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VOLTAMMETRIC BEHAVIOR OF MEDIATOR-MODIFIED ELECTRODE BY ELECTROCHEMICAL POLYMERIZATION OF NITROXYL RADICAL PRECURSOR CONTAINING PYRROLE SIDE CHAIN

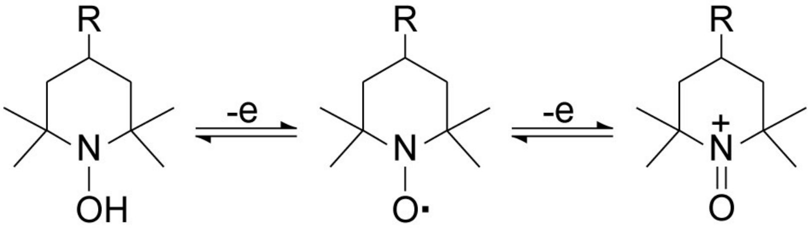
Tetsuya Ono, Makiko Tsunoda, Shigehiro Takahashi, Toshio Obata, Takanori Sone, and Yoshitomo Kashiwagi*

School of Pharmaceutical Sciences, Ohu University, 31-1 Misumido, Tomita-machi, Koriyama, Fukushima 963-8611, Japan Tel: +81-24-932-9146; Fax: +81-24-932-9146; E-mail: y-kashiwagi@pha.ohu-u.ac.jp

Abstract – This paper describes the voltammetric behavior of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl)-modified electrode prepared by the electrochemical polymerization of TEMPO-modified pyrrole. The modified electrode exhibits a symmetrical reversible redox wave at +0.7 V versus Ag/AgCl, which originates from the electron transfer between the pyrrole-polymerized layer and the electrode. The properties of the polymers on the electrode surface can be modulated by varying the applied polymerization potential. The TEMPO-modified electrode exhibits electrocatalytic activity for the oxidation of geraniol.

INTRODUCTION

Polypyrroles that conduct electricity in the oxidized state is normally obtained via the chemical or electrochemical oxidative polymerization of pyrroles.[1] The electrochemical polymerization method provides conducting polymers in the form of films adhered to the electrode surfaces. On the other hand, the organic nitroxyl radicals such as TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) and PROXYL (2,2,5,5-tetramethylpyrrolidine-1-oxyl) are usually stable radicals, and their oxidized species (i.e., an oxoammonium ion) can be easily prepared electrochemically by the one-electron oxidation of nitroxide (Scheme 1).[2] There exists literature that reports the preparation of a nitroxyl-radical-modified electrode by the electrochemical polymerization of TEMPO[3] or PROXYL[4] precursors containing pyrrole side chains for the electrocatalytic oxidation of alcohols. However, the electrochemical polymerization conditions and the properties of resulting polymers on the electrode surface have not been investigated in detail. We report here the voltammetric behavior of nitroxyl-radical-modified electrode prepared by the electrochemical polymerization of 4-(3-(pyrrole-1-yl)propoxy carbonyl)-TEMPO (**1**). It may be possible to modulate the properties of the conducting polymer by varying the applied polymerization potential.[5–7]

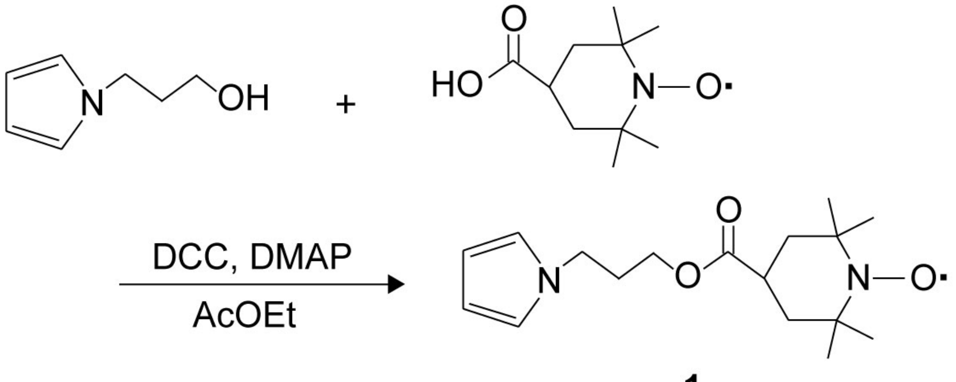


Scheme 1. Reversible redox system based on nitroxyl radical

RESULTS AND DISCUSSION

1. Characteristics of Monomer **1**

Pyrrole-based monomer **1** was synthesized from 1-(3-hydroxypropyl)pyrrole and 4-carboxy-TEMPO (Scheme 2). Cyclic voltammetry of monomer **1** was carried out in a MeCN solution containing 0.1 M TBAP as a supporting electrolyte. Figure 1 shows the cyclic voltammogram (CV) of monomer **1**, in which the reversible oxidation of a nitroxyl radical/oxoammonium ion redox system at +0.7 V and the irreversible oxidation of the pyrrole moiety at +1.32 V can be observed. Therefore, we have prepared polymer **1**-modified electrodes through the direct electrochemical polymerization of monomer **1** on the electrode surface by applying a film when a potential above +1.32 V.



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Scheme 2. Synthesis of TEMPO precursor containing pyrrole side chain (**1**)

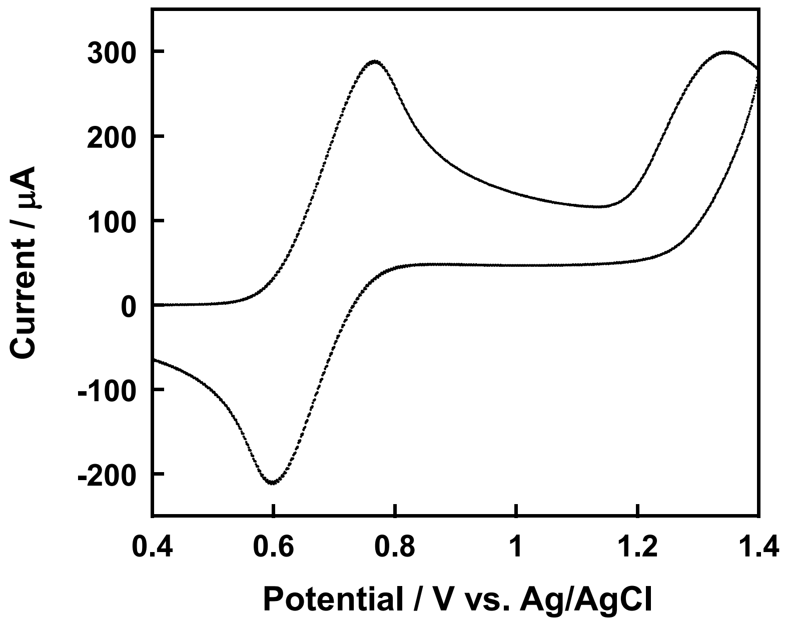


Figure 1. Cyclic voltammogram of 0.01 M monomer **1** at 200 mV s^{-1} in 0.1 M TBAP/MeCN

2. Electrochemical Polymerization

2.1. Electrochemical Polymerization by Repetitive Cyclic Voltammetric Scans

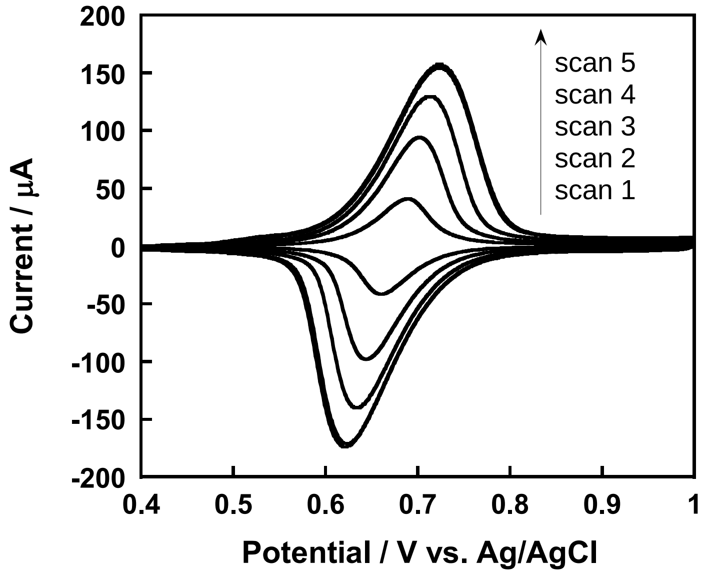
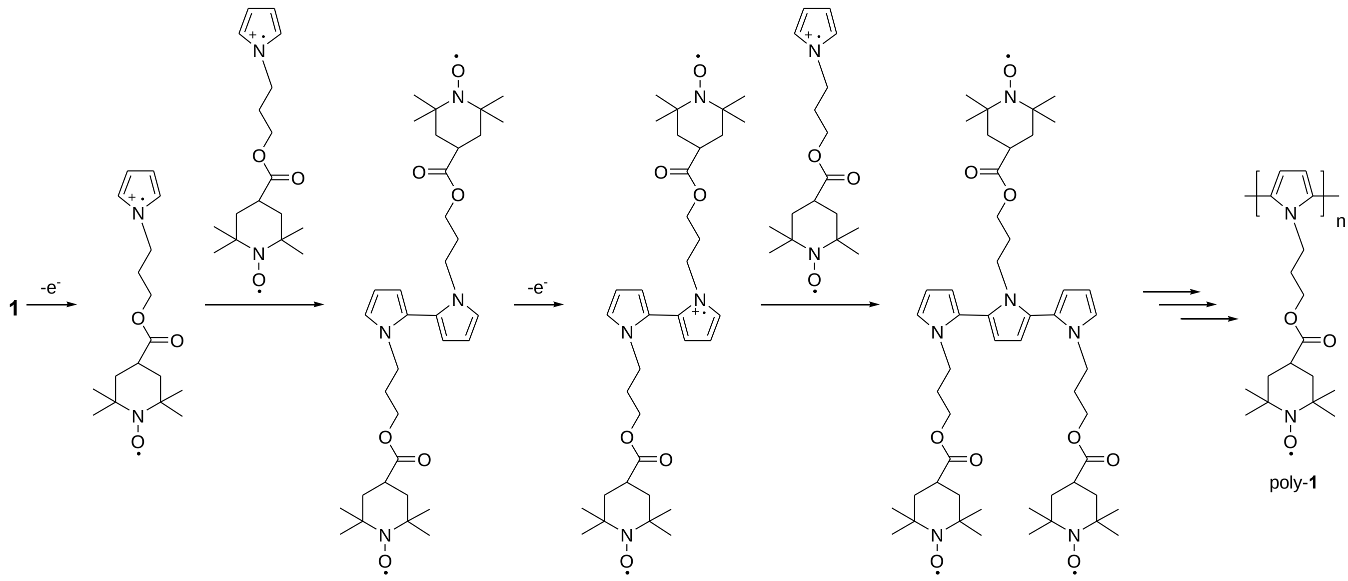


Figure 2. Cyclic voltammograms of the prepared poly-**1**-modified electrodes at 50 mV s^{-1} in 0.1 M TBAP/MeCN. The poly-**1**-modified electrodes were obtained by repeating cyclic voltammetric scans between +0.4 and +1.40 V at 100 mV s^{-1}



Scheme 3. A plausible mechanism of electrochemical polymerization of monomer **1**

Table 1. The characteristic features of poly-**1**-modified electrodes. The electrodes were obtained by repeating cyclic voltammetric scans between +0.4 and +1.40 V at 100 mV s^{-1}

Number of Scan	i_p^{a} / μA	ΔE_p / mV	Surface Concentration / nmol cm^{-2}
1	39	28	5.3
2	90	58	14.5
3	120	79	22.4
4	133	101	28.7
5	133	103	29.0

First, the poly-**1**-modified electrode was prepared by repeating cyclic voltammetric scans between +0.4 and +1.4 V at various scan rates in the presence of monomer **1**. The anodic and the cathodic peak currents of the CV were increased with an increase in the cyclic voltammetric scans (Figure 2). This suggests that poly-**1** was prepared on the electrode while repeating the oxidation and coupling reactions (Scheme 3). The polymer **1** was obtained more effectively in the solution of 0.01 M than in 0.001 and 0.1 M solutions (Figure 3). The characteristics of the prepared poly-**1**-modified electrodes at a scan rate of 100 mV s^{-1} are shown in Table 1. The polymer **1** on the electrode surface was considerably stable, and no deactivation was observed in CV after repeated potential scanning. The peak current of the CV was increased with an increase in the number of the scans; however, the peak current did not increase after four times. The oxidation potential of the modified electrodes was found at +0.72 to +0.74 V vs.

Ag/AgCl; the peak split between the anodic and cathodic peak potentials increased with the increase in the repeated scans. A linear relationship between the peak current and the scan rate in the cyclic voltammetry observed, suggesting the poly-**1** film was firmly immobilized on the electrode surface.[8] The amount of electroactive **1** on the electrode surface was determined to be ca. 5.2 – 29 × 10^{-9} mol cm^{-2} by integrating the oxidation current of the CV and applying Faraday's law. Therefore, the poly-**1**-modified electrode can be effectively provided by repetitive cyclic voltammetric scans with a scan rate of more than 100 mV s^{-1} in the solution of 0.01 M monomer **1**.

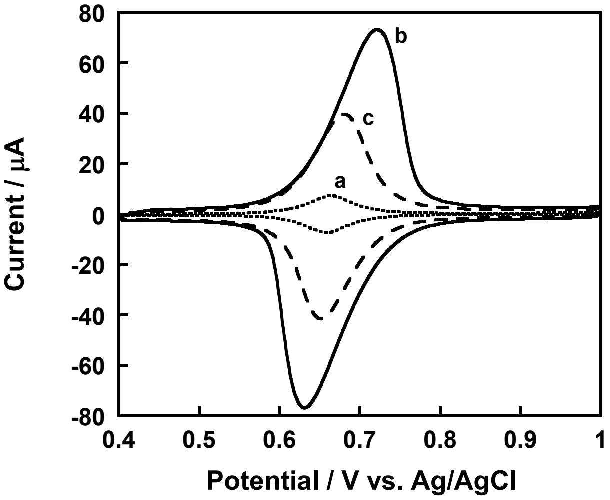


Figure 3. Cyclic voltammograms of the poly-**1**-modified electrodes. Concentration of monomer **1**: (a) 0.001 M, (b) 0.01 M, and (c) 0.1 M

2.2. Electrochemical Polymerization at Constant Potential

Based on the cyclic voltammetry result of monomer **1** (Figure 1), the preparation of the poly-**1**-modified electrode at a constant potential was performed at +1.40 V versus Ag/AgCl. The CVs and characteristics of the poly-**1**-modified electrodes prepared are shown in Figure 4 and Table 2, respectively. The constant potential polymerization was carried out in monomer **1** solution without stirring because poly-**1** did not form on the electrode surface in the stirred solution. The peak current of the CV increased with an increase in the electrolysis time. The poly-**1**-modified electrode obtained by the constant potential electrolysis for 45 s or longer exhibited a wide separation between the oxidation and reduction potentials. This implies that the electron transfer between the electrode and the mediator cannot be carried out smoothly because of a thick poly-**1** layer. On the other hand, the poly-**1**-modified electrode obtained by at 30 s or shorter electrolysis exhibited a reversible redox couple with the one-electron oxidation of the nitroxyl radical to the oxoammonium ion in the CV, suggesting a smooth electron transfer between the electrode and the mediator. A linear relationship between the peak current and the scan rate in the cyclic voltammetry for the poly-**1**-modified electrodes was observed.[8] The amount of electroactive **1** on the electrode surface was determined to be ca. 3.6 – 64 × 10^{-9} mol cm^{-2} by integrating the nitroxyl-radical oxidation current of the CV and applying Faraday's law.

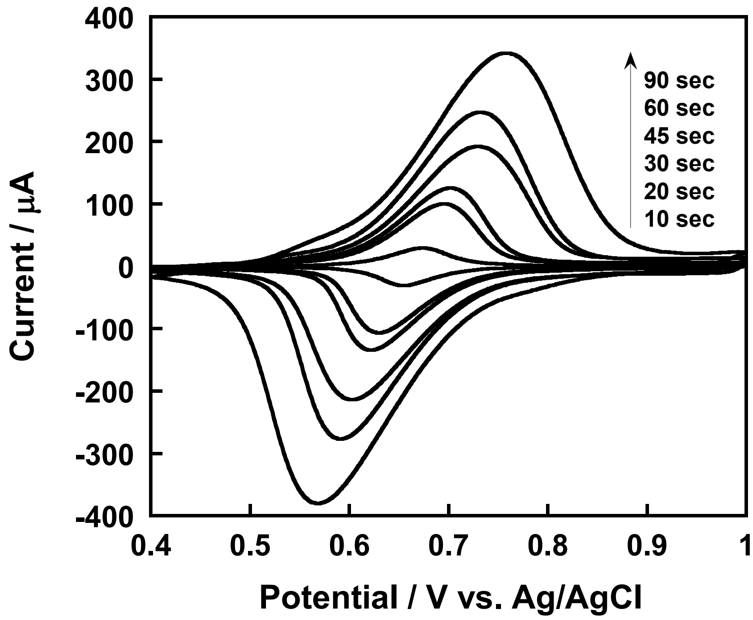
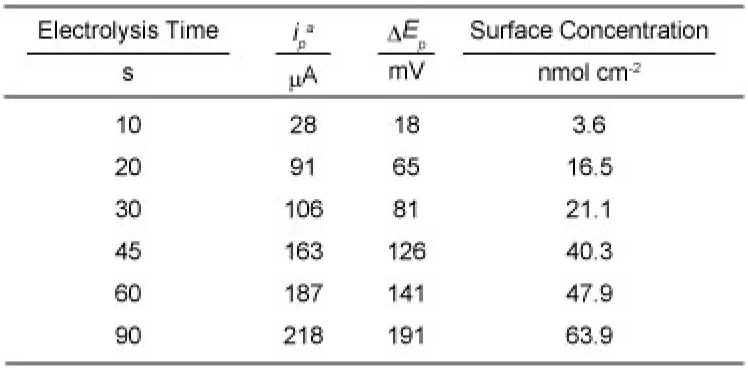


Figure 4. Cyclic voltammograms of the poly-**1**-modified electrode obtained by a constant potential at +1.40 V vs. Ag/AgCl

Table 2. The characteristic features of the poly-**1**-modified electrode prepared by constant potential electrolysis at +1.40 V vs. Ag/AgCl



Electrolysis Time s	i_p^a μA	ΔE_p mV	Surface Concentration nmol cm^{-2}
10	28	18	3.6
20	91	65	16.5
30	106	81	21.1
45	163	126	40.3
60	187	141	47.9
90	218	191	63.9

3. Electrocatalytic Activity for the Oxidation of Geraniol

Cyclic voltammetry was used for checking whether the electron transfer from the immobilized oxoammonium ion of the nitroxyl radical on the electrode surface to dissolved geraniol occurred. The CVs of the poly-**1**-modified electrode in the presence of geraniol and 2,6-lutidine are shown in Figure 5. The anodic peak current for geraniol was significantly enhanced in comparison with the blank voltammogram (the poly-**1**-modified electrode itself), and a small cathodic peak was observed on the reverse scan. The oxidation peak current was proportional to the concentration of geraniol. The ratio of the new oxidation peak's height to the reversible nitroxide oxidation peak height decreased with an increase in the scan rate. This shows that the immobilized nitroxyl radical on the poly-**1**-modified electrode is electrocatalytically active for the oxidation of geraniol because geraniol is not electroactive below +1.0 V versus Ag/AgCl. All these results are characteristic of the electrochemical catalysis of the oxidation of geraniol to geranial via the active oxoammonium ion oxidant (Scheme 4).[9, 10] A linear relationship between the anodic peak current and the concentration of geraniol from 1 to 200 mM was observed (Figure 6). This suggests that the present system may also be applicable to the quantitative analysis of geraniol.

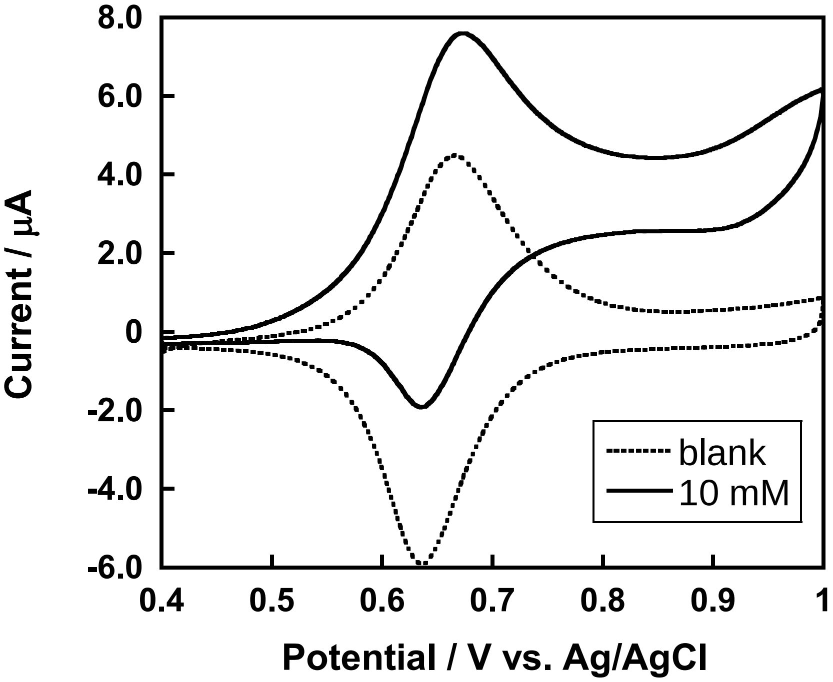


Figure 5. Cyclic voltammograms for poly-**1**-modified electrode in blank (dashed line) and in 10 mM geraniol and 20 mM 2,6-lutidine solution (solid line) at 10 mV s^{-1}

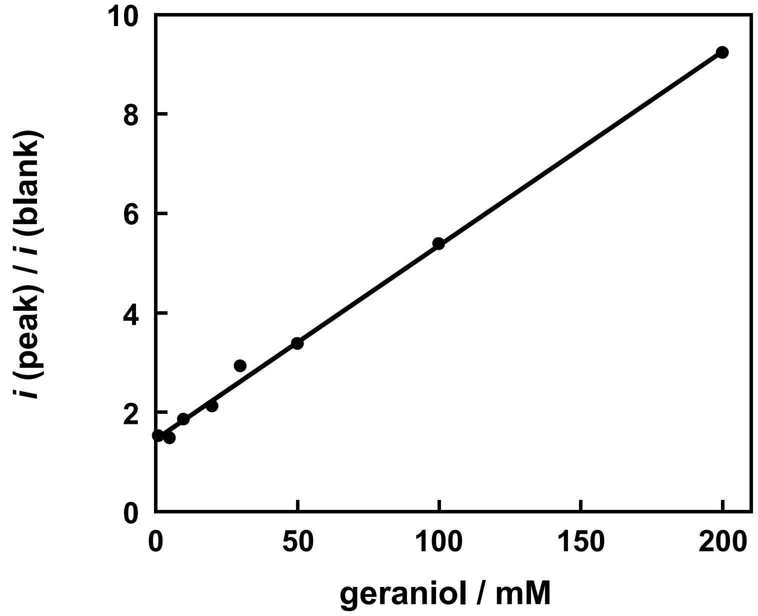
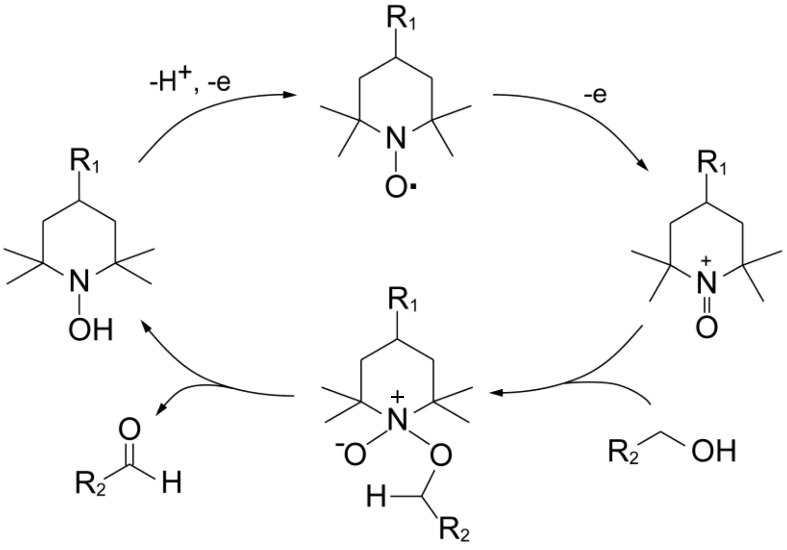


Figure 6. Anodic peak current in cyclic voltammograms of the poly-**1**-modified electrode as a function of the concentration of geraniol. Scan rate: 10 mV s^{-1}



Scheme 4. Mechanism of oxidation of geraniol to geranial with nitroxide

In summary, the nitroxyl-radical-modified electrode prepared by the electrochemical polymerization of the nitroxyl radical precursor containing pyrrole side chain exhibited a symmetrical reversible redox wave in CV. The properties of the immobilized polymers on the electrode surface could be modulated by varying the applied polymerization potential. Furthermore, this modified electrode exhibited electrocatalytic activity for the oxidation of geraniol. We are now studying the electrocatalytic oxidation of alcohols on this modified electrode.

EXPERIMENTAL

1. General Information

1-(3-Hydroxypropyl)pyrrole, 4-carboxy-TEMPO was purchased from Tokyo Chemical Industry Co., Ltd. 4-Dimethylaminopyridine (4-DAP), N,N'-dicyclohexylcarbodiimide (DCC), and tetra-n-butylammonium perchlorate (TBAP) were purchased from Nacalai Tesque, Inc. Acetonitrile (MeCN) was purified by using the method described in the literature.[11] All the other reagents used in this study were of the commercially available reagent grade. The electrochemical polymerization and the cyclic voltammetry characterization were conducted on a BAS ALS/CHi420A and a Nikko Keisoku Model NPGFZ-2501-A potentiogalvanostat, respectively.

2. Synthesis of TEMPO Precursor Containing Pyrrole Side Chain

1-(3-Hydroxypropyl)pyrrole (1.88 g, 15 mmol) and 4-carboxy-TEMPO (3.00 g, 15 mmol) were stirred in 30 mL of AcOEt in the presence of 4-DAP (18 mg, 0.15 mmol) at 0 ℃.[12] DCC (3.51 g, 17 mmol) in 20 mL of AcOEt 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 stirred overnight. The crude product was filtered, and the filtrate was purified using a silica gel column and 4:1 *n*-hexane/AcOEt as eluant. 4-(3-(Pyrrole-1-yl)propoxycarbonyl)-TEMPO (**1**) appeared as orange crystals (3.77 g, 82 % yield).

3. General Procedure for Electrochemical Polymerization

Electrochemical polymerization and characterizations were performed in a one-compartment cell with a platinum disk (0.07 cm^2) as a working electrode and a platinum wire as a counter electrode. A Ag/AgCl (0.1 M $(C_4H_9)_4NClO_4$ (TBAP) in MeCN) electrode was used as the reference electrode. All electrochemical polymerization experiments were performed in the MeCN solution with monomer **1** and 0.1 M TBAP as the supporting electrolyte. Characterizations (by cyclic voltammetry) of the polymer film were conducted in MeCN solutions with 0.1 M TBAP.

4. Electrocatalytic Activity for Oxidation of Alcohol

The electrocatalytic activity of the poly-**1**-modified electrode for the oxidation of geraniol was evaluated in a one-compartment cell with a platinum wire and a Ag/AgCl electrode. The electrolyte was 10 ml of MeCN solution containing geraniol as the substrate, 2,6-lutidine as the base, and 0.1 M TBAP.

ACKNOWLEDGEMENTS

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