Supporting Information for

Confinement of Photopolymerization and Solidification with Radiation Pressure

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1. Experimental procedure

Irradiating with UV light pulses (wavelength, ~355 nm; pulse duration, ~0.5 ns; repetition rate, ~10 kHz) from a pulsed diode-pumped UV laser (Nanolase, NV-0021x-100) induced local photopolymerization in the liquid resin. A conventional UV-curable acrylate solution KC1156A was provided by the JSR Corporation. Trimethylolpropane triacrylate (TMPTA, provided from Toagosei) containing 1 wt% photoinitiator (Irgacure 184, Chiba Specialty Chemicals) was also used. The solution was dropped onto a glass substrate (Matsunami, micro cover glass, thickness No.1). A continuous wave (CW) near-infrared laser beam (wavelength, ~1064 nm) from a Nd^{3+}:YAG laser (Spectron Laser Systems, SL902T) locally confined photopolymerization in the resin. Both laser beams were coaxially introduced into an optical microscope (Olympus, IX70) and focused at the same point through an objective (magnification, ~100; NA, ~1.35). The curing process was monitored via optical transmission images with a charge-coupled-device camera (FLOVEL, HCC-600) attached to the microscope. Micro-sized products of the solidified polymer were fabricated in the liquid resin on glass substrates, and then washed with ethanol to remove the uncured photopolymer. For clear scanning electron microscopic observations, the fabricated microstructures on the substrates were coated with a layer of Au (~30 nm thick) by vapor deposition.

2. Transient absorption spectra of the radical photoinitiator

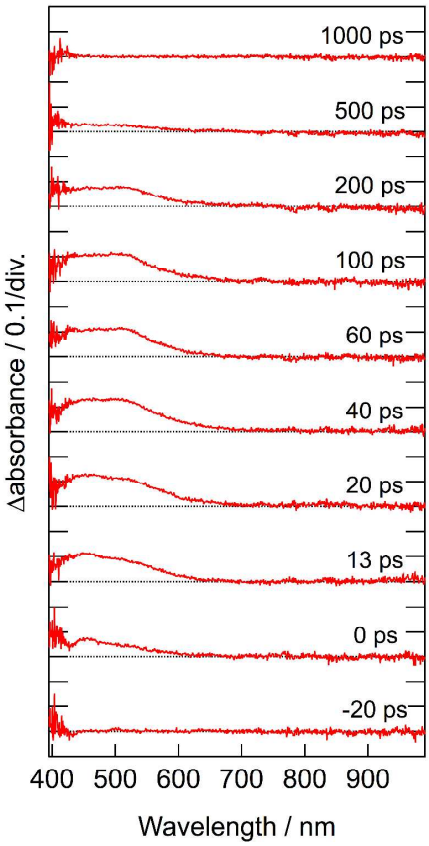

Fig. S1. Transient absorption (TA) spectra of the radical photoinitiator, Irgacure 184, in acetonitrile measured using our ps TA measurement system.[1,2] Third harmonics (355 nm) of a Nd^{3+}:YAG laser with a 15 ps (fwhm) duration and 0.5–1.0 mJ output power provided the excitation. Picosecond white continuum generated by focusing the fundamental pulse into a 10 cm quartz cell containing a D_2O and H_2O mixture (3:1) was employed as the monitoring light, and a 1 cm long sample cell was used in the transient absorption measurements. These TA spectra show that the excited states of the photoinitiator do not have an absorption band in the near infrared (NIR) region (around 1 μm). Hence, a stepwise multiphoton absorption does not occur when simultaneously irradiating with UV and NIR laser lights.

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[1] Miyasaka, H.; Moriyama, T.; Kotani, S.; Muneyasu, R.; Itaya, A. *Chem. Phys. Lett.*, 1994, **225**, 315.

[2] Miyasaka, H.; Moriyama, T.; Itaya, A. *J. Phys. Chem.*, 1996, **100,** 12609.

3. Scanning electron micrographs of solidified microstructures

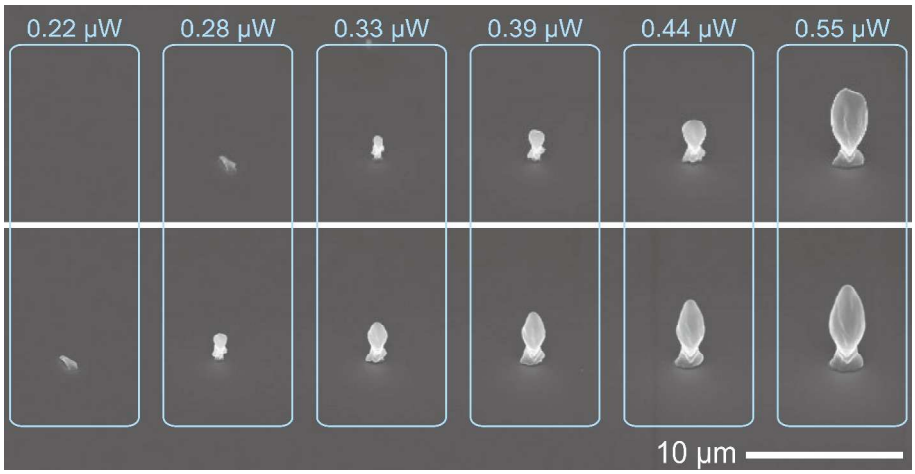

Figure S2. Scanning electron micrographs of TMPTA microdots solidified (upper) solely by UV laser polymerization and (lower) by simultaneously irradiating with UV and NIR (at 120 mW). TMPTA solution, including a small amount (1 wt%) of the radical photoinitiator, Irgacure184, solidified by focusing the UV laser light at the interface between the solution and glass surface. Applied UV light intensities are shown in the figures. Irradiation time for solidifying a position is 0.5 s per point. Threshold of the photopolymerization decreases upon simultaneous irradiations of UV and NIR lights, as seen in the results of Figs. 1a and 1b.

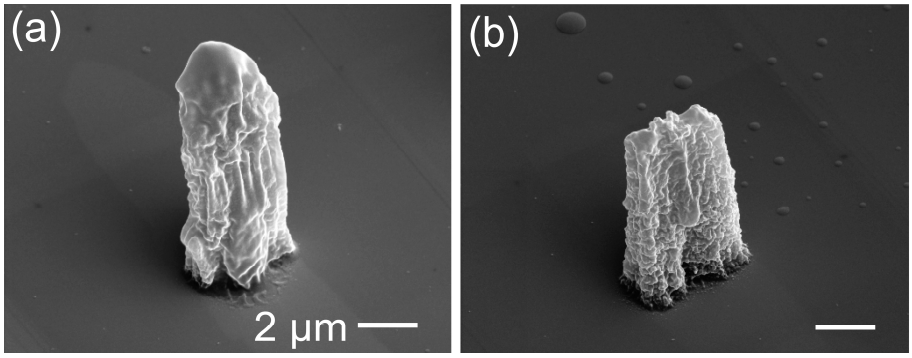

Figure S3. Scanning electron micrographs of solidified microstructures of KC1156A by (a) UV laser polymerization and (b) simultaneously irradiating with UV and NIR (at 120 mW) lights. Although these two structures are modelled by multiple irradiations at the same UV power, 0.078 μW, in the same manner, the resultant shapes differ. Similar to the experimental result shown in Fig. 2c, simultaneous irradiation of UV and NIR laser lights suppresses the dispersion of the reaction intermediates.

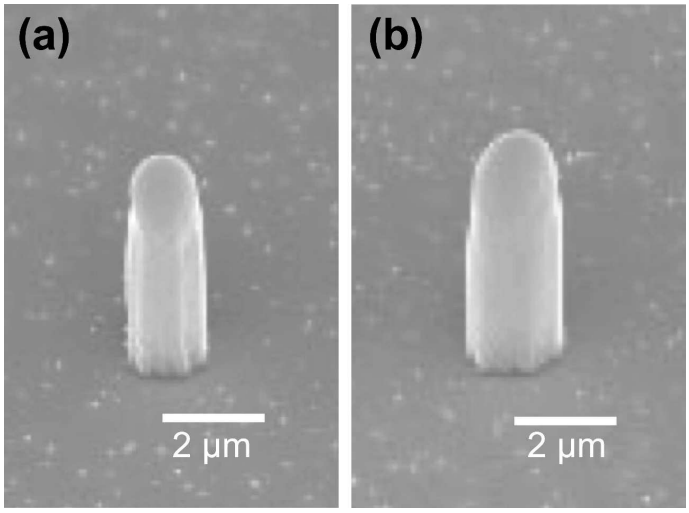

Figure S4. Scanning electron micrographs of solidified microcolumns of dipentaerythritol hexaacrylate (DPHA, provided from Toagosei), which includes 1 wt% radical photoinitiator, Irgacure184, by (a) multiple UV irradiations and (b) simultaneous UV and NIR (at 120 mW) irradiations. Columnar microstructures are produced in the same manner as ones shown in Fig. 2 according to the blueprint shown in Fig. 2d. DPHA solution has a higher viscosity (~5300 mP·s at 298K) than TMPTA (~85 mP·s at 298K) and KC1156A (~450 mP·s at 298K). Applied UV and NIR light intensities are 0.02 μW and 120 mW, respectively, and the irradiation time for solidifying a position is 0.5 s per point. The highly viscous medium prevents the dispersion of reaction intermediates such as polymer radicals and nanometer-sized crosslinked polymer particles from the focusing point of the UV light, resulting in a much smaller solidification volume even with only UV irradiation.

4. Temperature measurement at the focusing spot of the NIR laser beam in a photopolymerizable solution

Fluorescence correlation spectroscopy provides the translational diffusion coefficient of fluorescence dyes in solution based on autocorrelation analysis of the temporal fluctuations in the fluorescence intensity. This fluctuation originates from variations in the dye concentration due to the Brownian motion in the small detection volume of a confocal microscope. Autocorrelation function, $G(\tau)$, of this fluorescence fluctuation at the detection volumes of confocal microscopes is analytically derived as[3, 4]

$$G(\tau) = 1 + \frac{1}{N}\left(1 + \frac{p}{1-p}\exp\left(-\frac{\tau}{\tau_T}\right)\right)\left(1 + \frac{\tau}{\tau_D}\right)^{-1}\left(1 + \frac{\tau}{w^2\tau_D}\right)^{-1/2} \quad \text{(S1)}$$

Here N is the average number of fluorescence dye molecules in the confocal volume, τ_T is triplet lifetime of the fluorescence dyes, p is the fraction of the contribution of the triplet state, and τ_D is the diffusion time (or mean residence time) related to the translational diffusion coefficient D by eq. (S2). Structure parameter, w, is defined as $w = w_z/w_{xy}$ where w_{xy} and w_z are respectively the radius and axial length of the confocal volume with cylindrical shape ($V = 2\pi\, w_{xy}^2\, w_z$).

$$\tau_D = \frac{w_{xy}^2}{4D} \quad \text{(S2)}$$

If the translational diffusion of dye molecules obeys the Stokes–Einstein model, then translational diffusion coefficient, D, can be expressed as

$$D = \frac{kT}{6\pi\eta(T)a} \quad \text{(S3)}$$

where k is the Boltzmann constant, T is Kelvin temperature, $\eta(T)$ is the viscosity of the solution at temperature T, and a is the hydrodynamic radius of the probe molecules. Elimination of D between eqs. (2) and (3) gives the following equation.

$$\tau_D = \gamma\frac{\eta(T)}{T} \qquad \left(\gamma = \frac{6\pi a w_{XY}^2}{4k}\right) \quad \text{(S4)}$$

In eq. (S4), the temperature dependence of the viscosity $\eta(T)/T$ can be independently obtained by a viscometer, and the γ value can be obtained by the FCS measurement at a certain temperature (typically, room temperature, 294–295K). Hence, temperature, T, is estimated from τ_D obtained with FCS under the condition where the hydrodynamic diameter of dyes, a, and the structure parameter, w_{xy}, are constant in the temperature range examined. Note that the method estimates the average temperature inside the confocal volume because FCS provides the average translational diffusion velocity over fluorescent dyes passing through the confocal area. For more detail about the method, see Ref. 19.

The temperature dependence of the viscosity of the monomer (TMPTA) solution used in the present work was experimentally obtained using Ostwald's viscometer, as shown in Fig. S5(a). Figure S5(b) shows the fluorescence autocorrelation curves of rhodamine 123 (R123) in TMPTA in the presence of NIR laser light, and clearly demonstrates that the decay of the correlation curve becomes faster as the laser power increases. The value of diffusion time, τ_D, decreases as the incident NIR power increases (Fig. S5(b) inset). From the experimentally obtained values of τ_D, the temperatures at the focusing point of the NIR laser light were estimated, as shown in Fig. S5(c). The results indicate the coefficient of temperature elevation of TMPTA is 27 K/W.

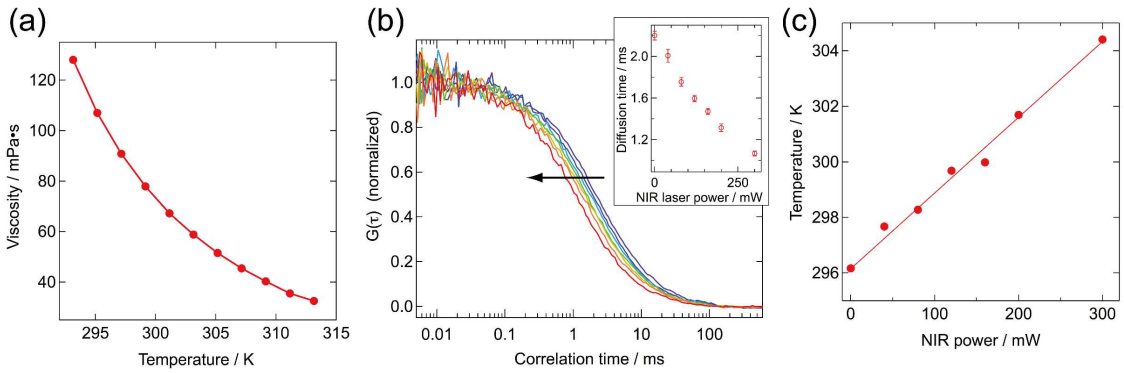

Figure S5. (a) Viscosity–temperature relation of TMPTA. (b) Fluorescence autocorrelation curves of R123 in the presence of the incident NIR laser light. (c) Temperature at the focusing point of the NIR laser light in TMPTA as a function of incident NIR laser power.

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[3] *Fluorescence Correlation Spectroscopy*, Rigler, R.; Elson, E. S., Eds.; Springer Series in CHEMICAL PHYSICS 65, Springer, Berlin, 2001.

[4] Krichevsky, O.; Bonnet, G., Reports on Progress in Physics, 2002, **65**, 251.

5. The complete citation for reference 17b

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