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Electrooxidation of Alcohols in an *N*-Oxyl-Immobilized Poly(ethylene-*co*-acrylic acid)/Water Disperse System

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The electrooxidation of alcohols in a disperse system with *N*-oxyl-immobilized polymer particles (**PE-*co*-AA-*N*-Oxyl**), prepared from poly(ethylene-*co*-acrylic acid) (**PE-*co*-AA-CO$_2$H**), as a disperse phase and an aqueous saturated NaHCO$_3$ containing 20 wt % NaBr as a disperse medium was successfully performed in a simple beaker-type undivided cell under constant-current conditions. The electrooxidation of alcohols proceeded in a similar manner by the use of **PE-*co*-AA-CO$_2$H** as a disperse phase, though the current efficiency decreased in some extent. Protection of most of the carboxylic acid moieties on the surface of **PE-*co*-AA-CO$_2$H** by esterification or amidation resulted in significant decrease of the product yields, suggesting that the carboxylic acid moieties on the surface of **PE-*co*-AA-CO$_2$H** would also act as a mediator for the electrooxidation of alcohols. Both the recovered **PE-*co*-AA-*N*-Oxyl** and the aqueous solution were used repeatedly for the electrooxidation of alcohols, thereby offering a formally closed system for the electrooxidation of alcohols.

The oxidation of alcohols into the corresponding carbonyl compounds is one of the most important organic transformations.[1] Many metallic oxidants as well as non-metallic oxidants have been developed. These oxidants are, however, used stoichiometrically or more, and the environmental stress derived from these oxidants could be no longer negligible. A catalytic methodology should be developed.

The electrooxidation of alcohols mediated with *N*-oxyl compounds has been intensively investigated as a prominent catalytic protocol. Historically, the electrooxidation of alcohols was first carried out in an organic solvent, such as acetonitrile or dichloromethane, containing a rather high concentration of the supporting electrolytes under a regulated potential in a divided cell.[2] These processes are, however, not satisfactory in terms of operational simplicity, manufacturing cost, and environmental stress.

Torii developed the electrooxidation of alcohols in an organic/aqueous two-phase system, e.g., CH$_2$Cl$_2$/H$_2$O, in which two-redox couples (*N*-oxyl/*N*-oxoammonium and Br$^-$/Br$^+$) work as mediators.[3] Electrolysis was carried out under a constant-current condition in a beaker-type undivided cell, and hence the operation became remarkably simple. However, there still remained serious problems in terms of environmental stress arising from the use of harmful organic solvents, such as dichloromethane.

One of the most promising accesses to the reduction of the environmental stress must be electrooxidation in water free from any organic solvents. Recently, organic reactions in water have received much attention, since water is cheap, safe, not flammable, environmentally benign, and easy to handle.[4] Many organic compounds are, however, poorly soluble in water, hence, we need some proper devices for the reaction of such water-insoluble compounds in water. We developed a silica-gel disperse water system, in which organic substrates and *N*-oxyl are adsorbed on silica-gel particles (ϕ 46–200 μm), and the silica-gel particles are dispersed in an aqueous disperse medium (20 wt % NaBr–Sat. NaHCO$_3$). In this system, *N*-oxyl, the starting materials, and the products are adsorbed on the silica-gel during the electrolysis because of the hydrophobic effect. The electrooxidation of alcohols proceeded smoothly to give the corresponding carbonyl compounds in good yields. One drawback of this system is, however, that the *N*-oxyl was excluded from the reaction system during the work-up process, and was contained in the products as a contaminant.

The immobilization of reagents and/or catalysts on solid supports is one of the keen projects in modern organic synthesis.[5] Solid-supported reagents and catalysts offer many advantages over their solution-phase counterparts, including ease of separation from the product mixture, minimizing of the waste-disposal problem, and the recycled use of the reagents and catalysts.[6] In the last decade, many solid-supported reagents and catalysts have been developed for the oxidation of alcohols.[7] For example, *N*-oxyl-immobilized polymer particles[8–11] and silica-gel[12] were prepared and applied as an oxidation catalyst. In this connection, we have developed the electrooxidation of alcohols in a disperse system with *N*-oxyl-immobilized polyethylene particles as a disperse phase and an aqueous saturated NaHCO$_3$ solution containing 20 wt % NaBr as a disperse medium.[13] It is interesting to note that both the *N*-oxyl-immobilized disperse phase and the aqueous disperse media could be recovered and used repeatedly. Consequently, all chemicals were used repeatedly for the electrooxidation of alcohols, thereby offering a totally closed system. In our continuing studies on the electrooxidation of alcohols in *N*-oxyl-immobilized polymer particles/water disperse systems, we found that *N*-oxyl-immobilized poly(ethylene-*co*-acrylic acid) particles could be successfully used as a disperse phase for the electro-

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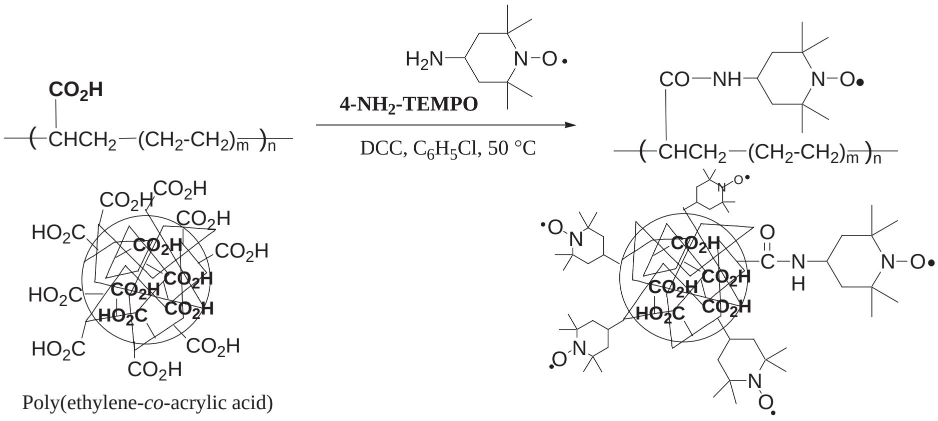


Poly(ethylene-*co*-acrylic acid)
5 wt% acrylic acid
(PE-*co*-AA-CO$_2$H)

PE-*co*-AA-*N*-Oxyl
(1a ~ 1f)

Scheme 1. Preparation of *N*-oxyl-immobilized poly(ethylene-*co*-acrylic acid).

oxidation of alcohols in water. A further investigation on the disperse electrolysis system let us consider that the carboxylic acid moieties on the polymer surface could also play a significant role in the electrooxidation of alcohols. Herein, we describe the electrooxidation of alcohols with *N*-oxyl-immobilized poly(ethylene-*co*-acrylic acid) as a disperse phase and an aqueous $NaHCO_3$ containing NaBr as a disperse medium. The role of carboxylic acid moieties on the polymer particles is also considered.

Results and Discussion

Preparation of *N*-Oxyl-Immobilized Poly(ethylene-*co*-acrylic acid). *N*-Oxyl-immobilized poly(ethylene-*co*-acrylic acid) particles **PE-*co*-AA-*N*-Oxyl** were prepared by the treatment of poly(ethylene-*co*-acrylic acid) **PE-*co*-AA-CO$_2$H** (5 g, containing 5 wt % acrylic acid) with 4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl **4-NH$_2$-TEMPO** (1.5×10^{-3}–4.0 mmol) in chlorobenzene in the presence of dicyclohexylcarbodiimide (DCC) at 50 °C for 2 d. The polymer particles were separated by filtration and washed successively with chlorobenzene, water, methanol, and ether. The solids were dried under reduced pressure to afford **PE-*co*-AA-*N*-Oxyl 1a–1f** (Scheme 1). The conditions and results are summarized in Table 1.

Table 1. Preparation of *N*-Oxyl-Immobilized Poly(ethylene-*co*-acrylic acid)[a)]

Entry	4-NH$_2$-TEMPO /mg	(mmol)	DCC /mg	(mmol)	Polymer particles
1	688	(4.0)	1033	(5.0)	**1a**
2	298	(1.7)	414	(2.0)	**1b**
3	37.0	(2.2×10^{-1})	51.2	(2.2×10^{-1})	**1c**
4	12.5	(7.3×10^{-2})	20.6	(1.0×10^{-2})	**1d**
5	2.50	(1.5×10^{-2})	4.10	(2.0×10^{-2})	**1e**
6	0.26	(1.5×10^{-3})	0.40	(2.0×10^{-3})	**1f**

a) Carried out by treatment with PE-*co*-AA-CO$_2$H (5.0 g) and 4-NH$_2$-TEMPO in chlorobenzene (20 mL) in the presence of DCC at 50 °C for 2 d.

In the IR spectra of **PE-*co*-AA-*N*-Oxyl 1a**, the absorption band at 1701 cm^{-1}, referred to as the carboxylic acid groups of **PE-*co*-AA-CO$_2$H**, decreased, and new absorption bands at 1653 and 1540 cm^{-1}, ascribed to the amide groups, appeared. Furthermore, a remarkable color change of the polymer particles from white to orange was observed. These results showed that the *N*-oxyl moieties were immobilized on the polymer surface. Notably, the adsorption band due to the carboxylic acid moiety still remained, even upon a treatment with an excess amount of **4-NH$_2$-TEMPO** (Entry 1).

Electrooxidation of Alcohol 2a in an *N*-Oxyl-Immobilized Poly(ethylene-*co*-acrylic acid)/Water Disperse System. Next, the electrooxidation of alcohols was investigated by the use of **PE-*co*-AA-*N*-Oxyl** as a disperse phase and aqueous saturated $NaHCO_3$ containing 20 wt % NaBr as a disperse medium. A typical procedure is as follows: a mixture of **PE-*co*-AA-*N*-Oxyl 1a** (500 mg) and 1-(4-chlorophenyl)ethanol (**2a**, 0.70 mmol) in an aqueous saturated $NaHCO_3$ containing 20 wt % NaBr (6 mL) was placed in a beaker-type undivided cell. After stirring for 5 min, two platinum electrodes (1.0×1.5 cm^2) were immersed into the mixture, and a constant current conditions (20 mA/cm^2, 1.56 h, 2.5 F/mol) was supplied at 0 °C under vigorous stirring. The work-up process was quite simple; thus, **PE-*co*-AA-*N*-Oxyl 1a** were separated by filtration and washed with EtOAc. The filtrates were extracted three times with EtOAc, and the extracts were combined with the washings. A GC analysis of the organic solution showed the formation of *p*-chloroacetophenone (**3a**) in 93% yield. Evaporation of the solvent, followed by short-path column chromatography (SiO_2, Hexane/EtOAc; 5/1), afforded **3a** in 87% yield (Table 2, Entry 1).

The presence of NaBr in the disperse medium was indispensable. When NaCl was used in the place of NaBr, only a small amount of ketone **3a** was obtained (Table 2, Entry 2). Sodium iodide was not effective at all (Entry 3). The electrooxidation of **2a** hardly occurred in the absence of the halide salts (Entry 4).

In a similar manner, the electrooxidation of alcohol **2a** using **PE-*co*-AA-*N*-Oxyl 1b–1f** with different amounts of the immobilized *N*-oxyl moieties was carried out (Table 3). Excellent yields of **3a** (>90%) were obtained when the electrolysis was carried out with **PE-*co*-AA-*N*-Oxyl** containing $\geqq 0.2$ mol % of *N*-oxyl moieties (**1a–1e**) (Entries 1–5). A slight decrease in yield to 82% was observed when the **PE-*co*-AA-*N*-**

Table 2. Electrooxidation of Alcohol **2a** with or without Halide Salts[a)]

Entry	NaX	**3a** Yield/%[b)]	**2a** Recov./%[b)]
1	NaBr	93 (87)[c)]	2 (2)[c)]
2	NaCl	12	77
3	NaI	—	94
4	—	3	89

a) Electrooxidation of **2a** (0.70 mmol) in a disperse system (**PE-*co*-AA-*N*-Oxyl 1a** (500 mg)/an aqueous saturated $NaHCO_3$ containing 20 wt% NaX (6 mL)) was carried out under a constant current conditions (20 mA/cm^2, 2.5 F/mol) in an undivided cell at 0 °C. b) Determined by GC analysis with acetophenone as an internal standard. c) Isolated yield in the parenthesis.

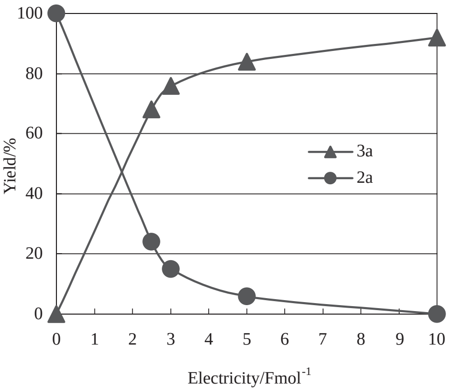
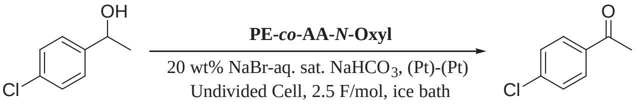


Fig. 1. Time course of the electrooxidation of alcohol **2a** with **PE-*co*-AA-CO_2H**.

Table 3. Electrooxidation of Alcohol **2a** with Different Amount of *N*-Oxyl[a)]



2a (0.70 mmol) **3a**

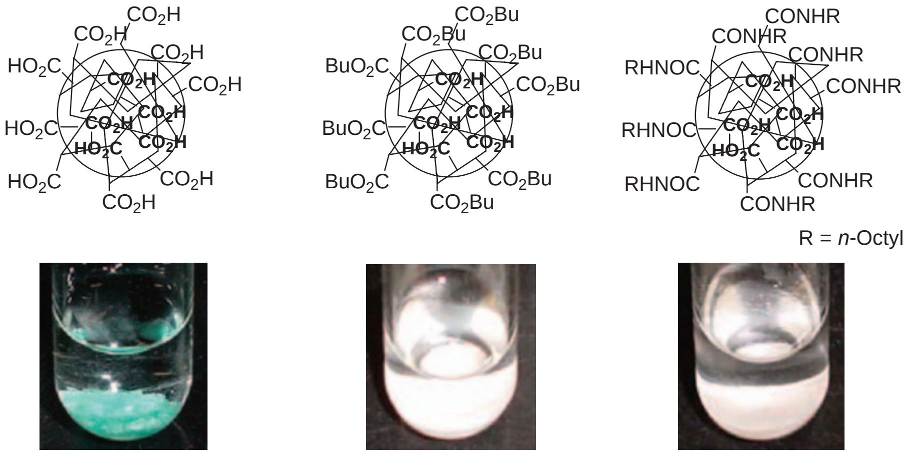
Entry	**PE-*co*-AA-*N*-Oxyl**	Amount of 4-NH_2-TEMPO[b)]	mol % vs **2a**[c)]	**3a** Yield/%[d)]	**2a** Recov./%[d)]
1	**1a**	>1	>50	94	—
2	**1b**	1/2	24	93	—
3	**1c**	1/16	3	90	3
4	**1d**	1/48	1	93	—
5	**1e**	1/240	0.2	90	—
6	**1f**	1/2400	0.02	82	8
7	**PE-*co*-AA-CO_2H**	0	—	68	24

a) Electrooxidation of **2a** (0.70 mmol) in a disperse system (**PE-*co*-AA-*N*-Oxyl** (500 mg)/an aqueous saturated $NaHCO_3$ containing 20 wt% NaBr (6 mL)) was carried out under a constant current conditions (20 mA/cm^2, 2.5 F/mol) in an undivided cell at 0 °C. b) Molar ratio of 4-NH_2-TEMPO used for the preparation of **PE-*co*-AA-*N*-Oxyl** vs the total carboxylic acid groups on **PE-*co*-AA-CO_2H**. c) mol % of *N*-oxyl moieties on the polymer surface against alcohol **2a**. d) The yields were determined by GC analysis with acetophenone as an internal standard.

Oxyl 1f (0.02 mol %) was used (Entry 6). It is of interest to note that the electrooxidation of **2a** proceeded to afford a moderate yield of **3a** (68%), even with **PE-*co*-AA-CO_2H**, which did not have the *N*-oxyl moieties (Entry 7). The time course of the electrooxidation of alcohol **2a** using **PE-*co*-AA-CO_2H** is illustrated in Fig. 1. An increase of the electricity to 5 and 10 F/mol resulted in increases of the yields of **3a** to 84 and 92%.

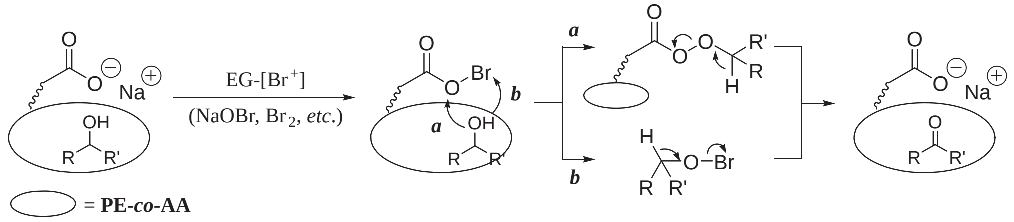
To obtain greater insight of the interface between the polymer particles and the aqueous solution, the carboxylic acid moieties on the surface of the polymer particles were protected by esterification and amidation, and the electrooxidation of alcohol **2a** was carried out with these protected polymer particles. **PE-*co*-AA-CO_2H** particles were treated with 1-butanol and with octylamine in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide in chlorobenzene at 80 °C for 4 d to afford the corresponding ester **PE-*co*-AA-CO_2-*n*-Bu** and amide **PE-*co*-AA-CONH-*n*-Octyl**, respectively. IR spectra of each of the protected polymer particles showed the characteristic absorption bands due to the ester and amide at 1736 and 1635 cm^{-1}, respectively. In both cases, however, the absorption bands due to the carboxylic acid moieties were also observed at 1701 and 1704 cm^{-1}. The presence of the carboxylic acid moieties on the surface of **PE-*co*-AA-CO_2H** was confirmed by a malachite green test.[14] Thus, to **PE-*co*-AA-CO_2H** particles placed in a test tube were added an ethanol solution of malachite green (0.072 M, 2 mL) and a single drop of Et_3N. After standing for 1 h at room temperature, the ethanol solution was discarded and the polymer particles were washed several times with methanol until the solution remained clear. The results are shown in Fig. 2. **PE-*co*-AA-CO_2H** particles showed green color after a treatment with malachite green (Fig. 2a). On the other hand, the protected polymer particles, **PE-*co*-AA-CO_2-*n*-Bu** and **PE-*co*-AA-CONH-*n*-Octyl**, did not show any color change after a treatment with malachite green in a similar manner (Figs. 2b and c), indicating that the carboxylic acid moieties on the surface of the protected polymer particles were almost completely protected.

The electrooxidation of alcohol **2a** was carried out with the protected polymer particles as a disperse phase to assay the



(a) (b) (c)

Fig. 2. Results of the malachite green color test; (a) **PE-*co*-AA-CO_2H**, (b) **PE-*co*-AA-CO_2-*n*-Bu**, and (c) **PE-*co*-AA-CONH-*n*-Octyl**.



Scheme 2. A plausible mechanism of the carboxylate ion-mediated electrooxidation of alcohol.

Table 4. Effect of Carboxylic Acid Moieties on the **PE-*co*-AA** Surface[a)]

Entry	Polymer particles	**3a** Yield/%[b)]	**2a** Recov./%[b)]
1	**PE-*co*-AA-*N*-Oxyl**	93	2
2	**PE-*co*-AA-CO_2H**	68	24
3	**PE-*co*-AA-CO_2-*n*-Bu**	24	64
4	**PE-*co*-AA-CONH-*n*-Octyl**	4	85

a) Electrooxidation of **2a** (0.70 mmol) in a disperse system (polymer particles (500 mg)/20 wt % NaBr–aq. sat. $NaHCO_3$ solution (6 mL)) was carried out under a constant-current conditions (20 mA/cm^2, 2.5 F/mol) in an undivided cell at 0 °C. b) The yields were determined by GC analysis with acetophenone as an internal standard.

Table 5. Recycle Use of the **PE-*co*-AA-*N*-Oxyl** and the Aqueous Media[a)]

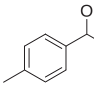
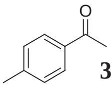
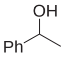
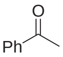
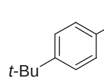
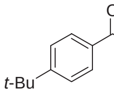
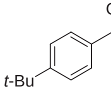
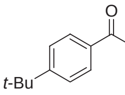
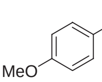
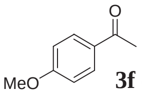
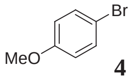
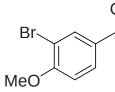
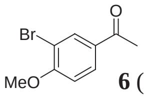
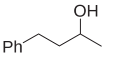
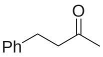
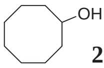
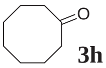
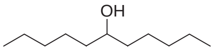
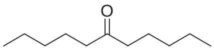
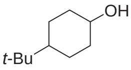
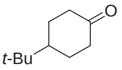
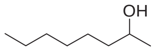
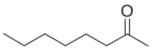
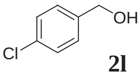
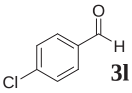
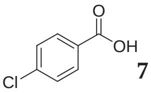
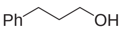
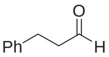
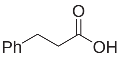
Run	**PE-*co*-AA-*N*-Oxyl** /mg	**3a** Yield/%[b)]	**2a** Recov./%[b)]
1	468	99	—
2	461	95	2
3	459	88	5
4	451	88	4
5	439	86	6

a) Electrooxidation of **2a** (0.70 mmol) in a disperse system (polymer particles (500 mg)/20 wt % NaBr–aq. sat. $NaHCO_3$ solution (6 mL)) was carried out under a constant-current conditions (20 mA/cm^2, 2.5 F/mol) in an undivided cell at 0 °C. b) Determined by GC analysis with acetophenone as an internal standard.

effect of the carboxylic acid moieties on the surface. Upon electrooxidation with **PE-*co*-AA-CO_2-*n*-Bu** and **PE-*co*-AA-CONH-*n*-Octyl**, the yields of ketone **3a** dramatically decreased to 24% and 4%, respectively (Table 4, Entries 3 and 4), in sharp contrast to the results with **PE-*co*-AA-*N*-Oxyl** and **PE-*co*-AA-CO_2H** (Entries 1 and 2). The significant decrease of the product yields suggests that the carboxylic acid moieties on the **PE-*co*-AA-CO_2H** surface also work as a mediator for the electrooxidation of alcohol. A plausible mechanism is illustrated in Scheme 2. Electro-generated active bromine species, such as sodium hypobromite and/or bromine, would react with carboxylate ion on the polymer particles to generate acyl hypobromite, which would, in turn, react with adsorbed alcohol **2a** on the polymer surface. A subsequent reaction through path **a** or **b** would afford the corresponding ketone **3a** together with carboxylate ion.[15]

In the electrooxidation of alcohol **2a** in the disperse system with **PE-*co*-AA-*N*-Oxyl** as a disperse phase and an aqueous saturated $NaHCO_3$ containing 20 wt % NaBr as a disperse medium, the **PE-*co*-AA-*N*-Oxyl** and the aqueous solution were easily recovered by filtration and a subsequent extraction process after the reaction. The recovered polymer particles **1a** and the aqueous solution could be used repeatedly for the electrooxidation of **2a**. After the first run, both the polymer particles (**1a**, disperse phase) and the aqueous solution (disperse medium) were recovered and used for the second run without any treatments. In a similar manner, the electrooxidation of **2a** was repeated totally 5 times. As shown in Table 5, no significant changes of the current efficiency and the conversion

Table 6. Electrooxidation of Alcohols in **PE-*co*-AA-*N*-Oxyl**/aq. NaBr–$NaHCO_3$[a)]

Entry	Substrate	Electricity/F mol^{-1}	Current/mA cm^{-2}	Products (Yield/%)[b)]	Recov./%[b)]
1	 **2b**	2.5	20	 **3b** (93)	—
2	 **2c**	2.5	20	 **3c** (92)	—
3	 **2d**	2.5	20	 **3d** (98)	—
4	 **2e**	2.5	20	 **3e** (87)	12
5	 **2f**	2.5	20	 **3f** (22)  **4** (19)  **5** (12)  **6** (19)	—
6	 **2g**	2.5	20	 **3g** (94)	3
7	 **2h**	2.5	20	 **3h** (66)	9
8		2.5	10	(72)	20
9	 **2i**	2.5	20	 **3i** (66)	32
10		2.5	10	(80)	12
11	 **2j**	2.5	20	 **3j** (52)	9
12		2.5	10	(53)	21
13	 **2k**	2.5	20	 **3k** (51)	31
14	 **2l**	2.5	20	 **3l** (78)  **7** (–)	—
15[c)]	 **2m**	2.5	20	 **3m** (21)  **8** (25)	27
16[d)]		5.0	20	**3m** (–) **8** (57)	17
17		10.0	20	**3m** (–) **8** (60)	—

a) Electrooxidation of alcohol **2** (0.70 mmol) in a disperse system (**PE-*co*-AA-*N*-Oxyl** (500 mg)/an aqueous 20 wt% NaBr–sat. $NaHCO_3$ solution (6 mL)) was carried out under a constant current conditions (20 mA/cm^2, 2.5 F/mol) in an undivided cell at 0 °C. b) Isolated yields after short-pass column chromatography. c) 3-Phenylpropyl 3-phenylpropanoate (8%) and 1,1-bis(3-phenylpropoxy)-3-phenylpropane (12%) were also obtained. d) 3-Phenylpropyl 3-phenylpropanoate (13%) was obtained.

yields were observed.

The **PE-*co*-AA-*N*-Oxyl**-dispersed water system was successfully applied to the electrooxidation of benzylic and aliphatic alcohols. The representative results are summarized in Table 6. The oxidation of benzylic alcohols **2b–2e** proceeded smoothly to afford the corresponding ketones **3b–3e** in good-to-excellent yields (Entries 1–4). On the other hand, 1-(4-methoxyphenyl)ethanol **2f** suffered considerable bromination on the 4-methoxyphenyl moiety to afford a mixture of 4-bromoanisole **4** (19%), 1-(3-bromo-4-methoxyphenyl)ethanol **5** (12%), and 3′-bromo-4′-methoxyacetophenone **6** (19%) together with *p*-methoxyacetophenone **3f** (22%).[12] The oxidation of aliphatic *sec*-alcohols **2g–2k** was similarly performed to afford the corresponding ketones **3g–3k** in 51–94% yields (Entries 6–13). The oxidation of **2h–2k** did not efficiently proceed under the standard condition (Entries 7, 9, 11, and 13). When the current density was decreased to 10 mA/cm^2, the yields of ketones **3h** and **3i** increased to 72 and 80%, respectively (Entries 8 and 10). The oxidation of 4-chlorobenzyl alcohol **2l** proceeded smoothly to afford the corresponding 4-chlorobenzaldehyde (**3l**, 78%), and no appreciable amount of carboxylic acid was obtained (Entry 14). In contrast, the oxidation of 3-phenyl-1-propanol **2m** afforded a mixture of the corresponding aldehyde **3m** (21%), 3-phenylpropanoic acid (**8**, 25%), 1,1-bis(3-phenylpropoxy)-3-phenylpropane (12%), and 3-phenylpropyl 3-phenylpropanoate (8%) (Entry 15). When an excess amount of electricity (5.0 and 10.0 F/mol) was passed, the yield of the corresponding carboxylic acid **8** increased to 57% and 60% (Entries 16 and 17).[2a,3c]

Conclusion

The electrooxidation of alcohols **2** proceeds smoothly in a disperse system with *N*-oxyl-immobilized poly(ethylene-*co*-acrylic acid) as a disperse phase and the aqueous saturated $NaHCO_3$ containing 20 wt% NaBr as a disperse medium. The electrooxidation of alcohol **2a** could be performed in a similar manner with **PE-*co*-AA-CO$_2$H** as a disperse phase to afford a moderate yield of the corresponding ketone **3a**. Protection of most of the carboxylic acid moieties on the polymer surface by esterification or amidation resulted in a significant decrease of the product yield, suggesting that the carboxyl moieties on the polymer surface would act as a mediator for the electrooxidation of alcohols. The disperse electrolysis system was successfully applied to various benzylic and aliphatic *sec*-alcohols. Both the *N*-oxyl-immobilized disperse phase and the aqueous medium could be easily recovered and used repeatedly for the electrooxidation of alcohols **2**. The organic solvent for washing the polymer particles and extracting the aqueous medium could also be recovered and reused, thus, offering a formally closed system for the electrooxidation of alcohols without the consumption of any chemicals.

Experimental

General Procedures. Unless otherwise noted, reagent-grade chemicals were purchased and used without further purification. Silica-gel for column chromatography was Merck Silica Gel 60 (43–60 µm). ^{1}H NMR spectra were recorded at 200 MHz on a Varian Gemini-200 instrument, and the chemical shifts were reported in parts per million (δ) downfield from internal Me_4Si. Infrared spectra (IR) were recorded on a JASCO VALOR-III spectrometer. Gas chromatography (GC) analyses were performed on a Yanaco GC 6800 with a Quadrex Corporation fused silica glass capillary column (methyl phenyl 5: 25 m × 0.25 µm i.d., column 100 °C, injector 270 °C, detector 300 °C, carrier gas, He; flow rate, 26 mL/min). GC yields were determined by use of acetophenone as an internal standard.

Electrolysis Apparatus. An undivided cell [2.7 cm diameter and 5.5 cm height (20 mL volume)] with a stirring bar was used. A METRONIX corporation model 543B regulated DC power supply was used as a source of electric current. Two platinum electrodes (1.0 × 1.5 cm^2) were placed parallel to each other 5 mm apart. The vessel was immersed in an ice bath maintained at 0–2 °C by external cooling.

Preparation of *N*-Oxyl-Immobilized Poly(ethylene-*co*-acrylic acid). A Typical Procedure: A mixture of poly(ethylene-*co*-acrylic acid) particles (containing 5 wt% acrylic acid, Aldrich, 5.0 g), 4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl (688 mg, 4.02 mmol), and DCC (1.03 g, 5.01 mmol) in chlorobenzene (30 mL) was heated at 50 °C for 2 d under an argon atmosphere. The poly(ethylene-*co*-acrylic acid) particles were separated by filtration and washed successively with chlorobenzene, H_2O, MeOH, and Et_2O (20 mL each). The solids were dried under reduced pressure to afford *N*-oxyl-immobilized poly(ethylene-*co*-acrylic acid) particles (**1a**, 4.90 g): orange solids; IR (KBr) 3325, 2903, 2855, 1702, 1636, 1467, 1377, 1243 cm^{-1}.

Electrooxidation of Secondary Alcohols to Ketones. A mixture of *N*-oxyl-immobilized poly(ethylene-*co*-acrylic acid) particles **1a** (504 mg) and 1-(4-chlorophenyl)ethanol (**2a**, 109.6 mg, 0.70 mmol) in an aqueous saturated $NaHCO_3$ containing 20 wt% NaBr was placed in a beaker-type undivided cell. After stirring for 5 min, two platinum electrodes (1.0 × 1.5 cm^2) were immersed into the reaction mixture, and a constant current conditions (30 mA, 1.56 h, 2.5 F/mol) was supplied at 0 °C under vigorous stirring. After electrolysis, the poly(ethylene-*co*-acrylic acid) particles were separated by filtration and washed with EtOAc. The aqueous layer was extracted three times with EtOAc. The extracts and the washings were combined and dried over Na_2SO_4. Most of the solvents were evaporated and the residue was chromatographed on a silica-gel column (hexane/EtOAc: 5/1) to afford *p*-chloroacetophenone[16] (**3a**, 94 mg, 0.61 mmol, 87%); a colorless liquid; $R_f = 0.52$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.60 (s, 3H, CH_3), 7.44 (d, $J = 8.6$ Hz, 2H, Ar), 7.90 (d, $J = 8.6$ Hz, 2H, Ar); IR (neat) 3007, 2970, 2904, 1687, 1589, 1572, 1176 cm^{-1}.

In a similar manner, the electrooxidation of alcohols **2b**–**2k** was carried out in the disperse system. The reaction conditions and results are summarized in Table 6.

***p*-Methylacetophenone (3b):**[16] A colorless liquid; $R_f = 0.62$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.41 (s, 3H, CH_3), 2.58 (s, 3H, $COCH_3$), 7.26 (d, $J = 8.3$ Hz, 2H, Ar), 7.86 (d, $J = 8.3$ Hz, 2H, Ar); IR (neat) 3033, 3004, 2923, 1683, 1607, 1575, 1406, 1358, 1183 cm^{-1}.

Acetophenone (3c):[16] A colorless liquid; $R_f = 0.58$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.61 (s, 3H, $COCH_3$), 7.42–7.60 (m, 3H, Ar), 7.96 (d, $J = 8.5$ Hz, 2H, Ar); IR (neat) 3061, 3005, 2961, 2916, 1686, 1583, 1266, 1181 cm^{-1}.

***p*-*t*-Butylacetophenone (3d):**[17] A colorless liquid; $R_f = 0.53$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.34 (s, 9H, *t*-Bu), 2.59 (s, 3H, CH_3), 7.48 (d, $J = 8.5$ Hz, 2H, Ar), 7.90 (d, $J = 8.5$ Hz, 2H, Ar); IR (neat) 3056, 2968, 2907, 2871, 1683, 1607 cm^{-1}.

1-(4-*t*-Butylphenyl)-1-propanone (3e):[18] A colorless liquid; $R_f = 0.69$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.22 (t, $J = 7.3$ Hz, 3H, CH_3), 1.34 (s, 9H, *t*-Bu), 2.99 (m, 2H, CH_2), 7.47 (d, $J = 8.5$ Hz, 2H, Ar), 7.91 (d, $J = 8.5$ Hz, 2H, Ar); IR (neat) 3057, 2967, 2907, 2874, 1687, 1607, 1565, 1228, 1110 cm^{-1}.

***p*-Methoxyacetophenone (3f):**[16] A colorless liquid; $R_f = 0.38$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.56 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 6.94 (d, $J = 9.0$ Hz, 2H, Ar), 7.94 (d, $J = 9.0$ Hz, 2H, Ar); IR (neat) 3010, 2970, 2841, 1675, 1601, 1577, 1260 cm^{-1}.

4-Bromoanisole (4): A yellow liquid; $R_f = 0.62$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.78 (s, 3H, OCH_3), 6.78, (d, $J = 9.1$ Hz, 2H, Ar), 7.38 (d, $J = 9.1$ Hz, 2H, Ar); IR (neat) 3006, 2938, 2838, 1579, 1489, 1291, 1171 $\mathrm{cm^{-1}}$.

1-(3-Bromo-4-methoxyphenyl)ethanol (5):[19] A yellow liquid; $R_f = 0.15$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 1.47 (d, $J = 6.4$ Hz, 3H, $\mathrm{CH_3}$), 1.80 (br, 1H, OH), 3.90 (s, 3H, $\mathrm{OCH_3}$), 4.84 (q, $J = 6.4$ Hz, 1H, –CH–), 6.88 (d, $J = 8.4$ Hz, 1H, Ar), 7.28 (d, $J = 8.4$ Hz, 1H, Ar), 7.57 (s, 1H, Ar); IR (neat) 3380, 2972, 2931, 2839, 1604, 1480, 1462, 1256, 1053 $\mathrm{cm^{-1}}$.

3′-Bromo-4′-methoxyacetophenone (6):[20] White solids; $R_f = 0.26$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 2.56 (s, 3H, $\mathrm{CH_3}$), 3.97 (s, 3H, $\mathrm{OCH_3}$), 6.94 (d, $J = 8.7$ Hz, 1H, Ar), 7.92 (d, $J = 8.7$ Hz, 1H, Ar), 8.17 (s, 1H, Ar); IR (KBr) 3082, 3060, 2991, 2927, 2851, 1674, 1593, 1498, 1357, 1169 $\mathrm{cm^{-1}}$.

4-Phenyl-2-butanone (3g):[21] A colorless liquid; $R_f = 0.43$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 2.14 (s, 3H, $\mathrm{CH_3}$), 2.74–2.91 (m, 4H, $\mathrm{–CH_2–CH_2–}$), 7.16–7.28 (m, 5H, Ar); IR (neat) 3063, 3027, 2924, 1717, 1603 $\mathrm{cm^{-1}}$.

Cyclooctanone (3h): A colorless liquid; $R_f = 0.78$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 1.30–1.44 (m, 2H), 1.49–1.60 (m, 4H), 1.81–1.94 (m, 4H), 2.41 (t, $J = 6.4$ Hz, 4H); IR (neat) 2923, 2856, 1701, 1467, 1411, 1333, 1147 $\mathrm{cm^{-1}}$.

6-Undecanone (3i):[22] A colorless liquid; $R_f = 0.83$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 0.89 (t, $J = 6.6$ Hz, 6H), 1.17–1.42 (m, 8H), 1.50–1.64 (m, 4H), 2.38 (t, $J = 7.4$ Hz, 4H); IR (neat) 2954, 2933, 2864, 1719, 1460, 1411, 1376, 1134 $\mathrm{cm^{-1}}$.

4-*t*-Butylcyclohexanone (3j):[23] White solids; $R_f = 0.63$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 0.92 (s, 9H), 1.39–1.49 (m, 3H), 2.05–2.14 (m, 2H), 2.30–2.44 (m, 4H); IR (KBr) 2964, 2949, 2857, 1727, 1472, 1367, 1224, 1163 $\mathrm{cm^{-1}}$.

2-Octanone (3k):[24] A colorless liquid; $R_f = 0.43$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 0.87 (t, $J = 6.6$ Hz, 3H), 1.25–1.31 (m, 6H), 1.52–1.60 (m, 2H), 2.13 (s, 3H), 2.43 (t, $J = 7.0$ Hz, 2H); IR (neat) 2955, 2861, 1718, 1459, 1412, 1360, 1165 $\mathrm{cm^{-1}}$.

Electrooxidation of Primary Alcohols in an *N*-Oxyl-Immobilized Poly(ethylene-*co*-acrylic acid) Dispersed Water System. A mixture of *N*-oxyl-immobilized poly(ethylene-*co*-acrylic acid) particles **1a** (475 mg) and 4-chlorobenzyl alcohol **2l** (100 mg, 0.70 mmol) in an aqueous saturated $\mathrm{NaHCO_3}$ containing 20 wt % NaBr was placed in a beaker-type undivided cell fitted with two platinum electrodes (1.0×1.5 $\mathrm{cm^2}$). A constant current conditions (30 mA, 1.56 h, 2.5 F/mol) was supplied at 0 °C under vigorous stirring. The polymer particles were separated by filtration and washed with EtOAc. The aqueous layer was extracted three times with EtOAc. The extracts and the washings were combined and dried over $\mathrm{Na_2SO_4}$. After evaporation of most of the solvents, the residue was chromatographed on a silica-gel column (hexane/EtOAc: 5/1) to afford 4-chlorobenzaldehyde **3l**[25] (77.2 mg, 0.55 mmol, 78%): white solids; $R_f = 0.60$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 7.52 (d, $J = 8.5$ Hz, 2H, Ar), 7.83 (d, $J = 8.5$ Hz, 2H, Ar), 9.99 (s, 1H, CHO); IR (KBr) 3007, 2970, 2904, 1687, 1589, 1572, 1176 $\mathrm{cm^{-1}}$. The aqueous solution was acidified with aq 5% HCl, and extracted with $\mathrm{Et_2O}$ (5 mL × 5). The combined extracts were dried over $\mathrm{Na_2SO_4}$, filtered, and concentrated under reduced pressure to afford no appreciable amount of the corresponding carboxylic acid **7**.

In a similar manner, the electrooxidation of alcohol **2m** was carried out. The reaction conditions and results are summarized in Table 6, Entries 15–17.

3-Phenylpropanal (3m):[25] A colorless liquid; $R_f = 0.37$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 2.78 (t, $J = 7.3$ Hz, 2H, $\mathrm{Ar–CH_2–}$), 2.97 (t, $J = 7.3$ Hz, 2H, $\mathrm{–CH_2CO}$), 7.18–7.34 (m, 5H, Ar), 9.83 (s, 1H, CHO); IR (neat) 3058, 3029, 2935, 1735, 1604, 1497, 1162 $\mathrm{cm^{-1}}$.

3-Phenylpropanoic Acid (8):[26] White solids; $R_f = 0.00$ (hexane/EtOAc: 5/1); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 2.69 (t, $J = 7.5$ Hz, 2H, $\mathrm{Ar–CH_2–}$), 2.97 (t, $J = 7.5$ Hz, 2H, $\mathrm{–CH_2CO}$), 7.17–7.34 (m, 5H, Ar); IR (KBr) 3060, 3032, 2935, 1697, 1497, 1305, 1221 $\mathrm{cm^{-1}}$.

1,1-Bis(3-phenylpropoxy)-3-phenylpropane: A colorless liquid; $R_f = 0.74$ (hexane/AcOEt: 5/1); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 1.82–2.00 (m, 6H, $\mathrm{–CH_2–}$), 2.70 (t, $J = 7.6$ Hz, 6H, $\mathrm{ArCH_2–}$), 3.39–3.49 (m, 2H, $\mathrm{OCH_2–}$), 3.56–3.68 (m, 2H, $\mathrm{OCH_2–}$), 4.48 (t, $J = 5.7$ Hz, 1H, CH), 7.17–7.32 (m, 15H, Ar); IR (neat) 3063, 3027, 2940, 2866, 1603, 1450, 1126, 1036 $\mathrm{cm^{-1}}$.

3-Phenylpropyl 3-Phenylpropanoate:[27] A colorless liquid; $R_f = 0.66$ (hexane/AcOEt: 5/1); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 1.93 (m, 2H, $\mathrm{–CH_2–}$), 2.63 (t, $J = 7.5$ Hz, 4H, $\mathrm{ArCH_2–}$), 2.96 (t, $J = 7.7$ Hz, 2H, $\mathrm{–CH_2CO}$), 4.09 (t, $J = 6.4$ Hz, 2H, $\mathrm{OCH_2–}$), 7.13–7.33 (m, 10H, Ar); IR (neat) 3064, 3028, 2950, 2858, 1753, 1604, 1162 $\mathrm{cm^{-1}}$.

Esterification of Poly(ethylene-*co*-acrylic acid). A mixture of poly(ethylene-*co*-acrylic acid) (1.01 g), 1-butanol (74.4 mg, 1.00 mol), and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (WSCI•HCl, 192 mg, 1.00 mmol) in chlorobenzene (15 mL) was heated at 80 °C for 4 d under an argon atmosphere. The polymer particles were separated by filtration and washed successively with aq 5% HCl (20 mL), $\mathrm{H_2O}$ (20 mL), and acetone (20 mL). The polymer particles were dried under reduced pressure to afford poly(ethylene-*co*-acrylic acid) butyl ester (**PE-*co*-AA-$\mathbf{CO_2}$-*n*-Bu**, 806 mg) as white solids; IR (KBr) 2919, 2851, 1736, 1701, 1541, 1465, 1375, 1165, 720 $\mathrm{cm^{-1}}$.

Amidation of Poly(ethylene-*co*-acrylic acid). A mixture of poly(ethylene-*co*-acrylic acid) (1.01 g), octylamine (108 mg, 0.84 mol), and WSCI•HCl (161 mg, 0.84 mmol) in chlorobenzene (15 mL) was heated at 80 °C for 4 d under an argon atmosphere. The polymer particles were separated by filtration and washed successively with aq 5% HCl (20 mL), $\mathrm{H_2O}$ (20 mL), and acetone (20 mL). The polymer particles were dried under reduced pressure to afford poly(ethylene-*co*-acrylic acid) octyl amide (**PE-*co*-AA-CONH-*n*-Octyl**, 813 mg) as white solids; IR (KBr) 3288, 2922, 2850, 1699, 1645, 1541, 1465, 720 $\mathrm{cm^{-1}}$.

Sensitive Color Test to Monitor the Presence of Carboxylic Acid Moieties on the Poly(ethylene-*co*-acrylic acid) Surface.[14] Poly(ethylene-*co*-acrylic acid) was placed in a test tube, to which was added a solution of malachite green (2 mL, 0.072 M) in EtOH and a single drop of $\mathrm{Et_3N}$. After standing for 1 h at room temperature, the green solution was discarded and the polymer particles were washed several times with methanol until the solution remained clear. **PE-*co*-AA-$\mathbf{CO_2H}$** was colored green.

References

1 a) “Comprehensive Organic Synthesis,” ed by B. M. Trost and I. Fleming, Pergamon Press, Oxford (1991), Vol. 7. b) R. C. Larock, “Comprehensive Organic Transformations,” VCH Publishers, Inc. (1989).

2 a) M. F. Semmelhack, C. S. Chou, and D. A. Cortés, *J. Am. Chem. Soc.*, **105**, 4492 (1983). b) Z. Ma, Q. Huang, and J. M. Bobbitt, *J. Org. Chem.*, **58**, 4837 (1993). c) Y. Kashiwagi, F.

Kurashima, C. Kikuchi, J. Anzai, T. Osa, and J. M. Bobbitt, *Tetrahedron Lett.*, **40**, 6469 (1999). d) Y. Kashiwagi, F. Kurashima, C. Kikuchi, J. Anzai, T. Osa, and J. M. Bobbitt, *Chem. Commun.*, **1999**, 1983. e) Y. Yanagisawa, Y. Kashiwagi, F. Kurashima, C. Kikuchi, J. Anzai, T. Osa, and J. M. Bobbitt, *Chem. Lett.*, **1996**, 1043. f) Y. Kashiwagi, Y. Yanagisawa, F. Kurashima, J. Anzai, T. Osa, and J. M. Bobbitt, *Chem. Commun.*, **1996**, 2745. g) T. Osa, Y. Kashiwagi, Y. Yanagisawa, and J. M. Bobbitt, *J. Chem. Soc., Chem. Commun.*, **1994**, 2535. Electrooxidation of carbohydrates in aqueous solution: h) K. Schnatbaum and H. J. Schäfer, *Eur. J. Org. Chem.*, **2003**, 351.

3 a) T. Inokuchi, S. Matsumoto, T. Nishiyama, and S. Torii, *J. Org. Chem.*, **55**, 462 (1990). b) S. Torii, T. Inokuchi, S. Matsumoto, T. Saeki, and T. Oki, *Bull. Chem. Soc. Jpn.*, **63**, 852 (1990). c) T. Inokuchi, S. Matsumoto, T. Nishiyama, and S. Torii, *Synlett*, **1990**, 57. d) T. Inokuchi, S. Matsumoto, and S. Torii, *J. Org. Chem.*, **56**, 2416 (1991). e) T. Inokuchi, P. Liu, and S. Torii, *Chem. Lett.*, **1994**, 1411. f) M. Kuroboshi, H. Yoshihisa, M. N. Cortona, Y. Kawakami, Z. Gao, and H. Tanaka, *Tetrahedron Lett.*, **41**, 8131 (2000).

4 a) S. Kobayashi, T. Wakabayashi, S. Nakayama, and H. Oyamada, *Tetrahedron Lett.*, **38**, 4559 (1997). b) S. Kobayashi and T. Wakabayashi, *Tetrahedron Lett.*, **39**, 5389 (1998). c) Y. Mori, K. Kakumoto, K. Manabe, and S. Kobayashi, *Tetrahedron Lett.*, **41**, 3107 (2000). d) K. Manabe, X.-M. Sun, and S. Kobayashi, *J. Am. Chem. Soc.*, **123**, 10101 (2001). e) K. Manabe, Y. Mori, T. Wakabayashi, S. Nagayama, and S. Kobayashi, *J. Am. Chem. Soc.*, **122**, 7202 (2000). f) K. Manabe, Y. Mori, and S. Kobayashi, *Tetrahedron*, **57**, 2537 (2001). g) S. Kobayashi and K. Manabe, *Acc. Chem. Res.*, **35**, 209 (2002). h) S. Kobayashi, R. Matsubara, Y. Nakamura, H. Kitagawa, and M. Sugiura, *J. Am. Chem. Soc.*, **125**, 2507 (2003). i) K. Manabe, S. Iimura, X.-M. Sun, and S. Kobayashi, *J. Am. Chem. Soc.*, **124**, 11971 (2002). j) "Organic Synthesis in Water," ed by P. A. Grieco, Blackie Academic & Professional, London (1998).

5 a) H. Danjo, D. Tanaka, T. Hayashi, and Y. Uozumi, *Tetrahedron*, **55**, 14341 (1999). b) Y. Uozumi, H. Danjo, and T. Hayashi, *Tetrahedron Lett.*, **39**, 8303 (1998). c) Y. Uozumi, H. Danjo, and T. Hayashi, *J. Org. Chem.*, **64**, 3384 (1999). d) Y. Uozumi and T. Watanabe, *J. Org. Chem.*, **64**, 6921 (1999). e) K. Shibatomi, T. Nakahashi, and Y. Uozumi, *Synlett*, **2000**, 1643. f) Y. Uozumi and Y. Kobayashi, *Heterocycles*, **59**, 71 (2003). g) Y. Uozumi, H. Danjo, and T. Hayashi, *Tetrahedron Lett.*, **38**, 3557 (1997).

6 a) G. Sourkouni-Argirusi and A. Kirschning, *Org. Lett.*, **2**, 3781 (2000). b) W. Minghu, Y. Guichun, and C. Zuxing, *React. Funct. Polym.*, **44**, 97 (2000). c) B. Hinzen and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, **1997**, 1907. d) M. Mülbaier and A. Giannis, *Angew. Chem., Int. Ed.*, **40**, 4393 (2001). e) G. Sorg, A. Mengel, G. Jung, and J. Rademann, *Angew. Chem., Int. Ed.*, **40**, 4395 (2001). f) S. Ficht, M. Mülbaier, and A. Giannis, *Tetrahedron*, **57**, 4863 (2001).

7 a) T. Miyazawa and T. Endo, *J. Polym. Sci.*, **23**, 2487 (1985). b) T. Miyazawa and T. Endo, *J. Mol. Catal.*, **49**, L31 (1988). c) T. Osa, U. Akiba, I. Segawa, and J. M. Bobbitt, *Chem. Lett.*, **1988**, 1423. d) F. MacCorquodale, J. A. Crayston, J. C. Walton, and D. J. Worsfold, *Tetrahedron Lett.*, **31**, 771 (1990). e) A. Dijksman, I. W. C. E. Arends, and R. A. Sheldon, *Chem. Commun.*, **2000**, 271. f) A. Dijksman, I. W. C. E. Arends, and R. A. Sheldon, *Synlett*, **2001**, 102. g) R. A. Sheldon, I. W. C. E. Arends, G.-J. T. Brink, and A. Dijksman, *Acc. Chem. Res.*, **35**, 774 (2002). h) S. Weik, G. Nicholson, G. Jung, and J. Rademann, *Angew. Chem., Int. Ed.*, **40**, 1436 (2001). i) C. Tanyeli and A. Gümüş, *Tetrahedron Lett.*, **44**, 1639 (2003).

8 a) C. Bolm and T. Fey, *Chem. Commun.*, **1999**, 1795. b) T. Fey, H. Fischer, S. Bachmann, K. Albert, and C. Bolm, *J. Org. Chem.*, **66**, 8154 (2001).

9 J. Yoshida, R. Nakai, and N. Kawabata, *J. Org. Chem.*, **45**, 5269 (1980).

10 J. Yoshida, H. Sohuku, and N. Kawabata, *Bull. Chem. Soc. Jpn.*, **56**, 1243 (1983).

11 J. Yoshida, J. Hashimoto, and N. Kawabata, *J. Org. Chem.*, **47**, 3575 (1982).

12 H. Tanaka, Y. Kawakami, K. Goto, and M. Kuroboshi, *Tetrahedron Lett.*, **42**, 445 (2001).

13 H. Tanaka, J. Kubota, S. Itogawa, T. Ido, M. Kuroboshi, K. Shimamura, and T. Uchida, *Synlett*, **2003**, 951.

14 Taddei and his co-workers developed a rapid and sensitive color test for monitoring the presence of the COOH on a solid resin using malachite green. If there are carboxylic acid moieties on the solid surface, the solid shows green color after the reaction of malachite green. M. E. Attardi, G. Porcu, and M. Taddei, *Tetrahedron Lett.*, **41**, 7391 (2000).

15 The protected polymer **PE-*co*-AA-CO$_2$-*n*-Bu** and **PE-*co*-AA-CONH-*n*-Octyl** showed negative result for malachite green test, whereas IR spectra of them showed the absorption bands due to the carboxylic acid moieties were also observed at 1701 and 1704 cm^{-1}. These indicate that carboxylic acid moieties on the surface of **PE-*co*-AA-CO$_2$H** were completely protected and those inside the polymer remained intact. The fact that the electrooxidation with **PE-*co*-AA-CO$_2$-*n*-Bu** and **PE-*co*-AA-CONH-*n*-Octyl** did not proceed indicates that the carboxylic acid moieties on the surface of the polymer can promote the electrooxidation, whereas those inside the polymer can not. This suggests that the substrate was adsorbed on the surface of the polymer.

16 S. Cacchi, G. Fabrizi, F. Gavazza, and A. Goggiamani, *Org. Lett.*, **5**, 289 (2003).

17 H. B. Kwon, B. H. McKee, and J. K. Stille, *J. Org. Chem.*, **55**, 3114 (1990).

18 H. Miyoshi, J. Iwata, K. Sakamoto, H. Hurukawa, M. Takada, H. Iwamura, T. Watanabe, and Y. Kodama, *J. Biol. Chem.*, **273**, 17368 (1998).

19 E. M. Brown, F. H. Fuller, S. C. Hebert, and J. E. Garrett, Jr., U.S. Patent 5688938 (1997); *Chem. Abstr.*, **128**, 30379j (1998).

20 R. G. Syvret, T. P. Nguyen, V. L. Bulleck, and R. D. Rieth, Eur. Pat. Appl., EP 1138657 A1 (2001); *Chem. Abstr.*, **135**, 272548a (2001).

21 J. Louie, C. W. Bielawski, and R. H. Grubbs, *J. Am. Chem. Soc.*, **123**, 11312 (2001).

22 A. Arase, M. Hoshi, and Y. Masuda, *Bull. Chem. Soc. Jpn.*, **57**, 209 (1984).

23 S. Torii, T. Inokuchi, and T. Sugiura, *J. Org. Chem.*, **51**, 155 (1986).

24 I. E. Markó, P. R. Giles, M. Tsukazaki, I. Chellé-Regnaut, A. Gautier, S. M. Brown, and C. I. Urch, *J. Org. Chem.*, **64**, 2433 (1999).

25 M. Fujii, K. Nakamura, S. Yasui, S. Oka, and A. Ohno, *Bull. Chem. Soc. Jpn.*, **60**, 2423 (1987).

26 J. Blum and B. Zinger, *J. Org. Chem.*, **43**, 2961 (1978).

27 S. Bhar and S. K. Chaudhuri, *Tetrahedron*, **59**, 3493 (2003).