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Polyhedral oligomeric silsesquioxanes as functional monomer to prepare hybrid monolithic columns for capillary electrochromatography and capillary liquid chromatography

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HIGHLIGHTS

- A POSS reagent was selected as monomer to prepare hybrid monolithic column.
- Two resulting hybrid monoliths were successfully applied for CEC and cLC.
- The hybrid poly(POSS-*co*-BPADMA) monolith exhibits better selectivity for PAHs.

GRAPHICAL ABSTRACT

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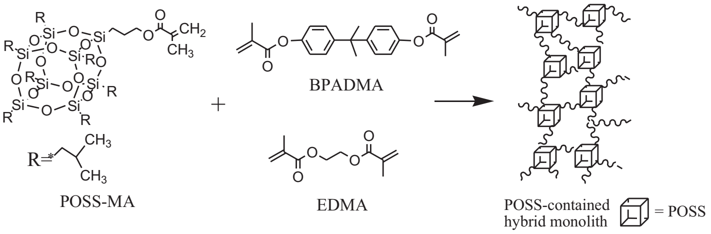

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ABSTRACT

A simple approach to fabricate hybrid monolithic column within the confines of fused-silica capillaries (75 μm i.d.) was introduced. A polyhedral oligomeric silsesquioxanes (POSS) reagent containing a methacrylate group was selected as functional monomer, and copolymerized with bisphenol A dimethacrylate (BPADMA) or ethylene dimethacrylate (EDMA) in the presence of porogenic solvents via thermally initiated free radical polymerization. After optimization of the preparation conditions, two POSS-containing hybrid monoliths were successfully prepared and exhibited good permeability and stability. By comparison of the separation efficiencies of the resulting poly(POSS-*co*-BPADMA) and poly(POSS-*co*-EDMA) monoliths in capillary electrochromatography (CEC) and capillary liquid chromatography (cLC), it was indicated the former has better column efficiencies for alkylbenzenes, phenols, anilines and PAHs in CEC and cLC than the latter. Particularly, the hybrid poly(POSS-*co*-BPADMA) monolith is more suitable for separation of PAHs due to π–π interaction between the analytes and aromatic rings in the surface of monolithic stationary phase.

1. Introduction

Nanomaterials have attracted extensive attention in the past decade due to the unique physical and chemical properties associated with their size and shape, and been widely applied in the fields of chemistry, physics, medicine and biology [1]. Taken advantage of their property of large surface area, to date, the nanostructured materials, such as carbon nanotubes, silica, magnetic and non-magnetic metal oxides, silver and gold nanoparticles, have been adopted in chromatographic and electrophoretic techniques, in which nanoparticles serve as additives, or permanent/dynamic capillary inner surface coatings in capillary electrophoresis (CE) [2–5], as stationary phases in capillary electrochromatography (CEC) [6–12] and gas chromatography (GC) [13,14], as well as liquid chromatography (LC) [15].

Monolithic materials, in situ formed within the confines of column tubings, capillaries or microchannels in microchips, have

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been widely applied for the separation of small molecules and large biomolecules because of easy preparation, versatile surface modification and chemistry. These excellent advantages have made the monolithic columns an attractive alternative to the packed and open-tubular columns in the field of microscale separation, including CEC and capillary liquid chromatography (cLC) [16–20]. The process of monolithic materials affords a variety of surface chemistries for the requirement of small and large molecules in several separation modes. Nanoparticles were recently explored to functionalize the monoliths with specific selectivity. The approaches are divided into two categories: (i) direct encapsulation of nanoparticles into the monolith in the process of polymerization[21–23] and (ii) modification of surface with nanoparticles after monolith formation[24–30]. The latter approach results in a remarkable increase in the effective surface area of monolith, which was successfully applied for CEC and cLC separation, and solid-phase extraction as well.

Polyhedral oligomeric silsesquioxanes (POSS) developed in the end of last century, with sizes of from 1 to 3 nm in diameter, can be thought of as the smallest possible particles of silica [31]. It was revealed that the incorporation of POSS derivatives into polymeric materials can lead to dramatic improvement in polymer properties including thermal stability, oxidation resistance, surface hardening, and improved mechanical properties, as well as reduction in flammability [32]. To date, POSS nanostructures have shown significant promise for use in catalyst supports and biomedical applications as scaffolds for drug delivery, imaging reagents, and combinatorial drug development etc. [33–35]. Recently, a POSS monomer of POSS-methacryl substituted was selected as the crosslinker to prepare an inorganic-organic hybrid monolithic column, which exhibits good mechanical and pH stabilities, probably due to the incorporation of the nanosized silica core of POSS into the monolith [36]. It offers a simple way to develop other POSS-containing hybrid monoliths by copolymerization with organic monomers for various application purposes [37]. Herein, PSS-(1-propylmethacrylate)-heptaisobutyl substituted (POSS-MA) (as shown in Fig. 1) was selected as functional monomer to fabricate hybrid monoliths, while both bisphenol A dimethacrylate (BPADMA) and ethylene dimethacrylate (EDMA) were selected as crosslinkers, respectively. Their property and efficiency were evaluated and compared in CEC and cLC.

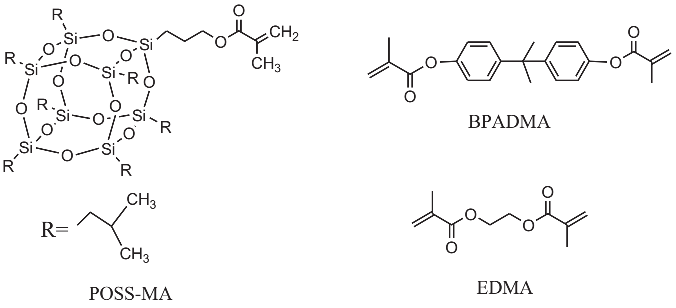

Fig. 1. Molecular structures of monomers: PSS-(1-propylmethacrylate)-heptaisobutyl substituted (POSS-MA), bisphenol A dimethacrylate (BPADMA) and ethylene, dimethacrylate (EDMA).

2. Experimental

2.1. Chemicals and materials

POSS-MA was purchased from Acros (NJ, USA). 1,4-Butanediol, 1-propanol, thiourea, benzene, toluene, ethylbenzene, propylbenzene and butylbenzene were from

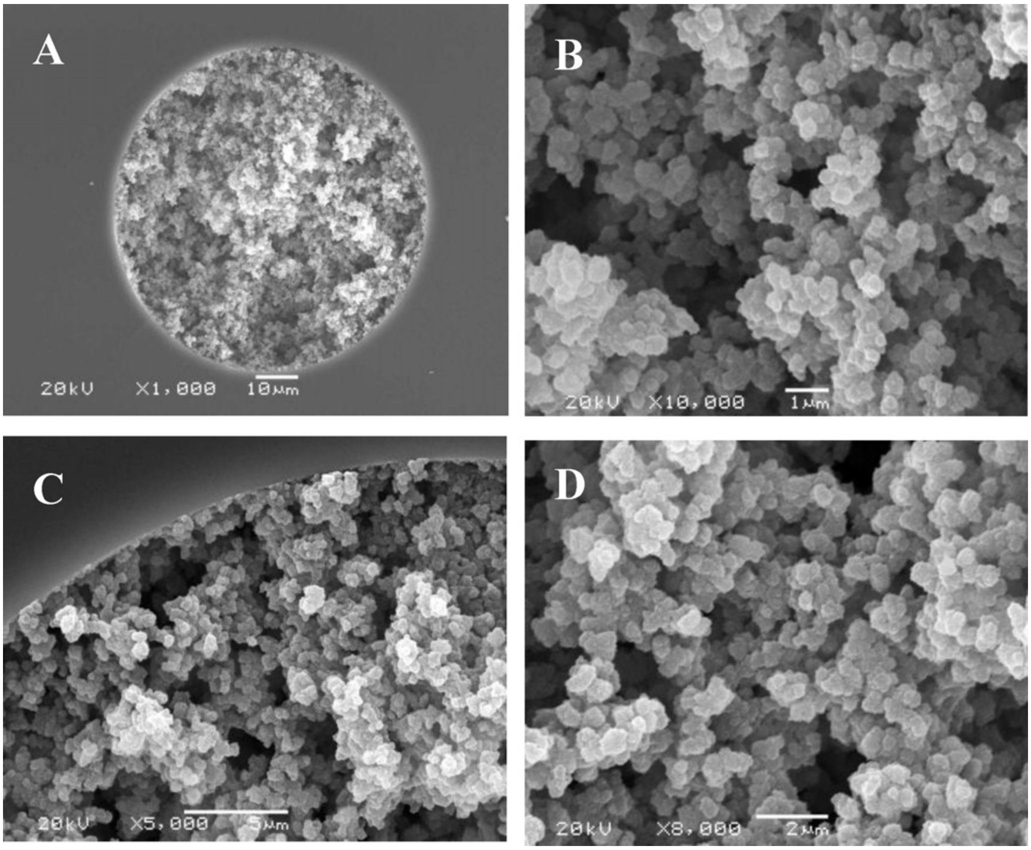

Fig. 2. SEM photographs of the poly(POSS-*co*-EDMA) (A and B) and poly(POSS-*co*-BPADMA) (C and D) monoliths.

Table 1
Composition of polymerization mixture for preparation of POSS containing hybrid monolithic columns.

Column[a]	EDMA (mg)	BPADMA (mg)	Propanol (μL)	Decanol (μL)	Toluene (μL)	Morphology[b]	Permeability ($\times 10^{-14}$ m^2)
A	30	–	150	–	40	Brown	–
B	30	–	180	–	–	Homogeneous	1.45
C	30	–	160	20	–	Homogeneous	3.15
D	30	–	150	30	–	Homogeneous	3.42
E	30	–	140	40	–	Homogeneous	1.69
F[c]	–	30	60	120	–	–	–
G	–	30	–	130	50	Detached	–
H	–	30	–	80	100	Transparent	–
I	–	30	120	–	60	Homogeneous	7.62
J	–	30	115	–	65	Homogeneous	5.05
K	–	30	110	–	70	Homogeneous	2.22
L	–	30	105	–	75	Homogeneous	0.665

[a] The 30 mg POSS-MA was added to all polymerization mixture for cLC and CEC, while AMPS (1% of total monomers, w w^{-1}) was added to the polymerization mixture to generate electroosmotic flow (EOF) for CEC. Other preparation conditions: polymerization temperature, 55 °C; AIBN, 1 mg.
[b] Which was observed with an optical microscope.
[c] The monomers could not be dissolved to form a homogeneous solution.

Tianjin Kermel Chemical Plant (Tianjin, China). EDMA, BPADMA, γ-methacryloxypropyltrimethoxysilane (γ-MAPS), 1-decanol, phloroglucinol, 4-cresol, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), 2,4-dichlorophenol and other standard reagents were all purchased from Sigma (St Louis, MO, USA). Azobisisobutyronitrile (AIBN) was obtained from Shanghai Chemical Plant (Shanghai, China) and recrystallized in ethanol prior to use. HPLC-grade acetonitrile (ACN) from Merck (Darmstadt, Germany) was used for preparation of mobile phases. Water used in all experiments was doubly distilled and purified by a Milli-Q system (Millipore, MA, USA). Other chemical reagents were of analytical grade. The fused-silica capillary with 75 μm i.d. and 365 μm o.d. was purchased from Reafine (Hebei, China).

2.2. *Preparation of hybrid monolith in a capillary*

The capillary was first rinsed with a 0.1 mol L^{-1} NaOH for 30 min, washed with water, followed by 0.1 mol L^{-1} HCl for 30 min, and finally, rinsed with water until the pH value of the outlet solution reached 7.0. The internal surface of the capillaries was then treated with γ-MAPS according to the procedures described elsewhere [38]. The pretreated capillary was filled with a solution of γ-MAPS, acetic acid and water (2/3/5, v/v/v) using a syringe, and kept at room temperature overnight with both ends sealed with rubber septa. Finally, the capillary was rinsed with ACN/water (4/1, v/v) to flush out the residual reagents and dried with a stream of nitrogen gas.

The polymerization solution consisting of functional monomer (POSS-MA), crosslinker (EDMA or BPADMA), initiator (AIBN) and porogens was mixed in an ultrasonic bath to form a homogeneous solution. Then, the mixture was purged with nitrogen for 10 min and introduced in the pretreated capillary (total length 40 cm) to a length of 28 cm, that is, the 12-cm long capillary was blank. With both ends sealed with silicon rubber, the capillary was immersed in a water bath at 55 °C for 16 h. The capillary column was then flushed with methanol using an HPLC pump to remove the residual reagents. Finally, a detection window was created by burning out a 2–3-mm segment in the blank section of capillary, which was located as close to the hybrid monolithic matrices as possible. The monolithic column was then cut to an effective length of 24.5 cm with a total length of 33 cm prior to use.

2.3. *Instrumentation and Methods*

The flow-through property of the resulting monoliths was characterized by measuring flow-induced back pressure with an Eksigent NanoLC pump (Livermore, CA, USA). The mobile phase was ACN. Each column was flushed for at least 30 min before measuring back pressure, and measurements were taken twice at each flow rates between 50 and 600 nL min^{-1}. The superficial permeability values [19] for these monoliths were calculated using Darcy's equation, $K = (F\eta L)/(\pi r^2 \Delta P)$, where K is the permeability, F the flow rate of mobile phase, η the viscosity of the mobile phase, L the column length, r the inner radius of the capillary and ΔP the pressure drop across the column.

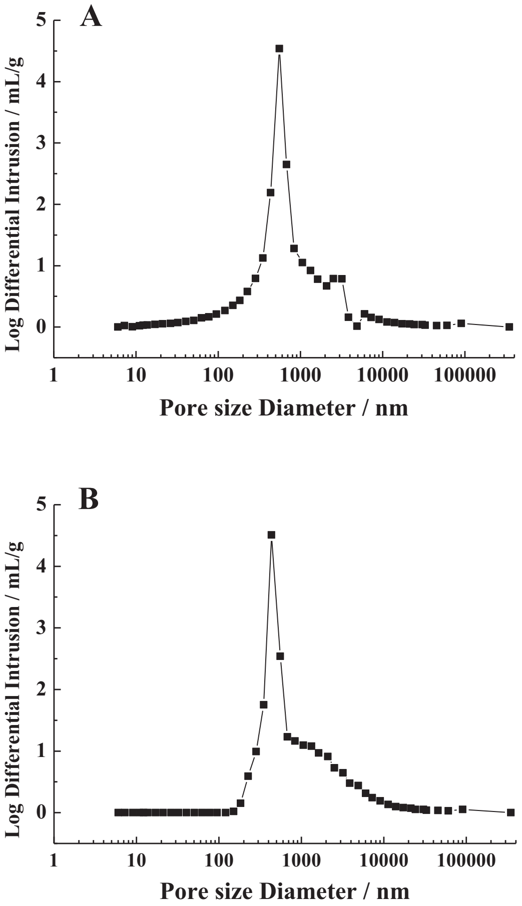

Fig. 3. Pore size distribution of the (A) poly(POSS-*co*-EDMA) monolith and (B) poly(POSS-*co*-BPADMA) monolith.

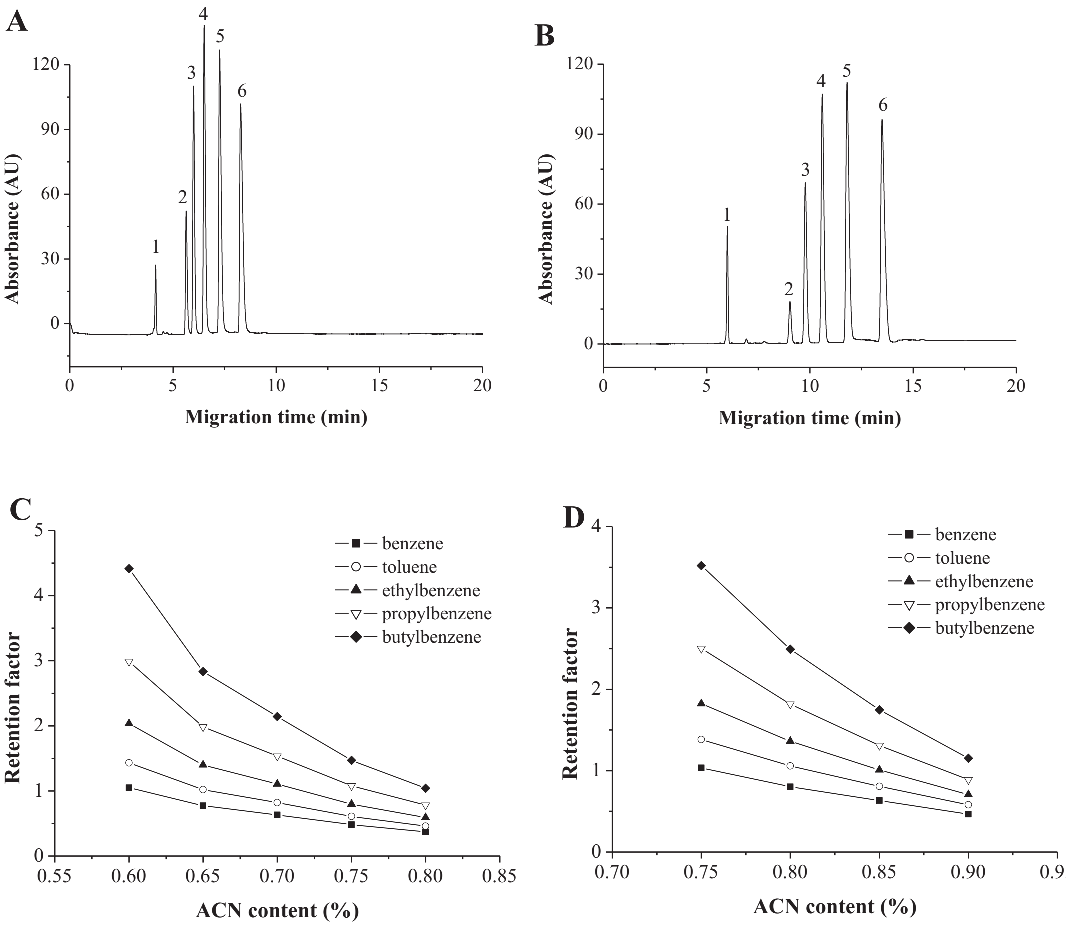

Fig. 4. Electrochromatograms for separation of alkylbenzenes on (A) poly(POSS-*co*-EDMA) and (B) poly(POSS-*co*-BPADMA) monoliths, and effects of ACN content in mobile phase on the retention factor of alkylbenzenes on (C) poly(POSS-*co*-EDMA) and (D) poly(POSS-*co*-BPADMA) monoliths. The analytes are thiourea (1), benzene (2), toluene (3), ethylbenzene (4), propylbenzene (5) and butylbenzene (6) with different concentrations. The mobile phases were 80% for (A) and 90% for (B) ACN/acetate buffer solution (10 mM, pH 7.0), respectively, while the mobile phase were acetate buffer solution (10 mM, pH 7.0) with various content of ACN for (C) and (D). The separation conditions were: electrokinetic injection, 4 kV for 3 s; separation voltage, (A), (B) 20 kV and (C), (D) 10 kV; detection, 214 nm. The effective separation column was 24.5 cm long while the total length was 33 cm.

Electrochromatographic experiments were performed on an Agilent CE system (Hewlett-Packard, Waldbronn, Germany) equipped with a UV detector. Data were acquired and processed with ChemStation software. The mobile phases composed of ACN with varying concentration of acetate buffer were filtered prior to use. All standard sample mixtures were dissolved in ACN with a concentration of 1.0–10.0 mg mL^{-1}. Prior to CEC, the column placed in the CE cartridge was preconditioned with running buffer for at least 30 min with an HPLC pump, and then equilibrated in the CE system by applying a voltage of 5 kV until stable current and baseline were achieved. Both electrokinetic injection of sample and separation were performed at room temperature, and the detection was set at wavelength of 214 nm. Thiourea was selected as EOF marker. The CEC retention factor of the neutral analytes tested, k_{CEC}, was calculated as: $k_{\mathrm{CEC}} = (t_r - t_0)/t_0$, where t_r is the migration time of the analyte and t_0 is the migration time of an unretained EOF marker. The EOF velocity was calculated by the equation, $\mu_e = lL/(Vt_0)$, where μ_e is the effective mobility, V is the applied voltage, t_0 is the migration time of the EOF marker, and l and L are the effective and total length of the capillary, respectively.

The cLC experiments were performed on LC system equipped with an Agilent 1100 micropump (Hewlett-Packard, Waldbronn, Germany) and a K-2501 UV detector from Knauer (Berlin, Germany). The detection wavelength was set at 214 nm. All chromatographic data were collected and evaluated using HW-2000 software from Qianpu Software Ltd. (Shanghai, China). The flow rate of pump was set at 40–200 μL min^{-1}. For obtaining a flow rate of nanoliter per minute (nL min^{-1}), a T-union connector was used to serve as a splitter, with one end connected to the monolithic column and another end connected to a blank capillary (50 μm i.d. × 100 cm in length). The actual flow rate in the monolithic column was 80–400 nL min^{-1}, resulting in split ratio about 1/500. A 7725i injector equipped with a 20 μL sample loop was connected between the micropump and T-union to load the samples with split mode. The other end of monolithic column was connected to a 15-cm long blank capillary (75 μm i.d.) by a polymeric tubing, where a detection window was made by removing the out polyimide coating of a fused-silica capillary with a razor blade.

Scanning electronic microscopic (SEM) images were obtained by using a JEOL JSM-5600 scanning microscope (Tokyo, Japan). Monolithic bulk material was prepared in a stainless-steel HPLC column (15 cm × 4 mm i.d.) as well as the preparation in a capillary column. The specific surface area was calculated from nitrogen adsorption/desorption measurements using a Quadrasorb SI surface area analyzer (Quantachrome, Boynton Beach, USA). Pore size distribution was measured on an Autopore IV 9500 (Micromeritics, Norcross, USA).

3. Results and discussion

3.1. Preparation of hybrid POSS-containing monoliths

The approach to prepare organic–silica hybrid monoliths generally makes use of sol-gel chemistry [39]. Meanwhile, an inorganic-organic hybrid monolithic column was simply fabricated by using a POSS reagent containing several methacrylate groups as crosslinker via free radical polymerization [36]. This process was the same as common organic polymer-based monoliths. Similarly, in this study, the POSS-MA containing one methacrylate group was selected as functional monomer to prepare POSS-containing hybrid monoliths by copolymerizing with other crosslinkers, EDMA or BPADMA. Several kinds of porogenic systems including 1-propanol/1,4-butanediol, toluene/dodecanol and cyclohexanol/decanol, which have been used for preparing methacrylate-based polymeric monoliths, were initially attempted to prepare POSS-containing hybrid monoliths. Unfortunately, these porogenic systems were not satisfactory because of the immiscibility of monomers POSS-MA and BPADMA, or poor homogeneity and permeability of the resulting monoliths. Table 1 lists several polymerization mixtures involving two crosslinkers, indicating the effect of porogens composition on the morphology and permeability of monoliths. When the mixture of 1-propanol and toluene was selected as porogens to prepare hybrid poly(POSS-*co*-EDMA) monolith (as for column A in Table 1), a brown monolith was observed with an optical microscope, and no noticeable liquid flow could be achieved even using a high-pressure LC pump. However, a homogeneous monolith was formed in the capillary when using 1-propanol as the sole porogenic solvent, providing a low permeability (as for column B). It was found that adding 1-decanol in porogenic mixture possibly generated macropores in poly(POSS-*co*-EDMA) monolith, and an increase of the proportion of 1-decanol led to an increase of permeability (as for columns C and D). It was worth noting that further increasing 1-decanol in the polymerization mixture would result in low permeability perhaps due to the swelling or collapse of hybrid matrices (as for column E). As a result, the optimal condition for column D was adopted for preparation of poly(POSS-*co*-EDMA) monolith in following experiments.

Similarly, the preparation condition of hybrid poly(POSS-*co*-BPADMA) monolith was optimized by varying composition of porogens. As shown in Table 1, the monomers of POSS-MA and BPADMA could not be dissolved in the 1-propanol/1-decanol mixture to form a homogeneous solution (as for column F), while a detached monolith or a transparent gel-like monolith was produced in the capillaries (as for columns G and H). The porogenic mixture of 1-propanol and toluene was finally found to yield a rigid, homogeneous porous poly(POSS-*co*-BPADMA) monolith. When the proportion of toluene in the mixture was increased from 33.3% to 41.7% (v/v), the permeability decreased significantly from 7.62×10^{-14} to 6.65×10^{-15} m^2 (as for columns I, J, K and L). This indicates that 1-propanol serves as a macroporogen in the preparation of poly(POSS-*co*-BPADMA) monolith, while toluene as a microporogen. As the column J exhibited moderate permeability, it was further evaluated by CEC and cLC in following experiments.

3.2. Characterization of hybrid POSS-containing monoliths

Fig. 2 presents the SEM photographs of the resulting poly(POSS-*co*-EDMA) monolith (column D) and poly(POSS-*co*-BPADMA) monolith (column J). It can be observed that the homogeneous matrices were well linked to the inner wall of capillary (Fig. 2A and C), as well as through-pores (Fig. 2B and D), which allow the fluid to pass the capillary and gave a good permeability. Actually, these POSS-contained monoliths look the same as common polymeric monolith. Pore size measurement also indicated that large pores (>1.0 μm in diameter) existed in poly(POSS-*co*-BPADMA) and poly(POSS-*co*-EDMA) monoliths, as shown in Fig. 3. Their specific surface areas were calculated as 10.6 (column D) and 13.7 (column J) m^2 g^{-1} based on nitrogen adsorption/desorption isotherm. The low specific surface area may be attributed to the absence of micropores and mesopores in the dry state [40,41].

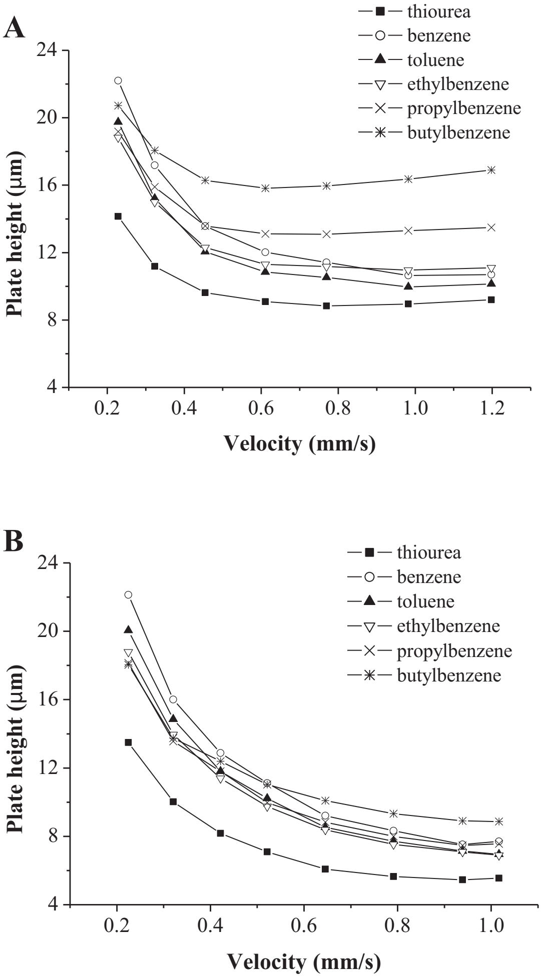

Fig. 5. Dependence of the plate height of analytes on the linear velocity of the mobile phase on (A) poly(POSS-*co*-EDMA) monolith and (B) poly(POSS-*co*-BPADMA) monolith. The mobile phases were (A) 80% ACN/acetate buffer solution (10 mM, pH 7.0) and (B) 90% ACN/acetate buffer solution (10 mM, pH 7.0), respectively. The separation conditions were: electrokinetic injection, 4 kV for 3 s; separation voltage, 5–30 kV. Other conditions as in Fig. 4.

The mechanical stability of two hybrid monoliths was examined by connecting a 20-cm long column to a NanoLC pump and using ACN as the mobile phase. The measured backpressures were all linearly ($R^2 = 0.999$) increased when the flow rate was increased from 50 to 500 nL min^{-1} (data not shown). These results indicated that the prepared hybrid monoliths possessed satisfying mechanical stability. Additionally, the run-to-run repeatability was accessed in terms of both t_0 and the retention factor of benzene when the mobile phase was 70% ACN/acetate buffer solution (10 mM, pH 7.0). It was obtained that the relative standard deviations (RSD) for them were less than 2.6 ($n = 5$), further indicating stable matrices in hybrid monolithic columns. The column-to-column and batch-to-batch preparation repeatability of these hybrid columns were similarly evaluated through the RSD for EOF velocity and

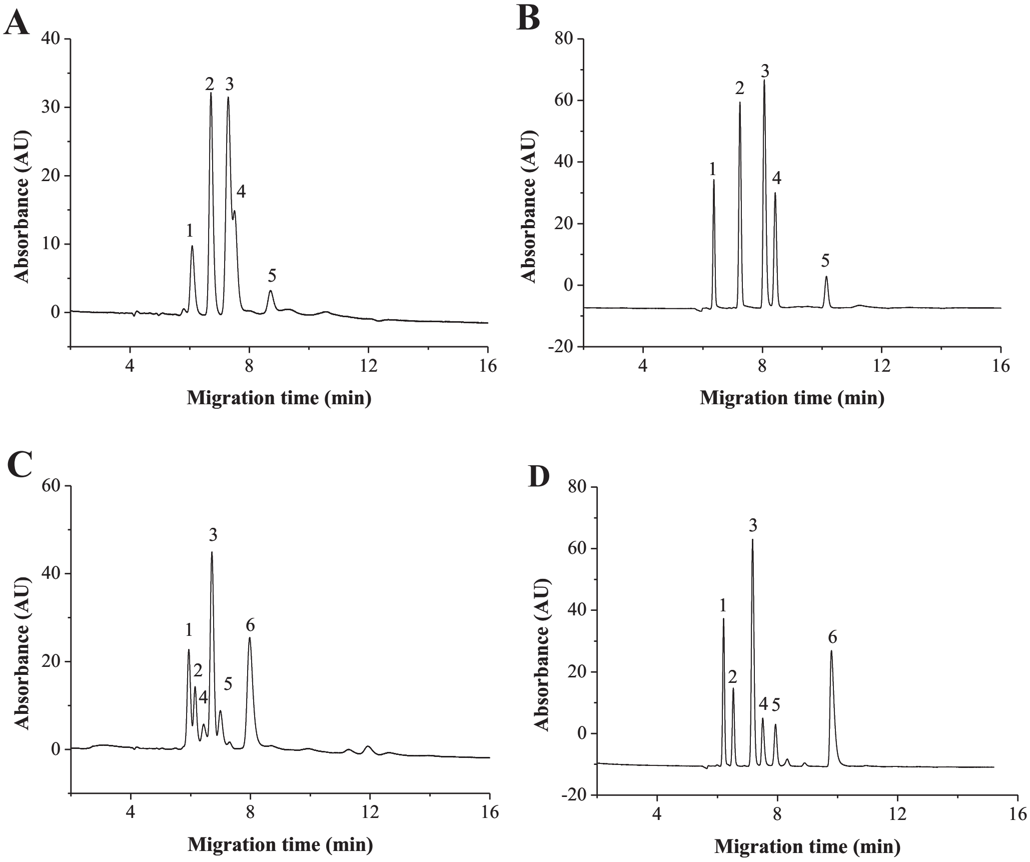

Fig. 6. Electrochromatograms for separation of (A and B) phenolic compounds and (C and D) basic compounds on (A and C) poly(POSS-*co*-EDMA) monolith and (B and D) poly(POSS-*co*-BPADMA) monolith, respectively. The analytes are (A and B) phloroglucinol (1), 4-cresol (2), 2,4-dichlorophenol (3), 4-*tert*-butylphenol (4), 2,4,5-trichlorophenol (5); (C and D) caffeine (1), 2,4-diaminotoluene (2), aniline (3), 4,4′-methylenedianiline (4), 2-nitroaniline (5) and 2,5-dichloro-4-nitroaniline (6). The mobile phases were 80% ACN/acetate buffer solution (10 mM, pH 7.0) for (A and C) and 90% ACN/acetate buffer solution (10 mM, pH 7.0) for (B and D), respectively. The separation voltage was 15 kV. Other conditions as in Fig. 4.

retention factor of benzene for CEC under the same CEC conditions. It was calculated that the repeatability based on column-to-column preparation from the same batch of polymerization solution, and batch-to-batch preparation of monoliths was less than 4.8% ($n = 5$) and 5.9% ($n = 5$) RSD, respectively, for two hybrid monolithic columns. The results indicated that the repeatability of hybrid monoliths was acceptable.

3.3. EOF study

As the monomer AMPS was fixed into two hybrid monoliths for CEC separation, the generation of a cathodic EOF was anticipated. The effect of ACN content in mobile phase on EOF was investigated. It was found that the EOF in poly(POSS-*co*-BPADMA) monolith was slightly increased from 1.54×10^{-8} to 1.58×10^{-8} $m^2 v^{-1} s^{-1}$ with an increase of ACN content from 75 to 90% (v/v) in the mobile phases, while EOF in poly(POSS-*co*-EDMA) monolith was slightly decreased from 1.76×10^{-8} to 1.67×10^{-8} $m^2 v^{-1} s^{-1}$ with an increase of ACN content from 60 to 80% (v/v) in the mobile phases. The phenomena may be related to both the size of the pores formed during the polymerization process and changes in dielectric constant and the magnitude of the zeta potential. The dependence of EOF on both pH and salt concentration in the mobile phases was measured with two hybrid monoliths. EOFs were nearly constant in the range of pH 2–8, as well as salt concentration in mobile phases ranging in 2–10 mM.

3.4. Separation of alkylbenzenes on hybrid monoliths and their efficiencies in CEC

The two POSS-containing hybrid monoliths were used to separate benzene homologues by CEC, and the results are presented in Fig. 4. It can be seen from Fig. 4A that the baseline separation of five alkylbenzenes on poly(POSS-*co*-EDMA) monolith was obtained within 15 min by applying voltage of 20 kV when the mobile phase was 80% (v/v) ACN/acetate buffer. Alkylbenzenes were eluted in the order benzene < toluene < ethylbenzene < propylbenzene < butylbenzene according to their hydrophobicity, illustrating the typical reversed-phase separation mechanism. A lot of isobutyl groups in the functional monomer of POSS reagent should be exposed at the surface of poly(POSS-*co*-EDMA) monolith, contributing hydrophobic retention property. As seen in Fig. 4B, similar result could be acquired on poly(POSS-*co*-BPADMA) monolith when using the mobile phase of 90% (v/v) ACN/acetate buffer. The selectivity factors of two adjacent alkylbenzene compounds were almost same in the range of 1.06–1.14 on the two columns, however, the resolution of benzene and toluene on poly(POSS-*co*-EDMA) monolith was 2.36, which was less than that on poly(POSS-*co*-BPADMA) monolith, 3.34 (Fig. 4A and B). This indicates that the latter has stronger hydrophobicity than the former, perhaps due to π–π interaction with the aromatic groups in monolith skeleton. This phenomenon was also observed in benzyl methacrylate (BMA) based organic monolith, poly(BMA-*co*-BPADMA)[38].

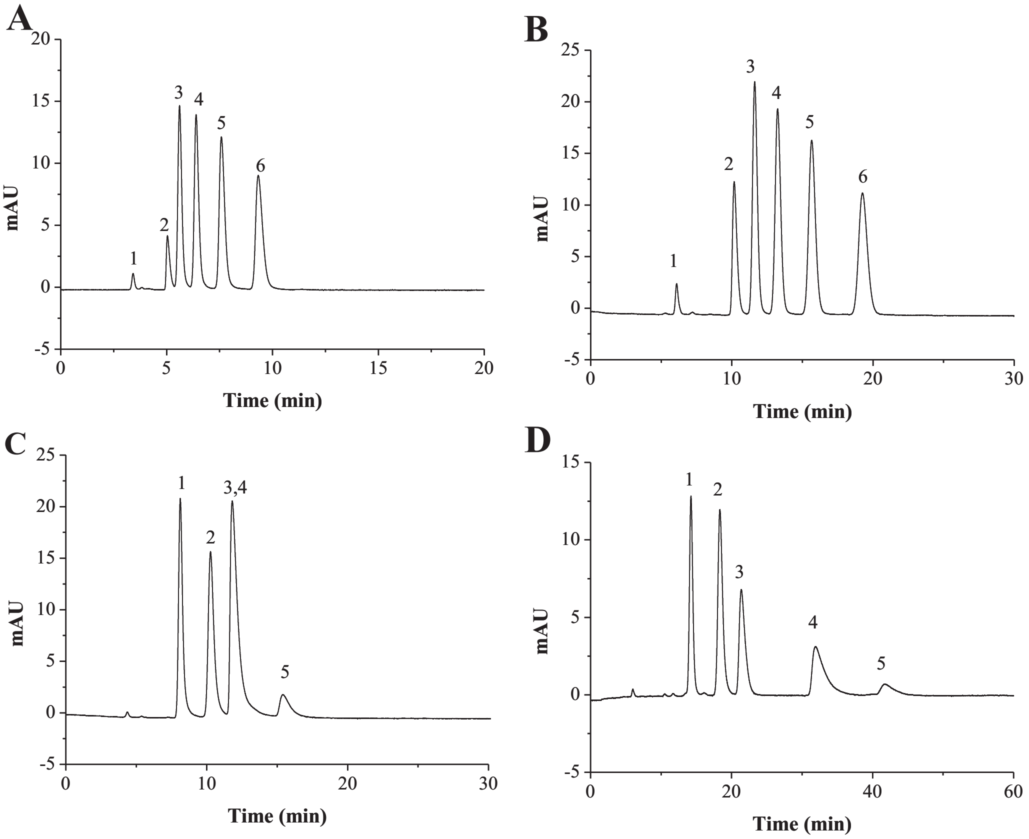

Fig. 7. Separation of (A and B) alkylbenzenes and (C and D) PAH compounds on (A and C) poly(POSS-*co*-EDMA) and (B and D) poly(POSS-*co*-BPADMA) monoliths by cLC, respectively. The analytes are (A and B) thiourea (1), benzene (2), toluene (3), ethylbenzene (4), propylbenzene (5) and butylbenzene (6); (C and D) naphthalene (1), acenaphthene (2), 4,4-dimethylbiphenyl (3), pyrene (4) and p-terphenyl (5). The mobile phases were 70% for (A and C), 80% for (B) and 85% for (D) ACN/water, respectively. Both hybrid monolithic capillary columns were 75 μm i.d. × 20 cm in effective length. Other cLC conditions: flow rate (before split), 60 μL min^{-1} for (A and C) and 50 μL min^{-1} for (B and D); detection wavelength, 214 nm.

Fig. 4C and D shows the effect of ACN content in mobile phases on the retention of 5 alkylbenzenes. It can be found that all retention factor on the poly(POSS-*co*-EDMA) monolith decreased with an increase of ACN content ranging from 60 to 80%, and the retention factor on the poly(POSS-*co*-BPADMA) monolith also decreased with an increase of ACN content ranging from 75 to 90%. Furthermore, the logarithm of these retention factors ($\log k$) linearly decreased with an increase of ACN content, where all linear correlation coefficients (R) were higher than 0.996. These results also confirmed reversed-phase retention mechanism for alkylbenzenes on the two hybrid monoliths.

The column efficiencies of the two hybrid monoliths in CEC were investigated by applying voltage ranging from 5 to 30 kV. Note that the relationship between voltage (5–30 kV) and current yielded good linearity (data not shown), suggesting that Joule heating is negligible. Fig. 5 shows the Van Deemter curves for two hybrid monoliths using unretained thiourea and retained five alkylbenzenes as analytes. The poly(POSS-*co*-EDMA) monolith exhibited the minimum plate height of 8.9 μm for thiourea, and of 10.7–15.8 μm for alkylbenzenes, corresponding to 113,000 and 93,000–63,000 theoretical plates per meter, while poly(POSS-*co*-BPADMA) monolith produced the minimum plate height of 5.5 μm for thiourea, and of 7.6–8.9 μm for alkylbenzenes, corresponding to 183,000 and 132,000–112,000 theoretical plates per meter. Obviously, poly(POSS-*co*-BPADMA) monolith exhibits better efficiency than poly(POSS-*co*-EDMA) monolith, and they both remained at high efficiency with the linear velocity ranging from 0.6 to 1.0 mm s^{-1} in CEC. Furthermore, it is obvious that the efficiencies for alkylbenzenes were remarkably lower than that for thiourea on the two hybrid monoliths. This result is consistent with those on the methacrylate-based monolithic columns in LC and CEC reported by Kok and co-workers [42]. It may be due to the existence of gel porosity, which dominates dispersion and retention dynamics of these two POSS-containing monoliths [40,41].

3.5. Separation of polar analytes on hybrid monoliths in CEC

The prepared hybrid monoliths were also applied for separation of polar weak acidic and basic aromatic compounds. It can be seen from Fig. 6A and B that baseline separation for all phenols on poly(POSS-*co*-BPADMA) monolith was obtained by using mobile phase of 90% ACN/acetate buffer solution (10 mM, pH 7.0) in 12 min, while 2,4-dichlorophenol and 4-*tert*-butylphenol could not be baseline-separated on poly(POSS-*co*-EDMA) monolith even after optimizing CEC conditions. The highest column efficiency was calculated at 206,000 theoretical plates per meter for phloroglucinol on poly(POSS-*co*-BPADMA) monolith. The separation of basic compounds usually suffers from serious tailing owing to the secondary interaction between the stationary phase and basic solutes using silica-based phases, which should be eliminated due to the neutral surface character of the POSS-containing monoliths. Fig. 6C and D presents the separation of six basic anilines on two hybrid monoliths. Satisfactory separation was obtained on poly(POSS-*co*-BPADMA) monolith without adding any competing amines in the mobile phase, and their column efficiencies were in the range of 103,000–191,000 theoretical plates per meter. However, these basic compounds could not be baseline separated on poly(POSS-*co*-EDMA) monolith. These results completely indicate that the poly(POSS-*co*-BPADMA) monolith offers not only excellent column efficiency but also good separation selectivity for aromatic analytes.

3.6. Separation of neutral compounds in cLC

The separation of alkylbenzenes and polyaromatic hydrocarbons (PAHs) on the two hybrid monoliths was also performed in cLC. The results are presented in Fig. 7. As shown in Fig. 7A and B, 5 alkylbenzenes could be baseline separated on poly(POSS-*co*-EDMA) and poly(POSS-*co*-BPADMA) monoliths with the mobile phase of 70% and 80% (v/v) ACN/water, respectively. It is evident that column efficiencies of 5 alkylbenzenes on poly(POSS-*co*-BPADMA) monolith in the range of 23,600–27,200 theoretical plates per meter were higher than those on poly(POSS-*co*-EDMA) monolith in the range of 18,900–22,100 theoretical plates per meter. Similarly, the phenomenon of efficiency depending on retention of analytes was also observed in cLC. Fig. 7C exhibits the chromatogram of separation of PAHs on poly(POSS-*co*-EDMA) monolith with the mobile phase of 70% (v/v) ACN/water. The 4,4-dimethylbiphenyl and pyrene were not separated on poly(POSS-*co*-EDMA) monolith under various of chromatographic conditions. However, the baseline separation of them could be achieved on poly(POSS-*co*-BPADMA) monolith with the mobile phase of 85% (v/v) ACN/water (as shown in Fig. 7D). It is further demonstrated that the poly(POSS-*co*-BPADMA) monolith exhibits better selectivity for PAH compounds due to π–π interaction with the aromatic groups of monolithic matrices. Although their column efficiencies in cLC were remarkably lower than those in CEC, these hybrid columns may be suitable for separation of proteins etc. due to their properties of good permeability and stability.

4. Conclusions

A novel kind of hybrid capillary monolithic column was successfully developed by using a POSS reagent containing one methacrylate group, POSS-MA, as the monomer via thermally initiated free radical polymerization. The preparation process was simple as common organic monoliths. After optimizing the composition of prepolymerization solution, two hybrid monoliths were obtained by copolymerization of POSS-MA and the crosslinkers, EDMA or BPADMA. The resulting hybrid monoliths exhibited good stability and separation efficiency, and could be applied for alkylbenzenes, phenols, anilines and PAHs in CEC or cLC. It offers a simple, facile approach to prepare the POSS-contained hybrid monoliths. Additionally, these hybrid monoliths are expected to be suited for biomolecular separation.

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