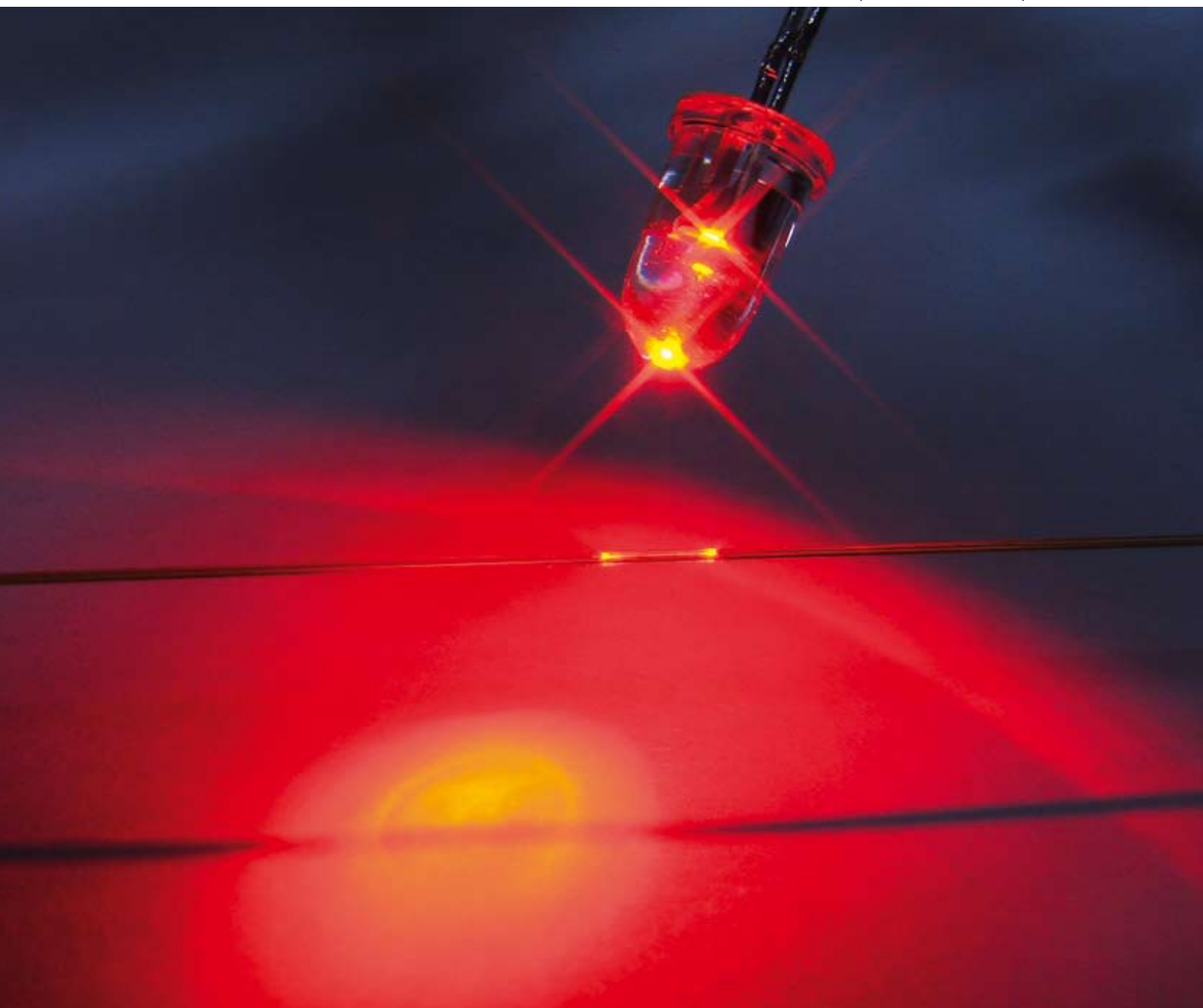


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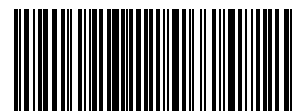
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Photoinitiated polymerisation of monolithic stationary phases in polyimide coated capillaries using visible region LEDs†

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The spatially controlled synthesis of poly(glycidyl methacrylate-co-ethylene dimethacrylate) monolithic stationary phases in polyimide coated fused silica capillaries by visible light induced radical polymerisation using a three-component initiator and a 660 nm light emitting diode (LED) as a light source is presented here.

Since the synthesis of the first organic monolith was reported by Svec and Fréchet in 1992,¹ monolithic stationary phases have been recognised as one of most innovative developments since the conception of chromatography by Tsvet in the early 1900s.² Initiation by heat¹ and ultraviolet (UV) radiation³ are the most common methods of inducing polymerisation, while other methods such as initiation by microwaves,⁴ γ -radiation⁵ and electron beam⁶ have been reported more recently. Photoinitiation is of particular interest as it is an excellent method of achieving sharp plugs of monolith in a specific location within a mold in a short amount of time.

Until recently, photoinitiation could be carried out only by using ultraviolet light and was therefore restricted to UV-transparent molds such as polytetrafluoroethylene (PTFE) coated fused silica capillaries³ and microfluidic chips made from poly(methyl methacrylate),⁷ glass⁸ or cyclic olefin copolymer.⁹ In this work the synthesis of organic polymer monoliths by radical polymerisation using red LEDs with emission max. at 660 nm to initiate polymerisation within polyimide (PI) coated fused silica capillaries is investigated. To the authors best knowledge this *communication* is the first example in the literature of the photoinitiated synthesis of organic polymer monoliths in polyimide coated fused silica capillaries with visible light in the red region of the spectrum.

The authors are aware of a publication in which Dulay *et al.*¹⁰ describe the synthesis of a silica sol-gel monolith in a polyimide coated capillary by cationic polymerisation using a cool fluorescent lamp equipped with a bandpass filter to

produce 470 nm light. Two recent papers also report the use of UV-LEDs to induce polymerisation both in a UV-transparent capillary⁷ and in solution.¹¹

Unlike PTFE, polyimide is strongly absorbing below approx. 500 nm, Fig. 1, therefore UV radiation cannot be used to induce efficient polymerisation within PI coated fused silica capillaries – light will be absorbed by the coating and will not pass into the capillary to initiate polymerisation. As the transmission of light through PI coated capillaries is already above 50% at 550 nm, photoinitiation of polymerisation can be carried out more efficiently using visible light above 550 nm. The ability to carry out polymerisation in polyimide coated capillaries is particularly useful as they are more durable than their UV-transparent (PTFE-coated) counterparts and are used in the vast majority of capillary separation applications.

The photoinitiated polymerisations described here have been carried out using LEDs as the light source. The benefits of using LEDs over classical light sources in both analytical chemistry¹² and photoinitiated polymerisation^{7,11} have been reported elsewhere. LEDs are cheap, small, robust and have long lifetimes (up to 100 000 h)¹¹ but their most important feature, with respect to their use in photoinitiated polymerisation, is their relatively small heat generation.¹¹ Using a 'cold' light source means that there is a remote chance that thermally initiated polymerisation is occurring simultaneously with the photoinitiation so thermal effects, such as enhanced diffusion

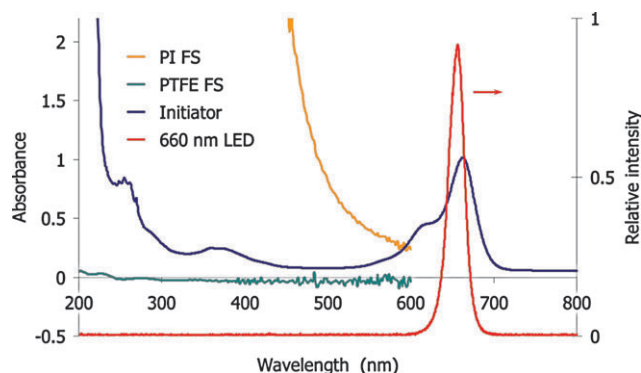


Fig. 1 Absorption spectra of PI and PTFE coated fused silica capillaries (spectra measured on Agilent 3D CE instrument, bare fused silica reference, all samples filled with deionised water for measurement), absorption spectrum of the dye sensitiser/borate salt complex and the emission spectrum of the 660 nm LED used for polymerisation (see ESI†).

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causing inhomogeneity towards the ends of the monolith, are unlikely.

In this study, a novel three-component photoinitiator mixture, consisting of a cyanine dye sensitizer with a borate counterion radical initiator and an alkoxy pyridinium salt, was used to start polymerisation of poly(glycidyl methacrylate-*co*-ethylene dimethacrylate). The initiator system is based on a commercially available *n*-butyltriphenyl borate salt of a cyanine dye, 3-butyl-2-[5-(1,3-dihydro-3,3-dimethyl-1-propyl-2*H*-indolylidene)-penta-1,3-dienyl]-1,1-dimethyl-1*H*-benzo[*e*]indolium (HNB 660, Spectra Group Ltd, USA). Efficient single electron transfer from the borate anion to the excited cyanine sensitizer is known to generate the cyanine radical and the butyl radical, along with phenyl borane.^{13–15} The butyl radical species are then able to initiate chain polymerisation. In contrast, the second co-initiator, *N*-methoxy-4-phenylpyridinium tetrafluoroborate (Sigma-Aldrich, Ireland) can abstract an electron from the excited state of the cyanine dye to produce a methoxy radical and pyridine *via* reductive cleavage of the N–O bond.¹⁶ Such a three-component system, proposed by Kabatc and Paczkowski,¹⁷ was shown to initiate polymerisation of 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate more efficiently than the cyanine/borate salt itself because it is capable of releasing two radical species as polymerisation initiators upon absorption of a single photon, while the overall rate of free radical formation is not controlled by the reverse electron transfer.¹⁷ Referring to the work of Kabatc and Paczkowski,¹⁷ a 10-fold molar excess of the alkoxy pyridinium salt was used in this study to ensure that the photoinitiated polymerisation of the monolithic stationary phases was as efficient as possible. The absorption properties of the cyanine ($\lambda_{\text{max}} = 660 \text{ nm}$) allow the use of red light which easily penetrates the polyimide coating to the internal cavity where the polymerisation mixture is held (Fig. 1).

A standard polyimide coated fused silica capillary (Polymicro Technologies, AZ, USA) was used as the mold for the synthesis of the organic polymer monolith by photoinitiated polymerisation (Table 1). Before polymerisation within the mold, the internal walls were pretreated with a silanising agent, 3-(trimethoxysilyl)propyl methacrylate (TMSPM) to ensure that the growing monolith is covalently anchored to the walls.^{18,19} Glycidyl methacrylate (GMA) and ethylene dimethacrylate (EDMA) were chosen as the monomer and cross-linker, respectively, with a mixture of acetonitrile, isopropanol and decanol as porogenic solvents.[†] After the pretreated capillaries were filled with the polymerisation

solution, the capillaries were masked using black electrical tape to ensure that only certain sections of the capillary were exposed to visible light to show that spatial control of the monolith formation within the polyimide coated capillary was possible.

The masked capillary was placed on a flat surface with the LED positioned perpendicular to it at a distance of 15 mm (Fig. 2 left). A 660 nm LED (Soanar, Australia) with a forward current of 30 mA was used and the polymerisation was allowed to proceed for 30 min. The resulting monolithic polymer was more completely formed on the side of the mold adjacent to the LED, while the opposite side had a thinner layer of polymer. The lens-like properties of the capillary walls and the high absorptivity of the dye sensitizer ($\epsilon_{\text{max}}^{660} = 230\,000 \text{ L mol}^{-1} \text{ cm}^{-1}$) are believed to be the reason for this occurrence. When the LED is perpendicular to the capillary the majority of light passes through the polyimide coating and the fused silica wall in a straight line with little scattering of the light rays. On reaching the cavity, the transmission of light through the polymerisation solution is hindered by the high absorptivity of the dye. Using the Beer–Lambert law to make an approximation of the light transmitted through the cavity, it is estimated that while approx. 50% of light is absorbed at the adjacent wall (within 1 μm of the wall) only 1.5% can be absorbed at the opposite wall (100 μm distance).[†] While diffusion of radicals and some light scattering do occur, the more common outcome is an inhomogeneous wall coating.

Keeping all other conditions constant, the LED was shifted incrementally towards the parallel. Moving the LED away from the perpendicular significantly improved the quantity and homogeneity of the polymer formed within the cavity. The optimum degree of polymerisation was achieved when the LED was positioned at approximately 60° to the normal (Fig. 2 right). At this angle there is increased light scattering within the walls of the capillary, which allows more radicals to be generated, giving a more homogeneous monolith. A small motor was also used to rotate the capillary at a rate of 17 rpm so light can penetrate more evenly through the capillary, this has previously been discussed by Eeltink *et al.*²⁰

A summary of the optimum conditions used to synthesise poly(GMA-*co*-EDMA) monoliths by visible light induced polymerisation is given in Table 1.

To characterise the monoliths synthesised under these conditions, optical microscopy, scanning electron microscopy and the measurement of flow resistance with respect to flow rate were used.

Scanning electron microscopy was used to show that the monoliths had completely filled the capillary and were well attached to the walls (Fig. 3 left).

Optical microscopy using blue LEDs to back light the capillary at a magnification of 10 \times (Fig. 3 right) showed that the plug of monolith has straight, sharp edges.

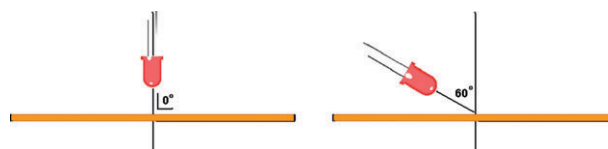


Fig. 2 Position of LED relative to the capillary during polymerisation.

Table 1 Optimum conditions for the synthesis of organic monolithic materials by visible light induced polymerisation

Monolith synthesis conditions	
LED	660 nm
Angle	Approx. 60° to the normal
Distance	15 mm
Current	30 mA
Reaction time	30 min
Mold	PI coated fused silica 375 μm o.d., 100 μm i.d.
Composition of polymerisation solution	See ESI

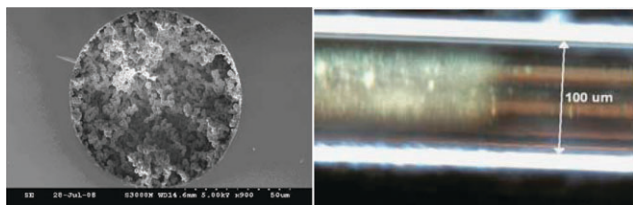


Fig. 3 Left: Scanning electron micrograph of a poly(GMA-co-EDMA) monolith synthesised under the optimum conditions and right: optical microscope image (10 \times) showing the sharp edges of the monolith within the capillary.

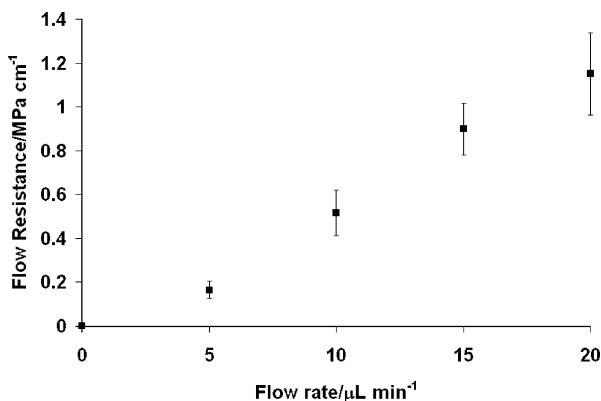


Fig. 4 Plot of flow rate ($\mu\text{L min}^{-1}$) vs. flow resistance (MPa cm^{-1}) for a poly(GMA-co-EDMA) monolith synthesised by visible light initiated polymerisation; error bars show an error of $\pm 1\sigma$.

Finally, the flow resistance of the monoliths was measured using a S-100 HPLC pump (Knauer, Germany) with HPLC grade methanol (Sigma-Aldrich, Ireland) as the eluent. These measurements were carried out on a batch of monoliths synthesised under the optimum conditions and were found to be reproducible, Fig. 4 ($n = 3$).

The flow resistance at $5 \mu\text{L min}^{-1}$ is 0.16 MPa cm^{-1} , which shows that these monoliths are suitable for low pressure separation applications such as those involving microfluidic chips and lab-on-a-chip systems.

The monoliths were encased in a poly(methyl methacrylate) chip similar to those used by Nie *et al.*^{21,22} to be used as electroosmotic pumps (EOPs). The monolith was flushed with 1 M NaOH for 3 h to attack the epoxy ring of the GMA and produce some negative charge on the surface which should create electroosmotic flow. Doing this produced a maximum flow rate of 274 nL min^{-1} using 2 mM phosphate buffer at pH 11 when the applied voltage was 2 kV; for comparison an unmodified commercial silica C18 monolith as EOP has been shown to give a flow rate of approx. 160 nL min^{-1} with 2 mM NaCl buffer at 2 kV.²² This value obtained from the modified GMA-EDMA copolymer shows an acceptable performance as an EOP. When the flow rate was measured without modification of the monolith, a negligible flow rate was obtained regardless of the voltage applied.

To conclude, for the first time the synthesis of organic polymers has been demonstrated by photoinitiated polymerisation in polyimide coated fused silica capillaries using visible

region LEDs as the light source. In comparison to thermal initiation, polymerisation time is significantly reduced with polymer generated in 30 min. Using LEDs as the light source instead of classical high powered light sources, interference from thermal effects during polymerisation is minimised. The monoliths synthesised here have been demonstrated as EOPs for microfluidic devices.

The here presented visible light photoinitiated polymerisation has a potential for use in other polyimide-encased microfluidic devices such as polyimide chips. In addition to photoinduced polymerisation within polyimide coated capillaries, there is potential for this method to be used for the grafting of species onto monolithic supports, which are currently impossible to photo-graft using conventional UV-initiated grafting methods, such as chromophoric monomers with strong absorbance in the UV region. This application is currently being examined.

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