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ANTIOXIDANT ACTIVITY OF POLYMERS BEARING HINDERED PHENOLIC GROUPS

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ABSTRACT

Polyallylamine and polystyrene beads were allowed to react with 3,5-dibutyl-4-hydroxybenzaldehyde (BHB) and *t*-butylhydroquinone (BHQ), respectively. The polymeric products, poly-Aa(BHB) and poly-St(BHQ) beads worked functionally as antioxidants. The antioxidant effect of the polymer beads in the oxidation of linoleic acid suspensions was investigated by both the ferric thiocyanate and thiobarbituric acid methods. The antioxidant activity of poly-St(BHQ) beads was higher than that of poly-Aa(BHB) ones. It was found that the antioxidant activity for 2 mg of 3,5-di-*t*-butyl-4-hydroxytoluene (BHT) corresponded to that for 11.7 g of poly-Aa(BHB) and that of 0.6 g of poly-St(BHQ). The polymer beads are potential antioxidants for foods since their separation from a food oil after their use is easy because of their insolubility.

INTRODUCTION

A number of synthetic food additives have been used to keep food fresh. It is obviously better for us to cut down their use to avoid their possible toxicity. Food additives such as BHT and 3,5-di-*t*-butyl-4-hydroxyanisole (BHA) have been effective antioxidants for a long time. Since their carcinogenic activity has been reported [1], their use as food additives has decreased drastically.

If polymers bearing hindered phenyl groups are added to a food oil as antioxidants, they can be separated easily from the oil before use. Even if ingested, they could not act as toxicants because of their indigestible and unabsorbable nature. Polymer containing antioxidant active moieties are expected to be safe and effective antioxidants for foods.

In this regard, polyallylamine (poly-Aa) and polystyrene (poly-St) beads were allowed to react with 3,5-dibutyl-4-hydroxybenzaldehyde (BHB) and *t*-butylhydroquinone (BHQ) to obtain antioxidant polymers, poly-Aa(BHB) and poly-St(BHQ) beads, respectively. The polymer containing butylated hydroxyphenyl (BHP) groups showed antioxidant activity.

A number of chemists have been interested in applying functionalized polymers as polymer drugs [2], immobilized enzymes [3], and polymer catalysts [4, 5]. However, only limited attention has been given to functional polymers for foods. Kato and Nakano carried out radical copolymerization of β -vinyl-oxy(3,5-di-*t*-butyl-4-hydroxy)benzoate with comonomers such as styrene or maleic anhydride and reported the antioxidant activities of the products [6]. These copolymers were not used as food additives. Dawson synthesized poly(vinylamine) bearing azo-dye moieties [7] but could not succeed in supplying it as a food additive.

EXPERIMENTAL

Materials

Poly-Aa beads were prepared from polyallylamine hydrochloride beads obtained from Nitto Boseki Co. [8, 9] by neutralizing with aqueous NaOH solution, washing with water, and drying *in vacuo*. Poly-St beads (200–400 mesh) were commercially supplied by Eastman Kodak and used after washing with methanol and water. Commercial BHB, BHQ, and α -tocopherol (α -Toc) were used without further purification. Linoleic acid was distilled under vacuum before use. Partially chloromethylated polystyrene beads were synthesized from poly-St beads and chloromethyl methyl ether. After chloromethylation, the polymer beads were washed with methanol and water and dried *in vacuo*. The polymer beads contained 44.8 meq chlorinated units/g polymer.

Poly-St(BHQ) Beads

BHQ (3.99 g, 24.0 mmol) was allowed to react with sodium metal in 55 mL dry tetrahydrofuran (THF). To the THF solution of BHQ sodium salt, partially chloromethylated poly-St beads (10.0 g, 44.8 meq Cl) were added and stirred at 50°C for 18 hours. The beads were filtered off through a sintered glass funnel and washed with an acid aqueous solution (pH 6). The beads were washed further with water, methanol, and THF in a Soxhlet extractor and dried under *vacuum*.

Poly-Aa(BHB) Beads

To 200 mL of a chloroform solution of BHB (20.5 g, 87.5 mmol), Poly-Aa beads (10 g, 175 mmol) were added and stirred at room temperature for 22.5 hours. The beads were filtered off through a sintered glass funnel, washed with chloroform in a Soxhlet extractor until the filtrate became transparent, and dried *in vacuo*.

Measurements

Visible absorption spectra were measured on a Hitachi Model 200-10 spectrophotometer. Infrared spectra were recorded by the KBr disk method on a Nicolet Model 5ZDX FT-IR spectrometer. Antioxidant activity was measured by the ferric thiocyanate and the thiobarbituric acid methods [10].

RESULTS AND DISCUSSION

Polymers Bearing Butylated Hydroxyphenyl Groups

Poly-Aa(BHB) beads were yellow and insoluble in organic solvents. The infrared spectrum of poly-Aa(BHB) had absorption bands at 1641 cm^{-1} for $\nu_{\text{C}=\text{N}}$, at 1607 cm^{-1} for $\nu_{\text{C}=\text{C}}$ of the phenyl rings, and at 3634 cm^{-1} for the monomeric —OH groups. Poly-St(BHQ) beads were pale yellow and insoluble in organic solvents. An absorption band at $3600\text{--}3700\text{ cm}^{-1}$ was attributed to monomeric hydroxy groups. The absorption bands at 1067 and 1264 cm^{-1} were due to the newly introduced ether groups.

Contents of butylated hydroxyphenyl groups in the polymers were determined from elemental analysis (C, H, and N) to be 1.5 meq/g poly-Aa(BHB) and 1.2 meq/g poly-St(BHQ), respectively. The antioxidant activities of poly-Aa(BHB) and poly-St(BHQ) beads were measured in ethanol-phosphate buffer solution including freshly distilled linoleic acid by the ferric thiocyanate and the thiobarbituric acid methods [10]. The antioxidative action of poly-Aa(BHB) and poly-St(BHQ) beads took place heterogeneously. In both cases of poly-Aa(BHB) and poly-St(BHQ) beads, the buffer solution of linoleic acid was transparent during the reaction in a manner similar to those of α -Toc and BHT. Figure 1 shows that the oxidation of linoleic acid was prevented with 0.1 g of the antioxidant polymer beads as well as with 2.0 mg of natural antioxidant, α -Toc.

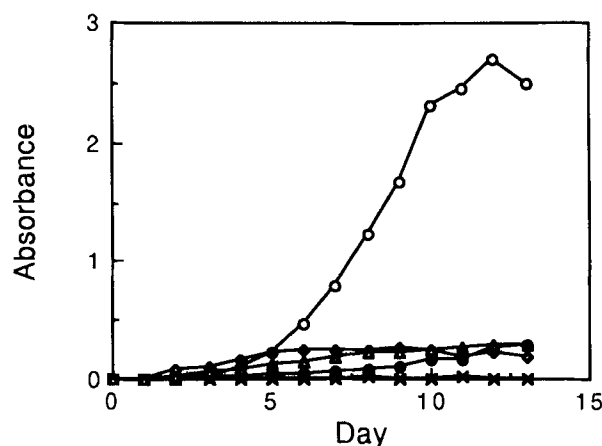


FIG. 1. Antioxidant effect of poly-Aa(BHB) and poly-St(BHQ) beads by the ferric thiocyanate method: (◇) poly-Aa(BHB), 0.1 g; (●) poly-St(BHQ), 0.1 g; (×) BHT, 2 mg; (△) α -Toc, 2 mg; and (○) control.

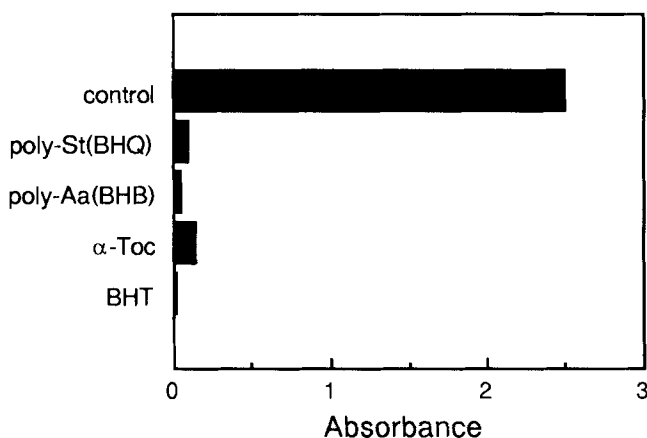


FIG. 2. Antioxidant effect of poly-Aa(BHB) and poly-St(BHQ) beads by the thiobarbituric acid method: poly-St(BHQ), 0.1 g; poly-Aa(BHB), 0.1 g; α -Toc, 2 mg; and BHT, 2 mg.

The antioxidant activities according to the thiobarbituric acid method (measured on the 13th day using 0.1 g of antioxidants polymer beads) were similar to those of the ferric thiocyanate method (Fig. 2). As the butylated hydroxy phenolic (BHP) group contents in α -Toc, BHT, and the polymers were not the same, it is impossible to compare the potency of their antioxidant activities directly.

The effect of BHP content of poly-Aa(BHA) and poly-St(BHQ) beads on antioxidant activity were measured by the ferric thiocyanate method. The initial rate of oxidation was estimated from the absorbance of the ferric rhodanide produced. The antioxidant activity of BHT, α -Toc and the polymer beads was defined as the reciprocal of the initial rate.

The correlation between the reciprocal values of the initial oxidation rate and the content of BHP groups in the polymer beads is shown in Fig. 3. The reciprocal of the initial rate for control (without antioxidant) and BHT (2 mg, content of BHT groups = 0.009 meq BHP/g BHT) are 560 and 4, respectively. The values for poly-Aa(BHA) and poly-St(BHQ) beads increased with an increase in the content of BHT groups in the polymers. The antioxidant activity of poly-St(BHQ) beads was higher than that for poly-Aa(BHB) ones. The hydrophobic groups on the surface of poly-St(BHQ) beads seem to have a stronger affinity for linoleic acid than those on poly-As(BHA) beads. The slopes suggested that the antioxidant activity for 2 mg BHT (9.1 μ eq BHP) corresponds to that for 11.7 g (11.7 g \times 1.5 meq BHP/g = 17.5 meq BHP) of poly-Aa(BHB) beads and that for 0.61 g (0.61 g \times 1.2 meq BHP/g = 0.73 meq BHP) of poly-St(BHQ) beads. Only 1/1900 (= 9.1 μ eq/17.5 meq) and 1/80 (= 9.1 μ eq/0.73 meq) of BHP groups in poly-Aa(BHA) and poly-St(BHQ) beads were effective for the antioxidant reaction, respectively. It seems that only BHP groups on the bead surface are involved in antioxidation of linoleic acid.

When polymer beads bearing hindered phenolic groups are added to a food oil as antioxidants, they can be separated easily from the oil before use because of their insolubility, and thus the ingestion of the antioxidant or its fragments can be avoided. In addition, their indigestible and unabsorbable nature will not allow them

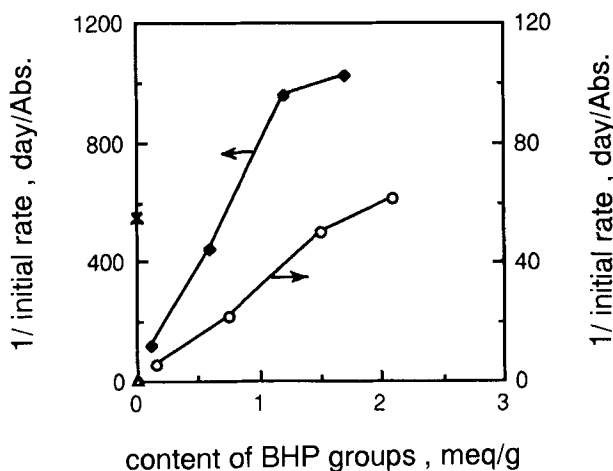


FIG. 3. Relationship between the reciprocal values of initial oxidation rate and the content of BHP groups in the polymers: (○) poly-Aa(BHB), (◆) poly-St(BHQ) beads, (×) BHT, and (△) control.

to exert any toxicity, even if they were consumed. Poly-Aa(BHB) and poly-St(BHQ) beads are expected to be safe and effective antioxidants for foods. We are investigating their toxicity.

CONCLUSION

Poly-Aa and Poly-St beads were reacted with BHB and BHQ to obtain antioxidant polymers, poly-Aa(BHB) and poly-St(BHQ) beads, respectively. The polymer containing butylated hydroxyphenyl (BHP) groups showed antioxidant activity. The antioxidant activity of poly-St(BHQ) beads was higher than that for poly-Aa(BHB) ones. The hydrophobic groups on the surface of poly-St(BHQ) beads seem to have a stronger affinity for linoleic acid than those on poly-As(BHA) beads. Only 1/1900 and 1/80 of BHP groups in poly-Aa(BHA) and poly-St(BHQ) beads were effective for antioxidant reaction, respectively. It seems that only BHP groups on the bead's surface are involved in antioxidation of linoleic acid. The polymer beads are potential antioxidants for foods since their separation from a food oil after their use is easy because of their insolubility.

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