

# New Approach to Rapid Generation and Screening of Diverse Catalytic Materials on Electrode Surfaces

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**Abstract:** This paper describes a general approach to rapid generation and screening of catalytic materials on electrode surfaces. The properties of the corresponding polymers, including catalytic performance, can be modulated by varying the monomer feed ratios, monomer concentrations, and applied polymerization potential. Thus, the generation of the polymeric TEMPO (2,2,6,6-tetramethylpiperidin-1-yloxy) catalysts was performed by electrochemical copolymerization of 2,2'-bithiophene with the TEMPO catalyst precursors containing pyrrole side chains. A library of catalyst films was obtained over a wide range of bithiophene/pyrrole ratios upon repeated scanning of the applied potential from +0.5 to +1.4 V (vs Ag/AgCl). The resulting catalyst films were utilized in both chemical and electrochemical oxidation of primary alcohols to aldehydes.

## Introduction

New routes to catalyst immobilization on solid supports have received considerable attention.<sup>1</sup> The ultimate goal in this field is to combine advantages inherent to homogeneous catalysis with the many virtues of heterogeneous catalysis.<sup>2</sup> The loss of catalytic activity through poisoning or leaching is the biggest problem that faces many immobilized catalysts. Thus, there is a growing need for the new types of catalytic materials that possess high stability and retain catalytic activity under a wide range of reaction conditions.

Electrochemistry is at the interface of solution and solid-phase chemistry, as reactions occur in the diffusion layer formed at the electrode surface.<sup>3</sup> We were intrigued by the possibility of using electrochemistry to generate copolymer film supports on electrode surfaces with the catalyst sites attached to the polymer chains. The resulting catalytic materials can then be used in either chemically or electrochemically driven redox processes. It is possible to modulate the composition and properties of the conducting copolymer by varying (1) monomer feed ratio,<sup>4</sup> (2) monomer concentrations,<sup>5</sup> and (3) applied polymerization potential.<sup>4b,c,5</sup> The latter parameter is unique to electrochemistry and offers a competitive advantage of using different redox-active monomers at the catalyst preparation stage. If the oxidation potentials of the monomers are different, it should be possible to obtain conducting copolymers with a high degree of variability in the composition of the catalyst matrix by fine-tuning the feed ratio as well as applied potential during

electropolymerization. The fact that maximum catalytic activity of a supported catalyst need not correlate with maximum ligand loading<sup>6</sup> warrants screening of surface compositions. This principle can be extended to generate arrays of copolymer films combinatorially<sup>7–9</sup> to identify the most active catalysts among them. Noteworthy, electrochemistry was recently introduced into the field of combinatorial catalysis.<sup>9</sup> A contribution from our lab describes the design and applications of the spatially addressable electrolysis platform (SAEP)<sup>10</sup> for parallel electro-synthesis which has led to the present idea of parallel electrochemical generation of arrays of copolymer film catalysts.

## Experimental Section

**General Information.** Acrylonitrile, pyrrole, *N*-hydroxysuccinimide, 4-amino-2,2,6,6-tetramethylpiperidinyloxy (free radical), 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (free radical), and 2,2'-bithiophene were purchased from Aldrich Chemical Co. Column chromatography was carried out using 230–400 mesh silica gel. <sup>1</sup>H NMR spectra were referenced to residual CHCl<sub>3</sub> (δ 7.26 ppm) and <sup>13</sup>C spectra were referenced to CDCl<sub>3</sub> (δ 77.2 ppm). Electrochemical polymerization and cyclic voltammetry characterization were conducted on a BAS CV-50W Voltammetric Analyzer (Bioanalytical Systems, Inc.) equipped with a BAS C3 three-electrode cell stand. Electrochemical oxidation of benzyl alcohol with the polymer catalyst poly(3-bithiophene) was performed with use of a laboratory DC power supply (GW, model GRP-3060D).

**Preparation of 3-(Pyrrol-1-yl)propionic Acid.** A modified literature procedure<sup>11</sup> was followed. Acrylonitrile (10 mL, 152 mmol) was added

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dropwise over a period of 30 min to a mixture of pyrrole (10 g, 149 mmol) and tetrabutylammonium hydroxide (3.0 mL of 40 wt % aqueous solution). The temperature was kept at  $-78\text{ }^{\circ}\text{C}$ . The reaction mixture was then allowed to warm to room temperature and was stirred for 1 h. The crude nitrile was hydrolyzed by refluxing with a solution of potassium hydroxide (10 g, 178 mmol) for 1 h in 15 mL of water. Acidification with 10 mL of 5% hydrochloric acid and extraction with ether (20 mL  $\times$  3) gave 15.3 g (74%) of product.

**General Procedure for Synthesis of Monomers 1–3.** 3-(Pyrrol-1-yl)propionic acid (0.70 g, 5.0 mmol) and 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (0.86 g, 5.0 mmol) were stirred in 20 mL of ethyl acetate at  $0\text{ }^{\circ}\text{C}$ . *N,N'*-Dicyclohexylcarbodiimide (DCC, 1.03 g, 5.0 mmol) in 10 mL of ethyl acetate was added slowly to the above mixture. A white precipitate of dicyclohexylurea was formed within 30 min. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The crude product was filtered and the filtrate was purified using a silica gel column and 60:40 hexane/ethyl acetate as eluent. Monomer **3** appeared as orange crystals (67% yield). Monomers **1** and **2** were prepared by a similar procedure using the corresponding TEMPO precursors.

**3-(Pyrrol-1-yl)propionic Acid 2,5-Dioxopyrrolidin-1-yl Ester (1).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.70 (t, 2H,  $J = 2.0$  Hz), 6.17 (t, 2H,  $J = 2.0$  Hz), 4.30 (t, 2H,  $J = 7.2$  Hz), 3.07 (t, 2H,  $J = 7.2$  Hz), 2.84 (s, 4H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  168.87, 166.41, 120.62, 109.13, 44.39, 33.76, 25.68.

**4-(3-(Pyrrol-1-yl)propionylamino)-2,2,6,6-tetramethylpiperidin-1-yloxy (2).** IR (KBr) 3312 (NH), 2975 (CH), 1651 (C=O), 1538 (NH), 728 (pyrrole)  $\text{cm}^{-1}$ . MS, *m/e* (rel intensity) 293 (43), 154 (40), 139 (80), 124 (78), 109 (82), 80 (100). HRMS 293.1857 (Calcd for  $\text{C}_{16}\text{H}_{25}\text{N}_3\text{O}_3$ : 293.1865).

**4-(3-(Pyrrol-1-yl)propionyl)oxy)-2,2,6,6-tetramethylpiperidin-1-yloxy (3).** IR (KBr) 2974, 2935 (CH), 1734 (C=O), 1166 (C–O), 727 (pyrrole)  $\text{cm}^{-1}$ . MS, *m/e* (rel intensity) 292 (11), 206 (18), 154 (21), 139 (19), 124 (33), 94 (63), 84 (100). HRMS 292.2142 (Calcd for  $\text{C}_{16}\text{H}_{26}\text{N}_3\text{O}_2$ : 292.2127).

**General Procedure for Electrochemical Polymerization.** Electrochemical polymerization and characterizations were performed in a one-compartment cell with a platinum disk ( $0.07\text{ cm}^2$ ) as working electrode and a platinum wire as counter electrode, respectively. A Ag/AgCl electrode was used as reference electrode. All electrochemical polymerization experiments were performed in acetonitrile solution with 0.1 M total monomer concentration and 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte. Repetitive cyclic voltammetric scans between +0.5 and +1.5 V led to the formation of a black electroactive film at the working electrode. Characterizations (by cyclic voltammetry) of the copolymer films were conducted in acetonitrile solutions with 0.1 M tetrabutylammonium tetrafluoroborate. Preparative scale copolymer films for catalytic reaction were obtained with a pair of platinum foil ( $5\text{ cm}^2$  each) electrodes as working and counter electrodes and a Ag/AgCl reference electrode.

**General Procedure for Alcohol Oxidation with Polymer Catalysts.** The reaction was performed in a 20 mL glass vial cooled in an ice–water bath. The platinum foil, covered with the polymer catalyst according to the procedure described above, was placed in the vial. A dichloromethane solution (5 mL) of the alcohol (0.2 M) and tetralin (0.1 M; as GC internal standard) were added followed by KBr (24 mg, 0.2 mmol). After the above mixture was cooled to  $0\text{ }^{\circ}\text{C}$ , 12 mL of aqueous NaOCl (diluted to a final concentration of 0.1 M and buffered by addition of  $\text{NaHCO}_3$  to a pH of 9.1) was added. The reaction mixture was then vigorously stirred for 1 h. The organic phase was separated, and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried over  $\text{MgSO}_4$ . After analysis by GC, the solvent was removed in vacuo, and the product was purified by column chromatography on silica gel with 80:20 hexane/ethyl acetate as eluent. The polymer film was washed three times with water, methanol, and dichloromethane (5 mL each), air-dried, and reused as such.

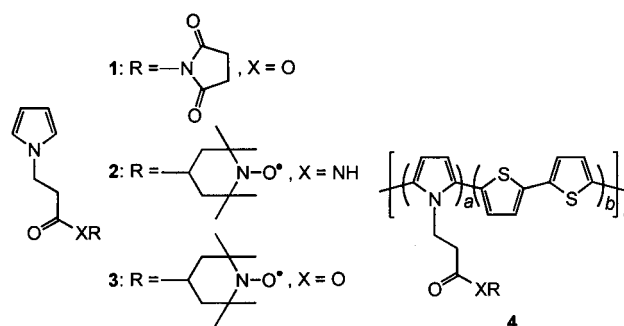
**Procedure for Electrochemical Oxidation of Benzyl Alcohol with Polymer Catalyst.** A solution of benzyl alcohol (108 mg, 1.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was placed in a 20 mL glass vial. To this solution was added 10 mL of an aqueous solution of NaBr (25%) buffered by addition of solid  $\text{NaHCO}_3$  to pH 8.6. Two platinum foil electrodes ( $2.5$

$\text{cm} \times 2.0\text{ cm}$ ) were immersed into the upper layer of the resulting biphasic mixture. The anode was precoated with the polymer catalyst poly(3-bithiophene). The mixture was electrolyzed under a constant current of  $20\text{ mA/cm}^2$  with moderate stirring until  $2.0\text{ F/mol}$  of electricity was passed. The organic layer was separated and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic extracts were dried over  $\text{MgSO}_4$  and concentrated in vacuo. The crude product was purified by column chromatography on silica gel with 80:20 hexane/ethyl acetate as eluent.

## Results and Discussion

Polypyrrole and polythiophene conduct electricity in the oxidized state and are normally obtained via chemical or electrochemical oxidative polymerization of pyrrole and thiophene, respectively.<sup>12</sup> The electrochemical polymerization method provides conducting polymers in the form of films adhered to the electrode surfaces. A number of catalysts were found among the polypyrroles derivatized with metal complexes.<sup>13</sup> We now wish to demonstrate implementation of a novel technique for conducting copolymer catalyst generation and screening. A specific example illustrates high-throughput generation and identification of new heterogeneous oxidation catalysts on electrode surfaces.

Our studies commenced with the generation of suitable conducting polymer precursors for heterogeneous TEMPO (2,2,6,6-tetramethylpiperidin-1-yloxy) oxidation catalysts.<sup>14</sup> Pyrrole-based monomers **1–3** were synthesized from 3-(pyrrol-1-yl)propionic acid.<sup>11</sup> It was envisaged that the pyrrole **1** could be utilized for post-polymerization catalyst loading while the pyrroles **2** and **3** could introduce catalyst sites via direct electropolymerization.



Direct electrochemical polymerization of **1** on a platinum electrode in acetonitrile produced a film, while monomers **2** and **3** could not be polymerized electrochemically. It is well-known that certain functional groups on the pyrrole side chain can prohibit polymerization.<sup>15</sup> Thus, we turned to copolymerization with bithiophene, known for its ability to initiate electrochemical polymerizations due to its low oxidation potential (+1.3 V vs SCE).<sup>16</sup> Gratifyingly, stable catalyst films of generic composition **4** were obtained over a wide range of bithiophene/pyrrole ratios upon scanning the potential from +0.5 to +1.4 V (vs Ag/AgCl). A typical time for catalyst generation

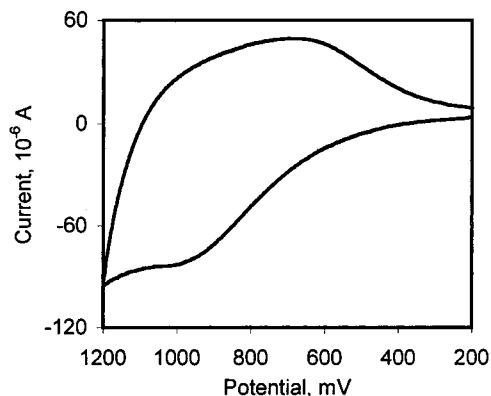
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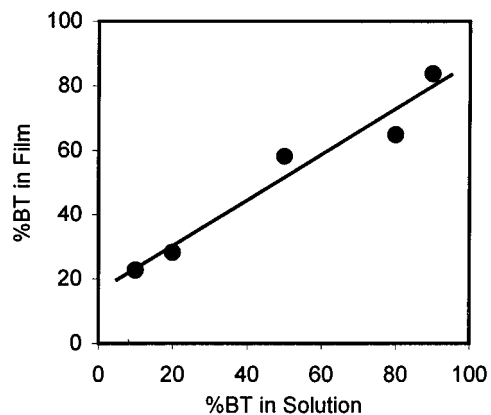
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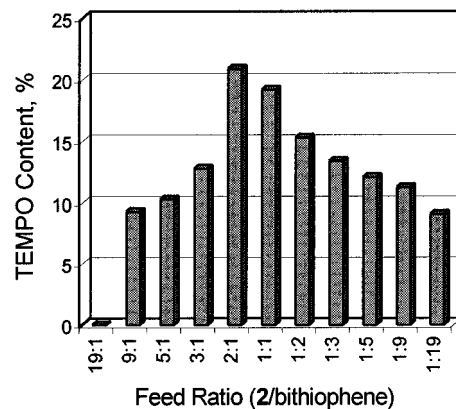
**Figure 1.** Cyclic voltammogram of the copolymer of **1** and bithiophene in acetonitrile (9:1 feed ratio of **1**/bithiophene) with 0.1 M  $\text{Bu}_4\text{N}^+\text{BF}_4^-$ .



**Figure 2.** Bithiophene composition in the catalyst matrix as a function of bithiophene fraction in solution.

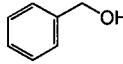
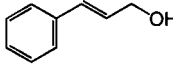
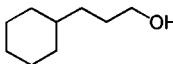
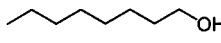
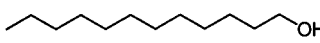
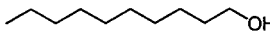
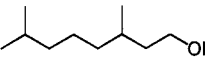
is 1–2 min. The cyclic voltammogram (Figure 1) of the copolymer film, obtained from a 9:1 mixture of **1** and bithiophene, displays a broad redox band extending from +1.0 to +0.6 V, where no distinctive redox bands for polypyrrole (+0.2 to 0.0 V) and polythiophene (+1.4 to +1.0 V) could be identified, indicating the polymer film is a copolymer instead of a polymer blend.<sup>4c</sup> The appearance of a single redox couple for the conducting copolymer has been correlated with uniform redox properties.<sup>4c</sup> Most importantly, in the case of the film produced from **1** and bithiophene, elemental analyses of the S/N ratios indicate that the bithiophene/pyrrole ratio in solution is in linear correlation with the film composition (Figure 2). This correlation provides a convenient way of varying the content of catalyst sites in the copolymer matrix when making an array of catalysts. In addition to the feed ratio as a means of generating diverse copolymeric materials, changing the position of the potential window during potentiodynamic electropolymerization can be used to vary the compositions of the resulting films. However, preliminary results indicate that the corresponding catalytic materials have low mechanical stability when potentials above +1.5 V vs Ag/AgCl are being applied.<sup>17</sup>

In the case of electrochemical copolymerization of bithiophene with the pyrrole monomer **2**, we have observed an interesting nonlinear behavior between the TEMPO content in the copolymer film and the fraction of **2** in solution (Figure 3). The TEMPO content was determined by correlating the integrated CV curve of the copolymer backbone with the CV curve of the TEMPO redox region. We believe that two effects, i.e., the initiating/promoting effect of bithiophene and inhibiting effect of the monomer **2**, determine this electrochemical polymeriza-



**Figure 3.** TEMPO content of the copolymer film as a function of the **2**/bithiophene feed ratio in solution.

**Table 1.** Oxidation of Primary Alcohols to Aldehydes with the TEMPO Catalyst Poly(2-bithiophene) Obtained from **2** and Bithiophene (2:1 feed ratio)

Substrate	Isolated Yield, %
	89
	86
	97
	92
	90
	91
	96

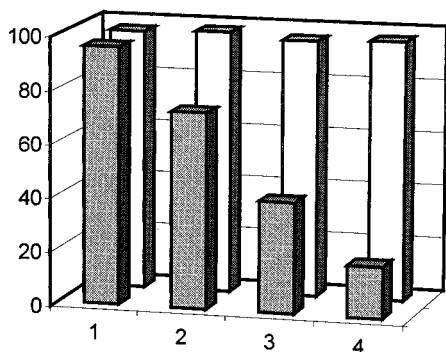
tion behavior. Presumably, at high bithiophene/pyrrole feed ratios, the initiating/promoting effect dominates and the TEMPO content in the film correlates with the **2**/bithiophene ratio. When more monomer **2** is present in solution, its inhibiting effect becomes predominant, and the TEMPO content decreases with increasing **2**/bithiophene feed ratio. Similar inhibiting behavior of one of the monomers in electrochemical copolymerization was previously observed.<sup>18</sup> The nonlinear behavior in the present case validates the combinatorial approach to conducting film catalysts for those precursors that require bithiophene “activation” for efficient film formation and compositional screening.

To illustrate the utility of the electrochemically generated materials in heterogeneous catalysis, we chose the TEMPO-catalyzed oxidation of primary alcohols to aldehydes with sodium  $\text{NaClO}/\text{NaBr}$  (Table 1).<sup>19</sup> The 2:1 feed ratio of **2**/bithiophene corresponds to the most active catalyst which was identified during initial catalyst screening. The typical amount of catalyst on a platinum foil electrode of 5  $\text{cm}^2$  area is

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**Figure 4.** Recyclability of the poly(2-bithiophene) (dark) and poly(3-bithiophene) (light) film catalysts for oxidation of benzyl alcohol to benzaldehyde (GC yield, %).

approximately 1.5  $\mu\text{mol}$ , estimated from the TEMPO content in the copolymer by integrating the CV curve. Thus, the catalyst loading is approximately 1.5 mol %, which corresponds to a minimum turnover frequency of 60/h for benzyl alcohol oxidation, a result comparable with the silica-supported TEMPO catalysts (90/h).<sup>19</sup> The catalytic activities of the films obtained using other feed ratios were also screened under the same alcohol oxidation conditions. For the films that correspond to 9:1 and 1:9 feed ratios of **2** and bithiophene, the respective yields for benzyl alcohol oxidation were 51% and 48%, consistent with the TEMPO loadings calculated from the CV experiments. Thus, the cyclic voltammetry can be used as a reliable screening tool. In a control experiment, a copolymer film of 1-butylpyrrole and bithiophene (1:1) was used for oxidation of benzyl alcohol. Less than 5% of benzaldehyde was detected by GC and 90% of starting material was recovered.

The recyclability of poly(2-bithiophene) catalyst was quite low: the yield of subsequent oxidation under the same conditions dropped to 19% after four runs. We were pleased to find that, by changing the amide bond in **2** into an ester bond (monomer **3**), the heterogenized catalyst poly(3-bithiophene), obtained with the optimized **3**/bithiophene feed ratio of 2:1, showed a significant improvement in catalytic performance. The catalytic activity of the film remained high after four runs (Figure 4). The yield dropped insignificantly (to 88%) after eight consecutive catalytic experiments. The improved performance

of the ester-based catalyst is most likely due to better mechanical properties of the adhered polymer.

To validate electrochemical oxidation as a complementary screening tool for catalytic activity, we explored the TEMPO modified platinum supports as anodes in the oxidation of alcohols. Direct oxidation of 1-octanol on a poly(3-bithiophene)-modified electrode in the presence of 2,6-lutidine<sup>20</sup> was unsuccessful. The peak current corresponding to TEMPO oxidation and reduction decreased significantly upon adding 2,6-lutidine to the alcohol solution in acetonitrile, indicating passivation of the electrode surface. However, the indirect, mediatory electrooxidation method<sup>21</sup> gave encouraging results. For the NaBr-mediated electrooxidation of benzyl alcohol in the  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  two-phase system on a modified platinum anode (**3**/bithiophene feed ratio = 2:1), the isolated yield of benzaldehyde was 63%. When an unmodified platinum electrode was used the isolated yield of benzaldehyde was 7% and the starting material was recovered.

In summary, we have developed a new approach to rapid generation and screening of diverse catalytic materials on electrode surfaces. Copolymerization of various ratios of film precursors yields diverse surfaces with modulated catalytic properties. In theory, the number of possible combinations is infinite. Bithiophene solves the problem of poor polymerizability of some pyrrole-substituted catalyst precursors. Rapid generation of modified electrodes should be made straightforward by copolymerizing libraries of pyrroles with bithiophene on arrays of electrodes.<sup>9</sup> The resulting materials can be applied in processes that are driven by either electrochemical or chemical redox systems. We are currently exploring the SAEP instrument<sup>10</sup> for parallel screening of film compositions for high-throughput generation of electrocatalysts.

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