Electronic Supporting Information

A facile versatile polymeric monolith for multiple separations

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1. Experimental section

1.1 Materials and Chemicals

Vinylbenzyl trimethylammonium chloride (VBTA), tris(2-acryloyloxyethyl) isocyanurate (TAEIC), 2-(methacryloyloxy)ethyltrimethylammonium methyl sulfate (META), Ethylene dimethacrylate (EDMA), 2,2'-azobisisobutyronitrile (AIBN), 3-(trimethoxysilyl)propyl methacrylate (λ-MAPS); Benzoic acid (B), 4-hydroxybenzoic acid (4-HB), 3,4-dihydroxybenzoic acid (3,4-DHB), 3,4,5-trihydroxybenzoic acid (3,4,5-THB), PAHs, Aromatic amines, phenol, catechol, resorcinol, hydroquinone, pyrogallol, thiourea, phloroglucinol were purchased from Aldrich (Milwaukee, WI, USA). Nucleobases, nucleoside and estrogens were purchased from Sigma (St. Louis, MO, USA). HPLC-grade methanol and ACN were purchased from Chemical Reagent Corporation (Shanghai, China). The water used throughout all experiments was double-distilled water. Other chemicals (Chemical Reagent Plant, Shanghai, China) were of analytical grade. The fused-silica capillaries with a dimension of 100-μm ID (375-μm OD) were purchased from the Yongnian Optic Fiber Plant (Hebei, China).

1.2 Instrumentation

Pressured capillary electrochromatography (pCEC) was performed on a Trisep-TM 2010GV CEC system (Unimicro Technologies, Pleasanton, CA, USA) equipped with a UV/Vis detector (190 – 600 nm), which is comprised of a microvolume pumps, a high-voltage power supply (−30 to +30 kV), a microfluid manipulation module (including a six-port injector), and a data acquisition module. Pressure was applied to the column inlet during the separation. A positive voltage was applied to the outlet of column, and the inlet of column was connected to the split valve and grounded. In this experiment,

the isocratic elution system was used.

Scanning electron micrographs (SEM) of the monolithic columns were carried out on an XL30 E scanning electron microscope (Philips, The Netherlands).

1.3 Preparation of poly(TAEIC-co-VBTA) monolith

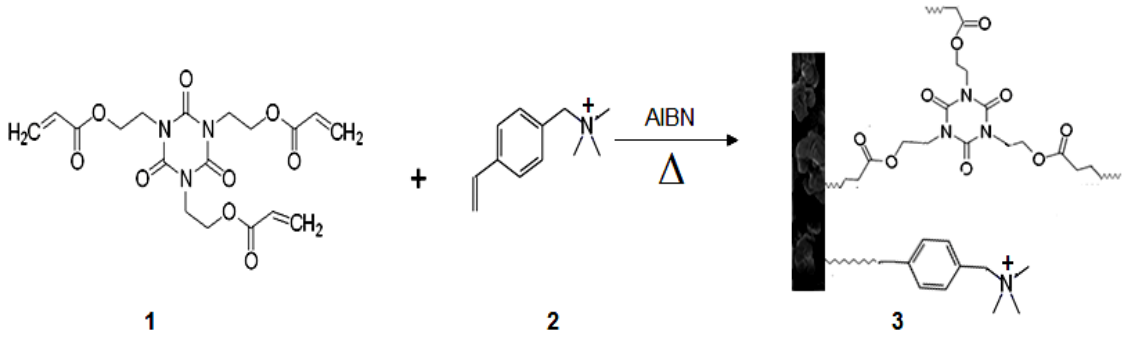
Prior to use, the inner wall of the capillary was firstly treated with λ-MAPS [S1]. Polymerization solutions weighing 2.0 g were prepared from monomers and porogenic solvents in ratios of 20:80 (monomers/solvents, w/w). The mixtures of monomers were weighed and dissolved in porogenic solvents consisting of methanol and dodecanol in various ratios (see Table S1). AIBN (4.0 mg, 1.0% with respect to total monomers, w/w) was added to the porogenic solvents. The polymerization mixture was vortexed and then ultrasonicated for 5 min, and then kept in ice until it was injected into the capillary for 35-cm length. The capillary was sealed and submerged into water bath at 60 °C for 20 h. The obtained monolith was washed with methanol to flush out the residual reagents. A detection window was created at 1-2 mm at the end of the polymer bed. Finally, the column was cut to a total length of 50 cm with an effective length of 30 cm.

Reference

S1. B. Xiong, L. Zhang, Y. Zhang, and H. Zou, *J. High Resolut. Chromatogr.*, 2000, **23**，67-72.

2. Results and discussions

2.1 Supporting Scheme



Scheme S1 Process of “one-step” in-situ copolymerization for poly(VBTA-co-TAEIC)

2.2 Supporting Figures

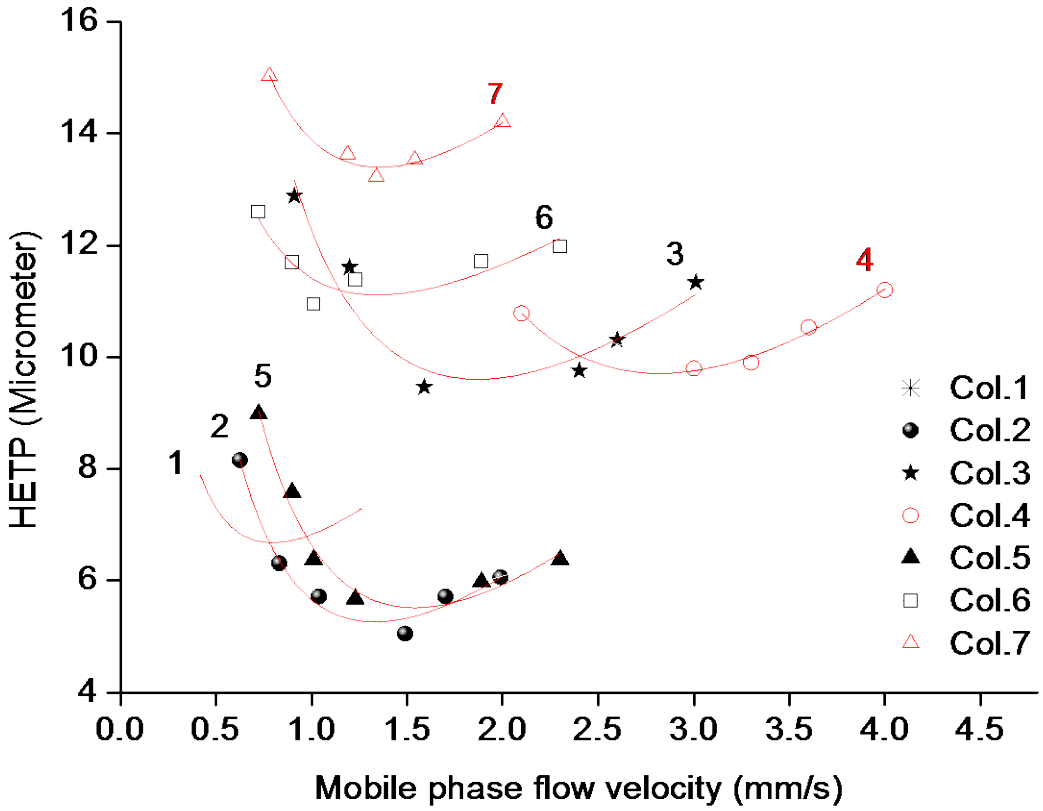


Fig. S1. Height equivalent to a theoretical plate (HETP) for various monolithic columns prepared from polymerization solution at different wt% of TAEIC and wt% of dodecanol. Experimental conditions: mobile phase, ammonium formate (5mM, pH 5.0), at 80% v/v ACN. pump flow: 0.1mL/min; applied pressure 0.8 MPa; applied voltage from +2 to +20 kV. The plate height is the average taken for thiourea.

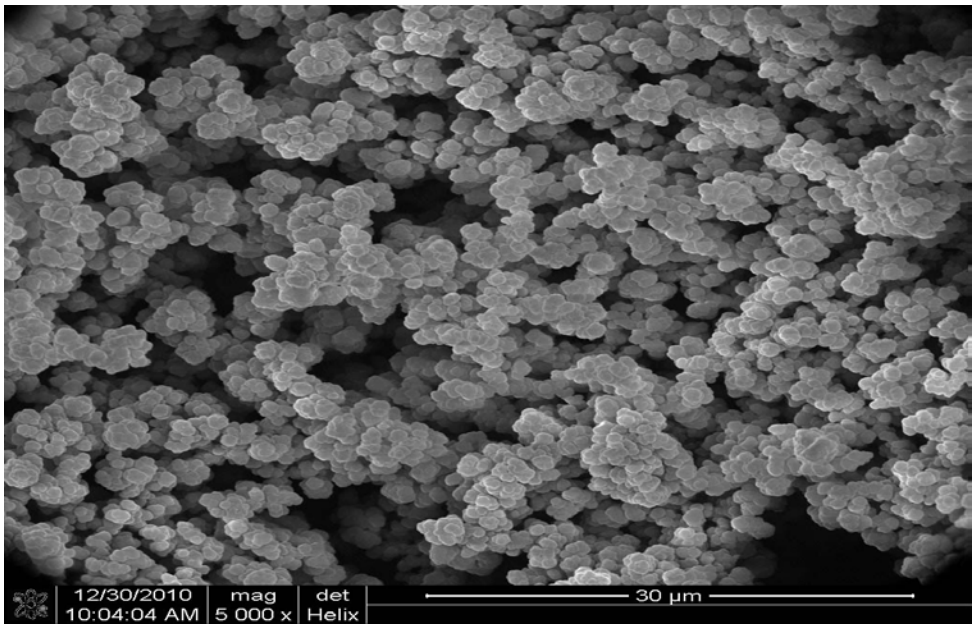


Fig. S2. Scanning electron microphotograph of monolithic column 2.

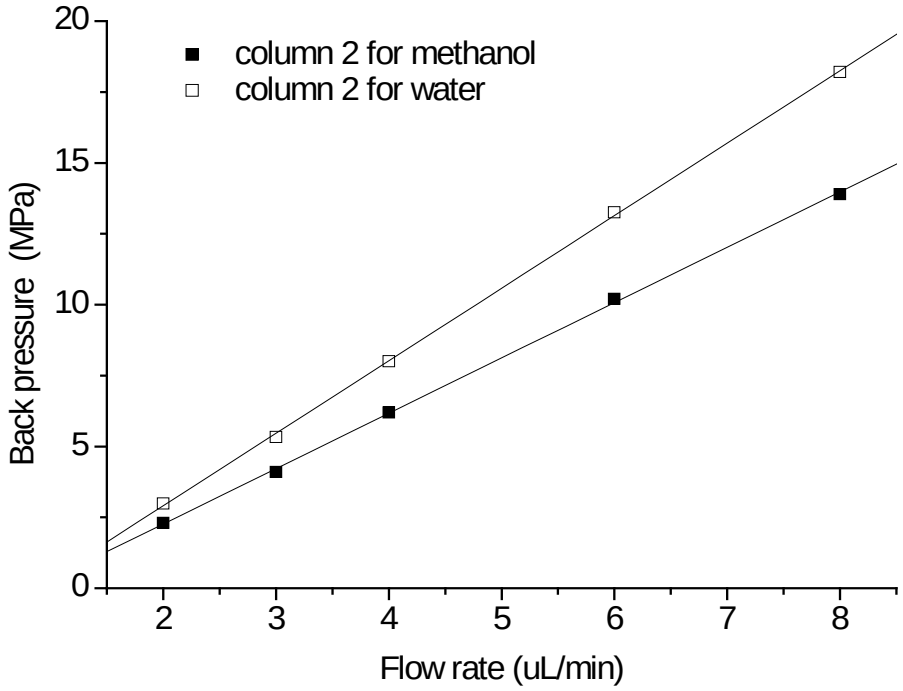


Fig. 3S. Dependence of the back pressure on the eluent flow-rate for column 2

2.2 Supporting Tables

Table S1 Different permeability of the monoliths prepared with different compositions of the polymerization solutions

Column designation	Monomer-to-solvent ratio	TAEIC [a)] (% w/w)	VBTA [a)] (% w/w)	Dodecanol [b)] (% w/w)	Permeability [c)], K ($\times 10^{-14}$ m^2)
Col.1	20:80	9.0	11.0	44.0	6.2
Col.2	20:80	9.0	11.0	48.0	12.8
Col.3	20:80	9.0	11.0	52.0	20.5
Col.4	20:80	9.0	11.0	56.0	29.1
Col.5	20:80	10.0	10.0	48.0	14.1
Col.6	20:80	8.0	12.0	48.0	10.7
Col.7	20:80	7.0	13.0	48.0	7.4
Col.8	30:70	13.5	16.5	42.0	n/a

a) Percentage of TAEIC or VBTA in the polymerization mixture.

b) Percentage of dodecanol in the polymerization mixture. The porogenic solvent was composed of methanol and dodecanol.

c) The permeability was measured by using 80/20 (v/v) acetonitrile/water. The viscosity of ACN/water (80/20, v/v) was 0.53 [Ref. S2].

n/a: the measurements could not be made because the columns were not applicable.

S2: (a) P.A. Bristow and J.H. Knox, *Chromatographia*, 1977,**10** : 279-289.

(b) X. Lin, X. Wang, T. Zhao, Y. Zheng, S. Liu and Z. Xie, *J. Chromatogr. A.* 2012, **1260**:174-182

Table S2 Van Deemter formula of different monoliths

Parameters [a)]	A	B	C	Correlation coefficient (R)	H_{min} [b)] (μm)
Col.1	0.99	2.27	3.57	0.9592	6.7
Col.2	-4.45	6.46	3.64	0.9899	5.2
Col.3	-3.55	12.3	3.51	0.9539	9.6
Col.4	-14.7	34.6	4.35	0.9913	9.8
Col.5	-6.3	9.13	3.85	0.9848	5.6
Col.6	3.64	3.83	3.7	0.9592	11.2
Col.7	3.98	6.56	3.37	0.9849	13.4

a）Van Deemter formula: $H = A + B/u + C \times u$

b）The minimum theoretical height (H_{min}) was calculated as $H_{min} = A + 2 (B \times C)^{1/2}$

Table S3 α (ribose) values of the nucleosides in different monoliths

Column designation	α(ribose)				References
	$k_{(uridine)}/k_{(uracil)}$	$k_{(adenosine)}/k_{(adenine)}$	$k_{(cytidine)}/k_{(cytosine)}$	$k_{(guanosine)}/k_{(guanine)}$	
Column B[a)]	5.59	1.69	2.93	2.14	S3
Amide-80	1.81	1.18	1.52	1.49	S4
ZIC-HILIC	2.53	1.08	1.71	1.75	S4

a. Column 2 was the obtained optimum poly(TAEIC-co-VBTA) column.;

α(ribose) defined as $k_{(nucleoside)}/k_{(nucleic\ base)}$

S3: this manusript.

S4: Y. Kawachia, T. Ikegamia, H. Takuboa,1, Y. Ikegamib, M. Miyamotoa and N. Tanaka, *J. Chromatogr. A*, 2011, **1218**: 5903- 5919