Electronic Supporting Information

Patterning Reactive Microdomains inside Polydimethylsiloxane Microchannels by Trapping and Melting Functional Polymer Particles

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1. Experimental Details

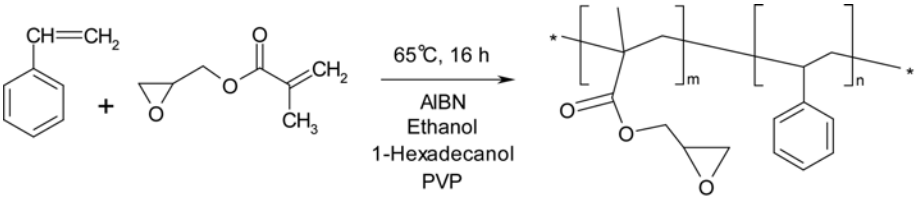
1-1. Materials

Si (100) wafers were obtained from KN Platz Corp. (Osaka, Japan). Negative photoresists, SU-8 2005, 2025, and 2050, were obtained from MicroChem Corp. (Newton, MA, USA). PDMS (Sylgard 184) was obtained from Dow Corning (Midland, MI, USA). Styrene, glycidyl methacrylate, 2,2'-azobis(isobutyronitrile) (AIBN), ethylenediamine, ethanol, and methanol were obtained from Wako Pure Chemical Ind., Ltd. (Osaka, Japan). Poly(*N*-vinylpyrrolidone) (K-30; PVP) and 1-hexadecanol were obtained from Nacalai Tesque Inc. (Kyoto, Japan). Fluorescein isothiocyanate (isomer I; FITC) was obtained from Sigma Aldrich Inc. (St. Louis, MO, USA). These chemicals were used without further purification.

1-2. Synthesis of monodisperse poly(styrene-co-glycidyl methacrylate) particles

Reactive polymer particles having an epoxy group as a functional group were synthesized via dispersion copolymerization in a polar solvent using styrene and glycidyl methacrylate as monomers (Scheme S1). Initially, 66.8 g of ethanol, 2.50 g of PVP, and 0.50 g of 1-hexadecanol were weighed in a 300-mL glass batch reactor equipped with a stirrer. The reactor was then heated from room temperature to 65 °C with agitation at 30 rpm. After heating, a mixture consisting of 4.0 g of glycidyl methacrylate, 16.0 g of styrene, and 0.20 g of AIBN was added. The reaction was carried out at 65°C for 16 hours with agitation at 30 rpm. After the polymerization, particles were recovered and washed three times with methanol via centrifugation.

Scheme S1. Synthesis of poly(styrene-co-glycidyl methacrylate) particles.



1-3. Microchannel fabrication

Microdevices were fabricated using the usual rapid prototyping and replica molding techniques, as described elsewhere.[1,2] First, a negative photoresist (SU-8 2005, 2025, or 2050) structure (master) was formed on a silicon wafer. The PDMS prepolymer was then poured onto the master, and after curing, the PDMS plate was peeled off. Then PDMS plates either with the microchannel or microwell structures were bonded, after being treated with O_2 plasma for 1 sec (at 100 W and 40 Pa of O_2) using a plasma reactor (PR-500, Yamato Scientific Co. Ltd., Japan). The positions of the microchannel and microwells were precisely aligned under an optical microscope using methanol as a lubricant. After bonding, the microdevice was placed in an oven at 200ºC for at least 2 hours to completely recover the surface hydrophobicity. The width, depth, and length of the microchannel were 200 μm, 170 μm, and 12 mm, respectively, while microwells with various shapes were employed.

1-4. Operation of particle trapping and melting

The particle trapping and melting were performed according to the following procedures. At first, ~2 μL of the particles suspension (1×10^5 particles per 1 μL) was dropped into the inlet reservoir and then pulled into the microchannel by aspiration from the outlet using a syringe pump (KDS250, KDScientific Corp., MA, USA) at a flow rate of 30 μL/h. Air

was then automatically introduced by continuing the aspiration through the microchannel. The behavior of particles was observed using an optical microscope (IX71, Olympus Corp., Tokyo, Japan), and movies were captured using a PC equipped with a CCD camera (DXC-151, Sony Corp., Tokyo, Japan). After trapping, residual methanol was removed by incubating the microdevice in an oven (ST-110, Espec Corp., Osaka, Japan) at 50°C for 1 hour. To fix the polymer matrix onto the microdomain, particles were melted in an oven (LCV-232, Espec Corp.) at 160°C under a vacuum condition (50 mmHg) for 2 hours. At each step, SEM images were taken using a SEM system (VE-8800, Keyence Corp., Tokyo, Japan).

1-5. Characterization of the patterned microdomain

To label the patterned region with FITC, we first introduced an aqueous solution of ethylenediamine (10% (w/w)) into the microchannel by using a syringe pump at a flow rate of 30 μL/h for 6 hours at room temperature. To completely wash out the ethylenediamine, distilled water was then introduced at a flow rate of 30 μL/h for 3 hours. Methanol containing FITC (0.5% (w/w)) was then introduced at a flow rate of 30 μL/h for 5 hours, and finally, the microchannel was washed thoroughly with methanol containing 1% (w/w) Tween 20 for 1 hour, and then distilled water. The fluorescence signal was observed by using a fluorescence microscope (IX-70, Olympus Corp.). In addition, the presence of the epoxy group on the patterned microdomain was directly observed via FT-IR spectrometry. After heating and melting the particles, PDMS plates were peeled apart and the patterned microdomain was observed using an FT-IR spectrophotometer and an IR microscope (FTIR-8400S and AIM-8800, Shimadzu Corp., Kyoto, Japan). Moreover, in the case of microwells packed with single particles, we examined the surface flatness by using a confocal laser profilometer (HD100D, Lasertec Corp., Kanagawa, Japan.).

2. Additional Results and Discussion

2-1. Movies of particle trapping

Movies of particle trapping in the microchannel are shown. Movie S1: particles trapped in 80 × 80 μm square wells, and Movie S2: particles trapped in wells composed of two overwrapping circles with diameters of 7 μm.

2-2. Enlarged SEM images showing particles trapping

Images shown in Figure 2 (g) are enlarged and shown in Figure S1.

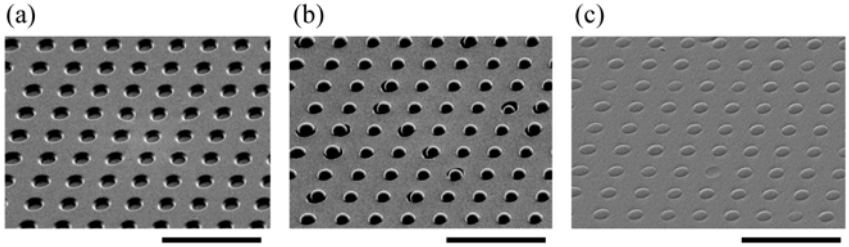


Figure S1. Enlarged SEM images showing particle trapping in circular-microwell array with a depth of 3.0 μm and a diameter of 7.0 μm; microwells (a) before particle introduction, (b) after trapping, and (c) after particle melting. Scale bar, 50 μm.

2-3. Efficiency of particle trapping

The efficiency of particle trapping was examined by using an array of circular microwells with different depths and diameters, and by increasing the number of injections. We fabricated circular microwells with diameters of 5~15 μm, and with depths of 2.3, 3.6, or 5.1 μm (Figure S2 (a)). When the diameter of the wells was smaller than the average particle diameter (6.8 μm), the ratio of the occupied wells was low (0~5% for 5 μm wells) regardless of the well depth (Figure S2 (b) – (d)). When the depth of the microwell was 2.3 μm, the ratio of the occupied wells was not high (40~70%) except for the wells similar in size to the particles (Figure S2 (b)). We consider that a relatively large shear force was exerted to particles in the case of shallow (2.3 μm in depth) and large (7~15 μm in diameter) wells, and consequently, particles that were once trapped flowed out of the wells, making the trapping efficiency relatively low. While in the case of the deeper (3.6 and 5.1 μm) and larger (7~15 μm in diameter) wells, almost all of the wells were completely occupied with particles after three injections (Figure S2 (c) and (d)).

In addition, we examined the ratio of the wells packed with the ideal number of particles, using the wells shown in Fig. 2 (d) - (f). As a result, in the case of wells shown in Fig. 2 (d), the trapping efficiency was higher than 95%, as is the case with single circular wells, which can clearly be seen in the supplementary movie. On the other hand, in the case of wells of Fig. 2 (e) and (f), the ratio of wells completely packed with the particles was not so high; the ratio of the square wells (Fig. 2 (e)) packed with four particles was ~30%, and that of the star-shape wells (Fig. 2 (f)) packed with three particles was ~50%, even after three times of particle introduction. This inaccuracy would mainly be due to the ununiformity of the particle size. That is, particles larger than the average size tended to flow out of the wells after trapping due to the relatively large shear force, in the case of such relatively wide and shallow wells. On the other hand, there are particles much smaller than the average size, although the ratio was not so high. Such small particles tended to remain in the wells, since the shear stress applied to such particles was not so high. Consequently, we sometimes observed the larger number of smaller particles stacked in these wells, instead of the ideal number of the average-size particles. We expect that this inaccuracy of particle trapping would be improved by using particles with a narrower size-distribution.

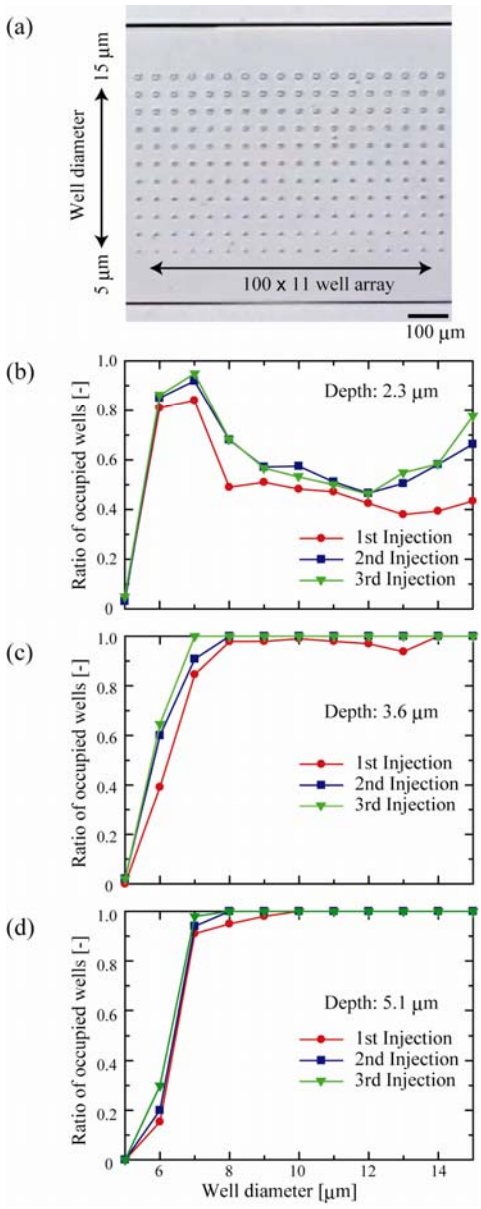


Figure S2. (a) Microscopic image showing the microchannel equipped with a circular-microwell array (100 × 11) used to examine the trapping efficiency of the particles. (b)-(d) The trapping efficiency of particles by varying the well diameter, well depth, and the number of the injections; the depths were (b) 2.3, (c) 3.6, and (d) 5.1 µm, respectively.

References

(1) Duffy, D. C.; McDonald, J. C.; Schueller, O. J. A.; Whitesides, G. M. *Anal. Chem.* **1998**, *70*, 4974-4984.

(2) Yamada, M.; Seki, M. *Anal. Chem.*, **2004**, *76*, 895-899.