Photo-initiated Polymerisation of Monolithic Stationary Phases in Polyimide Coated Capillaries Using Visible Region LEDs

Electronic Supplementary Information

Zarah Walsh, Silvija Abele, Brian Lawless, Dominik Heger, Petr Klán, Michael C. Breadmore, Brett Paull and Mirek Macka*

Decomposition of photoinitiators to radicals during initiation step of polymerisation[1]

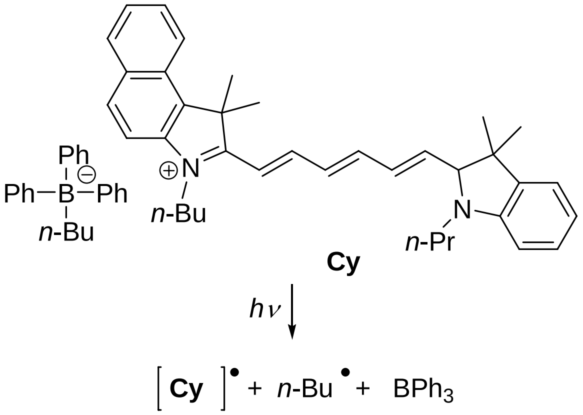

Fig.1 Decomposition of borate salt to phenyl borane and butyl radical via electron transfer

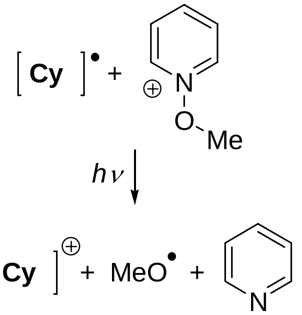

Fig.2 Decomposition of the alkoxypyridnium salt to pyridine and methoxy radical via electron transfer

A 5 μmol/L solution of cyanine-borate in isopropanol:acetonitrile 50:50 (V+V) in a standard cell of 10 mm pathlength was used for the spectrum taken of the initiator in Fig.1 in the main text.

Pre-treatment of the internal walls of the polyimide coated fused silica capillaries

Lengths of 100 μm i.d. polyimide coated fused silica capillary (Polymicro Technologies, AZ, USA) were flushed with 1 M NaOH, 0.1 M HCl and deionised H_2O, in that order, for 20 min each using a peristaltic pump (Perkin-Elmer Corp., MA, USA). The internal channel was then allowed to dry by leaving the capillary connected to the pump and pumping air for approx. 20 min. In the meantime, a 1:1 solution of the silanising agent 3-(trimethoxysilyl)propyl methacrylate (TMSPM) and acetone was made up in an eppendorf tube, sonicated for 3 min and purged with N_2 for 1 min. Once dry the capillary was filled with the TMSPM/acetone solution, the ends were sealed and the capillary was placed in a water bath for 20 h at 60 °C. Upon removal from the water bath the capillary was once again connected to the peristaltic pump and flushed with methanol for 30 min to remove all traces of silanising solution from the capillary. The capillary was then allowed to dry as before. Silanising the capillary before polymerisation allows the polymer monolith to grow from the walls increasing the mechanical stability of the resulting chromatographic stationary phase.

Synthesis of the poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) monolith

The polymerisation reaction solution consisted of 80 μl GMA (0.59 mmol), 80 μl EDMA (0.42 mmol), 60 μl acetonitrile, 80 μl isopropanol, 100 μl decanol, 4.2 mg N-methoxy-4-phenylpyridinium tetrafluoroborate (2.5% per weight of monomer) and 0.42 mg HNB 660 (0.25% per weight of monomer). The mixture was sonicated and purged with nitrogen. The resulting aquamarine coloured solution was then filled into polyimide coated capillaries, the ends were sealed with rubber septa and the capillary was masked with black electrical tape.

The 660 nm LED was positioned at 60° to the capillary and the capillary was placed in the grip of a small motor which was rotating at a constant speed of 17 rpm. The forward current through the LED was set at 30 mA and the polymerisation reaction was allowed to proceed for 30-40 min. After polymerisation was complete the capillary was flushed with several column volumes of methanol to remove traces of unreacted initiators and monomers.

Light transmission through the polyimide capillary

Approximation of light transmission through the internal cavity of the capillary was calculated based on the Beer-Lambert law and accounting for the light absorbed by the polyimide coating as shown in Fig.1 of the short communication.

The concentration of initiator used was 0.25% of the total amount of monomer present or 0.65 mM. Inserting this value into the Beer-Lambert law, along with the molar absorptivity coefficient of the cyanine/borate and a value for each pathlength from 1 to 100 μm, a graph was obtained plotting the decrease in transmission of the light from the LED with distance moving from the adjacent to the opposite side of the capillary. As mentioned in the communication, almost 50% of the light from the LED is absorbed by the polyimide coating at 660 nm, therefore the onset in this graph at a distance equal to zero was corrected by a factor of 0.5. The resulting graph is shown in Fig.3. It is evident from the graph that around 50 % of light is available to initiate polymerisation at the internal wall of capillary adjacent to LED, whereas only 1.5 % of light remains available at the opposite side of the capillary. This is one of the reasons why no monoliths of a satisfactory quality were obtained without rotation of the capillary.

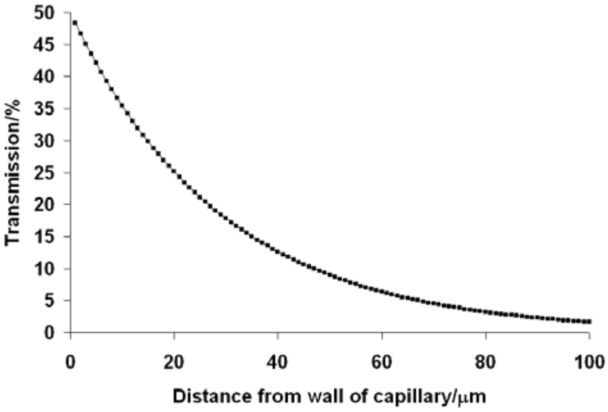

Fig.3 Graph showing the transmission of light through the internal cavity of the polyimide coated fused silica vs. the distance from the wall of the capillary adjacent to the LED when the % of initiator per weight of monomer is 0.25%

Characterisation of the Monoliths

Scanning electron microscopy was carried out using a S-3000N VP-SEM (Hitachi, Japan) at a working distance of 15 mm and an accelerating voltage of 5 kV (with low acceleration bias).

Optical microscopy was carrried out with a SVM340 Synchronized Video Microscope (LabSmith, USA).

[1] J. Kabatc and J. Paczkowski, *Journal of Photochemistry and Photobiology A: Chemistry*, 2006, **184**, 184.