Optimisation fabrication of butyl methacrylate monoliths

Eman Alzahrani

Chemistry Department, Faculty of Science, Deanship of scientific research, Taif University, 888-Taif, Kingdom of Saudi Arabia, e-mail: em-s-z@hotmail.com

ABSTRACT In this study, a butyl methacrylate-co-ethylene dimethacrylate (BuMA-co-EDMA) monolith was synthesised using UV-initiated polymerization. The effect of the energy of the UV light (254 and 365 nm), and the time of exposure to the UV light (8-22 min) on fabrication of the organic polymer monolith were investigated. The results of this investigation showed that the most suitable wavelength for the photoinitiated polymerisation reaction in this study was 365 nm. In addition, the finding of this study suggests that the optimum time of exposure to the UV light in order to prepare a porous rigid monolith was 20 min. Control of the porous properties of the organic polymer monolith was optimised by adjusting the composition of the porogenic solvents. In this study, eight different binary porogenic solvent systems containing 50 % of main solvent (MeOH) and 50 % of co-porogen (EtOH, ACN, chloroform, hexane, tetrahydrofuran, 1-propanol, ethyl acetate, and cyclohexanol) were studied. The characterisation of the bed structures of the fabricated monoliths was carried out by SEM analysis, BET model, and measuring the porosity and permeability of the monoliths. The results of this investigation show that the optimal binary porogenic solvent system to prepare the poly (BuMA-co-EDMA) monolith was MeOH/EtOH, which offers high porosity and permeability. In addition, this study found that replacing EtOH with 1-propanol enables the fabrication of the organic polymer monolith with a higher surface area (56.89 m2 g-1).

1. Introduction

An organic monolith is a single block of highly porous material that consists of polymer globules separated by numerous interconnected cavities (pores), and held together through extensive crosslinking[1]. The preparation of a polymer-based monolith is produced by a "moulding" process, which is relatively simple and straightforward compared with inorganic monoliths[2].

The important property of typical monolithic materials is high surface area, which can be increased by increasing the number of micropores. On the other hand, the permeability of the monolith requires macropores in order to allow liquid to flow through the monolith at a reasonable pressure[3]. Both the surface area and the hydrodynamic properties of the monolith depend on the pore size distribution of the monolith; therefore, a balance between the requirement of low flow resistance and high surface area must be found, and the ideal monolith should have both macropores in order to achieve sufficient permeability of the monolith, and micropores for high capacity[2, 4]. Many studies have been carried out to increase the surface area as well as the permeability of flow through the monolith by optimising the composition of the polymerisation mixture and the reaction conditions[5].

The most effective parameters in the fabrication of a polymer-based monolith that can affect its properties are the proportion of monomer to crosslinker, the polymerisation temperature or time of exposure to UV light, concentration of the initiator, and the percentage of the porogenic solvent system in the polymerisation mixture. The specific surface area and the pore size distribution are very sensitive to any variations of the listed parameters[6].

The purpose of using the porogenic solvent is to dissolve monomer, crosslinker, and photoinitiator without reacting during the polymerisation reaction in order to get a homogeneous solution. Moreover, the benefit of the porogenic solvent is to form the pores since the monomer is soluble in the porogen while the polymer is insoluble; therefore, the fraction of the solvent in the polymerisation reaction is related to the fraction of the pores in the monolith[7].

The aim of this study was to optimize fabrication of an organic polymer-based monolith. The reason for choosing this type of monolithic material is because the preparation of an organic polymer-based monolith is fast and simple. In addition, they are stable over a wide range of pH values, and can be washed without damage with caustic mobile phase[8].

2. Experimental

2.1. Chemicals and materials

Ethanol, acetonitrile, chloroform, hexane, tetrahydrofuran, 1-propanol, ethyl acetate, and cyclohexanol were purchased from Scientific Laboratory Supplies (Nottingham, UK). Methacrylate 99 % (BuMA), ethylene dimethacrylate 98 % (EDMA),and 2,2-dimethoxy-2-phenyl acetophenone 99 % (DMPA) were purchased from Sigma-Aldrich (Poole, UK).Blu-tack was purchased from Lyreco (Telford, UK).Draper 0-150 mm/0-6" Digital Vernier Caliper was purchased from Toolbox Ltd., (Lincoln, UK).Disposable plastic syringe (1ml) waspurchased from Scientific Laboratory Supplies (Nottingham,UK).

2.2. Instrumentation

A sonicator from Ultrawave Sonicator U 300HD (Cardiff, UK). UV lamp from Spectronic Analytical Instruments (Leeds, UK). A scanning electron microscope (SEM) Cambridge S360 from Cambridge Instruments (Cambridge, UK). HPLC analysis was carried out using a Perkin Elmer LC200 series binary pump, a Symmetry C8 column, 4.6 mm × 250 mm packed with silica particles (size 5 µm) from Thermo Fisher Scientific (Loughborough, UK) and a Perkin Elmer 785A UV/Visible Detector from Perkin Elmer (California, USA).

2.3. Fabrication of poly (BuMA-co-EDMA) monolith

Photoinitiated free radical polymerisation was utilised for

the preparation of the polymer-based monolith within the plastic syringe at room temperature under UV irradiation. The polymer-based monolith was prepared as described by Frechet et al[9]. with some modifications. The polymerisation mixture consisted of a monovinyl monomer, butyl methacrylate 99 % (BuMA), a crosslinker, ethylene dimethacrylate 98 % (EDMA), the free radical photoinitiator, 2,2-dimethoxy-2-phenyl acetophenone 99 % (DMPA), and the porogenic solvent system, which was a binary mixture of methanol and another solvent (50:50). The solvents that were investigated for fabrication of the organic monolith were ethanol, acetonitrile, chloroform, hexane, tetrahydrofuran, 1-propanol, ethyl acetate, and cyclohexanol. Table 1 shows the main components of the polymerisation mixture used for the preparation of the polymer-based monolith.

Table 1 The composition of the polymerisation mixture used for the preparation of the polymer-based monolith.

Type	Chemical	Weight (g)
Monomer	Butyl methacrylate (BuMA)	1.422
Crosslinker	Ethylene dimethacrylate (EDMA)	0.96
Porogenic solvent system	50:50 of main solvent (methanol) and other solvent (ethanol, acetonitrile, chlor form, hexane, tetrahydrofuran, 1-propanol, ethyl acetate, and cyclohexanol)	3.6
Photoinitiator	2,2-dimethoxy-2-phenyl acetophenone (DMPA)	0.024

The polymerisation mixture was sonicated for 10 min to dissolve the initiator and get a homogeneous solution using a sonicator and purged with nitrogen gas for 10 min to remove oxygen. A plastic syringe was filled with polymerization mixture and the ends of the tube were sealed with blu-tack. The tube filled with the polymerisation mixture was placed under the UV lamp at 254 nm or 360 nm at room temperature. After the polymerisation reaction, the monolithic materialswere flushed with methanol.

2.4. Monolithic material characterisation
2.4.1. SEM analysis
The morphology of the dried monolith was characterised by scanning electron microscopy (SEM) Images were obtained using an accelerating voltage of 20 kV and a probe current of 100 pA in high vacuum mode. The samples were coated with a thin layer of gold-platinum (thickness around 2 nm).

2.4.2. BET analysis
The physical properties of the bulk monolith (surface area, average pore diameter, and the pore volume) were studied by the Brunauer-Emmett-Teller (BET) model using a Surface Area and Porosity Analyser. The porous monolith was fabricated inside a 1 mL disposable plastic syringe using the same polymerisation mixture. The monolith rod was dried using N_2 gas. The porous properties of the monoliths were determined using the BET isotherms of nitrogen adsorption and desorption at 77 K. The isotherms were analysed to get the surface area according to the BET model. The pore volume and pore size distribution of pores within the monoliths were measured from the nitrogen adsorption isotherm using the BJH (Barrett-Joyner-Halenda) model.

2.4.3. Measuring porosity
The total porosity equal to the volume fraction of both the micron-scale and nm scale pores of the cylindrical monolith samples was measured as described by Fletcher et al[10]. The porosity was measured by weighing the monolith when dried (i.e. with all pores containing only air) and when filled with deionised water.

$$\emptyset_t = \frac{W_M - W_T}{dLR^2\pi}$$

(1)

Where and are the weights of the monolith when dried and when filled with water respectively, is the density of water (at 23 °C = 0.9975 g cm^{-3}), and and are the whole length and radius of the cylindrical monolith, respectively, which were measured using caliper. The measurement was repeated five times and the average was taken.

2.4.4. Permeability of the monolith
The permeability of the organic monoliths was investigated by measuring the backpressure generated while pumping deionised water using an HPLC pump at different flow rates through the monolith.[11] Then, the value of the pressure in the system was recorded.

3. Results and discussion
3.1. Fabrication of poly (BuMA-co-EDMA) monolith
A methacrylate-based monolith was chosen for the organic polymer-based monolith in this study as this is widely used[12]. The polymerisation mixture consisted of the monovinyl (BuMA) and divinyl monomer (EDMA) in the presence of porogenic solvents and a free radical initiator (DMPA). The free radical polymerisation reaction was initiated using UV light (photoinitiation process) at room temperature rather than using a water bath (thermal initiation process). Poly (butyl methacrylate-*co*-ethylene dimethacrylate) stationary phase was prepared as described by Frechet *et al*[9] using the same polymerisation mixture except the photoinitator was changed from 2,2'-azobis(2-methylpropionitrile) (AIBN) to DMPA to avoid formation of voids during the polymerisation reaction. The voids reported are thought to be due to the generation of nitrogen gas during polymerization [13].

3.2.Optimisation of fabricationof the organic monolith
It was very important before using the prepared poly (BuMA-*co*-EDMA) monolith to optimise its physical properties in order to get an organic monolith with high mechanical stability and good permeability. Many factors can affect the porous properties of a polymer-based monolith, such as the polymerisation time, the UV lamp power, monomer to porogen ratio, monomer to crosslinker ratio, concentration of the photoinitiator, and composition and type of

the porogenic solvent system[14, 15]. In this study, it was decided to investigate the energy of the UV light, time of exposure to the UV light, and the type of the porogenic solvent system.

3.2.1. Investigation of UV light energy and exposure time

Since the irradiation process was used to initiate the polymerisation reaction, the influence of the UV light energy on the preparation of the polymer-based monolith was investigated. The experiment was carried out by filling the plastic syringe with the polymerisation mixture and performing the polymerisation reaction using UV light with different wavelengths, 254 and 365 nm. It was expected that using the short wavelength (254 nm) would be best for the polymerisation reaction because short wavelength light provides more energy than longer wavelength (365 nm), since the wavelength is inversely proportional to the energy and the reaction time could be reduced by increasing the light energy. However, it was observed that the photoinitiation reaction was faster and more polymerisation was obtained by using the long wavelength, as was also observed by other groups[16]. The reason for that is acrylate monomers absorb the UV light in the range 200-300 nm, reducing "the energy dose" and decreasing the efficiency of the photoinitiator, when using UV light with a wavelength of 254 nm. Therefore, it was decided to use the longer wavelength (365 nm) for the polymerisation reaction in this study.

Fig. 1 Effect of the duration of exposure to the UV lamp on the formation of the poly (BuMA-co-EDMA) monolith.

the effect of the duration of exposure to the UV light on the preparation of the polymer-based monolith was examined at eight different time-points in order to find the most suitable time to complete the polymerisation reaction. The different exposure times investigated were 8, 10, 12, 14, 16, 18, 20, and 22 min. A good indication of forming continuous beds was the appearance of the porous polymer monolith, which was a bright white material. It was found that the irradiation time was an important factor affecting the polymerisation reaction as evident from Figure 1, which shows the difference in the appearance of the organic monoliths prepared in the sample vials. The first conclusion derived from the figure is related to the effect of the polymerisation time on the formation of the organic monolith. It was observed that the exposure time 8 min was not enough to fabricate the organic monolith in the sample vials. Therefore, the exposure time was increased by 2 min each time up to 20 min. It was observed that the white solid monolithic material was increased while the polymerisation mixture, which contained the unreacted monomeric materials and the casting solvents, was decreased. The polymerisation reaction was changed to 22 min, it was observed that there was no difference in the white solid monolithic material in the sample vial; however, it was found that the monolithic polymer tube could not be washed. The reason for that could be because increas-

ing the duration of exposure to the UV light can generate smaller pores and this can decrease the permeability of the monolith[11]. It was concluded that the optimum irradiation time to get polymer-based monolith in the tube was 20 min because the appearance of the polymeric monolithic stationary phases was satisfactory compared with the other monoliths, and the monolithic tube was still washable.

3.2.2. Investigation of porogenic solvent system

The composition of the binary porogenic solvent system was investigated to control the physical characteristics of the organic monolith. The purpose of changing the composition of the binary porogenic system was to find a porogenic solvent system that can offer a monolith with a high surface area[17, 18]. In addition, the chosen porogenic solvent system should offer macroporous materials, since the pore diameter can affect the permeability of the monolith.

A common solvent for the preparation of methacrylate-based monoliths is methanol (MeOH)[19, 20]. Therefore, it was used here as the main porogenic solvent with co-porogen that was one of ethanol, acetonitrile, chloroform, hexane, tetrahydrofuran, 1-propanol, ethyl acetate, or cyclohexanol. The effect of the porogenic solvent system on the properties of the organic monolith was studied by using the same polymerisation mixture, except the porogenic solvent was a mixture of methanol and co-porogen (50:50). The polymerisation mixture was placed in a 1 mL plastic disposable syringe and the polymerisation reaction was carried out under identical conditions. After the polymerisation reaction, samples of the monoliths were studied. Figure 2 shows the appearance of the poly (BuMA-*co*-EDMA) monoliths prepared using different porogenic solvent systems before washing them with methanol. The porogenic solvent systems that gave a bright white material besides methanol were MeOH/EtOH, MeOH/1-propanol, and MeOH/hexane.

Fig.2 The appearance of the poly (BuMA-co-EDMA) monoliths prepared using different porogenic solvent systems before washing them with methanol.

After preparation of the monolithic polymer rod, it was washed by Soxhlet extraction using methanol at 80 °C for 24 hours to remove the unreacted monomeric materials. The diameter of the cylindrical monolithic rod was meas-

ured using caliper to determine the degree of shrinkage in the prepared monolithic rod after washing with methanol. Figure 3 shows the difference in appearance of the poly (BuMA-*co*-EDMA) monoliths after washing with methanol. As can be seen in the figure, the monolithic polymer rods, which were not affected when they were washed with methanol and were not shrunk or swollencompared with MeOH only (4.06 ± 0.07 mm), were the monolithic rods prepared using MeOH/EtOH (4.04 ± 0.16 mm) and MeOH/1-propanol (4.12 ± 0.05 mm) while the rest of the monoliths were shrunk significantly.

Fig.3 The appearance of the poly (BuMA-co-EDMA) monoliths prepared using different porogenic solvent systems after washing them with methanol to remove the unreacted monomeric materials using Soxhlet extraction with methanol at 80 °C for 24 hours.3.3. Characterisation of the fabricated materials

3.3.1. SEM analysis

The effect of the solvent type on the bed structure of the fabricated polymer-based monolith was investigated by studying the morphology of the polymer-based monolith using SEM. Figure 4 presents the SEM micrographs showing the morphology of the polymer-based monoliths fabricated using different porogenic solvent systems. Evaluation of the SEM micrographs shows that the structure of the fabricated monoliths was homogeneous and macroscopically uniform. In addition, the skeleton size of the fabricated polymer monolith was very small; therefore, it was expected that the physical strength of the fabricated polymer monolith was low.

From the SEM micrographs, it was observed that there is a clear effect of the porogenic solvent system on the morphology of the fabricated polymer-based monoliths since the size of globules and pores of the prepared monoliths were not similar.It can be seen that the morphology of the fabricated polymer monolith using MeOH/EtOH was similar to that of the polymer monolith fabricated using MeOH only and the fabricated polymer monoliths contained large globules and large pore size. This means using MeOH/EtOH as a porogenic solvent can offer an organic monolith with good hydrodynamic properties (high permeability) that allow using high flow rate velocities due to the large globules and large pore size. In contrast, the polymer-based monolith prepared using a porogenic solvent of MeOH/1-propanol resulted in small globules and small pores between them, which can provide an organic monolith with high surface area. The organic monolith that was fabricated using MeOH/cyclohexanol results in a condensed monolith contained large globules and small pore

size. The rest of the monoliths were very condensed (the SEM micrographs are not shown).
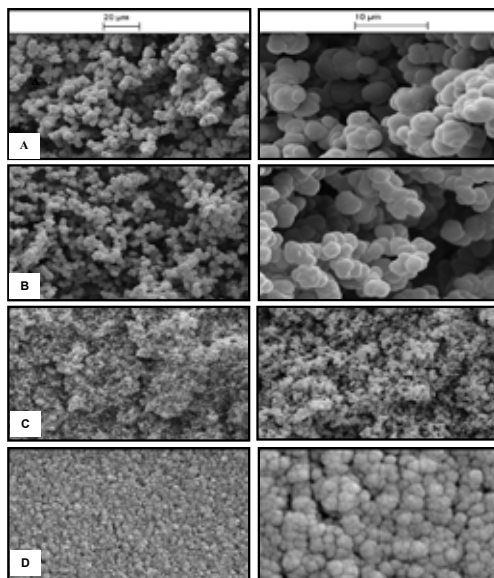

Fig.4 SEM micrographs of the poly (BuMA-co-EDMA) monoliths prepared using different porogenic solvent systems: (A) MeOH only, (B) MeOH/EtOH, (C) MeOH/1-propanol, and (D) MeOH/cyclohexanol.

3.3.2. BET analysis

The effect of the porogenic solvent type on the physical properties of the fabricated organic monoliths was investigated extensively. The important parameters that are sufficient for physical characterisation of the polymer-based monolith are the specific surface area (m^2 g^{-1}), and the pore size (nm)[21, 22].In this study, the surface area of the fabricated polymer-based monoliths and their pore size were measured using the BET analysis.

A high surface area of the prepared polymer-based monolith is desired in order to increase the binding capacity of the monolith[23].The bar chart 5 presents the surface areas of the polymer-based monoliths using different porogenic solvent systems. The result indicates that using MeOH/1-propanol as a porogenic solvent system resulted in a monolith with the largest surface area (56.89 m^2 g^{-1}). This result was expected since the SEM morphology of the monolith fabricated using this porogenic solvent system showed that it had small globules and pore size. The rest of the polymer-based monoliths prepared using different porogenic solvent systems had low surface areas, between 6.57 and 12.60 m^2 g^{-1}. In general, it was found that the surface areas of the prepared polymer-based monoliths were not very high.
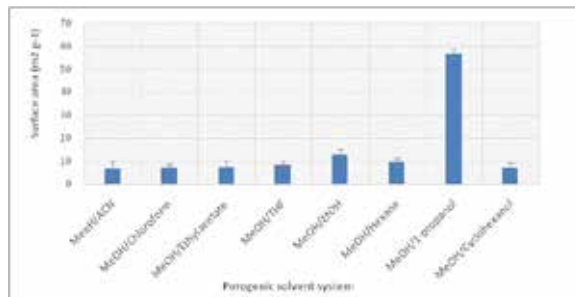

Fig.5 Effect of the composition of the porogenic solvent system on the total surface area of the prepared poly (BuMA-co-EDMA) monoliths using BET instrument, SD (n=3).

The size of the pores is a key factor for control of the hydrodynamic properties of the monolithic materials[24]. Large pore sizes within the monolithic material can lead to a decrease in the backpressure especially when the extraction is carried out in a microfluidic device. The pore size of the organic monoliths was also studied using the BET model. Figure 6 presents the effect of the porogenic solvent system on the pore size of the polymer-based monoliths. As can be seen in the figure, the diameter of the pores ranged between 4.73 and 12.93 nm, which places them in the mesopore range. It was found that the biggest pore size was obtained with the polymerisation mixture containing the porogenic solvent MeOH/EtOH (12.93 nm), followed by the organic monolith fabricated using MeOH/1-propanol (8.45 nm).
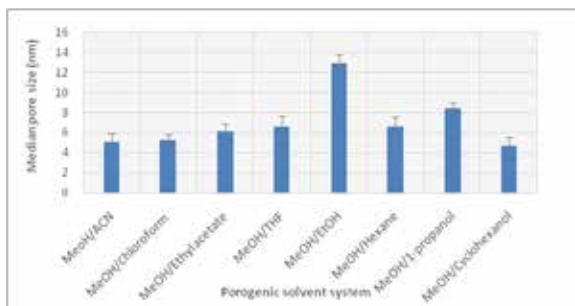

Fig.6 Effect of the porogenic solvent system on the median pore size of the prepared poly (BuMA-co-EDMA) monoliths using BET instrument, SD (n=3).

3.3.3. Measuring porosity
The porosity of the polymer-based monolith would be changed when it is exposed to organic solvents. Therefore, it is very important to study the effect of the porogenic solvent system on the porosity of the fabricated organic monolith, since there is a relation between the porosity of monolith and the backpressure; the higher the porosity, the lower the backpressure. Figure 7 presents the effect of the porogenic solvents on the porosity of the prepared organic monolith. As can be seen from the figure, the highest-porosity monolith was obtained when using a polymerisation mixture containing MeOH/EtOH as a porogenic solvent system (porosity = 0.08), followed by the monolith fabricated using MeOH/1-propanol (porosity = 0.05) compared with the rest of the fabricated organic monoliths.
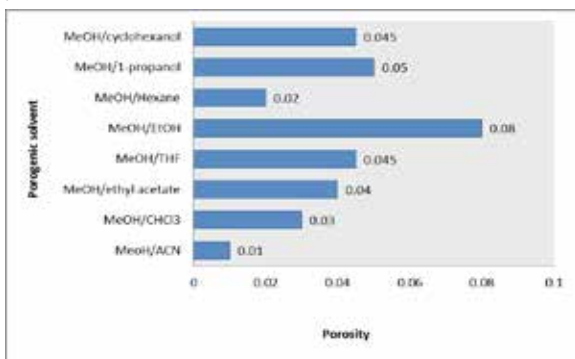

Fig.7 Effect of the porogenic solvent system on the porosity of the prepared poly (BuMA-co-EDMA) monoliths, SD (n=3). The porosity was calculated using equation 1, density of water at temperature 23 °C = 0.9975 g cm⁻³.

3.3.4. Measuring permeability
It is known that the porous polymer-based monoliths have a permeability to liquid flow through the network of canal-

like pores within the monolith[25].The permeability of the monolith is an important factor since high permeability of the monolith means low backpressure, a higher flow rate, and consequently a shorter analysis time[26]. However, an increase in the backpressure indicates that there is an interaction between the analyte and the surface of the monolith.The flow resistance of the monolithic beds was measured using the liquid chromatography pump system by passing deionised water at different flow rates through the various monoliths. Since the level of the backpressure can give information about the permeability of the monolith, the value of the backpressure (flow resistance) in the system was recorded. Figure 8 shows the relationship between the backpressure and the flow rate of the deionised water through the organic monoliths prepared using different porogenic solvent systems, which were MeOH only, MeOH/EtOH, and MeOH/1-propanol. The linearity of the relation was found to be good, with a correlation R^2 = 0.998 for all the prepared organic monoliths. The general conclusion that proceeds from measuring the backpressure is that the organic monoliths prepared using MeOH only, and MeOH/EtOH as porogenic solvent systems are characterised with low flow resistance and low backpressure for deionised water pumped through the monolith at different flow rates. The backpressure remains below a value of 350 psi at the high flow rate of 400 µL min⁻¹. The polymer-based monolith prepared using MeOH/1-propanol results in the same backpressure value but at a very low flow rate (19 µL min⁻¹). This result was expected since using MeOH/EtOH as a porogenic solvent system results in a monolith with high porosity, and large pore size. The permeability of the rest of the monoliths was not studied since the backpressures of these monoliths were too high and the experiment could not be completed.
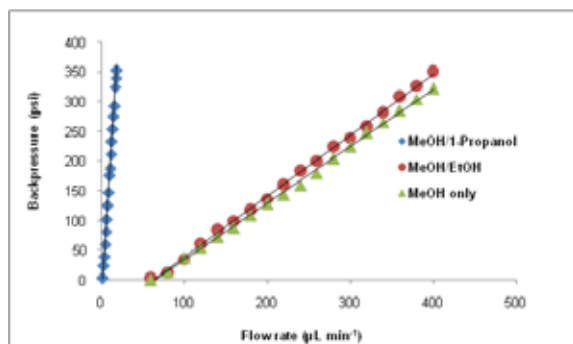

Fig.8 The relation between the backpressure and the flow rate of the deionised water through the poly (BuMA-co-EDMA) monoliths prepared using MeOH, MeOH/EtOH, and MeOH/1-propanol as porogenic solvent system.

4. Conclusion
In summary, the physical properties of the polymer-based monolith namely the surface area, pore size, porosity, and permeability can be substantially controlled by the porogenic solvent system. Based on the previous experiments, it was found that the most suitable porogenic solvent systems to prepare the butyl methacrylate monolith were MeOH/1-propanol, since it can offer an organic monolith with a high surface area, and MeOH/EtOH, since it can offer an organic monolith with high porosity and permeability.

REFERENCE 1. Arrua, R.D., M.C. Strumia, and C.I. Alvarez Igarzabal, Macroporous Monolithic Polymers: Preparation and Applications. Materials, 2009. 2(4): p. 2429-2466. | 2. Svec, F., Preparation and HPLC applications of rigid macroporous organic polymer monoliths. Journal of Separation Science, 2004. 27(10-11): p. 747-766. | 3. Svec, F., Porous polymer monoliths: Amazingly wide variety of techniques enabling their preparation. Journal of Chromatography A, 2010. 1217(6): p. 902-924. | 4. Yun Li, M.L.L., Biocompatible polymeric monoliths for protein and peptide separations. J. Sep. Sci., 2009. 32: p. 3369-3378. | 5. Svec, F. and J.M.J. Frechet, Kinetic Control of Pore Formation in Macroporous Polymers. Formation of "Molded" Porous Materials with High Flow Characteristics for Separations or Catalysis. Chemistry of Materials, 1995. 7(4): p. 707-715. | 6. Merhar, M., et al., Methacrylate monoliths prepared from various hydrophobic and hydrophilic monomers – Structural and chromatographic characteristics. Journal of Separation Science, 2003. 26(3-4): p. 322-330. | 7. Ma, G., et al., Multi-scale structures in emulsion and microsphere complex systems. China Particuology, 2005. 3(6): p. 296-303. | 8. Lubda, D., et al., Monolithic silica columns with chemically bonded β-cyclodextrin as a stationary phase for enantiomer separations of chiral pharmaceuticals. Analytical and Bioanalytical Chemistry, 2003. 377(5): p. 892-901. | 9. Yu, C., et al., Preparation of monolithic polymers with controlled porous properties for microfluidic chip applications using photoinitiated free-radical polymerization. Journal of Polymer Science Part A: Polymer Chemistry, 2002. 40(6): p. 755-769. | 10. Fletcher, P., et al., Permeability of silica monoliths containing micro- and nano-pores. J. Porous Mater., 2010. | 11. Chuda, K., et al., Characteristics and fluidic properties of porous monoliths prepared by radiation-induced polymerization for Lab-on-a-Chip applications. Radiation Physics and Chemistry, 2006. 75(1): p. 26-33. | 12. Lin, F.-Y. and W.-Y. Chen, Microcalorimetric Studies on the Interaction Mechanism between Proteins and Hydrophobic Solid Surfaces in Hydrophobic Interaction Chromatography: Effects of Salts, Hydrophobicity of the Sorbent, and Structure of the Protein. Analytical Chemistry, 2001. 73(16): p. 3875-3883. | 13. Bandilla, D. and C.D. Skinner, Protein separation by monolithic capillary electrochromatography. Journal of Chromatography A, 2003. 1004(1–2): p. 167-179. | 14. Rohr, T., et al., Photografting and the Control of Surface Chemistry in Three-Dimensional Porous Polymer Monoliths. Macromolecules, 2003. 36(5): p. 1677-1684. | 15. Wu, M., et al., Preparation and application of organic-silica hybrid monolithic capillary columns. ELECTROPHORESIS, 2011. 32(1): p. 105-115. | 16. Violaine Augustin, T.S., Frantisek Svec, Jean M. J. Fréchet CEC separation of peptides using a poly(hexyl acrylate-co-1,4-butanediol diacrylate-co-[2-(acryloyloxy)ethyl]trimethyl ammonium chloride) monolithic column. Electrophoresis, 2008. 29: p. 3875-3886. | 17. Samanidou, V.F., A.S. Ioannou, and I.N. Papadoyannis, The use of a monolithic column to improve the simultaneous determination of four cephalosporin antibiotics in pharmaceuticals and body fluids by HPLC after solid phase extraction—a comparison with a conventional reversed-phase silica-based column J. Chromatogr., B, 2004. 809: p. 175-182. | 18. Cabrera, K., et al., SilicaROD™ — A new challenge in fast high-performance liquid chromatography separations Trends Anal. Chem., 1998. 17: p. 50-53. | 19. Alzahrani, E. and K. Welham, Design and evaluation of synthetic silica-based monolithic materials in shrinkable tube for efficient protein extraction. Analyst, 2011. 136(20): p. 4321-4327. | 20. Altun, Z., Methacrylate-based monolithic packings, 2005, Karlstad University. | 21. Jal, P.K., S. Patel, and B.K. Mishra, Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions. Talanta, 2004. 62(5): p. 1005-1028. | 22. Beiler, B. and Á. Sáfrány, Polymer monoliths synthesized by radiation co-polymerization in solution. Radiation Physics and Chemistry, 2007. 76(8-9): p. 1351-1354. | 23. Potter, O.G. and E.F. Hilder, Porous polymer monoliths for extraction: Diverse applications and platforms. Journal of Separation Science, 2008. 31(11): p. 1881-1906. | 24. Xie, S., F. Svec, and J.M.J. Fréchet, Porous Polymer Monoliths: Preparation of Sorbent Materials with High-Surface Areas and Controlled Surface Chemistry for High-Throughput, Online, Solid-Phase Extraction of Polar Organic Compounds. Chemistry of Materials, 1998. 10(12): p. 4072-4078. | 25. Peters, E.C., et al., Molded Rigid Polymer Monoliths as Separation Media for Capillary Electrochromatography. 1. Fine Control of Porous Properties and Surface Chemistry. Analytical Chemistry, 1998. 70(11): p. 2288-2295. | 26. Nischang, I., F. Svec, and J.M.J. Fréchet, Downscaling Limits and Confinement Effects in the Miniaturization of Porous Polymer Monoliths in Narrow Bore Capillaries. Analytical Chemistry, 2009. 81(17): p. 7390-7396. |