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Preparation, characterization and application of polymethacrylate-based monolithic columns for fast and efficient separation of alkanes, alcohols, alkylbenzenes and isomeric mixtures by gas chromatography

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ABSTRACT

Application of monolithic columns in gas chromatography is still considered very limited. In this work, several polymethacrylate-based monolithic capillary columns were fabricated, characterized and used in gas chromatography. The five monomers used were: methyl methacrylate, (MMA), hexyl methacrylate (HMA), glycidyl methacrylate (GMA), 2-butoxyethyl methacrylate (BEMA) and isobornyl methacrylate (IBMA), while ethylene dimethacrylate was the crosslinker. The monoliths were synthesized in 30 cm length capillaries possessing inner diameters (i.d.) of 0.25 mm. The prepared monolithic columns were applied for separation of 3 series of homologous alkanes, alcohols and alkylbenzenes, as well as some isomeric mixtures. Van Deemter plots were used to optimize and compare the columns performance. The smaller methacrylates (MMA and GMA) exhibited higher porosity and permeability with low column backpressure values and poorer efficiency than the larger methacrylate monomers (HMA and BEMA). The columns prepared from IBMA monomer showed the highest pressure and the least separation efficiency. The fastest full separation of alkanes was achieved on HMA-*co*-EDMA column in about 3.0 min with resolution better than 2.73, while the fastest full separation of alcohols and alkylbenzenes was carried out using BEMA-*co*-EDMA column in less than 0.8 and 1.75 min with chromatographic resolution better than 1.27 and 1.85, respectively. Again, BEMA-*co*-EDMA column gave the best performance with the fastest and complete separation of all studied isomeric mixtures. For all tested series of solutes, the better separation efficiency was reached with tridecane, which gave 25,200 plates/m on the HMA-*co*-EDMA column. Another application was carried out using HMA-*co*-EDMA column for determination of myrcene and limonene, two monoterpenic isomers, in some fruit peels. Under the optimum GC conditions, a rapid separation of myrcene and limonene was achieved in less than 1.0 min with chromatographic resolution of 2.56. The highest contents of myrcene (0.131 mg/g) and limonene (1.225 mg/g) were measured in the hexane extracts of grapefruit and Egyptian orange, respectively. Finally, a comparison between the prepared columns and a commercial capillary column was performed. Based on the measured run time and HETP values, HMA-*co*-EDMA and BEMA-*co*-EDMA monolithic columns exhibited faster separation and higher efficiency for n-alkanes and alkylbenzenes than the TR-5 open tubular column, although they are 100 times shorter.

1. Introduction

The first investigations about monolithic materials and their applications in various fields were reported about five decades ago. Kubin et al. described in 1967 the first preparation of a polymethacrylate-based monolithic column and its application in HPLC [1], while Svec et al. proposed in 1996 the denomination of "monolithic stationary phases" which is now widely accepted [2]. These highly porous materials can be easily prepared *in-situ* inside the column and showed several advantages over conventional particulate stationary phases [3,4]. The development of new and efficient monolithic columns proved to be a prolific and innova-

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tive field which has attracted many fruitful research activities [4,5]. Thousands papers reported various methods for preparation of monolithic stationary phases and improvement of their efficiency in several chromatographic modes [6,7]. Compared to conventional packed columns, monolithic capillaries are a miniaturized separation system with many other advantages such as easy preparation, high separation efficiency, short analysis time and low solvent consumption [8,9]. Beside their main application as stationary phase in many chromatographic techniques, monolithic materials proved to be versatile and efficient adsorbents for extraction and separation of specific analytes. Due to the highly porous structure of monolithic materials which confers them a high specific surface area, their use as specific adsorbents instead of packed cartridges is increasing [9,10].

Three kinds of monolithic materials were developed: inorganic based on silica, organic consisting of a rigid porous polymer and organic-inorganic hybrid monoliths [11,12]. While inorganic silica-based materials are generally prepared by *sol-gel* method, organic based porous polymers are synthesized through a single-step polymerization of a mixture including suitable monomers, cross-linkers, porogenic solvents and an activator. All monolithic materials have a single-piece structure with a dense porous network. The density and size of these interconnected channels can be modulated to control the permeability and efficiency of the prepared monolithic stationary phase [13,14].

A large variety of monolithic columns were prepared, characterized and applied for separation of a wide range of analytes, from small solutes to large biomolecules. The success of this kind of new structures can be explained by their easy and inexpensive preparation, good permeability, low solvent consumption and high efficiency [12]. Many published papers and reviews reported successful applications of different kinds of monolithic columns for separation of various solutes such as pharmaceuticals, pollutants, food, chiral compounds and polymers [8,15–17]. In the last two decades polymer-based monoliths became more popular and many kinds were developed and successfully used for fast separation of various samples [16–18]. Most research efforts focused on preparation of new monolithic organic polymers and improvement of their chromatographic properties because they are easier to synthesize and to modify than silica-based monoliths [19,20]. In addition, these monolithic polymers could be widely used in different chromatographic modes such as reversed-phase liquid chromatography (RPLC), ion exchange chromatography (IEC), hydrophilic interaction chromatography (HILIC) and size exclusion chromatography (SEC) [17,21]. Monoliths based on organic polymers showed their ability to separate efficiently various macromolecules either natural such as peptides, proteins and nucleic acids or synthetic [20–22].

Svec and Frechet described in 1995 the preparation of a monolithic continuous bed based on macroporous copolymer glycidyl methacrylate-ethylene dimethacrylate and its use for HPLC separation of proteins [23]. Compared to other monolithic materials, methacrylate based columns have several advantages such as their simpler preparation, a wider range of pH stability, easy functionalization, as well as the availability of various monomers [24–26]. The main feature of monolithic columns is the single continuous piece of stationary phase which fills all the column volume. A uniform network of interconnected channels allows the flow of mobile phase through this porous material. The macropores, with a size in the μm range, provide this flow path and contribute to increase the column porosity and permeability while reducing the solute retention [9,18,27]. The fine porous structure of a monolith is due to mesopores which have a diameter in the nm range and afford a high active surface area for better separation efficiency. This characteristic structure is a key factor in the success of monolithic columns in terms of low back pressure, fast mass transfer of solutes and high efficiency [7,28,29]. On the other hand, if the monolith contains micropores which correspond to diameters less than 2 nm, the small solutes will tend to stagnate more; this will result in an increase of peak dispersion and a loss of efficiency. Therefore, preparation of highly efficient monolithic stationary phases requires a tight control of their porosity, in terms of pore size and distribution [12,30]. If the prepared monolith suffers from a lack of mesopores, its low specific area will induce a low retention for smaller solutes. Several procedures were applied to correct this defect including use of more suitable monomers and cross-linkers, incorporation of nanoparticles and hyper-crosslinking of the prepared monolith [12,31,32].

The first application of monolithic columns was carried out by Crawley in gas chromatography in 1969, but their use in GC remained very limited compared to their great success in HPLC [33,34]. Thus, most reports published later described their use in high performance liquid chromatography, using mainly fused silica capillary columns. In fact, the performance of monolithic stationary phases tested in GC was notably lower than that of commercially available open tubular capillary columns. While several detailed reviews described a great variety of monolithic columns successfully used in different HPLC modes, the first review about applications of monoliths in GC was published only in 2008 by Svec and Kurganov [4]. It was followed by a second review authored by Kurganov in 2008 [9].

Since polymethacrylate-based monoliths have a relatively low thermal stability, only few investigations were carried out on their applications in gas chromatography. However, some recent papers showed that methacrylate-based monolithic capillary columns can be successfully used in GC for fast separation of gases and light hydrocarbons, using a conventional non-modified chromatograph [34–36]. As for liquid chromatography, application of capillary monolithic columns in gas chromatography has several advantages: ease of preparation, fast and efficient separation, reduced carrier gas consumption [4].

The preparation of organic-based monolith columns is easily achieved in few steps by thermal or photo-induced polymerization inside the capillary of a mixture composed of suitable monomers, crosslinker, porogenic solvents and initiator. Among the available monomers, acrylates, methacrylates, styrenes and acrylamide were widely used; whereas divinylbenzene and ethylene dimethacrylate are common cross-linkers [8,18,20]. Several studies showed that the amount and properties of crosslinker greatly influences the porosity, permeability and chromatographic efficiency of the prepared column [12,18].

Polydivinylbenzene has been widely used as monolithic stationary phase in GC since 2000, because of its remarkable thermal stability until 380 °C. Since the permeability of monolithic columns is much lower than that of conventional open tubular capillaries, some research groups used a modified GC instrument working at carrier gas higher pressure [12,18]. The present work describes fabrication and characterization of five methacrylate-based monolithic materials including MMA-*co*-EDMA, HMA-*co*-EDMA, GMA-*co*-EDMA, BEMA-*co*-EDMA and IBMA-*co*-EDMA, then their use for some applications in gas chromatography.

2. Experimental

2.1. Chemicals and columns

Polyimide coated fused silica tubing (250 μm i.d.) was purchased from Restek (Bellefonte, USA). The chemicals used for preparation of monolithic columns in this work were acquired from Aldrich (Steinheim, Germany) as follows: 3-(trimethoxysilyl) propyl methacrylate (TMSM) 98%, ethylene dimethacrylate (EDMA)

98%, azo-bis-isobutyronitrile, hexyl methacrylate 98%, isobornyl methacrylate 98.5%, 2-butoxyethyl methacrylate 98%, methyl methacrylate 99% and glycidyl methacrylate 97%. All gases (methane, helium, hydrogen, nitrogen and air) of high-purity grade (99.9999%) were purchased from SIGAS (Riyadh, Saudi Arabia). Various alkanes, alkylbenzenes, alcohols and some isomeric compounds, all of the highest purity grade, and were obtained from BDH (England), Acros Organics (New Jersey, USA) and Riedel-de Haen (Seelze, Germany). Polar probes (diethylether, dichloromethane, tetrahydrofuran, chloroform and ethylacetate) all of the highest purity grade, were provided from Merck (Darmstad, Germany). HPLC grade acetonitrile was purchased from Fisher Scientific (Leicestershire, UK). Purified water was prepared with a Millipore system (Milli- Q Advantage Elix, Millipore S.A.S. 67120 Molsheim, France) and then filtered through a 0.22 μm nylon Whatman membrane (Maidstone, UK). All chemicals were used without further purification.

2.2. Capillary monolithic columns preparation

In order to clean and activate the capillary inner surface, the fused-silica tubing was rinsed first with acetone for 10 min. After that, it was rinsed with a 0.2 mol/L NaOH solution for 30 min and soaked in the same solution for 30 min, then rinsed with water and dried in air for 15 min, twice for each step. The tubing was then flushed with 0.2 mol/L HCl for 30 min and rinsed with water and dried in air for 15 min, twice for each step. After that, the capillary was rinsed with ethanol for 15 min, flushed with 40% TMSM solution in ethanol for 30 min and left with the same solution for 4 h, then rinsed with ethanol for 15 min and dried with nitrogen gas for 10 min. The activated capillary was then cut into pieces (about 32 cm length each) with a razor blade. In order to examine the effect of monomer type, three batches of columns have prepared, each batch contained five columns which only differ in monomer. Five monomers were used in this work and denoted as follows; methyl methacrylate (MMA), hexyl methacrylate (HMA), glycidyl methacrylate (GMA), 2-butoxyethyl methacrylate (BEMA) and isobornyl methacrylate (IBMA).

The composition of monomeric mixture used for each column preparation was 14% (v/v) monomer, 10% (v/v) ethylene dimethacrylate, 75% (v/v) porogen (mixture of propanol/1,4-butandiol = 50/50) and 1% (mass) of azo-bis-isobutyronitrile initiator. The total composition was mixed into a homogenous solution then sonicated and purged with nitrogen gas for 15 min. Each capillary column was then filled with the corresponding reactant solution and both ends were plugged with a piece of rubber, the polymerization was performed at 70 °C for 20 h. The prepared columns were then washed with acetonitrile overnight to remove the unreacted materials and porogenic solvents. After the washing, about 1 cm was cut from both capillary ends to get a total length of 30 cm for each column.

2.3. Characterization of the columns

The microscopic morphology of the monolithic materials was characterized using a JEOL (JSM-6380LA) SEM (Tokyo, Japan) analytical scanning electron microscope at 5 kV without further coating. The thermal stability of the monolithic materials was studied by thermo gravimetric analysis (TGA) with a Mettler-Toledo TGA/DSC Stare system (Schwerzenbach, Switzerland). The samples were heated from 25 to 500 °C at a heating rate of 10 °C/min. Columns porosity and permeability were determined using nano-LC 3000 RSLC Dionex Ultimate with UV detector (Sunnyvale, CA, USA).

2.4. Gas chromatography

All GC experiments were performed using a conventional chromatographic system (Thermo Scientific-Trace GC Ultra, USA) with Xcalibur software. The system included an oven with a temperature range of 40–400 °C at a heating rate of up to 870 °C/min. The investigated temperature range was 100–200 °C. The chromatograph used a split/splitless injector and a flame ionization detector (FID) with a 1:10 hydrogen/air mixture as the flame fuel. The carrier and makeup gas was dry, high-purity helium. Both the detector and the injector were adjusted to 200 °C. For the comparative study, TR-5 MS open tubular column, 30 m length 0.25 mm i.d. and 0.25 μm film was purchased from Thermo Scientific (Waltham, MA, USA).

3. Results and discussion

3.1. Columns preparation and characterization

In brief, preparation of capillary monolithic columns for chromatographic applications consists of two main steps; activation of the empty capillary inner wall and *in-situ* polymerization of the monomeric mixture in the column. The permeability and mechanical stability of the five prepared columns were evaluated under both HPLC and GC conditions. In HPLC, acetonitrile was used as eluent for the measurement of the pressure drop across the column at different flow rates ranging from 1.0 to 50 μL/min. Fig. 1(A) shows a directly proportional relationship between acetonitrile flow rate and column backpressure at 25 °C. The permeability values for the five columns were determined at 25 °C temperature while acetonitrile passed through the column at a volumetric flow rate of 0.5 μL/min. On the other hand, the total porosity of the prepared columns was evaluated in HPLC using uracil as unretained marker [25,26,37]. We noticed that the columns with shorter monomeric chain (MMA and GMA) exhibited higher porosity and permeability values than the longer methacrylate chains (HMA and BEMA). This effect was expected because a longer monomer chain induces an increase of the polymer volume with a reduction of the pore volume of the resulting monolithic phase. IBMA-*co*-EDMA column corresponded to the lowest porosity and permeability values, which could be explained by the higher volume of the isobornyl substituent. Both permeability and porosity values of the MMA-*co*-EDMA, HMA-*co*-EDMA and GMA-*co*-EDMA columns are very close to that published previously for similar columns [25,38,39] while (to the best of our knowledge) BEMA-*co*-EDMA and IBMA-*co*-EDMA monolithic columns are prepared for the first time. A linear dependence with regression factors ranging from 0.9991 to 0.9999 for all columns under HPLC and GC conditions indicates that the stationary phase permeability and stability of the two columns are excellent. The permeability and porosity values for the five columns are reported in Table 1.

Since conventional GC systems are designed to operate at a pressure less than 1000 kPa, the ratio of monomers to porogenic solvents was kept at minimum percentage but with significant contents to prevent high column backpressure and to provide stable and efficient stationary phases inside the columns. On the other side, helium was used in GC for estimation of the pressure drop across the columns at different flow rates ranging from 0.15 to 2.0 mL/min. Fig. 1(B) illustrates the effect of the flow rate through the prepared columns on backpressure using helium as carrier gas.

The morphological properties of the monolithic materials are considered as key factors affecting the separation efficiency of the capillary column. Representative SEM images of the monolithic columns are shown in Fig. 2(A–E). These pictures of the bulk region of columns demonstrate that the procedure for synthesis renders permeable monoliths with a continuous and uniform structure

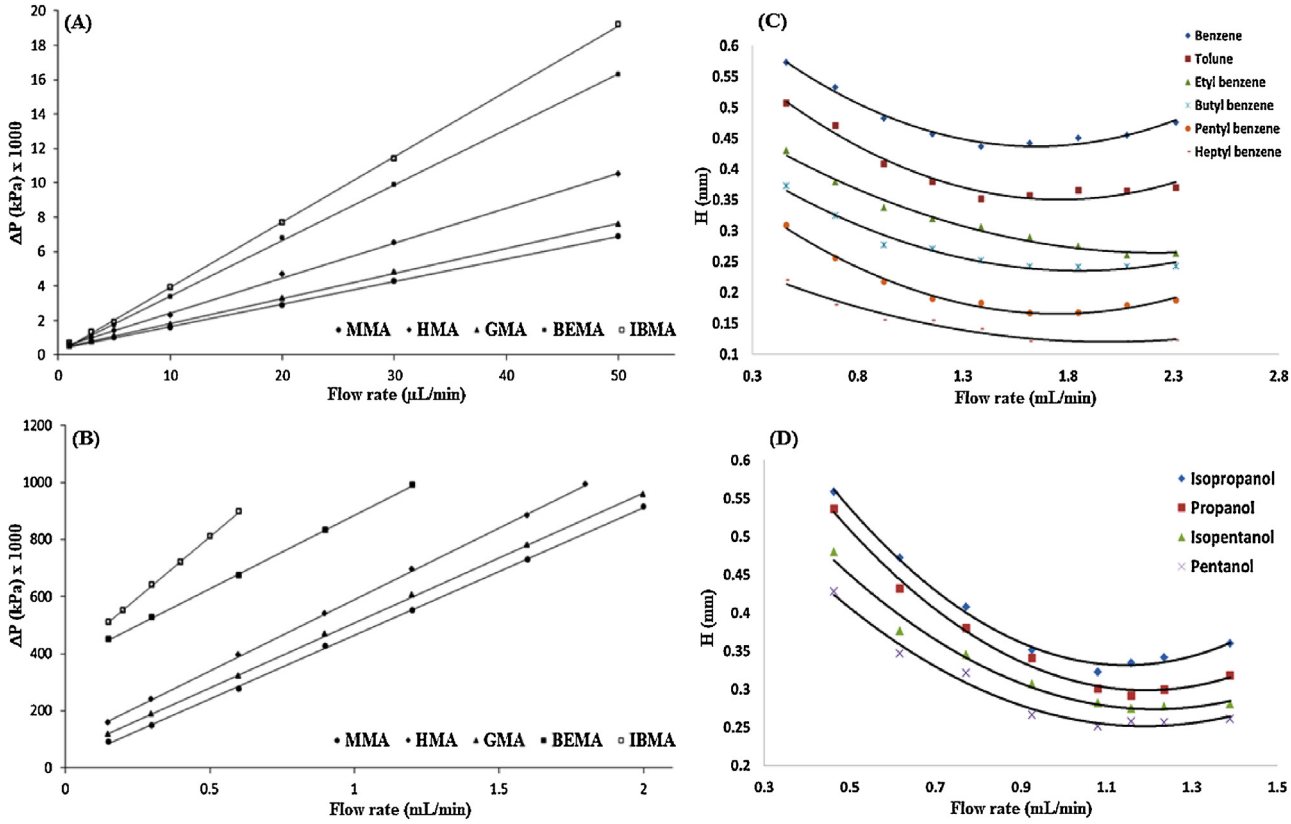

Fig. 1. Mechanical stability curves of the prepared columns: backpressure as a function of acetonitrile flow rate in HPLC (A). Mechanical stability curves of the prepared columns: backpressure as a function of helium flow rate as a carrier gas in GC (B). Van Deemter plots relating height equivalent to a theoretical plate and flow rate of the carrier gas (helium) for BEMA-*co*-EDMA column (C) and HMA-*co*-EDMA column (D).

Table 1
Porosity and permeability values of the prepared columns.

Column	Porosity	Permeability (m^2)	
		Acetonitrile[a]	Helium[b]
MMA-*co*-EDMA	0.85 ± 0.83%	1.74×10^{-13}	5.91×10^{-12}
HMA-*co*-EDMA	0.77 ± 1.14%	1.24×10^{-13}	4.13×10^{-12}
GMA-*co*-EDMA	0.82 ± 0.92%	1.58×10^{-13}	5.07×10^{-12}
BEMA-*co*-EDMA	0.74 ± 0.75%	1.02×10^{-13}	2.43×10^{-12}
IBMA-*co*-EDMA	0.71 ± 1.03%	9.15×10^{-14}	1.83×10^{-12}

[a] Measured by HPLC.
[b] Measured by GC.

and porosity. TGA data indicated that the porous monoliths of the five synthesized polymethacrylates did not undergo any significant thermal degradation below 225 °C for HMA-*co*-EDMA, 220 °C for MMA-*co*-EDMA, GMA-*co*-EDMA and IBMA-*co*-EDMA, and 210 °C for BEMA-*co*-EDMA. This good thermal behavior enables these monolithic columns to be operated routinely for GC applications at temperatures up to 200 °C, without observing any deterioration of their stability. A typical TGA profile for HMA-*co*-EDMA column is shown in Fig. 2(F).

3.2. *Separation of* n-*alkanes, alkylbenzenes and alcohols*

A number of monolithic capillary columns were prepared using five methacrylate monomers; MMA, HMA, GMA, BEMA and IBMA. To the best of our knowledge, this is the first application of 2-butoxyethyl and isobornyl methacrylate for fabrication of monolithic columns, and use in GC and even HPLC applications. After preparation of the capillary columns using several monomer compositions and experimental conditions, their chromatographic properties were then evaluated by separation of various mixtures in GC. For this purpose, three series of homologous consecutive compounds were tested: eleven linear alkanes ranging from pentane to pentadecane, five aliphatic alcohols from methanol to pentanol and eight alkylbenzenes from benzene to heptylbenzene. The three standard mixtures were separated under different isothermal and isobaric conditions or by programming the oven temperature in order to obtain the best resolution in the shortest time. The main chromatographic results and conditions obtained in these experiments are given in Table 2.

First, regarding investigations on *n*-alkanes, among the five tested methacrylate based monoliths, BEMA-*co*-EDMA column provided the fastest separation of C_5 to C_9 alkanes in 0.38 min (at 160 °C) because of its higher permeability, although pentane and hexane were partially resolved. The fastest and complete separation of the C_5—C_9 alkane series was achieved on the same column in less than 0.9 min (at 120 °C). The HMA-*co*-EDMA column allowed a fast separation of *n*-pentane to *n*-nonane in 0.68 min, while the eleven *n*-paraffins C_5—C_{15} showed a baseline resolution on the

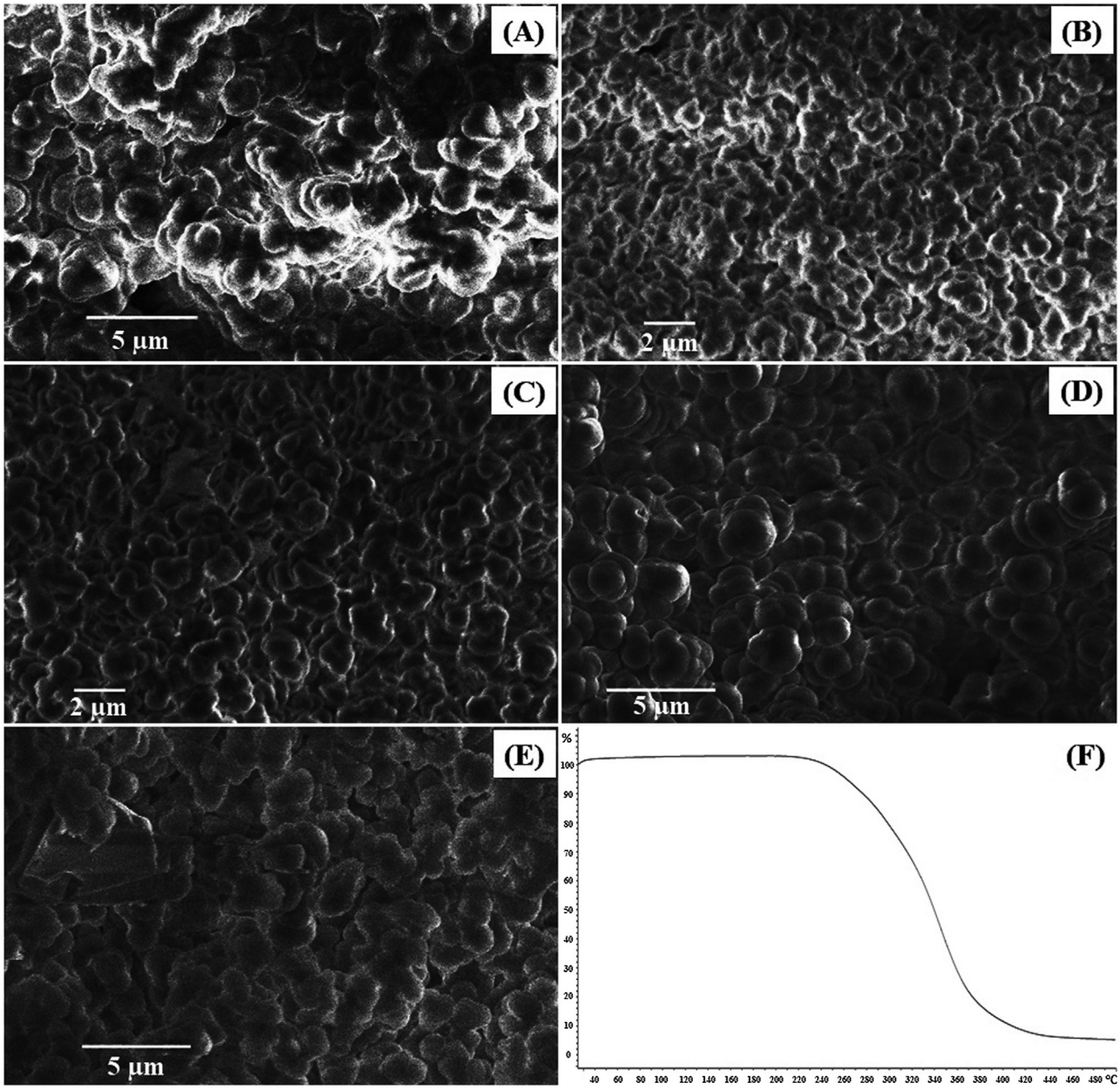

Fig. 2. Microphotographs of monolithic columns prepared with MMA-*co*-EDMA (A), HMA-*co*-EDMA (B), GMA-*co*-EDMA (C), BEMA-*co*-EDMA (D) and IBMA-*co*-EDMA (E). Thermogram of HMA-*co*-EDMA monolithic polymer (F).

hexyl methacrylate column in about three minutes, as it is shown in Fig. 3(A). In this experiment, tridecane gave a plate height of 0.04 mm corresponding to 25300 plates/m and a resolution of 3.80 between C_{13} and C_{14} (Table 2). Using IBMA-*co*-EDMA column, although the first five *n*-alkanes were eluted in about 5.86 min, pentane and hexane peaks were overlapping. The retention time of pentane was 1.54 min, compared to 0.156 and 0.108 min on BEMA-*co*-EDMA and HMA-*co*-EDMA columns, respectively. This result means that IBMA-*co*-EDMA monolith has a higher content of mesopores than in other columns, inducing thus a higher diffusion of analytes and more interactions, which led to broader peaks and increased retention due to longer path.

A full separation of light alkanes on BEMA-*co*-EDMA and HMA-*co*-EDMA columns was possible at 140 °C under a pressure of 900 kPa or using a programmed temperature from 100 to 160 °C at a fast rate. The results obtained using these two columns showed that both are able to achieve a fast and efficient separation of saturated hydrocarbons. The eleven successive alkanes from C_5 to C_{15} were baseline separated with a resolution higher than 1.20. The chromatogram on Fig. 3(B) corresponds to the result of the five lightest *n*-alkanes with IBMA-*co*-EDMA monolithic column; the total run time is higher than 12 min with broad and overlapping peaks. Peak broadening resulted from increasing the column temperature and thus this effect induced a lower resolution between alkanes for all columns.

For the *n*-alcohols series, a complete separation was achieved in a relatively short time on HMA-*co*-EDMA and BEMA-*co*-EDMA columns; the overall separation time was 3.4 and 0.8 min, respectively. Nevertheless, the resolution was higher on HMA-*co*-EDMA column but the retention was longer. As it was observed for *n*-alkanes, a marked peak broadening was noticed for alcohols separation on IBMA-*co*-EDMA column, with a longer run time of 11 min. This result was explained by the lower porosity and permeability

Table 2
Retention times, efficiency values and separation conditions of alkanes, alcohols and alkylbenzenes on monolithic columns.

Columns	Probes	t_R (min)	N (plates/m)	HETP (mm)	R_s	GC conditions
HMA-*co*-EDMA	pentane	0.108	3100	0.32	2.73	110 °C rise to 180 °C (50 °C/min), 1.2 mL/min
	hexane	0.158	2600	0.38	3.09	
	heptane	0.247	2700	0.37	3.37	
	octane	0.408	2400	0.42	4.32	
	nonane	0.683	5700	0.18	4.18	
	decane	0.983	8600	0.12	4.12	
	undecane	1.313	13300	0.08	3.99	
	dodecane	1.653	19000	0.05	3.90	
	tridecane	2.003	25200	0.04	3.80	
	tetradecane	2.393	23600	0.04	**4.23**	
	pentadecane	3.018	14700	0.07		
	methanol	0.360	2800	0.35	2.22	110 °C (isothermal), 1.5 mL/min
	ethanol	0.482	3400	0.30	4.37	
	propanol	0.855	3200	0.31	4.79	
	butanol	1.645	3000	0.34	**5.44**	
	pentanol	3.260	4000	0.25		
	benzene	0.428	2400	0.41	2.78	160 °C (isothermal), 1.2 mL/min
	toluene	0.632	3100	0.33	2.75	
	ethyl benzene	0.912	3100	0.33	2.94	
	propyl benzene	1.328	3500	0.29	3.82	
	n-butyl benzene	2.120	3800	0.26	3.85	
	pentyl benzene	3.360	3900	0.26	4.41	
	hexyl benzene	5.455	5100	0.20	**4.79**	
	heptyl benzene	9.037	4900	0.20		
BEMA-*co*-EDMA	pentane	0.156	3600	0.28	2.50	120 °C (isothermal), 2.2 mL/min
	hexane	0.215	3200	0.31	2.92	
	heptane	0.323	2600	0.40	3.64	
	octane	0.522	3700	0.27	**4.22**	
	nonane	0.895	3300	0.31		
	methanol	0.125	1800	0.57	1.27	110 °C (isothermal), 2.1 mL/min
	ethanol	0.155	1900	0.51	2.92	
	propanol	0.247	2300	0.43	3.76	
	butanol	0.418	3200	0.31	3.27	
	pentanol	0.722	1600	0.62		
	benzene	0.198	2300	0.44	1.85	180 °C (isothermal), 1.6 mL/min
	toluene	0.260	2700	0.37	1.92	
	ethyl benzene	0.337	3200	0.31	2.10	
	propyl benzene	0.433	4200	0.24	2.95	
	n-butyl benzene	0.603	4400	0.23	3.18	
	pentyl benzene	0.832	6200	0.16	4.06	
	hexyl benzene	1.168	9100	0.11	**4.57**	
	heptyl benzene	1.663	9000	0.11		
IBMA-*co*-EDMA	pentane	1.545	300	3.29	1.11	180 °C (isothermal), 0.1 rise to 0.2 mL/min (0.01 mL/min)
	hexane	2.303	530	1.87	1.47	
	heptane	3.583	660	1.52	1.45	
	octane	5.573	560	1.80	**1.39**	
	nonane	9.253	350	2.83		
	methanol	1.545	380	2.62	1.36	150 °C rise to 180 °C (15 °C/min), 0.2 mL/min
	ethanol	2.457	550	1.82	2.15	
	propanol	4.053	1700	0.60	1.89	
	butanol	6.067	990	1.01	**2.00**	
	pentanol	10.015	820	1.21		
	benzene	3.042	820	1.21	1.90	180 °C (isothermal), 0.2 mL/min
	toluene	4.612	1400	0.70	1.71	
	ethyl benzene	6.527	1300	0.81	1.65	
	propyl benzene	9.880	700	1.42	**1.98**	
	n-butyl benzene	16.243	1000	0.99		

of the column. The resolution factor between alcohols was greater than 1.20 for all couples, on the three tested columns.

A complete separation of the *n*-alkylbenzene series was achieved on BEMA-*co*-EDMA and HMA-*co*-EDMA columns in a total run time of 2.0 and 10.5 min, respectively. These aromatic hydrocarbons could be separated more quickly in 0.8 and 2.8 min on BEMA-*co*-EDMA and HMA-*co*-EDMA, the GC experimental conditions are presented in Table 2. Among the prepared and tested monolithic columns, BEMA-*co*-EDMA allowed the fastest separation of alkylbenzenes without any peak overlapping (Fig. 3(C)). The results obtained for alkylbenzenes on IBMA-*co*-EDMA column were not satisfactory and showed longer retention times and broader peaks which correspond to a poor efficiency. The poor resolution observed for this column could not be improved by any change in temperature or pressure. Hence, it was concluded that IBMA-*co*-EDMA column is not a suitable choice for a rapid and efficient separation of alkylbenzenes and light *n*-alkanes. Although the GMA-*co*-EDMA and MMA-*co*-EDMA columns were prepared using the same monomer composition and experimental conditions as other columns, their application for separation of n-alkanes, alcohols and alkylbenzenes gave bad results, (Fig. 3(D)). This could be explained by their high permeability and porosity which exceeded 80%.

3.3. Separation of isomer mixtures

In order to investigate the capability of the prepared columns to differentiate between structural isomers, some investigations

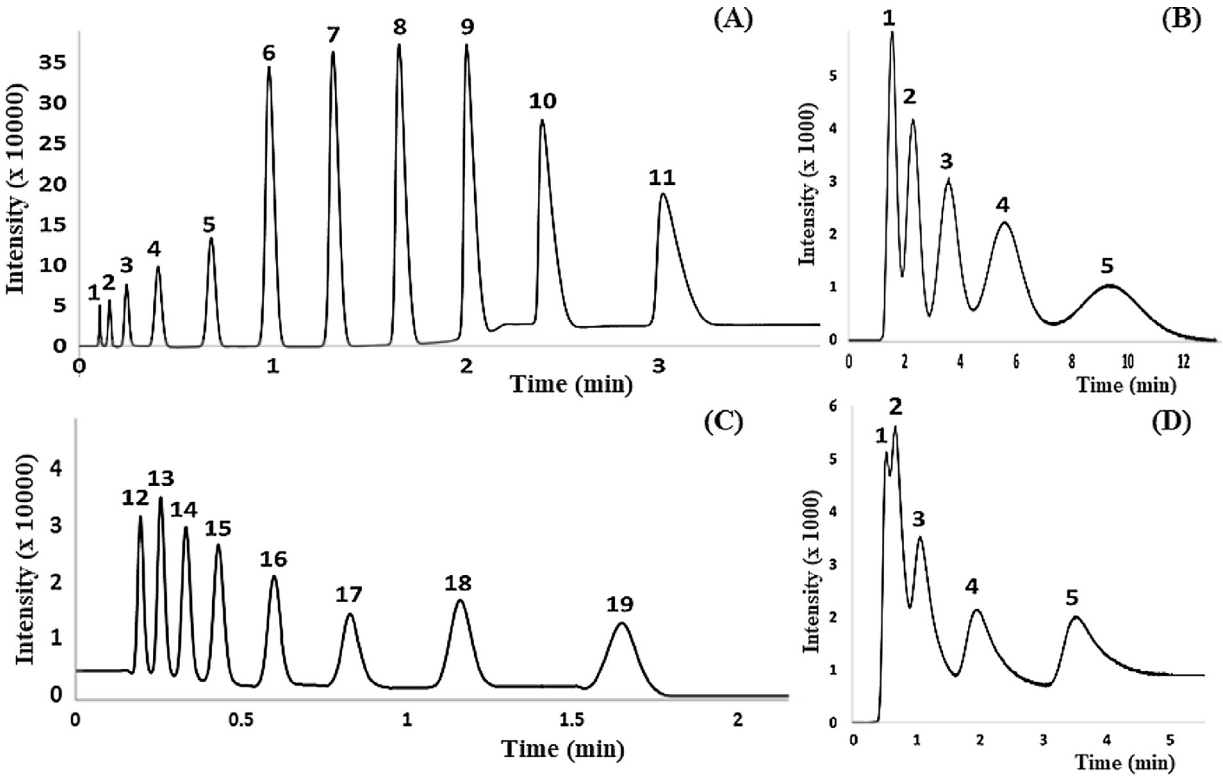

Fig. 3. GC separation of alkanes and alkylbenzenes using: (A) HMA-*co*-EDMA, (B) IBMA-*co*-EDMA, (C) BEMA-*co*-EDMA and (D) GMA-*co*-EDMA columns. Solutes are: (1) pentane, (2) hexane, (3) heptane, (4) octane, (5) nonane, (6) decane, (7) undecane, (8) dodecane, (9) tridecane, (10) tetradecane, (11) pentadecane, (12) benzene, (13) toluene, (14) ethyl benzene, (15) propyl benzene, (16) *n*-butyl benzene, (17) pentyl benzene, (18) hexyl benzene and (19) heptyl benzene.

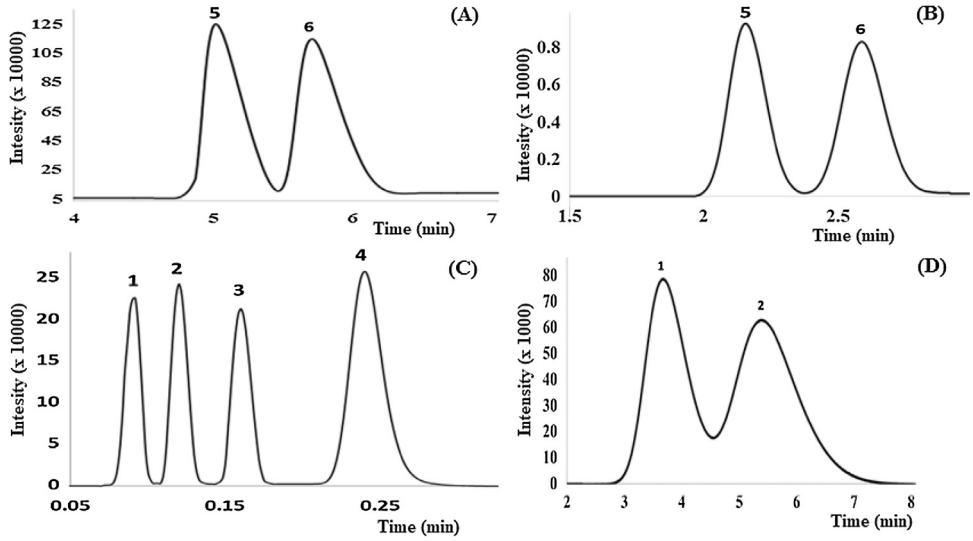

Fig. 4. Separation of isomeric mixtures using (A) HMA-*co*-EDMA, (B) BEMA-*co*-EDMA, (C) BEMA-*co*-EDMA and (D) IBMA-*co*-EDMA columns. Solutes are: (1) isopropanol, (2) propanol, (3) isopentanol, (4) pentanol, (5) *p*-xylene and (6) *o*-xylene.

were carried out on different mixtures. An excellent and fast separation of a mixture including two couples of isomeric alcohols (isopropanol/propanol and isopentanol/pentanol) was performed using BEMA-*co*-EDMA columns in approximately 0.25 min, using a programmed temperature from 100 to 160 °C and a helium flow rate of 1.7 mL/min (Fig. 4(C)). The same mixture was separated in about 0.5 min using HMA-*co*-EDMA; but with IBMA-*co*-EDMA each couple could be separated while the mixture showed co-elution. As it was obtained for homologous series, GMA-*co*-EDMA and MMA-*co*-EDMA columns were unable to resolve the alcohol isomers. BEMA-*co*-EDMA column gave the best performance with a fastest and complete separation of all the tested isomeric couples: isooctane/octane (0.4 min with $R_S = 2.23$), isobutyl benzene/*n*-butyl benzene (3.2 min, $R_S = 2.25$), *p*-xylene/*o*-xylene (2.7 min, $R_S = 1.68$) (Fig. 4(B)), and myrcene/limonene (2 min, $R_S = 2.38$) using a programmed temperature.

Also HMA-*co*-EDMA column showed an excellent separation of all couples which were fully resolved with high values under the same conditions but in longer times. The run time and resolution values for each couple were 0.45 min and $R_S = 1.63$ for

Table 3
Retention time, efficiency values and separation conditions of isomeric mixtures on monolithic columns.

Column	Probes	t_R (min)	N (plates/m)	HETP (mm)	R_s	GC conditions
HMA-*co*-EDMA	isopropanol	0.923	1600	0.63	2.72	110 °C (isothermal), 1.3 mL/min
	propanol	1.413	2900	0.34		
	isopentanol	2.418	6300	0.16	3.02	
	pentanol	3.097	10000	0.10		
	isooctane	0.308	2000	0.49	1.63	180 °C (isothermal), 1.1 mL/min
	octane	0.393	2700	0.37		
	isobutyl benzene	4.977	1700	0.59	1.75	120 °C (isothermal), 1.1 mL/min
	n-butyl benzene	6.807	1700	0.60		
	p-xylene	5.018	6600	0.15	1.41	100 °C rise to 160 °C (8 °C/min), 1 mL/min
	o-xylene	5.715	5900	0.17		
	myrcene	2.532	3900	0.26	1.72	150 °C (isothermal), 1 mL/min
	limonene	3.073	4500	0.22		
BEMA-*co*-EDMA	isopropanol	0.668	2500	0.40	3.17	100 °C rise to 160 °C (20 °C/min), 1.7 mL/min
	propanol	1.013	3700	0.27		
	isopentanol	1.668	6300	0.16	3.88	
	pentanol	2.322	8500	0.12		
	isooctane	0.252	2300	0.43	2.20	160 °C (isothermal), 1.6 mL/min
	octane	0.338	3900	0.26		
	isobutyl benzene	2.437	5800	0.17	2.25	140 °C (isothermal), 1.6 mL/min
	n-butyl benzene	3.000	6600	0.15		
	p-xylene	2.157	4400	0.23	1.68	120 °C rise to 160 °C (8 °C/min), 1.6 mL/min
	o-xylene	2.588	4600	0.22		
	myrcene	1.602	5900	0.17	2.38	150 °C (isothermal), 1.5 mL/min
	limonene	1.974	8000	0.13		
IBMA-*co*-EDMA	isooctane	0.832	210	4.74	5.56	160 °C (isothermal), 0.2 mL/min
	octane	7.643	750	1.33		
	isopropanol	3.678	560	1.78	1.30	150 °C (isothermal), 0.15 mL/min
	propanol	5.388	690	1.46		
	isobutanol	6.145	600	1.66	1.47	180 °C (isothermal), 0.15 mL/min
	butanol	9.252	780	1.28		
	isopentanol	4.617	700	1.43	1.40	160 °C (isothermal), 0.2 mL/min
	pentanol	6.775	750	1.34		

isooctane/octane, 7.0 min and $R_S = 1.75$ for isobutyl benzene/*n*-butyl benzene, 6.5 min and $R_S = 1.41$ for *p*-xylene/*o*-xylene (Fig. 4(A)), and 3.2 min and $R_S = 1.72$ for myrcene/limonene. Only four couples of isomers (isooctane/octane, isopropanol/propanol, isobutanol/butanol and isopentanol/pentanol) were resolved on IBMA-*co*-EDMA column with a peak resolution higher than 1.30. Representative isomeric mixture separations using IBMA-*co*-EDMA are shown in Fig. 4(D). The investigated isomeric mixtures could not be separated satisfactorily using GMA-*co*-EDMA and MMA-*co*-EDMA columns. The measured values of retention, separation efficiency and resolution for isomeric mixtures on the different monolithic columns are summarized in Table 3 .

3.4. Column efficiency

Van Deemter curves were plotted by calculating the efficiencies of the prepared columns and correlating the height equivalent to a theoretical plate (HETP) with the flow rate of the carrier gas (helium). These experiments were carried out for alkanes, alcohols and alkylbenzene series, as well as for isomeric alcohols which were investigated on the prepared columns at 110, 150, 160 and 180 °C, as shown on Fig. 1(C & D). The column flow rate was measured manually using a bubble flow meter over a range of pressure. As shown in Fig. 1(C & D), the van Deemter curves have a characteristic profile with decreasing HETP at low flow rates, then increasing at higher flow rate values after the optimum value which corresponds to the minimum HETP. For all tested series of solutes (*n*-alkanes, alcohols, alkylbenzenes and isomeric alcohols) it appears that for the same flow rate, a compound with a higher molecular weight corresponds to a lower HETP value, due to its higher retention.

The van Deemter curves were plotted by varying the carrier gas flow rate in the range up to 150 μL/min. For alkanes, the HETP ranged from 0.27 to 0.57 mm for BEMA-*co*-EDMA (Fig. 1(C)), 0.12–0.59 mm for HMA-*co*-EDMA and 1.5–3.6 mm for IBMA-*co*-EDMA columns. The optimum flow rate values corresponding to the lowest HETP were 2.1, 1.3 and 0.22 mL/min for BEMA-*co*-EDMA, HMA-*co*-EDMA and IBMA-*co*-EDMA, respectively. For separation of alkylbenzenes, the HETP ranged from 0.11 to 0.57 mm for BEMA-*co*-EDMA and 0.18–0.88 mm for HMA-*co*-EDMA; the value of flow rate that yielded the lowest HETP was 1.8 and 1.4 mL/min for BEMA-*co*-EDMA and HMA-*co*-EDMA columns, respectively. In the case of isomeric alcohols separation, the value of the optimum flow rate was 2.3 and 1.2 mL/min for BEMA-*co*-EDMA and HMA-*co*-EDMA columns, respectively; the HETP was in the range 0.37–0.72 mm for BEMA-*co*-EDMA, and 0.26–0.56 mm for HMA-*co*-EDMA (Fig. 1(D)).

When comparing the results obtained for all mixtures, the lowest HETP values were 0.12 mm (corresponding to 8600 plates/m) for octane, 0.26 mm (3900 plates/m) for pentanol, 0.27 mm (3600 plates/m) for isopentanol and 0.18 mm (5600 plates/m) for hexylbenzene on HMA-*co*-EDMA column. BEMA-*co*-EDMA column corresponded to a HETP value of 0.27 mm (3700 plates/m) for octane, 0.37 mm (2700 plates/m) for pentanol, 0.47 mm (2100 plates/m) for isopentanol and 0.11 mm (9400 plates/m) for hexylbenzene. It can be deduced that for alkanes, HMA-*co*-EDMA column exhibits a better efficiency than BEMA-*co*-EDMA; this could be explained by the lower polarity of HMA-*co*-EDMA monolith. In the case of separation of alkylbenzenes, the order is reversed as the column efficiency of BEMA-*co*-EDMA is higher. The van Deemter curves confirmed the superiority of the prepared HMA-*co*-EDMA and BMA-*co*-EDMA columns over the IBMA-*co*-EDMA columns, while a complete separation of most mixtures was not achieved using GMA-*co*-EDMA and MMA-*co*-EDMA columns, which have the highest permeability and porosity.

3.5. Quantitative analysis of myrcene and limonene in some fruits peel

The applicability and reliability of the prepared columns were also evaluated. For this purpose, HMA-*co*-EDMA column was selected for determination of myrcene and limonene isomers in

Table 4
Myrcene and limonene contents in some fruits peel.

Source of peel sample	Concentration (mg/g)	
	Myrcene	Limonene
Egyptian orange	ND[a]	1.225
Lemon	0.032	0.295
Clementina	ND	0.902
Valencia orange	ND	0.130
Grapefruit	0.131	0.632

[a] ND: not detected.

some fruits peel. HPLC grade hexane was added to the mixture as an internal standard (IS). The GC oven was isothermally heated at 150 °C. The injection port was held at 200 °C and the split valve was opened with split ratio of 1:5. Helium (99.9999% purity) was used as the carrier gas with a constant flow of 1.2 mL/min. The temperature of the detector (FID) was 200 °C and it was fed with 300:30 mL/min hydrogen/air gases. The column backpressure was registered at 905 ± 2 kPa. Under these GC conditions, a rapid separation of myrcene and limonene was achieved in less than 1.0 min with a chromatographic resolution of 2.56.

The results obtained showed that the calibration curves were linear over the solute to internal standard concentration ratio range of 0.006–1.28 with R^2 more than 0.9989. The detection limits of myrcene and limonene were 0.40 and 0.35 μg/mL, respectively at a signal-to-noise ratio of 3:1. A typical chromatogram of the standard mixture and calibration curves are shown in Fig. 5. The contents of myrcene and limonene in the studied fruits peel are presented in Table 4. While myrcene was not detected in Egyptian orange, Clementina and Valencia orange extracts, the highest contents of myrcene (0.131 mg/g) and limonene (1.225 mg/g) were obtained in the hexane extract of Grapefruit and Egyptian orange, respectively. These data indicated that the monolithic prepared columns could be used for routine analysis of various volatile compounds in real samples.

3.6. Comparison with commercial open tubular column

In order to complete the picture, a comparison of the separation efficiency between the prepared columns (30 cm long × 250 μm i.d.) and a commercial open tubular TR-5MS column (30 m long × 250 μm i.d.) was performed. Mixtures of alkanes and alkylbenzenes were injected onto the prepared columns using the optimum flow rate derived from the van Deemter curves, under isothermal conditions at 150 and 180 °C for n-alkanes and alkylbenzenes, respectively. Separation of the same samples were performed using the commercial open tubular column (TR-5MS) under its optimal conditions of temperature and flow rate.

Table 5 represents the results obtained using the prepared monolithic columns (BEMA-*co*-EDMA and HMA-*co*-EDMA) and the commercial TR-5 MS column at the optimum flow rate for each column, which corresponded to 2.3 and 1.2 mL/min for BEMA-*co*-EDMA and HMA-*co*-EDMA, respectively. According to this comparison, both monolithic columns separated the two mixtures faster than the open tubular column with similar efficiencies, as shown by their HETP values. These results show that our columns allow a complete and faster separation with a lower consumption of carrier gas, in spite of their much shorter length.

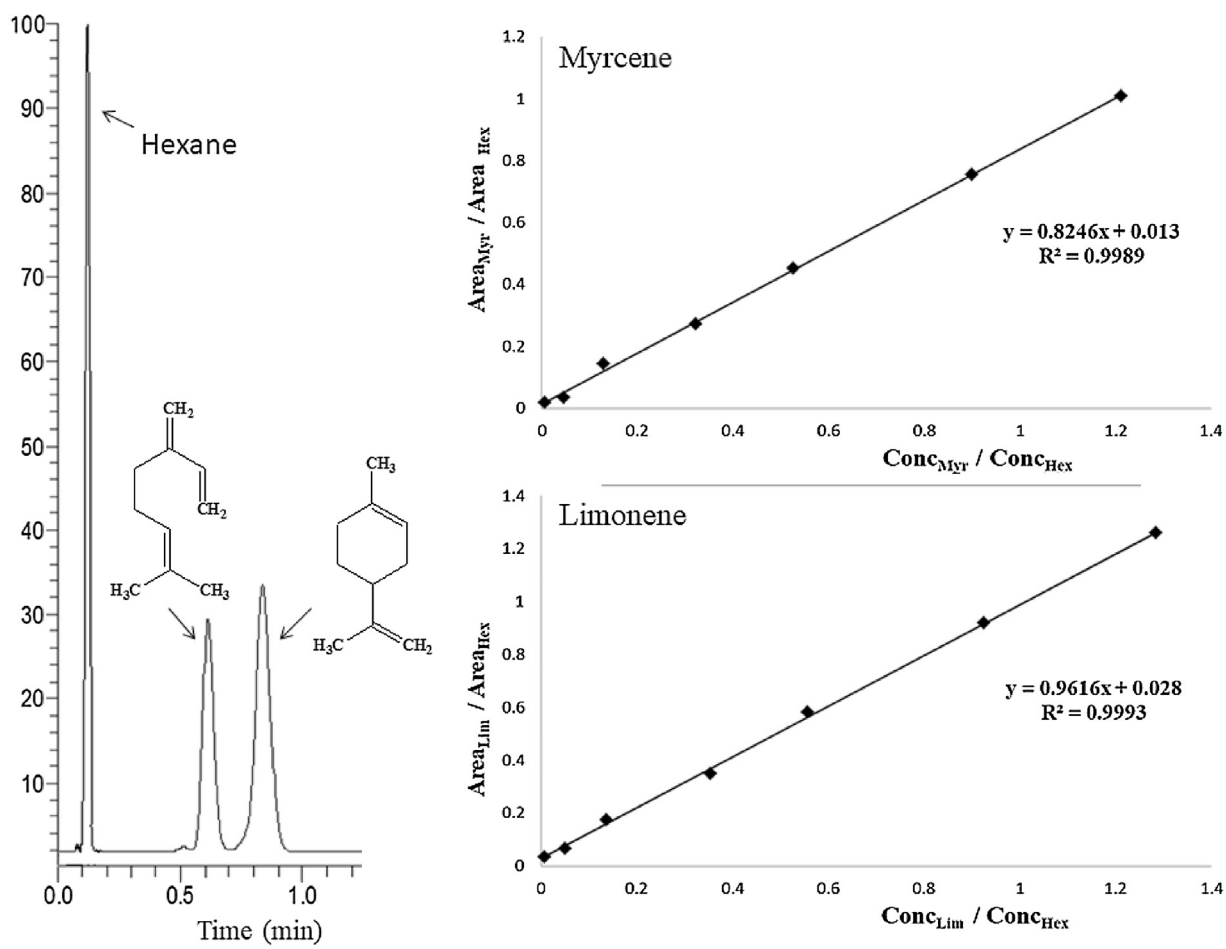

Fig. 5. Chromatogram of the standard mixture and calibration curves of myrcene and limonene using hexane as internal standard.

Table 5
Comparison between the efficiency of separation of a commercial column (TR-5 MS) and the monolithic columns (BEMA-*co*-EDMA and HMA-*co*-EDMA) at the optimum conditions for each column.

	t_R (min) HMA-*co*-EDMA (0.3 m)	N (plates/m)	HETP (mm)	t_R (min) TR-5 MS (30 m)	N (plates/m)	HETP (mm)
pentane	0.108	3100	0.32	0.826	2239	0.45
hexane	0.158	2600	0.38	0.972	2303	0.43
heptane	0.247	2700	0.37	1.315	2332	0.43
octane	0.408	2400	0.42	2.015	3517	0.28
nonane	0.683	5700	0.18	3.131	4435	0.23
benzene	0.198	2300	0.44	0.906	2491	0.40
toluene	0.260	2700	0.37	0.936	2466	0.41
ethyl benzene	0.337	3200	0.31	0.966	1689	0.59
propyl benzene	0.433	4200	0.24	1.064	2268	0.44
n-butyl benzene	0.603	4400	0.23	4.636	8831	0.11
pentyl benzene	0.832	6200	0.16	5.653	10507	0.10
hexyl benzene	1.168	9100	0.11	6.923	10171	0.10
heptyl benzene	1.663	9000	0.11	8.958	6737	0.15

4. Conclusion

Despite the intrinsic poor thermal stability of polymethacrylate-based monolithic columns which limits their use at high temperature, efficient and fast separations of various volatile mixtures of alkanes, alcohols, alkylbenzenes and isomeric compounds were successfully achieved using several prepared methacrylate-based monolithic capillary columns under normal GC conditions. As a whole, we found that each column presented unique advantages. For example, HMA-*co*-EDMA column was more suitable for rapid separation of alkane series, while BEMA-*co*-EDMA monolithic column showed better efficiency towards alcohols, alkylbenzenes and isomeric mixtures. In most cases, the separation efficiency, resolution and run time could be further improved using programmed temperature rather than isothermal conditions. When compared with a commercial open tubular capillary, both HMA-*co*-EDMA and BEMA-*co*-EDMA columns with only 30 cm length provided high efficiency and faster separation of alkanes and alkylbenzenes than the open tubular column with 30 m length.

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References

[1] M. Kubín, A generalized exponential function as a model of polymer distribution curves, Collect. Czech. Chem. Commun. 32 (1967) 1505–1517.
[2] F. Svec, J.M.J. Fréchet, New designs of macroporous polymers and supports: from separation to biocatalysis, Science 273 (1996) 205–211.
[3] X. Qiao, R. Chen, H. Yan, S. Shen, Polyhedral oligomeric silsesquioxane based hybrid monolithic columns: recent advances in their preparation and their applications in capillary liquid chromatography, Trends Anal. Chem. 97 (2017) 50–64.
[4] F. Svec, A.A. Kurganov, Less common applications of monoliths III. Gas chromatography: a review, J. Chromatogr. A 1184 (2008) 281–295.
[5] F. Wu, C. Xu, N. Jiang, J. Wang, C. Ding, Poly (methacrylic acid-co diethenyl-benzene) monolithic microextraction column and its application to simultaneous enrichment and analysis of mycotoxins, Talanta 178 (2018) 1–8.
[6] F. Svec, Y. Lv, Advances and recent trends in the field of monolithic columns for chromatography, Anal. Chem. 87 (2015) 250–273.
[7] F. Wang, A. Wei, X. Wang, H. Liu, L. Bai, H. Yan, Property evaluations and application for separation of small molecules of a nanodiamond-polymer composite monolithic column, Talanta 154 (2016) 237–248.
[8] Z.A.A.L. Othman, Preparation and characterization of alkyl methacrylate capillary monolithic columns, J. Saudi Chem. Soc. 16 (2012) 271–278.
[9] A. Kurganov, Monolithic column in gas chromatography: a review, Anal. Chim. Acta 775 (2013) 25–40.
[10] L. Liu, M. Zuo, J. Cheng, G. Matsadiq, H. Zhou, J. Li, Coupling polymer monolith microextraction to gas chromatography: determination of pyrethroids in water samples, Microchim. Acta 173 (2011) 127–133.
[11] K. Cabrera, D. Lubda, H.M. Eggenweiler, H. Minakuchi, K. Nakanishi, A new monolithic-type HPLC column for fast separations, HRC J. High Resolut. Chromatogr. 23 (2000) 93–99.
[12] H. Zhang, J. Ou, Y. Wei, H. Wang, Z. Liu, L. Chen, H. Zou, A novel polymeric monolith prepared with multi-acrylate crosslinker for retention independent efficient separation of small molecules in capillary liquid chromatography, Anal. Chim. Acta 883 (2015) 90–98.
[13] P. Jandera, Advances in the development of organic polymer monolithic columns and their applications in food analysis—a review, J. Chromatogr. A 1313 (2013) 37–53.
[14] C. Acquah, C.K.S. Moy, M.K. Danquah, C.M. Ongkudon, Development and characteristics of polymer monoliths for advanced LC bioscreening applications: a review, J. Chromatogr. B 1015–1016 (2016) 121–134.
[15] Y. Wu, H. Liu, S. Lin, M. Fuh, Quantification of 7-aminoflunitrazepam in human urine by polymeric monolith-based capillary liquid chromatography coupled to tandem mass spectrometry, Talanta 176 (2018) 293–298.
[16] J. Krenkova, F. Foret, F. Svec, Less common applications of monoliths: V. Monolithic scaffolds modified with nanostructures for chromatographic separations and tissue engineering, J. Sep. Sci. 35 (2012) 1266–1283.
[17] Y. Chen, Y. Shu, Z. Yang, X. Lv, W. Tan, Y. Chen, M. Ma, B. Chen, The preparation of a poly (pentaerythritol tetraglycidyl ether-co-poly ethylene imine) organic monolithic capillary column and its application in hydrophilic interaction chromatography for polar molecules, Anal. Chim. Acta 988 (2017) 104–113.
[18] K. Yusuf, A. Aqel, Z.A.L. Othman, A.Y. Badjah-Hadj-Ahmed, Preparation and characterization of alkyl methacrylate-based monolithic columns for capillary gas chromatography applications, J. Chromatogr. A 1301 (2013) 200–208.
[19] S. Lin, Y. Wu, T. Lin, M. Fuh, Preparation and evaluation of poly(alkyl methacrylate-co-methacrylic acid-co-ethylene dimethacrylate) monolithic columns for separating polar small molecules by capillary liquid chromatography, Anal. Chim. Acta 871 (2015) 57–65.
[20] J.C. Masini, F. Svec, Porous monoliths for on-line sample preparation: a review, Anal. Chim. Acta 964 (2017) 24–44.
[21] T. Zhu, K.H. Row, Preparation and applications of hybrid organic-inorganic monoliths: a review, J. Sep. Sci. 35 (2012) 1294–1302.
[22] M. Laher, T.J. Causon, W. Buchberger, S. Hild, I. Nischang, Assessing the nanoscale structure and mechanical properties of polymer monoliths used for chromatography, Anal. Chem. 85 (2013) 5645–5649.
[23] F. Svec, M.J. Fréchet, Molded rods of macroporous polymer for preparative separations of biological products, Biotechnol. Bioeng. 48 (1995) 476–480.
[24] Q. Wang, K. Peng, W. Chen, Z. Caoa, P. Zhu, Y. Zhao, Y. Wang, H. Zhoua, Z. Jianga, Development of double chain phosphatidylcholine functionalizedpolymeric monoliths for immobilized artificial membrane chromatography, J. Chromatogr. A 1479 (2017) 97–106.
[25] A. Aqel, Z.A.A.L. Othman, K. Yusuf, A.Y. Badjah-Hadj-Ahmed, A.A. Alwarthan, Preparation and evaluation of benzyl methacrylate monoliths for capillary chromatography, J. Chromatogr. Sci. 52 (2014) 201–210.
[26] Z.A.A.L. Othman, A. Aqel, H.A. Al Abdelmoneim, A.Y. Badjah-Hadj-Ahmed, A.A. Al-Warthan, Preparation and evaluation of long chain alkyl methacrylate monoliths for capillary chromatography, Chromatographia 74 (2011) 1–8.
[27] A. Maniquet, N. Bruyer, G. Raffin, F. Baco-Antionali, C. Demesmay, V. Dugas, J. Randon, Behavior of macroporous vinyl silica and silica monolithic columns inhigh pressure gas chromatography, J. Chromatogr. A 1504 (2017) 105–111.
[28] A. Khaparde, M.A. Vijayalakshmi, K.K.R. Tetala, Development of a metal/chelatepolyhydroxyethyl methacrylate monolith capillary for selective depletion of immunoglobulin G from human plasma for proteomics, J. Chromatogr. A 1517 (2017) 117–125.
[29] Z. Liu, J. Ou, H. Zou, Click polymerization for preparation of monolithic columns for liquid chromatography, Trends Anal. Chem. 82 (2016) 89–99.
[30] I. Nischang, Porous polymer monoliths: morphology, porous properties, polymer nanoscale gel structure and their impact on chromatographic performance, J. Chromatogr. A 1287 (2013) 39–58.

[31] E.J. Carrasco-Correa, A. Martínez-Vilata, J.M. Herrero-Martínez, J.B. Parra, F. Maya, V. Cerdà, C.P. Cabello, G.T. Palomino, F. Svec, Incorporation of zeolitic imidazolate framework (ZIF-8)-derived nanoporous carbons in methacrylate polymeric monoliths for capillary electrochromatography, Talanta 164 (2017) 348–354.
[32] T. Hong, X. Yang, Y. Xu, Y. Ji, Recent advances in the preparation and application of monolithic capillary columns in separation science: a review, Anal. Chim. Acta 931 (2016) 1–24.
[33] R.P. Crowley, Chromatographic columns, US Patent 3,422,605 (1969).
[34] K. Yusuf, A.Y. Badjah-Hadj-Ahmed, A. Aqel, T. Aouak, Z.A.A.L. Othman, Zeolitic imidazolate framework-methacrylate composite monolith characterization by inverse gas chromatography, J. Chromatogr. A 1443 (2016) 233–240.
[35] E.J. Carrasco-Correa, G. Ramis-Ramos, J.M. Herrero-Martínez, Evaluation of 2,3-epoxypropyl groups and functionalization yield inglycidyl methacrylate monoliths using gas chromatography, J. Chromatogr. A 1379 (2015) 100–105.
[36] J. Ji, C. Deng, W. Shen, X. Zhang, Field analysis of benzene, toluene, ethylbenzene and xylene in water by portable gas chromatography-microflame ionization detector combined with headspace solid-phase microextraction, Talanta 69 (2006) 894–899.
[37] A. Al-Rifai, A. Aqel, L. Al Wahibi, Z.A.A.L. Othman, A.Y. Badjah-Hadj-Ahmed, Carbon nanotube-based benzyl polymethacrylate composite monolith as a solid phase extraction adsorbent and a stationary phase material for simultaneous extraction and analysis of polycyclic aromatic hydrocarbon in water, J. Chromatogr. A 1535 (2018) 17–26.
[38] S.D. Chambers, F. Svec, J.M.J. Fréchet, Incorporation of carbon nanotubes in porous polymer monolithic capillary columns to enhance the chromatographic separation of small molecules, J. Chromatogr. A 1218 (2011) 2546–2552.
[39] A. Aqel, K. Yusuf, Z.A. Al-Othman, A.Y. Badjah-Hadj-Ahmed, A.A. Alwarthan, Effect of multi-walled carbon nanotubes incorporation into benzyl methacrylate monolithic columns in capillary liquid chromatography, Analyst 137 (2012) 4309–4317.