

# Preparation of Spherical Polymer Beads of Maleic Anhydride–Styrene–Divinylbenzene and Metal Sorption of Its Derivatives

N. OGAWA, K. HONMYO, K. HARADA, and A. SUGII, *Faculty of Pharmaceutical Sciences, Kumamoto University, 5-1 Oe-honmachi, Kumamoto 862, Japan*

## Synopsis

Compounds having acid anhydride moiety have been used for starting materials for many useful derivatives. Spherical crosslinked polymer beads of porous maleic anhydride–styrene–divinylbenzene copolymer are obtained by suspension polymerization. Glycerol is found to be a preferable dispersant to make spherical beads. The beads contained 93% of the anhydride and 7% of the free carboxyls. As one of applications, the beads were hydrolyzed or reacted with anhydrous hydrazine, and the metal sorption behavior of them was examined. The hydrolyzed beads show a similar sorption manner as a conventional cation exchange resin having carboxylic acid groups, but the hydrazide beads sorbed mercury(II) selectively over a wide pH range. This investigation suggests a simple preparative method for the insoluble spherical porous beads of the maleic anhydride copolymer.

## INTRODUCTION

In organic acid anhydride, maleic anhydride is easily copolymerized with many monomers and the anhydride groups in the polymers are effective polymeric acylating reagent and expected to have high reactivity with some compounds including amines. Copolymers of maleic anhydride and styrene or other monomers have been prepared by solution polymerization technique as fine powder.<sup>1,2</sup> Linear copolymers of maleic anhydride and ethylene or other monomers have been successfully used for the preparation of polyanionic water-insoluble derivatives of enzymes and protein enzyme inhibitors.<sup>3-5</sup> The linear copolymer is soluble in aqueous media, and usually additional crosslinkage with diamines such as hexamethylenediamine has been done. It is desirable to obtain spherical crosslinked maleic anhydride copolymer because spherical beads are more easily handled for a variety of chromatographic applications and the crosslinked polymers are insoluble in various kinds of solvents.

This article reports on the preparation of spherical porous copolymer beads of maleic anhydride (MA)–styrene (ST)–divinylbenzene (DVB) and an applicability of the beads as starting material of ion exchange or chelating resin.

## EXPERIMENTAL

St and DVB solution (nominally containing about 50% of DVB) were washed with 2*N* sodium hydroxide and water to remove inhibitor. The monomers were dried over anhydrous calcium chloride. MA, benzoyl per-

oxide, and glycerol used were reagent grade. Benzene and dioxane were distilled before use. The IR spectra of copolymer beads were recorded on a JASCO DS-701G spectrophotometer in KBr disks.

**Resin I (MA-ST-DVB Copolymer).** Polymerization was carried out under a nitrogen atmosphere. A mixture of 84 g of MA, 36 mL of ST, 36 mL of DVB, 62 mL of benzene, 62 mL of dioxane, and 3.2 g of benzoyl peroxide were added to a suspending medium of 540 mL of glycerol containing hydroxyethyl cellulose (1.1 g) and sodium chloride (27 g). The organic phase was at first dispersed in the suspending solution at 25°C; then the bath temperature was gradually raised to 70°C at a rate of 1°C/1.5 min and stirred for 2 h. The resulting beads were immersed in water and washed with water, methanol, benzene, and methanol and dried. About 60 g of white spherical beads (35–60 mesh) were obtained.

**Resin II.** Resin I (4 g) was refluxed with 100 mL of 2*N* sodium hydroxide and then washed with 2*N* hydrochloric acid and water and dried. The exchange capacity (H–Na) was 5.4 mmol/g.

**Resin III.** Resin I (15 g) was swollen in 50 mL of dioxane for 30 min and then 10 mL of anhydrous hydrazine was added and refluxed for 3 h. The resulting beads were washed successively with water, methanol, 2*N* hydrochloric acid, and water, and then dried. Nitrogen content of the beads was 7.9%.

The content of anhydride and free carboxyl groups in resin I was determined as follows: (1) the total amounts of anhydride and free carboxyl groups: after hydrolysis of resin I (100 mg) with 2*N* sodium hydroxide (1 mL) in sealed glass tube in a water bath (80°C) for 3 h, the mixture was transferred into a beaker with 10 mL of methanol and titrated with 0.1*N* methanolic hydrochloric acid using phenolphthalein as a indicator. The difference in titration between blank and sample was a measure of total amount of anhydride and carboxyl groups. (2) The amount of anhydride groups<sup>6</sup>: in a parallel experiment, the intact resin I (100 mg) and redistilled morpholine (800 mg) was sealed in a glass tube and heated to 80°C for 3 h. The reaction mixture was transferred into a beaker with 10 mL of dioxane. After addition of 10 mL of acetic acid, unreacted morpholine was titrated potentiometrically with 0.2*N* perchloric acid in acetic acid. The difference in titration between the blank and sample was a measure of anhydride groups. The amount of anhydride and free carboxyl groups initially presented in the resin was calculated from the two titration values.

Sorption of metal ions on resins II and III. To a glass-stoppered test tube containing 100 mg of the beads, 9 mL of 0.5*M* acetic acid-nitric acid (pH 1–2) or 0.5*M* acetic acid–0.5*M* sodium acetate (pH 3–7), and 1 mL of 0.1*M* metal ion solution were added; then the mixture was shaken at room temperature for 24 h. The beads were filtered off on glass-wool and the amount of metal remaining in the filtrate was determined by complexometric titration, atomic absorption spectrometry, or colorimetry. In the case of column study, <sup>203</sup>Hg was used as a tracer.

## RESULTS AND DISCUSSION

MA copolymerizes with many monomers to produce mainly a 1:1 ratio of the monomer sequence in the copolymer.<sup>7</sup> When MA and DVB were copolymerized, the product was very rigid and seemed to be difficult to

modify chemically; therefore, ST was added to the monomers to create a distance between crosslinkages.

An aqueous solution, usually used for a dispersing medium in suspending polymerization, cannot be used in the case of MA, because MA is soluble in water and easily hydrolyzed, and the hydrolyzed acid strongly inhibits the copolymerization. In this experiment, glycerol was used as a suspending medium for MA solution. The solution in glycerol is expected to be stable for hydrolysis and production of polyester unless the temperature is too high.<sup>8</sup> Ethylene glycol was also used as a medium, but the spherical beads were not obtained. When benzene was used as a solvent of the monomers as usual, the surface of the beads obtained were uneven, so dioxane was added to benzene and white spherical beads (resin I) were successfully obtained. A microscopic photograph of resin I is shown in Figure 1. The spherical porous beads are easily controlled in size by adjusting stirring speed in this polymerization process, and are stable for break on swelling of the beads.

As one of application of the beads, derivatives of resin I were prepared and metal sorption behavior of them were examined. Resin II was obtained by the hydrolysis of resin I, and resin III was prepared by a reaction of resin I and anhydrous hydrazine. Infrared spectra of resins I-III are shown in Figure 2. Resin I shows characteristic absorption bands at 1852 and 1775  $\text{cm}^{-1}$  for acid anhydride. Generally, acid anhydride reveals two strong absorption bands between 1885-1725  $\text{cm}^{-1}$ , and the infrared spectrum of resin I in this region is similar to that of succinic anhydride. The anhydride content of resin I determined by a similar method reported by Johnson and Funk<sup>6</sup> was 2.6 mmol/g. The exchange capacity (H-Na) of resin II was 5.4 mmol/g, and the infrared spectrum shows characteristic absorption at 1710  $\text{cm}^{-1}$  due to free carboxylic acid. When resin II was refluxed with xylene to change carboxylic acid groups to anhydride, it was changed easily to resin I. On the other hand, when commercially available Amberlite IRC-50 (H-form), methacrylic acid copolymer, was refluxed with xylene in a similar manner as above, the absorption of acid anhydride was scarcely observed in the infrared spectrum. This suggests that the carboxylic acid groups in resin II exist closely each other. Resin III shows a absorption at 1700  $\text{cm}^{-1}$  due to carbonyl groups (amid) and contained 7.9% (5.6 mmol/g) of nitrogen.

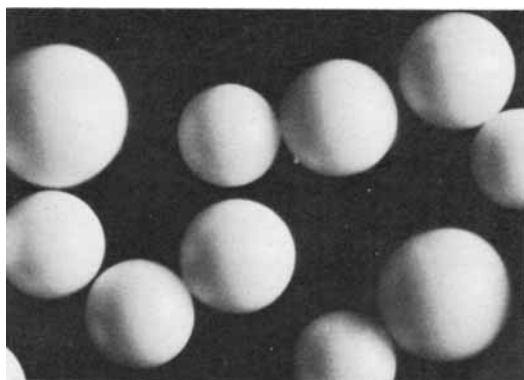


Fig. 1. Microphotograph of resin I.

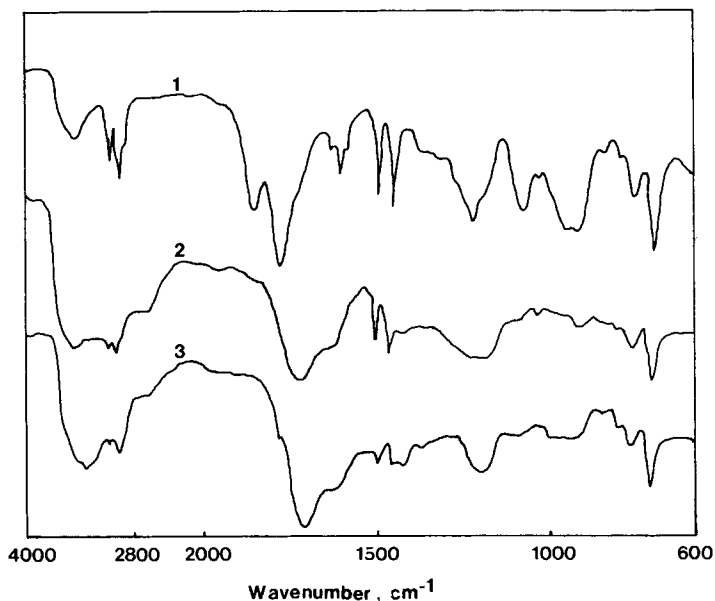
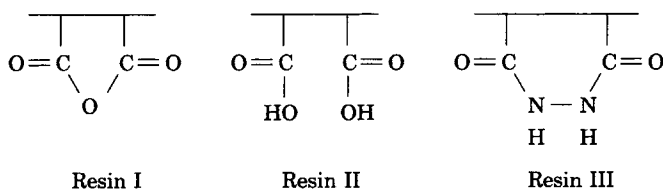


Fig. 2. Infrared spectra of resins in KBr disks: (1) resin I; (2) resin II; (3) resin III.

From the analytical and spectral data of resin III, presence of cyclic hydrazide groups are expected.



Sorption of some metal ions on resins II and III are shown in Figures 3 and 4. The metal sorption manner of resin II was similar to that of Amberlite

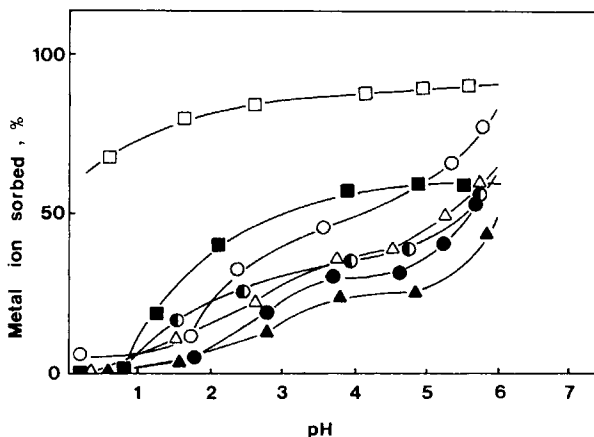


Fig. 3. Sorption behavior of metal ions on resin II. Metal solution:  $1 \times 10^{-2}M$ ; resin: 100 mg; shaking time: 24 h: (○) Cu(II); (●) Co(II); (△) Zn(II); (▲) Ni(II); (□) Hg(II); (■) Th(IV); (●) U(VI).

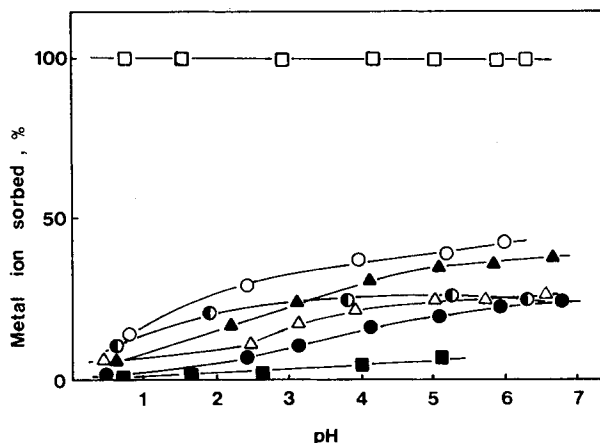


Fig. 4. Sorption behavior of metal ions on resin III. Conditions and symbols are same as those in Figure 2.

IRC-50, and no striking selectivity was found. However, resin III showed high selectivity for mercury(II) over a wide pH range [capacity for mercury(II) at pH 7.0, 3.00 mmol/g]. Cyclic maleic hydrazide and an ion-exchange resin prepared by a condensation of resorcinol and formaldehyde in the presence of the hydrazide have been reported to have strong affinity for mercury(II).<sup>9</sup> It is supposed that the cyclic hydrazide groups on resin III contribute conveniently to the sorption of mercury(II).

The sorption of mercury(II) on resin III in the presence of diverse metal ions [100 times of mercury(II)] was examined, and the result is shown in Table I. The diverse metal ions tested did not interfere with the sorption of mercury(II). The breakthrough experiment was carried out by a column operation in which a feed solution containing tracer scale of <sup>203</sup>Hg(II) was allowed to pass through the column packed with 2 g of resin III, and the result is shown in Figure 5. About 25 bed volumes of feed solution can be passed through with leakage of less than 1% of <sup>203</sup>Hg(II) in the effluent.

In conclusion, spherical MA copolymer beads are easily prepared by the proposed method including the use of glycerol as a dispersant. The beads

TABLE I  
Sorption of Mercury(II) from Acetate Buffer (pH 7.0) in the Presence of Diverse Metal Ions on Resin III<sup>a</sup>

Diverse metal (0.1M)	Hg(II) sorption (%)
Sr(II)	100.0
Cu(II)	99.6
Co(II)	99.5
Zn(II)	99.9
Pb(II)	99.9
Cd(II)	100.0
Ni(II)	99.8
U(VI)	99.4

<sup>a</sup> Mercury(II) solution: 0.001M, 100 mL; resin: 100 mg.

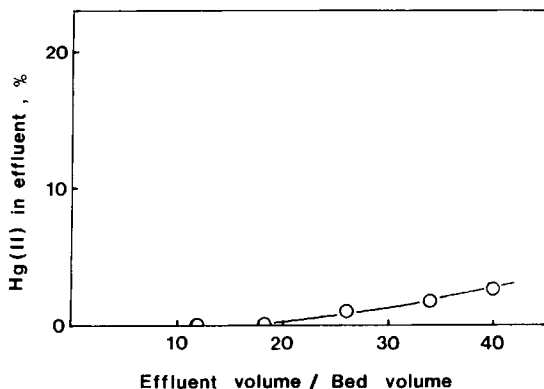


Fig. 5. Breakthrough curve for mercury. Column: resin III, 2 g (1 × 8 cm). Feed: tracer concentration of Hg(II) in 0.5M acetate buffer (pH 6), 8000 cpm/mL. Flow rate: 1 mL/min.

obtained seem to be useful as a starting material for ion-exchange or chelating resin and are also expected to apply to other fields such as biological sciences.

### References

1. D. Braun, H. Cherdron, and W. Kern, *Praktikum der Makromolekularen Organischen Chemie*, Dr. A. Hüthig Verlag, Heideberg, 1966; transl. to Japanese by Y. Iwakura, Asakura Shoten Co., Tokyo, 1968, p. 161.
2. J. H. Johnson, *Macromolecular Syntheses*, J. A. Moore, Ed., Wiley, New York, 1977, Coll. Vol. 1, p. 45.
3. Y. Levin, M. Pecht, L. Goldstein, and E. Katchalski, *Biochemistry*, **3**, 1905 (1964).
4. R. A. Zingaro and M. Uziel, *Biochim. Biophys. Acta*, **213**, 371 (1970).
5. H. Fritz, H. Schult, M. Wiedemann, and E. Werle, *Z. Physiol. Chem.*, **348**, 308 (1967).
6. J. B. Johnson and G. L. Funk, *Anal. Chem.*, **27**, 1464 (1955).
7. F. R. Mayo, F. M. Lewis, and C. Walling, *J. Am. Chem. Soc.*, **70**, 1529 (1948).
8. W. R. Sorensen and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, 2nd ed., Wiley-Interscience, New York, 1968, p. 447.
9. E. Blasius and M. Laser, *J. Chromatogr.*, **11**, 84 (1963).

Received December 13, 1983

Accepted January 12, 1984