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Conference Paper (Contributed)

Semiconducting Copolymeric Polythiophene Films*

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We describe the incorporation of a specific binding site into a semiconducting matrix. The specific binding is boronic acid which was incorporated into a semiconducting polythiophene film. This semiconducting polymer was shown to have new semiconducting properties.

INTRODUCTION

Polymer matrices have now been built to involve site specific receptors. These receptor sites have been called templates and can be used for molecular recognition.^{1,2,3} In some ways the templated site in the polymer cavity is analogous to an enzymatic site.¹ Such templated polymer systems show promise of enhancing selectivity in chromatographic separations of organic molecules.

It is also known that certain aromatic-like compounds, such as pyrrole, pyridine, and thiophene undergo anodic polymerizations which can be given semiconducting properties under controlled oxidizing conditions.⁴ The electrical conductivities of these polymers can be changed by either altering the counterion or changing its concentration as the »dopant.« We will describe the preliminary experiments which show that semiconducting copolymers can be prepared in the polythiophene series and that these copolymers have binding sites suitable for surface binding studies or templating.

The copolymer system chosen in this study is thiophene/thiophenyl boronic acid. The dopant used is fluoride ion, obtained from lithium tetrafluoroborate.

The system is shown below in Figure 1.

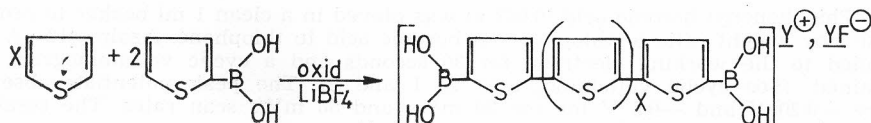


Figure 1. The copolymer system to be constructed in this study.

* Based on a contributed paper presented at the 7th »Ruđer Bošković« Institute's International Summer Conference on the Chemistry of Solid/Liquid Interfaces, Red Island — Rovinj, Croatia, Yugoslavia, June 25—July 3, 1986.

The thiophenyl boronic acid is unavailable commercially and had to be prepared for this study. Boronic acids react readily with alcohols and diols. Thus when the boronic acid is incorporated into the copolymer, the resulting semiconductor should respond to alcohols binding to its surface. The terminal boronic acid functionality could be used to bind a sugar molecule between two polymer chains. This is illustrated by preparing a glucose template from thiophenyl boronic acid.

EXPERIMENTAL

*Thiophenyl Boronic Acid*⁵

Magnesium turnings (565) were placed in a 250 ml round bottom flask equipped with a magnetic stirrer and a reflux condenser. Slowly dropped in a mixture of 4.25 ml of 2-bromo thiophene and 100 ml of diethyl ether. The resulting Grignard was filtered into a dropping funnel and slowly dripped into a stirred solution of 6.85 ml of Trimethyl borate in 100 ml diethyl ether at -70°C . After the mixture had stirred overnight, 10 ml of distilled water was added. After a few minutes a white precipitate fell out, the yellow ether solution decanted and the ether was removed. To the brownish remains were added 10 ml of distilled water and the mixture was refluxed for 2 hours. The hot solution was filtered. The resulting precipitate was recrystallized from hot water. The melting range of the resulting crystals was $122-125^{\circ}\text{C}$. Infrared analysis showed major IR absorption bands at: 3300 cm^{-1} , broad, due to O—H; 1560 cm^{-1} , sharp, due to C—C; 1440 cm^{-1} , sharp, due to C—H; 1380 cm^{-1} , due to S—S; 1195 cm^{-1} , due to B—C and 1100 cm^{-1} , due to B—O. The nuclear magnetic resonance spectrum obtained in deuterated DMSO contained peaks at: δ 7.70, 1 H, a triplet due to the proton with two neighbors on the thiophene ring; δ 8.26, 2 H, due to the other protons on the thiophene ring; δ 8.86, 2 H due to the O—H protons.

*Incorporation of Thiophenyl Boronic Acid into Polymeric Thiophene*⁶

A standard solution of 0.376 M thiophene and 0.519 M lithium tetrafluoroborate was prepared. From this, 1 ml was pipetted into a 1 ml beaker. The beaker was fitted with a stopper containing a platinum working electrode, a saturated Ag/AgCl reference electrode and a counter electrode. A current of $412\text{ }\mu\text{A}$ was applied to the working electrode for 30 seconds. A cyclic voltammogram was then obtained at 20 mV/s and 50 mV/s scan respectively which was identical to previously reported voltammogram for thiophene on platinum. The shiny green film was then peeled off the working electrode. It appeared continuous and tough.

Thiophenyl boronic acid (0.0016 g) was then placed in a clean 1 ml beaker and 1 ml of the standard thiophene solution was added. This provided 5% by weight of thiophenyl boronic acid to thiophene in the beaker. The solution was stirred, and $412\text{ }\mu\text{A}$ was applied for 30 seconds. A cyclic voltammogram was then obtained. A slight shift in the anodic potential was observed (Table I). The anodic potentials observed were -0.25 V and -0.18 V for the 20 mV/s and 50 mV/s scan rates respectively. The green film peeled off the electrode was not as tough and slightly flaky.

Thiophenyl boronic acid (0.063 g) was played in a clean 1 ml beaker to provide a 20% by weight ratio of thiophenyl boronic acid to thiophene. Again, $412\text{ }\mu\text{A}$ was applied to the working electrode for 30 seconds and a cyclic voltammogram was obtained. (See cyclic voltammograms C, 1 and 2). The peak potentials observed were -0.20 V and -0.5 V for the 20 mV/s and 50 mV/s scan rates. The resulting film was very brittle and flaky when peeled off.

*Thiophenyl Boronic Acid-Glucose Complex*⁷

Thiophenyl boronic acid, 0.0029 g and 0.022 g D-glucose were crushed in a watch glass to a fine powder. A small amount of this was placed in a capillary tube and placed in a Melt-Temp apparatus. The temperature was raised until both

components melted. This temperature was maintained for 5 minutes. The capillary tube was then crushed and extracted with petroleum ether. The ether was removed from the extract and the residue was used to obtain an infrared spectrum. The major absorption bands were at: 3450 cm^{-1} , due to O—H; 2975 cm^{-1} , due to C—H; 1540 cm^{-1} , due to C—C; 1450 cm^{-1} , due to C—H; 1380 cm^{-1} , due to S—C, and 1210 cm^{-1} , due to B—O. This spectrum was different from the glucose spectra and the thiophenyl boronic acid spectrum, and is consistent with a dithiophenyl borate ester of glucose, most likely the furanose form.

RESULTS AND DISCUSSION

For this study we wished to incorporate simple functionality in an organic semiconducting matrix. This simple functionality must readily bind to other molecules, that is, rapidly establish an equilibrium with a substrate. Boronic acids are known to bind readily and reversibly with alcohols and polyalcohols such as sugars. The incorporation of a boronic acid functionality into thiophene was accomplished easily using established methods. In turn, this substituted thiophene could be reacted with glucose to give a disubstituted glucose molecule suitable for incorporation into a semiconducting matrix as a template.

Cyclic voltammograms, as shown in Figure 2. and the reduced data in Table I clearly reveal that the thiophenyl boronic acid was incorporated

TABLE I

*Electrochemical Data From Cyclic Voltammograms**

Trial	Thiophene (M)	Lithium tetrafluoroborate (M)	Thiophenyl boronic acid (M)	Peak anodic 20 mV/s	Potential 50 mV/s
1	0.376	0.519	—	—0.45 V	—1.05 V
2	0.376	0.519	0.012	—0.25 V	—0.81 V
3	0.376	0.519	0.049	—0.20 V	—0.50 V

* Solutions were in benzonitrile. Reference electrode was Ag/AgCl, working electrode was Pt and the counter electrode was Al. (Model 362 Scanning Potentiostat, EG + G Princeton Applied Research).

into the semi-conducting matrix. The measured current was directly proportional to the scan rate, as theory suggests for a surface bound species as opposed to the electrochemistry of a solution phase species. The incorporation of the thiophenyl boronic acid was observed as a drop in the measured current that was proportional to the molar ratio of the thiophenyl boronic acid present in solution. The observed shifts in the potential, the broadening of the peaks and the appearance of shoulders at the peaks (Figure 2.) all suggest that the thiophenyl boronic acid was incorporated into the matrix.

By removing the matrix from the platinum electrode, it was easy to observe a loss of mechanical strength in the film with increased mole fraction of thiophenyl boronic acid. This would be expected if the boronic acid functionality terminated the polymer chain, as shown in Figure 1.

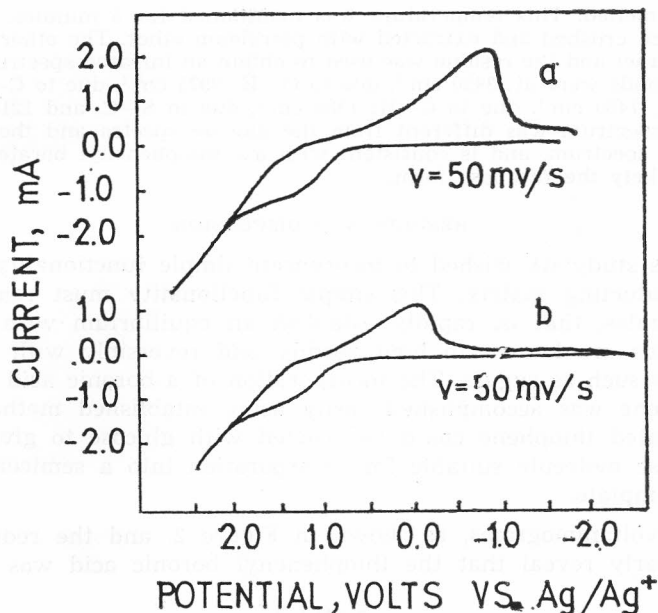


Figure 2. The cyclic voltammetry showing incorporation of thiophenyl boronic acid into a semi-conducting polythiophene film.

Although this is a preliminary report, we show that copolymeric semi-conducting films can be constructed and that these films can incorporate functionality suitable for binding studies and templating. Eventually, these should lead to a new class of chemical sensors, as suggested recently.⁸

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SAŽETAK

Poluvodički filmovi kopolimernog politiofena

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Dan je preliminarni izvještaj o inkorporaciji specifične funkcionalne skupine u poluvodičku matricu. Ta specifična funkcionalna skupina je borna kiselina koja je umetnuta u poluvodički film politiofena. Ona postaje specifično mjesto vezivanja glukoze. Novo stvoreni kopolimer ima i nova poluvodička svojstva.