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RESEARCH ARTICLE OPEN ACCESS

Characterization Of Monolithic Column Methacrylate Polymer Based Modified by Dietylamine and Dimetylamine

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Abstract:

The monolithic methacrylate polymer-based column has higher polarity and better stability in work in a wide range of acidity (pH) degrees so that it can be used as an alternative stationary phase in ion chromatography. Therefore, in this study monolithic columns made in fused silica capillary column by in situ polymerization reaction using glicydil methacrylate as monomers; ethylene dimethacrylate as a crosslinker; 1-propanol, 1,4-butanadiol and water as porogen; diethylamine (DEA) and dimethylamine (DMA) as modifiers. The monolithic column that has been polymerized, the morphological form will be characterized using Scanning Electron Microscopy (SEM), the functional group is characterized by the Fourier Transform Infra-Red Spectroscopy (FTIR). Monolithic columns have good mechanical stability with permeability 9.88 x 10^{-7} mL/m for modification of diethylamine and for modification of dimethylamine 10.5 x10^{-7} mL/m.

Keywords — **Monolithic column, polymer based methacrylates, ion chromatography**

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I. INTRODUCTION

Ion chromatography has developed from using conventional columns which are relatively large into smaller (micro) sized columns [1]. In 1981, Daido Ishii used a micro column to separate samples in serum. The use of micro columns has advantages compared to conventional columns, one of which is the relatively smaller column size with a small stationary phase and mobile phase with a small volume and low flow rate. So that it can produce waste with a small volume especially if it is used for analysis with toxic mobile phases and the volume of samples analyzed also becomes less. The analyte component can be separated because of the influence of the difference in electrostatic force between the analyte ion and the functional group on the stationary phase where the analyte component can be detected on the detector [2].

The monolithic column was successfully applied as a separation medium in ion chromatography because it has several advantages, namely simple manufacturing, availability of various types of precursors, having a typical pore structure, low system pressure and better permeability. Making a monolithic column is known as a monolithic technique that is by entering a stationary phase into a column by mixing several types of monomer solutions (amino acids, nucleotides, monosaccharides and fatty acids).

The initiator to initiate the formation of a polymer with a certain particle size depending on the type of initiator used. The cross-linker solution is a compound that has a low molecular weight with a hydroxyl group or amine group which functions to make the polymer more elastic and less swelling power. Porogens function to make shafts on polymer compounds that are formed. Then these

monomers will form polymers with macromolecules of the basic monomer units. Monolithic columns that have a porous structure will reduce diffusion paths and flow resistance compared to containerized columns [3].

Methacrylate based polymers provide higher polarity and better stability over a wide pH range (2-12). Glicydil methacrylate has a very reactive epoxy ring and can be converted into an ion exchange group with a ring opening reaction from its compounds . Addition of the monomer methacrylate in the polymerization mixture can increase the surface area of the monolith so that the performance of the separation of small molecules can be increased[4].

Monolithic column will be used as a separation medium in ion chromatography. Ion chromatography has evolved from using conventional columns that are relatively large to smaller or micro sized columns[5]. Ion chromatography has became a reliable analytical technique for determining cations or anions in various sample at lower concentration[6].

II. MATERIALS AND METHODS

a. Materials and Instruments

This study needs materials used for fabrication monolithic polymer column is Glycidyl methacrylate (GMA), 1,4-butanediol,Dimethylaime (DMA),Diethylamine(DEA), 3-propyl methacrylate ,ethylenedimethacrylate(EDMA),azobisisobutyronitrile(AIBN) and also several materials used for separation analysis.

The instrumentations used in this study included instruments for synthesis and characterization of monolithic column. Such as liquid romatografi capillary system, gas-tight syringer, capillary column, polytetrafluoroethylene (PTFE), waterbath.

Instruments used for characterization consisted of Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR).

b. Procedure

1. Making a Monolith Column

a. Pre-treatment

The capillary column is cut (100 mm x 0.32 mm id x 0.75 mm od). Flowed to 1M NaOH capillary column with flow rate of 4 µL / min for 30 minutes (washing the column). And finally the capillary column was rinsed with 1M HCl with a flow rate of 4 µL / min for 30 minutes. Then the capillary column is filled with ɣ-MAPS solution (15 mL ɣ-MAPS in 0.35 mL acetone) until it is fully filled and both ends of the capillary column are closed with PTFE. The capillary column was inserted into the *waterbatch* for 24 hours at 60 ^{0} C. The capillary column was removed from the *waterbatch* and rinsed with acetone with a flow rate of 4 µL / min for 30 minutes. Then the capillary column was dried with N_2 gas for 30 minutes.

b. Polymerization

The polymer precursor solution was made by weighing 0.002 g of the AIBN initiator and mixed with 0.09 mL GMA (monomer); 0.03 mL EDMA (crosslinker); 0.105 mL 1,4-butanadiol; 0.06 ml deanol; 0.015 mL of water (porogen). The polymer solution was homogenized in ultrasonification for 5 minutes. After being homogeneous, the polymer solution is loaded into the capillary column until it is fully filled and closes both ends with PTFE. Entered into *waterbatch* for 24 hours at 60 ^{0} C. The column was removed from the *waterbatch* and rinsed using 0.5 mL methanol with a flow rate of 4 µL / min to remove parogen solution and other solutions which did not react.

c. Modification of Monolith Columns with Dietylamin(DEA) and Dimetylamin(DMA)

DEA and DMA are used to act as functional groups where anion exchange and anion separation occur. The capillary column has been filled with a modified stationary phase polymer with 0.5 mL DMA dissolved in 0.5 mL ethanol (1: 1 v / v) at a rate of 4 µL / minute. The column was heated for 4 hours at 80 ^{0} C. The column was removed from the oven and rinsed with 0.5 mL methanol with a flow rate of 4 µL / min. The same treatment modifier was replaced with 0.5 mL DEA dissolved in 0.5 ml ethanol (1: 1 v / v)[7].

2. Characterization of Monolithic Columns by *Scanning Electron Microscopy* (SEM)

Characterization using SEM aims to determine the morphological form of the monolithic column that has been made . Small pieces of monolithic column are placed on the sample site. The process of visualizing and photographing the surface morphology of the monolithic column using SEM is done by operating a computer that has been directly connected with SEM equipment and instrumentation.

3. Characterization of Monolith Columns with *Fourier Transform Infrared Spectroscopy* (FT-IR)

Characterization using FT-IR aims to determine the functional groups contained in the monolithic column that has been made. Material filled with monolithic column was removed from the *fused sillica capilary column* to obtain a fine powder. Then taken and placed in the sample place on the FT-IR tool for analysis.

4. Column Permeability Measurement

Column permeability is determined by measuring column pressure. Column pressure measurement is carried out by flowing the water motion phase with the flow rate. The permeability curve is made based on the flow rate (µL / minute) and pressure (MPa) produced. The permeability of the resulting column can be calculated using the formula:

$$K^0 = \frac{V\eta L}{\pi r^2 \Delta P}$$

K^0 = column permeability (mLm)
V = linear phase of the mobile phase (mL / s)
Ƞ = dynamic viscosity of the mobile phase (Pa s)
L = column length (m)
r = radius of column (m)
ΔP = pressure difference (Pa)

III. RESULT AND DISCUSION

1. Fabriaction a Monolithic Column

The anion exchange monolith column was made through an insitu polymerization reaction consisting of three stages. The first is the initial treatment of the *capillary column* using ɣ-MAPS. Second, the formation of a polymer matrix using AIBN as an initiator, GMA as a monomer, EDMA as a crosslinker and a porogen mixture consisting of 1-propanol, 1.4 butanadiol and water. Finally, the modified monolithic column uses dimethyl amin and diethyl amin to obtain an anion exchange group.

The composition of the mixture of monomers, crosslinkers and porogens, and the conditions of the polymerization reaction and modifications will affect the structure of the monolithic column. Approximate scheme forming reaction monolithic columns *methacrylate-based polymer* in general can be seen in Figure 1.

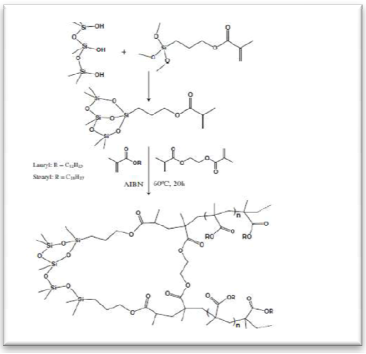


Figure 1 . Estimated reaction scheme for monolithic column formation

The form of anion exchange monolith column that has been made can be seen in Figure 2

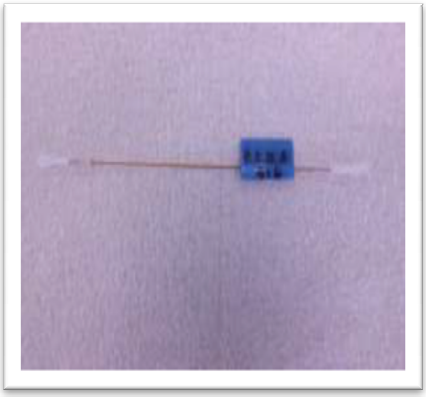
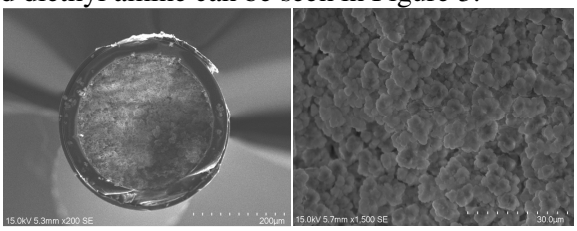


Figure 2 . Anion exchange monolith column (0.32 mm id x 0.45 mm od) [8]

2. Characterization of Monolithic Columns by *Scanning Electron Microscopy* (SEM)

The shape of the surface morphology of monolithic columns is an important parameter that can affect the ability and efficiency of separation. The morphological shape of the monolith column that was made was characterized using SEM. The results of SEM characterization of monolithic columns modified with dimethyl amine and diethyl amine can be seen in Figure 3.



(a) (b)

Figure 3. SEM results
in modified monolithic *methacrylate-based polymer* columns with DEA and DEA
(0.32 mm id x 0.45 mm od)
(a). 200X magnification, (b). Zoom in 3000X.

From the SEM results in Figure 3 (a) it can be seen the morphological shape of the solid monolithic column and the polymer formed sticking well to the wall in the *silica capillary column* used. The successful attachment of polymers formed on the column walls used is greatly influenced by success in the initial treatment stage. At the initial treatment ɣ-MAPS is passed so that the methoxysilyl group at ɣ-MAPS reacts with a silanol group of wall surfaces in the *silica capillary column to* form a –Si-O-Si-C bond so that the polymer formed can stick to the wall in the column.

From the SEM results in Figure 3 (b) it can be seen that on the surface of the monolithic column column there are small particles that have a spherical and homogeneous shape. Small particles scattered in the aggregate monolithic column form a skeleton. The pores in the skeleton (mesopore) are not clearly visible because of the very small size. While the pores between skeletons (macropore) can be clearly seen.

The particle size of column fill material can affect the results of separation. The smaller the particle size, the surface area will be greater so that more and more anion exchange groups are contained in the column. Column size will also affect the results of separation. The smaller the column size, the smaller the period of the column, which means the number of stationary phases in the column is also less. The interaction between the analyte which will be separated with the stationary phase will be smaller so that the analyte can separate with a faster retention time. This can cause the analyte not to separate completely or the resulting analyte peak is still wide[9].

3. Characterization of Monolith Columns with *Fourier Transform Infrared Spectroscopy* (FT-IR)

Characterization with FT-IR aims to estimate the functional groups found in the anion exchanger monolithic column that has been made. Results of FT-IR characterization of monolithic columns before and after modification with dietylamine DEA) and dimetylamine (DMA).

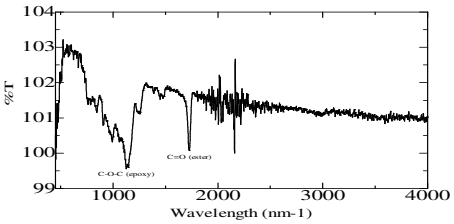


Figure 4 . FT-IR spectum is a monolithic column before being modified

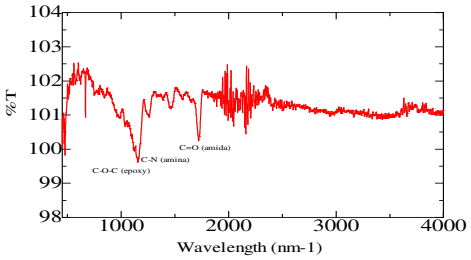


Figure 5 . FT-IR spectum after monolithic column modified

From Figure 4 it can be seen that the monolithic column before modification has two peaks, first at wave number 1729.83 cm cm $^{-1}$, and second peak at wave number 1152.26 cm $^{-1}$. The absorption area found in wave numbers between 1700-1750 cm $^{-1}$ is an area for absorption C=O (esters) and the area found in wave numbers

between 1000-1250 cm $^{-1}$ is an area for COC (epoxy) uptake.

From Figure 8 it can be seen that the monolith column after modification has three peaks. The first peak at wave number 1720.19 cm $^{-1}$ is estimated to be the peak of C = O (amide). The second peak at wave number 1477.21 cm $^{-1}$ is estimated to be the peak of CN (amide). The third peak at wave number 1169.62 cm $^{-1}$ is estimated to be the peak of COC (epoxy) and CN (amine) where the peak is overlapping with the peak COC (epoxy). It can be estimated that in the monolithic column a reaction occurs between trimethylamine and the C = O group (esters) of the monomers to produce amide compounds with quaternary amides as anion exchange groups and the reaction between trimethylamine and COC (epoxy) from the monomer produces amine compounds with quaternary amines as clusters anion exchanger.

4. Column Permeability Measurement

Permeability is the ability of the stationary phase to be fed by the mobile phase. The column permeability is determined by measuring the pressure at various flow rates using water as the mobile phase. The permeability values of the columns obtained were 9.88 x 10 $^{-7}$ mL / m modified DMA and 10.5 x10 $^{-7}$ mL / m for the DEA modification . Monolithic columns are said to have good permeability if the permeability value is around 19x10 $^{-7}$ mL/m [10]. Thus the monolithic column which has been modified with dietylamine and dimetylamine has quite good permeability.

The permeability value of the monolithic column is strongly influenced by the type and composition of the porogen. Smaller molecular weight porogens will form smaller pores, while larger molecular weight porogens will form larger pores. The high porogen composition in the polymerization solution mixture will provide greater permeability so that the mobile phase and sample solution can flow through the column at lower pressures.

However, the low porogen composition in the polymerization solution mixture will give smaller permeability so that the mobile phase and sample solution flow past the column at higher pressures. The higher the flow rate used, the higher the pressure produced. This shows that the monolithic column has good mechanical stability.

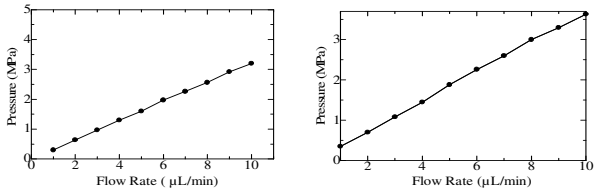


Figure 6. Curve showing the permeability of column (a). Modified DEA (b). DMA modification

IV. CONCLUSION

Based on the results of the research conducted, it can be concluded that:

The monolithic column is made on the *fused silica capillary* by *insitu* polymerization reaction using glycidyl methacrylat as a monomer; ethylene dimethacrylate as a crosslinker; 1-propanol, 1,4-butanadiol, and water as porogen;Diethylamine and dimethylamine as modifiers. The morphological form of the monolith column that has been made solid and the polymer formed attaches well to the wall in the *fused silica capillary* used. Small particles scattered over the monolithic column are estimated to have a particle size of around 0.67 µm. From the results of the FT-IR it was estimated that in the monolithic column a reaction between diethylamine and dimethylamine with COC (epoxy) from the monomer produced amine compounds with tertiary amines as ion exchange guggus. Monolithic columns have good mechanical stability with permeability of mL / m.

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