

Synthesis of Copolymer Beads with Various Phenolic Derivatives Attached via Different Linkages and Their Antioxidation Activity

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ABSTRACT: Macroporous copolymer beads with various phenolic derivatives introduced via three types of linkages—amide, methylene, and ether—were prepared from chloromethyl styrene/tetra(ethylene glycol) dimethacrylate copolymer beads. The antioxidation activity of these phenolic copolymer beads was investigated by the measurement of the inhibition activity against the hydroperoxidation of 1,4-dioxane. The phenolic copolymer beads with the dihydroxybenzene moiety exhibited the highest antioxidation activity, and the antioxidation activity of methylene- or ether-linked phenolic copolymer beads was higher

than that of amide-linked copolymer beads. Thus, the antioxidation activity of the phenolic copolymer beads was affected by not only the kinds of phenolic moieties attached but also the type of linkage group. In addition, the swelling of the copolymer beads in an organic solvent was greatly affected by the linkage type of the phenolic copolymer beads. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1031–1038, 2008

Key words: antioxidants; functionalization of polymers; macroporous polymers

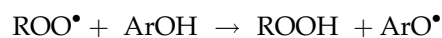
INTRODUCTION

Many kinds of peroxides are known to be influential in industrial chemistry or in our lives. For example, peroxides, such as hydrogen peroxide and benzoyl peroxide, are used as sterilizers or initiators for polymerization and so forth.¹ It is also known that most aliphatic ethers contain small amounts of their hydroperoxides, which are formed by light irradiation in the presence of oxygen during storage.^{2,3} Moreover, it is known that fats and oils are subjected to the polymerization or generation of lipid hydroperoxides by light irradiation in the presence of oxygen during storage. These phenomena mean that fats or oils are degraded by oxidation. It has been reported that the deterioration of organic compounds due to oxidation occurs via the formation of peroxide radicals.⁴ Phenolic compounds, such as catechol, hydroquinone, and methoxyphenol, have been reported to act as inhibitors of radical chain reactions during the autoxidation of such organic compounds.^{5–10} Furthermore, many researchers have reported on polymeric antioxidants that have antimigration and long-term application advantages.^{11–14} In almost all of these reports, polymeric antioxidants

were synthesized by the introduction of low-molecular-weight antioxidants onto the polymer side chains, and they were used as antioxidants and light stabilizers for plastic products.

We have been studying polymeric antioxidants prepared from porous styrene beads. Previously, we reported on porous chloromethyl styrene (CMS)/tetra(ethylene glycol) dimethacrylate (TEGDM) copolymer beads with phenolic derivatives attached via an amide linkage. They exhibited inhibition activity against the photogeneration of 1,4-dioxane hydroperoxide in the presence of oxygen by UV irradiation.¹²

To date, many researchers have studied the antioxidation mechanism of phenolic compounds from theoretical or experimental points of view.^{15–17} Bolland and Have¹⁸ reported that the antioxidant properties of phenols are due to their ability to quench the chain carrying peroxy radicals of the substrate by transfer of the hydroxyl hydrogen to form hydroperoxides as follows:



where ROO^\bullet denotes the peroxy radical and ArOH represents the antioxidant phenol.

On the other hand, in 1988, Scott¹⁹ reported that electron-donating groups in the aromatic nuclei of phenolic compounds increase antioxidant activity, whereas electron-withdrawing groups decrease it, and substituents that delocalize the electron in the

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aryloxy or arylaminy radicals increase the antioxidant activity.

Brigati et al.²⁰ determined the bond dissociation enthalpies of O—H bonds in several phenolic compounds containing electron-withdrawing or electron-donating substituents in the para position of 2,6-di-*tert*-butyl phenols by means of the electron paramagnetic resonance (EPR) radical equilibration technique. Moreover, they reported that electron-withdrawing substituents such as —NO₂ and —COOH induce an increase in the bond dissociation enthalpy of the O—H bond. Thus, they decrease the antioxidant activity of phenols, whereas electron-donating substituents such as —CH₃ and —OCH₃ in the para position have the opposite effect.

In these reports, many researchers have indicated that the influence of the number of phenolic hydroxy groups on the benzene nucleus is smaller than the influence of the structure of the phenolic compound on the antioxidation ability.^{21–26} In our previous studies,^{27,28} copolymer beads containing various phenolic derivatives were synthesized, and the radical quenching abilities were evaluated. In the results, the radical quenching abilities were much affected by the position of the hydroxy group and the type of linkage between the phenolic moiety and polymer matrices.

In this study, to develop antioxidant copolymer beads with higher antioxidation activity, we synthesized CMS–TEGDM copolymer beads containing various phenolic derivatives attached via electron-donating groups (methylene or ether linkages) instead of an electron-withdrawing group (amide linkage), and we investigated the antioxidation activity of the copolymer beads by measuring the inhibition activity against the generation of 1,4-dioxane hydroperoxide. In addition, the effect of the chemical structure of the copolymer beads with phenolic derivatives attached via different types of linkages on the antioxidation activity is discussed.

EXPERIMENTAL

Materials

CMS was purchased from Tokyo Kasei Co. (Tokyo, Japan) and was purified by the elimination of inhibi-

tors via passage through an activated alumina column. TEGDM as a crosslinking reagent was purchased from Sigma-Aldrich Japan Co. (Tokyo, Japan) and used without further purification. α,α' -Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. *N,N*-Dimethylformamide (DMF) was purchased from Wako Chemical Co. (Osaka, Japan) and purified by distillation under reduced pressure (50°C/12 mmHg) after drying overnight in the presence of a molecular sieve (Wako Chemical). 1,4-dioxane (for HPLC grade) was purchased from Wako Chemical and passed through an activated alumina column to eliminate hydroperoxides. Other chemical compounds were reagent-grade and were used as received.

Preparation of macroporous TEGDM–CMS (RTC) copolymer beads

RTC copolymer beads were prepared by suspension copolymerization in water with cyclohexane as a porogen as described in a previous report.²⁹ A solution of CMS (0.34 mol) and TEGDM (0.038 mol), cyclohexane (72 cm³, 120 vol % with respect to the total monomers), and AIBN (5.3 mmol) as an initiator were poured into a glass reaction flask with 500 cm³ of a 0.2% (w/v) hydroxyethyl cellulose aqueous solution. The mixture was stirred until the monomer solution was dispersed as fine droplets. After sealing, the flask was heated to 70°C, and the mixture reacted with stirring for 4.5 h (Fig. 1). After polymerization, the product was filtered off, washed with hot (80°C) water several times, and immersed in methanol overnight. After drying, copolymer beads with a favorable diameter (32–60 mesh) were selected with a screen mesh. The surface area and mean pore diameters were measured with a Micromeritics 2010C automatic analyzer (Norcross, GA) equipped with a high-stability, 1-Torr pressure transducer. The chloromethyl group content in the copolymer beads was determined by the measurement of the chlorine content by the combustion method.³⁰

Introduction of phenolic derivatives into the copolymer beads

Various phenolic derivatives were attached onto RTC via different linkages with the methods

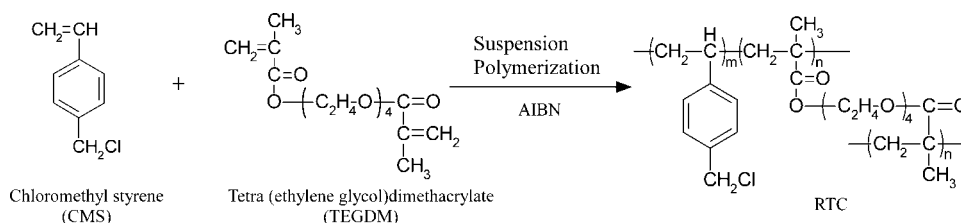


Figure 1 Synthesis of macroporous copolymer beads with chloromethyl groups.

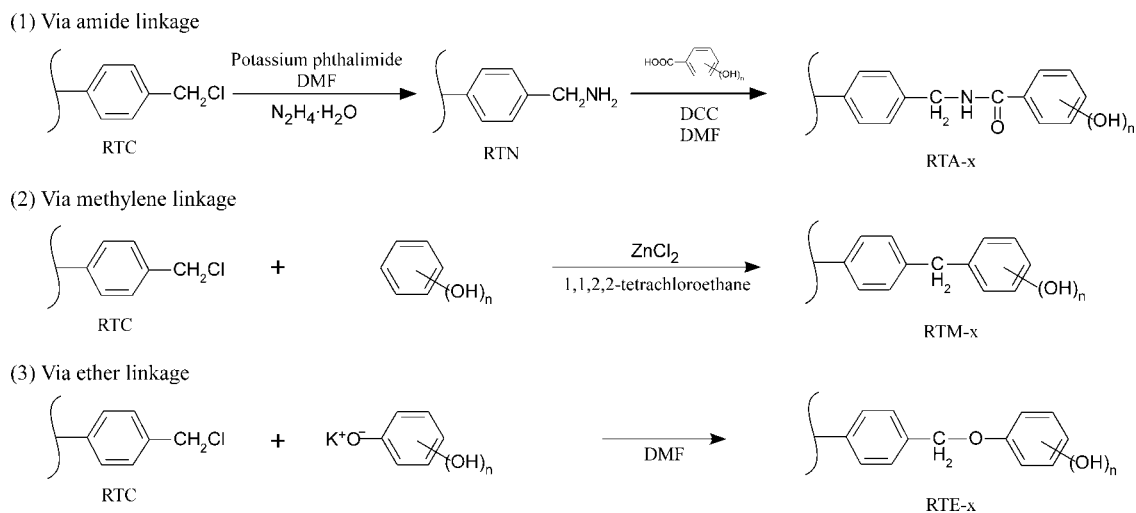


Figure 2 Synthesis of copolymer beads with phenolic derivatives attached via three types of linkages.

described next. The contact surface of porous copolymer beads exerts a large influence on the activity. Although introducing functional group onto porous polymer beads while maintaining the microstructure is difficult, to prevent the collapse of the porous structure, the modification was conducted under mild conditions and with a lower number of steps.

Amide linkage²⁹

Macroporous copolymer beads containing phenolic derivatives attached via an amide linkage were prepared by a two-step reaction [Fig. 2(a)]. RTC (10 g) and potassium phthalimide (0.054 mol; 2.5 molar ratio with respect to chloromethyl groups in the copolymer beads) were stirred in anhydrous DMF at 100°C for 5 h. The resulting beads were filtered off and washed with deionized water and ethanol. After drying, the copolymer beads were refluxed in a hydrazine monohydrate ethanol solution (ethanol/hydrazine monohydrate = 4/1 v/v) at 100°C for 6 h. After refluxing, the copolymer beads were immersed in a 2N NaOH aqueous solution at room temperature for 2 h, washed several times with ethanol and deionized water, and then washed by Soxhlet extraction with methanol for 12 h. After drying, copolymer beads containing benzylamino groups (RTN) were obtained. The introduction of benzylamino groups was confirmed by IR spectrometry and by the introduction of nitrogen atoms as determined by elemental analysis.

Next, the RTN copolymer beads (2 g) and benzoic acid derivatives with phenolic hydroxy groups [4-hydroxybenzoic acid (1), 3,5-dihydroxybenzoic acid (2), 3,4-dihydroxybenzoic acid (3), 2,4-dihydroxybenzoic acid (4), or 3,4,5-trihydroxybenzoic acid (5); 1.2 molar ratio with respect to the benzylamino groups] were added to 30 cm³ of DMF and stirred at 0–5°C for about 30 min. An amount of *N,N'*-dicyclohexyl-

carbodiimide (DCC) equal to that of the phenolic derivatives dissolved in a portion of DMF was added dropwise to the aforementioned mixed solution over a period of 3 min at 0–5°C. After the addition, the mixture was stirred at 0–5°C for 2 h, then at 20°C for 2 h, and further at 60°C for 4 h. After the removal of urea derivatives, the copolymer beads were filtered off and washed with methanol several times and then were washed by Soxhlet extraction with methanol for 24 h. After drying, copolymer beads containing phenolic derivatives [RTA-*x* (*x* = 1–5)] were obtained.

The content of phenolic derivatives introduced onto the copolymer beads was estimated by the measurement of the content of unreacted benzylamino groups. That is, the content of phenolic derivatives attached to the copolymer beads was calculated from the difference in the anion-exchange capacity of the copolymer beads before and after the reaction. The anion-exchange capacity²⁹ of the copolymer beads was measured as follows.

Copolymer beads (0.25 g) were placed in an Erlenmeyer flask, and 50 cm³ of a 0.1 mol/dm³ HCl solution was added to the flask. The mixture was shaken at 30°C for 15 h, and the copolymer beads were filtered off. A 2 mol/dm³ NaHCO₃ solution and 5 cm³ of a 2% (w/v) starch solution were added to 10 cm³ of the supernatant. The anion-exchange capacity was then determined by titration of chloride ions in the supernatant with a 0.1 mol/dm³ AgNO₃ solution with fluorescein as an indicator. The obtained value of the anion-exchange capacity indicated the benzylamino group content in the copolymer beads.

Methylene linkage^{31,32}

Immobilization of phenol derivatives via methylene groups was carried out by a Friedel–Crafts reaction

as described later [Fig. 2(b)]. 1,4-Hydroxybenzene (**6**; 2.0 molar ratio with respect to chloromethyl groups) was dissolved in 50 cm³ of 1,1,2,2-tetrachloroethane, and RTC (2 g) and a fine powder of zinc chloride (at an equal molar ratio to **6**) were dispersed in the solution. The mixture was stirred at 0°C for 1 h, at 70°C for 1.5 h, and then at 100°C for 6 h. After the reaction, the copolymer beads were filtered off, washed with acetone and deionized water several times, and then washed by Soxhlet extraction with acetone for 24 h. After drying, copolymer beads with a phenol moiety attached by a methylene linkage (RTM-6) were obtained.

Ether linkage³³

The scheme of the synthesis of copolymer beads with **6** or 1,3,5-trihydroxybenzene (**7**) immobilized via ether linkages is shown in Figure 2(c). The monopotassium salt of **6** or **7** was prepared by treatment with potassium hydroxide (1/2 molar ratio with respect to **6** and 1/3 molar ratio with respect to **7**) in DMF at room temperature under stirring. RTC (2 g) and the monopotassium salt were added to 30 cm³ of DMF and stirred at 110°C for 24 h. After the reaction, the copolymer beads were treated with a 1 mol/dm³ HCl solution to completely convert the attached phenolic moiety to the H type and then washed by Soxhlet extraction with methanol for 24 h. After drying, copolymer beads with a phenolic moiety attached by an ether linkage (RTE-6 and RTE-7) were obtained. The phenolic moiety content in the copolymer beads was estimated from the difference in the chloromethyl group contents before and after the reaction.

Measurement of the inhibition activity of the copolymer beads against the generation of 1,4-dioxane hydroperoxide

Dried copolymer beads (1.0 g) were placed in a quartz test tube, and 10 cm³ of purified 1,4-dioxane was added. After oxygen was bubbled into the test tube for 5 min in the dark at 25°C, the tube was sealed, and UV light (<380 nm, ca. 5 mW/cm²; high-pressure mercury lamp, SHL-100UVQ2, Toshiba Co., Tokyo, Japan) was irradiated onto the tube from a distance of 20 cm with magnetic stirring. The hydroperoxide content of 1,4-dioxane generated was determined by iodometry as follows.¹⁸ The copolymer beads were removed by decantation, and a 0.12 mol/dm³ FeCl₃ acetic acid solution and 0.2 cm³ saturated KI aqueous solution were added to 5 cm³ of 1,4-dioxane containing hydroperoxide under an N₂ atmosphere. Deionized water (10 cm³) was added and titrated with a 0.02 mol/dm³ sodium thiosulfate solution with a 1 wt % starch solution as an indica-

tor. A blank test was performed with the same procedure with purified 1,4-dioxane only. The concentration of 1,4-dioxane hydroperoxide was calculated as follows:

Concentration of hydroperoxide in

$$1,4\text{-dioxane (mmol/dm}^3) = [(v - b) \times c] / (V \times 2) \quad (1)$$

where v is the volume of the titrant added to the 1,4-dioxane containing hydroperoxide (dm³), b is the volume of the titrant for the blank test (dm³), c is the concentration of the titrant (mmol/dm³), and V is the volume of titrated 1,4-dioxane (dm³).

The inhibition ratio was calculated from the concentration of hydroperoxide generated as follows:

$$\text{Inhibition ratio (\%)} = [C]_{R6} / [C]_{B6} \times 100 \quad (2)$$

where $[C]_{R6}$ is the concentration of hydroperoxide in the presence of the copolymer at 6 h and $[C]_{B6}$ is the concentration of hydroperoxide without copolymers at 6 h.

Measurement of the swelling ratio of copolymer beads in 1,4-dioxane

The bulk volume of 1 g of dried copolymer beads was measured in a 10-cm³ glass cylinder, and then 5 cm³ of 1,4-dioxane was poured into the cylinder. The bulk volume of the copolymer beads in 1,4-dioxane was measured at intervals of several hours at 25°C. The swelling ratio was calculated as follows:

$$\text{Swelling ratio} = V_w / V_d \quad (3)$$

where V_w is the bulk volume (cm³) of wet copolymer beads in 1,4-dioxane and V_d is the bulk volume (cm³) of dried copolymer beads.

RESULTS AND DISCUSSION

Preparation of the copolymer beads with phenolic moieties attached via different linkages

Macroporous copolymer beads (RTC; CMS/TEGDM molar ratio in the feed = 90 : 10) were prepared by the suspension copolymerization of CMS and TEGDM with AIBN as an initiator. RTC, which was obtained with 120 vol % porogen (with respect to the monomers), had a chlorine content of about 5.0 mmol/g. RTC had a 1.1 cm³/g pore volume, a 500-Å average pore radius, and a 30 m²/g specific surface area.

The anion-exchange capacity of the aminated resin (RTN) was 4.8 mmol/g. The anion-exchange capacity was appropriate for the value calculated from the nitrogen content with elemental analysis

TABLE I
Content of Phenolic Derivatives in Copolymer Beads Attached via Three Types of Linkages

Copolymer	Bond type	Attached phenol derivative ^a	Conversion (%)	Content of phenolic moiety (mmol/g)
RTA-1	Amide	1	87.5	2.8
RTA-2	↑	2	80.9	2.5
RTA-3	↑	3	93.2	2.8
RTA-4	↑	4	77.9	2.5
RTA-5	↑	5	83.2	2.5
RTM-6	Methylene	6	86.8	3.2
RTE-6	Ether	6	86.8	3.3
RTE-7	↑	7	66.2	2.6

^a Shown in Figure 3.

(within the experimental error). These results indicate that the molar ratio of CMS to TEGDM of the copolymer beads was 88:12, and about 88% of chloromethyl groups in RTC were converted to benzyl amino groups.

Amide linkage

The introduction of phenolic derivatives was brought about by the reaction of benzylamino groups in RTN with carboxyl groups in various benzoic acids containing phenolic hydroxy groups (1–5). The content of the phenolic moiety attached to the copolymer beads was estimated by the change in the anion-exchange capacity of the copolymer beads before and after the modification. The conversion (%) of amino groups of RTN to amide groups is listed in Table I (see Fig. 3). The phenolic moiety content in RTA-*x* is shown in Table I together with the abbreviations for the copolymer beads obtained.

Methylene linkage

6 was introduced into the RTC copolymer beads via methylene linkages. The phenolic moiety content attached onto the copolymer beads was estimated by the difference in the chloromethyl group contents before and after the modification. The conversion ratio and phenolic moiety content in RTM-6 are shown in Table I. The phenolic moiety content was nearly equal to that of RTA-*x*.

Ether linkage

6 and **7** were introduced into the RTC copolymer beads via ether linkages. The conversion ratios and contents of the phenolic moiety in RTE-6 and RTE-7 are shown in Table I together with the abbreviations for the copolymer beads obtained. The conversion ratio of RTE-7 was lower than that of the other copolymers. Although we tried to increase the con-

version ratio by changing the reaction conditions, we could not obtain a higher value than the one shown in Table I. The reason for this low conversion ratio and a better method are still not clear. We used RTE-7 in our examination because a comparison of the inhibition ability was carried out with copolymer beads containing equimolar amounts of phenolic moieties.

The IR spectra of RTC, RTN, and copolymer beads with dihydroxybenzene moieties attached via different linkages (RTA-2, RTE-7, and RTM-6) are shown in Figure 4. Absorption bands at 1600 and 3370 cm^{-1} , assignable to $-\text{NH}_2$, were observed in RTN. Absorption bands at 1670 (amide I) and 1530 cm^{-1} (amide II) appeared in RTA-2. Absorption bands at 1470 cm^{-1} , assignable to $-\text{CH}_2\text{O}-$, were observed in RTE-7. In all modified copolymer beads, the absorption band at 1260 cm^{-1} due to $-\text{CH}_2\text{Cl}$ was reduced, and a broad absorption peak at 3300–3500 cm^{-1} due to phenolic hydroxy groups was observed. In the case of RTM-6, no new significant absorption band other than that for the absorption of phenolic hydroxy groups was observed. These results indicate

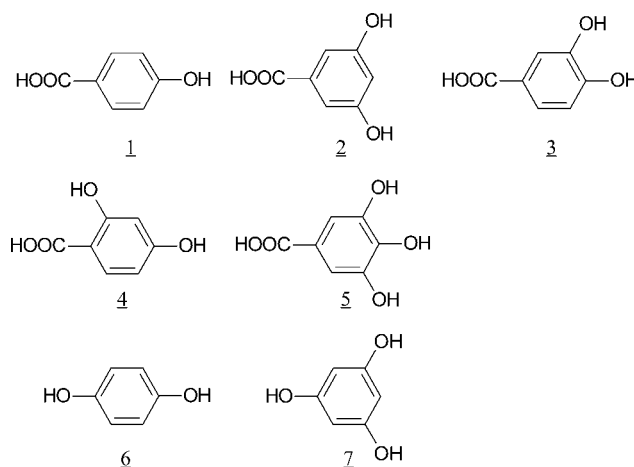


Figure 3 Structures of the introduced phenolic derivatives.

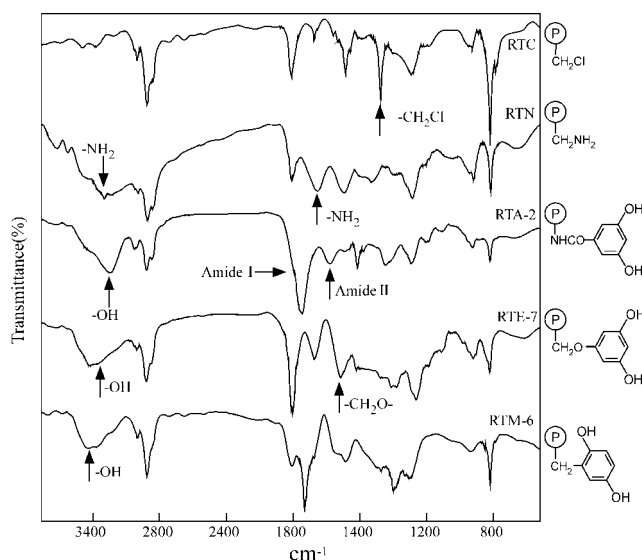


Figure 4 IR spectra of RTC, RTN, RTA-2, RTE-7, and RTM-6.

that the dihydroxybenzene moiety was attached via different linkages on the copolymer beads.

Inhibition against the generation of 1,4-dioxane hydroperoxide in the presence of copolymer beads with phenolic moieties attached via an amide linkage

Figure 5 shows the time line of the concentration of hydroperoxide generated in 1,4-dioxane in the absence or presence of copolymer beads with various phenolic moieties containing different numbers of phenolic hydroxy groups (RTA-1, RTA-2, and RTA-5). RTC with no phenolic derivatives had no inhibition activity. Figure 5 indicates that all the copolymer beads with phenolic moieties attached via amide linkages exhibited inhibition activity, and the

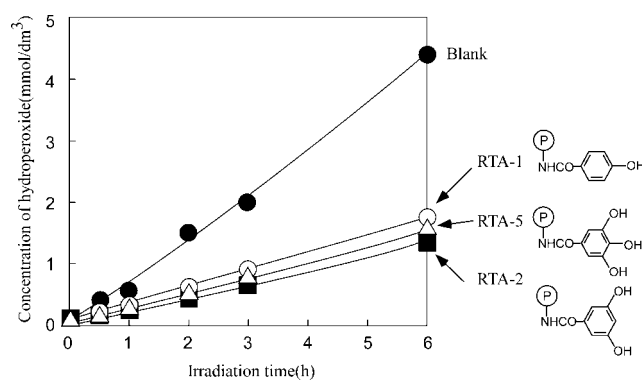


Figure 5 Inhibition against the generation of 1,4-dioxane hydroperoxide by UV irradiation with the copolymer beads with phenolic derivatives containing different numbers of phenolic hydroxy groups attached via amide linkages.

TABLE II
Inhibition Ratio of Copolymer Beads with Phenolic Derivatives

Copolymer	Bond type	Inhibition ratio (%)
RTA-1	Amide	60.2
RTA-2	↑	69.7
RTA-3	↑	80.0
RTA-4	↑	76.9
RTA-5	↑	65.3
RTM-6	Methylene	72.0
RTE-6	Ether	75.5
RTE-7	↑	79.5

order of inhibition activity of the copolymer beads was as follows:

$$\text{RTA-2} > \text{RTA-5} > \text{RTA-1}$$

The inhibition ratios of the copolymer beads were calculated from the results in Figure 5 and are shown in Table II. The inhibition ratio indicates that the inhibition ability of the copolymer beads and the order of the inhibition ratios were the same as those shown in the results in Figure 5. It was found that the order of magnitude of the inhibition activity of the copolymer beads did not correspond to the number of phenolic hydroxy groups in the attached phenolic moieties and that the copolymer beads with the dihydroxybenzene moiety exhibited the highest inhibition activity of the copolymer beads used.

Next, the inhibition activities of the copolymer beads with two phenolic hydroxy groups at different positions on the benzene nucleus were investigated. RTA-2, RTA-3, and RTA-4 were used in this experiment. The results are also shown in Table II. All these phenolic copolymer beads, which had two phenolic hydroxy groups at different positions on the benzene nucleus, exhibited high inhibition activity against the generation of 1,4-dioxane hydroperoxide. The order of the inhibition activity was as follows:

$$\text{RTA-3} > \text{RTA-4} > \text{RTA-2}$$

The reason for the differences between the inhibition activities of these copolymer beads is not obvious at present.

Inhibition activity of copolymer beads with phenolic moieties attached via different types of linkages

In 1988, Scott¹⁹ reported that electron-donating groups [methylene or methoxy (ether) groups] in aromatic nuclei increase antioxidant activity, whereas electron-withdrawing groups (amide or carboxyl groups) decrease it, and substituents that delocalize the elec-

tron of the aryloxy or arylaminy radicals increase the antioxidation activity. In our study, to investigate the effect of the type of linkage by which the phenolic moieties are attached to the copolymer on the antioxidation activity, we prepared copolymer beads with hydroxybenzene moieties attached via different linkages. In comparing the inhibition activities of RTA-1, which had an amide linkage, and RTE-6, which had an ether linkage, we found that the inhibition activity of RTE-6 was significantly higher than that of RTA-1 (Table II). This result indicates that electron-donating groups at the para position of the aromatic nucleus enhanced the inhibition activity against the generation of 1,4-dioxane hydroperoxide.

Next, the inhibition activities of phenolic copolymer beads with two phenolic hydroxy groups attached via three different types of linkages (amide, methylene, or ether bonds) were compared (Table II). Of the three types of copolymer beads used, only RTM-6 had two phenolic hydroxy groups that were at positions different from those in RTA-2 and RTE-7. Although it is preferable to prepare copolymer resins with methylene linkages in the same structure, this synthesis has not yet been achieved with RTC. It was found that the order of the inhibition activity of the copolymer beads was as follows:



Although the structures are not exactly the same and a strict comparison will not be achieved, this result also indicates that the antioxidation activity of RTC with dihydroxybenzyl groups attached via methylene or ether linkages is higher than that in which the groups are attached via an amide linkage. In other words, electron-donating groups in the aromatic nuclei enhanced the inhibition activity, whereas electron-withdrawing groups suppressed it.

Swelling ratios of copolymer beads with phenolic moieties attached via different types of linkages

During the measurements of the inhibition activities of the copolymer beads, it was apparent that the swelling ratios of the copolymers differed. It should be considered that the contact surface areas of the copolymers may have been changed by the swelling ratios. To investigate the effect of the swelling of the copolymer beads, the swelling ratios were measured in 1,4-dioxane. The results are shown in Figure 6. The swelling ratios of the copolymer beads increased with time and approached equilibrium in 30 min. The order of the magnitude of the swelling ratios was as follows:

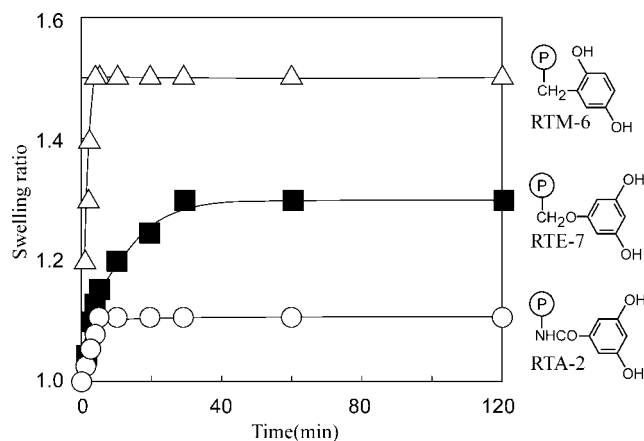


Figure 6 Time dependence of the swelling ratio of the copolymer beads with two phenolic hydroxy groups attached via different linkages in 1,4-dioxane.

A clear difference was observed between the swelling ratios of the three copolymer beads. This was due to the differences between the polar characters of the linkage groups. The lowest swelling ratio (for RTA-2 in 1,4-dioxane) was due to the higher polarity of the amide groups in comparison with the other types of linkages.

Thus, it has been found that the type of linkage group via which phenolic derivatives are attached to the copolymer greatly affects the swelling ratio of the copolymer beads in 1,4-dioxane, and a higher swelling ratio results in an increase in the inhibition activity for hydroperoxide generation.

We mentioned previously that copolymer beads with different phenolic moieties attached via amide linkages exhibited clear differences in inhibition activity against the generation of 1,4-dioxane hydroperoxide, as shown in Table II and Figure 5. In that case, the swelling ratios of the copolymer beads were almost the same, regardless of the kind of phenolic moiety attached. This indicates that the inhibition activities of copolymer beads with various phenolic moieties attached via amide linkages are affected by the kind of phenolic moiety attached.

CONCLUSIONS

Porous copolymer beads with various phenolic moieties attached via amide, methylene, or ether linkages were prepared from CMS/tetramethylene dimethacrylate copolymer beads. Of the copolymer beads with phenolic derivatives attached via amide linkages, copolymers containing two hydroxy groups showed the highest inhibition activity against the generation of 1,4-dioxane hydroperoxide. The copolymers with phenolic derivatives attached via methylene or ether linkages exhibited higher inhibition ability than the copolymer with an amide link-

age because of the electron-donating effect. It was found that the type of linkage group via which the phenolic moieties were attached affected not only the antioxidation activity but also the swelling ratio of the copolymer beads in 1,4-dioxane.

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