak polaron transition.

The conductivity of poly(aniline-*co*-AB) was measured to confirm the relationship between the intensity of the polaron peak and the concentration of dopants ($B(OH)_2$). The conductivity of poly(aniline-*co*-AB) was measured with a solid sample obtained by distilling off the water from the polymer solution in the self-doped state without additional doping. A plot of conductivity versus mole ratio of aniline/AB for each sample is given in Figure 3. There is little change in the conductivity as the molar ratio of [aniline]/[AB] decreases from 16 to 8. Further decreases from 8 to 2 result in increasing conductivity. For ratios less than 2, the conductivity begins to decrease. This data is consistent with the polaron peaks in the UV−vis spectra shown in Figure 2. The conductivity of the copolymer at a molar ratio of 2.0 is approximately 2 orders of magnitude higher than that of boronic acid homopolymers. The highest conductivity observed in the molar ratio of [aniline]/[AB] = 2:1 suggests

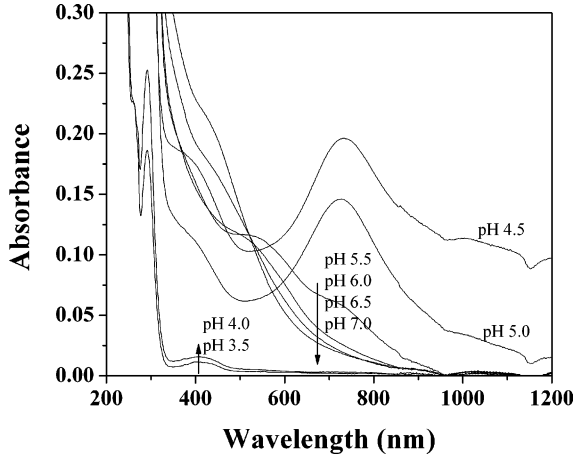


Figure 1. UV−vis−NIR absorption spectra of poly(AB) at various pH values (3.5−7.0).

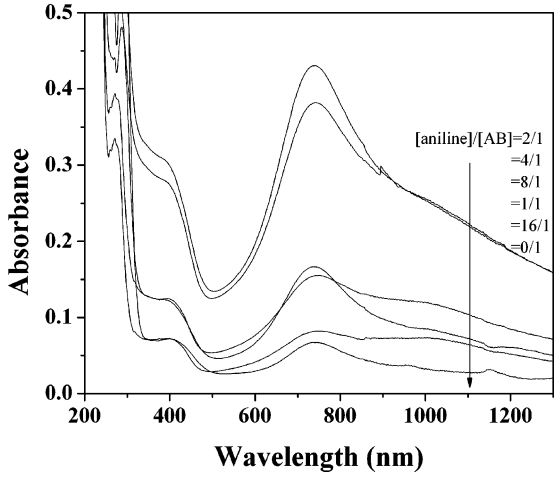


Figure 2. UV−vis−NIR absorption spectra of self-doped poly(aniline-*co*-AB) at different [aniline]/[AB] ratios at pH 4.5.

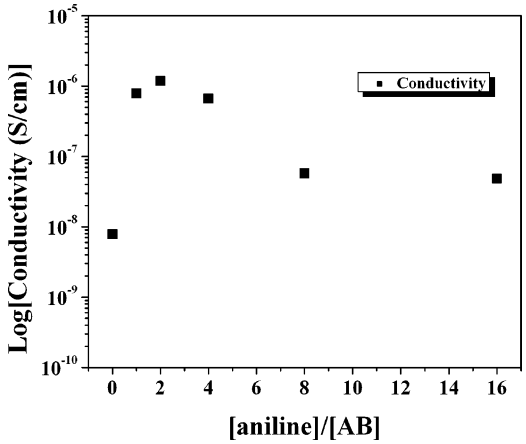


Figure 3. Conductivity of self-doped poly(aniline-*co*-AB) with different aniline ratios.

that a 2:1 ratio is the best condition to synthesize the copolymer to observe the maximum change in the polaron absorption and highest conductivity.

As the intensity of the polaron absorption at 740 nm shows the maximum for the copolymer with a mole ratio of [aniline]/[AB] = 2:1, this composition of the copolymer was used to investigate the effect of the addition of various saccharides on the absorption spectra at pH 4.5. Concentration-dependent changes in the spectra by the addition of various saccharides

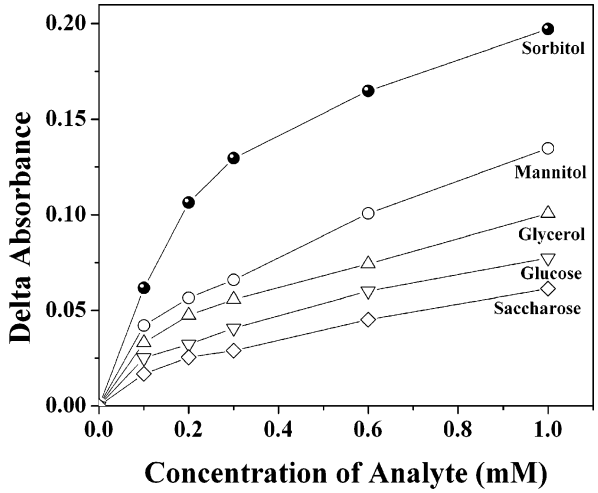


Figure 4. Change in the absorption of **P2** at 740 nm upon the addition of various saccharides in varying concentrations (pH 4.5).

such as sorbitol **4**, glucose **5**, saccharose **6**, mannitol **7**, and glycerol **8** (see Scheme 2) in **P1** was observed in an aqueous solution at 740 nm. The concentration-dependent changes of the absorbance of **P2** at 740 nm are plotted in Figure 4. These results show the change in absorption spectra by different interactions between self-doped poly(aniline-*co*-AB)/SPS and various saccharides at pH 4.5. As can be seen from Figure 4, sorbitol caused the strongest changes in the absorption, followed by mannitol, glycerol, glucose, and saccharose. Its change in absorption intensity was increased with an increase in the molar ratio of each saccharide. The binding of the each saccharide was reversible, albeit slow. The changes that occurred in the unidentified absorption spectra by the binding of saccharides were interpreted in one or more of the following ways in previous reports:[40] (i) steric hindrance, (ii) the loss of hydrogen bonding, (iii) the loss of positive charge, and (iv) the difference of interlayer interaction extent between electron-deficient boron and electron-rich nitrogen by the insertion of a saccharide. However, in this experiment, the decrease of a polaron transition band at 745 nm was used as a reference to monitor the binding of sugar molecules with boronic acids of the polyaniline. Therefore, the decrease of a polaron peak is probably caused by the loss of protons due to covalent bonds formed with sugar molecules in the polyaniline, and this results in the dedoping of polyaniline. Although the addition of sugar molecules increases the acidity of boronic acid,[41] the binding of saccharide molecules on the boronic acid leaves the nitrogen neutral, which may cause the decrease of the polaron peak. The decreasing absorbance intensity varied in the order sorbitol > mannitol >glycerol > glucose > saccharose, which was the same as that observed in the previously reported chemically synthesized sensor. However, the change of polaron intensity in the self-doped poly(aniline-*co*-AB) was approximately a few hundred times higher than that of the copolymer that was reported previously.[40] This large increase in sensitivity may be due to the fact that the polymer is in solution form, caused by the aid of SPS. Unlike solid film, the solution may facilitate more boronic acids in the polymer to interact with sugar molecules. Another advantage of this copolymer synthesized with the aid of SPS is that it is water soluble, which may reduce the response time to bind the sugar molecules.

A trace of the CVs of poly(aniline-*co*-AB) in the presence of various concentrations of sorbitol is shown in Figure 5. Two redox couples are shown at negative and positive potentials, respectively. The CV data indicate that poly(aniline-*co*-AB)

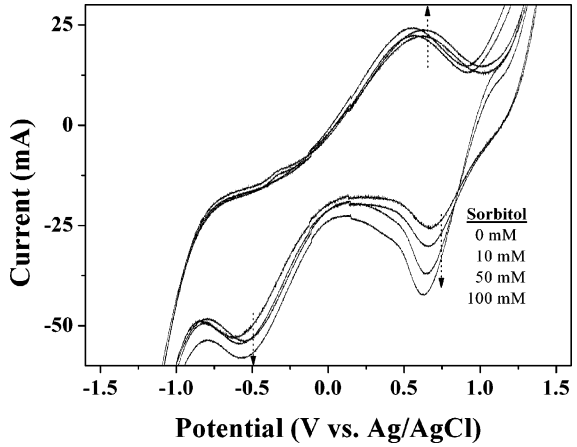


Figure 5. CVs of poly(aniline-*co*-AB) containing esterified boronic acid by various concentrations of Sorbitol in TBAFP6 acetonitrile solution at room temperature.

containing sorbitol is electroactive, having a prominent cathodic and a broad peak at 0.62 and −0.54 V as well as the characteristic two broad anodic peaks at 0.55 and −0.76 V. These peaks result from the redox process of the polyaniline backbone and esterification between boronic acid and polyols attached to the conducting polymer.[40] As can be seen from Figure 5, 100 mM sorbitol caused the strongest changes in the current value. Although there is a potential shift at the cathodic and anodic peaks, the current intensity obtained upon the addition of sorbitol changed sharply at a potential of 0.62 V, and the change was less pronounced at potentials of −0.54 and 0.55 V, respectively. The current response of poly(aniline-*co*-AB) solution to sorbitol increased with an increase in the sorbitol concentration. However, a change in the anodic peak concentration did not produce a significant change in the electroactivity. The dedoping process might occur because the binding of polyols onto the boronic acid prevent the nitrogen in the polyaniline from doping by boronic acids.

Conclusions

Poly(aniline-*co*-AB) was successfully synthesized with the aid of the anionic polyelectrolyte SPS at mild pH conditions. This poly(aniline-*co*-AB) complex underwent changes in the absorption spectra upon the addition of saccharides at pH 4.5 in the water-soluble state. The effects of weak dopants, $B(OH)_2$ by changing the mole ratio between aniline and AB by acting as a self-dopant in **P1**, were conveniently monitored by UV−vis absorption spectra. The UV−vis spectra showed that $B(OH)_2$ functioned as a dopant when its concentration was lower; however, at higher concentrations, it worked as a bulky pendant group and decreased the conductivity of polyaniline. This conductivity dependency on the mole ratio of AB monomers allowed the modulation of electrical properties of the copolymer. The response of the poly(aniline-*co*-AB) solution by the addition of saccharides in the UV−vis absorption spectra and CVs (particularly in cathodic reaction at 0.65 V) was increased gradually with increasing concentration of saccharides due to the dedoping of poly(aniline-*co*-AB). The sensitivity of water-soluble copolymer to detect saccharides was superior to the copolymer film synthesized by chemical methods. The results clearly demonstrated that poly(aniline-*co*-AB) is useful for sensing saccharides and is advantageous over other sugar-sensitive materials because of the ease of fabrication, prominent sensitivity, and highly applicable possibility in the physiological pH range, even though selectivity is still limited.

Acknowledgment. We acknowledge U.S. Army NSRDEC for financial support.

Supporting Information Available. FT-IR transmission spectra of polyaniline, poly(AB), and poly(aniline-*co*-AB), and in situ UV−vis−NIR spectra change of poly(AB) during the reaction time. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Robertson, R. N. *The Lively Membranes*; Cambridge University Press: New York, 1983.
(2) Elsaa, L. J.; Rosenberg, L. E. *J. Clin. Invest.* **1969**, *48*, 1845−1849.
(3) De Marchi, S.; Cecchin, E.; Basil, A.; Proto, G.; Donadon, W.; Jengo, A.; Schinella, D.; Jus, A.; Villalta, D.; De Paoli, P.; Santini, G.; Tesio, F. *Am. J. Nephrol.* **1984**, *4*, 280−284.
(4) Baxter, P.; Goldhill, J.; Hardcastle. P. T.; Taylor, C. J. *Gut* **1990**, *31*, 817−820.
(5) Yasuda, H.; Kurokawa, T.; Fuji, Y.; Yamashita, A.; Ishibashi, S. *Biochim. Biophys. Acta* **1990**, *1021*, 114−118.
(6) Fedoak, R. N.; Gershon, M. D.; Field, M. *Gasteroenterology* **1989**, *96*, 37−40.
(7) Yamamoto, T.; Seino, Y.; Fukumoto, H.; Koh, G.; Yano, H.; Inagaki, N.; Yamada, Y.; Inoue, K.; Manabe, T.; Imura, H. *Biochem. Biophys. Res. Commun.* **1990**, *170*, 223−230.
(8) James, T. D.; Linnane, P.; Shinkai, S. *Chem. Commun*. **1996**, 281−286.
(9) James, T. D.; Samankumara, K. R. A. S.; Shinkai S. *Angew. Chem. Int. Ed*. **1996**, *35*, 1910−1922.
(10) James, T. D.; Shinkai, S. *Top. Curr. Chem*. **2002**, *218*, 159−162.
(11) Bielecki, M.; Eggert, H.; Norrild, J. C. *J. Chem. Soc., Perkin Trans. 2* **1999**, 449−451.
(12) Arimori, S.; Bosch, L. I.; Ward, C. J. *Tetrahedron Lett.* **2001**, *42*, 4553−4555.
(13) (a) Gough, D. A.; Armor, J. C. *Diabetes* **1995**, *44*, 1005−1009. (b) Heller, A. *Annu. Rev. Biomed. Eng.* **1999**, *1*, 153−175.
(14) (a) Soundararajan, S.; Badawi, M.; Kohlrust, C. M.; Hageman, J. H. *Anal. Biochem.* **1989**, 125−134. (b) Maestas, R. R.; Prieto, J. R.; Kuehn, G. D.; Hageman, J. H. *J. Chromatogr.* **1980**, 225−231.
(15) Tsukagoshi, K. S. S. *J. Org. Chem.* **1991**, *56*, 4089−4091.
(16) (a) DiCesare, N.; Lakowicz, J. R. *Chem. Commun.* **2001**, 2022−2023. (b) Arimori, S.; Bell, M. L.; Oh, C. S.; Frimat, K. A.; James, T. D. *J. Chem. Soc., Perkin Trans. 1* **2002**, 803−808. (c) Sandanayake, K. R. A. S.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1083−1084. (d) Kukrer, B.; Akkaya, E. U. *Tetrahedron Lett.* **1999**, *40*, 9125−9128. (e) DiCesare, N.; Lakowicz, J. R. *Tetrahedron Lett.* **2001**, *42*, 9105−9108. (f) Gao, X.; Zhang, Y.; Wang, B. *Org. Lett*. **2003**, *5*, 4615−4618.
(17) Boeseken, J. *Adv. Carbohydr. Chem.* **1949**, *4*, 189−210.
(18) Kuivila, H. G.; Keough, A. H.; Soboczenski, E. J. *J. Org. Chem.* **1954**, *19*, 780−783.
(19) Wu, W. H.; Greene, C. *Clin. Chem.* **1986**, *32*, 1193.
(20) Yoon, J.-Y.; Czarnik, A. W. *J. Am. Chem. Soc.* **1992**, *114*, 5874−5875.
(21) James, T. D.; Linnane, P.; Shinkai, S. *Chem. Commun.* **1996**, 281−288.
(22) Shinmori, H.; Takeuchi, M.; Shinkai, S. *Tetrahedron* **1995**, *51*, 1893−1902.
(23) Norrild, J. C.; Sotofte, I. *J. Chem. Soc., Perkin Trans.* **2002**, *2*, 303−311.
(24) Yamamoto, H.; Ori, A.; Ueda, K.; Dusemund, C.; Shinkai, S. *Chem. Commun.* **1996**, 407−408.
(25) Wulff, G. *Pure Appl. Chem.* **1982**, *54*, 2093−2102.
(26) Reddinger, J. L.; Reynolds, J. R. *Adv. Polym. Sci.* **1999**, *145*, 57−122.
(27) Focke, W. W.; Wnek, G. E.; Wei, Y. *J. Phys. Chem.* **1987**, *91*, 5813−5818.
(28) Genies, E. M.; Lapkowski, M.; Tsintavis, C. *New J. Chem.* **1988**, *15*, 373−377.
(29) MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 317−332.
(30) Liu, W.; Kumar, J.; Tripathy, S.; Senecal, K. J.; Samuelson, L. *J. Am. Chem. Soc.* **1999**, *121*, 71−78.
(31) MacDiarmid, *A. G. Angew. Chem., Int. Ed*. **2001**, *40*, 2581−2590.
(32) Stafstrom, S.; Bredas, J. L.; Epstein, A. J.; Woo, H. S.; Tanner, D. B.; Huang, W. S.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1987**, *59*, 1464.

(33) Ginder, J. M.; Epstein, A. J. *Phys. Rev. B* **1990**, *41*, 10674−10685.
(34) Wudl, F.; Angus, R. O.; Lu, F. L.; Allemand, P. M.; Vachon, D. J.; Nowak, M.; Liu, Z. X.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3677−3684.
(35) Brewer, S. H.; Allen, A. M.; Lappi, S. E.; Chasse, T. L.; Briggman, K. A.; Gorman, C. B.; Franzen, S. *Langmuir* **2004**, *20*, 5512−5520.
(36) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*, 2nd ed.; Academic Press: New York, 1975; pp 335−337.
(37) Yu, I.; Deore, B. A.; Recksiedler, C. L.; Corkery, T. C.; Abd-El-Aziz, A. S.; Freund, M. S. *Macromolecules* **2005**, *38*, 10022−10026.
(38) Deore, B. A.; Yu, I.; Aguiar, P. M.; Recksiedler, C. L.; Kroeker, S.; Freund, M. S. *Chem. Mater.* **2005**, *17*, 3803−3805.
(39) Deore, B. A.; Yu, I.; Freund, M. S. *PCT Int. Appl.* **2005**, 30.
(40) Pringsheim, E.; Terpetschnig, E.; Piletsky, S. A.; Wolfbeis, O. S. *Adv. Mater.* **1999**, *11* (10), 866−868.
(41) Li, J.; Xu, X.; Zhang, Y. *Tetrahedron Lett.* **2003**, *44*, 9349−9351.

BM070421+