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Rapid Fabrication Of Poly(Methyl Methacrylate) Capillary Electrophoresis Microchips By In Situ Surface Polymerization

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ABSTRACT

In situ surface polymerization of methyl methacrylate (MMA) have been employed for the fabrication of poly(methyl methacrylate) (PMMA) capillary electrophoresis microchips. MMA containing thermal and ultraviolet (UV) initiators was allowed to partially prepolymerize under heat and was subsequently sandwiched between a nickel template and a PMMA plate. The images of microchannels on the template could be precisely replicated during the UV-initiated polymerization of the molding solution on the surface of the PMMA plate at room temperature within 30 min.

KEYWORDS

Microchip;
Capillary electrophoresis;
Poly(methyl methacrylate);
Amperometric detection;
Microfabrication.

INTRODUCTION

Polymers are becoming the most promising materials for the microfluidic devices because they are cheaper and easier to be manipulated than glass based substrates and can be produced with mass-replication technologies, such as injection molding and hot embossing[1,2]. Poly(methyl methacrylate) (PMMA) has been particularly useful for microfluidic chips with the features of low price, excellent optic transparency, and good electric and mechanical properties[2,3]. Existing procedures for fabricating PMMA chips include laser ablation, imprinting, injection molding, etc[4-6]. Recently, methods based on the in situ polymerization of methyl methacrylate (MMA) in molds have been developed for the fabrication of PMMA microchips with the aids of ultraviolet (UV) light[7] or heat[8]. To define the dimension of the microchips, a rigid frame with a rectangular cavity was sandwiched between a hard plate and a template to form molds[7,8]. The volume shrinkage of the MMA molding solution was inevitable during molding, resulting in bubble formation in the PMMA substrate. Additional molding solution usually had to be added to the cavity in the mold during polymerization. Another bottleneck of the existing molding methods is the long polymerization time (6 to 12 h) that is not compatible with the mass production. In this work, a novel method based on in situ surface polymerization of MMA on PMMA plates have been developed for the rapid fabrication of PMMA capillary electrophoresis (CE) microchips. The time for the complete polymerization of the molding solution was significantly reduced to less than 30 min.

The newly fabricated PMMA chips (16 mm × 70 mm) had simple cross layouts, with a four-way injection cross connected to three reservoirs and the separation channel. The PMMA chip consisted of a 60 mm-long separation channel (between the injection cross and the detection reservoir) and a 5 mm-long injection channel. The two channels crossed each other halfway between the sample and the unused reservoirs, at 5 mm from the run buffer reservoir. The channel was 40 μm deep and 50 μm wide. The nickel master template composed of a positive relief structure of nickel for the channels was made at the Research Institute of Micro/Nano Science and Technology in Shanghai Jiaotong University (Shanghai, China) by using a SU-8 (a negative photoresistor) based UV-LIGA technology. Benzoin ethyl ethter (BEE, 0.2% w/v, an UV initiator) and 2-2'-azo-bis-isobutyronitrile (AIBN, 0.2% w/v, a thermal initiator) were dissolved in MMA and the mixed solution was allowed to prepolymerize in an 85 °C water bath for ~15 min to generate a molding solution.

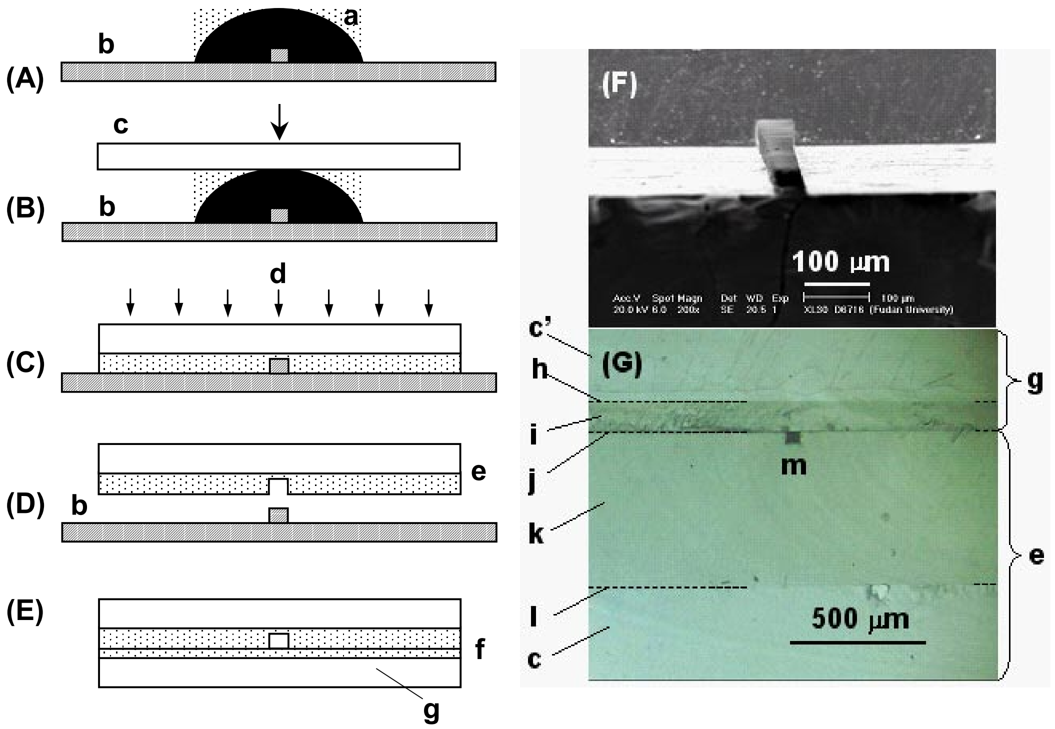

Figure 1: Schematic of the microfabrication process.

(A) casting the MMA prepolymer molding solution (a) on a nickel template (b)

(B) sandwiching (a) between (b) and a comercial PMMA plate (c)

(C) exposing the sandwich mold to the UV light (d)

(D) demolding of the polymerized PMMA channel plate (e)

(E) thermal bonding of (e) and the cover plate (g) to form the complete microchip (f)

(F) scanning electron micrographs (SEM) of the cross sections of (A) an unsealed microchannel in (e)

(G) microscopic image (×100) of the cross sections of the channels in (f). SEM conditions: accelerating voltage, 20 kV; magnification, ×200. (h) the interface between the PMMA plate (c') and the synthesized PMMA layer (i), (j) the boundary between the cover plate (g) and the channel plate (e), (k) the synthesized PMMA layer with microchannels replicated inside, (l) the interface between (c) and (k), (m) the channel outlet.

To fabricate the channel plate, about 1.5 ml of the molding solution (Figure 1a) was cast directly on the nickel template (b) along the raised separation channel. Subsequently, the PMMA plate (c, 70 mm × 16 mm × 1 mm) was carefully covered on the molding solution and pressed slightly until that all the interspaces between the nickel template and the PMMA plate were filled by the molding solution (Figure 1c). The excess solution could flow out and agglomerated along the edge of the PMMA plate on the nickel template and could prevent the ingress of air bubbles as a result of the shrinkage during in situ polyperization. Subsequently, the sandwich mold (Figure 1c) was exposed to UV light (d, 365 nm). Complete polymerization of the molding solution was accomplished within 30 min at 25°C. During the polymerization, the images of microchannels on the nickel template were precisely replicated into the synthesized PMMA layer on the surface of PMMA plate (c). Demolding was accomplished by sonicating the mold in a 40 °C water bath for 10 min. Figure 1f illustrates the scanning electron micrographs (SEM) of the cross sections of an unsealed microchannel in the PMMA substrate. The cover plate (g) was fabricated in the same way as the PMMA channel plate (e) except the nickel template was replaced by a glass slide (75 mm × 25 mm × 1 mm). Prior to sealing, the edges of the channel plates were cut off and 2 mm-diameter access holes were drilled at the ends of channels to create reservoir ports. The cover and the channel plate were cleaned by sonicating in doubly distilled water and isopropanol for 1 min each and were dried. Subsequently, the plates were aligned (Figure 1e) and sandwiched between two glass slides, clamped together using six binder clips (25 mm), and were placed in a 108 °C convection oven for 10 min. The bonded chip (f) was then allowed to cool slowly to the room temperature and was removed from the glass slides.

The detection reservoir port of the microchip was cut off to facilitate the end-column ampero metric detection (AD) and the chips were placed in a Plexiglas holder in which the detection and high-voltage electrodes were configured. The effective length of the separation channel was 55 mm (from cross-section to the channel outlet). Details of the CE-AD system have been described previously[9]. A stainless steel guiding tube (400 μm I.D. × 700 μm O.D.) was attached to the holder for the precise alignment between the channel outlet and the carbon disc detection electrode fabricated in a fused silica capillary (320 μm I.D. × 450 μm O.D.)[6]. The sample solution was loaded into the separation channel by applying +1500 V to the sample reservoir for 2 or 3 s, while the detection reservoir grounded and other reservoirs floating. In the existing methods[5] only one UV or thermal initiator was employed. The polymerization of MMA can only be initiated by UV light or heat. In this work, both UV or thermal initiators were used to form a highly efficient initiate system. The in situ surface polymerization initiated by UV light were performed using different mixtures of MMA solutions with BEE when the content of AIBN was fixed at 0.2% w/v. When the amount of BEE was 0.05, 0.1, 0.2, 0.3, and 0.4 % w/v, the polymerization time of the molding solution was 95, 66, 28, 15, and 11 min, respectively. A 0.2% BEE level was proved to be optimal for the complete curing of the substrates, while providing high quality structures.

The thermal initiator, AIBN, allowed MMA to prepolymerize to a high extent so that the time for the complete polymerization of the molding solution under UV light was significantly reduced to less than 30 min. The solid contents in the molding solution was approximately 36% (w/w). Because the image of the relief on the nickel template was precisely replicated into just a thin layer of synthesized PMMA on the surface of a commercially available PMMA plate (Figure 1c), the heat released from the polymerization was minimized and the molding procedure was greatly simplified. Although the volume shrinkage of the molding solution was inevitable during molding, no bubble formation was found because no rigid space or frame was sandwiched between the nickel template (Figure 1b) and the PMMA plate (Figure 1c) in this work. As shown in Figure 1g, the microchip was composed of four layers. The synthesized layers (Figure 1i and k) that formed the microchannel (Figure 1m) were sandwiched between two commercial PMMA plates (Figure 1c and c′).

The analytical performance of the new PMMA microchips was demonstrated by separating cat-

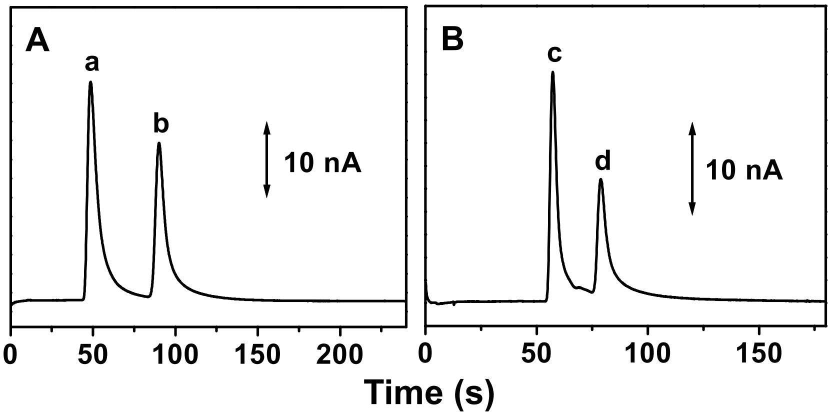

Figure 2: Electropherograms for a mixture
(A) containing 200 μM dopamine (a) and 200 μM catechol (b) or (B) 200 μM 1,2-phenyldiamine (c) and 200 μM 2-methylaniline (d). Conditions: separation and injection voltage, +1500 V; injection time, 3 s (A) and 2 s (B); running buffer, 10 mM phosphate buffers (A, pH 6.5; B, pH 4.5); detection electrode, 320 μm diameter carbon disc electrode; detection potential, +0.80 V (vs. Ag/AgCl wire).

echolamine analytes and two aromatic amines of environmental concern coupled to end-column AD. As indicated from Figure 2a, the PMMA electrophoresis microchip provides baseline-resolved well-defined peaks for 200 μM dopamine (a) and 200 μM catechol (b) within 100 s. The number of theoretical plates for dopamine was determined to be greater than 6780 plates/m. The sensitivities of dopamine and catechol are 143.5 and 102.1 nA/mM, respectively. Figure 2b displays the electropherograms for a mixture containing 200 μM 1,2-phenyldiamine (c) and 200 μM 2-methylaniline (d). The two aromatic amines could be separated on baseline with well-defined peak shapes within 90 s, indicating the present PMMA CE microchips might be attractive tools in the environmental monitoring.

CONCLUSION

A simple and rapid fabrication method for PMMA microchip based on the in situ surface polymerization has been developed in this study, holding considerable promise for the mass production of microchips. This flexible and simple surface molding methodology may also find more applications for the fabrication of other polymer microfluidic devices.

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