Supplementary Material (ESI) for The Analyst

UV-LED photopolymerised monoliths

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Electronic Supplementary Information

Pretreatment of fused silica capillaries or channels of microfluidic chips

Silanization with 3-(trimethoxysilyl)propyl methacrylate (TMSPM) of inner capillary walls or chip channels in order to provide good attachment of the formed monolith to the walls was conducted using the method introduced by the group of Svec[4, 8, 12]. In brief, Polymicro transparent poly(tetrafluoroethylene) (PTFE) coated fused silica capillaries (100 μm i.d., Composite Metal Services Ltd.) were flushed with 1.0 M NaOH, 0.1 M HCl and distilled water for 10 min each, then dried with nitrogen for 10 min. The capillary was filled with the silanization mixture (0.5 ml acetone, 0.5 ml TMSPM), capillary ends were sealed with a rubber septum and the capillary was left in a water bath for 20 h at 60ºC. Then the surface modified capillary was flushed with methanol (10 min), and dried with nitrogen (10 min). In case of microfluidic chips (channels N5 and N2 of 320 μm and 640 μm depth, respectively, of cyclo-olefin copolymer (COC) microfluidic snake mixer slide SMS0104, ThinXXS Microtechnology AG) ethanol was used instead of acetone, and the chip with the silanization solution was kept overnight at room temperature.

Photopolymerisation

Methacrylic monoliths were synthesised using glycidyl methacrylate (GMA) as a main monomer and ethylene dimethacrylate (EDMA) as a crosslinker (1:1 in volume). Mixture of cyclohexanol and decanol (1:2) was used as porogenic solvent[2]. All chemicals were purchased from Sigma Aldrich.

The photopolymerisation experiments followed generally well established procedures[2, 3, 23] with details briefly summarised as follows. A typical polymerisation mixture (400 μl) consisted of 60 μl GMA, 60 μl EDMA, 1.26 mg (1% to monomer) photoinitiator (DAP or MK), 95 μl of cyclohexanol, and 185 μl of decanol (1:2). Monomer/solvent ratio used was 30/70 to 40/60 (v/v). After sonication and purging with nitrogen polymerisation mixture was filled into the silanized fused silica capillary or channel of microfluidic chip and both ends were sealed with a rubber septum or micro plug. Prior to photopolymerisation, the capillary was masked using an opaque microtight sleeve of 395 μm i.d. (F-185, Upchurch Scientific), microfluidic chip was masked with black adhesive tape.

The setup for photopolymerisation experiments (Fig. 1): The LED (255 nm or 370 nm, see Tab.1) was positioned at a distance of 0 to 30 mm (*L* in Fig. 1) from the capillary or chip and capillary/chip was exposed to UV light for the desired length of time (5 - 60 min). After polymerisation the residual monomer and solvents were flushed out with methanol (1 μl/min) using HPLC pump (Waters 510) and the monolith in the channel was dried by the stream of nitrogen (5 min).

SEM characterisation

Scanning electron microscopy (SEM) system used was a Hitachi S-3000N. All samples were gold-sputtered prior to imaging in order to minimise charging and improve the image quality (contrast).

Backpressure characterisation

The backpressures of the obtained monoliths were measured using Applied Biosystems 400 Solvent Delivery System (water, 1 μl/min, 20ºC). The measured values of 6-56 bars/cm were compared with monolith backpressure values (normalised for the same conditions 100 μm i.d., 1 μl/min, water) given by Rohr *et al*[4] for the same concentration of methacrylic monomers and the same exposure time (10 min) as demonstrated below.

Table Example of backpressure recalculations when comparing literature value with data obtained in this study

	Rohr *et al*[4] (Fig. 5)	**This study**
Capillary i.d.	100 μm	100 μm
Eluent	Water	Water
Volumetric flow rate (F, μl/min)	0.1 μl/min	1 μl/min
Length of monolith (L, cm)	8.5 cm	3.5 cm
Measured backpressure (Δp, MPa))	0.5 MPa	20 bars
Calculated per 1 cm column length (Δp/L, MPa/cm)	0.5 MPa / 8.5 cm = 0.0588 MPa/cm	20 bars / 3.5 cm = 5.71 bars /cm
MPa to bar conversion	0.588* bars / cm	---
Calculated for flow rate F= 1 μl/min	**5.88 bar/cm ≈ 6 bar/cm**	**5.71 bar/cm ≈ 6 bar/cm**

*1 Pa = 10^{-5} bar, *i.e.* 0.1 MPa = 1 bar

Microfabrication of microfluidic chip

A polymethylmethacrylic (PMMA) chip with micromilled channels was used for photopolymerisations of GMA/EDMA to create monolithic electro-osmotic pump (EOP). PMMA chip was designed using CAD 3D Excalibur software (Progressive software corporation, USA) and were micromilled as described by F.-Q. Nie *et al.*[26]. In brief, the channels within the PMMA plates were fabricated through direct micro-milling (Datron 3D M6, Datron tecchnology Ltd., Milton Keynes, UK). Ten 0.4 mm x 0.4 mm channels, each 10 mm long, were milled. Two access holes (2 mm x 2 mm) were drilled at both ends of the channels for reservoir and outer power conections. One blank PMMA top-plate of equal size was bonded with the premilled PMMA chip using pressure adhesive polyester film (ARcare 8890, SAdhesives Research Ltd., Limerick, Ireland).
Photopolymerisation of methacrylic monoliths was performed (as described above) in the channels using 15% and 30% of monomer (GMA/EDMA) in the polymerisation mixture.

EOP measurements
EOP measurements were conducted according to F.-Q. Nie *et al.*[26] A 0 - 30 kV power supply (Unimicro technologies Inc., Pleasanton, USA) connected to platinum wire electrodes was used to apply all voltages. Two 10 mm long polyetheretherketone (PEEK, Upchurch Scientific) tubings were firmly inserted into the inlet and outlet holes and glued to prevent the leakage during pumping. Two plastic vials serving as working fluid reservoirs were connected to the channel inlet and outlet through PVC tubings. Monolithic columns were pressure filled with working electrolyte (0.2 mM sodium acetate buffer, pH 3.5) and equilibrate 20 min before the measurements were made. Voltages from 0.2 kV were applied to open channel and monolithic channels and obsereved currents (2 - 50 μA) were measured.