



# Polymer supported amino bis-(*cis*-propan 2,3 diol) functions for removal of trace boron from water

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## Abstract

Reaction of diallylamine with crosslinked terpolymer beads of glycidyl methacrylate–methyl methacrylate–ethylene glycol dimethacrylate yields corresponding polymers with diallylamino functions ( $2.4 \text{ mmol g}^{-1}$ ). *Cis*-dihydroxylation of the allyl groups with hydrogen peroxide, in presence of  $\text{OsO}_4$  catalyst yields polymer supported amino-bis(*cis*-propane 2,3-diol) functions with 81.7% of conversion yields. The resulting polymer resin having vicinal *cis*-diol functions is a high capacity ( $1.77 \text{ mmol g}^{-1}$ ) boron-specific sorbent and useful for extraction of trace boric acid (105.1 ppm) from aqueous solutions in about 20 min.

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## 1. Introduction

Boron removal is of special importance due to its plant stunning effect. Presence of boric acid higher than 4 mg per liter in water have been reported to accelerate decay of fruit trees. Citrus plantations are especially susceptible to excessive boron concentration in the irrigation water [1].

The development of new boron-specific chelating resins with large capacity, high selectivity, and high uptake rate has held much interest both for the sepa-

ration of boron isotopes in nuclear-related fields and for the recovery and removal of borate from geothermal waters and boron containing wastewaters.

Three or more hydroxyl functions can bind boric acid tightly by forming either neutral boron esters or borate complex anion with a proton as counter ion. Hydroxyl functions are specific in boron binding. Having six hydroxyl functions, sugar derivatives such as sorbitol and mannitol have exceptionally high boron binding abilities.

In accordance with this key principle, poly (styrene)-based resin with *N*-methyl D-glucamine functions, emerged in the mid 1960s [2], and has been reported as boron-specific sorbent.

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This resin has excellent efficiency in boron uptake although some activity loss is observed in regenerations by acid [3].

In a related study, Japanese workers demonstrated that additional amine functionality is essential for high levels of boron chelating [4].

Based on this principle, in our previous study we have demonstrated that, glycidyl methacrylate based gel polymers with *N*-methyl *D*-glucamine functions are very useful in removal of trace boric acid [5,6]. These polymers are efficient and regenerable in boron sorption process.

Vicinal diol containing compounds are versatile materials for chelation with boric acid and borates [7].

Under the light of these studies, in the present work we have prepared glycidyl methacrylate based resin with *vic-cis* diol functions to attain better boron sorptions. Boron uptake ability and regeneration conditions of the resulting polymer resin have been investigated.

## 2. Experimental

### 2.1. Materials

All the chemicals used were analytical grade. Glycidyl metacrylate (GMA), (Fluka), methyl metacrylate (MMA) (Fluka), Ethylene glycol dimetacrylate (EGDMA) (Fluka), diallylamine, (E-Merck), sorbitol (Fluka), Osmium tetroxide (E-Merck).

### 2.2. Preparation of GMA–MMA–EGDMA terpolymer beads

The terpolymer beads were prepared by suspension polymerization of GMA (0.4 mol), MMA (0.5 mol), EGDMA (0.1 mol) as described before [8]. Epoxide content was determined as  $3.20 \text{ mmol g}^{-1}$  ( $3.16 \text{ mmol g}^{-1}$ ) by pyridine–HCl method [9].

### 2.3. Modification of the bead polymer by diallylamine

Ten grams of the bead polymer were added portion wise to the stirred solution of 15 ml diallylamine in 40 ml of DMF at  $0^\circ\text{C}$ . The mixture was

placed on a continuous shaker and shaken for 24 h at room temperature and the reaction content was heated at  $80^\circ\text{C}$  for 3 h.

The reaction content was filtered and washed with excess of water and 150 ml of methanol, respectively. The filtered product was dried under vacuum at room temperature for 24 h. The dry product weighted 12.8 g.

### 2.4. Determination of the accessible double bond densities

This was determined by bromine addition method as follows: To avoid interference of tertiary amine bromine interaction, first, the tertiary amine groups were blocked by  $\text{H}_2\text{SO}_4$ . For this purpose 20 ml 0.1 N  $\text{H}_2\text{SO}_4$  was added to 0.125 g of the resin sample and left to stand for 1 h. The resin was filtered, washed with alcohol and ether. Then the sample was dried under vacuum for 24 h at room temperature.

Bromine [ $1.5 \text{ ml}$  ( $2.91 \times 10^{-2} \text{ mol}$ )] was added to cold  $\text{CCl}_4$  and diluted to 50 ml. To 10 ml of this solution, there was added 0.125 g of the beads sample prepared above. The bottle was tightly stoppered and mounted on a continuous shaker. After shaking for 24 h at room temperature, the mixture was filtered and 4 ml of the filtrate was mixed with 5 ml of 20% KI solution. The mixture was titrated with 0.1 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution until disappearance of the color of elemental iodine. Titer (38.5 ml) (42.2 ml for 4 ml of blank) indicates about 4.08 mmol (theoretical: 3.93 mmol) double bond per gram of the resin.

### 2.5. *Cis*-dihydroxylation of the resin with diallyl amino groups

Hydrogen peroxide [6.5 ml (63.6 mmol)] (30% w/w) was added to 30 ml of *tert*-butanol in a separatory funnel. After shaking for 5 min, organic phase was separated and dried with anhydrous sodium sulfate. To this solution 10 g of the resin with diallyl amine functions was added. Then 0.05 g  $\text{OsO}_4$  was added to the mixture and stirred at  $50^\circ\text{C}$  for 24 h. Thereafter, modified bead product was filtered and washed with ethyl alcohol and excess of water. In order to destroy the *N*-oxide, the

product was mixed 100 ml of 0.5 M HCl solution, and left to stand for overnight. Then it was washed with excess of water, 200 ml of 1 M NaOH solution and distilled water (250 ml), respectively. After final washing with 20 ml alcohol and 20 ml ether, the product was dried at room temperature for 24 h under vacuum. The yield was 11 g.

*Cis*-dihydroxylation yield was assigned indirectly based on final amine content which was estimated by titration, as follows. Firstly, 0.25 g of resin samples was wetted with 5 ml distilled water (4 h), then 0.1 M HCl was added to the mixture. After filtration, 2 ml of the filtrate was titrated with 0.02 M NaOH. Titer (1.4 ml) corresponds to 1.73 mmol g<sup>-1</sup> of amine content (theoretical: 2.05 mmol g<sup>-1</sup>). This result reveals an 81.7% of conversion yield in the *cis*-dihydroxylation.

#### 2.6. Determination of the boron loading capacity

Maximum boron loading capacity of the resin was determined by interaction of 0.25 g of the polymer sample. The sample was wetted with 5 ml of distilled water for 4 h. Three grams of H<sub>3</sub>BO<sub>3</sub> (4.852 × 10<sup>-2</sup> mol) was dissolved in water and diluted to 100 ml. Twenty five milliliter of this solution was added to the above mixture and the mixture was shaken on a shaker for 24 h at room temperature. After filtration, the residual boron content of the solution was determined titrimetrically based on 2 ml of the filtrate which was transferred in 10 ml of 0.5 M sorbitol solution using phenolphthalein indicator. This solution was titrated with 0.06 M NaOH (*F*=0.946) solution. Titer (13.2 ml) (13.7 ml for the blank) gave a 1.77 mmol H<sub>3</sub>BO<sub>3</sub> sorption per gram of the polymer sample.

#### 2.7. pH-dependent boron sorption

A series of buffer solution was prepared (100 ml of each) by using appropriate combination of 0.2 M sodium acetate and 0.2 M acetic acid solutions for pH 2, 4.05, 5 and 0.06 M sodium hydrogen phosphate and 0.06 M potassium dihydrogen phosphate for pH 8, respectively.

In each buffer solution, 1.5 g (24.3 mmol) H<sub>3</sub>BO<sub>3</sub> was dissolved and made up 50 ml, so that the final concentration will be 0.485 M.

Table 1

Boron sorption characteristics of the resin at room temperatures

| H <sub>3</sub> BO <sub>3</sub> (M) | pH           | Capacity (mmol g <sup>-1</sup> ) |
|------------------------------------|--------------|----------------------------------|
| 0.485                              | Non-buffered | 1.77                             |
| 0.485                              | 2.0          | 1.04                             |
| 0.485                              | 4.05         | 1.53                             |
| 0.485                              | 5.0          | 1.66                             |
| 0.485                              | 8.0          | 1.79                             |

The resin samples (0.5 g of each) were interacted with 20 ml of H<sub>3</sub>BO<sub>3</sub> (9.704 mmol) in buffer solutions for 24 h. Then, the solutions were filtered and diluted with distilled water. Residual boron contents of the filtrates were assigned colorimetrically ( $\lambda = 585$  nm) by carminic acid method [10].

The data was shown in Table 1.

#### 2.8. Kinetics of boron sorption

Batch kinetics experiments were carried out using 9.70 × 10<sup>-3</sup> M boric acid solutions as follows: The resin (1 g) was interacted with 50 ml of the boric acid solution. While stirring with a magnetic bar, aliquots (5 ml) were taken at appropriate time intervals and filtered. Residual boron contents of the filtrate were determined colorimetrically as described above. The data derived were used to build up the concentration–time plots in Fig. 1.

#### 2.9. Desorption of the loaded resin

Acid leaching method was used for desorption of the boron as follows:

Loaded resin sample (0.25 g) was left in contact with 5 ml of water for 4 h. Then 20 ml of 2.5 M HCl solution was added and stirred at room temperature for 24 h. It was filtered and 2 ml of the filtrate was titrated with 0.05 M KOH solution in the presence of phenolphthalein indicator. At the end of neutralization of the excess hydrochloric acid, 10 ml of 0.5 M D-sorbitol solution was added to the mixture. Additional KOH solution (0.4 ml) reveals a 1.6 mmol of desorbed boron per gram of loaded sample.

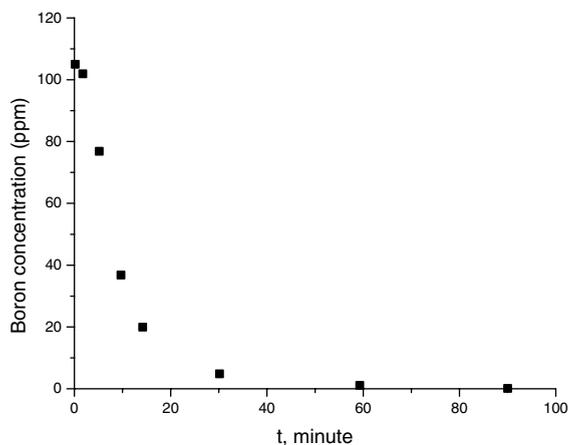


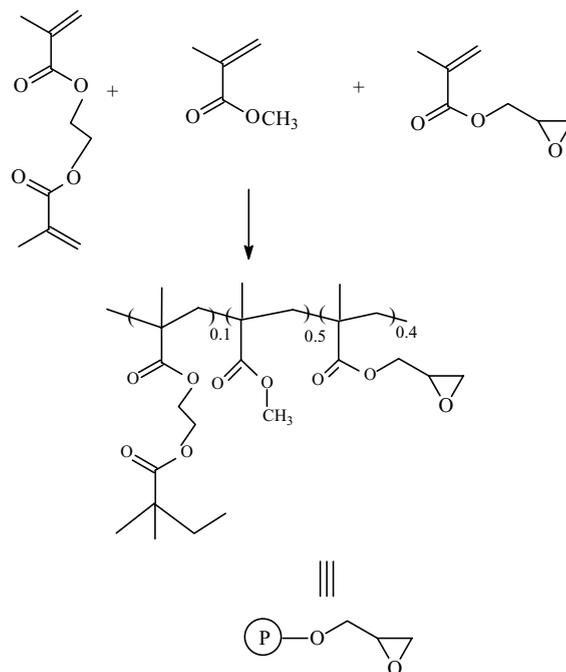
Fig. 1. Boron uptake kinetics of resin (1 g) using artificial boric acid solution with 105.1 ppm initial boron concentration.

### 3. Results and discussion

Polymer supported imino propane diols have shown to be very useful in boron sorption from aqueous solutions as described in our previous study [11]. Boron sorption, in that case, occurs mostly by neutral boron ester formation. Tetra coordinated chelation by borate formation, however, is being prevented sterically due to fact that, hydroxy groups in the *vic*-diols are mostly *trans* to each other.

*Cis*-diols, on the other hand, are known to have far more reactivity in forming boron esters and tetra-valent borates. Based on this consideration, we have targeted to prepare crosslinked polymer resins with amino bis-propanediols in which dihydroxy groups are in *cis* position. For this purpose, we have preferred a glycidyl methacrylate based crosslinked polymer as support, due to easy modification of the epoxy groups involving. GMA based polymer beads used were prepared by suspension terpolymerization of GMA (0.4 mol), MMA (0.5 mol), EGDMA (0.1 mol) as outlined in Scheme 1.

Modification of the terpolymer beads by well-known reaction sequences: (i) treatment with allyl amine and (ii) subsequent *cis*-dihydroxylation with  $\text{OsO}_4$  catalyst yields the expected polymer resin with *cis*-propanediol functions (Scheme 2).



Scheme 1. Preparation of GMA based spherical bead terpolymer.

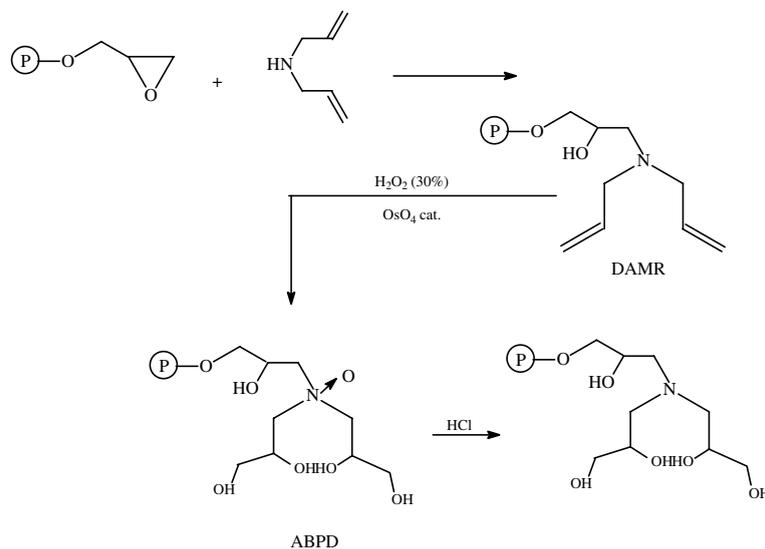
Reaction with excess of diallylamine gave almost quantitative conversion as has been inferred from titrametric analysis of the amine content ( $2.4 \text{ mmol g}^{-1}$ ) of the product (theoretical value  $2.41 \text{ mmol g}^{-1}$ ). Also the double bond content of this product (bromine addition method) reveals a  $4.08 \text{ mmol g}^{-1}$  allyl group which is fairly consistent with the theoretical value of  $3.93 \text{ mmol g}^{-1}$ .

The *cis*-dihydroxylation yield in the second step was inspected indirectly by acid titration of amino groups. This analysis gave  $1.73 \text{ mmol g}^{-1}$  amino group which indicates a 81.7% of *cis*-dihydroxylation yield.

Obviously *N*-oxide is expected to form during reaction with  $\text{H}_2\text{O}_2$ . The *N*-oxide is destroyed by treating with HCl solution for 24 h and subsequent reaction with NaOH solution.

### 4. Boron sorption

Experiments show that the resin with two *cis*-dihydroxy functions is a boron-specific sorbent



Scheme 2. Preparation of crosslinked polymer resin with amino-bis (propane *cis* 2,3 diol) groups.

with a capacity of  $1.77 \text{ mmol g}^{-1}$ . This amount is in good agreement with  $1.73 \text{ mmol g}^{-1}$  amino group content. This implies that each bis-(amino propane glycol) function involves in chelating with boron. In other words, two *cis*-propane diol functions attached to amino group show very high reactivity in boron binding.

Sorption kinetics from highly diluted boric acid solutions (105.1 ppm) shows that sorption of boron is reasonably fast and boron concentration reduces below 5 ppm in about 20 min (Fig. 1).

Increasing pH of the boric acid solution increases the capacity (Table 1) as expected. At low pHs the capacity is about 60% of the maximum capacity. High capacities in basic and neutral regions are due to stabilization of anionic borate ester moieties. This result is in agreement with the previous results.

## 5. Regeneration of the sorbent

We have also studied recovery of boric acid from loaded samples. Interestingly back extraction with 2 M  $\text{H}_2\text{SO}_4$  was not successful whereas desorption did occur with 2 M HCl solutions. The reason of the difference is ambiguous yet. Boron (1.6 mmol) releasing by HCl solution implies that

about 53.3% of boric acid sorbed can be recovered in the first contact of the acid solution. Second acid treatment provides a total 79.0% of boron desorption. Further acid leaching results in 91% of boron release from the resin.

Although, we have not studied sorption efficiency of the regenerated resin. It is more likely reusable considering with our previous works on the subject.

This result can be ascribed to bonding of boric acid tightly with *cis*-dihydroxy functions, which was not the case for the resin with *trans*-dihydroxy groups.

## 6. Conclusion

*Vic-cis*-dihydroxyl groups are fast in boron binding. When compared this resin with the resins having *trans*-dihydroxy groups (which we have described before [11]) there is no additional advantage regarding the capacities. Moreover, desorption of the loaded boron by acid leaching is somewhat difficult when compared to those for the resin with *trans*-dihydroxy groups. Nevertheless this material presented in this work is fast boron binding and expected to be beneficial in application view point.

**References**

- [1] N. Nadav, *Desalination* 124 (1999) 131.
- [2] W.R. Lyman, A.F. Preuss, US Pat. 2 (1957) 813,838.
- [3] R.M. Roberts, *Ind. Eng. Chem. Prod. Res. Div.* 10 (1971) 356.
- [4] L. Yoshimura, Y. Miyazaki, F. Ota, S. Matsuoka, H. Sakashita, *J. Chem. Soc., Faraday Trans.* 94 (1998) 683.
- [5] N. Bıçak, H.O. Ozbelge, L. Yılmaz, B.F. Senkal, *Macromol. Chem. Phys.* 201 (2000) 577.
- [6] N. Bıçak, N. Bulutçu, F. Senkal, M. Gazi, *React. Funct. Polym.* 47 (2001) 175.
- [7] M. Matsumoto, K. Kondo, *Separ. Sci. Technol.* 32 (1997) 983.
- [8] H.B. Sonmez, B.F. Senkal, N. Bıçak, *J. Polym. Sci. Part A. Polym. Chem.* 40 (2002) 3068.
- [9] S. Sigga, *Quantitative Organic Analysis*, third ed., Wiley, New York, 1967.
- [10] J.T. Hatcher, L.V. Wilcox, *J. Anal. Chem.* 22 (1950) 567.
- [11] B.F. Senkal, N. Bıçak, *React. Funct. Polym.* 55 (2003) 27.