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# Polymer monolithic methacrylate base modified with tosylated-polyethylene glycol monomethyl ether as a stationary phase for capillary liquid chromatography

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## ABSTRACT

A polyethylene glycol (PEG) monolithic column was successfully prepared in situ for the separation of inorganic anions in ion exchange capillary chromatography. By attaching PEG-groups into the methacrylate-based polymer, the number of theoretical plates was improved from 1433 to 3346 plates/m (when nitrate was used as the analyte). The retention behavior of iodate, bromate, nitrite, bromide and nitrate was observed under various salt aqueous solutions. The retention was based on cations trapped among PEG chain and the positively charged pyridine that work as the anion exchange sites in the PEG monolith. The relative standard deviations (RSDs, for  $n=7$ ) of retention time, peak height and peak area were less than 2.27% for all the analyte anions. The PEG monoliths showed satisfactory mechanical stability and did not swell or shrink significantly with swelling propensity value of 0.34 and 0.64 for methanol and THF, respectively. This stationary phase was successfully applied to the determination of these anions in seawater as well as public drinking water samples.

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## 1. Introduction

Monolithic beds have recently been developed for liquid chromatography (LC) [1]. Their advantages include low column backpressure, simple preparation, requirement of very small amount of stationary phase for a single column, wide application, no use of retaining frits to hold the stationary phase and ease of modification. The porous monoliths consist mesopores and through-pores, which makes them highly porous compared to conventional particle-packed columns. Consequently, monolithic column can conduct the eluent with high flow rate. Basically, monoliths can be synthesized from inorganic material such as silica [2–5] or organic materials such as polymer [6,7] that contain a cross-linking agent, monomers and some porogen in a column tube by in-situ polymerization.

Polymer monolithic stationary phases for ion exchange chromatography (IEC) were fabricated and the separation efficiency was investigated in this study. The fabrication of the polymer

monolith usually involves a reactive moiety of the monolith; in this case epoxy group was used, which is then directly modified with functional groups that contain ion-exchange property, such as amino groups [6].

Polyethylene glycol (PEG) is a hydrophilic macromolecule, which only shows mild hydrophilic interaction with proteins at higher salt concentration, and hardly affected the bioactivity of protein under adequate protein purification condition [4]. PEG-functionalized polymer monolith provides the stationary phase for the separation of large and small molecules [6,8]. PEG have been used for stationary phase in reversed phase liquid chromatography. Beside hydrophobic interaction, PEG could also be used for the separation of anions even though PEG does not possess any ion exchange site. Several packing materials which were physically coated and chemically bonded by PEG for IEC have been developed while materials in the form of monolith have been very limited. Rong et al. developed and examined the PEG stationary phase by physically coating for ion chromatography. Lim et al. and Takeuchi et al. have successfully examined the PEG bonded stationary phase for separation of inorganic anions [9–12]. Linda et al. has successfully reacted the PEG with primary amino groups of an aminopropylsilica packing column for separation of inorganic anions [13]. The PEG moiety could form a helix-like conformation in the organic-aqueous media. The separation of anions based on trapping the eluent cations fixed on the oxygen atoms of the PEG chain by ion-dipole interaction that work as the anion-exchange site for separation of anions [14]. Furthermore, the trapping of the

*Abbreviations:* GMA, glycidyl methacrylate; EDMA, ethylene dimethacrylate; AIBN, 2,2'-azobisisobutyronitrile; Tosylated-PEG, tosylated-polyethylene glycol monomethyl ether; THF, tetrahydrofuran; RSD, relative standard deviation; SEM, scanning electron microscopy; HETP, height equivalent to a theoretical plate;  $\gamma$ -MAPS, 3-(trimethoxysilyl) propyl methacrylate; SP, swelling propensity; IEC, ion exchange chromatography

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**Table 1**  
Various polymerization conditions.

Column	Monomer <sup>a</sup> % (v/v)	Crosslinker <sup>b</sup> % (v/v)	Porogen <sup>c</sup> % (v/v)	Mixture ratio <sup>d</sup>	Modification condition <sup>e</sup>	N <sub>Max</sub> (plates/m)
M1	7.5	2.5	90	10/90	75 °C, 6 h	*
M2	15	5	80	20/80	75 °C, 6 h	3346
M3	22.5	7.5	70	30/70	75 °C, 6 h	5275
M4	30	10	60	40/60	75 °C, 6 h	1558
M5	17.5	2.5	80	20/80	75 °C, 6 h	4383
M6	12.5	7.5	80	20/80	75 °C, 6 h	3076
M7	10	10	80	20/80	75 °C, 6 h	1389
M8	15	5	80	20/80	75 °C, 4 h	2944
M9	15	5	80	20/80	75 °C, 5 h	3218
M10	15	5	80	20/80	75 °C, 7 h	*
M11	15	5	80	20/80	75 °C, 8 h	*

\* Not applicable.

<sup>a</sup> Glycidyl methacrylate (GMA) was always used as a monomer.

<sup>b</sup> Ethylene dimethacrylate (EDMA) was used as a cross-linker.

<sup>c</sup> Three kind of alcohols i.e. ethanol, 1,4-butanediol and decanol were used as porogen.

<sup>d</sup> The volume ratio of monomer+cross-linker to porogen.

<sup>e</sup> 1,4-Dioxane and pyridine were used as the solvents of tosylated-PEG during the modification.

cations on the PEG is similar with trapping on the crown ethers since crown ethers are cyclic PEG, but the former is more flexible [9]. The PEG monoliths have been made and synthesized from PEG-functionalized monomers or cross-linkers for size-exclusion, cation-exchange, and anion-exchange chromatography. Monolithic columns have higher permeability than particle packed columns, which lead to rapid separation of analytes. However, PEG monoliths for the separation of anions have been little reported in the literature. The focus of this study is a polymeric monolith, which requires shorter fabrication time and more robust over a wide range of pH compared to silica-based monoliths. PEG was introduced into the monolith using pyridine will be prepared to improve the column efficiency in the separation of anions since for the PEG stationary phase bromide and nitrite coelute. The PEG monolith was then used as the stationary phase for the rapid and direct determination of inorganic anions in seawater sample as well as public drinking water sample in capillary ion chromatography.

## 2. Experimental

### 2.1. Chemicals

Glycidyl methacrylate (GMA) (97%) and ethylene dimethacrylate (EDMA) (97%) were obtained from Wako while *n*-decyl alcohol, 3-(trimethoxysilyl)propyl methacrylate ( $\gamma$ -MAPS, 98%) and 2,2'-azobisisobutyronitrile (AIBN) were obtained from TCI (Tokyo, Japan). 1,4-Butanediol, pyridine and 1,4-dioxane were obtained from Nacalai Tesque (Kyoto, Japan). Polyethylene glycol monomethyl ether *p*-toluenesulfonate (tosylated-PEG, M.W.1000) was obtained from Aldrich (Rockford, IL, USA). Potassium chloride was of extra pure reagent grade (Nacalai Tesque). Purified water was produced in the laboratory by using a GS-590 water distillation system (Advantec, Tokyo, Japan). All the solutions used in this study were prepared from extra pure reagents obtained from Nacalai Tesque.

### 2.2. Preparation of monolithic column

The fused silica capillary tube (0.320 mm i.d.  $\times$  0.450 mm o.d.) was purchased from GL Sciences (Tokyo, Japan). Fused silica capillary tube was washed using 1 M NaOH solution, deionized water and 1 M HCl in sequence. 30% (v/v) of  $\gamma$ -MAPS in acetone was used for providing methacrylate groups on the inner wall surface of the capillary tube; the tube was sealed at both ends and thermally treated in a water bath at 60 °C for 24 h. Thereafter, the

capillary tube was washed with acetone and dried using nitrogen gas for 30 min. As shown in Table 1, mixture solutions of monomer, cross-linker and porogen were prepared at various compositions. Then, 0.2 mL of the solution was completely mixed with 2 mg of AIBN, i.e. the polymerization initiator. The mixture solution was then subjected to ultrasonic vibration for 5 min before it was injected into the pretreated capillary tube. Thermal polymerization was carried out in the water bath at 60 °C for 24 h. The capillary tube was rinsed with methanol thoroughly after polymerization to remove unreacted reagent and porogenic solvents. The morphology of the monolith was examined by using scanning electron microscopy (SEM; S-4800, Hitachi, Tokyo, Japan).

### 2.3. Modification of glycidyl methacrylate base

Subsequently, polyethylene glycol (PEG) group was attached into the glycidyl methacrylate monolith using polyethylene glycol monomethyl ether tosylate (tosylated-PEG). Tosylated-PEG was dissolved in 0.5 mL of 1,4-dioxane and pyridine (50/50, v/v). The solution was passed through to the glycidyl methacrylate monolith and the reaction was carried out by heating in the oven at 75 °C for 4–8 h, followed by washing with methanol at a flow-rate of 4  $\mu$ L/min for 2 h.

### 2.4. Capillary liquid chromatography

The chromatographic separation was carried out using a capillary LC system constructed by an L.TEX-8301 Micro Feeder (L.TEX corporation, Tokyo, Japan) equipped with an MS-GAN 050 gas-tight syringe (0.5 mL, Ito, Fuji, Japan) as a pump, a Model 7520 (Rheodyne, Cotati, CA, USA) injector with an injection volume of 0.2  $\mu$ L, a 100 mm  $\times$  0.32 mm i.d. of microcolumn and a UV-1575 intelligent UV/vis detector, (JASCO, Tokyo, Japan) that was operated at 210 nm. The data was acquired using a Chromatopac C-R7A data processor (Shimadzu, Kyoto, Japan). The inlet pressure was monitored with an L.TEX-8150 Pressure Sensor (L.TEX).

## 3. Results and discussion

### 3.1. PEG-monolith preparation

PEG monolith was prepared firstly from polymerization of GMA and EDMA under normal temperature for polymerization condition (60 °C) and was modified using Tosylated-PEG dissolving into 1,4-dioxane and pyridine. The good composition of monolith is a

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