



Electrostatically attached highly branched anion-exchange phases derived from diamines and diepoxides

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ABSTRACT

A new synthesis approach for the preparation of highly branched anion exchange materials utilizing diamine and diepoxide reagents is described. Unlike previously reported condensation polymers prepared from primary amine and diepoxide reagents, anion exchange polymers prepared from diamines and diepoxide reagents exhibit exceptionally low affinity for polyvalent ions. Use of anion-exchange materials synthesized utilizing this new synthetic method for the analysis of common inorganic anions is demonstrated.

1. Introduction

Ion chromatography is a type of ion exchange chromatography where all components of the analytical system are optimized for conductivity detection. Suppressed ion chromatography, was first described by Small et al. in 1975 [1]. In ion chromatography, it is highly beneficial to be able to utilize a hydroxide mobile phase for the analysis of anions and a hydronium mobile phase for the analysis of cations. When such mobile phases are combined with the appropriate suppressor device, the suppression product is essentially deionized water with analyte anions in the hydronium form or analyte cations in the hydroxide form, depending upon the operating mode. Thus, the combination of hydroxide containing mobile phases with a cation-exchange suppressor device allows for the maximum possible signal-to-noise ratio for the analysis of anions via conductivity detection. Likewise, the combination of hydronium containing mobile phases with an anion-exchange suppressor device enables the maximum possible signal-to-noise ratio for the analysis of cations via conductivity detection. For that reason, from the very beginning of ion chromatography, there has been a strong motivation to develop stationary phases optimized for these mobile phases.

Another factor driving the interest in hydroxide and hydronium mobile phases in ion chromatography is the development of eluent generator technology, enabling the production of contaminant-free high-purity mobile phases. Initial eluent generators used low-pressure membrane devices with a flowing source and destination fluid stream [2]. Further improvements in eluent generator design allowed the eluent generator to be placed in the high-pressure portion of the flow path immediately before the injection valve. Eluent generation initially used an electrically polarized bed of resin [3], but ultimately the best

option proved to be a reinforced membrane sandwiched between the electrolyte reservoir and the high-pressure eluent stream [4]. This methodology provides lowest possible suppressed conductivity mobile phases with minimal baseline shifts under gradient elution conditions. Although eluent generators can be used to make other mobile phases, eluent generators are ideally suited for the preparation of high-purity hydroxide and high-purity hydronium mobile phases.

Stationary phases in ion chromatography have been steadily evolving over the past 40 years since the initial introduction of ion chromatography. Initially, stationary phases for anion analysis in ion chromatography were designed for use with carbonate eluent [5]. Stationary phases at the time used a quaternized vinylbenzyl chloride-divinylbenzene (QVBC-DVB) anion-exchange latex, electrostatically attached to a surface sulfonated polystyrene-divinylbenzene (S-DVB) copolymer bead. Such phases worked well with carbonate eluents, but hydroxide proved to be a very ineffective eluent species for such materials.

What followed were a series of improvements in stationary phases to increase the elution strength of hydroxide. First, the number of beta hydroxyl groups associated with the quaternary anion-exchange sites was increased from 1 to 2 in the IonPac AS5 and IonPac AS5A. These phases significantly improved the elution power of hydroxide but still required more than 50 mM hydroxide to elute trivalent anions. Next, stationary phase designs based on styrenic epoxide monomers were introduced. These phases allowed the synthesis of anion-exchange polymers where the number of beta hydroxyl groups associated with the quaternary anion-exchange sites was increased from 2 to 3 in the IonPac AS11 and IonPac AS11-HC. These phases allowed the use of substantially lower hydroxide concentrations than with earlier phases. Still, these phases exhibited poor peak shape for polarizable anions,

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requiring the addition of solvent to the mobile phase to at least partially mitigate these effects.

In 2003, this lab began exploring the synthesis and application of hyperbranched anion-exchange materials for ion chromatography. This new class of ion exchange materials, using an aliphatic backbone with ether linkages exhibited surprisingly good selectivity for both polarizable anions such as perchlorate and hexafluorophosphate along with good retention and selectivity for highly hydrated anions such as fluoride and acetate. One noticeable weakness of such materials is their relatively poor divalent anion selectivity. For example, the earliest commercially available hyperbranched anion-exchange materials (e.g., the IonPac AS19 or the IonPac AS20) exhibit marginal sulfate-carbonate selectivity and can't separate sulfate from sulfite, something that conventional anion exchange materials based on cross-linked styrenic monomers can easily accomplish.

While early work [6–8] described the use of several different reagents for the preparation of such materials, the bulk of the work in this lab and the work of others has been limited to the use of methyl amine (MA) and 1,4-Butanediol diglycidyl ether (BDDGE) to produce hyperbranched anion-exchange materials. The use of ethylene glycol diglycidyl ether and glycerol diglycidyl ether were detailed in one case [8], but further work with these reagents since then has not appeared. Three groups have explored the use of hyperbranched anion-exchange materials covalently attached to silica substrates [9–12]. However, in all cases, only hyperbranched anion-exchange materials based on MA and BDDGE were investigated. Others have investigated the use of hyperbranched structures on the surface of various polymeric substrates [13–23] and carbonaceous substrates [24]. In nearly all cases, only hyperbranched anion-exchange materials based on MA and BDDGE was investigated.

There has been limited work examining reagents beyond the most widely used MA and BDDGE reagents. Two papers have examined possible alternatives to BDDGE. One paper compared the use of BDDGE or resorcinol diglycidyl ether with various quaternizing tertiary amines [22] while work in this lab has included investigation of the utility of ethylene glycol diglycidyl ether as well as glycerol diglycidyl ether for the synthesis of hyperbranched anion exchange materials [8]. In addition, one paper studied the effect of the incorporation of glycine at various points in hyperbranched structures on anion-exchange selectivity [23]. Additional work in our lab has involved the study of the effect of symmetrical diamines where both amine moieties on each end of the diamine molecule were tertiary amines [25]. This work showed that divalent anion selectivity was strongly influenced by incorporation of diamines into the hyperbranched structure. Interestingly, this work also showed that the length of the methylene spacer between the two tertiary amine end groups strongly influenced the selectivity of anion-exchange materials for divalent anions. However, thus far there has been no work investigating the use of symmetrical diamines where both ends of the diamine molecule are primary amines. It is reasonable to expect that such reagents would also have useful properties for influencing the selectivity of divalent anions and for increasing the cross-link of hyperbranched structures given the fact that diprimary amines are capable of reacting with up to six epoxy moieties. Fig. 1a illustrates the situation when diepoxides are allowed to react with a pendant secondary amine group as in the case when MA is the functionalizing reagent. In this case, a maximum of two branches will be created with each reaction cycle of first primary amine and then diepoxide. Fig. 1b represents the situation where the amine reagent is a diamines with two primary amine moieties. When such a reagent is allowed to react with the pendant epoxide moiety and then the reaction product is allowed to react with an excess of diepoxide reagent, significantly more branch points are created with each reaction cycle. Such a reaction cycle can create up to five branch points for each reaction layer. It is expected that hyperbranched polymers synthesized using this reaction scheme

will produce materials with significantly different selectivity for polyvalent anions compared to the more widely studied methyl amine/diepoxide system.

2. Materials and methods

2.1. Equipment

All chromatography was performed on a Thermo Fisher Scientific (Waltham, MA, USA) Dionex ICS-5000 + ion chromatography system comprised of a DP pump module, an EG eluent generator module, a DC chromatography module and an AS autosampler. The system used Chromeleon 7.2 software for data analysis. The EG eluent generator module contained a KOH EGC500 eluent generator cartridge, a CR-ATC eluent purifier cartridge, and a degasser cartridge. The DC chromatography module column compartment was operated at 30 °C, the conductivity cell operated at 35 °C, and a 4 mm AERS suppressor was used for all the chromatographic separations while in a 15 °C temperature control zone. Potassium hydroxide eluent produced by the eluent generator was used for all separations except in the case of the separation shown in Fig. 9B where a lithium hydroxide eluent generator was used. The eluent flow rate in all cases was 1.0 mL/min. A Dionex GP-50 pump was used to deliver reaction reagents to the column. Reactions took place while the column was submerged in a Shel Lab 2 L water bath with the cover in place to minimize water loss.

2.2. Reagents

All reactions utilized BDDGE, 95 + % purity which was obtained from Sigma-Aldrich. It was dissolved in deionized water immediately before use. Solutions were not kept longer than eight hours to avoid excessive levels of hydrolyzed product that can form spontaneously when epoxy reagents are left in contact with water. Both 1,4-butanediol diamine, 99% purity, 2,2'-(Ethylenedioxy)bis(ethylamine), 98% purity and MA solution, 40% by weight in water were obtained from Sigma-Aldrich.

2.3. Stationary phase synthesis

All columns were in PEEK column hardware, with either 4 mm internal diameter or 5 mm internal diameter and 250 mm in length as noted below.

2.3.1. Synthesis of a hyperbranched phase with a methyl amine containing ground layer followed by four 2,2'-(Ethylenedioxy)bis(ethylamine) layers (column 1)

A 4 mm internal diameter by 250 mm length PEEK column was packed at 8 mL per minute and 60 °C for 20 min using 5 g of damp, surface sulfonated 6.55 μm particle size, 55% divinylbenzene-45% ethylvinylbenzene resin with a surface area of 20.8 m² per gram. The basement layer was applied to the packed column while submerged in a water bath, passing a BDDGE-MA solution mixture dissolved in deionized water (1:1 mol ratio, 0.36 M with respect to each reagent) through column at 70 °C for 90 min at a 0.5 mL/minutes flow rate and then a rinse with deionized water at 0.5 mL/minute followed by 4 additional layers, each layer consists of the following reaction “cycle” while at 70 °C:

1. Pass a 10% aqueous solution BDDGE solution through column for 10 min at a 0.5 mL/minutes flow rate and then allow to react for an additional 20 min with the flow off.
2. Rinse for 5 min with deionized water at a 0.5 mL/minutes flow rate.
3. Pass a 1 M 2,2'-(Ethylenedioxy)bis(ethylamine) (EDBEA) aqueous solution through the column for 10 min while at a 0.5 mL/minutes

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