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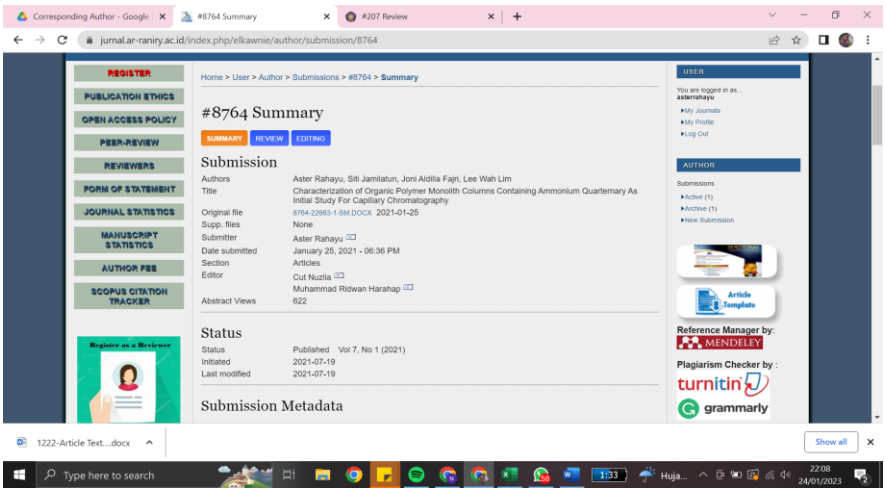
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CHARACTERIZATION OF ORGANIC POLYMER MONOLITH COLUMNS CONTAINING AMMONIUM QUARTENARY AS INITIAL STUDY FOR CAPILLARY CHROMATOGRAPHY

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Abstract: The polymerization process with a simple step has become the centre of attention of several researchers. Various polymers have been developed but still, use the post-modification method. In this research, quaternary ammonium monolith organic polymer has been prepared using a simple single thermal method. Monomer 2 - [(Methacryloyloxy) ethyl] trimethylammonium and ethylene dimethacrylate crosslinker polymerized in fused-silica capillary (100 mm, 0.32 mm i.d. x 0.45 mm o.d.). In order to achieve the perfect macropores, three types of compounds were used as porogen, namely isopropyl alcohol, PEG 400 and ethanol. Polymerization is carried out using a "one-pot approach". Characterization of surface morphology of quaternary ammonium monolithic polymer was carried out using a Scanning Electron Microscope (SEM), and functional groups were characterized by Fourier Transform Infrared Spectroscopy (FTIR). The polymer's pore size distribution was obtained, ranging from 1.29 to 3.33 µm. Organic polymers contain good amine functional groups.

Keywords: *Monolith, Organic polymer, One-pot approach, Ammonium quarternary, Polymerization, Capillary*

1. Introduction

Polymers are large molecules composed of a series of monomers that are interconnected by the presence of crosslinkers. Monolith polymers can be broadly divided into two types, namely organic polymers and inorganic polymers (Rahayu *et al.*, 2015). Inorganic polymers are usually based on silica and have been widely used as a stationary phase in cation separation and detection of cation levels in drinking water (Rahayu *et al.*, 2015) polar compounds (Yang *et al.*, 2013) and several other macromolecular compounds in the chromatography method (Iwasaki *et al.*, 2012). Besides the perfect separation and detection results, this inorganic polymer has disadvantages, including a long total manufacturing time and a limited variety of polymer-forming materials (Zhong *et al*., 2010, Lalli *et al*., 2020).

Organic polymers have been developed and applied as a stationary phase in separating compounds or ions in chromatographic methods. Besides, monolith polymers ability to provide pore space also serves as an alternative to the adsorbent. Among them is the absorption of several heavy metals in the form of ions or organic compounds. The Cr (VI) ion can be adsorbed using a magnetic polymer containing an amine group (Zhao *et al*., 2013, Zhao *et al*., 2010). Methacrylate-based organic polymers with the epoxy methacrylate ring-opening method have been successfully prepared and used in the absorption of Cu (II) (Shen *et al*., 2012) and Hg (II) ions (Pan *et al*., 2014, Pan *et al*., 2012). In addition to ions, organic polymers have been successfully applied to absorption. Organic compounds such as Bisphenol A (BPA) (Zhao *et al*., 2013), Bovine Serum Albumin (BSA) (Shamim *et al.*, 2007) and

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Making the polymer uses two stages, namely the polymerization stage and the advanced modification stage. This advanced modification stage aims to add the desired active side according to the intended purpose and application. Not many of these organic polymers are made using only the "one-pot approach" method with simple steps where the polymerization process with a simple step is the centre of several researchers attention.

This research aims to synthesize monolithic polymers with quaternary ammonium groups using a straightforward one-pot approach as an alternative to the stationary phase in capillary system liquid chromatography for the separation of anions and cations. In this research, monolithic polymers containing quaternary amine groups will be polymerized from monomer 2-[(Methacryloyloxy)ethyl] trimethylammonium with ethylene dimethacrylate as a crosslinker with a short and straightforward method, namely "one-pot approach". In the polymerization stage, several factors that influence the reaction and the polymer formed will be studied, including temperature and the composition of the polymer-forming monomers and porogens. The surface characteristics of the polymer monolith will also be investigated. The monolithic polymer that already contains the quaternary amine functional group will be characterized and used as the stationary phase in the capillary system liquid chromatography to separate organic compounds.

2. Material And Methods

2.1 Materials

The materials used in this study included 2- [(Methacryloyloxy) ethyl] trimethylammonium chloride solution (META), Ethylene dimethacrylate (EDMA) (Wako 1st Grade, Japan), 2,2'-azobisisobutyronitrile (AIBN) (Trade TCI Mark), Isopropyl alcohol (IPA) (Wako 1st Grade), Polyethylene glycol (PEG) 400, 3- (trimethoxysilyl) - propyl methacrylate (γ-MAPS) (Nacalai Tesque, Kyoto, Japan), ethanol (Wako 1st Grade), solution standard nucleotides (Uracil), toluene, 0.1 M NaOH, 0.1 M HCl (Nacalai Tesque, Kyoto, Japan), deionized water (water that has a known conductivity and is specifically used for ion chromatography) GS-590 water distillation system (Advantec, Tokyo, Japan).

2.2 Apparatus

The equipment used in this study included the Scanning Electron Microscope (SEM) S-4800 (Hitachi, Tokyo, Japan), Fourier Transform InfraRed (FTIR) Spectrum 400 Series Perkin Elmer.

2.3 Synthesis of quaternary ammonium organic polymer monoliths

Making organic polymer monoliths in silica capillaries begins with pre-treatment by rinsing the capillaries with 0.1 M NaOH, 0.1 M water and 0.1 HCL and acetone flowed into the column a flow rate of 2.5 µL/min for 60 minutes sequentially. The column was dried by flowing nitrogen gas for 30 minutes. 30% (γ-MAPS) was dissolved in acetone and flowed into

the column then both ends of the column were closed. The column which already contains the solution (γ-MAPS) is placed in a water bath with a temperature of 60 ºC for 24 hours. The capillary column was rinsed again with acetone at a flow rate of 2.5 µL / min for 60 minutes and dried by flowing nitrogen gas for 30 minutes.

The polymerization stage was carried out by making a polymer solution with an initial composition of 1.25 mL 2- (Methacryloyloxy) ethyl] trimethylammonium chloride solution, 0.375 mL ethylene dimethacrylate, 1.75 mL isopropyl alcohol, 0.35 mL ethanol, 1.4 mL PEG 400, 2 mg 2,2'-azobisisobutyronitrile was put into the vial bottle. The mixture is stirred until well blended. The solution mixture was put into the silica capillary, and then both ends tube were tightly sealed and placed into a water bath with a temperature of 60 ˚C and 24 hours. Then the monolith polymer is rinsed with methanol to remove residual reaction and residue. Monolith polymers as the stationary phase are suitable for capillary system liquid chromatography on uracil and toluene separation.

2.4.Characterization of compounds

The surface morphology of quaternary ammonium organic polymer monoliths was characterized using Scanning Electron Microscope (SEM) and Fourier Transform InfraRed (FTIR).

3. Discussion

3.1 Synthesis of polymeric organic monoliths

The Organic polymer monolith containing quaternary ammonium is synthesized by the direct method in the capillary column I.D 0.32 mm x 100 mm with single thermal polymerization known as one-pot approach method. The synthesis was carried out using a monomer that already has a quaternary ammonium functional group, in this study was used 2-[(methacryloyloxy) ethyl] trimethylammonium. To form a structural polymer union series, and Ethylene dimethacrylate as crosslinker. Monomers contained quaternary ammonium groups which can act as active groups for strong anion exchangers. This active group is very useful in the separation process of either anion solution or organic solution. The polymer formed by the "one-pot approach" method in the capillary column has a scheme of the expected reaction shown in Figure 1. The quaternary ammonium functional group in the META-EDMA polymer monolith is contributed by the META monomer, where quaternary ammonium is the active group for the anion exchange.

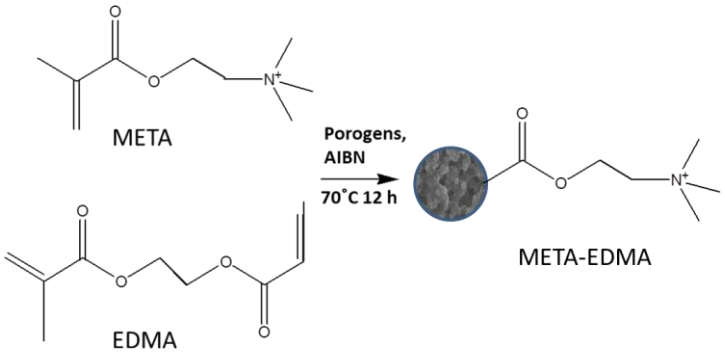


Figure 1. Scheme of the expected reaction of organic polymer

In this organic polymer monolith polymerization process, the ratio between monomer and porogen ratio is 20:80. Meanwhile that 20% is a mixture of monomer and crosslinker which consists of a percentage ratio of the composition, namely 50% is META, and 50% is EDMA. Meanwhile, 80% of the total polymer solution is porogen. Three types of organic compounds that act as porogen. Isopropyl alcohol, polyethylene glycol with a molecular weight of 400 and ethanol. These three solutions worked to form macropores on the surface of the polymer monolith that is formed. Visually, an organic polymer monolith forms a white solid, as shown in Figure 2.

Figure 2. The visual form of the quaternary ammonium organic polymer.

3.2 Characterization of organic polymer monoliths

3.2.1 Using Fourier Transform Infrared (FTIR)

Fourier Transform Infrared (FTIR) was carried out to determine the presence of amine compounds. The amine group itself is used as a strong anion-exchanger group. In addition, it is possible to predict the monolith column's possible reactions from the FTIR spectrum. The FTIR spectrum of an organic polymer monolith was shown in Figure 3. From Figure 3 it can be seen that the organic polymer monolith column has five peaks, namely the first peak at wave number 1020.3 cm^{-1}, the second peak at wave number 1352.2 cm^{-1}, the third peak at wavenumber 1723.6 cm^{-1}, peak fourth at wave number 2875.3 cm^{-1}, and the fifth peak at wavenumber 3433.6 cm^{-1}. The absorption area contained in the wavenumber between 1150-1085 cm^{-1} is the absorption area for the C-O (stretching) functional group. The high intensity of the principal peak in organic polymer monolith describes many oxygen-containing groups after the polymerization process. The number of oxygen-containing groups came from either from ethyleneglycol dimetharyate or 2-[(Methacryloyloxy) ethyl] trimethylammonium. The absorption area in the wavenumber between 1250-1020 cm-1 is the absorption area for C-N (amine). The absorption area in the wavenumber around 1650-1580 cm^{-1} is N-H's absorption area (amine). These amine groups are contributed by functional monomers that used. The absorption area in the wavenumber between 2853-2962 cm-1 is the absorption area for C-H (stretching). The absorption area in the wavenumber between 3000-3600 cm^{-1} is the O-H functional group (Silverstein *et al.*, 2005). It can be concluded that the bond and functional groups are thought to come from the presence of a polymerization reaction involving an initiator, monomer, crosslinker, and porogen.

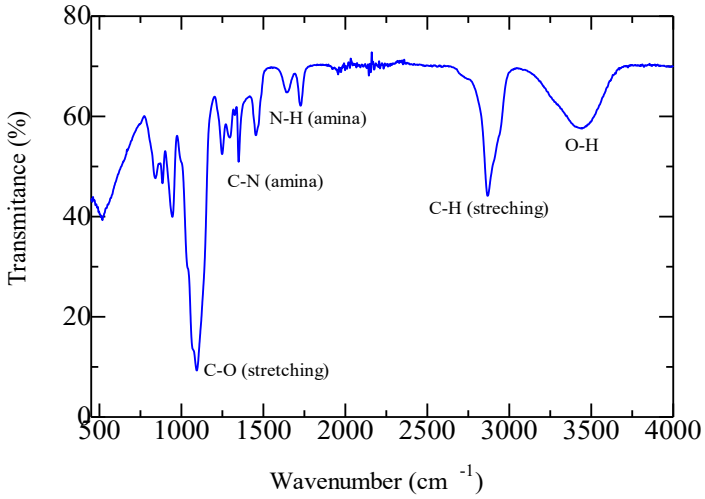
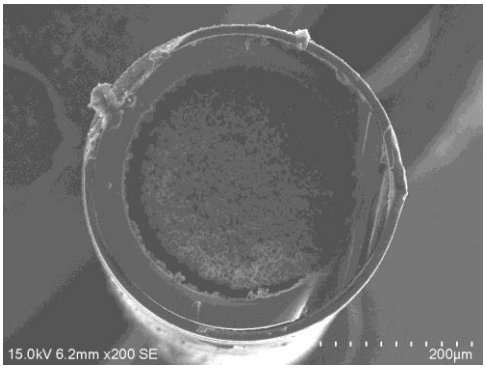


Figure 3.Fourier Transform Infrared (FTIR) spectrum of organic polymer monoliths.

3.2.2 Scanning Electron Microscope (SEM)

The surface morphology of the organic polymer monolith is one of the parameters to determine the polymer monolith adhesion condition to the capillary column's inner wall.

Besides, SEM analysis can also analyze the distribution of pores formed by using porogen in polymer solutions. The porogen used will form macropores, which are the distance between one polymer union and another. SEM results can be seen in Figure 4.



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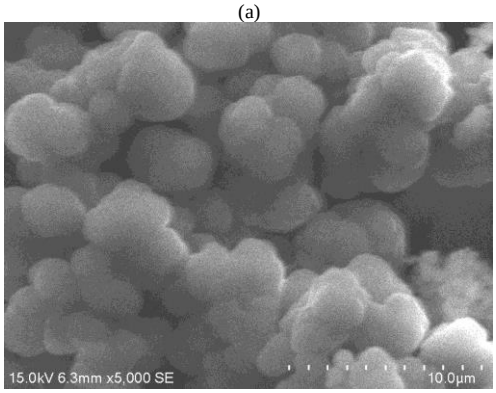
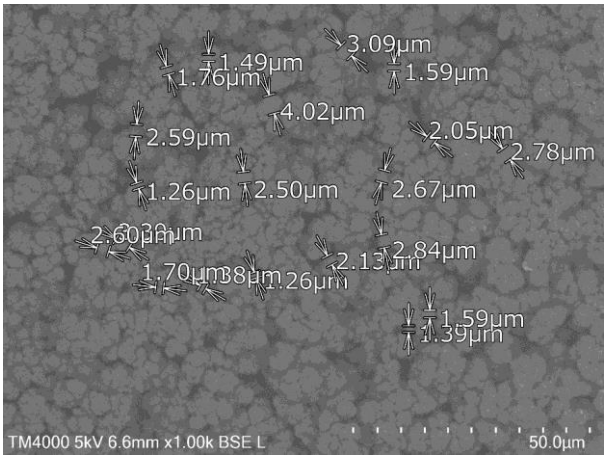


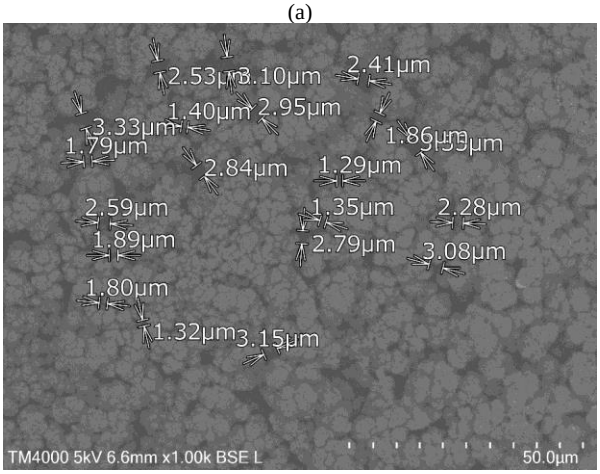
(b)

Figure 4.The surface morphology of the organic polymer monolith with the magnification of 200x (a) and 5000x (b)

Figure 4 shows if the capillary column surface analysis is carried out by enlarging it 200 times (a) and 5000 times (b). From the results of the SEM photos in Figure 4. (a) there is a sufficient optimal adhesion between the inner wall surface of the capillaries and the organic polymer monoliths formed. The capillary column's pre-treatment process using 30% (γ-MAPS) dramatically affects the adhesion results between the monolith formed and the walls in the capillary column. 30% (γ-MAPS) acts as a surface laxative in the capillary column walls coated with silanol groups. Whereas in Figure 4. (b), we can see the distribution of polymer unions and macropores' formation from organic polymer monolith. The macropores are perfectly formed and relatively evenly distributed. In Figure 5, you can see the size distribution of the union and pore created. The union's size formed on the organic polymer monolith can be seen in Figure 5 (a), about 1.26-3.09 µm for each union. And the pore size distribution formed can be seen in Figure 5 (b), around 1.29-3.33µm.



(a)



(b)

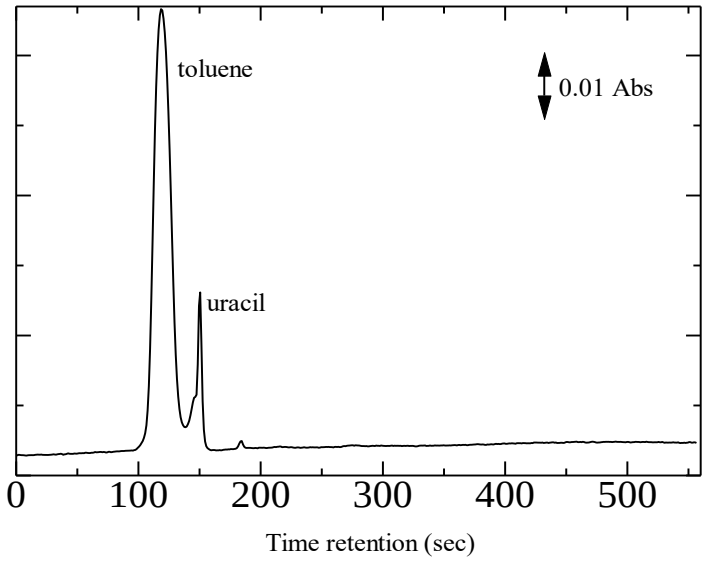
Figure 5. Surface morphology of organic polymer monolith, union size distribution (a) and pore size (b).

From the results of the excellent union and pore size distribution on the polymer surface of the capillary column that is formed, the column can be used as the stationary phase in a liquid chromatography system with a reasonably good system pressure below 2 MPa.

3.3. Separation of Uracil and Toluene

In order to observe the ability of the organic polymer monolith as stationary phase in liquid chromatography capillary system, as the initial study, uracil and toluene were used as analytes. Acetonitrile 90% was used as the mobile phase. The chromatographic result was shown in Figure 6. Figure 6 shows that toluene and uracil could separate correctly with the retention time of toluene 1.9 minutes and uracil 2.4 minutes. At the highest concentration of acetonitrile (90%), toluene elutes first and then continue with uracil. These show that the organic polymer monolith column can work on non-polar compounds. The interaction during the separation was a reverse-phase condition. This result could be a good start for applying

organic polymer monolith ammonium quaternary as stationary phase in liquid chromatography capillary system.



4. Conclusions

An organic polymer monolith containing quaternary ammonium was successfully direct synthesized in the capillary column using one-pot approach method using 2-[(Methacryloyloxy) ethyl] trimethylammonium as monomer, Ethylene dimethacrylate as crosslicer, isopropyl alcohol, PEG 400 and ethanol as a porogen. The surface morphology of the monolith column was formed by the presence of a macropore distribution with a size range of 1.29-3.33 µm and a distribution of polymer unions with a size range of 1.26-3.09 µm. From the FTIR results, it can be seen that the organic polymer monolith column contains an amine functional group (C-N) derived from the quaternary ammonium functional group in the monomer used.

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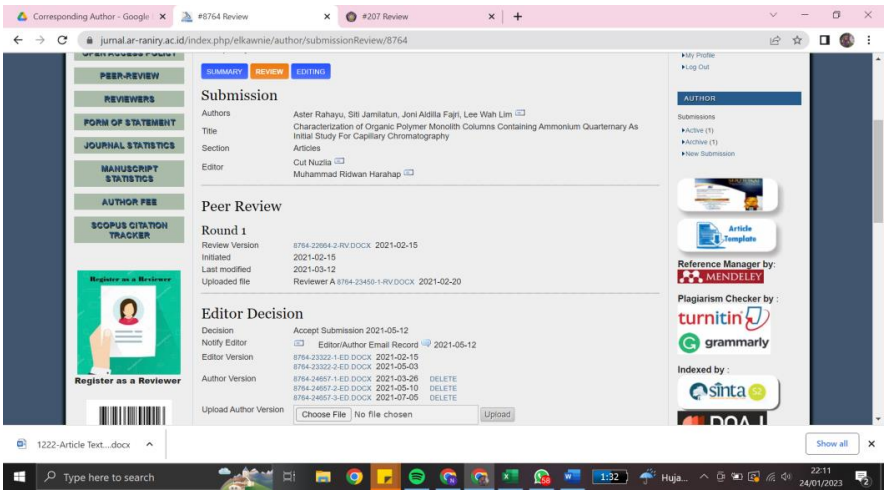
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7. Material And Methods

2.1 Materials

The materials used in this study included 2- [(Methacryloyloxy) ethyl] trimethylammonium chloride solution (META), Ethylene dimethacrylate (EDMA) (Wako 1st Grade, Japan), 2,2'-azobisisobutyronitrile (AIBN) (Trade TCI Mark), Isopropyl alcohol (IPA) (Wako 1st Grade), Polyethylene glycol (PEG) 400, 3- (trimethoxysilyl) - propyl methacrylate (γ-MAPS) (Nacalai Tesque, Kyoto, Japan), ethanol (Wako 1st Grade), solution standard nucleotides (Uracil), toluene, 0.1 M NaOH, 0.1 M HCl (Nacalai Tesque, Kyoto, Japan), deionized water (water that has a known conductivity and is specifically used for ion chromatography) GS-590 water distillation system (Advantec, Tokyo, Japan).

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I.e. Chemicals A, B and C were purchased from Wako. Chemical D was obtained from Merck and etc.

2.2 Apparatus

The equipment used in this study included the Scanning Electron Microscope (SEM) S-4800 (Hitachi, Tokyo, Japan), Fourier Transform InfraRed (FTIR) Spectrum 400 Series Perkin Elmer.

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2.3 Synthesis of quaternary ammonium organic polymer monoliths

Making organic polymer monoliths in silica capillaries begins with pre-treatment by rinsing the capillaries with 0.1 M NaOH, 0.1 M water and 0.1 HCL and acetone flowed into the column a flow rate of 2.5 µL/min for 60 minutes sequentially. The column was dried by flowing nitrogen gas for 30 minutes. 30% (γ-MAPS) was dissolved in acetone and flowed into the column then both ends of the column were closed. The column which already contains the solution (γ-MAPS) is placed in a water bath with a temperature of 60 ºC for 24 hours. The capillary column was rinsed again with acetone at a flow rate of 2.5 µL / min for 60 minutes and dried by flowing nitrogen gas for 30 minutes.

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The polymerization stage was carried out by making a polymer solution with an initial composition of 1.25 mL 2- (Methacryloyloxy) ethyl] trimethylammonium chloride solution, 0.375 mL ethylene dimethacrylate, 1.75 mL isopropyl alcohol, 0.35 mL ethanol, 1.4 mL PEG 400, 2 mg 2,2'-azobisisobutyronitrile was put into the vial bottle. The mixture is stirred until well blended. The solution mixture was put into the silica capillary, and then both ends tube were tightly sealed and placed into a water bath with a temperature of 60 ˚C and 24 hours. Then the monolith polymer is rinsed with methanol to remove residual reaction and residue. Monolith polymers as the stationary phase are suitable for capillary system liquid chromatography on uracil and toluene separation.

7.4.Characterization of compounds

The surface morphology of quaternary ammonium organic polymer monoliths was characterized using Scanning Electron Microscope (SEM) and Fourier Transform InfraRed (FTIR).

8. Discussion

3.1 Synthesis of polymeric organic monoliths

The Organic polymer monolith containing quaternary ammonium is synthesized by the direct method in the capillary column I.D 0.32 mm x 100 mm with single thermal polymerization known as one-pot approach method. The synthesis was carried out using a monomer that already has a quaternary ammonium functional group, in this study was used 2-[(methacryloyloxy) ethyl] trimethylammonium. To form a structural polymer union series, and Ethylene dimethacrylate as crosslinker. Monomers contained quaternary ammonium groups which can act as active groups for strong anion exchangers. This active group is very useful in the separation process of either anion solution or organic solution. The polymer formed by the "one-pot approach" method in the capillary column has a scheme of the expected reaction shown in Figure 1. The quaternary ammonium functional group in the META-EDMA polymer monolith is contributed by the META monomer, where quaternary ammonium is the active group for the anion exchange.

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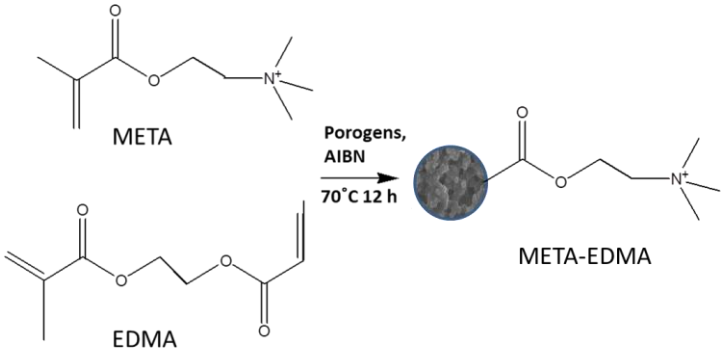

Figure 1. Scheme of the expected reaction of organic polymer

In this organic polymer monolith polymerization process, the ratio between monomer and porogen ratio is 20:80. Meanwhile that 20% is a mixture of monomer and crosslinker which consists of a percentage ratio of the composition, namely 50% is META, and 50% is EDMA. Meanwhile, 80% of the total polymer solution is porogen. Three types of organic compounds that act as porogen. Isopropyl alcohol, polyethylene glycol with a molecular weight of 400 and ethanol. These three solutions worked to form macropores on the surface of the polymer monolith that is formed. Visually, an organic polymer monolith forms a white solid, as shown in Figure 2.

Figure 2. The visual form of the quaternary ammonium organic polymer.

3.2 Characterization of organic polymer monoliths

3.2.1 Using Fourier Transform Infrared (FTIR)

Fourier Transform Infrared (FTIR) was carried out to determine the presence of amine compounds. The amine group itself is used as a strong anion-exchanger group. In addition, it is possible to predict the monolith column's possible reactions from the FTIR spectrum. The FTIR spectrum of an organic polymer monolith was shown in Figure 3. From Figure 3 it can be seen that the organic polymer monolith column has five peaks, namely the first peak at wave number 1020.3 cm^{-1}, the second peak at wave number 1352.2 cm^{-1}, the third peak at wavenumber 1723.6 cm^{-1}, peak fourth at wave number 2875.3 cm^{-1}, and the fifth peak at wavenumber 3433.6 cm^{-1}. The absorption area contained in the wavenumber between 1150-1085 cm^{-1} is the absorption area for the C-O (stretching) functional group. The high intensity of the principal peak in organic polymer monolith describes many oxygen-containing groups after the polymerization process. The number of oxygen-containing groups came from either from ethyleneglycol dimetharyate or 2-[(Methacryloyloxy) ethyl] trimethylammonium. The absorption area in the wavenumber between 1250-1020 cm-1 is the absorption area for C-N (amine). The absorption area in the wavenumber around 1650-1580 cm^{-1} is N-H's absorption area (amine). These amine groups are contributed by functional monomers that used. The absorption area in the wavenumber between 2853-2962 cm-1 is the absorption area for C-H

(stretching). The absorption area in the wavenumber between 3000-3600 cm^{-1} is the O-H functional group (Silverstein *et al*., 2005). It can be concluded that the bond and functional groups are thought to come from the presence of a polymerization reaction involving an initiator, monomer, crosslinker, and porogen.

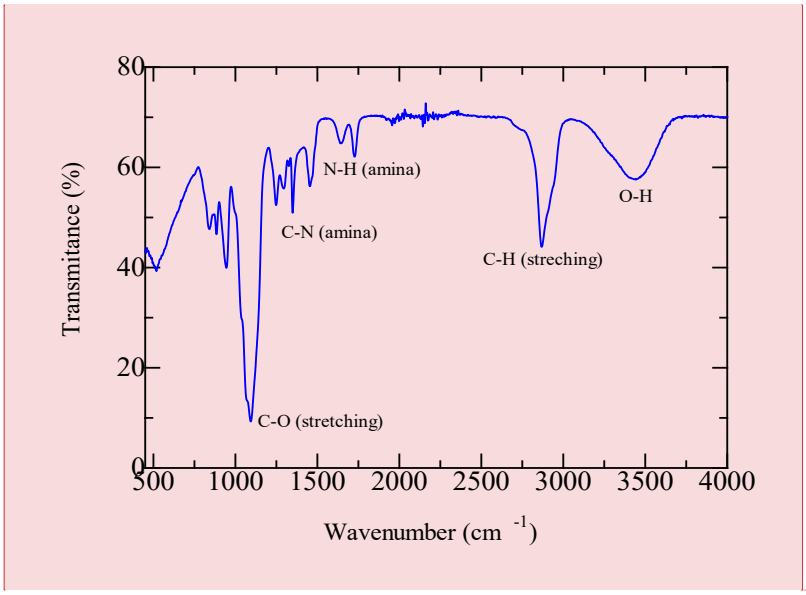

Figure 3.Fourier Transform Infrared (FTIR) spectrum of organic polymer monoliths.

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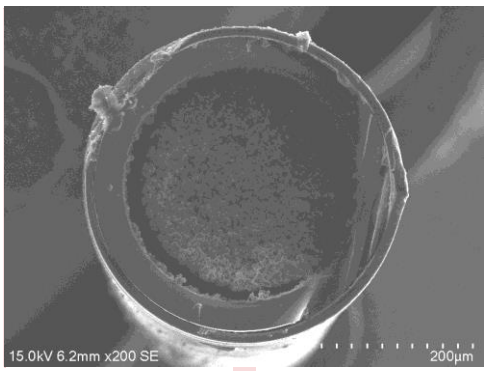
3.2.2 Scanning Electron Microscope (SEM)

The surface morphology of the organic polymer monolith is one of the parameters to determine the polymer monolith adhesion condition to the capillary column's inner wall. Besides, SEM analysis can also analyze the distribution of pores formed by using porogen in polymer solutions. The porogen used will form macropores, which are the distance between one polymer union and another. SEM results can be seen in Figure 4.



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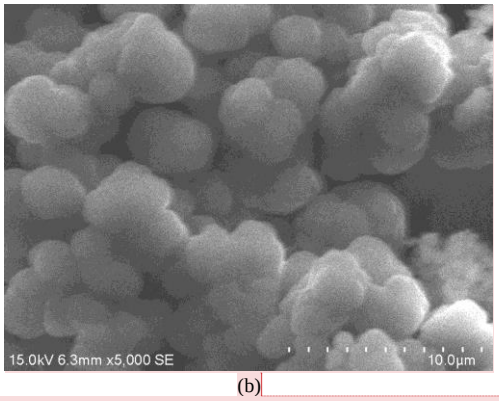
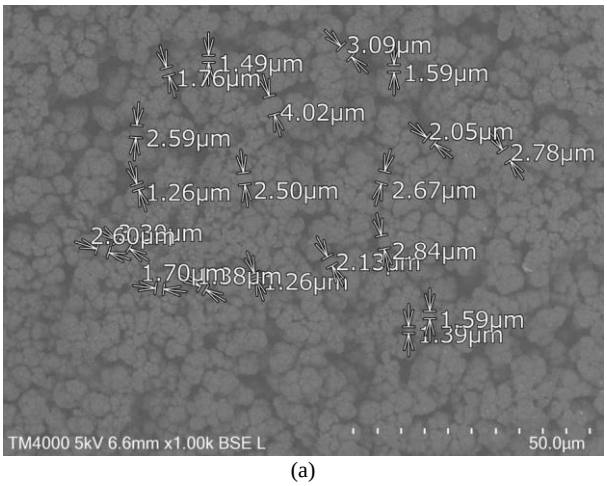


(b)

Figure 4.The surface morphology of the organic polymer monolith with the magnification of 200x (a) and 5000x (b)

Figure 4 shows if the capillary column surface analysis is carried out by enlarging it 200 times (a) and 5000 times (b). From the results of the SEM photos in Figure 4. (a) there is a sufficient optimal adhesion between the inner wall surface of the capillaries and the organic polymer monoliths formed. The capillary column's pre-treatment process using 30% (γ-MAPS) dramatically affects the adhesion results between the monolith formed and the walls in the capillary column. 30% (γ-MAPS) acts as a surface laxative in the capillary column walls coated with silanol groups. Whereas in Figure 4. (b), we can see the distribution of polymer unions and macropores' formation from organic polymer monolith. The macropores are perfectly formed and relatively evenly distributed. In Figure 5, you can see the size distribution of the union and pore created. The union's size formed on the organic polymer monolith can be seen in Figure 5 (a), about 1.26-3.09 µm for each union. And the pore size distribution formed can be seen in Figure 5 (b), around 1.29-3.33µm.



(a)

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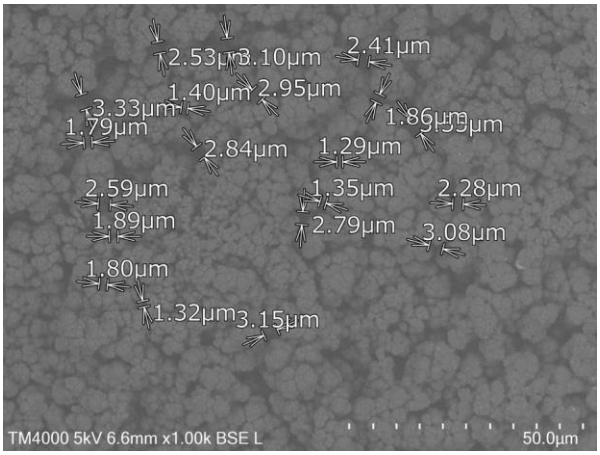

(b)

Figure 5. Surface morphology of organic polymer monolith, union size distribution (a) and pore size (b).

From the results of the excellent union and pore size distribution on the polymer surface of the capillary column that is formed, the column can be used as the stationary phase in a liquid chromatography system with a reasonably good system pressure below 2 MPa.

3.3. Separation of Uracil and Toluene

In order to observe the ability of the organic polymer monolith as stationary phase in liquid chromatography capillary system, as the initial study, uracil and toluene were used as analytes. Acetonitrile 90% was used as the mobile phase. The chromatographic result was shown in Figure 6. Figure 6 shows that toluene and uracil could separate correctly with the retention time of toluene 1.9 minutes and uracil 2.4 minutes. At the highest concentration of acetonitrile (90%), toluene elutes first and then continue with uracil. These show that the organic polymer monolith column can work on non-polar compounds. The interaction during the separation was a reverse-phase condition. This result could be a good start for applying organic polymer monolith ammonium quaternary as stationary phase in liquid chromatography capillary system.

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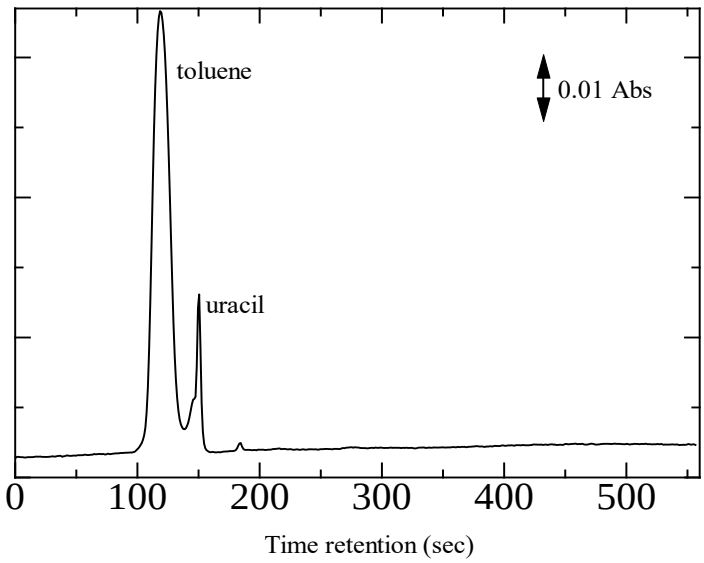

9. Conclusions

An organic polymer monolith containing quaternary ammonium was successfully direct synthesized in the capillary column using one-pot approach method using 2-[(Methacryloyloxy) ethyl] trimethylammonium as monomer, Ethylene dimethacrylate as crosslicer, isopropyl alcohol, PEG 400 and ethanol as a porogen. The surface morphology of the monolith column was formed by the presence of a macropore distribution with a size range of 1.29-3.33 µm and a distribution of polymer unions with a size range of 1.26-3.09 µm. From the FTIR results, it can be seen that the organic polymer monolith column contains an amine functional group (C-N) derived from the quaternary ammonium functional group in the monomer used.

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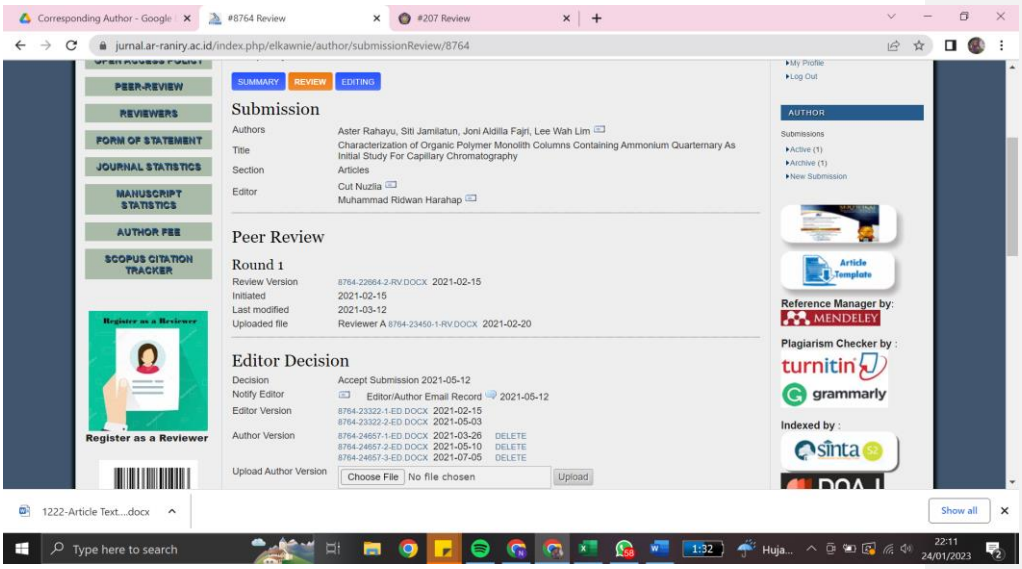
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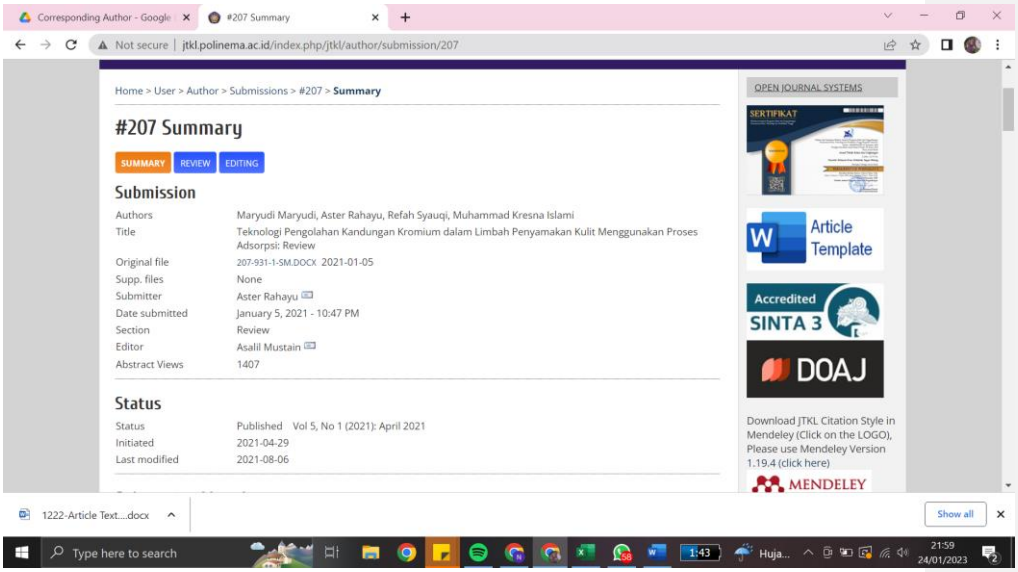
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CHARACTERIZATION OF ORGANIC POLYMER MONOLITH COLUMNS CONTAINING AMMONIUM QUARTERNARY AS INITIAL STUDY FOR CAPILLARY CHROMATOGRAPHY

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Abstract: The polymerization process with a simple step has become the centre of attention of several researchers. Various polymers have been developed, although in general, they use polymerization with a post-modification method. A quaternary ammonium monolith organic polymer has been prepared using a simple single thermal method in this research. 2-(Methacryloyloxy)-N,N,N-trimethylethanaminium chloride was as the monomer, and ethylene dimethacrylate was as crosslinker. The polymerization proceeded in fused-silica capillary (100 mm, 0.32 mm i.d. x 0.45 mm o.d.) using a one-pot approach method. To achieve the perfect macropores, isopropyl alcohol, PEG 400, and ethanol were used as porogen. Characterization of the surface morphology was carried out using a Scanning Electron Microscope (SEM), and the existence of an amine group was characterized by Fourier Transform Infrared Spectroscopy (FTIR). The distribution size of pores in the polymer was in the range of 1.29 to 3.33 µm.
Keywords: *Monolith, Organic polymer, One-pot approach, Ammonium quarternary, Polymerization, Capillary*

Abstrak: Polimerisasi dengan proses yang sederhana dan simpel menjadi pusat perhatian beberapa peneliti. Berbagai macam polimer telah dikembangkan, akan tetapi pada umumnya menggunakan polimerisasi dengan metode *post-modification*. Pada penelitian ini, polimer organik yang mengandung amonium kuartener dalam bentuk monolit dengan polimerisasi yang menggunakan suhu tunggal dan sederhana telah dilakukan. *2-(Methacryloyloxy)-N,N,N-trimethylethanaminium chloride* digunakan sebagai monomer dan *ethylene dimethacrylate* sebagai *crosslinker*. Polimerisasi dilakukan dengan metode *one-pot aaproach* di dalam kapiler silika (100 mm, 0,32 mm i.d. x 0,45 mm o.d.). Untuk mendapatkan makropori yang sempurna, isopropil alkohol, PEG 400 dan etanol digunakan sebagai porogen. Karakterisasi morfologi permukaan dilakukan dengan menggunakan *Scanning Electron Microscope* (SEM), dan *Fourier Transform Infrared Spectroscopy* (FTIR) untuk mengidentifikasi gugus fungsi gugus amina yang terdapat pada polimer. Ukuran distribusi pori pada polimer berkisar antara 1,29 sampai 3,33 µm.
Kata kunci: Monolitik, Polimer organik, *One-pot approach*, Amonium kuartener, Polimerisasi, kapiler

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Introduction

Polymers are large molecules composed of a series of monomers that are interconnected by the presence of crosslinkers. Monolith polymers can be broadly divided into two types, namely organic polymers and inorganic polymers (Rahayu *et al.,* 2015). Inorganic polymers are commonly based on silica and are widely used as a stationary phase. Several kinds of research have been reported in terms of application of inorganic polymers, such as separation and detection of cation levels in drinking water (Rahayu *et al.,* 2015), protein (Zhao *et al.,* 2012), tryptic digests of bovine serum albumin (BSA) (Zhang *et al.,* 2011), levodopa, carbidopa, benserazide, dopamine, and 3-O-methyldopa in plasma samples (Grecco *et al.,* 2020), polar compounds (Yang *et al.,* 2013) and other macromolecular compounds (Iwasaki *et al.,* 2012). However, time-consuming manufacturing and a limited variety of polymer-forming materials were obtained as disadvantages of inorganic polymer (Zhong *et al*., 2010, Lalli *et al*., 2020).

Organic polymers have been developed and applied as a stationary phase for separating compounds or ions in the chromatography system. The existence of pore in the monolith polymer can be served as an adsorbent. Some polymers have been widely used in the adsorption of several heavy metals and organic compounds. The Cr (VI) ion could be adsorbed using a magnetic polymer containing an amine group (Zhao *et al*., 2013, Zhao *et al*., 2010), removal of Pb^{2+}, $Cu^{2+,}$ and Zn^{2+} (Mokadem *et al*., 2020), trace Cd (II) in biological samples (Chen *et al.,* 2020), and removal of Pb(II) from water medium (Naushad *et al.,* 2020). Methacrylate-based polymers with the epoxy ring-opening method have been successfully prepared and applied for separation of organic compounds such as Bisphenol A (BPA) (Zhao *et al*., 2013), Bovine Serum Albumin (BSA) (Shamim *et al.*, 2007), alkylbenzene (Wang *et al.,* 2014), pentachlorophenol (Pan *et al.*, 2014), and enantioseparation (Angga *et al.,* 2019). Furthermore, it is also applied for the adsorption of some ions, such as Cu (II) (Shen *et al*., 2012) and Hg (II) ions (Pan *et al*., 2014, Pan *et al*., 2012). Overall, many of these polymers are applied as the stationary phase in the chromatography system.

Polymerization uses two-stage processes, namely the polymerization stage and the advanced modification stage. This advanced modification stage aims to add the desired active side group according to the intended purpose and application. However, a few organic polymers are synthesized using a one-pot approach method. This method was taking the attention of several researchers due to the simple step of the polymerization process.

The synthesizing of monolithic polymers with quaternary ammonium groups using a straightforward one-pot approach as a stationary phase in capillary system liquid chromatography will be the objective of this research. The monolithic polymers containing quaternary amine groups will be polymerized from 2-(Methacryloyloxy)-N,N,N-trimethylethanaminium chloride (META) and ethylene dimethacrylate (EDMA) with a short, simple and straightforward method, namely one-pot approach. The morphology surface of the polymer will be characterized before applying as the stationary phase in the capillary system liquid chromatography to separate organic compounds.

Material And Methods

Materials

The materials are purchased from a different source. 2-(Methacryloyloxy)-N,N,N-trimethylethanaminium chloride (META), Ethylene dimethacrylate (EDMA), Isopropyl alcohol (IPA), ethanol were purchased from Wako 1st Grade, Japan, 2,2'-azobisisobutyronitrile (AIBN) was purchased from Trade TCI Mark, Japan, poly(ethylene oxide) Mn. 400 (PEG 400), 3-(trimethoxysilyl)-propyl methacrylate (γ-MAPS), uracil, toluene, 0.1 M NaOH, 0.1 M HCl were purchased from Nacalai Tesque, Kyoto, Japan, deionized water (water that has a known conductivity and is specifically used for ion chromatography) from GS-590 water distillation system (Advantec, Tokyo, Japan).

Apparatus

The surface morphology of quaternary ammonium organic polymer monoliths was characterized using Scanning Electron Microscope (SEM) S-4800 (Hitachi, Tokyo, Japan) mainly, the size of single unions macropores formed. Furthermore, identifying the functional group in the polymer was carried out using Fourier Transform Infrared (FTIR) Spectrum 400 Series (Perkin Elmer).

The chromatographic system was performed to separate uracil and toluene 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 μL, a 100 mm x 0.32 mm i.d. of microcolumn and a UV-1575 intelligent UV/Vis detector, (JASCO, Tokyo, Japan) that was operated at 254 nm. The data was acquired using a data processor CDS-Lite ver.5.0 (LA soft, Chiba, Japan).

Synthesis of quaternary ammonium organic polymer monoliths

Synthesize of organic polymer monoliths was started with pre-treatment of the inner wall of capillary silica. The capillary column was rinsed with 0.1 M NaOH, 0.1 M water, 0.1 HCL and flowed with acetone into the column flow rate of 2.5 μL/min for 60 minutes sequentially. The column was dried by flowing

nitrogen gas for 30 minutes. 30% (γ-MAPS) in acetone filled into the column, and then both column ends sealed. The anchor inner wall of the capillary column is allowed at 60 ºC for 24 hours in the water bath. The capillary column was rinsed with acetone at a flow rate of 2.5 µL/min for 60 minutes and dried with nitrogen gas for 30 minutes.

Initially, the polymerization stage was carried out by preparing a mixture solution according to previous research with major modification (Rahayu *et al.,* 2015); 1.25 mL of META, 0.375 mL of EDMA, 1.75 mL of isopropyl alcohol, 0.35 mL of ethanol, 1.4 mL of PEG 400, and 2 mg 2,2'-azobisisobutyronitrile. The mixture solution was homogenized before filling into the pretreated capillary column. Subsequently, the polymerization was allowed at 60 ˚C for 24 hours in the water bath. The obtained polymer was rinsed with methanol to remove the residual reaction. Monolith polymers were applied in capillary system liquid chromatography for *the* separation of uracil and toluene.

Discussion

Synthesis of polymeric organic monoliths

The organic polymer monolith containing quaternary ammonium was synthesized directly in the capillary column (100 mm, 0.32 mm i.d. x 0.45 mm o.d.) with a single thermal polymerization one-pot approach method. The synthesis was carried out using a monomer containing a quaternary ammonium functional group. Quaternary ammonium groups in monomers act as strong anion exchangers and work well to separate either anion or organic compounds. The scheme of the expected reaction polymerization one-pot approach method is shown in Figure 1. The functional monomer introduced the quaternary ammonium in the organic polymer, which quaternary ammonium is the active group for the anion exchange.

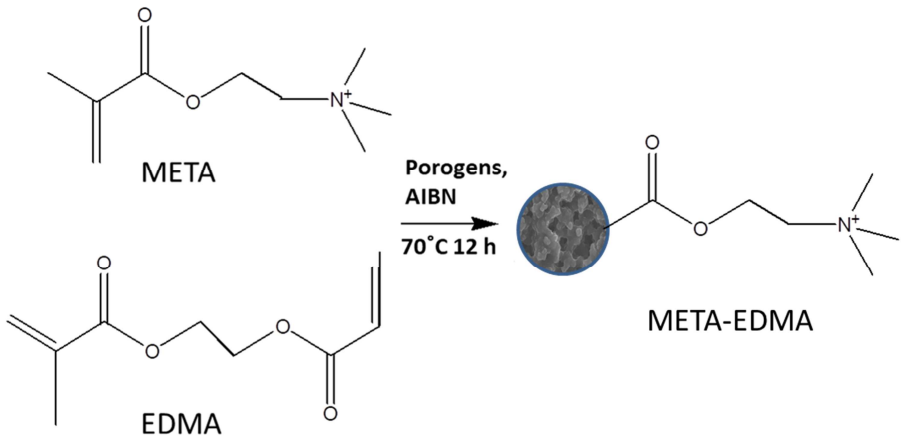


Figure 1. Scheme of the expected reaction of organic polymer

In the polymerization of organic polymer monolith, the ratio between monomer and porogen ratio was 20:80. Meanwhile, 20% was a mixture of monomer and crosslinker, and 80% was porogen. Interm of 20% for monomer and crosslinker, 50% of monomer, and 50% crosslinker were used. Three organic compounds acted as porogen, such as Isopropyl alcohol, polyethylene glycol 400, and ethanol. These three solutions worked to form macropores on the surface. Visually the polymer formed was solid white, as shown in Figure 2.

Figure 2. The visual organic polymer contained quaternary ammonium.

Characterization of organic polymer monoliths Using Fourier Transform Infrared (FTIR)

Fourier Transform Infrared (FTIR) was carried out to determine the presence of amine compounds. The amine group itself was used as a strong anion-exchanger. The FTIR spectrum of organic polymer monolith was shown in Figure 3. In Figure 3, it can be seen that detected five peaks in the organic polymer monolith column. These five peaks were the first peak at wave number 1020.3 cm^{-1}, the second peak at wave number 1352.2 cm^{-1}, the third peak at wavenumber 1723.6 cm^{-1}, the fourth at wave number 2875.3 cm^{-1}, and the fifth peak at wavenumber 3433.6 cm^{-1}. The absorption area in the wavenumber between 1150-1085 cm^{-1} refers to the C-O (stretching) absorption area. The high intensity of the principal peak in organic polymer monolith describes many oxygen-containing groups after the polymerization process. The number of oxygen-containing groups came from either ethylene glycol dimetharyate or 2-[(methacryloyloxy) ethyl] trimethylammonium. The absorption area in the wavenumber between 1250-1020

cm-1 refers to C-N (amine) absorption area. Subsequently, the absorption area in the wavenumber around 1650-1580 cm^{-1} refers to N-H (amine) absorption area. These amine groups are contributed by functional monomers that are used. The absorption area in the wavenumber between 2853-2962 cm-1 refers to the C-H (stretching) absorption area. Then, in the wavenumber between 3000-3600 cm^{-1}, it relates to O-H functional group (Silverstein *et al*., 2005). It can be concluded that existing bonds and functional groups are thought to come from the presence of a polymerization reaction involving an initiator, monomer, crosslinker, and porogen.

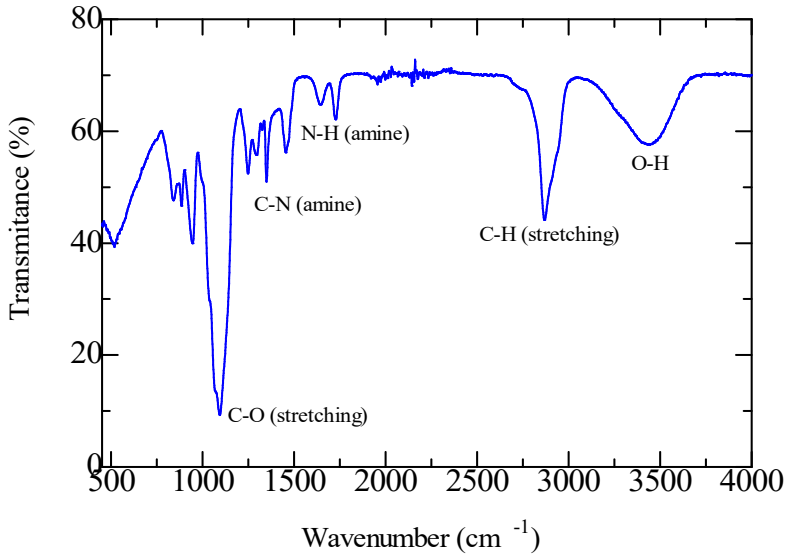
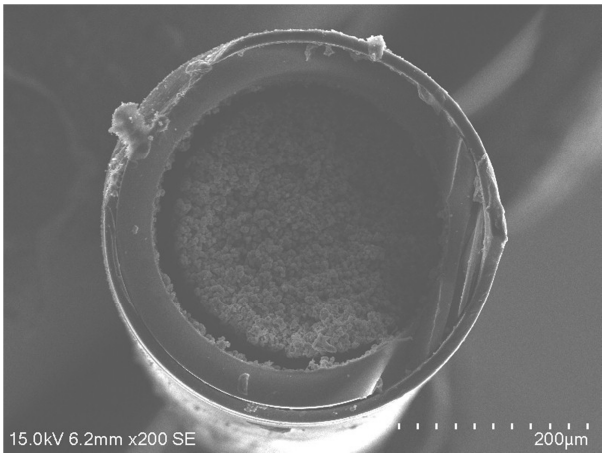


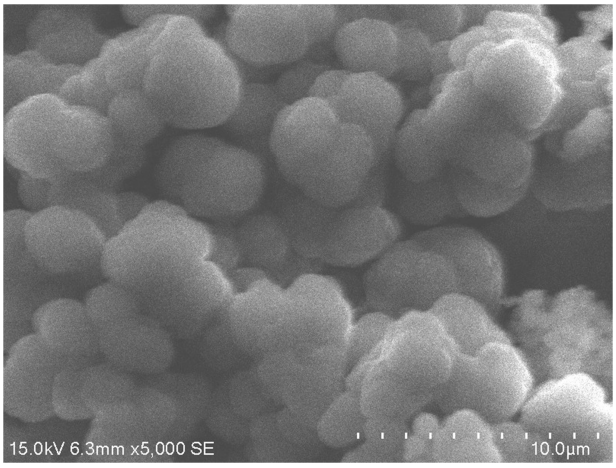
Figure 3. Fourier Transform Infrared (FTIR) spectrum of organic polymer monoliths.

Scanning Electron Microscope (SEM)

The morphology of the organic polymer monolith is one of the essential parameters to determine the adhesion condition of the polymer with an inner wall of the column. Furthermore, the range distribution of pores formed by using porogen in polymer solutions also can be observed. The porogen-created macropores as the distance between one polymer union and another. The morphology photo of the organic polymer monolith can be seen in Figure 4.



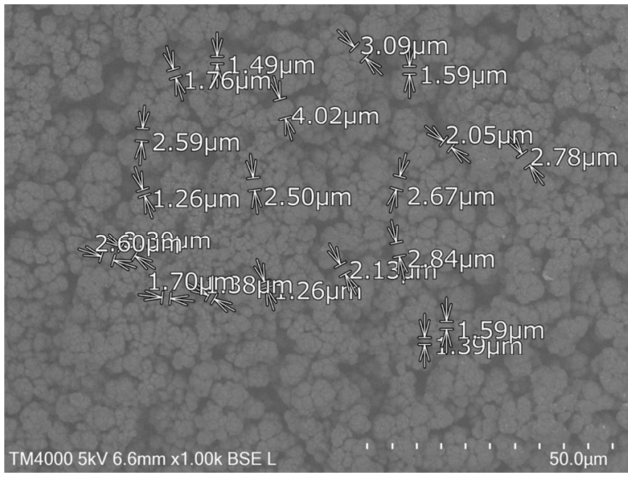
(a)



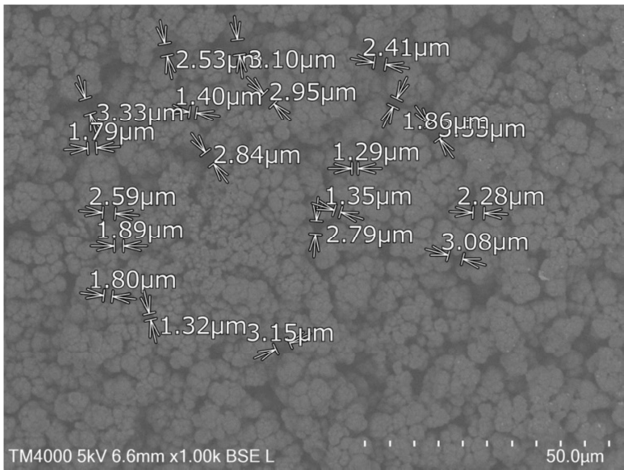
(b)

Figure 4. The morphology of the organic polymer monolith. (a). The magnification of 200x. (b). The magnification of 5000x

Figure 4 shows the performance of the organic polymer attaching into the inner wall of the capillary column by enlarging 200 and 5000 times. In Figure 4.(a). there is a sufficient optimal adhesion between the inner wall surface of the capillary and the organic polymer monoliths. The pre-treatment process in the capillary column using γ-MAPS dramatically affected the adhesion results for attaching the polymer to the inner wall of the capillary. The surface capillary column coated by the silanol group was perfectly laxative by γ-MAPS. Furthermore, Figure 4.(b). shows the distribution of unions and macropores in the organic polymer monolith. The macropores were significantly formed and evenly distributed. Subsequently, the size distribution of the union and macropores are shown in Figure 5. The range size for the union and macropore is 1.26-3.09 µm and 1.29-3.33µm, respectively.



(a)



(b)

Figure 5. The morphology of organic polymer monolith. (b). Distribution size of the union. (b). Distribution size of macropore

According to the distribution size union and macropore range, the organic polymer could be applied as a stationary phase for the capillary chromatography system. It is promoting good results with a reasonably good system pressure below 2 MPa.

Separation of Uracil and Toluene

The separation of organic compounds was conducted to observe the ability of organic polymer monolith as the stationary phase in the liquid chromatography capillary system. Uracil and toluene were used as analytes for the initial study. The separation of uracil and toluene by the liquid chromatography capillary system is shown in Figure 6. It can be seen that the toluene and uracil could be appropriately separated. The retention time of toluene and uracil are 1.9 minutes

and 2.4 minutes, respectively. Toluene was eluted first and then continued with uracil when 90% acetonitrile was used as eluent. These show that the organic polymer monolith column could work in non-polar compounds by reverse-phase mode. This result is promising for applying organic polymer monolith ammonium quaternary as a stationary phase in the liquid chromatography capillary system.

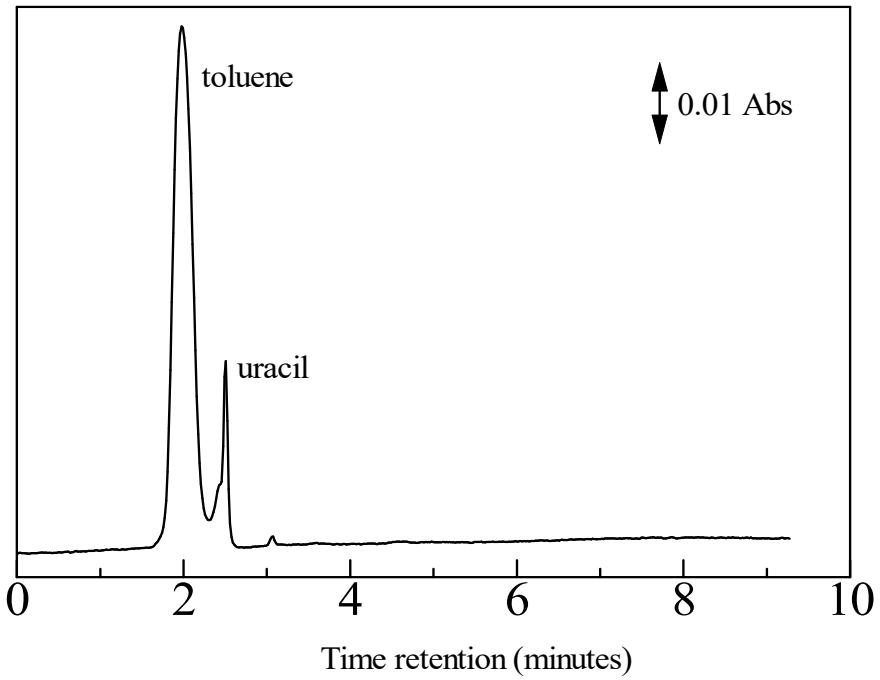


Figure 6. Separation of uracil and toluene by liquid chromatography capillary system. Experimental conditions: column: organic polymer containing ammonium quarternary monolithic (100 mm, 0.32 mm i.d. x 0.45 mm o.d.); mobile phase: 90% acetonitrile; flow rate: 3 µl/min; detection wavelength: 254 nm, injection volume: 0.02 µm.

Conclusions

An organic polymer monolith containing quaternary ammonium was successfully synthesized in the capillary column using a one-pot approach method. 2-(Methacryloyloxy)-N,N,N-trimethylethanaminium chloride acted as a monomer, Ethylene dimethacrylate as a crosslinker, and three kinds of solution as porogen; isopropyl alcohol, PEG 400, and ethanol. The organic polymer monolith also contained an amine functional group (C-N) derived from the quaternary ammonium active group for separating uracil and toluene. The range distribution size of the union and macropore is 1.26-3.09 µm and 1.29-3.33µm, respectively.

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