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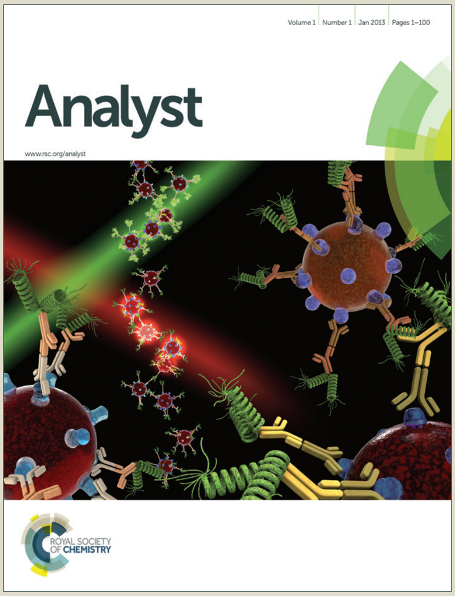

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ARTICLE TYPE

Preparation of polyhedral oligomeric silsesquioxane based hybrid monoliths by thiol-ene click chemistry for capillary liquid chromatography

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A facile organic-silica hybrid monolith was prepared by thiol-ene click reaction of polyhedral oligomeric silsesquioxane methacryl substituted (POSS-MA) with 1,4-bis(mercaptoacetoxy) butane (BMAB) using toluene and dodecanol as a porogenic system. The effects of the ratio of POSS-MA/BMAB and porogenic solvents and click reaction temperature on the morphology, permeability and column performance of the resulting POSS-BMAB hybrid monoliths were studied in detail. A uniform monolithic network with high porosity was obtained. The POSS-BMAB hybrid monolith exhibited good permeability and high thermal and mechanical stability. A series of test compounds including alkylbenzenes, polycyclic aromatic hydrocarbon, phenols, anilines were used to evaluate the retention behaviors of the POSS-BMAB hybrid monolith in capillary liquid chromatography. The prepared POSS-BMAB hybrid monolith exhibited typical reversed-phase chromatographic behavior toward neutral solutes. The minimum plate height of this hybrid monolith was determined as 12.6 and 13.7 μm for thiourea and benzene, respectively. These results demonstrate that thiol-ene click chemistry can provide a facile and robust approach for the preparation of POSS-based hybrid monolith.

1. Introduction

Monolithic columns have been developed as an alternative to classic particles packed columns for chromatographic separations in high performance liquid chromatography (HPLC), capillary liquid chromatography (cLC) and capillary electrochromatography (CEC). [1-3] In comparison with traditional packed columns, monolithic columns possessed a continuous porous structure, high porosity and large through-pore size with small-size skeletons, resulting in good column permeability and high mass transfer efficiency. Based on the nature of the matrix, monolithic columns can be mainly categorized into three types: organic polymer-based, silica-based and organic-silica hybrid monolithic columns.[4] In recent years, the organic-silica hybrid monolithic column have received more and more attention as it exhibit higher mechanical stability, better resistance to organic solvents and wide-pH-range tolerance.[5]

Over the last decade, click chemistry has attracted considerable attention on preparation chromatographic materials due to advantages such as simplicity, compatibility with aqueous media, high reaction yields and specificity.[6] The copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) was the first example of click chemistry, which is currently the most commonly click reaction used. Chu et al.[7] have extensively studied the CuAAc reaction for the preparation of separation materials for HPLC and have reported the benefits of this click reaction. However, CuAAc reaction has some drawbacks such as leaving heavy metal ions in the stationary phase and the explosive nature of azides.[8,9] Thiol-ene click reaction is a novel click chemistry reaction, which is a potential choice for copper-free click chemistry to complement the CuAAC.[10] The thiolether linkage formed serves as a strong and stable covalent bond, which is able to withstand harsh conditions. Thiol-ene click chemistry has been widely employed for the preparation of stationary phases in separation science. The most commonly used approach for elaboration of functionalized columns consists in a traditional two-step process in which a bare silica or polymer support was synthesized and subsequently post-modified via thiol-ene click chemistry.[11-22] However, the process of post-modification is always time-consuming and boring, although diverse functional groups can be introduced onto surface of stationary phase through this strategy. The more straightforward approach is the so-called "one-pot" sol-gel process, where tetramethoxysilane and 3-mercaptopropyltrimethoxysilane were adopted as co-precursors and vinyl-containing organic monomers were used as functional moieties.[23-26] Recently, Zou's group successively developed photoinduced thiol-ene polymerization reaction for fast preparing macroporous hybrid monoliths and and application in cLC.[27]

Cubic polyhedral oligomeric silsesquioxanes (POSS) with the unique cage-like structures and nanoscale dimensions has been used as a new cross-linker and has emerged for the preparation of hybrid-silica monolith.[28] POSS-based silica hybrid monolith has become one of the hottest topics in the region of hybrid organic-silica monolith due to unique properties including facile polymerization, good rigidity, and abundant functional moieties for the flexible modification.[29,30] With a simple in situ polymerization, many functionalized POSS-based silica hybrid monoliths have been fabricated conveniently with good robustness, high column efficiency and absence of residual silanol groups, and used for cLC or CEC.[31-34] Polyhedral oligomeric silsesquioxane methacryl substituted (POSS-MA) is one kind of derivative of POSS with multiple vinyl groups, which can be used for thiol-ene click chemistry. However, to the best of our knowledge, no studies on thiol-ene click chemistry for preparation of POSS-based monolithic column have been reported so far.

Herein, we developed a novel POSS-based hybrid monolith for cLC by thiol-ene click reaction of POSS-MA with BMAB. The synthetic procedure was simple and efficient without any special handling. The influences of the ratio of POSS-MA/BMAB and porogenic solvents and click reaction temperature on the morphology, permeability and column performances of the hybrid monoliths were investigated in detail. The obtained POSS-BMAB monolithic capillary columns exhibited good mechanical strength, solvent and thermal stability. The chromatographic performance of POSS-BMAB hybrid monolith for the separation of alkylbenzenes (ABs), polycyclic aromatic hydrocarbon (PAHs), phenols and anilines were evaluated in detail.

2. Experimental

2.1 Reagents and materials

Polyhedral oligomeric silsesquioxane methacryl substituted (cage mixture, n = 8, 10, 12, POSS-MA) was purchased from Sigma (St. Louis, MO, USA). γ-Methacrylyloxypropyltrimethoxysilane (γ-MAPS) and dodecanol were purchased from Alfa Aesar (Ward Hill, MA, USA). 1,4-Bis(mercaptoacetoxy) butane (BMAB) and alkylbenzenes (ABs) were purchased from TCI (Shanghai, China). Azobisisobutyronitrile (AIBN) was obtained from Tianjin Chemistry Reagent Factory (Tianjin, China) and recrystallized in ethanol prior to use. Thiourea, polycyclic aromatic hydrocarbons (PAHs), phenols, anilines and HPLC-grade methanol (MeOH) and acetonitrile (ACN) were obtained from Shanghai Chemical Reagents Corporation (Shanghai, China). All other reagents were of analytical grade. Ultrapure water used for the preparation of solutions was produced by a Milli-Q water system (Millipore, Bedford, MA, USA). Fused-silica capillary of 75 μm i.d. and 375 μm o.d. was obtained from Hebei Yongnian Optical Fiber Factory (Hebei, China).

2.2. Instrumentation

All chromatographic experiments were performed on a TriSep-2100 pressurized CEC system (this instrument can also be utilized as cLC system, Unimicro Technologies, Pleasanton, CA, USA). The Fourier transform infrared (FT-IR) spectra (4000-400 cm^{-1}) in KBr were recorded using a PE Spectrum One FT-IR spectrometer (PE, USA). Scanning electron microscope (SEM) was carried out on a FEI Quanta 200 FEG SEM (Philips, The Netherlands). Thermo gravimetric analysis (TGA) was performed on a Pyris Daimond TG (PE, USA). Micromeritics ASAP 2020M (Micromeritics, USA) were used to determine the Brunauer-Emmett-Teller (BET) surface areas of POSS-BMAB hybrid monoliths.

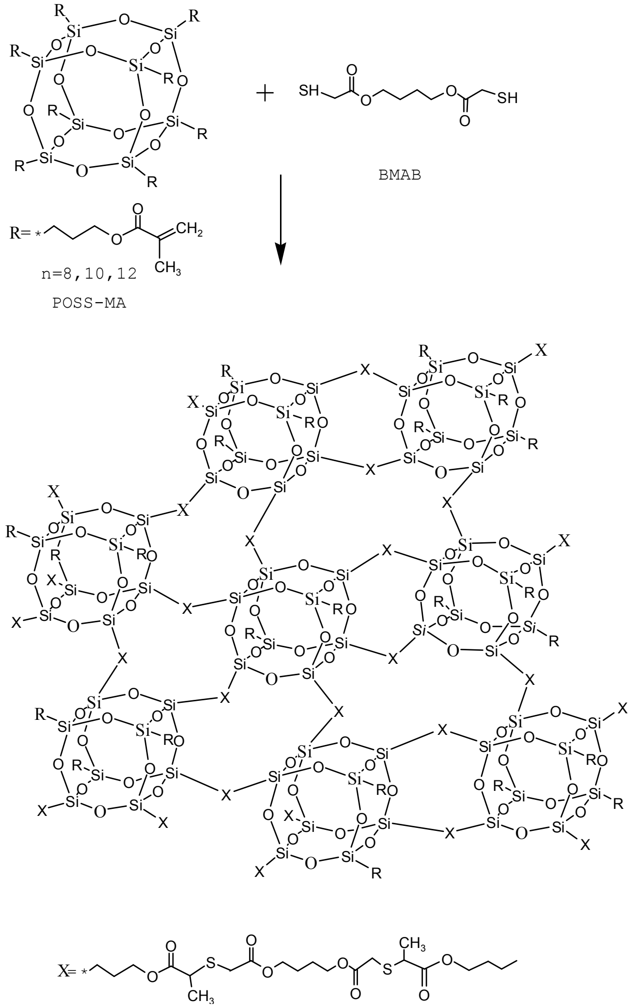

Fig.1 Preparation of the hybrid monoliths via thiol-ene click reaction of POSS-MA with BMAB

2.3. Preparation of POSS-BMAB hybrid monolith

Prior to surface modification by thiol-ene click chemistry, a 50% γ-MAPS methanol (v/v) solution was used to introduce the vinyl groups onto the inner surface of capillary according to a previously described procedure [35].

The POSS-based hybrid monolith was prepared by using an in situ radical polymerization method. POSS-MA, BMAB, dodecanol, toluene and AIBN with different composition as listed in Table 1 were mixed under ultrasonication to form a homogeneous solution. Whereafter, the mixture was manually injected into the pretreated capillary to an appropriate length with a syringe. With the both ends sealed with rubber stoppers, the capillary was submerged into a thermostatic bath (50-60℃) for 12 h. Finally, the obtained monolithic capillary columns were flushed with MeOH to remove the residual monomers and porogens.

2.4 Calculations

The permeability (K) is calculated by the following formula: [36]

$$K = \frac{F \times \eta \times L}{\Delta P \times \pi \times r^2}$$

Table1. Composition of polymerization mixture for the preparation of POSS-BMAB hybrid monoliths

Column	POSS-MA/BMAB (mol/mol)	Toluene (mg)	Dodecanol (mg)	T (℃)	Back pressure (MPa)	Permeability ($\times10^{-14}$ m^2)	*k* (benzene)	BET suface area (m^2/g)
A	1 : 1.0	110	200	55	>25(too hard to pump)	---	---	---
B	1 : 1.5	110	200	55	16.1	0.47	0.39	268.5
C	1 : 2.0	110	200	55	12.2	0.63	0.28	221.3
D	1 : 2.5	110	200	55	1.3	6.16	0.17	130.5
E	1 : 3.0	110	200	55	0.3	30.80	0.35	42.0
F	1 : 1.5	110	200	50	0.8	9.33	0.38	---
G	1 : 1.5	110	200	60	1.0	7.59	0.21	---
H	1 : 1.5	70	240	55	<0.2(slack, detached)	---	---	---
I	1 : 1.5	90	220	55	0.4	22.73	0.36	---
J	1 : 1.5	130	180	55	>25(too hard to pump)	---	---	---

[a]Other preparation conditions: POSS-MA, 50mg; AIBN, 2mg.

Where F is the volume flow rate of the eluent, η is the dynamic viscosity of the mobile phase, L is the column length, and ∆P is the pressure drop across the column. In this work, MeOH was used as mobile phase and corresponding value of dynamic viscosity was 0.580×10^{-3} kg/(ms) at 25 ℃.[37]

3. Results and discussion

3.1 Preparation of POSS-BMAB hybrid monolith

The POSS-BMAB hybrid monolith was prepared by a simple single-step thiol-ene click reaction of POSS-MA with BMAB. Since the morphology and permeability of hybrid monoliths were significantly affected by composition of prepolymerization solution and reaction temperature, several parameters such as the ratio of POSS-MA/BMAB and porogenic solvents, and click reaction temperature were systematically optimized as shown in Table 1.

Herein, the prepolymerization solutions with the different molar ratios of POSS-MA/BMAB from 1:1 to 1:3 were examined (column A-E, Table 1). It was observed that the back pressure and BET suface area of the hybrid monoliths gradually decreased with the decrease of the ratio of POSS-MA/BMAB, and the permeability of corresponding monoliths increased from 0.47 $\times10^{-14}$ to 30.80 $\times10^{-14}$ m^2. The SEM images of column B-E were also detected and displayed in Fig. 2. It could be seen that these hybrid monoliths have the morphology of a continuous skeleton and macro through-pores and good attachment to the inner wall of the capillary. It is interesting that the different ratio of POSS-MA/BMAB in the prepolymerization solution obviously affects the morphological structures of hybrid monoliths. For example, continuous reticular skeleton was observed in column B and C, while the nanoglobular aggregated morphology was obtained in column D and E. This finding is similar to the results reported previously by Zou's group.[27] The significant difference in morphology may be attributed to the phase separation process. The increase of BMAB crosslinker content may result in high local degree of polymerization and form crosslinked nanoglobular polymers separating from solvents.[38] Fig. 3 shows the separation of ABs on POSS-BMAB hybrid monoliths with

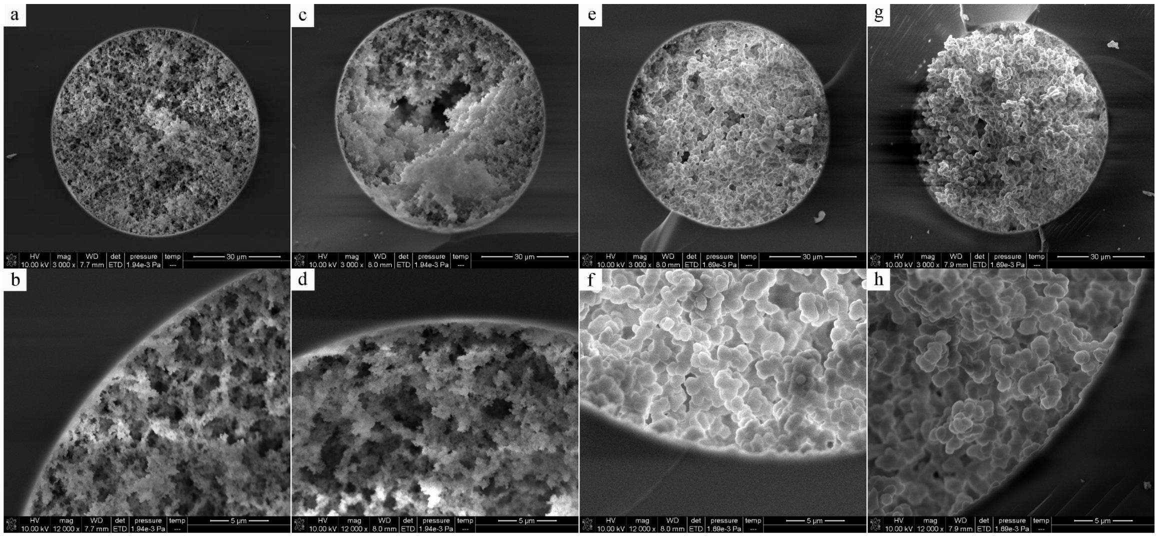

Fig.2 SEM images of hybrid monoliths of Column B (a, b), Column C (c, d), Column D (e, f) and Column E (g, h)

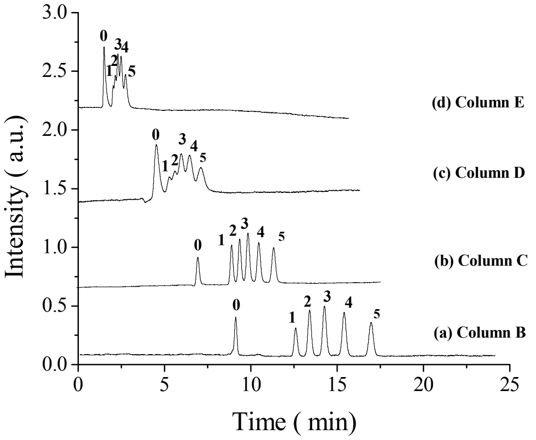

Fig. 3 Effect of the ratio of POSS-MA/BMAB on separation of ABs on POSS-BMAB hybrid monoliths. Conditions: mobile phase, ACN/H_2O (75/25, v/v); flow rate, 0.05 mL/min; detection wavelength, 214 nm; POSS–BMAB monoliths: 52 cm ×75 μm i.d. (30 cm effective length); supplement pressure, 1000 psi (a and b), 75psi (c and d). Solutes 0, thiourea; 1, benzene; 2, toluene; 3, ethylbenzene; 4, propylbenzene; 5, butylbenzene.

different molar ratio of POSS-MA/BMAB. It was observed that increasing the molar ratio of POSS-MA/BMAB in polymerization mixture improved retention and separation efficiency. Considering peak efficiency and retention of analytes, the molar ratio of POSS-MA/BMAB with 1:1.5 (column B in Table 1) was chosen for the further experiments.

Similar to the other radical polymerization synthesis of polymer monoliths, the thiol-ene click reaction temperature is an important factor in formation of hybrid monoliths. In this experiment, the effect of thiol-ene click reaction temperature on the permeability, back pressure and retention value of benzene were showed in Table 1. High permeability but low column efficiency and resolution were obtained as the click reaction temperature was set at 50 and 60 ℃ (Fig. 4a and c). In contrast, good chromatographic performance was observed on column B with a dense reticular monolithic network when the reaction temperature of 55 ℃ was applied (Fig. 4 b).

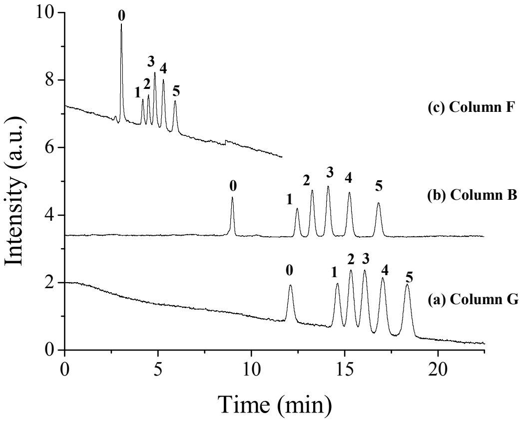

Fig. 4 Effect of thiol-ene click reaction temperature on separation of ABs on POSS-BMAB hybrid monolith. Conditions: supplement pressure, 1000 psi (a, b), 75psi (c). Other conditions are same as in Fig. 3

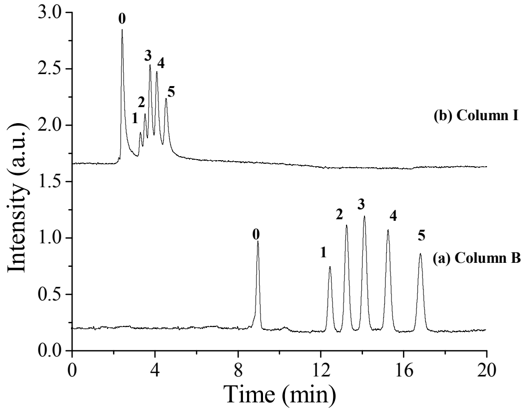

Fig. 5 Effect of the ratio of toluene-dodecanol on separation of ABs on POSS-BMAB monoliths. Conditions: supplement pressure, 1000 psi (a), 100psi (b). Other conditions are same as in Fig. 3

A binary porogenic system of toluene-dodecanol was employed, where toluene and dodecanol acted as a good solvent for POSS-MA and BMAB, respectively. As shown in Table 1, the ratio of toluene/dodecanol was investigated from 70:240 to 130:180 (w/w). The results demonstrated that the ratio of toluene/dodecanol higher than 130:180 resulted in high back pressure more than 25.0 MPa. Contrarily, the hybrid monolith was too slack when using the ratio of toluene/dodecanol lower than 70:240. Fig. 5 showed the effect of the ratio of toluene/dodecanol on the separation of ABs on POSS-BMAB hybrid monoliths. By comparing the separation efficiency for ABs on columns B and I, ABs were co-eluted with column I whereas baseline resolution was observed for column B. Based on above experiment results, column B was considered to be the optimal, and chosen for the further experiments.

3.2 Characterization of POSS-BMAB hybrid monolith

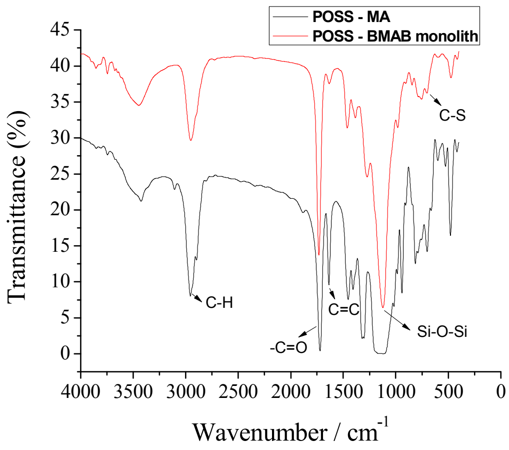

Fig. 6 FT-IR spectra of POSS-MA and POSS-BMAB hybrid monolith (Column B).

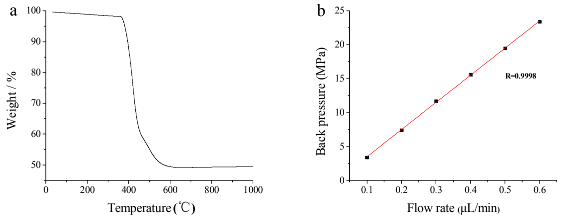

Fig. 7 TGA of POSS-BMAB hybrid monolith at a heating rate of 10℃ /min in air (a) and the relationships between flow rate and the back pressure drop of POSS-BMAB hybrid monolith (b)

FT-IR spectroscopic analysis was used to characterize thiol-ene click reaction. As can be seen from Fig. 6, the signals of characteristic peaks of C=C stretches (1630 cm^{-1}) were almost complete disappear, which associated with the presence of vinyl groups of the POSS-MA monomer. In addition, the appearance of new C–S adsorption (700 cm^{-1}) associated with the covalent linkage between POSS-MA and BMAB. These results confirmed that the thiol-ene click reaction of POSS-MA monomer with BMAB crosslinker.

The thermal stability of POSS-BMAB hybrid monolith was investigated by TGA. As can be seen from Fig. 7a, an endothermic mass loss began from 360 ℃ and continued up to 600 ℃ as a result of the pyrolysis of organic moieties, indicating good thermostability of POSS-BMAB hybrid monolith. Column pressure drops were measured using MeOH to evaluate the mechanical stabilities of the synthesized POSS-BMAB hybrid monolith. As can be seen from Fig. 7b, a good linear dependence of flow rate on column back pressure even at high pressure was observed, indicating these monoliths have good mechanical stability.

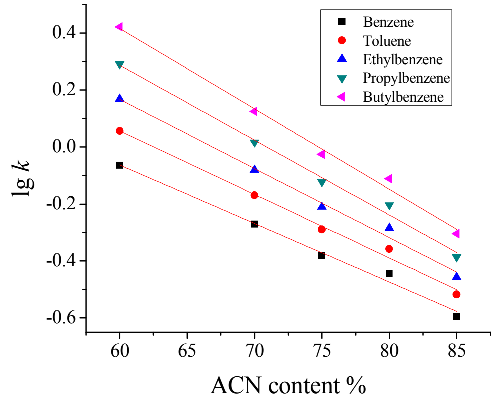

Fig. 9 The effect of ACN content in mobile phase on the retention factor lg *k* of ABs on Clumn B. Conditions are same as in Fig.3

To evaluate POSS-BMAB hybrid monolith column efficiency, the dependence of column efficiency on the linear velocity of the mobile phase was investigated. Fig. 8 showed the Van Deemter plots of thiourea and benzene. The minimum plate heights of 12.6 and 13.7 μm were achieved for thiourea and benzene, which were corresponding to the column efficiencies of 79,400 and 73,000 plates/m, respectively. Compared with the previous report on poly(POSS-co-bisphenol A dimethacrylate) monolith [38] with 23,600–27,200 plates/m for five ABs, the proposed POSS-BMAB hybrid monolith exhibited higher column performance. Also, it can be seen that the column efficiency was satisfactory over a range of linear velocity from 0.3 to 0.9 mm/s. Additionally, the good reproducibility for column B was demonstrated with the intra-day RSDS (≤0.5%, *n*=5) and day-by-day RSDS (≤1.5%, *n* = 5) for the retention factors of ABs. The column-to-column reproducibility was similarly evaluated through the RSD for retention factor of ABs at the same conditions. It was calculated that the reproducibility based on column-to-column preparation from the same batch of polymerization solution, was less than 5.3% (n = 3). No significant decline of column efficiency (<4.5%) and retention factors (< 3.6%) of five ABs were observed during the course of the stability study when comparing cLC runs performed at the start of the study and after performing over 200 injections within two months. These results indicate that the prepared POSS-BMAB hybrid monolith has good stability and reproducibility.

Owing to the hydrophobicity of the POSS-MA, the resulting hybrid monoliths were applicable to chromatographic separation

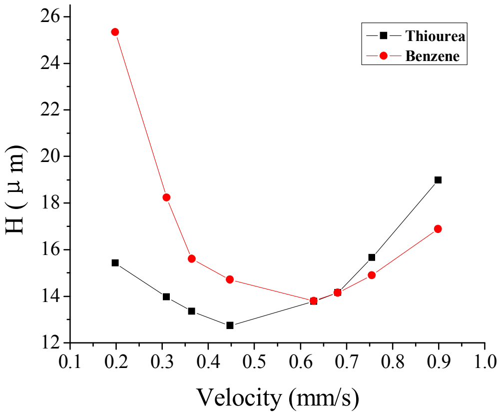

Fig. 8 Dependence of the plate height of analytes on the linear velocity of mobile phase by the Column B. Conditions: mobile phase, ACN/H_2O (75/25, v/v). Other conditions are same as in Fig.3

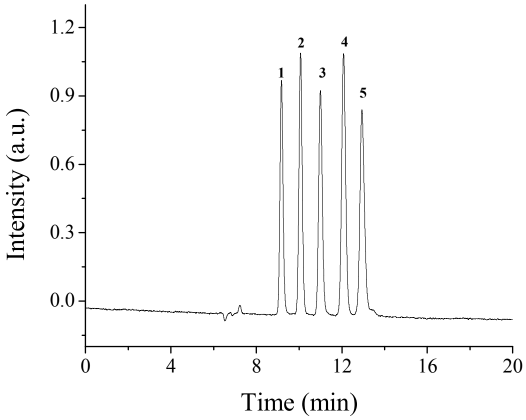

Fig. 10 Separations of PAHs on the column B in RP-cLC. Conditions: mobile phase, ACN-H_2O (90/10, v/v). Other conditions are same as in Fig. 3. Solutes 1, naphthalene; 2, fluorene; 3, phenanthrene; 4, fluoranthene; 5, pyrene.

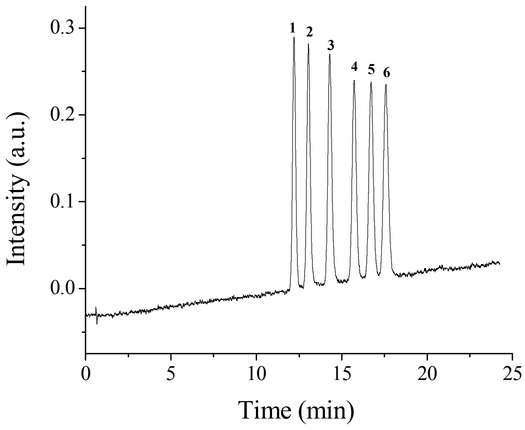

Fig. 11 Separations of phenols on the colunm B. Contionditons: mobile phase, ACN/H_2O (55/45, v/v). Other conditions are same as in Fig. 3. Solutes 1, phloroglucinol; 2, hydroquinone; 3, 2-aminophenol; 4, 4-methoxyphenol; 5, phenol; 6, 4-nitrophenol.

in reversed-phase (RP) mode. The retention properties of POSS-BMAB hybrid monolith were investigated using ABs as model compounds. Typical baseline separation of a mixture of ABs was showed in Fig. 5a. The retention and the elution order of ABs are benzene < toluene < ethylbenzene < propylbenzene < butylbenzene, which is well in agreement with the hydrophobicity of the ABs. Effect of varying ACN content in the mobile phases in the range 60-85 % (v/v) on the retention factors of ABs was investigated. It appears that the lg k almost linearity of decrease with increasing the content of organic modifier, where all linear correlation coefficients (R) were higher than 0.9941 (Fig. 9). All these effects can be deduced that the separation of ABs on the POSS-BMAB hybrid monolith was based on typical RP chromatographic retention mechanism.

3.3. Chromatographic performance

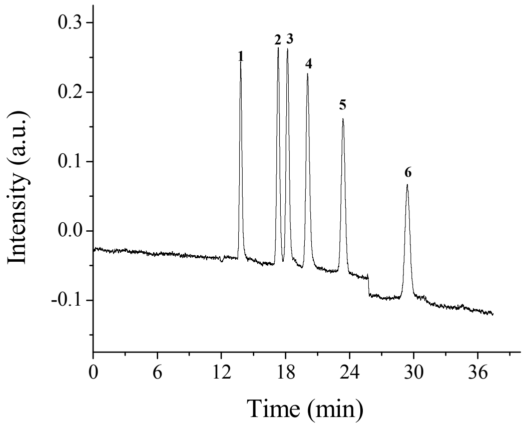

Fig. 12 Separations of anilines on the column B in cLC. Conditions: mobile phase, ACN/H_2O (65/35, v/v). Other conditions are same as in Fig. 5. Solutes 1, o-phenylenediamine; 2, aniline; 3, p-toluidine; 4, benzidine; 5, 2,4-dinitroaniline; 6, 1-aminonaphthalene.

The chromatographic performance of POSS-BMAB hybrid monolith was investigated by separating PAHs, phenols and anilines in cLC. Fig. 10 represents the separation of five PAHs in cLC using ACN/H_2O (90/10, v/v) as mobile phase. Five PAHs were well separated with column efficiency up to 53,800-69,900 plates/m according to their hydrophobicity in order from low to high, which indicated the retention mechanism was based on the hydrophobic interaction.

The prepared hybrid monoliths were also applied for separation of polar weak acidic compounds. A mixture of six phenols was used to survey the chromatographic performance of the POSS-BMAB hybrid monolith. As can be seen from Fig. 11, good separation of all these polar weak acidic compounds was achieved with the mobile phase containing ACN/H_2O (55/45, v/v). The high column efficiency for all phenols ranged from 56,600 to 69,200 plates/m.

As is well known, separation of basic compounds is still a troublesome task on traditional silica-based stationary phase in HPLC due to the secondary interactions between basic analytes and residual silanol groups of the stationary phases, which often lead to peak tailing and increased retention. However, this problem should be eliminated due to the neutral surface character of the POSS-BMAB hybrid without silanol groups. The separation of weak basic compounds on the POSS-BMAB hybrid monolith was also investigated. Fig. 12 presents the separation of six basic anilines on POSS-BMAB hybrid monolith. Good peak shape and high separation efficiency were observed for the separation of six basic analytes on POSS-BMAB hybrid monolith without adding any competing amines in the mobile phase. For instance, the tailing factors and column efficiency of six anilines were in the range of 1.05-1.18 and 53,800-64,500 plates/m respectively. These results demonstrated the higher separation ability of the POSS-BMAB hybrid monolith in RP-cLC.

4. Concluding remarks

In this work, a novel POSS-based hybrid monolith was facilely synthesized by thiol-ene click reaction of POSS-MA with BMAB. The synthetic method was very simple and convenient. The obtained POSS-BMAB hybrid monolith exhibited good permeability and thermostability and high mechanical stability. A typical RP chromatographic retention mechanism was observed for separation of the neutral analytes such as ABs. The POSS-BMAB hybrid monolith was also demonstrated its excellent chromatographic performance for separation of ABs, PAHs, phenols and anilines in RP-cLC mode. These successful separations suggest that the proposed hybrid monolith is a good separation media for complex sample analysis.

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Notes and references

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1 R.D. Arrua, T.J. Causon and E.F. Hilder. *Analyst*, 2012, **137**, 5179.
2 T.L. Chester. *Anal. Chem.*, 2013, **85**, 579.
3 P. Aggarwal, H.D. Tolley and M.L. Lee. J. Chromatogr., A, 2012, **1219** 1.
4 M. Wu, R. Wu, Z. Zhang and H. Zou. *Electrophoresis*, 2011, **32**, 105.
5 J. Ou, H. Lin, Z. Zhang, G. Huang, J. Dong and H. Zou. *Electrophoresis* 2013, **34**, 126.
6 A. Marechal, R. El-Debs, V. Dugas and C. Demesmay. *J. Sep. Sci.*, 2013, **36**, 2049.
7 C. Chu and R. Liu. *Chem. Soc. Rev*., 2011, **40**, 2177.
8 Z. M. Guo, A. W. Lei, Y. P. Zhang, Q. Xu, X. Y. Xue, F. F. Zhang and X. M. Liang. *Chem. Commun.,* 2007, **24**, 2491.
9 Bräse, S., Gil, C., Knepper, K. and Zimmermann, V. *Angew.Chem. Int. Ed.,* 2005, **44**, 5188.
10 Hoyle C E, Bowman C N. *Angew. Chem. Int. Ed.,* 2010, **49**, 1540.
11 A. Shen, Z. Guo, L. Yu, L. Cao and X. Liang. *Chem. Commun.,* 2011, **47**, 4550–4552
12 Y. Chen, M. Wu, K. Wang, B. Chen, S. Yao, H. Zou and L. Nie. *J. Chromatogr., A,* 2011, **1218**, 7982.
13 Y. Chen, K. Wang, H. Yang, Y. Liu, S. Yao, B. Chen, L. Nie, and G. Xu. *J. Chromatogr., A,* 2012, **1233**, 91.
14 K. Wang, Y. Chen, H. Yang, Y. Li, L. Nie and S. Yao. *Talanta,* 2012, **91**, 52.
15 Y. Lv, Z. Lin, F. Svec. *Analyst*, 2012, **137**, 4114.
16 X. Peng, T. Liu, S. Ji and Y. Feng. *J. Sep. Sci.*, 2013, **36**, 2571.
17 A. Shen, X. Li, X. Dong, J. Wei, Z. Guo and X. Liang. *J. Chromatogr., A,* 2013,**1314**, 63.
18 X. Cheng, X. Peng, Q. Yu, B. Yuan and Y. Feng. *J. Chromatogr., A,* 2013, **1302**, 81.
19 I. Tijunelyte, J. Babinot, M. Guerrouache, G. Valincius and B. Carbonnier. *Polymer,* 2012, **53** , 29.
20 A. Laaniste, A. Marechal, R. El-Debs, J. Randon, V. Dugas and C. Demesmay. *J. Chromatogr., A,* 2014, **1355**, 296. 21 X. Yao, T. Thatt, Y. Tan, Y. Wang. *J. Chromatogr., A*, 2014, **1326** 80.22 Z. Liu, J. Ou, H. Lin, H. Wang, J. Dong and H. Zou. *J. Chromatogr., A,* 2014, **1342**, 70.
23 Y. Liu, Y. Chen, H. Yang, L. Nie and S. Yao. *J. Chromatogr., A,* 2013, **1283**, 132.
24 M. Chen, J. Zhang, Z. Zhang, B. Yuan, Q. Yu and Y. Feng. *J. Chromatogr., A,* 2013, **1284**, 118.
25 Z. Lin, X. Tan, R. Yu, J. Lin, X.i Yin, L. Zhang and H. Yang. *J. Chromatogr., A*, 2014, **1355**, 228.
26 H. Yang, Y. Chen, Y. Liu, L. Nie and S. Yao. *Electrophoresis,* 2013, **34**, 510.
27 Z. Liu, J. Ou, H. Lin, Z. Liu, H. Wang, J. Dong and H. Zou. *Chem Commun.,* 2014, **50**, 9288.
28 M. Wu, R. Wu R. Li, H. Qin, J. Dong, Z. Zhang and H. Zou. *Anal. Chem.,* 2010**, 82,** 5447.
29 X. Lin, N. Zheng, J. Wang, X. Wang, Y. Zheng and Z. Xie. *Analyst*, 2013, **138**, 5555.
30 H. Lin, J. Ou, Z. Zhang, J. Dong and H. Zou. *Chem. Commun.,* 2013, **49**, 23.
31 H. Lin, Z. Zhang, J. Dong, Z. Liu, J. Ou and H. Zou. *J. Sep. Sci.*, 2013, **36**, 2819.
32 X. Lin, X. Wang, T. Zhao, Y. Zheng, S. Liu and Z. Xie. *J. Chromatogr., A*, 2012, **1260**,174.
33 X. Xiong, Z. Yang, Y. Li, L. Xiao, L. Jiang, Y. Chen, M. Ma and B. Chen. *J. Chromatogr., A*, 2013, **1304***,* 85.
34 J. Ou, Z. Zhanga, H. Lin, J. Dong and H. Zou, *Anal. Chim., Acta*, 2013, **761**, 209.
35 J. Ou, G.T.T. Gibson and R.D. Oleschuk. *J. Chromatogr., A,* 2010, **1217**, 3628.
36 P.A. Bristow and J.H. Knox. *Chromatographia,* 1977, **10**, 279.
37 P.S. Nikam, L.N. Shirsat and M. Hasan, *J. Chem. Eng. Data.,* 1998, **43**,732..
38 C. E. Hoyle, T. Y. Lee and T. Roper, *J. Polym. Sci. Part A: Polym. Chem.*, 2004, **42**, 5301.