



# Covalently-bonded hyperbranched poly(styrene-divinylbenzene)-based anion exchangers for ion chromatography



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## ARTICLE INFO

### Article history:

Received 22 July 2016

Received in revised form

15 September 2016

Accepted 6 October 2016

Available online 7 October 2016

### Keywords:

Ion chromatography

Poly(styrene-divinylbenzene)

Anion exchanger

Hyperbranched functional layer

Determination of anions

## ABSTRACT

A number of covalently-bonded hyperbranched poly(styrene-divinylbenzene)-based (PS-DVB) anion exchangers having functional ion exchange layers of different branching degrees are prepared and investigated. The attachment of the hyperbranched functional layers to the substrate surface is realized via anchor secondary amino groups inserted into the polymeric backbone by means of acylation with acetic anhydride followed by reductive amination with methylamine. Further modification of the obtained secondary amino groups is provided by repeating the steps of alkylation with 1,4-butanediol diglycidyl ether (1,4-BDDGE) and amination of the terminal epoxide rings with methylamine (MA). The variation of the number of cycles including modification with 1,4-BDDGE and MA results in selectivity alterations for the obtained anion exchangers. Chromatographic parameters of the obtained stationary phases are evaluated using the model mixtures of anions ( $F^-$ ,  $HCOO^-$ ,  $Cl^-$ ,  $EtCOO^-$ ,  $BrO_3^-$ ,  $NO_2^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$ ) with hydroxide and carbonate/bicarbonate eluents. The anion exchangers show the increase of  $NO_2^-/EtCOO^-$  and  $NO_2^-/BrO_3^-$  selectivity and the decrease of  $EtCOO^-/Cl^-$  selectivity with increasing the number of modification cycles. In case of anion exchanger obtained after three modification cycles, the calculated values of column efficiencies for polarizable  $NO_2^-$  and  $Br^-$  are up to 18,000 and 16,000 N/m, respectively.

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## 1. Introduction

Nowadays the development of novel polymer-based anion exchangers with improved selectivity and efficiency remains one of the priority tasks in modern ion chromatography (IC) because of the increasing demand in determining higher number of anions in the samples with more and more complex matrices [1–7]. Because of their mechanical and chemical stability in highly alkaline solutions, copolymers of divinylbenzene with styrene or ethylvinylbenzene (PS-DVB and EVB-DVB, respectively) having high crosslinking degree are the most suitable substrates for obtaining anion exchangers for the most sensitive suppressed IC mode with potassium hydroxide eluent [8]. Selectivity and efficiency of the stationary phases based on PS-DVB and EVB-DVB strongly depend not only on the characteristics of substrate particles, but also on the surface chemistry [1].

The most popular approaches in the design of the anion exchangers for IC are aimed at shielding polymeric substrate surface with rather hydrophilic functional layers in order to avoid possible non-ionic interactions of polarizable anions, such as bromide, nitrate, iodide, perchlorate etc. with aromatic backbone of the particle [1,9–12]. Better hydration of ion-exchange sites in such hydrophilic layers results in considerable decrease of the affinity of less hydrated polarizable anions for those sites [13–15].

Among all known modification techniques [4], the creation of hyperbranched functional ion-exchange layers nowadays attracts a lot of attention because of its simplicity and flexibility in terms of providing considerable selectivity variations. Another advantage of such approach is the possibility to construct functional layers of different hydrophilicity, which effectively shield the substrate surface from the undesirable interactions with polarizable anions, and prevent analytes diffusion into the pores of polymeric particle [2,16–23].

The method of creating hyperbranched anion exchangers initially proposed in Ref. [16] includes the preparation of basement polymer layer in situ by the reaction of diglycidyl ethers with primary amines in the presence of sulfonated EVB-DVB particles,

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which results in electrostatic attachment of the obtained condensation polymer to the substrate surface [1,16]. Further branching is provided by subsequent modification of the obtained product with diglycidyl ether and methylamine (MA), and the branching degree increases with every modification cycle [16]. The authors noted high selectivity of the obtained anion exchangers and excellent peak shape for a wide variety of anions. They also showed the possibility of altering selectivity by varying the type of diglycidyl ether and reaction conditions. Another advantage of the proposed approach is the possibility of in-column modification, which allows testing the column after each reaction cycle before further modification without the need for repacking procedures.

Covalent bonding of hyperbranched layers was later proposed on the surface of aminated silica [20–22], copolymer of 1,4-di(2-hydroxy-3-methacryloyloxypropoxy)phenol [17,18,21], and carbon nanotubes [24,25], which were further electrostatically attached to sulfonated PS-DVB. The authors of Ref. [26] successfully applied hyperbranching technique to modify microspheres of poly(glycidylmethacrylate-divinylbenzene) with different ratios of monomers, which resulted in obtaining high-capacity anion exchangers. In all cases MA and 1,4-BDDGE were used as aminating and alkylating agents, and the use of 1,4-BDDGE was explained by its commercial availability in higher purity in comparison with other diepoxides [16].

All covalently-bonded anion exchangers reported in the Ref. [17–24] were tested for the separation of 7 standard inorganic anions, namely, fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate. For all types of the substrates used for the synthesis of those anion exchangers, it was noted that increasing the number of modification cycles leads to the significant improvement of separation selectivity independently from the way of attaching hyperbranched functional layer to the substrate surface. It allows one to suppose that hyperbranching can also be a promising technique for improving the selectivity of chemically derivatized anion exchangers based on PS-DVB, which separation abilities are usually limited to 7 standard inorganic anions, as reported in Ref. [1,8,23–25,27].

Earlier we reported the preparation of chemically derivatized anion exchangers having covalently-bonded functional layers of different hydrophilicity obtained via the modification of aminated 3  $\mu\text{m}$  PS-DVB particles with various diglycidyl ethers and tertiary amines [15]. Such anion exchangers demonstrated high efficiency (up to 68,000 N/m for chloride) and good selectivity for the separation of 7 standard inorganic anions and formate, but no other anions of weakly retained organic acids or oxyhalides could be separated from that mixture. At the same time, the retention of polarizable anions, such as chlorate and iodide, was too high to elute them within reasonable time even using gradient elution. That was probably due to the incomplete shielding of hydrophobic surface of PS-DVB with branched ion exchange layer and thus, high impact of non-ionic interactions on the retention of less hydrated highly polarizable anions.

The covalent attachment of hyperbranched functional layers can provide better shielding of the surface of chemically derivatized aminated PS-DVB substrates and potentially help to increase not only selectivity, but also efficiency of the obtained anion exchangers. In addition, unlike silica- and acrylate-based stationary phases [1,26,28], PS-DVB-based anion exchangers are fully compatible with highly alkaline mobile phases because of high stability of aromatic copolymer in the whole pH range. Therefore, such anion exchangers can be used in the most sensitive suppressed IC mode with hydroxide eluent in isocratic and gradient modes.

This work reports the preparation of 3 chemically derivatized anion exchangers based on PS-DVB with covalently attached hyperbranched functional layers of different branching degrees. The aim of this study is to investigate chromatographic properties of the

prepared stationary phases and to evaluate the applicability of hyperbranching technique for chemically derivatized PS-DVB particles, as well as the influence of the branching degree of the functional layer on selectivity and efficiency of such anion exchangers.

## 2. Experimental

### 2.1. Instrumentation

“Mettler” Thermostat (Mettler GmbH & Co. KG, Schwabach, Germany), “Laboport” vacuum pump (KNF Neuberger, Tranton, New Jersey, USA), “Sapphire 6580” ultrasonic bath (Sapphire, Moscow, Russia), “Eurostar” mechanical stirrer (IKA-Werke, Staufen, Germany) were used for the syntheses.

A Dionex ICS 3000 Ion Chromatography system (Dionex part of Thermo Scientific, Sunnyvale, CA, USA) equipped with a gradient pump, an autosampler and a conductivity detector with an ion suppressor was used for IC with potassium hydroxide as an eluent. A Dionex ICS 1600 Ion Chromatography system equipped with a conductivity detector with an ion suppressor was used for IC with sodium carbonate and bicarbonate as eluents. Data acquisition and processing were controlled by Chromeleon 6.8 and Chromeleon 7.0 (Dionex part of Thermo Scientific, Sunnyvale, CA, USA). The 100 mm  $\times$  4.0 mm i.d. stainless steel columns were used as housing for all the studied stationary phases, and slurry packed at 250 bar using a K-1900 pump (Knauer, Berlin, Germany).

### 2.2. Reagents

All chemicals had reagent and analytical-reagent grade and were purchased from Sigma-Aldrich (Russia) and TCI Chemicals (Japan). PS-DVB microspherical particles (crosslinking degree of 50%, particle size 11.0  $\mu\text{m}$ , surface area 600  $\text{m}^2/\text{g}$ ) were used for all syntheses.

### 2.3. Synthesis of the anion exchangers

The synthesis of PS-DVB with secondary amino groups was performed on the loose polymer as described in Ref. [8], but the procedures for acylation and reductive amination were optimized for adjusting ion-exchange capacity. The scheme of the further modification of aminated PS-DVB is presented in Fig. 1. The packing procedure and the measurement of anion exchange capacity of the columns were completed in accordance with Ref. [8]. The list of the obtained anion exchangers, numbers of modification cycles and anion exchange capacities are given in Table 1. Anion exchanger A3 was obtained from aminated PS-DVB via batch synthesis after 3 cycles of modification with 1,4-BDDGE and MA (each reaction was conducted at 60  $^\circ\text{C}$  for 1 h). Anion exchangers A4 and A5 were obtained using dynamic in-column modification of A3 as described in Ref. [16]. The amount of alkylating and aminating agents at all modification steps was 1.5 mmol per gram of dry resin, all reactions were conducted at 60  $^\circ\text{C}$  in water bath. For anion exchangers A4 and A5 the necessary amounts of 1,4-BDDGE and MA were calculated in accordance with the mass of the resin in the column A3. Each reagent was dissolved in 15 mL of deionized water and passed through the column with the flow rate of 0.25 mL/min successively. The columns were rinsed with deionized water after each modification step. The subsequent increase of ion-exchange capacity with every following modification cycle is caused by increasing the amount of quaternary ammonium groups with increasing the branching degree of hyperbranched functional layer. The capacities of all obtained anion exchangers allow them to be used in suppressed IC mode. There were no significant differences in the back pressure of the columns A3, A4 and A5 operated at the flow rate

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