Preparation of porous polymer monoliths by radiation induced polymerization

PhD Thesis

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INTRODUCTION AND AIMS

Porous polymer monoliths represent a new class of materials discovered in the early 90’s that revolutionized liquid chromatography. These separation media are bulk porous materials in which pores form channels along the whole column that allows clear flow-through of liquids. Material transfer goes mainly through macropores, while the separation - in meso- and micropores. Pore size and distribution are controlled by preparation conditions and can be tailored for a given task.

Monoliths have many different applications, both of general and specific character. The most important area is liquid chromatography, where they are used as separation media. Stationary phases based on monoliths include hydrophilic/hydrophobic, affinity, size exclusion and ion exchange columns. The main advantages of these packing materials are the lack of dead space, faster material transport, shorter separation time (could be minutes instead of hours) and that the column can be attached to the chromatographic system immediately after the preparation.

Due to the high specific surface area these polymers can be used also for other analytical applications, like supports, adsorbents, solid phase reagents, in complex synthesis, enzyme support and lab-on-chip devices.

In traditional methods used for monolith preparation – thermal and photoinitiated polymerization – the thermal sensitivity of the initiator, long reaction time, type and thickness of the column walls all affect and limit the preparation process and the porous properties of the obtained monoliths. However, these drawbacks can be eliminated by using polymerization process induced by ionized radiation.

In case of this alternative preparation method the properties of the end product are independent of the initial temperature and of the thickness/material of column walls, the polymerization starts without initiators (the monolith will
be free of additional materials) and the reaction time is very short. Mariano Grasselli and Ágnes Sáfrány used this technique for the first time to prepare porous monoliths. Porous properties of monoliths prepared from the same initial monomer mixture were altered in a wide range by dose, dose rate and temperature. Monomer concentration and the use of different porogen solvents were another two parameters affecting strongly the porous properties of the formed materials.

The aim of my work was to prepare different porous polymer monoliths using $\gamma$-radiation induced radical polymerization and to investigate the effect of preparation conditions on the porous properties of these materials.

Firstly, homopolymers from diethylene-glycol dimethacrylate (DEGDMA) monomer using different solvents (alcohols, ethyl acetate, acetone and tetrahydrofurane) and their combinations were prepared. The effect of preparation conditions (dose, dose rate and temperature) on porous properties were investigated using flow-through measurements, scanning electron microscopy, nitrogen absorption and mercury intrusion porosimetry methods.

Next, monoliths from mixtures of DEGDMA – used as crosslinker – and 2-hidroxy-ethyl acrylate (HEA), glycidil methacrylate (GMA), butyl methacrylate (BMA), N-isopropyl acrilamide (NIPAAm) copolymers with different ratios were prepared. In addition to the above methods, the obtained samples were also investigated with Fourier-transform infrared spectroscopy.

Since monoliths are mainly used in analytics, and especially in liquid chromatography, some experiments were performed in order to test the applicability of these copolymer monoliths for chromatographic separation of selected organic materials.

**EXPERIMENTAL METHODS**

The porous structure of polymer monoliths was investigated by using
different techniques. **Flux** was measured using a chromatographic pump (Liquochrom Model 2010, LMIM, Hungary). For these measurements monoliths were prepared in teflon tubes that were attached to the system using standard chromatographic fittings. **Morphology** was investigated using scanning electron microscopy (JEOL JSM 5600 LV). After the irradiation, the samples were dried and coated with thin film of sputtered platinum-palladium or gold (JEOL JFCI 300AutoFine Coater). The pore size distribution was determined using *mercury intrusion porosimetry* at the Department of Chemistry, University of California, Berkeley (Autopore III 9400) and at Pannon University (Carlo Erba, 70 típusú). **Gas adsorption** measurements were performed at Zrínyi Miklós National Defense University, at Budapest University of Technology and Economics (Quantachrome Autosorb-1) and at Pannon University (Micromeritics, ASAP 2000). **Liquid chromatographic** tests were performed on Jasco MD-2015 Plus and Jasco PU-2089 Plus HPLC pumps. The *FTIR* spectra were recorded with diffuse reflectance attachment (Unicam Mattson Research Series 1 (UMRS1) FTIR spectrometer).

**NEW SCIENTIFIC RESULTS**

I.

a. Flux measurements performed on DEGDMA homopolymer monoliths showed that at least 20 kGy dose is required for the formation of rigid polymer framework. When using smaller doses, because of the low level of crosslinking polymer network could not yet develop, and pores did not exist. With increasing dose both flux and pore size decrease.

b. Rigid polymer network requires dose rates above 10 kGy/h. Higher dose rate means higher rate of radical formation and faster crosslinking, which results in bigger pores and higher flux. With increasing dose rate both flux and
pore size increase.

c. Higher synthesis temperature increases the average pore size. At higher temperatures the formed polymer chains move more rapidly and the crosslinking takes place faster, but the precipitation occurs earlier. The increasing temperature promotes the dissolution of the polymer. Therefore, at higher temperatures the polymerization centers (nuclei) are formed by polymer chains having higher molecular weight; this will lead to bigger polymer spheres and, as a consequence, bigger voids between them.

d. Increasing monomer concentration decreases the flux until it stops completely. For high DEGDMA concentrations the high crosslinking of the polymer results in very small pores and the eluent cannot flow through the column. 20-40 vol.% monomer concentration required to prepare monoliths with good flow-through characteristics.

II.

a. For DEGDMA-HEA copolymer monoliths, the increase of the 2-hydroxiethyl acrylate comonomer concentration resulted in bigger pores and enhancement of the hydrophilic character of the surface.

b. The increase of N-isopropyl acrylamide comonomer concentration resulted in bigger pores too. With NIPAAm concentrations higher than 12 w.% in binary solutions, hydrogels were obtained instead of monoliths.

c. In addition to bigger pores the higher concentration of butyl methacrylate comonomer causes also enhancement of hydrophobic properties of pore surface.

d. In case of glycidil methacrylate, the higher concentration results in smaller pores and higher affinity of the surface for protein immobilization.
III.

a. In case of homopolymer monoliths solvents can be divided into two groups: small pores were observed in monoliths prepared from systems with one type of solvents (acetone, acetonitrile, ethyl acetate and tetrahydrofurane), while large pores form with the others (first of all alcohols). This difference is caused by different solubility of the monomer and the polymer in solvents of the two groups.

b. The decreasing solubility parameter of alcohols resulted in decreasing pore size of the obtained copolymer monoliths. When using different alcohols with the same comonomer system, the pore size was found to decrease in the order of BMA<HEA<GMA.

c. In monoliths prepared with binary solvent systems, where a macro-porogen (ethyl acetate, acetone, acetonitrile, tetrahydrofurane) and an alcohol (methanol, ethanol, 2-propanol) solevent were mixed, highest flux was achieved with 20-30 vol.% content of micro-porogen. Alcohols were found to weaken the strong micro-porogen effect of other organic solvents.

IV.

Nucleic acids and amino acids were successfully separated from proteins on LC columns made of functionalized porous polymer monoliths prepared using radiation initiation polymerization. These packings could be good alternatives for monolithic HPLC packing materials prepared using thermal and/or photoinitiated polymerization. Monolith columns prepared from 2-hydroxy ethil acrylate and N-isopropyl acrylamide comonomers were found to be very promising environmentally friendly separation media, since organic solvents were not required during HPLC separations performed on them.
LIST OF PUBLICATIONS


BOOK CHAPTERS

Sáfrány, Á., Beiler, B., Radiation synthesized functional polymer supports with tailor-made properties for separation and purification IAEA-TECDOC-1465, 53-67 (2005)

2. Beiler, B., Sáfrány, Á., Pórusos polimer monolitok előállítása sugárzásos polimerizációval, KKKI Kutatóközponti tudományos napok, 2005, oral presentation


5. Beiler, B., Sáfrány, Á., Hidrofil karakterű kopolimer monolitok előállítása sugárzásos polimerizációval, Őszi radiokémiai napok, 2006, oral presentation