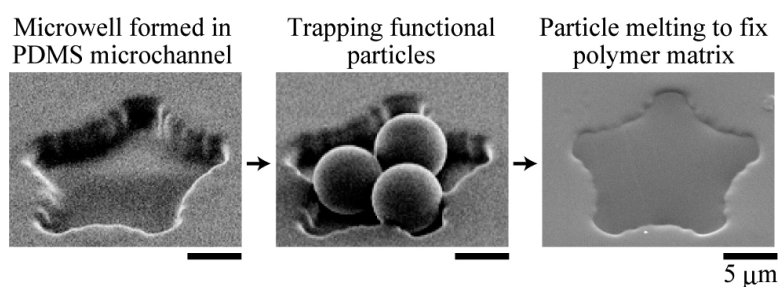## Communication

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Microwell formed in PDMS microchannel → Trapping functional particles → Particle melting to fix polymer matrix

5 μm

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

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During the past decade, the advent of microfluidic devices has dramatically accelerated chemical and biological studies in a miniaturized platform, including the controlled synthesis of fine chemicals and the biological analysis of single cells.[1] Polydimethylsiloxane (PDMS) is an especially well adapted material for microdevices, due to the simplicity and reproducibility in fabrication processes.[2] On the microscale, one of the key factors for the successful manipulation of chemical/biological substances is the surface properties.[3] Tremendous efforts have hitherto been made to develop techniques that are compatible for modifying the surface properties of PDMS microchannels,[4] even though PDMS is chemically inert. Among the various techniques for surface modification, local modification of the microchannel surface facilitates the construction of highly functional microsystems as well as related new applications, including the formation of stable liquid/liquid or gas/liquid interfaces for chemical processing systems[5] and the control of biomolecule attachment or cellular patterning.[6] Several attempts at modifying the local surface of PDMS microchannel have been made via selective photoirradiation through a mask[7] or the selective-filling technique.[8] These techniques, however, have limitations with regard to flexibility in design, resolution, or chemical reactivity for further utilization.

In this Communication, we present a simple and versatile technique for patterning reactive microdomains inside the PDMS microchannel with high spatial resolution. We employ polymer microparticles having an epoxy group as the carrier of the functional group (Figure 1). We employ a microchannel equipped with microwells on its floor and introduce particle suspension into the microchannel, followed by the introduction of air. Due to the difference in densities of the medium and particles, particles gradually precipitate and accumulate in the wells. Also, the receding meniscus formed at the air/liquid interface exerts lateral capillary forces on the particles,[9] trapping particles only inside the wells. We then fix the polymer matrix onto the local surface by heating and melting the trapped particles. The epoxy group on the modified region will be available as a starting material for the design of compounds with various functional groups, which would facilitate a variety of applications such as micropatterning of grafted polymers, biomolecules, or cultivated cells inside the microchannel.

In the present study, we synthesized monodisperse poly(styrene-*co*-glycidyl methacrylate) particles via dispersion copolymerization[10] and obtained particles with an average diameter of 6.8 μm (CV of 7.0%) and a melting point of ~135 °C. PDMS microchannels having microwells were prepared by bonding two PDMS plates with either a microchannel or microwells. Before introduction of
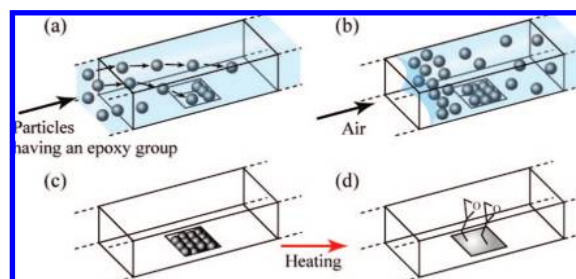

Figure 1. Schematic illustrations of the patterning of microdomains using functional particles: (a) introduction of particle suspension, (b) introduction of air, (c) trapped particles in the well, and (d) particle melting to fix the functional polymer matrix.
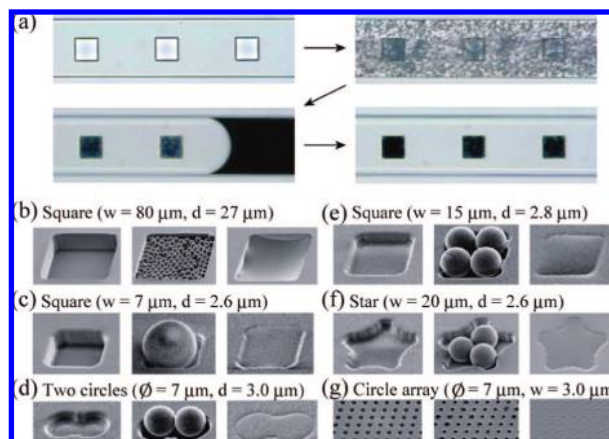

Figure 2. (a) Microscopic images showing particle trapping in 80 × 80 μm wells, before and during particle introduction, air introduction, and after the trapping. The flow direction was left to right. The channel width is 200 μm. (b–g) SEM images of various types of microwells, before and after trapping particles, and after melting the particles. See Supporting Information for movies of particle trapping and an enlarged version of panel (g).

the particles, the microchannel was rendered completely hydrophobic by incubating in an oven at 200 °C for at least 2 h. A small aliquot (~2 μL) of the particle suspension in methanol was dropped onto the inlet port, and it was introduced into the microchannel by aspirating from the outlet. After trapping, the microdevice was heated at 160 °C to melt the particles and fix the polymer matrix.

Optical microscope images show the trapping processes of particles in 80 × 80 μm square wells (Figure 2a). During flow through the microchannel, the particle concentration gradually increased, since particles tended to precipitate onto the bottom surface of the microchannel, making the flow speed of particles lower than the average flow rate of the medium. The introduced

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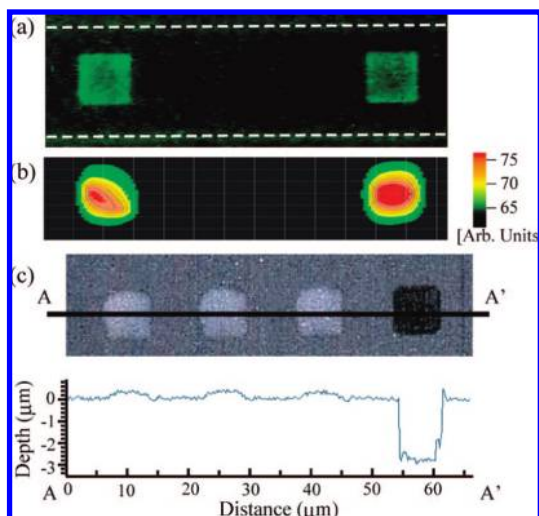[§] Chiba University.

Figure 3. (a) Fluorescence image of the microdomain (80 × 80 μm) coupled with ethylenediamine and FITC. Microchannel walls are outlined with broken lines. (b) Microscopic FT-IR image of the microchannel (80 × 80 μm) showing the absorbance at 900 cm⁻¹. (c) Microscopic image of the three occupied and one unoccupied microwells, and the corresponding surface profile along the line A−A′. The well shape corresponds to that in Figure 2c.

air then formed the receding meniscus, and particles accumulated only inside the wells by means of capillary force. We did not observe nonspecific adhesion of particles at the channel corner or on the wall, which would be due to the weak interaction of the hydrophobic surface of PDMS and the relatively hydrophilic particles in methanol. Note that particles tended to adhere onto the channel surface nonspecifically when the recovery of channel hydrophobicity was insufficient. Figure 2b shows scanning electron microscopy (SEM) images of the microwells before and after particle accumulation as well as after particle melting, taken after the bonded PDMS plates were peeled apart. Each microwell was almost fully packed with ∼700 particles, but after melting, the surface profiles of the modified region became concave due to the void volume of the accumulated particles.

In contrast to the large wells, we expected that the use of wells with a depth smaller than the particle diameter would result in a flat surface for the patterned microdomain. We employed various types of microwells to be packed with 1−4 particles per well (Figure 2c−g). As a result, particles were precisely stacked only inside the wells, regardless of the well shape, even when the well depth was smaller than the particle radius. In the case of a well array (Figure 2g), not all of the wells were completely occupied with the particles with a single injection; the trapping efficiency was ∼90%. However, multiple introduction of the particle suspension resulted in complete trapping (Figure S2, Supporting Information), since particles that were trapped once hardly flowed out of the wells when the well-depth was larger than about one-third of the particle diameter. In addition, the closest packing was observed in microwells with 3 or 4 particles (Figure 2e,f), although the ratio of the wells with closest packing was not so high (30−50%), mainly due to the presence of particles smaller than the average size (see Supporting Information for details).

We next examined the presence of functional groups on the patterned microdomains by using 80 × 80 μm square wells. At first, the epoxy group was reacted with ethylenediamine and fluorescein isothiocyanate (FITC) in a stepwise manner. As shown in Figure 3a, the modified region was successfully stained with

the fluorescent dye. In addition, we directly observed the absorbance of the epoxy group at 900 cm⁻¹ by using microscopic FT-IR.[11] The modified region specifically showed strong absorbance (Figure 3b), demonstrating the presence of the epoxy group. In addition, the surface flatness was examined using a confocal laser profilometer in the case of microdomains patterned with single particles. We confirmed that the combination of microwells and particles with appropriate volumes created the highly flat surface of the microdomains (Figure 3c). In this case, the surface roughness was less than 300 nm, which is sufficiently small that no disturbance would arise when a fluid flow is introduced.

In summary, we have demonstrated a facile and reproducible method for patterning reactive microdomains inside PDMS microchannels. The presented method introduces a novel mechanism that utilizes the microscale air/liquid interface of a particle suspension in combination with the chemical reactivity of functional particles and provides a robust means of achieving precise patterning without a need for complex operations or devices. We consider that the use of smaller-size particles and wells would further improve the resolution of modification. In addition, we expect that the mechanism presented here can be extended to other types of particles or microchannel materials when particles of proper surface characteristics are employed.

Supporting Information Available: Experimental details, additional results and discussion, and movies of particle trapping. This material is available free of charge via the Internet at http://pubs.acs.org.

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