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Highly crosslinked polymeric monoliths for reversed-phase capillary liquid chromatography of small molecules

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ABSTRACT

Seven crosslinking monomers, i.e., 1,3-butanediol dimethacrylate (1,3-BDDMA), 1,4-butanediol dimethacrylate (1,4-BDDMA), neopentyl glycol dimethacrylate (NPGDMA), 1,5-pentanediol dimethacrylate (1,5-PDDMA), 1,6-hexanediol dimethacrylate (1,6-HDDMA), 1,10-decanediol dimethacrylate (1,10-DDDMA), and 1,12-dodecanediol dimethacrylate (1,12-DoDDMA), were used to synthesize highly cross-linked monolithic capillary columns for reversed-phase liquid chromatography (RPLC) of small molecules. Dodecanol and methanol were chosen as "good" and "poor" porogenic solvents, respectively, for these monoliths, and were investigated in detail to provide insight into the selection of porogen concentration using 1,12-DoDDMA. Isocratic elution of alkylbenzenes at a flow rate of 300 nL/min was conducted for all of the monoliths. Gradient elution of alkylbenzenes and alkylparabens provided high resolution separations. Optimized monoliths synthesized from all seven crosslinking monomers showed high permeability. Several of the monoliths demonstrated column efficiencies in excess of 50,000 plates/m. Monoliths with longer alkyl-bridging chains showed very little shrinking or swelling in solvents of different polarities. Column preparation was highly reproducible; the relative standard deviation (RSD) values ($n = 3$) for run-to-run and column-to-column were less than 0.25% and 1.20%, respectively, based on retention times of alkylbenzenes.

1. Introduction

Monolithic stationary phases for liquid chromatography (LC) were introduced in the late 1980s and early 1990s [1–4] with promise of overcoming some limitations of conventional packed columns [5]. Monoliths are often called continuous porous beds, continuous polymer rods or continuous column supports [1]. Their unique hydrodynamic [6] and mass transfer characteristics [7] have improved the separation efficiency for high-molecular-weight compounds [8]. Monolithic columns are much easier to prepare and no frits are needed. They can provide rapid separations because they have high column permeability. Furthermore, the column porosity is not dependent on particle size, but can be optimized and controlled during the preparation process [9]. The attractive advantages of monolithic columns have been described in many excellent reviews [5,9–13]. Compared to packed columns, monoliths cannot form void volumes caused by poor packing, since they form as a continuous rod. This means that most of the through-pores can be used for mobile phase flow, which leads to high permeability.

Inorganic (silica) monolithic columns were introduced in 1996 using a sol–gel process [14,15], and are characterized by a bimodal pore size distribution. Large through-pores allow them to be used with high flow rates and low back pressure. The smaller pores provide high surface area. This helps to improve the resolution of small molecules. However, separations of high molecular weight compounds, such as proteins, are limited by the low number of small macropores (50–100 nm) [7,13].

Monolithic stationary phases can also be synthesized from organic monomers. The most commonly used organic monomers are styrene, acrylates, methacrylates, acrylamides and methacrylamides. Most monoliths prepared from these monomers have been used for the separation of peptides and proteins [16,17]. However, such polymeric materials also exhibit several disadvantages. Compared to inorganic monoliths, organic polymeric monoliths generally suffer from significantly lower chromatographic efficiencies for low-molecular weight compounds. This is due to a distinctive difference in pore-size-distribution between polymeric and inorganic monoliths. Inorganic monoliths usually contain both macropores and mesopores (5–40 nm), which are needed for the separation of small molecules [18,19]. In contrast, organic

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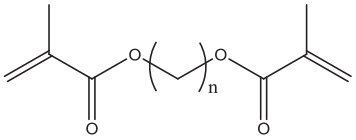


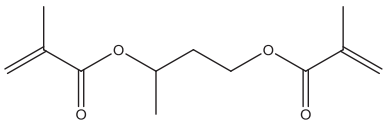
n = 4, 1,4-Butanediol dimethacrylate (1,4-BDDMA)

n = 5, 1,5-Pentanediol dimethacrylate (1,5-PDDMA)

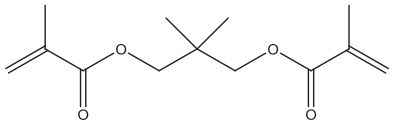
n = 6, 1,6-Hexanediol dimethacrylate (1,6-HDDMA)

n = 10, 1,10-Decanediol dimethacrylate (1,10-DDDMA)

n = 12, 1,12-Dodecanediol dimethacrylate (1,12-DoDDMA)



1,3-Butanediol dimethacrylate (1,3-BDDMA)



Neopentyl glycol dimethacrylate (NPGDMA)

Fig. 1. Chemical structures of n-alkanediol dimethacrylate monomers.

monoliths are usually more suitable for the separation of high molecular weight compounds due to their monomodal macropore-distribution [13]. In addition, organic polymeric monoliths can swell or shrink with organic solvents in the mobile phase, leading to reduced chromatographic performance and poor mechanical stability [20]. Recently, several publications have reported the separation of small molecules with organic monoliths [21–23]. However, most applications still focus on high-molecular-weight compounds.

A conventional polymerization system for monolith preparation includes initiator, functional monomer, crosslinking monomer and porogen or porogen mixture. It has been reported that higher crosslinker concentration can provide higher mechanical stability and higher surface area [6,20,22–30]. Our recent work has suggested that significant advantages are realized when using a single-monomer/crosslinker in the synthesis, including straightforward optimization of the polymerization solution, improved column-to-column reproducibility, better mechanical stability and higher surface area due to the highly crosslinked network [23,31].

In this study, we introduce a group of highly cross-linked polymeric monolithic stationary phases prepared from single alkanediol methacrylate based monomers. The structures of these monomers are shown in Fig. 1. The morphologies and separation performances of these monoliths were studied in this work. These monoliths were successfully used for separation of low-molecular-weight compounds, such as alkylbenzenes and parabens.

Table 1
Compositions of selected monomers.

Monolith	Composition[a] (g/wt%)[b]		
	Monomer	Methanol	Dodecanol
1,3-BDDMA	0.36/31.86	0.46/40.71	0.31/27.43
1,4-BDDMA	0.36/32.14	0.38/33.93	0.38/33.93
NPGDMA	0.36/31.86	0.31/27.43	0.46/40.71
1,5-PDDMA	0.36/32.43	0.34/30.63	0.41/36.94
1,6-HDDMA	0.36/31.86	0.52/46.02	0.25/22.12
1,10-DDDMA	0.36/31.58	0.51/44.74	0.27/23.68
1,12-DoDDMA	0.36/31.30	0.50/43.48	0.29/25.22

[a] All monoliths contained 1 wt% DMPA to monomer.
[b] wt% related to total polymerization mixture.

2. Experimental

2.1. Chemicals and reagents

2,2-Dimethoxy-2-phenylacetophenone (DMPA, 99%) and 3-(trimethoxysilyl)propyl methacrylate (TPM, 98%) were purchased from Sigma–Aldrich (St Louis, MO, USA); 1,5-pentanediol dimethacrylate (1,5-PDDMA) and 1,10-decanediol dimethacrylate (1,10-DDDMA) (see Fig. 1) were purchased from Polysciences (Warrington, PA, USA); and 1,3-butanediol dimethacrylate (1,3-BDDMA), 1,4-butanediol dimethacrylate (1,4-BDDMA), neopentyl glycol dimethacrylate (NPGDMA), 1,6-hexanediol dimethacrylate (1,6-HDDMA) and 1,12-dodecanediol dimethacrylate (1,12-DoDDMA) (see Fig. 1) were gifts from Sartomer (Exton, PA, USA). Water, methanol, decanol, dodecanol, propylbenzene, butylbenzene, amylbenzene and uracil were also obtained from Sigma–Aldrich; acetonitrile (ACN), iso-butanol, and ethylbenzene were purchased from Fisher Scientific (Pittsburgh, PA, USA); toluene was purchased from Mallinckrodt (Phillipsburg, NJ, USA); tetrahydrofuran (THF) was purchased from Curtin Matheson Scientific (Houston, TX, USA); and methyl paraben, ethyl paraben, propyl paraben and butyl paraben were purchased from Fluka (Buchs, Switzerland). All porogenic solvents and chemicals for monolith and mobile phase buffer preparations were HPLC or analytical reagent grade, and were used as received. Buffer solutions were prepared with HPLC water and filtered through a 0.22-μm membrane filter.

2.1.1. Polymeric monolith preparation

First, UV-transparent fused silica capillary tubing (75-μm i.d., 375-μm o.d., Polymicro Technologies, Phoenix, AZ, USA) was treated with TPM in order to anchor the polymer to the capillary wall. The treatment procedures were reported by Vidič et al. [32] and Coutios et al. [33].

Monomer solutions were prepared in 1-dram (4 mL) glass vials by admixing initiator, monomer, and porogen solvents (see Table 1 for reagent compositions). Each solution was vortexed and then degassed by sonication for a few seconds to avoid excessive evaporation of methanol. Then, the reaction mixture was introduced into one end of the silanized capillary by capillary action. The other end of the capillary was left empty for UV detection. After filling with solution, the capillary was sealed with rubber septa at both ends and placed directly under a PRX 1000-20 exposure unit UV lamp (390 ± 15 nm, 1000 W, TAMARACK Scientific, Corona, CA, USA). Monoliths obtained after exposing with UV light from 1 to 6 min were flushed with methanol and then water until stable pressure readings were obtained. Similar back pressures (per unit column length) and morphology (based on microscope images) were observed when the polymerization time was longer than 3 min. Therefore, a polymerization time of 3.5 min was selected for all monoliths. After a monolithic column was prepared, it was then flushed with methanol and water sequentially using an HPLC pump

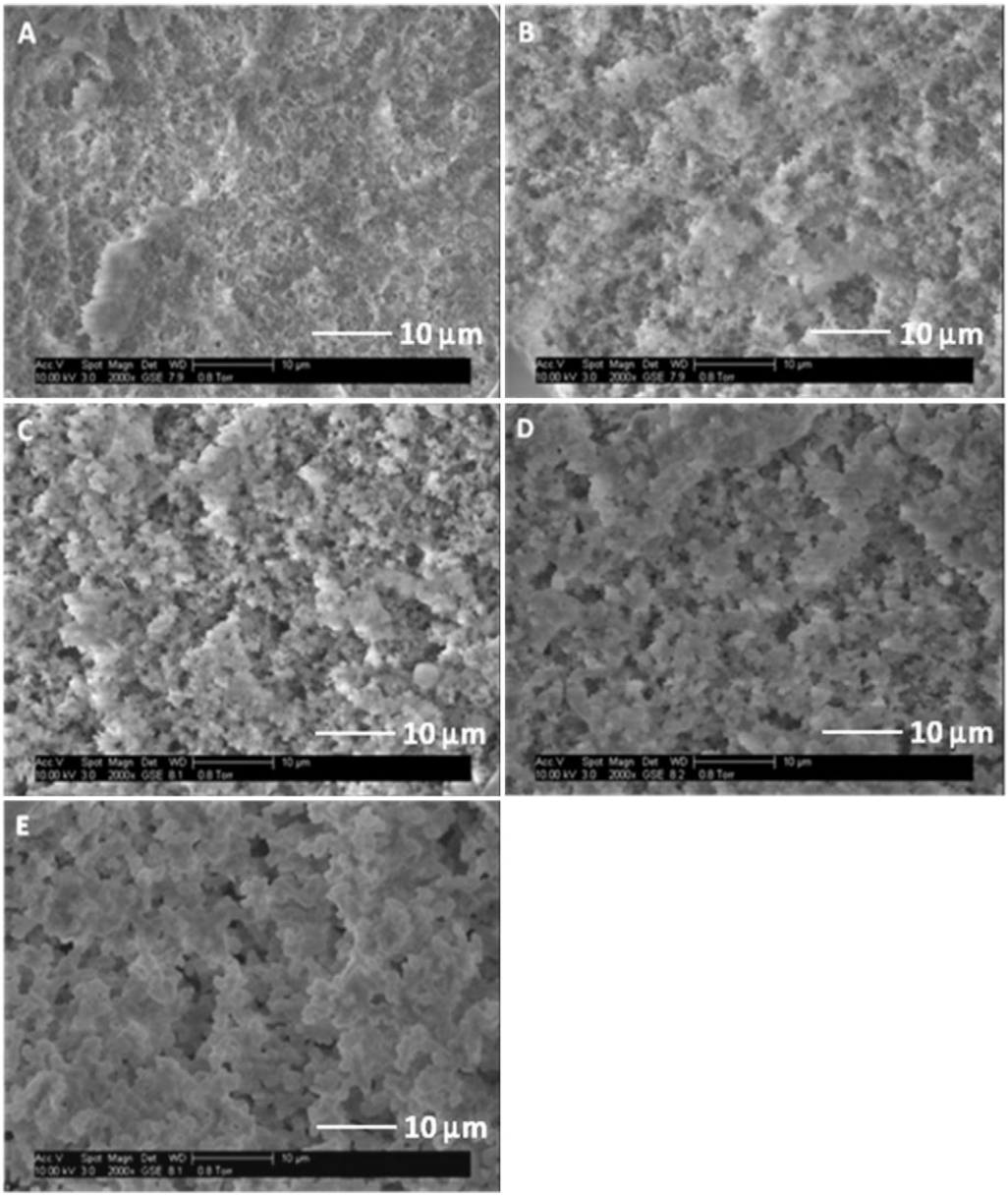


Fig. 2. SEM images of poly(1,12-DoDDMA) monoliths prepared with different percentages of methanol in methanol/dodecanol solution: (A) 59.3%, (B) 61.5%, (C) 63.3%, (D) 64.3%, and (E) 66.5%.

to remove porogens and possible unreacted residual monomers. The monolithic columns were characterized by scanning electron microscopy using an FEI Philips XL30 ESEM FEG (Hillsboro, OR, USA) without coating with a conductive gold layer.

2.1.2. Capillary liquid chromatography

An Eksigent Nano 2D LC system (Dublin, CA, USA) was used to conduct all chromatographic experiments. The injection volumes were 20 nL for alkylbenzenes and 30 nL for alkylparabens. The two mobile phase components for gradient elution of alkylbenzenes and alkylparabens in RPLC were water (mobile phase A) and acetonitrile (mobile phase B). On-column detection was performed using a Crystal 100 variable wavelength UV–vis absorbance detector. Chrom Perfect software (Mountain View, CA, USA) was used for data collection and treatment. UV absorbance was monitored at 214 nm.

3. Results and discussion

3.1. Selection of porogens

The selection of porogenic solvent or solvent combination is an important step in the preparation of monoliths. One of the monomers, 1,12-DoDDMA, was chosen for detailed study of porogen selection. Several solvents with different polarities were used to synthesize the monoliths. It was found that 1,12-DoDDMA formed a monolith when dissolved in methanol and iso-butanol after UV light initiation. A soft or hard transparent gel was obtained with polymerization using toluene, THF, or ACN, indicating that these were potentially "good" solvents for 1,12-DoDDMA. Rigid macroporous monoliths were found when methanol and iso-butanol were combined with decanol or dodecanol. Toluene, THF, and ACN still resulted in gels when combined with decanol and dodecanol. Although 1,12-DoDDMA could form monoliths with

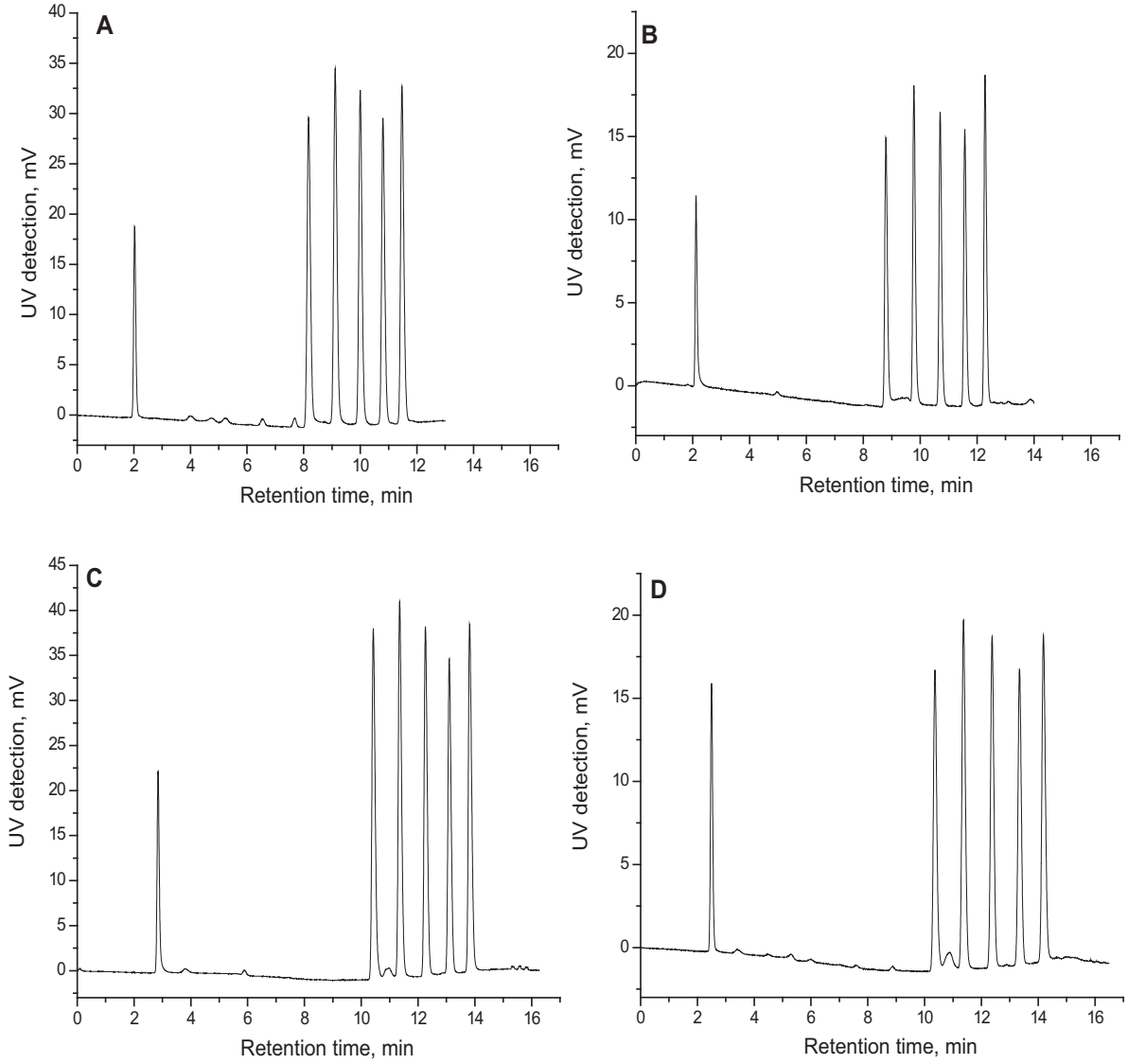


Fig. 3. (A), (B), (C), and (D) are RPLC separations of alkylbenzenes on monoliths synthesized from 1,5-PDDMA, 1,6-HDDMA, 1,10-DDDMA, and 1,12-DoDDMA, respectively. *Conditions*: 16 cm × 75 μm i.d. monolithic column; mobile phase component A was water, and B was acetonitrile; linear A–B gradient from 40% to 100% B in 10 min, and then isocratic elution with 100% B; 300 nL/min flow rate; on-column UV detection at 214 nm. Peak identifications: uracil, toluene, ethylbenzene, propylbenzene, butylbenzene and amylbenzene in order of elution.

decanol, the monoliths gave very poor chromatographic performance. When iso-butanol was combined with dodecanol, the final monolith gave very high back pressure (over 3000 psi at a mobile phase flow rate of 100 nL/min). Therefore, a combination of methanol and dodecanol appeared to be the best porogen system for the 1,12-DoDDMA monolith. The ratio of monomer to total porogens was investigated and the final ratio was set at 31.3:68.7. Table 2 shows the effect of methanol (poor solvent) to dodecanol (good solvent) ratio on back pressure in forming rigid monoliths from 1,12-DoDDMA. Fig. 2 shows SEM images of these monoliths, which indicate that the pore size becomes larger with an increase in methanol to dodecanol ratio.

3.2. Separation of small molecules

We obtained rigid structural monoliths using all of the monomers. All could be used to separate alkylbenzenes and parabens. Fig. 3 shows gradient elution chromatograms of uracil, toluene, ethylbenzene, propylbenzene, butylbenzene, and amylbenzene with the monoliths listed in Table 1. The flow rate was 300 nL/min and the gradient was 40–100% B in 10 min. A mixture of ACN and water (70%/30%, v/v) was used as the solvent for the alkylbenzene sample (0.25%, v/v each alkylbenzene

Table 2
Effect of methanol percentage in methanol/dodecanol solutions on column back pressure for a poly(1,12-DoDDMA) monolith.[a]

% Methanol[b]	Column back pressure (MPa)[c]
59.3	22.36 ± 0.49
61.5	12.76 ± 0.16
62.5	4.81 ± 0.10
64.3	3.20 ± 0.09
66.5	0.24 ± 0.01

[a] *Conditions*: 10 cm × 75 μm i.d. monolithic column, methanol, 300 nL/min flow rate.
[b] Percentage of mass.
[c] Average of three trials ± standard deviation.

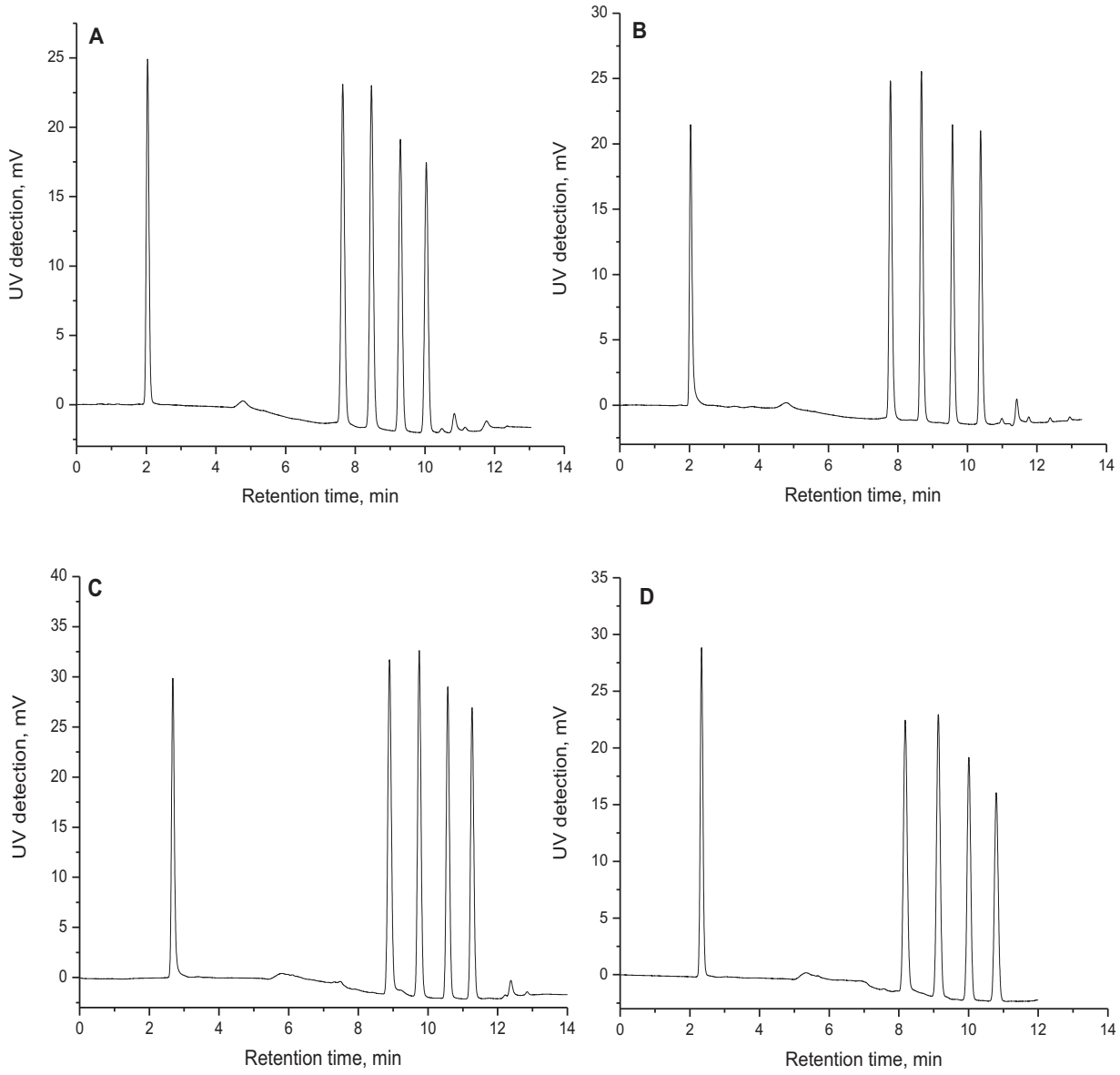


Fig. 4. (A), (B), (C), and (D) are RPLC separations of alkyl parabens on monoliths synthesized from 1,5-PDDMA, 1,6-HDDMA, 1,10-DDDMA, and 1,12-DoDDMA, respectively. *Conditions*: 16 cm × 75 μm i.d. monolithic column; linear A–B gradient from 20% to 100% B in 10 min, and then isocratic elution with 100% B; 300 nL/min flow rate; on-column UV detection at 214 nm, other conditions are the same as in Fig. 3. Peak identifications: uracil, methylparaben, ethylparaben, propylparaben and butylparaben, in order of elution.

standard). As can be seen in Fig. 3, all peaks had good symmetries and narrow peak widths at half peak height, ranging between 8.7 and 5.2 s for the alkylbenzenes. Fig. 4 shows gradient elution chromatograms of alkyl parabens. The flow rate was 300 nL/min and the gradient was 20–100% B in 10 min. A mixture of ACN and water (30%/70%, v/v) was used as solvent for the alkylparaben sample (0.7 mg/mL each alkylparaben standard). Columns prepared from 1,4-BDDMA, 1,3-BDDMA, and NPGDMA can also separate alkylbenzenes and alkyl parabens using the same conditions as in Figs. 3 and 4 (chromatograms not included). The resolution obtained using these columns was not as good as for poly(1,5-PDDMA), poly(1,6-HDDMA), poly(1,10-DDDMA), and poly(1,12-DoDDMA). Monoliths with longer alkyl-bridging chain length showed greater retention of both alkylbenzenes and alkylparabens, which was due to an increase in hydrophobicity of the monolith with longer alkyl-bridging chain.

Fig. 5 shows the elution of alkyl benzenes using a 1,6-HDDMA monolithic column with different gradients and flow rates. The six compounds were eluted within 8 min with better resolution using a 10 min gradient from 40% to 100% B and a flow rate of 600 nL/min in Fig. 5B compared to Fig. 5A. As expected, a shallower gradient led to longer elution time, and provided better resolution. For example, resolution values for toluene and ethylbenzene were 3.79 and 5.20 in Fig. 5A and C, respectively. The same trend was observed when a shallower gradient was used to separate alkylparabens with this column.

3.3. Chromatographic efficiency measurements

Column efficiencies were measured for all of the alkanediol dimethacrylate monoliths. The theoretical plate numbers varied between 30,000 and 35,500 plates/m for uracil as an unretained

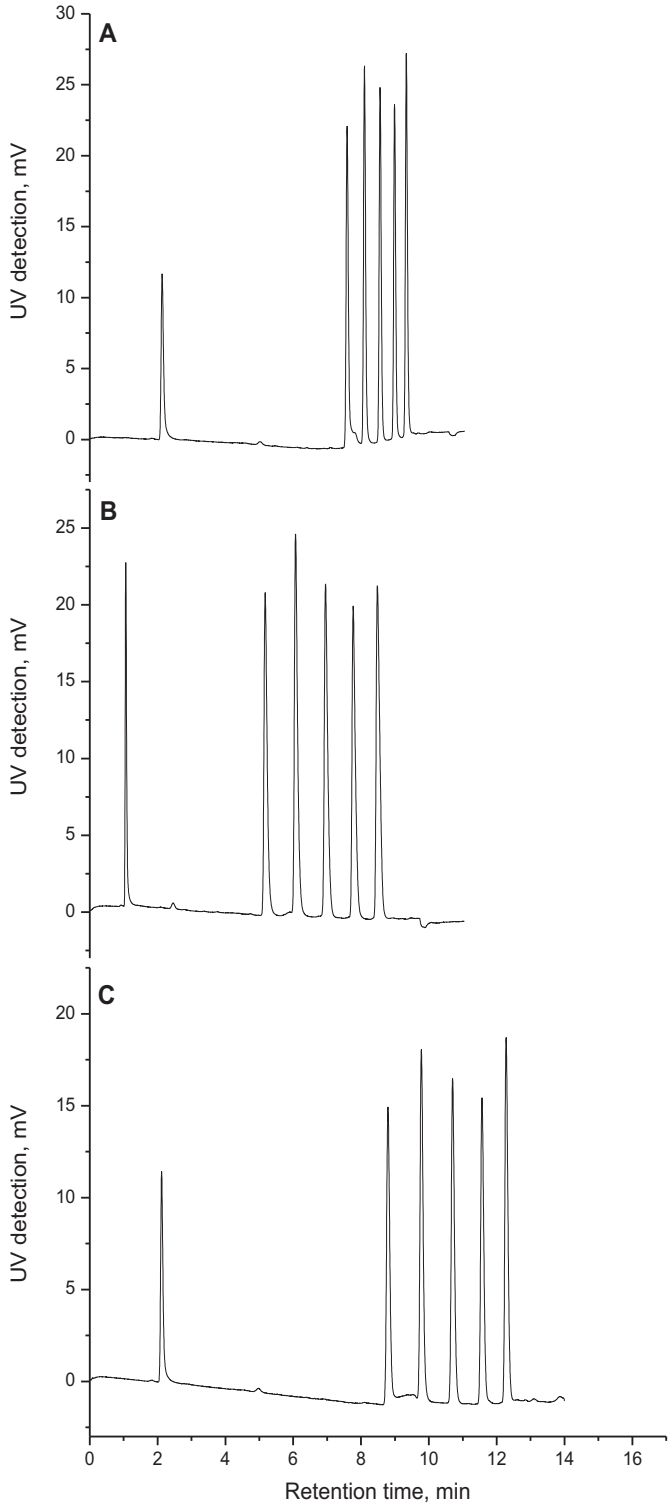


Fig. 5. Separations of alkyl benzenes on 1,6-HDDMA monolithic column. *Conditions*: linear A–B gradient from 40% to 100% B in (A) 5 min, 300 nL/min flow rate, (B) 10 min, 600 nL/min flow rate, and (C) 10 min, 300 nL/min flow rate; other conditions are the same as in Fig. 3.

compound at 120 nL/min (0.45 mm/s) flow rate, which was the optimized flow rate for the 1,6-HDDMA monolithic column based on its van Deemter curve (Fig. 6). The isocratic conditions used were 30% water/70% acetonitrile (v/v), 300 nL/min flow rate, and on-column UV detection at 214 nm.

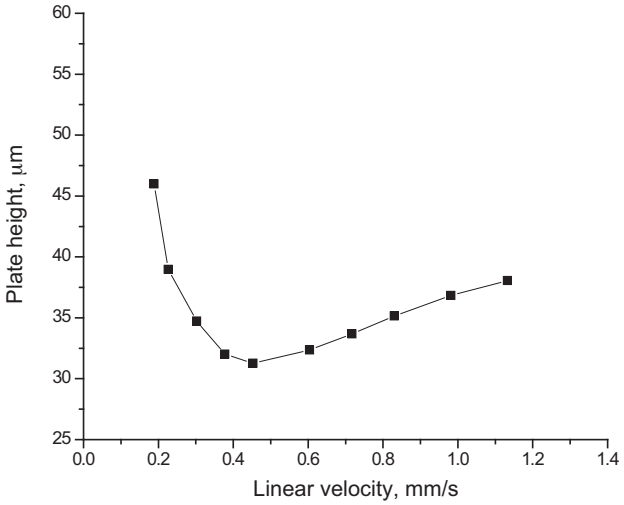


Fig. 6. Plate height versus linear velocity for a 1,6-hexanediol dimethacrylate monolithic column using uracil as an unretained compound. *Conditions*: 16 cm × 75 μm i.d. column; mobile phase component A was water, and B was acetonitrile; 30% A/70% B mobile phase.

The plate numbers for all of the monolithic columns were between 14,000 and 35,000 plates/m measured using uracil at 300 nL/min (i.e., 1.13 mm/s). Other conditions were the same as above. The column efficiencies (N/m)/retention factors (k) for toluene as a retained compound for all of the monolithic columns were 14,879/0.384 (1,4-BDDMA), 19,593/0.320 (1,3-BDDMA), 35,147/0.622 (1,5-PDDMA), 48,877/0.538 (NPGDMA), 51,610/0.890 (1,6-HDDMA), 53,779/0.573 (1,10-DDDMA), and 49,323/1.411 (1,12-DoDDMA). Fig. 7 shows chromatograms of alkylbenzenes using two different monolithic columns under isocratic conditions. The efficiencies of the alkanediol dimethacrylate-based monoliths with alkyl chains greater than C5 were comparable [21,34,35].

Two monomer pairs (i.e., 1,3-BDDMA and 1,4-BDDMA, and NPGDMA and 1,5-PDDMA) were used to compare monoliths from branching and non-branching alkyl groups of the same carbon number. The monoliths, especially NPGDMA, with two branching groups in the alkyl bridge between the two dimethacrylate groups gave higher efficiencies (plates/m) when compared to their corresponding linear isomeric polymers (19,593/0.320 and 14,879/0.384 for 1,3-BDDMA and 1,4-BDDMA, respectively, and 48,877/0.538 and 35,147/0.622 for NPGDMA and 1,5-PDDMA, respectively). This is most likely due to differences in monolith morphology and pore size distribution of the monoliths prepared from the different monomers.

3.4. Monolith morphologies

Fig. 8 shows SEM images of monoliths synthesized from 1,4-BDDMA, 1,3-BDDMA, NPGDMA, 1,5-PDDMA, 1,6-HDDMA, 1,10-DDDMA, and 1,12-DoDDMA. From the SEM images, we see that all seven monoliths formed with small globules. However, poly(1,10-DDDMA) and poly(1,12-DoDDMA) have much smaller globules than the other five dimethacrylate-based monoliths, which resulted in higher back pressures and sharper chromatographic peaks than obtained using the other three monoliths formed from linear alkanediol dimethacrylates.

3.5. Column permeability and stability

Column permeability was used to evaluate the stability of the monoliths. To obtain plots of back pressure versus flow rate,

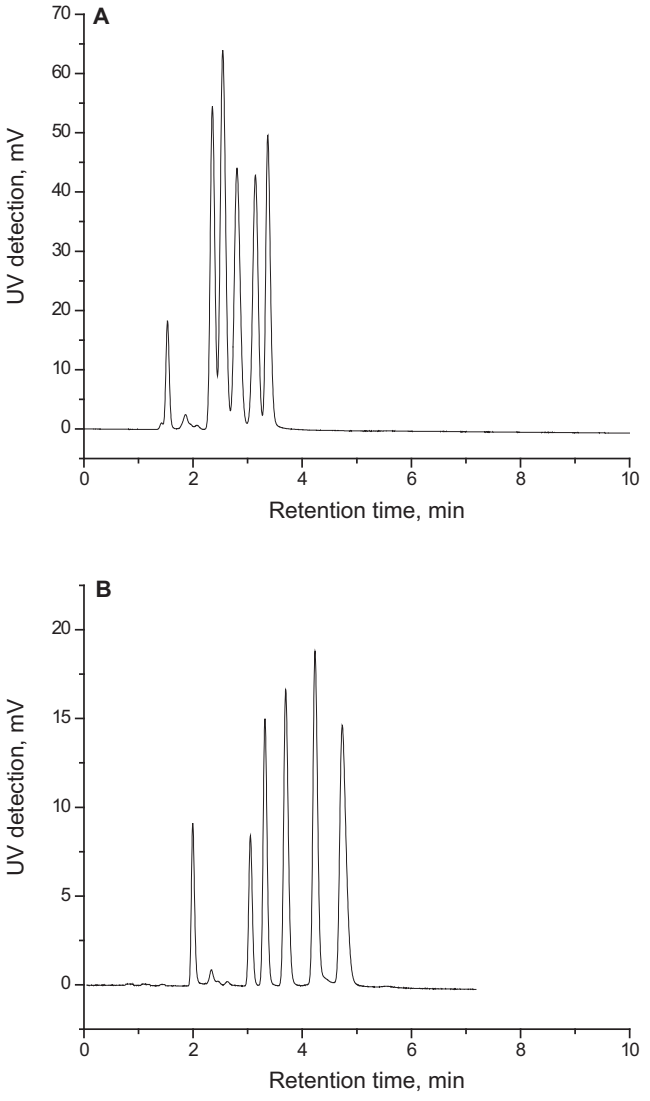


Fig. 7. Isocratic separations of alkylbenzenes on monoliths synthesized from (A) 1,3-BDDMA and (B) 1,6-HDDMA. *Conditions*: 16 cm × 75 μm i.d. monolithic column; mobile phase component A was water, and B was acetonitrile; 30% A/70% B mobile phase; 300 nL/min flow rate; on-column UV detection at 214 nm. Peak identifications: uracil, toluene, ethylbenzene, propylbenzene, butylbenzene and amylbenzene in order of elution.

acetonitrile, methanol and water were pumped through a 16-cm long monolithic column at six different flow rates from 0.05 to 0.5 μL/min. Linear relationships between back pressure and flow rate (R > 0.999 for all monoliths) clearly indicated that the monoliths were mechanically stable (data not included). The permeabilities calculated based on Darcy's law are listed in Table 3. For 1,5-PDDMA, 1,6-HDDMA, 1,10-DDDMA, and 1,12-DoDDMA monolithic columns, the results were similar for all three solvents, indicating that these monoliths shrank or swelled very little in solvents of different polarities. Monoliths with shorter alkyl-bridging chains, especially poly(1,4-BDDMA), had greater permeabilities. This may be due to the fact that monoliths with shorter alkyl-bridging chains have less hydrophobicities.

3.6. Reproducibility of poly(1,6-HDDMA)

In addition to good chromatographic performance, reproducibility and stability are basic requirements for a monolithic column, especially when the column is to be used for routine

Table 3
Permeabilities of poly(alkanediol dimethacrylate) monolithic columns using different liquids.

Liquid	Relative polarity[a]	Viscosity (mPa s)[b]	Permeability ($\times 10^{-14}$ m^2)[c,d]						
			1,4-DDMA	1,3-BDDMA	NPGDMA	1,5-PDDMA	1,6-HDDMA	1,10-DDDMA	1,12-DoDDMA
Water	1.00	0.89	22.57 ± 3.88	4.48 ± 0.39	0.77 ± 0.07	7.12 ± 1.11	5.52 ± 1.14	0.96 ± 0.01	1.07 ± 0.10
Acetonitrile	0.46	0.37	39.44 ± 5.08	6.10 ± 0.24	2.99 ± 0.64	8.16 ± 0.20	5.80 ± 0.23	0.77 ± 0.02	1.08 ± 0.04
Methanol	0.76	0.54	16.33 ± 3.90	6.44 ± 0.22	0.72 ± 0.10	6.42 ± 0.08	4.81 ± 0.28	0.74 ± 0.01	0.99 ± 0.02

[a] Relative polarity data are from Ref. [36].
[b] Viscosity, η, data are from online CRC Handbook of Chemistry and Physics, 89th ed., CRC, Boca Raton, FL, 2008–2009.
[c] Permeability $k = \eta Lu/\Delta P$, where η is the viscosity, L is the column length (16 cm in this case), u is the solvent linear velocity, and ΔP is the column back-pressure.
[d] Average of six trials at different flow rates ± standard deviation.

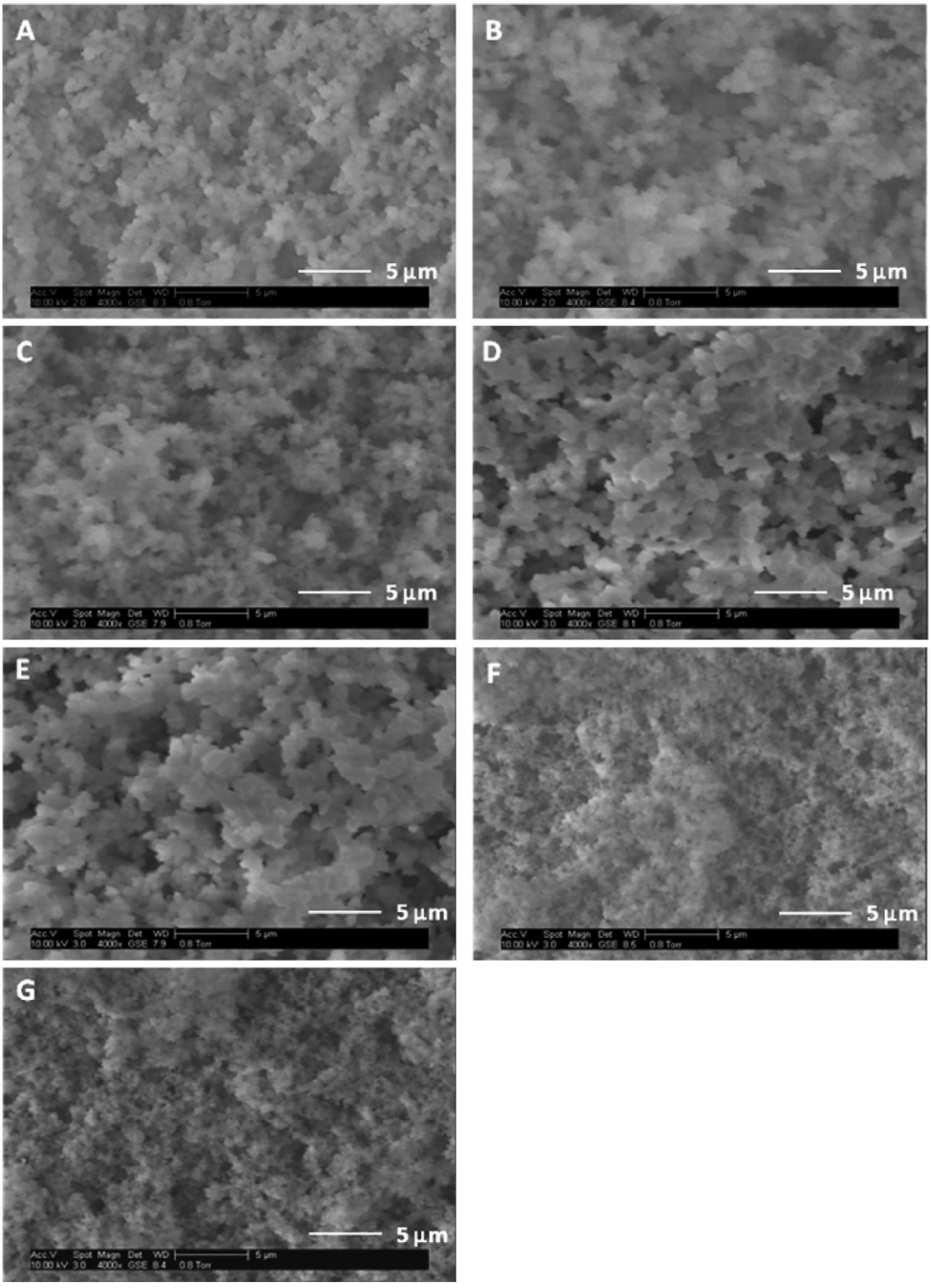


Fig. 8. SEM images of monoliths. (A) Poly(1,4-BDDMA), (B) poly(1,3-BDDMA), (C) poly(NPGDMA), (D) poly(1,5-PDDMA), (E) poly(1,6-HDDMA), (F) poly(1,10-DDDMA), (G) poly(1,12-DoDDMA); see structures in Fig. 1.

analysis. Run-to-run and column-to-column reproducibilities (see Table 4) were measured for the poly(1,6-HDDMA) monolithic column. The run-to-run and column-to-column RSD values based on retention times ($n = 3$) were 0.25% and 1.20%, respectively. More than 60 runs were conducted to test the stability of the poly(1,6-HDDMA) monolithic column (Table 1). There was no noticeable change observed in column performance. Due to the highly crosslinked network, monoliths synthesized from single crosslinking monomers typically exhibited excellent stability, as demonstrated here and in our previous work [23,26].

Table 4
Retention times of uracil and alkylbenzenes showing column-to-column reproducibility of three independently prepared 1,6-HDDMA columns.[a]

	Retention time (min)					
	Uracil	Toluene	Ethylbenzene	Propylbenzene	Butylbenzene	Amylbenzene
Column 1	2.12	8.79	9.78	10.70	11.57	12.28
Column 2	2.11	8.77	9.77	10.69	11.56	12.26
Column 3	2.07	8.79	9.78	10.71	11.58	12.28
Relative standard deviation (RSD)	1.20%	0.14%	0.07%	0.09%	0.07%	0.08%

[a] Conditions are the same as in Fig. 3.

4. Conclusions

New monolithic RPLC stationary phases based on single monomers were synthesized using UV-initiated free radical polymerization. These new monolithic columns were successfully used for the separation of low-molecular weight compounds under RP conditions. SEM images were taken which showed different globule sizes for monoliths made from different dimethacrylates. Smaller globules resulted in higher back pressures and sharper chromatographic peaks. Among the monoliths prepared from linear alkanediol dimethacrylates, poly(1,10-DDDMA) provided the highest efficiency (plates/m) overall. Investigation of two pairs of isomer monomers showed that monoliths with branching groups in the alkyl bridge between the two dimethacrylate groups gave higher efficiencies compared to their linear counterparts. Gradient elution of alkylbenzenes and alkylparabens was achieved with high resolution using all seven columns. The test analytes were completely separated in 15 min using 300 nL/min (1.13 mm/s) flow rate. Good run-to-run and column-to-column ($n = 3$) reproducibilities were observed, which are mainly attributed to the use of single monomers in their preparation.

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