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Electrochemical Detection of Alcohols and Carbohydrates at a Glassy Carbon Electrode Coated with a Poly(phenylene oxide) Film Containing Immobilized 2,2,6,6-Tetramethylpiperidinyl-1-oxyl (TEMPO)

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Electrochemical polymerization of 4-(3-hydroxyphenylacetyamino) -2,2,6,6-tetramethylpiperidinyl-1-oxyl (1) as a tool to immobilize 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) to the surface of a glassy carbon (GC) electrode has been examined. Voltammetric studies showed that anodic treatment in H_2O-MeCN (4 : 1) containing 1, $NaHCO_3$, and $NaClO_4$ with cycled or constant potentials provides access to a GC electrode coated with a poly(phenylene oxide) film containing immobilized TEMPO, which functions well as a catalyst for the electrochemical oxidation of alcohols. The TEMPO-modified electrode was applied to flow injection analysis (FIA) of alcohols and carbohydrates with an amperometric mode at a low applied potential. The results of FIAs demonstrated that reproducible and stable responses in the present system are obtained, not for hydrophobic alcohols, but for hydrophilic ones such as carbohydrates, although the former will be detected with a higher sensitivity than the latter. The observed phenomena seem to originate from the interaction of both alcohols and their oxidized products with the hydrophobic poly(phenylene oxide) film on the electrode surface.

Key words electrochemical detection; alcohol; carbohydrate; immobilized 2,2,6,6-tetramethylpiperidinyl-1-oxyl; poly(phenylene oxide) film

Previously, it was demonstrated that flow injection analysis (FIA) of alcohols and carbohydrates is effectively achieved by a simple electrochemical detection system when the carrier solution contains 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO).[1)] The system takes full advantage of the feature of TEMPO as a mediator of the oxidation of alcohols into aldehydes or ketones:[2—6)] the detection of alcohols is realized in terms of the anodic response resulting from the formation of an electrocatalytic cycle including TEMPO in the presence of alcohols (Chart 1). It is of great interest that the electrochemical method permits the detection of carbohydrates at as low a potential as 0.4 V *vs.* saturated calomel electrode (SCE) with a glassy carbon (GC) electrode, since carbohydrates are generally hard to oxidize at common carbon electrodes, leading to low sensitivity and selectivity on electrochemical detection. Namely, the methodology will provide a feasible solution to the problem; several approaches based on different concepts have been explored so far.[7—16)]

For practical application of the methodology to an electrochemical detection system in high-performance liquid chromatography (HPLC), two methods have been envisioned: post-mixing of a TEMPO carrier solution; confinement of TEMPO to an electrode surface. The latter technique will be more advantageous from the viewpoint of simplicity in constructing HPLC systems as well as from an economical standpoint. Thus, our attention has been directed to preparing a TEMPO-modified GC electrode and evaluating its utility in FIA for alcohols and carbohydrates. Immobilization of nitroxide radicals such as TEMPO on electrode surfaces was previously achieved as follows: a film-coating technique with polypyrrole bounded to 3-carboxy-2,2,5,5-tetramethyl-Δ3-pyrroline-1-oxyl (PROXYL-CO_2H),[17)] poly(acrylic acid) modified with 4-amino-TEMPO,[6)] or polysiloxane derivatized with PROXYL-CO_2H[18)]; or a self-assembly technique with thiooctic acid bounded to 4-amino-TEMPO.[19)] Among them, the polysiloxane films containing PROXYL-CO_2H were shown to work as catalytic electrodes even in aqueous solutions, which is preferred for analytical purposes. However, the preparation of such polysiloxanes and coating with the polymers seems rather troublesome. Thus, the electrochemical formation of poly(phenylene oxide) film[20—23)] was chosen as a tool to prepare a TEMPO-modified GC electrode, taking into consideration the stability of a polymer film in aqueous solutions, the feasible regulation of the amount of immobilized TEMPO, and easy access to a monomer bounded to 4-amino-TEMPO. Herein, we describe that FIA for alcohols and carbohydrates can be achieved using a GC electrode coated

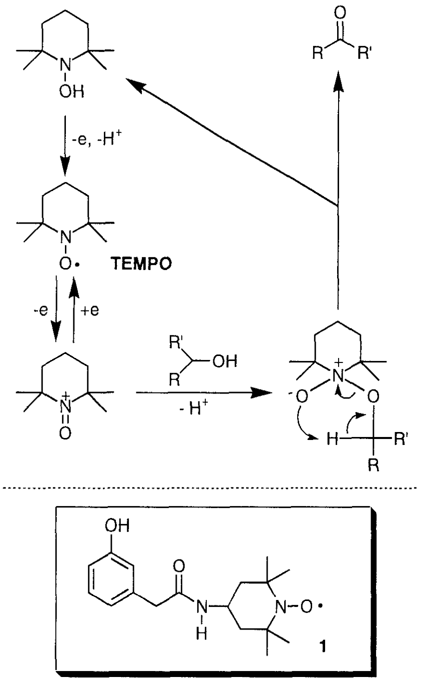

Chart 1

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with the polymer electrochemically formed from **1** (Chart 1) as an electrochemical detector.

Results and Discussion

Figure 1 shows cyclic voltammograms of **1** (1 mM) in H_2O–MeCN (4 : 1) containing 0.1 M $NaClO_4$ at a GC electrode. When the voltammetry was cyclized 5 times, the anodic peak around 1.10 V due to oxidation of the phenolic site in **1** was gradually reduced, while a reversible wave centered at 0.64 V, ascribed to the redox couple including a TEMPO moiety in the monomer, became larger. The rapid decrease in anodic current around 1.10 V is reminiscent of the reported voltammetric behaviors of various phenols to give poly(phenylene oxide) films.[21,23] After being treated with the successive potential sweep and washed with H_2O and MeCN, the GC electrode exhibited a reversible wave centered at 0.63 V on the voltammogram in MeCN containing only 0.1 M $NaClO_4$ (Fig. 2a). The peak separation of the redox wave was 5 mV, where the cathodic and anodic peaks are nearly mirror images of one another. The anodic peak current exhibited a proportionality against a potential sweep rate between 10—100 mV/s. These voltammetric results are consistent with general descriptions of how the success of an immobilization procedure manifests itself in certain electrochemical measurements.[24] Thus, it has been proved that the anodic oxidation of the phenol moiety in **1** at a GC electrode allows the formation of a poly(phenylene oxide) film containing immobilized TEMPO on the electrode surface.

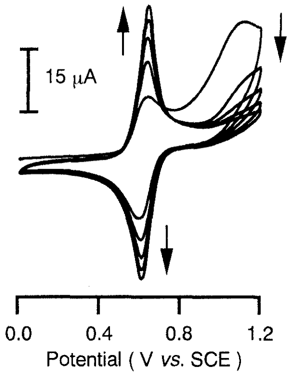

Fig. 1. Voltammograms Cycled 5 Times for **1** (1 mM) in H_2O–MeCN (4 : 1) Containing $NaClO_4$ (0.1 M) at a GC Electrode with a 10 mV/s Potential Sweep Rate

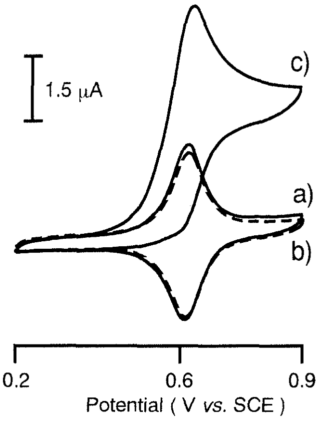

Fig. 2. Cyclic Voltammograms of a TEMPO-Modified GC Electrode in MeCN Containing $NaClO_4$ (0.1 M)

a) a blank solution; b), c) allyl alcohol (10 mM) in the absence (broken line) and presence of 2,6-lutidine (10 mM), respectively: potential sweep rate, 10 mV/s.

The utility of the TEMPO-modified GC electrode for the detection of alcohols coupled with the electrocatalytic oxidation was then examined. The reversible voltammetric wave observed at the modified electrode in MeCN was little affected by the addition of allyl alcohol, as shown in Fig. 2b. However, the catalytic oxidation of the alcohol at the modified GC electrode was induced by the addition of 2,6-lutidine (Fig. 2c): the oxidation current was enhanced more than twice, and the cathodic wave disappeared. The observed behavior is closely in line with the generally accepted mechanism for the catalytic oxidation of alcohols (Chart 1), where the presence of a base is essential. The results also indicate that the poly(phenylene oxide) film on the TEMPO-modified GC electrode offers sufficient permeability for alcohols to enter the catalytic process. Although the results are not described, the voltammetric behaviors of TEMPO-modified GC electrodes obtained under various conditions were also examined in the absence and presence of allyl alcohol and the base. Comparison of the results indicated that the electrochemical polymerization of **1** is most effectively achieved in an aqueous solution containing $NaHCO_3$ and 20% MeCN as a cosolvent, affording a TEMPO-modified GC electrode with the best performance as a catalytic electrode, namely, with the following voltammetric features: immobilized TEMPO exhibits a redox wave with the best reversibility and the largest response in the absence of any additives; the addition of allyl alcohol and 2,6-lutidine induces the largest incremental change in the anodic response of immobilized TEMPO; thus, the largest catalytic current available for detecting alcohol is realized. Accordingly, a solution of **1**, $NaHCO_3$, and $NaClO_4$ in H_2O–MeCN (4 : 1) was employed for the electrochemical polymer-coating of the GC surfaces for further examination.

A GC plate required in the FIA of alcohols was modified by controlled potential electrolysis at 0.8 V *vs.* SCE in the monomer solution, where the amount of immobilized TEMPO (Γ_{TEMPO}, mol/cm^2) was controlled coulometrically. After electrolysis, the treated plate was subjected to the voltammetry in MeCN containing only $NaClO_4$ in order to confirm the confinement of TEMPO and to estimate Γ_{TEMPO} from the charge of the oxidation peak.[24] To establish the best conditions for the FIA of alcohols using the TEMPO-modified GC electrode, the effects of the applied potential (E_{ap}) and Γ_{TEMPO} were examined. The evaluation was performed by comparing the peak currents (I_{p}) for allyl alcohol, and the ratio between I_{p} and background current (I_{bg}) under the following conditions: carrier solution, aqueous solution of $NaHCO_3$ (10 mM) and NaCl (0.1 M); flow rate, 0.5 ml/min; injection volume, 20 μl. Representative FIA responses for the alcohol are illustrated in Fig. 3.

As summarized in Table 1, the FIA responses were obtained at potentials higher than 0.4 V (runs 1—3), and a more positive E_{ap} induced a larger I_{p} for the alcohol. However, the FIA responses at 0.7 or 0.8 V suffered from

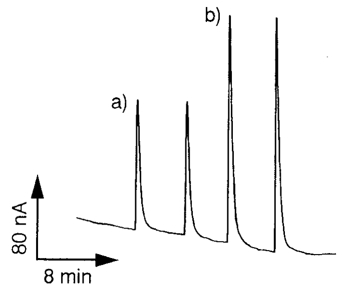

Fig. 3. Typical FIA Responses for a) 0.5 mM and b) 1.0 mM Allyl Alcohol

Flow conditions: immobilized TEMPO, $\Gamma_{\mathrm{TEMPO}}=9.2\times10^{-9}$ mol/cm^2; carrier solution, aqueous solution of $NaHCO_3$ (10 mM) and NaCl (0.1 M); applied potential, 0.6 V *vs.* SCE; flow rate, 0.5 ml/min; injection volume, 20 μl.

Table 1. The Effect of the Applied Potential (E_{ap}) in FIA for Allyl Alcohol (1 mM) Using a TEMPO-Modified GC Electrode upon Peak and Background Currents (I_p, I_{bg})[a]

Run	E_{ap} (V *vs.* SCE)	I_p (nA)(RSD, %)[b]	I_p/I_{bg}
1	0.2	0	0
2	0.3	0	0
3	0.4	14 (5.7)	0.56
4	0.5	70 (3.1)	0.97
5	0.6	223 (2.7)	1.24
6	0.7	444 (6.2)	0.91
7	0.8	460 (14.2)	0.90

a) FIA conditions are the same in Fig. 3 except for E_{ap}. *b)* Relative standard deviation ($n=3$).

Table 2. The Effects of the Amount of Immobilized TEMPO (Γ_{TEMPO}) and the Supporting Electrolyte in the Mobile Phase in FIA for Allyl Alcohol (1 mM) with TEMPO-Modified GC upon Peak and Background Currents (I_p, I_{bg})[a]

Run	Supporting electrolyte	Γ_{TEMPO} (10^{-9} mol/cm^2)	I_p (nA)	I_p/I_{bg}
1	$NaHCO_3$ (10 mM) + NaCl (0.1 M)	0	0	0
2	$NaHCO_3$ (10 mM) + NaCl (0.1 M)	4.7[b]	231	0.29
3	$NaHCO_3$ (10 mM) + NaCl (0.1 M)	9.0[c]	266	1.11
4	$NaHCO_3$ (10 mM) + NaCl (0.1 M)	11.9[d]	256	0.98
5	$NaHCO_3$ (10 mM) + NaCl (0.1 M)	13.0[e]	238	0.88
6	$NaHCO_3$ (10 mM) + NaCl (0.1 M)	13.9[f]	226	0.78
7	NaCl (0.1 M)	8.8[c]	53	0.41
8	$NaHCO_3$ (10 mM)	9.0[c]	42	0.26
9	$NaHCO_3$ (1 mM) + NaCl (0.1 M)	9.2[c]	140	0.52
10	$NaHCO_3$ (0.1 M) + NaCl (0.1 M)	9.2[c]	265	0.80
11	NaOH (10 mM) + NaCl (0.1 M)	9.2[c]	42	0.14

a) FIA conditions are the same as in Fig. 3 except for Γ_{TEMPO}. *b—f)* TEMPO was immobilized electrochemically by passing electricity of 20, 50, 60, 70, and 100 mC, respectively; for details, see Text.

low reproducibility as well as substantially large I_{bg}, as shown by the values of relative standard deviation (RSD) and I_p/I_{bg} in runs 6 and 7. Thus, 0.6 V seemed to be the applied potential of choice for the present FIA. As for the influence of Γ_{TEMPO}, the electricity consumption allowed in the electrochemical film-formation was not proportional to the number of active catalytic sites on the surface, that is, the sensitivity of the FIA responses for allyl alcohol (runs 2—6 in Table 2). This observation can be ascribed to the thickness of the polymer film containing immobilized TEMPO, which was not determined in this work, and yet, is believed to be in good proportion to the amount of electricity consumption in the electrochemical modification. The ionic conductivity of the thicker film will be lower, probably due to insufficient penetration of supporting electrolytes to the film. This will prevent a potential applied to a TEMPO-modified electrode from developing a potential gradient sufficient to allow an effective electron transfer between the electrode and all TEMPO sites in the polymer film. Thus, some of the immobilized TEMPO on the modified electrodes prepared at the expense of a large amount of electricity consumption, such as in runs 5 and 6, might be foreign to the electrochemical catalytic oxidation of allyl alcohol, which is expressed as the FIA peak. Based on the results, the electrochemical polymerization of **1** at the expense of 50 mC was likely to immobilize the catalyst on a GC electrode in the highest current and chemical yields, providing a modified electrode with the best electrochemical performance suitable for analytical purposes. No FIA response under the above conditions was obtained for allyl alcohol unless a GC electrode was electrochemically treated in the monomer solution (run 1). The results in runs 3 and 7—11 in Table 2 compare with the effects of the supporting electrolyte in a carrier solution. As can be expected, $NaHCO_3$ was essential in realizing the detection of allyl alcohol in a highly sensitive manner: I_p obtained without $NaHCO_3$ decreased to about 20% of that with the base (runs 3, 7). The FIA with a carrier solution containing only $NaHCO_3$ (10 mM) resulted in a large decrease in I_p (run 8), indicating that NaCl (0.1 M) as a supporting electrolyte is also essential to the present system. Among the media containing the base of 1, 10, and 100 mM, the highest I_p and I_p/I_{bg} were observed on employing the second (runs 3, 9, 10). Replacement of $NaHCO_3$ by NaOH induced a large loss in the FIA response (run 11). This observation would be explained by a deactivation of the immobilized TEMPO in the presence of NaOH, probably due to a base-induced degradation of the anodically generated nitrosonium ion.[2] It is noteworthy that Γ_{TEMPO} was satisfactorily reproducible as far as the electricity in the electrolysis was controlled in forming the polymer film (runs 3, 7—11).

Based on the results described so far, the relationship between the FIA responses and the concentration of allyl alcohol or glucose was examined under the following conditions: electricity in the electrochemical immobilization of TEMPO, 50 mC; applied potential, 0.6 V *vs.* SCE; carrier solution, aqueous solution of $NaHCO_3$ (10 mM) and NaCl (0.1 M); flow rate, 0.5 ml/min; injection volume, 20 μl. The response correlated linearly with a concentration of allyl alcohol from 0.1 to 1.0 mM (slope and correlation coefficient, 180.4 mA/M and 0.999), as shown in Fig. 4. A similar correlation line was obtained for glucose (slope and correlation coefficient, 31.5 mA/M and 0.982), yet the sensitivity for the carbohydrate was much lower than that for allyl alcohol.

The present FIA was also applied for the detection of various types of alcohols. The dependency of the FIA responses upon the structure of alcohols is listed in Table 3, where the response obtained for each alcohol was normalized against that for allyl alcohol. Comparison of

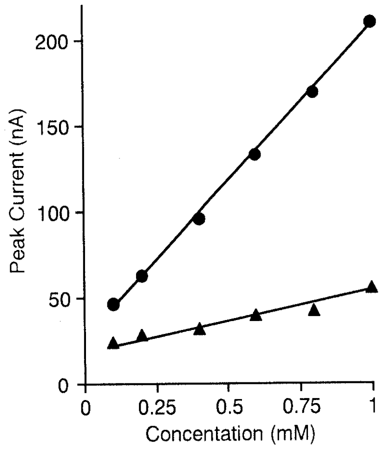

Fig. 4. Calibration Curves Obtained by FIA for Allyl Alcohol (Circles) and Glucose (Triangles) at a TEMPO-Modified GC Electrode

Flow conditions are the same as in Fig. 3.

Table 3. Responses for Various Alcohols (1 mM) in FIA with a TEMPO-Modified GC Electrode[a)]

Run	Alcohol	Relative response[b)]	Run	Alcohol	Relative response[b)]
1	Allyl alcohol	1.00	11	Diethylene glycol	0.33
2	1-Propanol	0.35	12	Triethylene glycol	0.31
3	1-Butanol	0.64	13	Tetraethylene glycol	0.30
4	1-Pentanol	0.97	14	Glucose	0.24
5	1-Hexanol	1.69	15	Galactose	0.28
6	Ethylene glycol	0.35	16	Rhamnose	0.19
7	1,3-Propanediol	0.32	17	Mannose	0.20
8	1,4-Butanediol	0.53	18	Arabinose	0.21
9	1,5-Pentanediol	0.50	19	Xylose	0.24
10	1,6-Hexanediol	0.63	20	Fructose	0.15

a) FIA conditions are the same as in Fig. 3. *b)* Against the FIA response for allyl alcohol.

the results for 1-alkanols and 1,ω-alkanediols (runs 2—5, 6—10) has suggested that the longer the alkyl chain of an alcohol, the higher the response attained in the FIA with the TEMPO-modified GC electrode. In other words, the hydrophobicity of alcohols will be a determinant of the sensitivity in the present detection system. In fact, high hydrophilicity of $HO(CH_2CH_2O)_nH$ ($n=2$—4) and carbohydrates seems to be responsible for the relatively low responses (runs 11—20). The dependence of the FIA responses upon the hydrophobicity of alcohols can be explained as follows: the poly(phenylene oxide) film formed from **1** is expected to be hydrophobic, permitting hydrophobic alcohols to permeate into the film and to encounter the oxidized form of immobilized TEMPO more effectively than hydrophilic alcohols.

The present method is likely to give reproducible and stable FIA responses not for hydrophobic alcohols but for hydrophilic ones, as demonstrated by the results obtained when a sample solution of 1-pentanol or glucose was successively injected 30 times (Fig. 5). For 1-pentanol, the FIA response observed at injection number 30 was 78% of that for the first injection: reproducible signals were afforded only for the first 10 injections, the RSD being 2.0%; thereafter, the peak current gradually decreased injection by injection (0.92 nA/injection). On the other hand, glucose was detected in a highly reproducible manner (RSD, 2.0%). The gradual electrode passivation observed on the detection of 1-pentanol can be attributed to the adsorption of the oxidation product, probably pentanal, through its hydrophobic interaction with the poly(phenylene oxide) film.

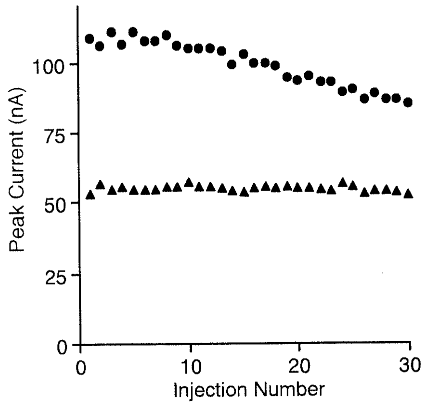

Fig. 5. FIA Responses for 30 Injections of 1-Pentanol (Circles) and Glucose (Triangles)(each 1 mM) at a TEMPO-Modified GC Electrode

Flow conditions are the same as in Fig. 3.

The results described so far demonstrate that TEMPO, immobilized on the surface of a GC electrode through the anodic formation of a poly(phenylene oxide) film, functions well as a catalyst for the electrochemical oxidation of alcohols, and this characteristic provides a useful approach to the electrochemical detection of hydrophilic alcohols such as carbohydrates by a FIA under aqueous basic conditions, where the modified electrode carries good physical and electrochemical stability. The observation allows the expectation that the present methodology will find a practical application to HPLC with an amperometric mode at a satisfactory low potential, although the sensitivity in the detection of hydrophilic alcohols should be improved and the problem of electrode fouling in the case of hydrophobic alcohols remains to be solved. These requirements will be satisfied by the judicious molecular-design of a TEMPO-bound phenol monomer so that its electrochemical polymerization might bring about the formation of a less hydrophobic film on a GC electrode. Further studies on these points are under way.

Experimental

Deionized and distilled water was used throughout the present study. MeCN was distilled from P_2O_5. All other chemicals were of reagent grade and were used without further purification. Infrared (IR) spectra were taken on a JASCO VALOR-III spectrometer. Mass spectra (MS) were recorded at 70 eV with a direct inlet system on a JEOL JMS-HX100 spectrometer. Cyclic voltammograms were recorded with a potentiostat (Huso, Model 315A) equipped with an X-Y recorder (Riken Denshi, Model F-5C) or with a computer controlled electroanalysis system (Cypress Systems, Inc., Model CS-1090). A three-electrode configuration was employed: a bare or modified GC electrode as the working electrode, an SCE as the reference electrode, and a platinum wire electrode as the counter electrode. All voltammetric measurements were carried out at room temperature. A potentiostat/galvanostat (Hokuto Denko, Model HA 301) connected to a coulomb/amperehour meter (Hokuto Denko, Model HF201) was used for modification by electrolysis.

4-(3-Hydroxyphenylacetylamino)-2,2,6,6-tetramethyl piperidinyl-1-oxyl (1) This compound was prepared by the coupling of 4-amino-TEMPO and 3-hydroxyphenylacetic acid in the presence of dicyclohexylcarbodiimide (DCC) according to the known procedure.[25] IR (KBr): 3282, 2977, 2940, 1645 cm^{-1}. MS: *m/z* 305 (M^+). *Anal.* Calcd for $C_{17}H_{25}N_2O_3$: C, 66.86; H, 8.25; N, 9.17. Found: C, 66.60; H, 8.27; N, 8.96.

Electrode Modification For a GC disk electrode: GC disks (GC 30, 3 mm i.d.) were obtained from Tokai Carbon and fabricated as previously described.[26] Before the modification, a GC electrode was polished mechanically by a polishing system (Maruto, ML-150P) with a polishing paper (♯1200) followed by alumina powder (0.05 μm) on a polishing cloth, sonicated in deionized water, MeOH, and $CHCl_3$ for 5 min each, then dried with a stream of nitrogen. The cleaned electrode was subjected to cyclic voltammetry in H_2O–MeCN (4 : 1) containing **1** (1 mM) and $NaClO_4$ (0.1 M), where a potential sweep between 0—1.2 V *vs.* SCE was repeated 5 times at 0.1 V/s and room temperature. After the treatment, the electrode was thoroughly washed with water and MeCN, and was subjected to the voltammetry in MeCN containing only $NaClO_4$ (0.1M) at 10 mV/s between 0.2 and 0.9 V *vs.* SCE, in order to determine Γ_{TEMPO} from the charge of an observed anodic peak and the geometric area of the GC electrode. For a GC plate electrode: GC plates (GC30, 15 × 30 × 3 mm) were obtained from Tokai Carbon and were polished and cleaned by the procedure described above. Using an undivided cell equipped with the GC plate, a Pt foil, and an SCE as an anode, a cathode, and a reference electrode, respectively, controlled-potential electrolysis was carried out in H_2O–MeCN (4 : 1) containing **1** (1 mM), $NaHCO_3$ (10 mM), and $NaClO_4$ (0.1 M) at 0.8 V, where 50 mC of electricity had been allowed to be consumed. The back and sides of the modified electrode were wiped with $CHCl_3$ to remove the polymer from these planes: the front of the modified electrode is considered as the plane facing a counter electrode during the electrolysis for the modification. The modified electrode was further washed with water and MeCN, and was subjected to the procedure for estimating Γ_{TEMPO} before being placed in the electrochemical cell.

FIA All measurements were performed at room temperature with an FIA system consisting of a plunger pump (Shimadzu, LC-5A), an injector with a 20 μl sample loop (Shimadzu, SIL-1A), a high-sensitivity potentiostat equipped with a low-pass filter (Huso, HECS 318 and 974), a thin-layer electrochemical cell (a flow cell from a Shimadzu L-ECD-6A electrochemical detector), and a recorder (Rikadenki, R-50). The reference electrode was an SCE. All sample solutions were prepared from a carrier solution.

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