



Polymerisation and surface modification of methacrylate monoliths in polyimide channels and polyimide coated capillaries using 660 nm light emitting diodes

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ABSTRACT

An investigation into the preparation of monolithic separation media utilising a cyanine dye sensitizer/triphenylbutylborate/*N*-methoxy-4-phenylpyridinium tetrafluoroborate initiating system activated by 660 nm light emitting diodes is reported. The work demonstrates multiple uses of red-light initiated polymerisation in the preparation of monolithic stationary phases within polyimide and polyimide coated channels and the modification of monolithic materials with molecules which absorb strongly in the UV region. This initiator complex was used to synthesise poly(butyl methacrylate-co-ethylene dimethacrylate) and poly(methyl methacrylate-co-ethylene dimethacrylate) monolithic stationary phases in polyimide coated fused silica capillaries of varying internal diameters, as well as within polyimide micro-fluidic chips. The repeatability of the preparation procedure and resultant monolithic structure was demonstrated with a batch of poly(butyl methacrylate-co-ethylene dimethacrylate) monoliths in 100 μm i.d. polyimide coated fused silica capillary, which were applied to the separation of a model protein mixture (ribonuclease A, cytochrome C, myoglobin and ovalbumin). Taking an average from 12 chromatograms originating from each batch, the maximum relative standard deviation of the retention factor (k) for the protein separations was recorded as 0.53%, the maximum variance for the selectivity factor (α) was 0.40% while the maximum relative standard deviation in peak resolution was 8.72%. All maxima were recorded for the Ribonuclease A/Cytochrome C peaks.

Scanning electron microscopy confirmed the success of experiments in which poly(butyl methacrylate-co-ethylene dimethacrylate) monoliths were prepared using the same initiation approach in capillary and micro-fluidic chips, respectively. The initiating system was also applied to the photo-initiated grafting of a chromophoric monomer onto poly(butyl methacrylate-co-ethylene dimethacrylate) monoliths within poly(tetrafluoroethylene) coated fused silica capillaries.

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1. Introduction

From the first report of photo-initiated synthesis of monolithic separation media by Viklund et al. [1] in 1997, UV light as the initiating source remains the state of the art for the production of controlled lengths of polymeric monolith within UV transparent moulds. Despite the popularity of this technique and the advances in light sources over the years, from mercury lamps [1], to fluorescent lamps [2], to light emitting diodes (LEDs) [3], there remains two major disadvantages to this approach. Firstly, the mould must be UV transparent to allow UV light to pass into the cavity to initiate polymerisation, which excludes the use of the standard and most durable polyimide coated capillaries. Secondly, the monomers and

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porogens either must not absorb UV light or must absorb at a wavelength removed from the $\lambda_{\max}$ of absorbance of the initiator, excluding the use of strong UV absorbers such as styrenes.

Several important advances in chromatographic technology have brought the issue of mould transparency to the foreground. The first of these is the recent introduction of the Agilent HPLC Chip, which employs specifically designed micro-fluidic chips fabricated from laser ablated laminated polyimide layers [4]. The second is the growing use of monolithic separation media in gas chromatographic applications, where polyimide coated capillaries are commonly used [5,6]. These show that there is a real need for a method of photo-initiated polymerisation which can be used with polyimide and polyimide coated moulds. While thermally initiated polymerisation is capable of producing monolithic materials within polyimide moulds the disadvantages of this method are that the polymerisations are generally rather long, in the region of 20 h, and there is no spatial control over the location of the monolith in the capillary [1,7]. UV initiated polymerisation allows spatial control of the monolith formation and reduced polymerisation times but cannot be used with polyimide coated capillaries due to absorption of the UV light by the polyimide coating. Visible light initiated polymerisation in the red region is the ideal solution to the issues arising from both of these methods, it too gives control over the location of the polymer in the capillary but without the need to remove the polyimide layer and average polymerisation times are far shorter than those recorded for thermally initiated polymerisations [8]. Additionally, as with UV initiated polymerisation, the polymerisations can be carried out at room temperature and there is the possibility for post-synthesis functionalisation of the monolith surface in a well-defined area using the same initiating system.

Dulay et al. [9] made the first advances in this area by presenting the visible light initiated synthesis of a sol-gel monolith within polyimide coated fused silica capillaries, performed using a cool fluorescent lamp emitting at 470 nm.

More recently, the authors of this present work were successful in further shifting the wavelength of the initiating light source into the red region, showing the first preparation of poly(glycidyl methacrylate-co-ethylene dimethacrylate) [poly(GMA-co-EDMA)] monoliths within polyimide coated fused silica capillaries [8]. In this case the reaction was initiated using a novel three component initiator system consisting of a cyanine dye/borate salt complex (3-butyl-2-[5-(1,3-dihydro-3,3-dimethyl-1-propyl-2H-indolylidene)-penta-1,3-dienyl]-1,1-dimethyl-1H-benzo[e]indolium triphenyl butyl borate, HNB660) and a secondary co-initiator (*N*-methoxy-4-phenylpyridinium tetrafluoroborate, MPPB) using a diode emitting at 660 nm [see electronic supplementary information (ESI) for structures].

This current work presents the full investigation of the novel initiating system and its utilisation to prepare organic polymer monoliths within polyimide coated fused silica capillaries and polyimide moulds. The synthesis of both poly(butyl methacrylate-co-ethylene dimethacrylate) [poly(BuMA-co-EDMA)] and poly(methyl methacrylate-co-ethylene dimethacrylate) [poly(MMA-co-EDMA)] monoliths in capillaries is demonstrated and the application of the poly(BuMA-co-EDMA) monoliths to the separation of a model protein mixture is shown, confirming that the monoliths produced using this method have porous structures and rigidity comparable to those prepared via the standard UV light initiated method and can be applied to chromatographic separations. Additionally, some specific and novel examples of the potential of this method for the synthesis and modification of monolithic separation media are also shown, (i) within polyimide micro-fluidic chips, and (ii) the application of the initiator system to facilitate the photo-initiated grafting of UV absorbing monomers on pre-existing monolithic scaffolds. The above applications of this new technology show the versatility of this approach and bring common polyimide moulds into the

range of moulds in which photo-initiated monolith synthesis can be carried out, which until recently [8,9] was not possible.

2. Experimental

2.1. Reagents

Acetic acid (ACS reagent grade, 99.7%), acetonitrile (HPLC grade, 99.9%), butyl methacrylate (BuMA, 99%), cytochrome C from bovine heart, 1-decanol (99%), ethylene dimethacrylate (EDMA, 98%), ethanol (spectrophotometric grade), formic acid (ACS reagent grade, 88%), methanol (HPLC grade, 99.9%), methyl methacrylate (MMA, 98%), myoglobin from equine skeletal muscle, *N*-methoxy-4-phenylpyridinium tetrafluoroborate (97%), ovalbumin from chicken egg white, 1-propanol (HPLC grade, $\geq 99.9\%$), ribonuclease A from bovine pancreas and 3-(trimethoxysilyl)-propyl methacrylate (TMSPM, 98%) were all purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA and Wicklow, Ireland). All chemicals were used as received with the exception of BuMA, MMA and EDMA, which were purified before use by passing over a bed of basic aluminium ($\sim 58 \text{ \AA}$) to remove inhibitors. 3-Butyl-2-[5-(1,3-dihydro-3,3-dimethyl-1-propyl-2H-indolylidene)-penta-1,3-dienyl]-1,1-dimethyl-1H-benzo[e]-indolium triphenyl butyl borate (HNB660) was purchased from Spectra Group Limited, Inc. (Millbury, OH, USA) and used as received. A monomeric spiropyran presenting a free vinyl terminal chain, 1'-(9-decenyl)-3',3'-dimethyl-6-nitrospiro[2H-1]-benzopyran-2,2'-indoline (SPM), was synthesised from a procedure described by McCoy et al. [10], which is outlined in the ESI. Water used in these experiments was obtained from a Milli-Q Ultrapure water filtration system from Millipore (Billerica, MA, USA).

2.2. Materials

Light emitting diodes (LEDs) were obtained from Roithner Laser Technik GmbH (Vienna, Austria) ($\lambda_{\max} = 660 \text{ nm}$, optical power = 3.5 cd at 20 mA) and MCD Electronics Ltd. (Albuquerque, NM, USA) ($\lambda_{\max} = 660 \text{ nm}$, optical power = 0.5 cd at 20 mA). Strip-board for fabrication of the LED arrays (shown in the ESI) and commercial power supply units operated in a constant voltage mode to power the LEDs were purchased from Maplins Electronics (Rotherham, UK). A small commercially available motor with a variable speed of rotation (Peats Electronics, Dublin, Ireland) was used at low speeds (ca. 34 rpm) for the polymerisation of standard poly(BuMA-co-EDMA) monoliths in capillary and for photo-initiated grafting. A second in-house fabricated motor, rotating at higher speeds of ca. 120 rpm, was used for the synthesis of standard poly(MMA-co-EDMA) using the LED array.

50–100 μm i.d. polyimide and 100 μm i.d. PTFE coated fused silica capillaries were purchased from Polymicro Technologies (Phoenix, AZ, USA). Polyimide micro-fluidic chips, with an internal channel 0.2 mm $\times$ 0.2 mm $\times$ 68 mm, were generously provided by Agilent Technologies (Santa Clara, CA, USA).

2.3. Instrumentation

Spectra of polyimide sheets were taken with a Cary 50 UV-vis spectrometer from Varian Inc., (Palo Alto, CA, USA). Optical micrographs of monolith filled micro-fluidic chips were taken with a TE200 optical microscope from Nikon (Tokyo, Japan) while filled capillaries were imaged using an EMZ-8TR video microscope (Meiji Techno, Saitama, Japan). Scanning electron micrographs of all poly(MMA-co-EDMA) monoliths were taken with an S-3400N Variable Pressure Scanning Electron Microscope from Hitachi (Tokyo, Japan) while poly(BuMA-co-EDMA) filled capillaries and chips were

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