ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Multilayered film microreactors fabricated by one-step thermal bonding technique with high reproducibility and their applications

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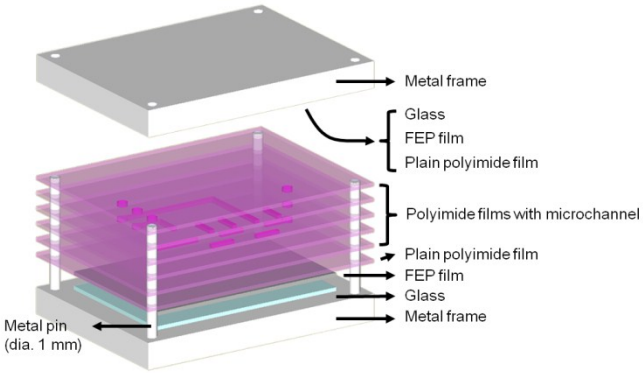
Fabrication of pressure tolerant hydrophilic PI film microdevice O/W droplet

To generate hydrophilic surface, we used UV laser (355 nm, ESI, USA) and adhesive PI film (Kapton EKJ film, Dupont, USA) as an internal layer. Typically, two pieces of PI (Kapton HN film, 125 μm of thick, Dupont, USA) as top and bottom layers were ablated by UV laser to form in/outlet holes (1 mm diameter) and Y-shaped microchannel (200 μm wide and 60 μm deep) having a rough surface with undulations of a few tens of micrometer. After laser ablation, the films were cleaned by washing with acetone in ultrasound and dried under nitrogen. A film (25 μm thick) of double-sided adhesive PI film was punched using laser to form a Ψ-shaped open-channel (60 μm wide for channel of dispersion phase and 200 μm wide for main channel) with a through-hole (1 mm diameter). The microchannel included an inner channel that was 25 μm deep and 60 μm wide for the dispersal phase, and two outer channels surrounding the inner flow that were 145 μm deep and 200 μm wide for a continuous phase. The four corners of each film were holed (1 mm diameter) to provide guides to align the film patterns. The internal adhesive film (25 μm thick) with an open channel was sandwiched between two pieces of the ablated 125 μm thick PI films by inserting metal pins through the holes at the film corners to be aligned. Additionally, Teflon films (190 μm thick, Dupont, USA) with a softening point at 260~280 °C were placed as cushions of the stacked layers to homogeneously distribute the applied pressure over the film to enhance the bonding reliability. One plain PI film was placed at each of the top and bottom of set of aligned PI films to prevent inflow of soft Teflon film. Finally the PI-based microchannels were bonded by pressing a set of the stacked films between two glass slides at 300 °C under a pressure of 10 kPa for at least 1 h. After simple one-step bonding of layered films, Teflon films were removed with plain PI films together. The sealed PI film 3D microdevices were fixed using a buckle-type aluminium chip holder (ICH-03, IMT, Japan) or metal holders to connect the inlet/outlet holes by using a screw type of Teflon ferrule without using any adhesive materials.

Fabrication of pressure tolerant hydrophobic PI film microdevice for W/O droplet

For hydrophobic surface on PI film microdevice, the PI film (125 μm thick) was initially punched by UV laser to form a open Ψ -shaped microchannel (125 μm deep and 200 μm wide) with orifice (50 μm wide, 125 μm height and 175 μm of length) for flow focusing. Each PI film was spin-coated at 1000 rpm for 30 sec with fluoropolymer as a thermal adhesive layer (ND-110, Neoflon, DAIKIN, Japan) using 60 % solid loading of aqueous solution containing a 150 nm thermoplastic FEP (fluoroethylene propylene) nanopowder. Subsequent evaporation of the solvent at 100 ^{o}C for 10 min rendered a 5 μm thickness FEP layer on PI film. Four corners of each film holed with 1 mm diameter were passed through metal pins to align the features between channels and in/outlet holes. Finally, the patterned PI film was sandwiched between two sheets of the non-patterned but FEP coated PI films and bonded through the same method as aforementioned.



Scheme S1. A scheme for typical alignment of PI films. Laser ablated PI films are aligned and stacked on metal frame by inserting metal pins with precise diameter of 1 mm into the holes at the film corners. And whole set are proceeded to further bonding step at 300 °C under a pressure of 10 kPa for at least 1 h.

Pressure tolerance of the film microfludic device

The microchannel was fabricated by laser with dimension of 50 μm deep, 200 μm wide, and 4 cm long on the PI film. After laser ablation, double-layered PI microchannels were fabricated with adhesive PI film and FEP coated PI film for the hydrophilic and the hydrophobic microchannel, respectively. The bonding strength of the sealed PI film microdevice was measured by connecting a high-performance liquid chromatography (HPLC) pump (SP-930D, Younglin, Korea). The HPLC pump was used to infuse the water into the film microdevice in the range of 0.1~10 mL/min. Furthermore, the burst pressure inside the microdevice with one-end open microchannel (closed outlet, open inlet) was recorded while rapidly pumping the water at 10 mL min^{-1} through the device until the microchannel was ruptured to leak. Three sets of identical experiments were conducted for average values within the standard deviation range.

Application for O/W and W/O droplet at high throughput

The emulsion droplets were produced using the fabricated PI film microdevices. To form O/W emulsion, hexadecane (Sigma-Aldrich) and 0.25 mmol of fluorescent water (Fluorescein sodium salt, Sigma-Aldrich) with 2 wt% surfactant (sodium dodecyl sulfate, SDS, Sigma-Aldrich) were infused into the hydrophilic PI film microdevice at various flow rates. For alternative droplets, PLGA micro/nanoparticles were prepared using poly(lactic-co-glycolic acid) (PLGA) (molecular weight = 50,000 ~ 75,000, lactide:glycolide = 85 : 15) dissolved in solvent (such as dichloromethane and acetonitrile) at concentrations of 1~3 wt%; the continuous phase was 1 wt% poly(vinyl alcohol) (PVA) (87%~89% hydrolyzed) in water. To generate W/O emulsion, water was injected into the center channel, and hexadecane with 1 % surfactant (Span-80, Sigma-Aldrich) was infused into the outer channels at various flow rates. For PLGA nanoparticles, 10 mg/mL of PLGA were dissolved in acetonitrile. Polymer solution and water flow rates were controlled by syringe pumps (PHD 2000, Harvard Instruments, USA).

Partial reduction of ester to aldehyde using DIBALH

The FEP-coated PI film microdevice was fabricated through the same method of as aforementioned. The dimension of microchannel was 125 μm height, 300 μm wide, 15 mm length for reaction part and 125 μm height, 300 μm

wide, 10 mm length for quenching part, respectively. The volume of reactor for reaction was 56 nL.

At first, absolute hexane or toluene was infused into PI film microdevice for removing oxygen and water. Solutions of ester (0.2 M in toluene, prepared under nitrogen), DIBALH (1 M in toluene, Sigma-Aldrich) and methanol (neat) were injected to the FEP coated hydrophobic PI film microdevice. After a steady state was reached the mixture was collected and then treated with a saturated aqueous solution of potassium sodium tartrate, diluted with diethyl ether and stirred until 2 clear phases were obtained. The organic phase was then analyzed by GC-MS (Agilent 5975C GC/MSD System, Agilent Tech., USA/Germany).

Hexanal: The spectral data was identical to those commercially available hexanal.

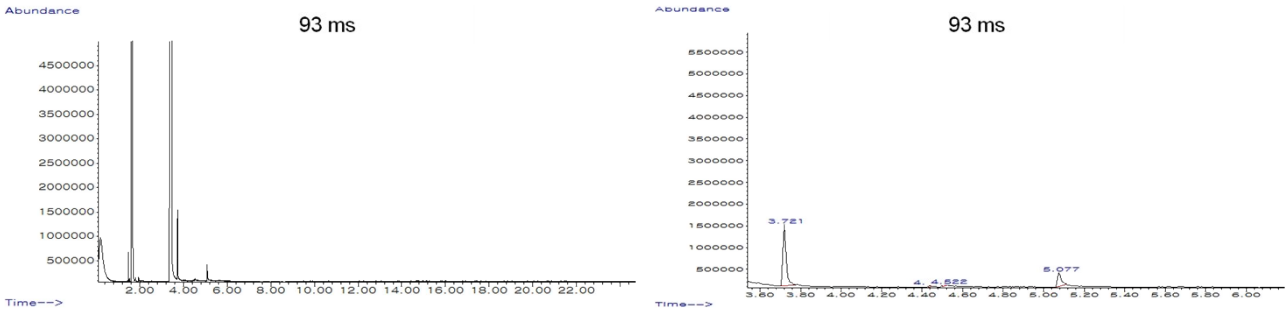


Figure S1. GC-MS peak of DIBALH reduction at 93 ms

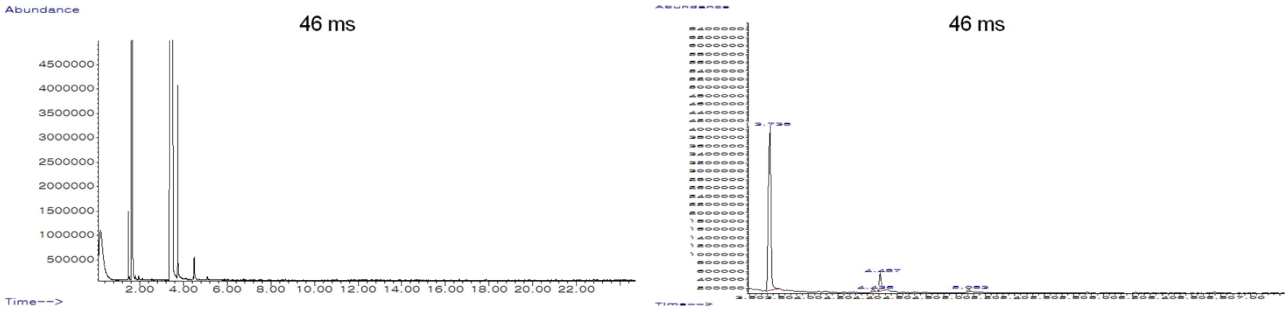


Figure S2. GC-MS peak of DIBALH reduction at 46 ms

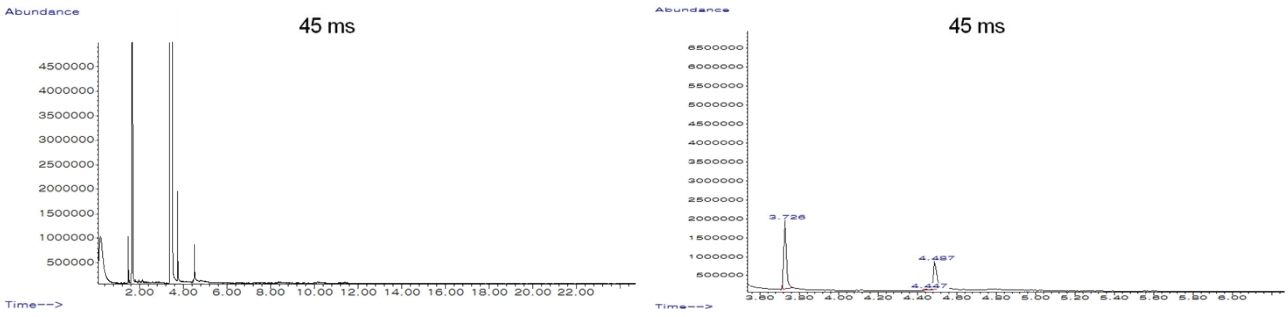


Figure S3. GC-MS peak of DIBALH reduction at 45 ms

Biphasic interfacial reactions in 3D membrane dual PI film microdevice with shower structure

The 3D membrane dual PI film microdevice with shower structure was fabricated through the FEP coated method of as aforementioned. The dimension of microchannel was 125 μm height, 800 μm wide, 10 mm length that the end of microchannel in the top PI film was overlapped with the beginning of the microchannel in the bottom PI film through square hole array in internal PI film, alternately. The junctions of membrane at internal PI film between top and bottom microchannels consisted of 20 times 5 x 5 hole array with 50 μm of diameter and 20 times square hole (800 μm x 800 μm). Total length of microchannel was 52 cm and the internal volume was around 52 μL. For simple Aza-Michael reaction, 1 M diethyl acetylenedicarboxylate (Sigma-Aldrich) in toluene and 1.2 M piperidine (Sigma-Aldrich) in water was infused into 3D membrane dual PI film microdevice at total 400 μL/min. After a steady state was reached, the mixture was collected. The organic phase was then analyzed by GC-MS.

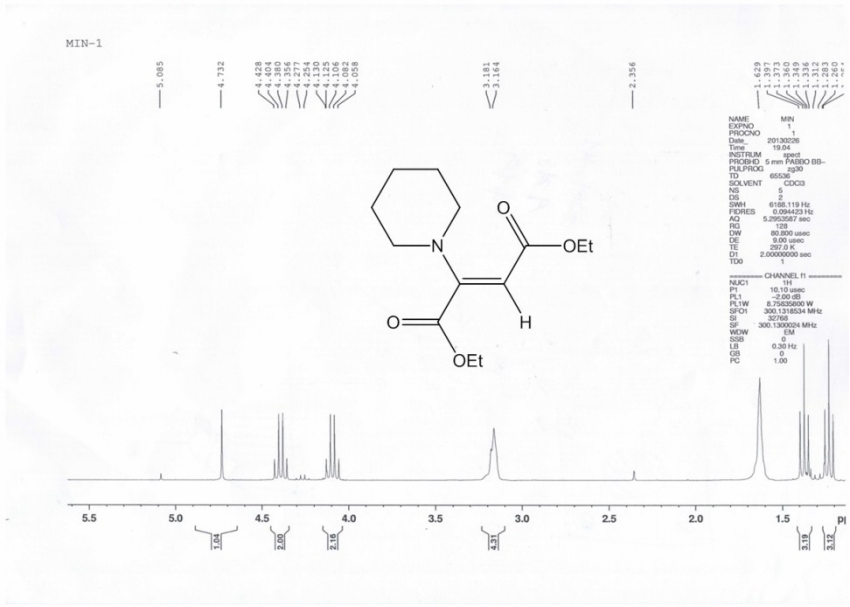


Figure S4. H-NMR peak of (Z) diethyl 2-(piperidin-1-yl)fumarate

(Z) diethyl 2-(piperidin-1-yl)fumarate: The crude product was analyzed by GC-MS and ^{1}H-NMR. The spectral data was identical to those reported in the literature.

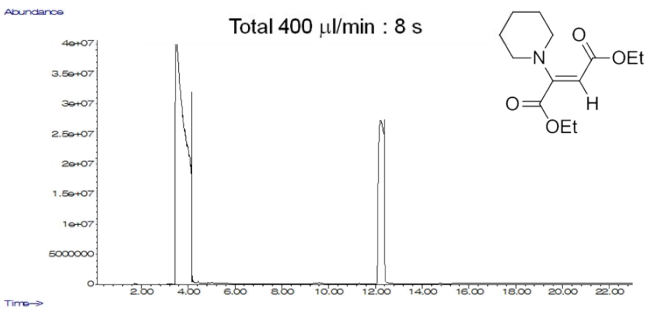


Figure S5. GC-MS peak of (Z) diethyl 2-(piperidin-1-yl)fumarate

(Z) diethyl 2-(4-methylpiperazin-1-yl)fumarate: The crude product was analyzed by GC-MS and ^{1}H-NMR. The spectral data was identical to those reported in the literature.

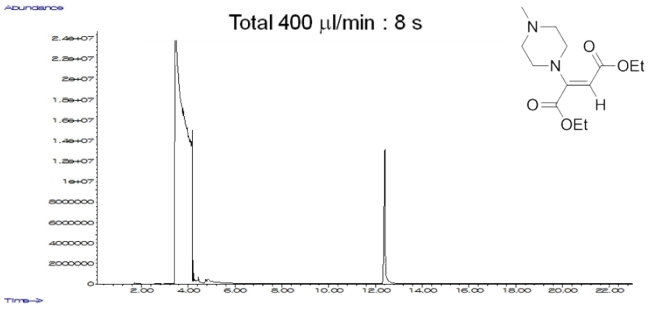


Figure S6. GC-MS peak of (Z) diethyl 2-(4-methylpiperazin-1-yl)fumarate

(Z) diethyl 2-(pyrrolidin-1-yl)fumarate: The crude product was analyzed by GC-MS and ^{1}H-NMR. The spectral data was identical to those reported in the literature.

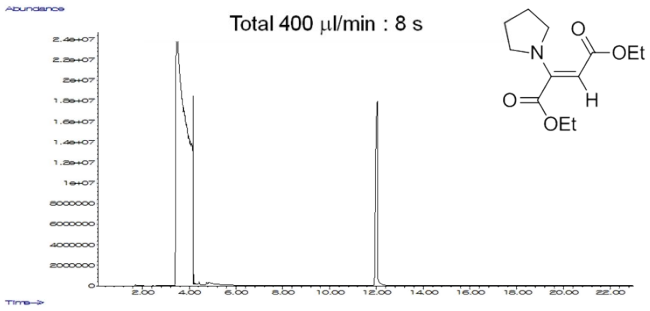


Figure S7. GC-MS peak of (Z) diethyl 2-(pyrrolidin-1-yl)fumarate