One-pot synthesis of polymer monolithic column by combination of free radical polymerization and azide-alkyne cycloaddition "click" reaction and its application in capillary liquid chromatography

Supporting Information

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SUMMARY

This supporting information file includes experimental section, additional results and information as described in the text of the main article. Including:

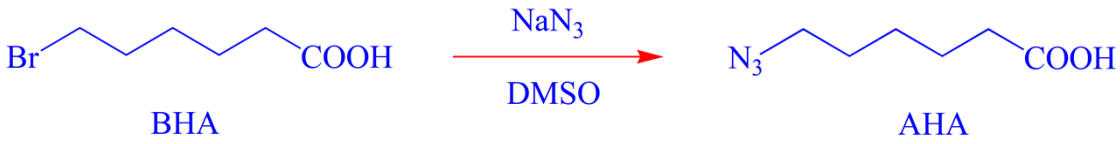
Experimental

Synthesis of 6-azidohexanoic acid

6-Bromohexanoic acid (6.5 g, 33.3 mmol) and sodium azide (6.5 g, 100mmol) were dissolved in DMSO and stirred at room temperature for 8 h. The reaction mixture was then dissolved in CH_2Cl_2, washed with $NaHCO_3$ aqeous solution (1 mol/L), and hydrochloric acid (0.1 mmol/L), dried over $MgSO_4$, and concentrated by rotary evaporation. Residual DMSO was removed by Kugelrohr distillation at 120℃. Distillation at 160℃ gave 6-azidohexanoic acid (AHA) as a colorless liquid (2.98 g, 57 %). The schematic synthesis of AHA was shown in Fig.S1 (Supporting Information). The product was characterized by IR, electrospray ionization mass spectrometry (ESI-MS) and NMR with results as follows: IR: 2090 cm^{-1} for N=N=N. ESI-MS, *m/z* at 156.1 [$M-H^-$] and 180.1 [$M+Na^+$] for $C_6H_{11}N_3O_2$. ^1H NMR ($CDCl_3$, 300 MHz): δ ($CHCl_3$ = 7.26 ppm) 11.43 (br, 1H, COO*H*), 3.28 (t, 2H, CH_2N_3), 2.38 (t, 2H, CH_2COOH), 1.65 (m, 4H, $CH_2CH_2CH_2CH_2CH_2$), 1.43 (m, 2H, $CH_2CH_2CH_2CH_2CH_2$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ ($CHCl_3$ = 77.0 ppm) 180.1 (*C*=O), 51.2 (CH_2N_3), 33.9 (CH_2COOH), 28.5 ($CH_2CH_2N_3$), 26.2 (CH_2CH_2 CH_2N_3), 24.2 (CH_2CH_2COOH) ppm.

Preparation of bulk monolith via free radical polymerization combined with CuAAC click chemistry

For FT-IR characterization and measurement of pore properties, bulk monolith was synthesized as follow: AHA (36 μL), PMA (31 μL), EDMA (29 μL), DMSO (200 μL), 1-dodecanol (219 μL), catalyst CuI (0.2 mg), and initiator AIBN (1 mg) was added to a small centrifuge tube. The obtained prepolymerization mixture was sonicated for 20 min and then purged with nitrogen for 10 min. Afterwards the centrifuge tube was submerged into water bath at 70 ℃ for 24 h. The cured bulk monolith was extracted with methanol, 20 mM EDTA solution and water to remove residuals. For the following characterization, the bulk monolith was cut into small pieces and grinded using mortar and pestle. Then the grinding powders were dried in a vacuum at 50 ℃ for two days.



BHA AHA

Fig.S1 Scheme for synthesis of AHA.

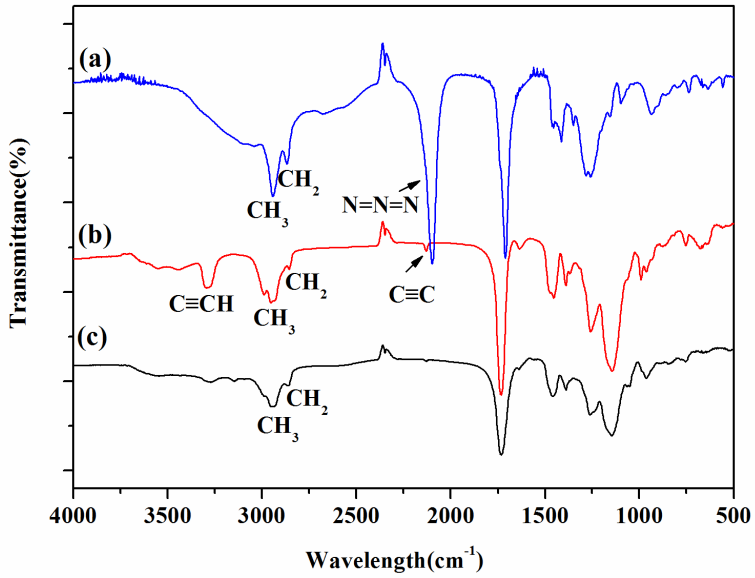


Fig.S2 FT-IR spectra of AHA (a), poly (PMA-co-EDMA) monolith (b) and poly (AHA-co-PMA-co-EDMA) monolith (c).

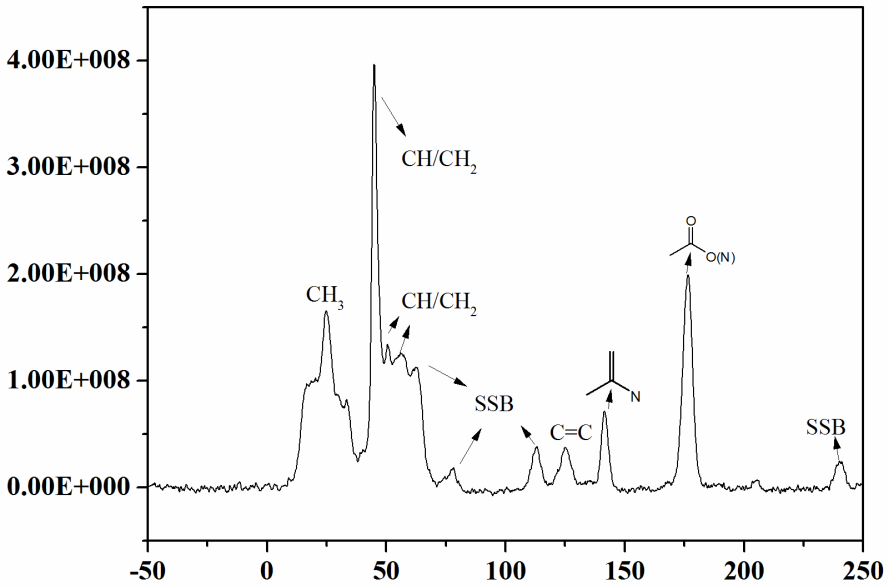


Fig.S3 ^{13}C nuclear magnetic resonance (NMR) spectra of poly (AHA-co-PMA-co-EDMA) monolith.

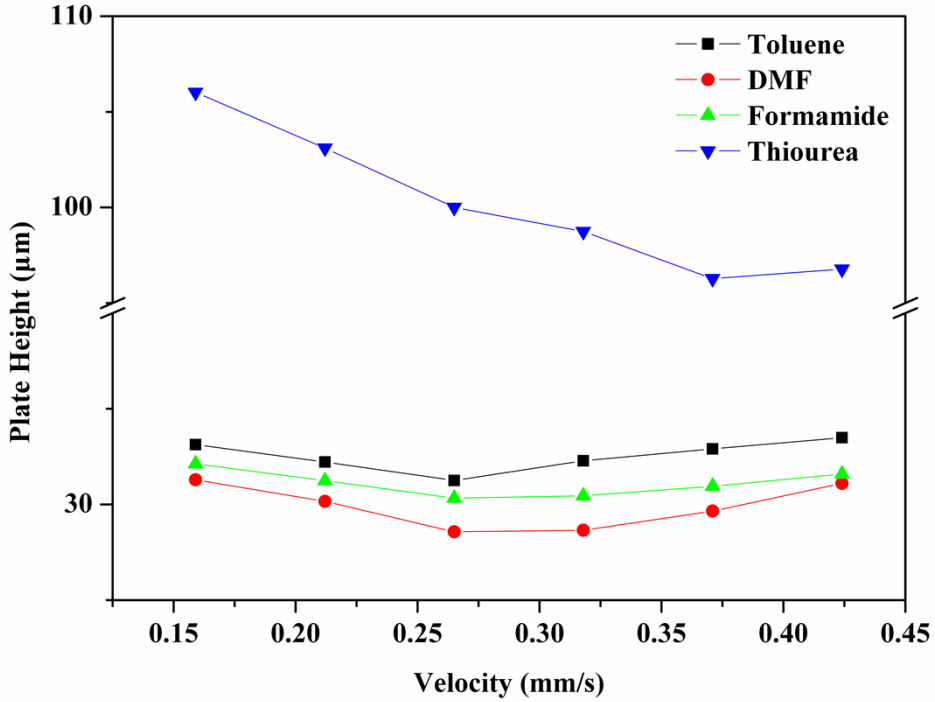


Fig.S4 Dependence of the plate height of four test solutes on the linear velocity of the mobile phase by the poly (AHA-co-PMA-co-EDMA) monolithic capillary column.

Conditions: monolithic capillary column, effective length of 25 cm × 100 i.d., total length of 50 cm; mobile phase, 100% ACN; Flow rate(actual flow rate after splitting): 0.05 mL/min (125 nL/min); Detection wavelength: 214 nm.

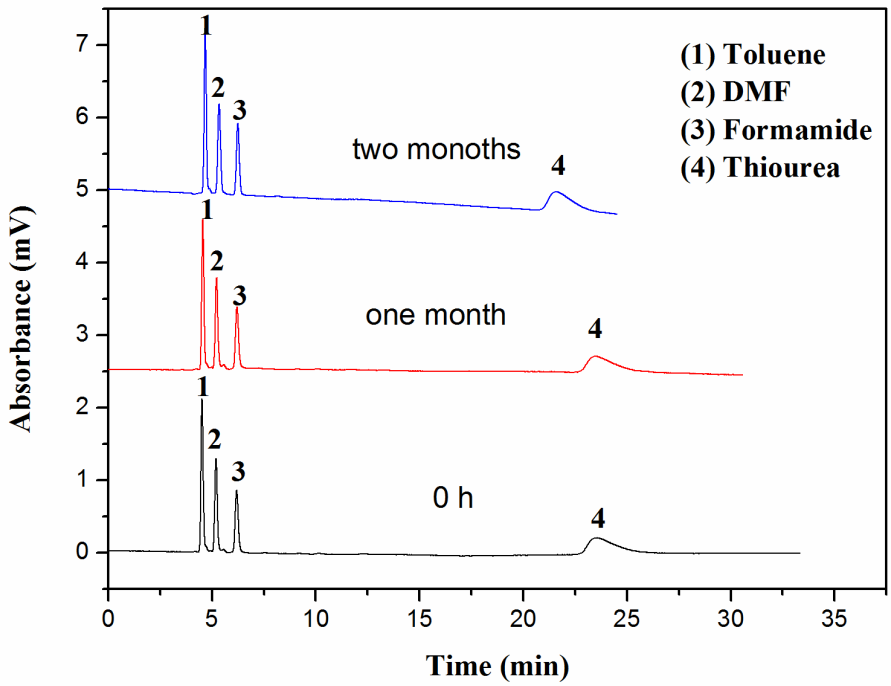


Fig.S5 Separation of four test solutes on the poly (AHA-co-PMA-co-EDMA) monolith immediately after its preparation, after one month and after two month. Conditions: ACN/water: 100/0 (v/v %); Flow rate(actual flow rate after spiltting): 0.05 mL/min (125 nL/min); Pump pressure: 3.0 MPa; Detection wavelength: 214 nm; the analytes are (1) toluene (100 ppm); (2) DMF (100 ppm); (3) formamide (100 ppm); (4) thiourea (100 ppm).

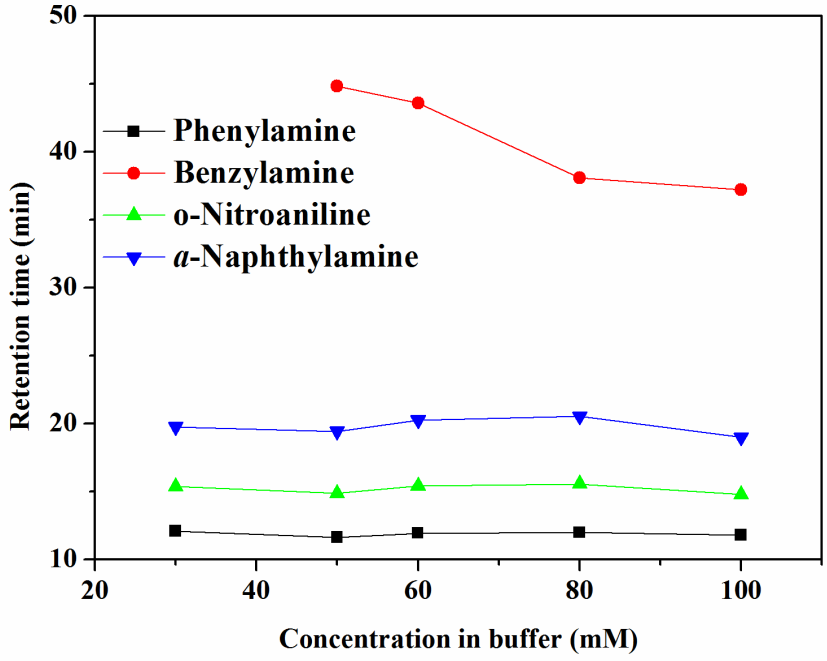


Fig.S6 Effect of salt concentration on retention time of anilines on the poly (AHA-co-PMA-co-EDMA) monolithic column.

Conditions: Mobile phase: PB (pH 5.5) containing 45% (v/v) ACN with various concentration in buffer; Pump pressure: 6.4 MPa; Flow rate (actual flow rate after splitting): 0.05 mL/min (125 nL/min); Detection wavelength: 214 nm.

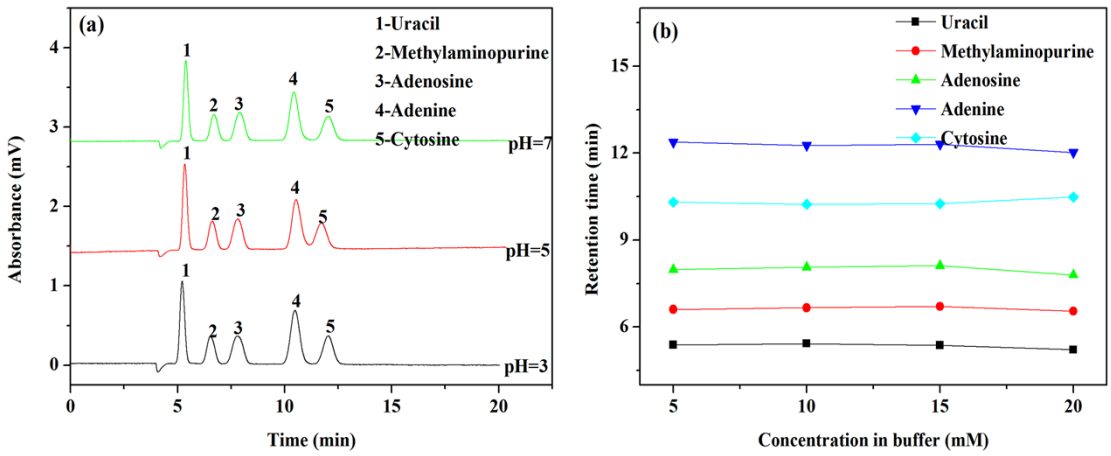


Fig.S7 (a) Separation of five nucleosides and nucleobases at varying pH on the poly (AHA-co-PMA-co-EDMA) monolith and (b) effect of salt concentration on retention time of nucleosides and nucleobases on the poly (AHA-co-PMA-co-EDMA) monolith.

Conditions for (a): Mobile phase: 20 mM PB containing 88% ACN with various pH;

Flow rate (actual flow rate after splitting): 0.05 mL/min (125 nL/min); Pump pressure: 4.2 MPa; Detection wavelength: 214 nm; For (b), all the conditions are same as (a) except for pH 3.0; The analytes are (1) uracil (100 ppm); (2) methylaminopurine (100 ppm); (3) adenosine (100 ppm); (4) adenine (100 ppm); (5) cytosine (100 ppm).