Novel In-Capillary Polymeric Monoliths Arising from Glycerol Carbonate Methacrylate for Flow-Through Catalytic and Chromatographic Applications

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1. Materials and Methods

1.1. Experimental:

Glycerol carbonate methacrylate (GCMA) was supplied by Specific Polymers. Ethylene glycol dimethacrylate (EGDMA, 98%), 3-(Trimethoxysilyl)propyl methacrylate (γ-MAPS, 98%), Sodium borohydride ($NaBH_4$, ≥98%), Sodium hydroxide (NaOH, 1 M), Hydrochloric acid (HCl, 0.1 M for HPCE), , 2,2-Dimethoxy-2-phenylacetophenone (DMPA, 99%), Toluene (anhydrous, 99.8%), 1-Dodecanol (≥98%) and 4-Mercaptobutyric acid were purchased from Sigma Aldrich. 2,2'-Azobisisobutyronitrile (AIBN, 98%) was obtained from Acros Organics. 4-Nitrophenol (*p*-nitrophenol, 99%), Potassium tetrachloroplatinate (K_2PtCl_4, 99,9% metal basis), 1-Octanethiol (98%) and Allylamine (98%+) were purchased from Alfa Aesar. Acetone, HPLC grade Acetonitrile (ACN) and Ethanol absolute (anhydrous) were supplied by Carlo Erba. n-Nonane comes from VWR Chemicals. All reagents were used without further purification. 18.2 MΩ deionized water was filtered through a Milli-Q Plus purification pack. Fused silica capillaries with a UV-transparent external coating (100 µm I.D.) were obtained from Polymicro Technologies.

1.2. Instrumentation:

An HPLC pump (Shimadzu LC-10ATVP) was used to flush monolithic columns with 2-nitrophenol solutions along with mobile phase. Spectrolinker XL-1500 UV Crosslinker (Spectronics Corporation) equipped with eight lamps (8 × 15W, 365 nm) was used to photoinitiate the polymerization. UV-Vis spectra were recorded on a Cary 60 UV-Vis Spectrophotometer from Agilent Technologies. Chemical Structure of the monoliths was investigated using a Raman apparatus XPlora One from Horiba Jobin Yvon equipped with a

laser at 638 nm. Samples were investigated in different places to control the homogeneity. The acquisition time was fixed at 1 min. Scanning Electron Microscopy (SEM) investigations of the materials were performed with a MERLIN microscope from Zeiss equipped with InLens, EBSD and SE2 detectors using a low accelerating tension (2-3 kV) with a diaphragm aperture of 30 μm. Prior to analyses, the samples were coated with a 4-nm layer of palladium/platinum alloy in a Cressington 208 HR sputter-coater. All chromatographic experiments were carried out using a Dionex Ultimate 3000 HPLC RSLC nanosystem (Sunnyvale, CA, USA) equipped with a 10 nL In-line split loop manual injector and a Dionex VWD 3400 RS detection system operating at a fixed wavelength λ = 214 nm.

1.3. Synthesis of the GCMA-based functionalized monolithic capillaries

The synthesis of the (GCMA-*co*-EGDMA) monolithic columns relies on a three-step process involving *(i)* the synthesis of the porous methacrylate matrix ; *(ii)* the chemical modification of the matrix with allylamine and *(iii)* a thiol-ene reaction with either mercaptobutyric acid or 1-octane thiol.

1.3.1. Surface pre-treatment of the capillaries

In order to ensure the stability of the monolithic column, the inner wall of the capillaries was submitted to a vinylization step. 3-(Trimethoxysilyl)propyl methacrylate (γ-MAPS) was used as a bifunctional reagent allowing for the covalent attachment of the polymeric material onto the wall of the capillaries. The procedure was as follows: fused silica capillaries were treated with 1 M NaOH for 1h at room temperature and subsequently heated for 2 h at a temperature of 100 °C. Capillaries were flushed with 0.1 M HCl for 10 min, rinsed with deionized water for 10 min and then with acetone for 15 min. Thereafter, capillaries were purged with dry nitrogen gas for 2 h at a temperature of 120 °C. 30% (v/v) 3-(trimethoxysilyl)propyl methacrylate solution in toluene was allowed to react overnight with inner silanols at room temperature. Last, the capillaries were rinsed with toluene for 15 min and dried under a stream of nitrogen gas for 1 h. The capillaries thus treated were stored at 4 °C prior to use.

1.3.2. *In situ* synthesis of the porous monolith

In order to find the adequate mixture to realize further experiments, the porous monolith was prepared through a photochemically-driven free radical polymerization reaction. Different solutions were tested, consisting of variations of the following combination: GCMA as a functional monomer, EGDMA as a crosslinker, toluene and dodecanol (or nonane, depending of the samples) as porogenic solvents and AIBN as an initiator (4 mg, 1% w/w with respect to the total amount of monomers). Mixtures were sonicated for about 15 min to obtain homogeneous solution. The pre-treated capillary was completely filled with the polymerization mixture by immersing the inlet of the capillary into a reservoir and by pushing through the solution previously prepared under nitrogen pressure (3 bar). After flushing with a large excess of polymerization solution, both ends of the capillary were sealed with rubber septa and the capillary was placed within a Spectrolinker XL-1500 UV and irradiated under an overall intensity of 8 $J.cm^{-2}$ (800 s). After the polymerization was completed, the septa were removed and the monolith capillary was washed with ACN for 1 h (5 $\mu L.min^{-1}$) to remove the unreacted monomers and the porogenic solvent. Subsequently, back pressure in the as-prepared capillaries was measured in order to determine their permeability.

1.3.3. *In situ* functionalization of the porous monolith with allylamine

The carbonate cycles stemming from the GCMA monomer were functionalized with alkene groups through nucleophilic substitution. The reaction was performed *in situ* by flushing the monolith capillary with a solution of allylamine (1 M = 160 µL in 2 mL of ACN in a reservoir) pushed under nitrogen pressure (50 bars) during 2 h at room temperature. Thereafter, the monolithic capillary was washed with ACN for 1 h in order to remove the unreacted allylamine. The nucleophilic substitution yield was evaluated through *in-situ* Raman spectroscopy performed on monolithic capillary samples.

1.3.4. Thiol-ene reaction with thiol based molecules

The capillary was flushed by anhydrous absolute ethanol for 1 h to remove the previous solvent. Then, the surface-grafted alkene moieties provided the reactive sites for the modification by thiol-containing molecules (*e. g.* 4-mercaptobutyric acid or 1-octanethiol) *via* thiol-ene-based “click” chemistry. Photochemical thiol-ene reaction was proceeded as follows: mercaptobutyric acid (0.1M) or 1-octanethiol (1 M) and DMPA (4 mg, 1 wt%) were

dissolved in 2 mL of absolute ethanol. The solution was flushed into the capillary during 2 h under UV light (λ = 365 nm). Then the capillary was rinsed with pure absolute ethanol during 1 h to remove unreacted reagents. Conversion of double bonds was evaluated through *in situ* Raman spectroscopy performed on monolithic capillary samples.

1.4. *In situ* formation of platinum nanoparticles

The carboxyl-modified capillary was flushed first, with deionized water during 10 minutes, and then with a solution of 43 mg of K_2PtCl_4 into a 2 mL mixture of water during 30 min. it was then rinsed with H_2O during 10 minutes to remove the non-adsorbed platinum ions. Then a solution of 7 mg of $NaBH_4$ (0.1 M) in water was flushed during 1 h. Finally the capillary was washed 10 min deionized water.

1.5. Reduction of *p*-nitrophenol by heterogeneous catalysis

A freshly prepared solution containing 200 µL of *p*-nitrophenol (5 mg in 10 mL of H_2O), 200 µL of $NaBH_4$ (114 mg in 10 mL of water) in 5 mL of deionized water was injected in the loop (20 µL, Rheodyne) of a HPLC pump system, the solution coming out from the in-capillary PtNPs decorated monoliths was collected and then analysed by UV-Vis spectrophotometry. To undoubtedly evidence the catalytic effect of PtNPs, blank tests were performed with monolithic microreactors without nanoparticles.

1.6. Reversed-Phase Separation of Hydrophobic Analytes by Capillary High Pressure Liquid Chromatography (nano-LC)

The capillary modified with 1-octanethiol was used in the resolution of 4 alkylbenzenes, namely toluene, *n*-propylbenzene, *n*-pentylbenzene and 1-phenylhexane. DMF was chosen as the unretained compound. The flowrate was fixed at 0.4 $\mu L.min^{-1}$ and the mobile phase was constituted by a mixture of ACN/water (60/ 40 v/v). 10 nL of the analyte mixture was injected. In a second time, the mobile phase composition was modified so as to determine to clearly evidence the reversed-phase chromatographic mode by plotting the logarithm of

retention factor versus % amount of ACN ranging from 50 to 65 % (v/v) for each of the analytes.

Table S1. Composition of polymerization mixtures used for the preparation of in-capillary monoliths with the corresponding permeabilities.

Polymerization Mixture	% v/v toluene/DOH[a]	% v/v toluene/C_9H_{20}	% w/w monomers/solvents	% w/w GCMA/EGDMA	B_0[b] (10^{-14} µm²)
1	75/25	-	36.2/33.8	34.4/65.6	4.31
2	-	50/50	36.2/63.8	34.4/65.6	0.89
3	40/60	-	39.2/60.8	34.4/65.6	1.83
4	100/0	100/0	36.2/63.8	34.4/65.7	12,21
5	0/100	-	36.2/63.8	34.4/65.8	[a]
6	50/50	-	36.2/63.9	34.4/65.9	3,56
7	25/75	-	36.2/63.10	34.4/65.10	[a]
8	60/40	-	36.2/63.11	34.4/65.11	5,23
9	-	0/100	36.2/63.12	34.4/65.12	[a]
10	40/60	-	36.2/63.13	34.4/65.13	[a]
11	40/60	-	44,2/55.8	34.4/65.14	1,08
12	40/60	-	49,8/50,2	34.4/65.15	1,78
13	40/60	-	39,2/60,8	25,1/74,9	11,60
14	40/60	-	39,2/60,8	43,8/56,2	16,74

[a] Permeability impossible to measure due to monolithic capillary clogging

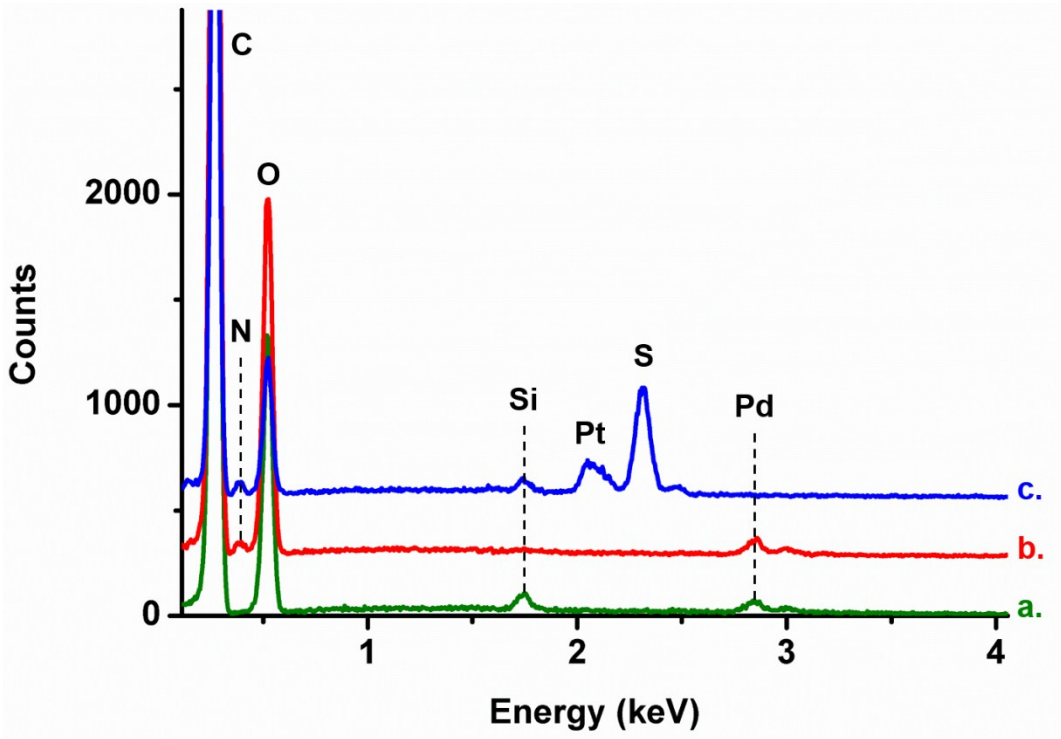

Figure S1. *In-situ* EDX semi-quantitative analysis of monolithic GCMA-based capillary before (a) and after functionalization with allylamine (b) and subsequent thiol-ene addition of 1-octane thiol (c).