

Anti-fouling epoxy coatings for optical biosensor application based on phosphorylcholine

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Abstract

Epoxy polymers containing phosphorylcholine (PC) groups were prepared by the copolymerization of glycidyl methacrylate and 2-methacryloyloxyethyl phosphorylcholine (MPC), and used as a coating material for an oxygen sensing membrane, in order to protect it against bio-fouling by microorganisms. The copolymers had good film forming properties. The cured polymer films had excellent adhesion properties and were transparent at the wavelength of more than 300 nm. The cross-linking reaction of the polymer films increased with increasing amount of MPC units in the copolymer, and the addition of an aliphatic diamine significantly enhanced the cross-linking reaction of the copolymer films. The cured epoxy copolymers show a high anti-fouling effect, which was observed by incubating *E. coli* on the copolymer films. The coatings of the cured epoxy copolymer did not interfere with the performance of the optical oxygen sensing membrane. Thus, the epoxy copolymers containing PC groups are very useful as an anti-fouling coating material for the optical biosensing membranes.

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1. Introduction

Sensors have been used for the continuous monitoring of various parameters such as the pH changes, and O₂ or CO₂ concentration in bio-reactor, environmental or clinical systems. However, one of the most serious problems in such sensing systems is the surface fouling caused by various foreign materials such as proteins, cells and microorganisms, which induce a decrease in the sensitivity and life-time of the sensors. Such surface fouling finally leads to sensor failure as a consequence of the interruption of the analyte transport into the sensing layer. Therefore, it is vital to protect against or minimize the fouling of the surface of sensors caused by the build-up of foreign materials.

Several polymer systems have been reported to prevent or minimize the bio-fouling of coatings. For example, biocides embedded in a copolymer matrix [1], polymers containing phosphorylcholine (PC)-substituted methacrylate units [2], anti-

microbial *N*-halamine polymer [3], fluoroalkyl diol-containing polyurethanes [4], poly(ether) grafted poly(urethanes) [5], and plasma polymers of hexamethyldisiloxane/O₂ [6], were found to be effective as anti-fouling coatings.

One of the most effective methods of making an anti-fouling coating is to use polymers containing PC groups, which mimic a bio-membrane surface. It is known that the major component of the outer surface of the cell membrane consists of the zwitterionic lipid PC. The PC surface provides an inert surface for the biological reactions of proteins and glycoproteins minimizing bio-fouling. Polymers containing PC groups have properties that reduce bio-fouling as well as resist protein adsorption and cell adhesion [7], and have been used in various biomedical applications to prevent bio-fouling [8].

Polymers containing PC groups were found to be suitable as a coating for devices which need to be endowed with anti-fouling properties. However, such polymers have poor mechanical properties due to the zwitterionic PC groups which absorb large amounts of water. It has generally been found that many of polymers containing PC groups possess inherently poor mechanical properties. Therefore, such polymer systems are not suitable for those devices in which the materials are exposed to mechanical forces.

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On the other hand, coating materials based on epoxy resins have attracted considerable attention in many areas of technology. This is due to the fact that epoxy resins can be processed relatively easily, and the cured epoxy resins have good mechanical and chemical properties. For this reason, epoxy resins have been widely used as surface coatings, adhesives, painting materials, laminates, encapsulants, polymer composites, and insulating materials for electronic devices, etc. [9,10].

In the present study, epoxy polymers containing PC groups were applied to anti-fouling optical sensor coating materials in order to improve the mechanical properties of the anti-fouling coatings, since epoxy polymers have an exceptional combination of properties such as easy processability, high safety, excellent solvent and chemical resistance, toughness, low shrinkage on curing, good electrical, mechanical and corrosion resistance along with excellent adhesion to many substrates [11]. The cured PC-containing epoxy polymers were used as a coating material for oxygen sensing membranes and their feasibility as a sensor coating material was examined.

2. Experimental

2.1. Materials and instruments

2-Chloro-2-oxo-1,3,2-dioxapholane (COP) and trimethylamine (TMA) were purchased from Aldrich Chemical Company and used without further purification. 4,4'-Methylenebis(cyclohexylamine) (MCA) and 4,4'-methylenedianiline (MDA) were obtained from the Tokyo Kasei Chemical Company and used as received. 2-(2-Oxo-1,3,2-dioxaphosphoxyloxy)ethyl methacrylate (OPEMA), and 2-methacryloyloxyethyl phosphorylcholine (MPC) [12], and ruthenium(II) tris(4,7-diphenyl-1,10-phenanthroline) perchlorate (Ru-DPP) [13] were prepared by using the procedures described in the literatures.

The molecular weight was determined using a dynamic light scattering (DLS) spectrophotometer model DLS-8000HL from Otsuka Electric Co. X-ray photoelectron spectra (XPS) were obtained using a Thermo Co. instrument model Multi-Lab 2000. The optical images of *E. coli* were taken using a Hitachi model S-4700 scanning electron microscope (SEM). Fluorescence spectra were recorded using a Hitachi model F-4500 fluorescence spectrophotometer. Adhesion tests were performed using a F107 Cross Hatch Cutter KIT from Elcometer Instruments.

2.2. Polymerization

The reaction conditions used for preparing the copolymers are shown in Table 1. Corresponding amounts of glycidyl methacrylate (GMA), MPC, and azobisisobutyronitrile (AIBN) were dissolved in 20 mL of a THF and MeOH (7:3, v/v) solvent mixture. The mixture was charged into a cap tube and purged with nitrogen for 20 min. The tube containing the mixture was sealed under nitrogen and polymerization was carried out at 60 °C for 16 h. The resulting polymer was isolated by precipitation into *n*-hexane and subsequently redissolved in CHCl₃ and purified by reprecipitation into *n*-hexane. The precipitated polymer was collected by filtration, and dried in vacuo for 6 h at room temperature.

IR (KBr pellet, cm⁻¹): 3700–2600 (broad, medium), 3050, 2943, 1732, 1480, 1400, 1220, 1149, 1085.

2.3. Film preparation

A 5.0 wt.% copolymer solution was prepared by dissolving the polymer (50 mg) and diamine (2.5 mg) in CHCl₃ (1.0 mL). The polymer solution was filtered through a 0.45 μm Milipore filter, and spin coated on a silicon wafer or a small Confocal dish at 400 rpm for 10 s on the 1st run and 1200 rpm for 20 s on the 2nd run. The film on the silicon wafer was dried in vacuo at 40 °C for over 6 h.

2.4. Adhesion test

A 20 wt.% polymer solution was prepared by dissolving the copolymer-I (2.0 g) and MDA (0.1 g) in CHCl₃ (10 mL). The polymer solution was cast on a glass plate (20 mm × 25 mm) and the film on the glass plate was cured at 80 °C for 20 min. Thickness of the film was 58 μm. The adhesion test was performed with a cross-hatch cutter using ASTM test method B (cross-cut tape test) [14].

2.5. Insoluble fraction

The copolymer films on the silicon wafer, with or without the diamine, were cured at various heating temperatures for 20 min. Thickness of the film was 1.76 μm. The cured copolymer films were dipped in CHCl₃ for 10 min and subsequently dried in vacuo at 40 °C for 4 h. The insoluble fraction of the copolymer

Table 1
Polymer composition and physical properties

Copolymer	Monomer ^a		AIBN (mg)	MPC in feed (mol%)	MPC unit ^b found (mol%)	Yield (%)	\bar{M}_n^c ($\times 10^5$)
	GMA (g)	MPC (g)					
I	1.00	0.11	10.0	5.0	2.0	72	1.20
II	1.00	0.21	10.0	10.0	6.6	78	0.93
III	1.00	0.32	10.0	15.0	13.0	63	0.99

^a Polymerization was carried out with 1 wt.% AIBN at 60 °C for 16 h.

^b Determined from XPS.

^c Determined from DLS-8000HL.

films was calculated from the following equation:

$$\text{Insoluble fraction (\%)} = \frac{\text{Absorbance at } 1730 \text{ cm}^{-1} \text{ after dipping}}{\text{Absorbance at } 1730 \text{ cm}^{-1} \text{ before dipping}} \times 100.$$

2.6. Anti-fouling effect

The anti-fouling effect of the polymer films was studied by cultivating *E. coli* JM109 in a confocal dish (35 mm × 10 mm) which was cured after being coated with the copolymer film. The number of *E. coli* adhered on the polymer film was counted.

2.6.1. Preparation of dye solutions

Crystal violet solution was prepared by mixing crystal violet (2.0 g) in 95% ethanol (20 mL) and ammonium oxalate (0.8 g) in H₂O (80 mL), and the solution was stored at room temperature for 24 h before using. Iodine solution was prepared by dissolving iodine (1.0 g) and KI (2.0 g) in H₂O (90 mL). A 2.5 wt.% safranin O dye solution was prepared by dissolving safranin O (0.25 g) in a 95% ethanol (10 mL) and H₂O (90 mL) mixture.

2.6.2. Bioadhesion studies

The copolymer film coated on the confocal dish was cured at 80 °C for 20 min and sterilized with 254 nm UV light. *E. coli* JM109 (3 mL) was seeded in LB medium and activated by incubating it in a shaking incubator at 37 °C for 24 h at 180 rpm. The activated *E. coli* (9 μL) was added to a culture medium (291 μL) in a small confocal dish (9 mL), which was cured after being coated with the copolymer. The *E. coli* in the confocal dish was incubated at 37 °C for various incubating times. The film incubated with *E. coli* on the confocal dish was washed carefully with distilled water, and put into a beaker containing 600 mL of distilled water. The beaker containing the confocal dish was shaken in a shaking bath for 3 min at 150 rpm and the confocal dish was washed again with distilled water.

After washing the film on the confocal dish, it was dried at 60 °C for 1 h, and the *E. coli* adhered on the film were sterilized by exposing them to a flame. The adhered *E. coli* were dyed with crystal violet (0.3 mL) for 1 min, treated with iodine solution (0.3 mL) for 1 min, washed with 95% ethanol, and finally dyed with safranin O (0.3 mL) solution. The pictures of the adhered *E. coli* were taken by using a SEM and the number of adhered *E. coli* was counted in three different areas (20 μm × 23 μm) and averaged.

2.7. Application to oxygen sensor

An optical sensing membrane was prepared by immobilizing Ru-DPP, a fluorescence dye used for oxygen sensing on a quartz plate by the sol-gel method [15]. A 5 wt.% solution of copolymer-I (50 mg) containing MCA (2.5 mg, 5 wt.% of copolymer) in CHCl₃ (1 mL) was cast on an optical sensing membrane, and the coated film was cured at 80 °C for 20 min. The optical sensing membrane, which was coated with the cured

copolymer film, was put into a sample adaptor in a specially devised fiber optic oxygen sensing system which was connected to a fluorescence spectrophotometer. The changes in the fluorescence intensity of the immobilized Ru-DPP on the sensing membrane were observed at 480 nm (excitation wavelength) and 590 nm (emission wavelength) as a function of the O₂ concentration in an Ar atmosphere.

3. Results and discussion

3.1. Polymerization

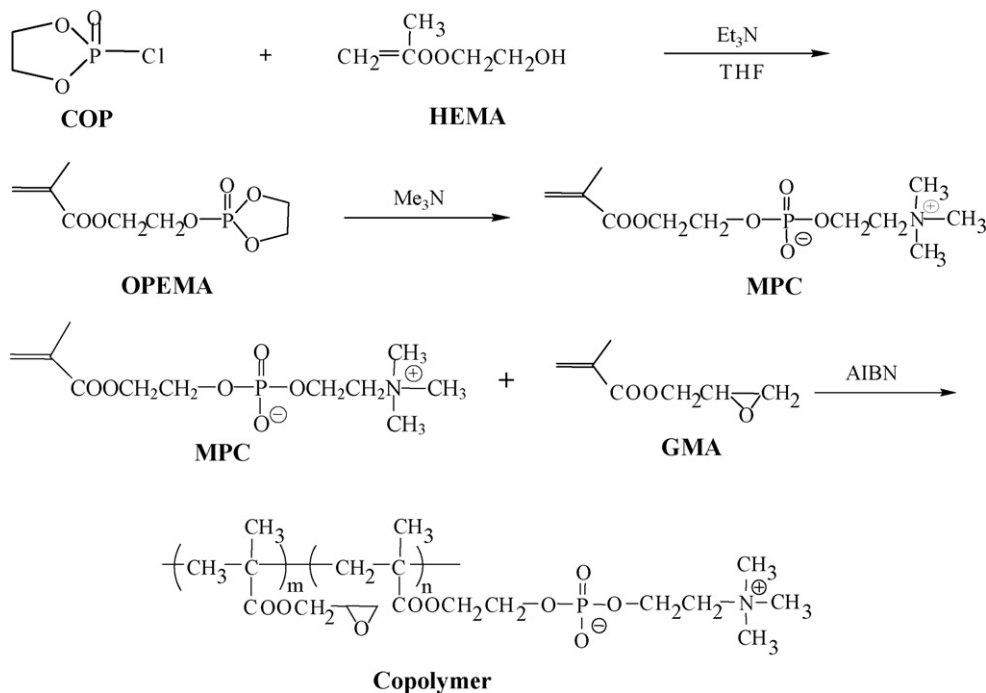
The preparation of the monomers and their polymerization are performed as shown in Scheme 1. OPEMA was synthesized from the reaction of HEMA and COP in the presence of triethylamine. A viscous liquid was obtained after the removal of triethylammonium chloride from the reaction mixture by double filtrations. The reaction temperature should be maintained in the range of –20 to –30 °C, since COP is very reactive and the reaction generated a large amount of heat. MPC, a monomer containing the PC group was synthesized from the reaction of OPEMA with an excess amount of trimethylamine in acetonitrile. The reaction should be carried out under anhydrous conditions.

Polymerization was carried out with GMA, a monomer containing an epoxy group, and MPC in the presence of AIBN. The copolymer was soluble in CHCl₃, but insoluble in THF, alcohol, and water. Copolymer III, which contains 13.0 mol.% of MPC units, became insoluble in chloroform when the polymer was stored at room temperature. Therefore, copolymer III was stored in the form of a 10 wt.% solution in chloroform.

Table 1 shows reaction conditions and physical properties of the polymers. The concentration of MPC units found in the copolymers by XPS was lower than that in feed. This seems to be due to the reactivity of GMA being higher than that of MPC. The number average molecular weight of the copolymers was in the range of 1.0–1.2 × 10⁵. No clear T_g was observed in the DSC measurements.

The copolymers have a good film forming properties. A clear and transparent film was obtained with copolymer-I after curing. Fig. 1 shows the UV–vis transmittance spectra of the PGMA and cured copolymer-I films on a quartz plate. The PGMA and copolymer-I films were transparent at the wavelength of more than 250 and 300 nm, respectively. The copolymer films were transparent in the visible region. Therefore, this result indicates that the cured copolymer films would not interfere with the fluorescence spectrum of Ru-DPP, an O₂ sensing compound, which was coated on a sensing membrane, since the fluorescence spectrum of Ru-DPP ranged from 400 to 700 nm.

Adhesion is one of the most important properties of the coated film. The adhesion of the cured copolymer films on a glass plate was tested by using a cross-hatch cutter. The evaluation of the adhesion by the ASTM cross-cut tape test indicated that the cured copolymer films belong to classification 5B, which means that the edge of the cuts were completely smooth and none of the square of the lattice were detached. Thus, the cured copolymer films had excellent adhesion properties.



Scheme 1.

3.2. Cross-linking reaction

The cross-linking reaction of the (epoxy) copolymers was studied in order to improve the physical properties of the coated polymer films. Fig. 2 shows the changes of the insoluble fraction of the copolymer films on a silicon wafer as a function of the heating temperature. The insoluble fraction of the PGMA film was less than 10% up to a heating temperature of 140 °C, whereas that of the copolymer films increased with increasing the amount of MPC units in the copolymer. This seems to be due to the catalytic effect of the quaternary ammonium groups in the MPC unit, since it was reported that quaternary ammonium compounds can be used as epoxy curing catalysts [16].

The cross-linking reaction of the epoxy groups was catalyzed by the addition of an amine. The effect of a diamine on the insoluble fraction of the copolymer films was studied, in order to increase their cross-linking efficiency. Fig. 3 shows the insoluble

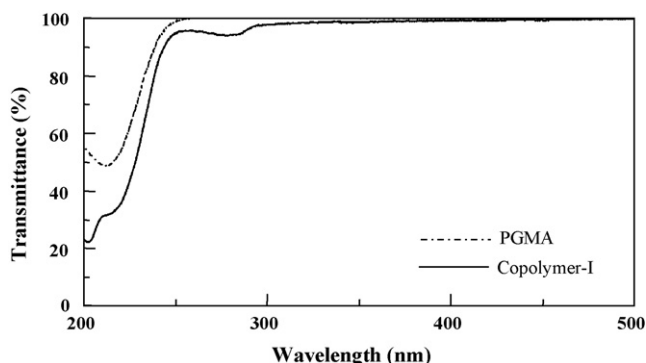


Fig. 1. The UV-vis transmittance spectra of the PGMA and copolymer-I films on the quartz plate.

fraction of the copolymer-I films containing a diamine on a silicon wafer as a function of the heating temperature. The insoluble fraction was effectively increased by the addition of the diamine, and the aliphatic diamine (MCA) was found to be far more effective than the aromatic diamine (MAN).

Generally, the cross-linking reaction of the epoxy polymers took place at a relatively high temperature and their cross-linking

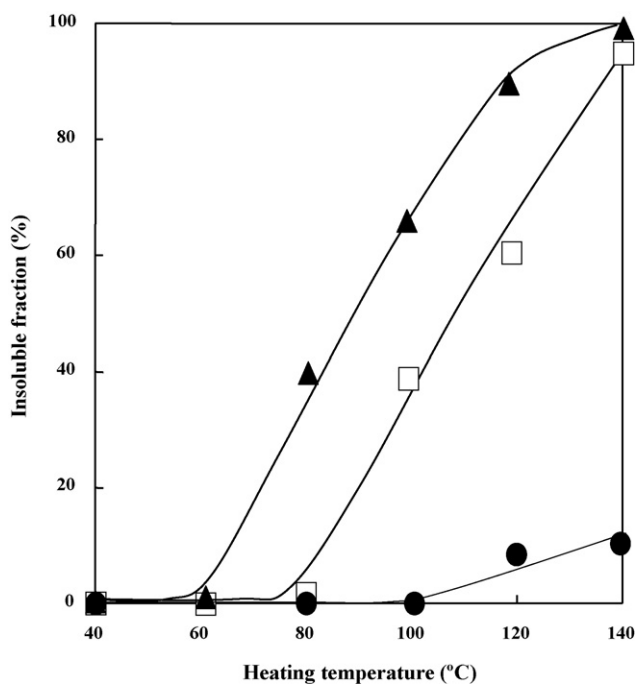


Fig. 2. The changes of the insoluble fraction of the copolymer films on a silicon wafer as a function of the heating temperature: PGMA (●), copolymer-I (□), copolymer-II (▲). The cured films were dipped in CHCl_3 for 10 min.

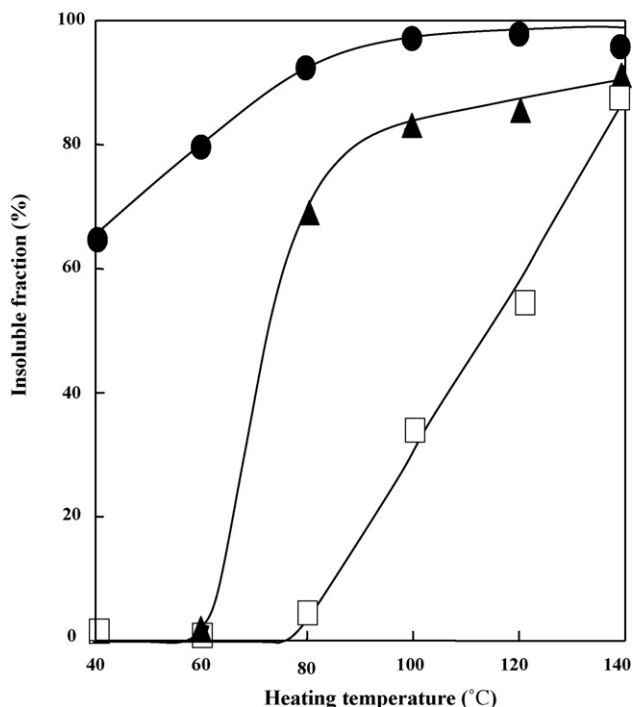


Fig. 3. The changes of the insoluble fraction of the copolymer-I films (□) containing MCA (●) and MDA (▲) on the silicon wafer as a function of heating temperature.

efficiency was low at temperatures below 140 °C. However, the above result indicates that the cross-linking reaction of the epoxy copolymers took place at a relatively low temperature (>80 °C) with a high efficiency (>90%) due to the addition of an aliphatic diamine. This result suggests that the epoxy copolymers prepared in this study would be useful as an anti-fouling coating material for plastic substrates, such as plastic optical fiber, which needed low temperature curing.

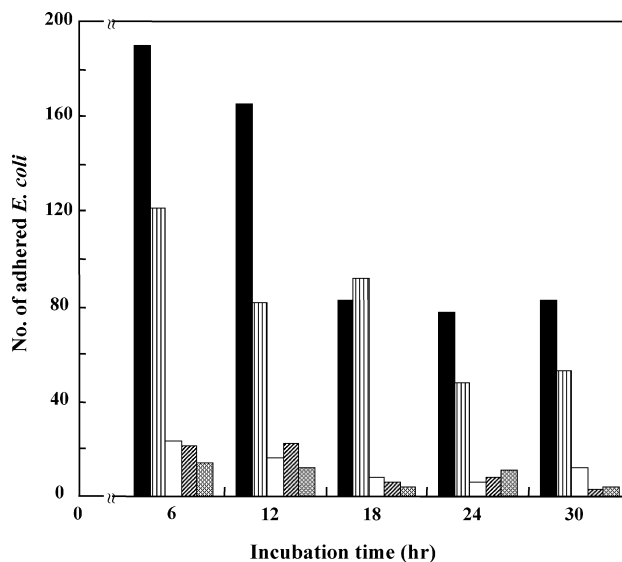


Fig. 5. The number of *E. coli* adhered on the glass plate (■), PGMA (▨), and the cured copolymer-I (□), copolymer-II (▧), and copolymer-III (▩) films as a function of the incubation time in an area of 20 μm × 23 μm.

3.3. Anti-fouling effect

The anti-fouling effect was observed by incubating *E. coli* on the cured copolymer films and counting the number of adhered *E. coli*. Fig. 4 shows the SEM pictures of the *E. coli* adhered on the glass plate, PGMA, and the cured copolymer films. A number of *E. coli* were adhered on the glass or PGMA films. However, few *E. coli* were found to be adhered on the cured copolymer films. It is likely that the anti-fouling effect of the cured copolymer films was not affected by the amount of MPC units in the copolymer.

Fig. 5 shows the number of *E. coli* adhered on various substrates as a function of the incubation time in an area of

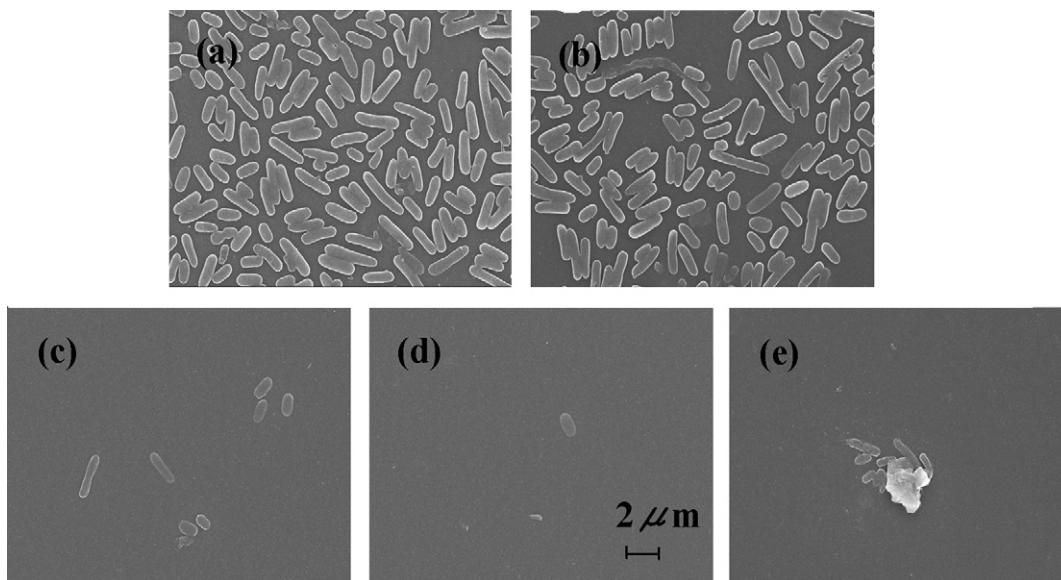
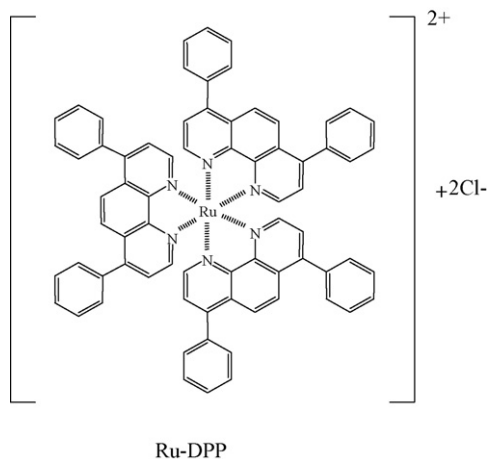


Fig. 4. The SEM pictures of the *E. coli* adhered on (a) a glass plate, (b) PGMA, and the cured (c) copolymer-I, (d) copolymer-II, and (e) copolymer-III films on the glass plate. *E. coli* was incubated at 37 °C for 6 h with 180 rpm in a shaking incubator.



Scheme 2.

20 μm \times 23 μm . A number of *E. coli* were adhered on the glass plate and PGMA films, but few *E. coli* were found on the cured copolymer films. The number of adhered *E. coli* reached a maximum at an incubation time of 6 h, and then gradually decreased. This result indicates that the epoxy copolymers containing PC groups have a high anti-fouling effect.

3.4. Application to optical oxygen sensor

The feasibility of the epoxy copolymers to be used as a coating material for the optical oxygen sensor was examined. Scheme 2 shows the chemical structure of Ru-DPP, a ruthenium(II) complex used as a dye for optical oxygen sensors, and Scheme 3 shows an optical sensing system used for the measurement of the O_2 concentration. An epoxy coated optical oxygen sensing membrane consists of two layers on a quartz plate. Ru-DPP was immobilized on a glass plate by the sol-gel method, and copolymer-I was coated on the Ru-DPP layer and cured.

The epoxy coated optical oxygen sensing membrane was put into the sample holder of the optical O_2 sensing system. Excitation light was irradiated onto the Ru-DPP contained in the optical

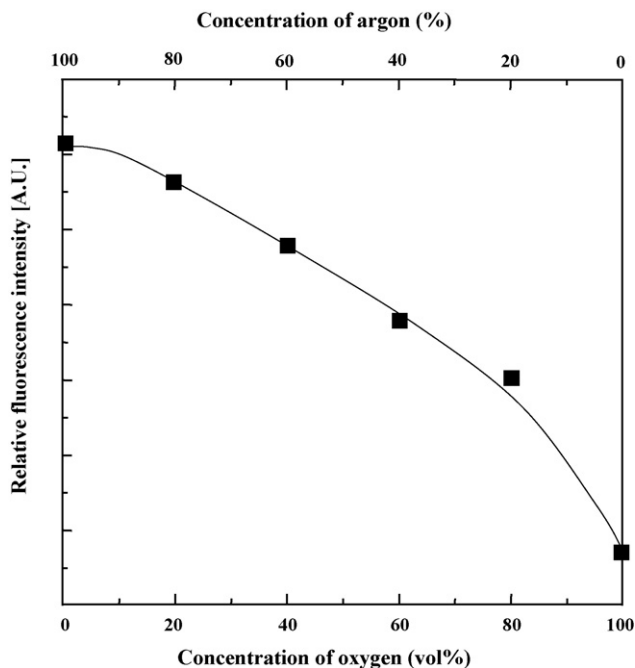
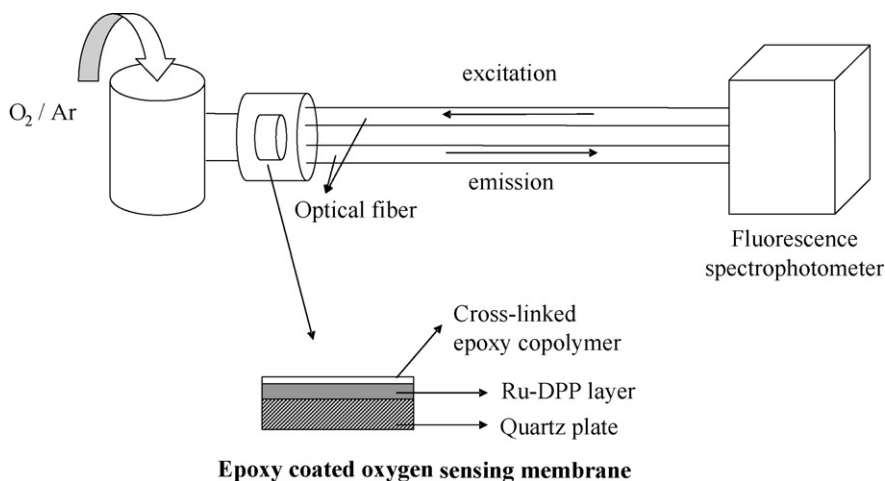


Fig. 6. The changes in the fluorescence intensity at 590 nm of Ru-DPP layer in the optical sensing membrane coated with cured copolymer I, as a function O_2 concentration at the excitation wavelength of 480 nm.

sensing membrane through an optical fiber from the light source of a fluorescence spectrophotometer. The fluorescent light emitting from the Ru-DPP layer was guided to the detector of the fluorescence spectrophotometer through an another optical fiber.

Fig. 6 shows the changes in the fluorescence intensity at 590 nm of the Ru-DPP layer in the optical biosensor membrane, coated with cured copolymer I, as a function of the O_2 concentration. The fluorescence intensity decreased linearly with increasing O_2 concentration. This is due to the dynamic quenching of Ru-DPP fluorescence by the oxygen molecule. This result indicates that the cured epoxy copolymer coating does not interfere with the performance of the optical oxygen sensing membrane.



Scheme 3.

The quenching response of the polymer based oxygen sensors depends on the polymer matrix as well as indicator dyes. Generally, for dyes in the fluid solution in the presence of a quencher Q, the reduction in photoluminescence intensity (I) normally follows the Stern-Volmer (SV) equation:

$$\frac{I_0}{I} = 1 + K_q \tau_0 [Q]$$

where $[Q]$ is the molar concentration of quencher, K_q the second-order quenching rate constant, τ the excited state lifetime, and the subscript 0 refers to the values in the absence of quencher. When the quencher is introduced into the system as a gas, one commonly measures the intensity as a function of external partial pressure P_{O_2} . For oxygen sensors that are based on polymer films, it is often convenient to express the SV equation in a more phenomenological form [17]:

$$\frac{I_0}{I} = 1 + K_{SV} P_{O_2}$$

where the SV constant K_{SV} contains all of the constants that relate oxygen partial pressure (P_{O_2}) to the changes in intensity and lifetime.

Fig. 7 shows the SV plot of the luminescence intensity ratios of immobilized and epoxy coated Ru-DPP on a glass plate as a function of partial pressure of oxygen. The typical SV plot shows a very good linearity over the entire range of oxygen partial pressure suggesting that the dye exists in a single uniform quenching environment even though the dye was immobilized by the sol-gel method and coated with epoxy resin.

Values of K_{SV} vary among probes and higher values of K_{SV} indicate that the dye is more sensitive to oxygen quenching. The measured K_{SV} value was $1.47 \times 10^{-3} \text{ Torr}^{-1}$. This value is lower than that in liquid solution (0.12 Torr^{-1} in absolute ethanol at 25°C), but comparable to that in homogeneous polymer matrix

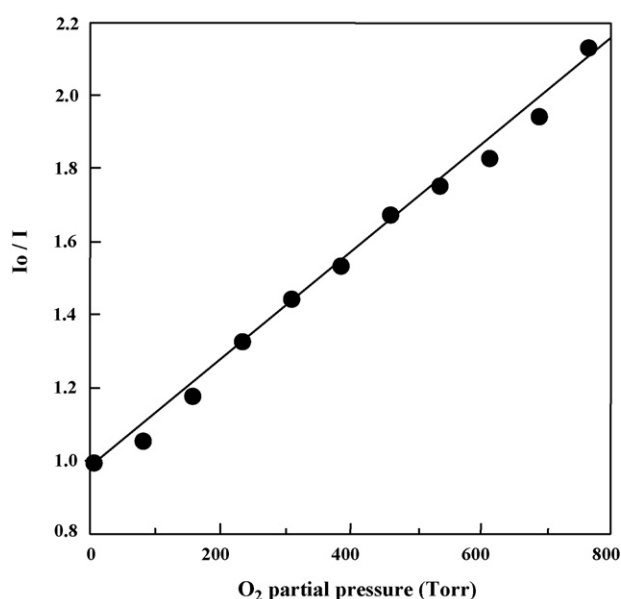


Fig. 7. Stern-Volmer plot of Ru-DPP at 480 nm (ex)/590 nm (em) as a function of O_2 partial pressure. Ru-DPP was immobilized on a glass plate by sol-gel method and cured after coating with copolymer-I.

($3.6 \times 10^{-3} \text{ Torr}^{-1}$ in polystyrene) [18]. These results indicate that the anti-fouling epoxy coating does not affect the performance of the optical oxygen sensing membrane.

4. Conclusion

The experimental results clearly demonstrate that the epoxy copolymers containing PC groups are very useful as a coating material for optical sensing membranes. The cured epoxy copolymers constitute suitable coating materials for the optical oxygen sensing membrane due to their high transparency, excellent anti-fouling effect, good physical properties, and lack of interference with the performance of the optical biosensor. Furthermore, it is very likely that the epoxy copolymers can be applied to various anti-fouling coating materials which need high chemical resistance and good mechanical properties.

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Biographies

Kyu Ho Chae received his BS degree from Seoul National University, Korea in 1972, and his MS and PhD degree in the area of organic photochemistry from Korea Advanced Institute of Technology (KAIST) in 1975 and 1979, respectively. He was a post-doctorial fellow at Johns Hopkins University, USA in 1982–1983. He has been a member of the Faculty of the Applied Chemistry Department, Chonnam National University, Korea since 1979, where he is now a full professor since 1990. His research interests lie in the area of photosensitive and photo-functional polymers, and polymer materials for bio-photonics applications.

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