A rapid synthetic method of organic polymer-based monoliths in room temperature ionic liquid reaction medium via microwave-assisted vinylization and polymerization

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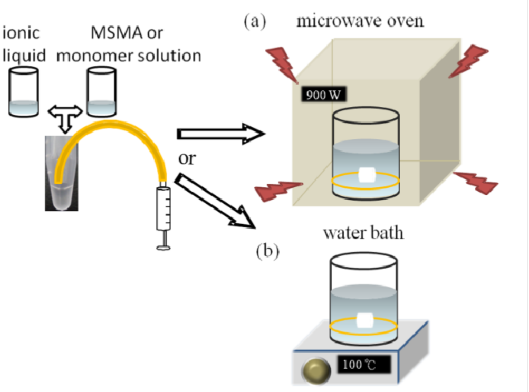
Supporting information

Experimental details

Prior to monolith preparation, vinyl moieties have to be carried on capillary inner wall in order to anchor the polymeric monolith on the capillary while polymerization proceeds. First, a 100-μm I.D. capillary column was filled with vinylization solution composed of MSMA mixed with methanol or [C_6mim][BF_4] (50 %, v/v). Once both ends of the capillaries were sealed with epoxy adhesive, the capillaries were heat-treated either in water bath at 100 ^oC or microwave oven (900 W, SAMPO RE-1002SM) in a beaker with RT water (Scheme 1). Next, the preparation of monolithic column was carried out below. A solution composed of monomers, reaction medium (solvents) and initiator was used to prepare the monolithic materials. This solution was made by dissolving initiator (AIBN, 1 mg), charged monomer (VBSA, 1 mg, only used for CEC application) in various monomer solutions, which included BMA, DVB, St or EDMA. Reaction medium, which consisted of volatile organic solvent (cyclohexanol and NMP), water or ILs ([C_6mim][BF_4]), was slowly added to the monomer mixture. The mixture solution was sonicated for 15 min until it became homogeneous, then it was used to fill the vinylized capillary by syringe injection. After both ends of the capillary were sealed with epoxy adhesive resin, the capillaries were heat-treated in (a) water bath at 100 ^oC or (b) microwaved (900 W) in a beaker with RT water (Scheme 1). An LC pump was used to wash the monolithic column first with methanol to remove the unreacted reagents and then with the mobile phase to condition the monolithic columns for subsequent CEC and nano-LC/MS analyses. All other conditions were the same with previous reports.[14a] The compositions of monomer and reaction medium for these monolith preparations (BMA-DVB, St-DVB and BMA-EDMA) are shown in the supplementary information). The CEC separations were performed with an applied voltage of 25 kV at 25 ^oC where a mixture of acetronitrile (ACN) and the phosphate buffer (5 mM) in a volume ratio of 55:45 was used as the mobile phase. The analyte solution was electrokinetically injected at 5 kV for 3 s and detected by an UV detector at 214 nm. Mobile phase compositions in nano-LC/MS were 90%:10% ACN:

H_2O (B) and 100% H_2O (C) using 1 M ammonia water to adjust pH. Paraben analytes (1 ppm each) were separated with a gradient elution program as follows: 1-70% B in 25 min and reduced to 1% in 35 min. Analytes were detected via on-line nanoESI-ion trap mass spectrometer operated in a negative mode wherein the molecular ion signals ($[M-H]^-$ form) of parabens with *m/z*'s 151 (methyl), 165 (ethyl), 179 (propyl) and 193 (butyl) were monitored.



Scheme 1. Column vinylization and monolith synthesis with IL solvent under a) microwave heating and b) 100°C water bath

The composition of monomer and reaction medium for BMA-DVB, St-DVB and BMA-EDMA monolith preparation

Table 1 shows the composition of monomer and reaction medium for BMA-DVB, St-DVB and BMA-EDMA monolith preparation used in the study as well as in previous papers, wherein a single IL solvent $[C_6mim][BF_4]$ synthesized successfully all three types of organic polymer-based monoliths. In comparison with conventional methods,[a-c] in which the type and ratio of organic solvents used as reaction medium need to be optimized carefully in order to produce adequately porous monoliths, this proposed method using single IL as reaction medium in the study avoids the complicated process.

Table 1 Composition of monomer and reaction medium in the monolith preparation.

Monolith	Monomer (%, v/v)	Reaction medium (%, v/v) in the study	Reaction medium (%, v/v) in previous paper
BMA-DVB	BMA (7.27) DVB (13.91)	[C_6mim][BF_4] (69.67)	cyclohexanol (36.07) and *N*, *N*-dimethylacetamide (36.06)[a]
St-DVB	St (7.39) DVB (11.09)	[C_6mim][BF_4] (77.64)	cyclohexanol (47) and *N*, *N*-dimethylacetamide (47)[b]
BMA-EDMA	BMA (9.6) EDMA (14.4)	[C_6mim][BF_4] (70)	1-propanol (30.54) and 1,4-butanediol (29.46)[c]

[a] H.Y. Huang, Y. J. Cheng, W. L. Liu, Y. F. Hsu, S. Lee, *J. Chromatogr. A*, **2010** 1217, 5839-5847.

[b] H.Y. Huang, Y. J. Cheng, C. L. Lin, *Talanta* 2010, 82, 1426-1433.

[c] E. C. Peters, M. Petro, F. Svec, and J. M. J. Fréchet, *Anal. Chem.* **1997,** 69, 3646-3649.

Conversion yields of BMA-DVB monolith syntheses

BMA-DVB monoliths prepared with different heat-treatment approaches were characterized by measuring their conversion yields at various reaction times. The monolith for conversion yield measurement was prepared in the same way as the monolithic columns but was placed in a glass vial. After a 100° C thermal heating or a 900W microwave irradiation at various reaction times, the monolithic polymer formed in the vial was Soxhlet extracted with methanol for 17 h, vacuum dried overnight, and then was directly used for the measurement of conversion yield. The conversion yield of polymerization reaction, which was obtained by comparison of the weight of the original monomer and the monolithic polymer, was summarized in Table 2. The results indicated that their conversion yields significantly increased with reaction time, and rapidly reached to 60 % within 10 min either in microwave or water bath. This could be attributed to the increased polarity of the IL solvent which improved propagation rate in free radical reaction, while, its high viscosity reduced termination rate in polymerization; as a result, fast reaction rates were acquired. In addition, by comparison, microwave heating provided a better conversion yield with brief reaction time (3 or 5 min), possibly because microwave irradiation produces efficient internal heating to induce molecule reactions which is consistently observed with previous works on microwave-assisted chemistry. [11]

Table 2 Conversion yields of BMA-DVB monoliths prepared with [C_6mim][BF_4] IL as reaction medium

	Conversion yield (%)[a]	
heating time (min)	Water bath at 100 °C	Microwave irradiation
1	6.6 (± 2.9)	0.0 ± (0.0)
3	28.7 (± 0.6)	54.7 (± 2.5)
5	44.3 (± 1.0)	63.2 (± 0.3)
10	65.8 (± 3.0)	59.7 (± 1.3)

[a] n=3. The value in parenthesis indicates the standard deviation of conversion yield in percentage.

Preparation of St-DVB and BMA-EDMA monoliths

St-DVB and BMA-EDMA monoliths were also successfully synthesized within 5 min both in 100 °C water bath and microwave heating with [C_6mim][BF_4] as reaction medium. Figure 1 shows the morphology of St-DVB and BMA-EDMA (i.e. SEM images) with 3 or 5 min reaction time chosen according to their optimal chromatographic results. Similar to BMA-DVB monoliths reported in the study, the two monoliths also had many porous channels when this IL solvent was used instead of conventional volatile solvents as reaction medium.

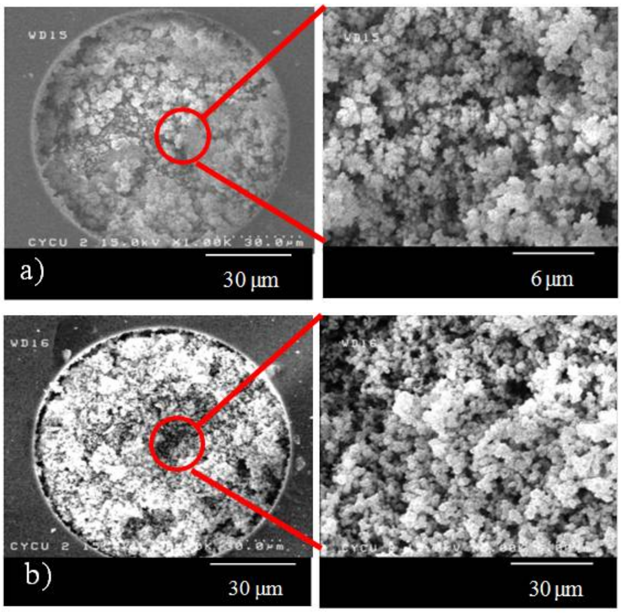


Figure 1. SEM images of a) St-DVB and b) BMA-DVB monolithic columns using ionic liquid as reaction solvent. Heat-treatment: microwave irradiation, 900 W, 5 min for a) and 3 min for b).

Because of good permeability and sieving effect, the two monoliths are promising candidates for chromatographic stationary phases. Their chromatographic performances were further evaluated by the separation of six alkyl benzenes in CEC system. The CEC chromatograms derived from the optimal composition of mobile phase and operation conditions are shown in Figure 2. The BMA-EDMA monolithic column afforded a baseline separation within 10 min with high peak symmetry and separation efficiency. In the case of St-DVB monolith, however, serious peak tailing was observed, that could be due to a stronger π-π interaction between the aromatic analytes and St-DVB monolith stationary phase, that has been mentioned in previous report (*Huang et al, J. Chromatogr. A,* ***2010*** *1217, 5839-5847*).

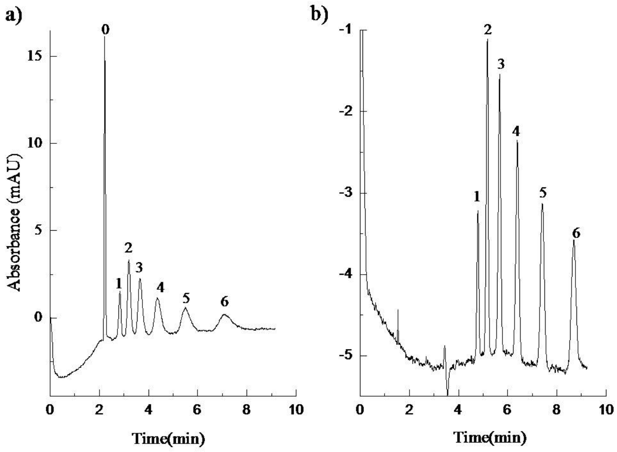


Figure 2. CEC separation of neutral aromatic compounds on a) St-DVB and b) BMA-EDMA monolithic columns prepared using [C_6mim][BF_4] solvent via microwave irradiation (5 min for a) and 3 min for b)). Peak identity: 0) thiourea, 1) benzene, 2) toluene, 3) ethylbenzene, 4) propylbenzene, 5) butylbenzene, 6) pentylbenzene.

Chromatographic performances of BMA-DVB monoliths

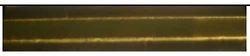
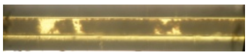
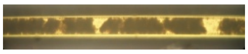
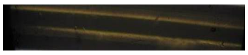
Table 3 shows the qualitative and quantitative performances of the BMA-DVB monolithic column prepared by the proposed column vinylization and monolith synthesis procedures (i.e. [C_6mim][BF_4] solvent used as reaction medium combined with microwave heating (5 min)). Without internal standard calibration, the RSD of the analytes' retention times were in the range of 0.04 to 0.21 % on a single column, and were in the range of 2.8 to 5.7 % for three columns produced on different days. In addition, the peak area RSDs for the six analytes were in the range of 0.90 to 4.7 % on a single column and on three columns produced on different days after internal standard calibration. These results indicated that the rapidly prepared monolith materials indeed provided comparable qualitative and quantitative performances with conventionally synthesized ones.

Table 3 Column performance of BMA-DVB monolith[a]

analyte	Retention time reproducibility		Peak area reproducibility	
	run-to-run	column-to-column	run-to-run	column-to-column
	R.S.D.[b](%)	R.S.D.(%)	R.S.D.(%)	R.S.D.(%)
Thiourea	0.21	2.77	1.08	0.91
Benzene	0.08	3.06	4.74	4.11
Toluene	0.08	3.27	3.22	4.69
Ethylbenzene	0.07	3.65	2.23	4.03
Propylbenzene	0.19	4.20	2.44	4.74
Butylbenzene	0.04	5.00	1.81	1.69
Pentylbenzene	0.11	5.67	0.90	2.51

[a] Values were obtained based on three intra-day replicates on the same column (run-to-run) or three different columns (column-to-column) (n=3). [b] relative standard deviations.

Table 4 Effect of type of reaction medium and heat-treatment on vinylization procedure in monolithic column.[a]

Reaction medium	Heat-treatment (time) [c]	OM image [d]
Methanol	water bath (35°C, 17h)	
	microwave (5 min)	
IL solvent [b]	water bath (5 min)	
	microwave (5 min)	

[a] Monolithic materials were prepared using BMA and DVB monomers mixed with $[C_6min][BF_4]$ as reaction solvent under microwave irradiation (900 W, 5 min).
[b] $[C_6mim][BF_4]$. [c] 100 °C water bath or 900 W microwave oven for microwave irradiation.
[d] Optical microscope images were magnified at ×100.