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Rapid formation of acrylated microstructures by microwave-induced thermal crosslinking

Seung Hwan Lee,[1,2] *Won Gu Lee,*[1,2] *Bong Geun Chung,*[1,2] *Jae Hong Park,*[1,2] *Ali Khademhosseini*[1,2]*

[1]Center for Biomedical Engineering, Department of Medicine, Brigham and Women's Hospital, Harvard Medical School, Cambridge, MA 02139, USA.

[2]Harvard-MIT Division of Health Sciences and Technology, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

*E-mail: alik@rics.bwh.harvard.edu

Experimental Part

Materials

Poly(ethylene glycol)$_n$ diacrylates (PEG$_n$DA) (n = 3, 4, 9, 10) and PEG$_n$ dimethacrylates (PEG$_n$DMA) (n = 4, 9) were individually purchased from Polysciences, Scientific Polymer Products, and Sigma-Aldrich. 3-(trimethoxysilyl)propyl methacrylate (TMSPMA), 2,2´-azobisisobutyronitrile (AIBN) and 2,2-dimethoxy-2-phenyl acetophenone (DPA) were purchased from Sigma-Aldrich. Microscope glass slides (75×25 mm^2) were purchased from Fisher Scientific. Poly(dimethylsiloxane) (PDMS) molds were fabricated by curing

prepolymer (Sylgard 184, Essex Chemical) on silicon masters patterned with SU-8 photoresist.

Characterization

Structures of PEG_4DA monomers and polymers were analyzed by using the conventional Fourier transform infrared spectroscopy (FTIR) spectrometer (Bruker ALPHA) with OPUS software. FTIR spectra were measured in an attenuated total reflection (ATR) mode. The data represent the average of 24 scans in the region between 4000 and 500 cm^{-1} at a resolution of 2 cm^{-1}. Samples were prepared after microwave-induced heating, conventional thermal heating and UV irradiation. After preparation of polymerization, all phase contrast images (10× and 2×) were taken on an inverted biological microscope (Nikon Eclipse Ti-S, USA) with SPOT advanced software. Representative image of a crosslinked PEG_4DA microspots in Figure S1 was taken by scanning electron microscope (SEM) (Carl Zeiss, ULTRA 55, Germany). The ratio of the projected area for each spot was calculated by analyzing phase contrast images using Image J software. The temperature of silicon wafer and glass slide after microwave irradiation was measured by using an infrared (IR) thermometer (OAKTON, WD35629, USA) at 23°C.

General procedure of TMSPMA-coated glass slide preparation

The glass slide was initially coated with TMSPMA, which provided an anchor for acrylate macromers during polymerization. Glass slides were cleaned with piranha solution (H_2O_2 : H_2SO_4 = 3 : 7) for 1h and washed 3 times with distilled deionized water (DDW) and 99% ethanol. 140 glass slides were stacked in a sealed box and coated with 4 mL of TMSPMA at 80°C for 24 h. Subsequently, the glass slides were washed 3 times with ethanol to remove excess TMSPMA, and cured in an oven (120°C) for 1h.

Microarray Preparation

Fresh stock solutions (1 mL) were prepared with neat acrylate monomers (1 mL) with and without a 1% (w/v) AIBN (10 mg). The solutions (100 μL) were immediately placed in 96-well plates. Microprinting was carried out by using a MicroGrid 600 robotic microarrayer (MGII600, Genomic Solutions, Harvard Bioscience, USA). The acrylate monomers were printed using the arrayer with the MicroSpot 10k pin on the TMSPMA-coated glass slides under atmospheric conditions at 23 °C. To account for the different viscosities of the acrylated macromers, various aspects of printing such as pin washing time, pin speed, and pin priming were controlled. After printing, the acrylate monomers were crosslinked by using microwave or UV irradiation.

To crosslink the PEG acrylate microarrays by using microwave-induced heating, a silicon wafer (5.5 × 5.5 cm^2) was placed inside household domestic microwave oven (120 V_{ac}, 60 Hz, 1.3 kW, Avanti products). Uncrosslinked acrylate-printed glass slides were then placed on the silicon wafer and cured for specific durations. For UV irradiation curing, OmniCure®S1000 was used for a long wave UV irradiation (20 mW/cm^2) for 600 s. The distance between sample glass slide and UV resource was 15 cm. To fabricate PEG-microwells, uncrosslinked PEG_4DA (10 μL) was molded in the void space between PDMS mold patterned with microscale posts and a TMSPMA-coated glass slide. After curing, all glass slides were cooled and washed with DDW.

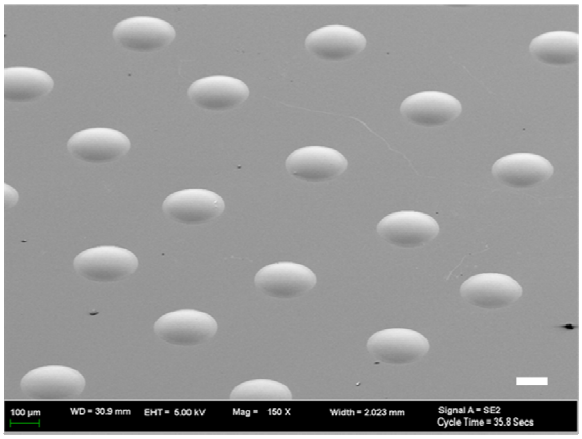

Figure S1. SEM image of microspots of PEG_4DA crosslinked by using the microwave-induced thermal crosslinking. Scale bar is 100 µm.

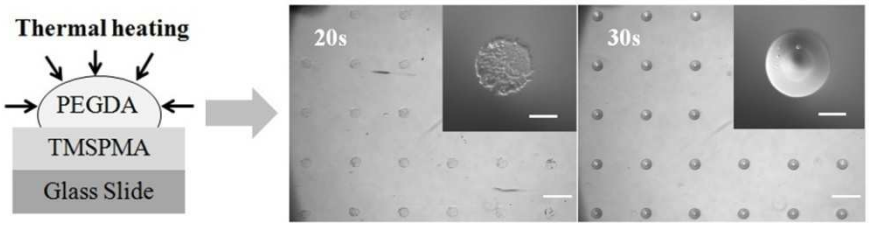

Figure S2. Schematic and phase contrast images of polymerized PEG_4DA by thermal curing (190°C) with 1 % AIBN for 20 s and 30 s. Scale bars are 100 µm (top inset) and 500 µm.

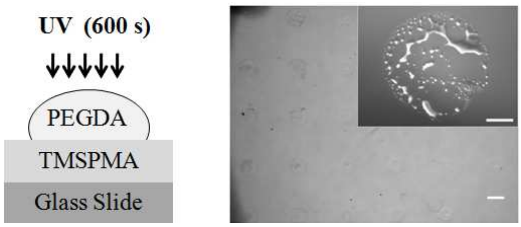

Figure S3. Schematic and phase contrast images of polymerized PEG_4DA microarray by UV irradiation curing for 600 s. Scale bars are 100 µm (top inset) and 300 µm.

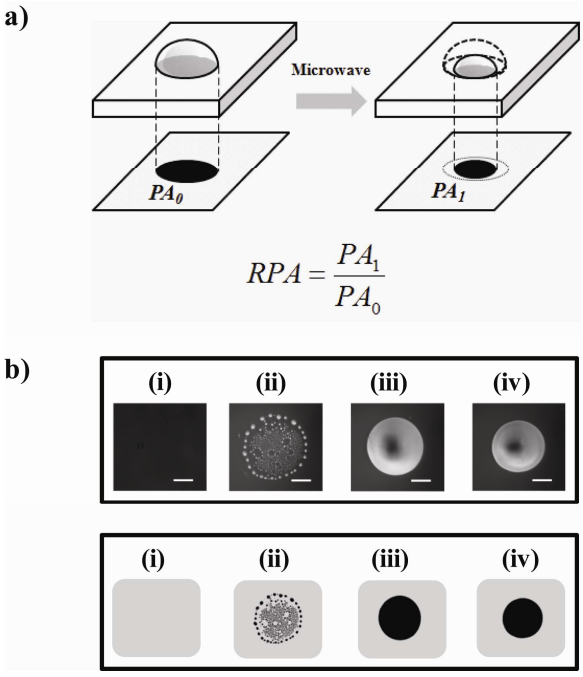

Figure S4. Polymerization of PEG_4DA under the four different crosslinking conditions: (i) UV irradiation (20 mW/cm^2) without DPA for 600 s, (ii) UV irradiation with 1% DPA for 600 s, (iii) UV irradiation with 1% DPA for 600 s and then exposure to microwaves for 9 s, and (iv) microwave-induced heating for 9 s. (a) Ratio of projected areas (*RPA*) induced with an initial projected area (PA_0) and a projected area after crosslinking (PA_1). (b) Phase contrast images of crosslinked PEG_4DA microspots in the individual polymerization and projected areas of the phase contrast images analyzed by Image J software. Scale bar is 100 µm.

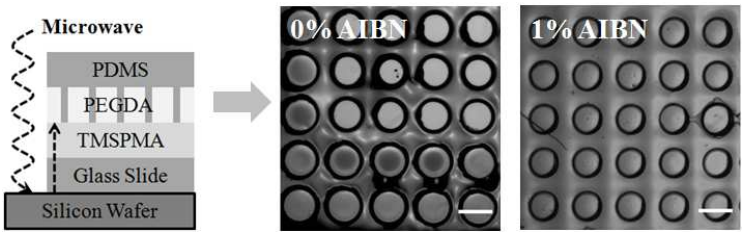

Figure S5. Schematic and phase contrast images of polymerized PEG_4DA microwells by microwave-induced crosslinking with and without 1% AIBN for 12 s and 9 s, respectively. Scale bars are 500 μm.

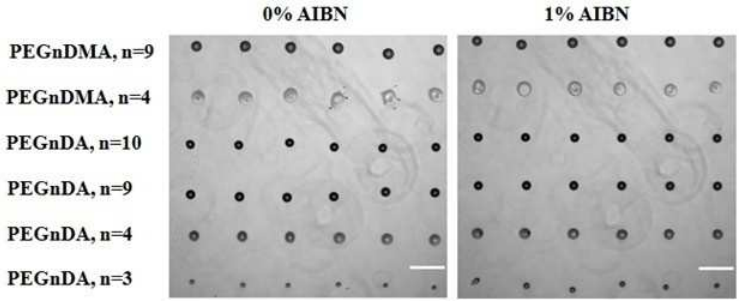

Figure S6. Phase contrast images of crosslinked PEG-based acrylate monomers by using microwave-induced heating with and without 1% AIBN for 9 s. Scale bar is 500 μm.