

Sorbitol-Modified Poly(*N*-glycidyl styrene sulfonamide) for Removal of Boron

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ABSTRACT: A sorbitol-containing resinous polymer has been prepared starting from crosslinked polystyrene–10% divinylbenzene (DVB) resin beads (720–840 μm) by the following series of reactions: (1) chlorosulfonation, (2) sulfonamidation with *N*-propylamine, (3) condensation of sulfonamide with epichlorohydrin, and (4) modification with sorbitol. The resulting sorbitol-modified polymer has been demonstrated to be an efficient and regenerable specific sorbent for removal of boron in parts per million (ppm) levels. Kinetics of boron sorption and regeneration of the polymer were investigated.

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Key words: boron uptake; boron-specific resin; sorbitol-modified polymer; poly(styrene sulfonamide) with glycidyl pendant groups

INTRODUCTION

Epoxy groups have a unique reaction capability. They undergo ring opening with various compounds possessing hydroxyl, amine, or activated methylene groups. For this reason, polymers with epoxy (oxirane) groups offer numerous functionalization possibilities in mild reaction conditions. Glycidyl methacrylate is the only commercially available vinyl monomer carrying oxirane group. Its polymer, poly(glycidyl methacrylate) has been represented as an alternative key material for preparing functional polymers.¹ Reasonable hydrolytic stability of the ester group in its polymer makes it preferable as a relatively inert support. Epoxidation of carbon–carbon double bonds in polymers is another alternative route to prepare oxirane-bearing polymers, such as epoxidized polybutadiene.²

One of the common ways to obtain oxirane function is condensation of phenols with epichlorohydrin. In this way, *O*-substituted glycidyl compounds are obtained. This methodology is already

being used to obtain various bis(glycidyl) compounds.³ Sulfonamides differ from carboxylic acid amides in that they have reasonable stability towards acid and base hydrolysis.⁴ They also form alkali salts with aqueous NaOH or KOH solutions. Sulfonamides can condense with alkyl halogenides to give corresponding *N*-alkyl sulfonamides.⁵

In the present work, this analogy has been extended to polymeric sulfonamides. We have demonstrated that poly(styrene sulfonamide) crosslinked with divinylbenzene (DVB) can be transformed into its corresponding *N*-glycidyl derivative by condensation with epichlorohydrin.

In the study, the glycidyl-bearing polymer has been modified with sorbitol via ring opening of the epoxy group. The resulting modified resin has been used to remove boron in ppm levels.

Boron removal is important for agriculture. Although any physiological effect of boron on human being or animals has not been reported so far, it is extremely harmful for plants. 4 ppm of boron in irrigation water has been accepted as an upper limit of concentration for plants.⁶

On the other hand, boron contamination is increasing everywhere in the world due to wide-

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spread exploitation of detergents containing sodium perborate as a brightening agent.

There are many methods in the literature for removal boron. Coagulation with lime, ferrous, and aluminium salts⁶ and adsorption by clays⁷ are reported to be useful only for concentrated boron solutions and not for trace quantities. Solvent extraction,⁸ sorption by MgO,⁹ and complexation with cellulose itself and its derivatives¹⁰ have been demonstrated to be effective for removal of boron in rather low concentrations.

Another route to remove boron from geothermal sources is to use a commercial boron-specific polymer, IRA-743. This material is obtained by condensation of *N*-methyl glucose amine with crosslinked chloromethylated polystyrene. By using this material, it is possible to reduce boron concentration below 1 mg L⁻¹ in water.¹¹ However, it has been demonstrated that, after regeneration with (10%) sulfuric acid, this polymer loses 14% of its original capacity, probably due to acid-catalyzed side reactions through amino groups and phenyl rings.¹²

In order to overcome this drawback, in this study, a new and efficient polymeric sorbent has been developed, and its boron uptake characteristics have been investigated.

EXPERIMENTAL

Preparation of Spherical Beads of Crosslinked Styrene–10% DVB Copolymers

This was prepared according to the procedure described elsewhere.¹³ The resulting spherical beads were sieved, and the 720–840 μm fraction was used for further modifications.

Chlorosulfonation of the Styrene–DVB Resin Beads

The reaction was performed by treatment of styrene–DVB spherical beads with chlorosulfonic acid at 0°C, as described before.¹³ The degree of the chlorosulfonation was determined by boiling the product with a 10% NaOH solution for 4 h. The chlorine content of the solution was determined by the mercuric thiocyanate method.¹⁴ The chlorine analysis was found to be 3.24 mmol g⁻¹, which corresponds to 51.2% chlorosulfonation.

Sulfamidation of the Chlorosulfonated Resin by Propylamine

Sulfamidation of the chlorosulfonated resins was performed by treating the resin samples with an

excess of propylamine in dimethoxyethane. A typical procedure is as follows. The chlorosulfonated resin (16 g) is placed in a 250-mL round-bottom flask, which is kept in an ice bath. Cold dimethoxyethane (40 mL) is added to the flask. While stirring, the mixture of 40 mL (0.596 mol) of propylamine with 20 mL of dimethoxyethane is added dropwise to the reaction mixture in the flask. Stirring is continued for 24 h at room temperature. The content of the flask is filtered and washed with 20 mL of ethanol and excess of water. To remove HCl, the product is dispersed in 100 mL of 5% NaOH and stirred for 30 min. The solution is decanted, and 100 mL of water is added to it and boiled for 30 min. While hot, the mixture is filtered and washed successively with excess of water and 20 mL of ethanol. The resulting product is dried *in vacuo* at 40°C for 24 h (yield 17 g). Conversion yield was found to be 100%, based on the sulfamide content of the product (see below). The theoretical yield should be 17.2 g. The minor difference of the practical yield can be explained in terms of mechanical losses.

Determination of the Sulfamide Content

For the determination of the sulfamide content of the sulfamidation product, 0.5 g of sample was interacted with 1.5 g of KOH in 15 mL of methanol for 24 h. After filtration, 3 mL of the filtrate was diluted to 25 mL with distilled water and titrated conductometrically with 0.4M HCl solution. By comparison with the result for the unreacted solution, the sulfamide content was found to be 3.01 mmol g⁻¹, which indicates a quantitative conversion.

Substitution of Epichlorohydrin with Polystyrene (*N*-Propyl sulfonamide resin)

11 g of the resulting polymer, bearing glycidyl pendant units, was interacted with 6 g. KOH in 40 mL of methanol, which is a two-times excess of the stoichiometric amount, for 16 h at room temperature. The content of the flask was filtered and washed with 100 mL of methanol and dried. The potassium salt of the polymer was transferred into a 250-mL flask, and 20 mL of epichlorohydrin was added to the flask. The content of the flask was stirred for 72 h at 50°C, then filtered and washed with 20 mL of acetone, excess of water, and 20 mL of acetone. The vacuum-dried product weighed 13.3 g.

Determination of the Epoxy Content

The epoxy content of the glycidyl-bearing polymer was determined by the pyridine-HCl method.¹⁵ From this experiment, the epoxy content of the resin was found to be 2.4 mmol g^{-1} resin, which corresponds to 98.4% conversion.

Modification of the Glycidyl Group with Sorbitol

10 g of the glycidyl-bearing polymer was interacted with the solution of 50 g (0.275 mol) of sorbitol in 150 mL of 2-methyl pyrrolidone in a 500-mL volume flask. 0.5 mL of triethylamine was added as catalyst. While stirring, the content of the flask was heated at 80°C for 8 h under reflux. The modified polymer was filtered and washed with excess of water and 30 mL of ethanol. The product was dried at 40°C for 24 h *in vacuo*; yield was 13.08 g.

Determination of Loading Capacity of the Sorbitol-Modified Polymer

Maximum loading capacity of the sorbitol-modified polymer was determined by interaction of 0.3

g of the polymer sample with an aqueous solution of 50 mL (0.42 M) H_3BO_3 for 24 h. After filtration, boron content of the filtrate was determined conductometrically based on 0.5 mL of aliquots transferred in 25 mL of 0.45 M sorbitol solution. The sorbed amount was obtained by differentiation of boron contents of the interacted and noninteracted boron solutions. This experiment indicates that the boron-loading capacity is 1.22 mmol g^{-1} resin.

Kinetics of Boron Sorption

Kinetics of boron sorptions were carried out by batch kinetic experiments as follows. 0.5 g of sorbitol-modified resin was soaked in 25 mL ($8.4 \times 10^{-2} \text{ M}$) of H_3BO_3 solution. While stirring at room temperatures, 0.5-mL samples were taken out at appropriate time intervals to follow the concentration of boron remaining unreacted in the solution. Based on these data, the time-dependence variation of boron sorption was plotted, as shown in Figure 1.

In order to investigate the efficiency of the poly-

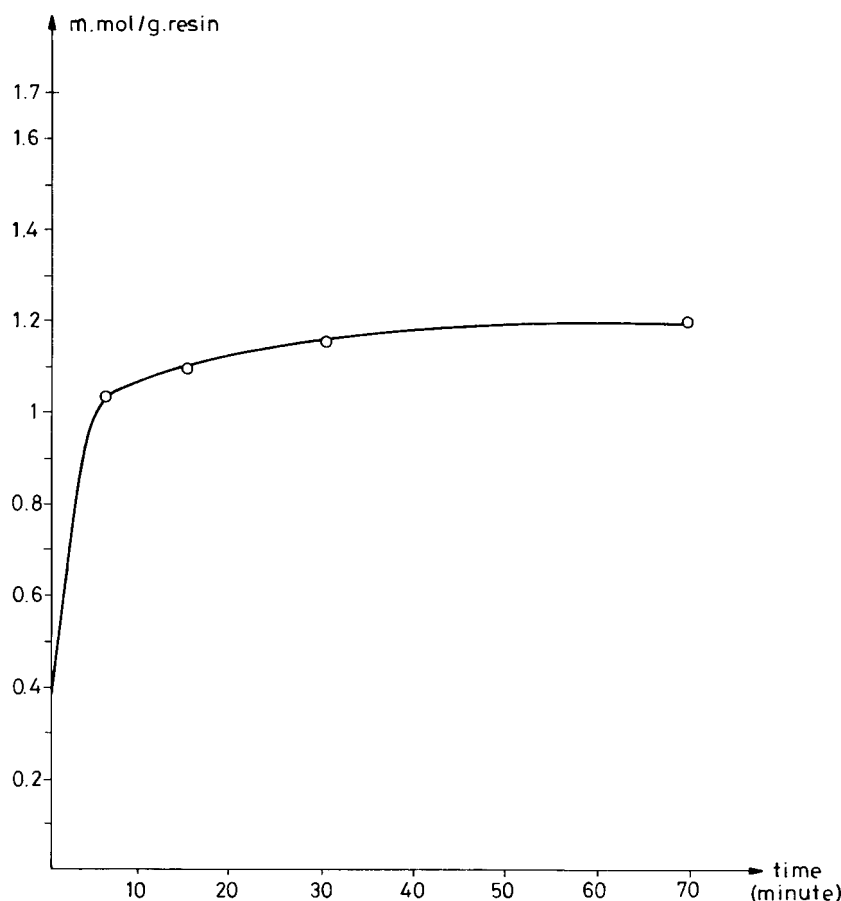


Figure 1 Boron sorption kinetics of the resin (from $8.39 \times 10^{-2} \text{ M}$ boric acid solution).

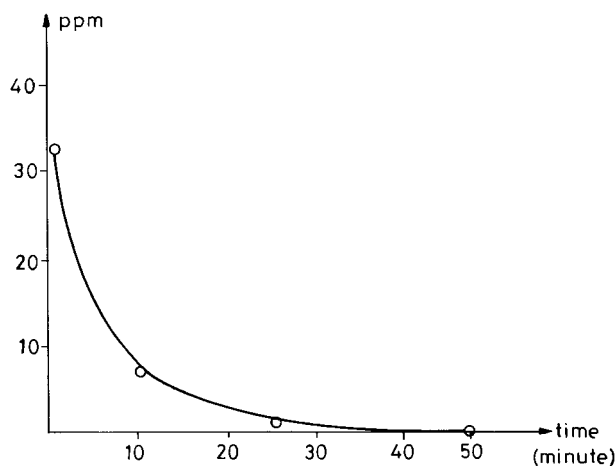


Figure 2 Concentration–time plots of the diluted boron solution (32.8 ppm) contacting with 1 g of polymer sample.

mer for trace quantities of boron, similar experiments were performed using 32.8-ppm boron solution. Variation of the boron content of the solution was determined similarly and is shown in Figure 2.

RESULTS AND DISCUSSION

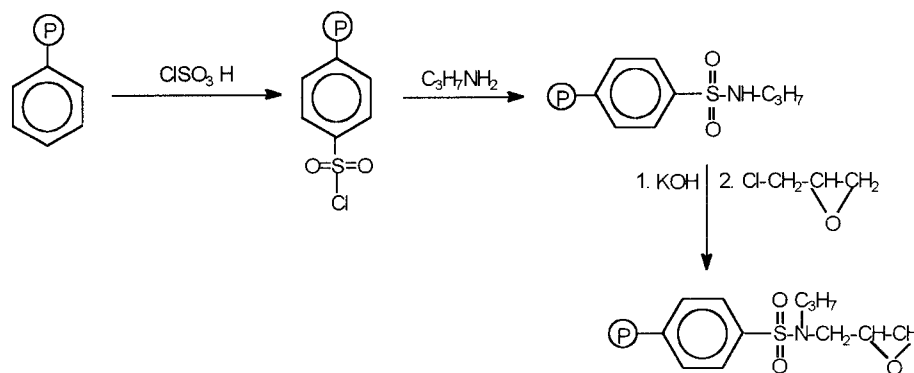
Based on the condensation reaction of sulfonamides with alkyl halogenides, in the present study, the potassium salt of poly(styrene sulfonamide) has been condensed with epichlorohydrin to give the corresponding *N*-glycidyl derivative according to the reaction sequences outlined in Scheme 1.

The following steps are involved: (1) chlorosulfonation, (2) sulfamidation, and (3) condensation

with epichlorohydrin. Conversion yields in each step were followed by proper analyses of the functional groups incorporated.

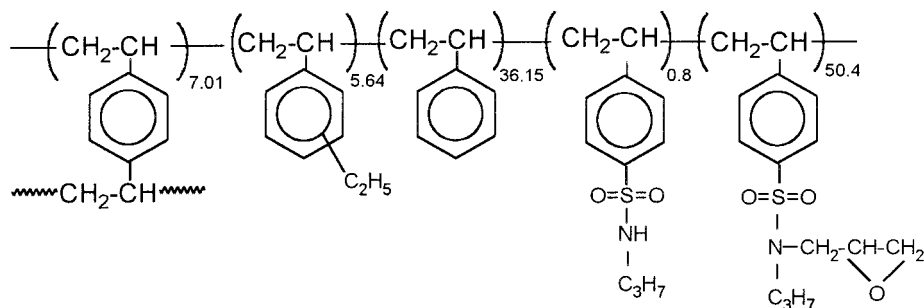
Polymer Characterization

When a 720–840 μm size of polystyrene beads is used, chlorine analysis indicates 51.2% of chlorosulfonation. In the second step, the reaction with *N*-propyl amine is almost quantitative. This was confirmed by acid titration of the filtrate of KOH solution, which was contacted with the sulfamidation product. In the third step, the potassium salt of the sulfamidation product was directly interacted with an excess of epichlorohydrin. Epoxide analysis of the resulting *N*-glycidyl derivative, by the pyridine–HCl method, indicated 98.4% conversion of sulfamide groups. Based on these analyses, the full structure of the glycidyl-bearing polymer is shown in Scheme 2. Easy ring opening of the oxirane (epoxy) group on the polymer provides a wide variety of functionalization possibilities to prepare new functional polymers. Transformation in each step may be followed by the Fourier transform infrared (FTIR) spectra of the products in Figure 3. Asymmetric and symmetric stretching vibrations of the sulfone group, observed at 1380 and 1170 cm^{-1} , shift to lower frequencies, 1317 and 1154 cm^{-1} , respectively, in the sulfamidation product. Also, a new band observed at 3250 cm^{-1} belongs to N–H stretching vibration. This is clear-cut evidence of the transformation. After substitution with epichlorohydrin [Fig. 3(c)], this band disappears completely due to incorporation of the glycidyl function. A new band, observed at 3050 cm^{-1} , can be due to the epoxide



(P): crosslinked polyethylenic chain

Scheme 1



Scheme 2

ring because aromatic C—H vibrations expected at the same region are not clearly observed for the case of chlorosulfonated and sulfamidation products. Also, symmetric and asymmetric vibrations of the epoxy ring are observed at 1250 and 950 cm^{-1} , respectively.

In this study, the glycidyl group of the polymer obtained was used for attachment of a sorbitol function to the polymer. The reaction was carried out in a solution of *d*-sorbitol in 2-methyl pyrrolidone, using triethylamine as catalyst, as shown in Scheme 3. The boron uptake capability of the sorbitol-modified polymer was investigated. Unfortunately, up to the present, we have not found an appropriate method for determination of sorbitol content of the polymer. Elemental microanalysis was useless, owing to the fact that the samples could not be burned up completely, even at 1000°C. For this reason, a functionalization degree with sorbitol is lacking quantitative evidence.

However, a rough estimation, based on the 30.8% of weight increase after functionalization, implies a 63.0% conversion of the epoxide groups with sorbitol. Because of the high reactivity of oxirane, the polymer is expected to react quantitatively with sorbitol under the conditions studied. However, adjacent epoxide groups can react with hydroxyl groups of the same sorbitol molecule, and this must be responsible for low functionalization with sorbitol.

Incorporation of sorbitol into the polymer may be followed qualitatively by the FTIR spectra. The only difference observed in the FTIR spectra of the sorbitol-modified product is the high intensity of OH stretching vibrations. The absorption band associated with OH stretching vibrations becomes stronger in comparison to the one observed in Figure 3(c) arising from the moisture of KBr.

Boron Uptake Capability of the Polymer

In this section of the study, boron uptake and regeneration conditions of the sorbitol-modified polymer

were investigated. The boron-loading capacity of the polymer was found to be 1.22 mmol g^{-1} .

Provided that each epoxide function is consumed for attachment of one sorbitol molecule and each sorbitol is used for one boric acid molecule, the theoretical capacity must be around 1.74. The practical value of the loading capacity is about 70% of the theoretical capacity. Kinetic experiments show that sorption of boron from aqua solutions (pH 6.5) is reasonably fast, and the equilibrium is established in about 30 min. (Fig. 1).

In order to follow the efficiency of the polymer against trace quantities of boron, the same kinetic experiments were performed by using 32.8-ppm concentrations of boric acid. Variation of the boron concentration of aqueous solution is shown in Figure 1. This figure indicates that 30 min of interaction is sufficient to remove all the boron content and that the resin is efficient for trace quantities. The polymer loaded with boron can be regenerated by acid treatment. However, when the desorption of the boron is performed with 0.4M HCl for 3 h only 46% of the boron is released from the loaded samples. In order to attain complete boron removal, this procedure should be repeated at least 4 times. After washing with 0.1M NaOH solution and an excess of distilled water, the regenerated polymer becomes active and can be reused for the next cycle. Although we have not studied variation of the activity of samples regenerated more than 2 times, according to our preliminary experiments, boron-loading capacities of the regenerated samples are almost the same as those of the original polymer.

In conclusion, this study reveals the following:

1. Glycidyl group can be incorporated into polystyrene sulfonamides, by condensation with epichlorohydrin, in high yields.
2. The oxirane ring on the polymer offers many functionalization possibilities, through ring opening in mild conditions. The sorbitol-mod-

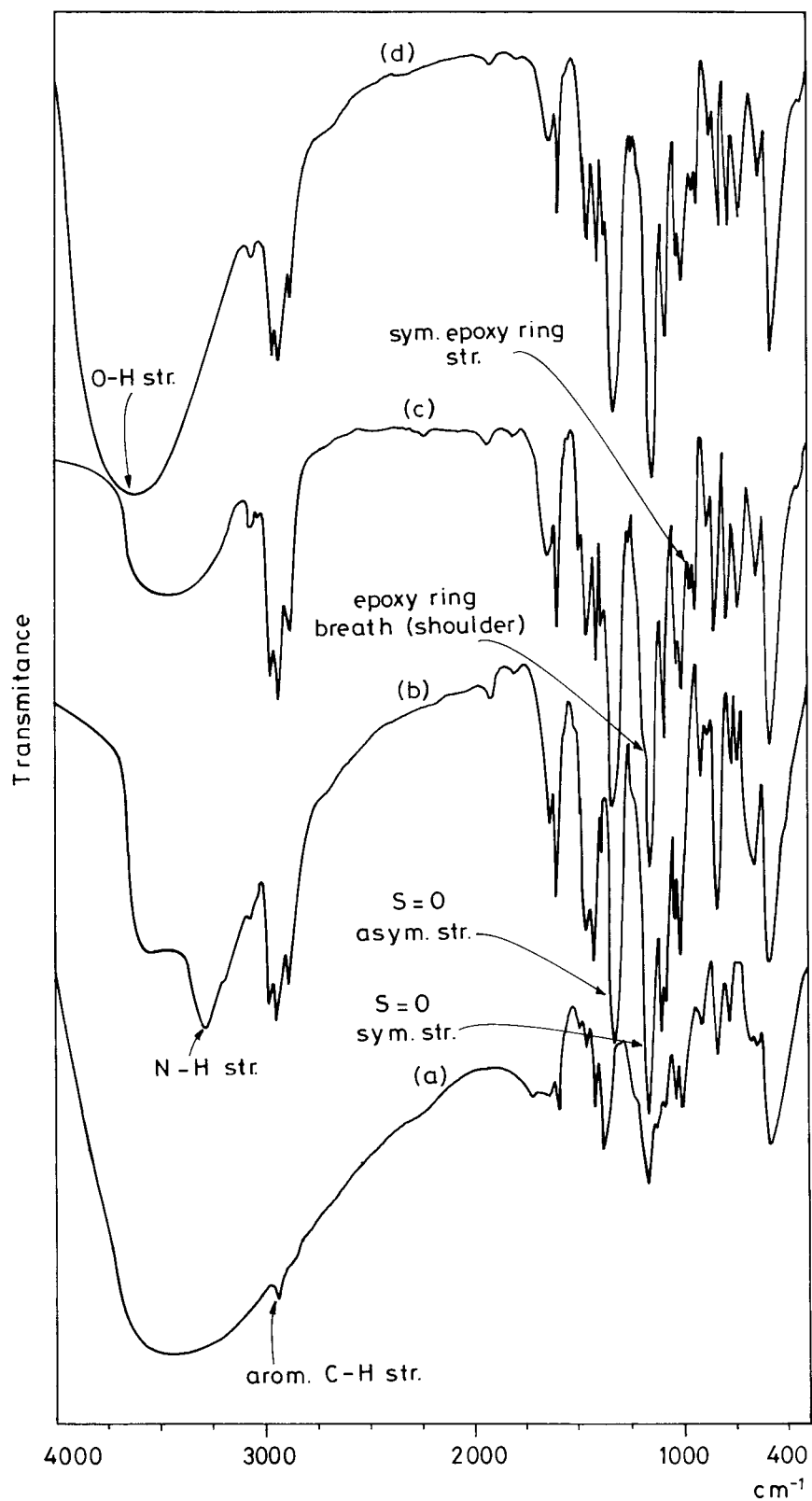
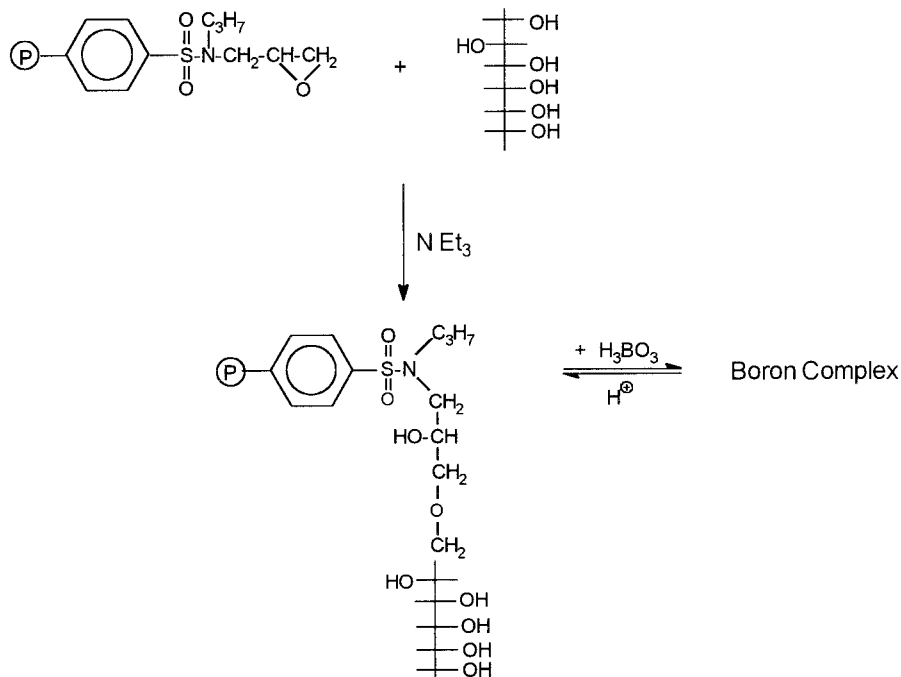


Figure 3 (a) FTIR spectra of chlorosulfonated polystyrene resin, (b) the sulfamidation product, (c) the glycidyl-bearing polymer and (d) the sorbitol-modified polymer.



Scheme 3

ified polymer presented is a specific sorbent for removal of boron, even in trace quantities.

3. Due to the relatively high hydrolytic stability of the sulfamide linkage, the polymeric sorbent can be regenerated without losing its reactivity.
4. The sorbitol-modified polymer may be of interest for large-scale applications, owing to the acceptable prices of the starting chemicals.

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