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Confinement of Photopolymerization and Solidification with Radiation Pressure

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Supporting Information

ABSTRACT: Controlling chemical reactions within a small space is a significant issue in chemistry, and methods to induce reactions within a desired position have various potential applications. Here we demonstrate localized, efficient photopolymerization by radiation pressure. We induced a one-photon UV polymerization of liquid acrylate solutions in the optical-trapping potential of a focused near-IR (NIR) laser beam, leading to the confinement of solidification to a minute space with dimensions smaller or equal to one-fifth of the wavelength of the NIR laser. Our approach can produce solidification volumes smaller than those achievable with conventional one-photon polymerization, thus enabling the production of tiny polymeric structures that are smaller than the diffraction limit of the trapping light. This is the first demonstration of a radiation pressure effect on a photochemical reaction.

In the 19th century, Levedev experimentally confirmed the existence of radiation pressure,[1] and in 1986, Ashikin developed a practical tool, the so-called optical tweezer, using strong radiation pressure from lasers.[2] To manipulate and fabricate small materials, the optical tweezing method has contributed to advances in various research areas, including micro total analysis systems,[3] microdevices,[4] colloid science,[5] and bioscience.[6] Moreover, optical trapping has been applied to nanoparticle patterning,[7] spectroscopic investigations of individual J-aggregates,[8] and laser-induced crystallization of organic molecules.[9] The underlying mechanisms for these processes have been investigated from experimental[10] and theoretical[11] viewpoints. Additionally, radiation pressure has been widely utilized to process and fabricate polymeric materials; examples include the laser-induced phase transition of a polymeric gel by nonresonant laser exposure,[12] connection of small spheres of polymers,[13] and formation of small polymeric assemblies with various structures.[14−16] Although these investigations have reported interesting results, the aforementioned studies used prepared polymers and did not demonstrate how radiation pressure controls the chemical reaction. This is because the chemical reactivity and diffusion of individual small molecules in solution are not usually affected by radiation pressure.

On the other hand, we have confirmed experimentally that an amphiphilic random copolymer with a gyration radius of 5.5 nm can be successfully trapped.[14] Thus, it is plausible that a photochemical reaction involving polymerization could be designed to demonstrate the effect of radiation pressure on a chemical reaction. Because the reaction intermediates cannot be monitored spectroscopically and the reaction dynamics is difficult to follow, we employed herein a type of product analysis; that is, we observed the solidified microstructures and compared the photopolymerization results with and without radiation pressure. This allowed us to demonstrate confinement of a reaction to a small volume (less than one-fifth the wavelength of the laser light) by radiation pressure.

Figure 1a shows scanning electron microscopy (SEM) images of polymerized microdots produced by spot irradiation for 0.5 s using a UV laser. The acrylate solution KC1156A (JSR Corporation) underwent photopolymerization upon UV irradiation [see the Supporting Information (SI)]. After the polymerized microdots were washed with ethanol and dried, they were examined using SEM. A UV laser beam was focused at the interface between the solution and a coverslip. Irradiation at powers of >0.15 μW successfully produced microstructures on the coverslip even after washing. On the other hand, at low laser powers of 0.11 and 0.095 μW, the solid products collapsed during the washing process. At powers of $\leq$0.076 μW, the SEM image did not show any structures. Moreover, we could not detect product formation in the optical transmission image during UV irradiation. These results indicate that the reaction intermediates produced by photoirradiation diffuse out from the focusing area of the UV light, preventing the generation of permanent products on the surface because of the low concentration of polymers in this UV power range ($\leq$0.076 μW).

Figure 1b shows SEM images of the microdots produced by simultaneous irradiation with a UV laser and an NIR laser (120 mW) for 0.5 s and subsequent washing similar to Figure 1a. Simultaneous irradiation using the NIR laser beam on the spot

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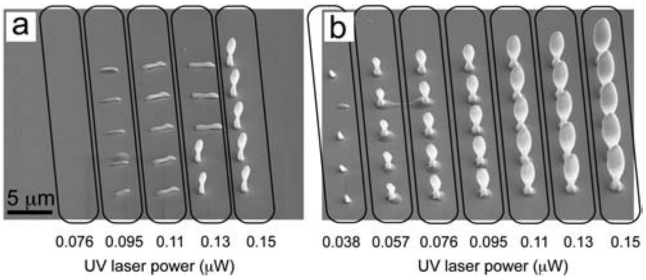

Figure 1. SEM images of photopolymerized microdots of KC1156A remaining on a glass surface after (a) irradiation with a UV laser for 0.5 s and (b) simultaneous irradiation with a UV laser and an NIR laser (at 120 mW output power) at the same position for 0.5 s. Incident UV laser powers are denoted in the figure.

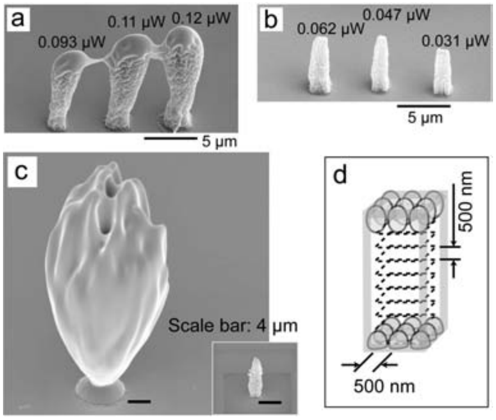

Figure 2. (a, b) SEM images of three microstructures produced by (a) UV laser polymerization and (b) simultaneous irradiation with UV and NIR lasers. In both cases, the solution (KC1156A) was exposed point by point using a 3D scanning stage according to the blueprint illustrated in (d). Applied UV powers are shown in the figures, and the irradiation time was 0.5 s per point. (c) SEM images of the TMPTA microstructures. The columnar structure on the left was fabricated by irradiation solely with a UV laser at a power of 0.28 μW, while the smaller structure on the right was fabricated by simultaneous irradiation with UV (0.28 μW) and NIR (120 mW) lasers using an irradiation time of 1.0 s per point. (d) Model structure (blueprint) for the microstructures in (a−c).

where UV exposure was carried out induced the production of microdots more efficiently. Even at UV laser powers of $\leq 0.076\ \mu$W, where microdots were not formed with UV irradiation alone (Figure 1a), clear images were observed (Figure 1b). Moreover, simultaneous irradiation with two lasers led to the formation of microproducts with volumes larger than those produced without NIR light.

It is well-known that multiphoton excitation with an ultrashort NIR laser pulse can produce this kind of microstructure.[17] As the photoinitiator in the present system has absorption bands only at wavelengths shorter than 360 nm, three-photon absorptions were required to photoexcite the initiators using a continuous-wave (CW) NIR laser beam at 1064 nm. The cross-section of the three-photon absorption was typically too small to induce an effective excitation by the CW laser light with an intensity of 5−50 MW/cm^2 at the present focusing point.[18] Actually, irradiating solely with NIR laser light did not produce any microproducts in the present system.

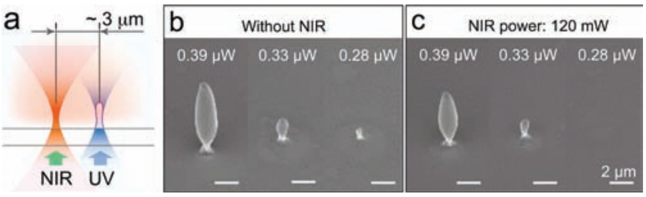

Figure 3. (a) Schematic illustration of the spatial relationship between the UV and NIR laser irradiation, where the latter was focused ~3 μm from the focus of the UV light. (b) SEM image of polymeric microdots cured by irradiating the TMPTA solution solely with the UV laser for 1 s as a function of laser power (as denoted in the picture). (c) SEM image of polymeric microdots cured by irradiating the TMPTA solution with a UV laser for 1 s as a function of laser power (as denoted in the image) in the presence of NIR laser light (120 mW). Simultaneous irradiation with the UV and NIR beams at the separated points decreased the size of the microdots.

To demonstrate the effect of radiation pressure on photopolymerization and solidification, we employed simultaneous irradiation with the two lasers to produce three-dimensional (3D) microstructures using a scanning stage. Figure 2a shows an SEM image of three microstructures produced by irradiation only with a UV laser. The microproducts produced without additional NIR irradiation exhibited larger and more obscure shapes in comparison with the model structure (Figure 2d). Moreover, the tops of the three microstructures were connected by polymerization. On the other hand, the microstructures prepared by irradiation with both the UV and NIR lasers gave fine, tiny shapes similar to the model structure shown in Figure 2d. These results clearly indicate that NIR irradiation results in the efficient production of microstructures as well as the confinement of polymerization, leading to the formation of structures in a minute area.

To confirm this effect of the NIR laser, we prepared microstructures at the same UV power (0.28 μW for 1 s) with and without NIR irradiation. Figure 2c clearly shows that the microstructure formed by irradiation only with UV light was much larger than that obtained using both NIR and UV light, indicating that polymers produced by UV irradiation diffuse to surrounding areas not irradiated by the UV laser. Additionally, the size of the microstructures decreased in highly viscous solutions (Figure S4 in the Supporting Information). On the other hand, the microstructure formed using two laser beams maintained a tiny, fine structure close to the model, although the same UV laser power was applied (for details, see Figure S2). The polymerization system using other monomers yielded similar results (Figure S3).

In general, the polymerization process can be divided into three reactions: chain initiation, chain propagation, and chain termination. The local temperature elevation induced by NIR irradiation may significantly affect these reactions. In the present system, irradiating the initiator with UV light resulted in chain initiation, negligibly influenced by the temperature effect. However, the present systems underwent a chain propagation reaction in the neat monomer liquid, and the reaction rate should increase as the temperature is elevated. Actually, organic compounds typically exhibit a slight absorption in the NIR range due to overtone absorptions of vibrational transitions.

Local heating of a solution by NIR light at 1064 nm could elevate the local temperature, so the temperature around the focal point of the NIR laser was estimated by fluorescence correlation spectroscopy (FCS).[19] The coefficient of temperature elevation for trimethylolpropane triacrylate (TMPTA) was

27 K/W (see Figure S5 and ref 19 for details). In the present case, the temperature elevation at the focal point of the NIR laser was estimated to be 5−10 K under the present conditions (<300 mW). In addition, it was confirmed that the temperature remained nearly constant up to several micrometers from the focusing point of the NIR beam because of the fast thermal conduction of organic solvents[20] (typically, several μm/μs). Hence, heating should have a strong effect, even for positions a few micrometers away from the focusing point of the NIR laser.

To clarify the effect of local heating, we produced microstructures using the optical setup shown in Figure 3a, where the NIR laser was focused ∼3 μm from the focal point of the UV laser. Figure 3b,c shows that irradiation with NIR light 3 μm from the UV light formed microstructures with smaller volumes than those produced by irradiation with UV at the same output power. Moreover, the microstructure was not detected at a UV power of 0.28 μW with NIR laser light. These results indicate that temperature elevation suppresses the formation of microstructure, probably because polymer diffusion is accelerated.

Thus, the present efficient and localized solidification can be ascribed to efficient trapping of long intermediate oligomers and polymers by radiation pressure. Equation 1 gives F_r, the force under the radiation pressure leading to the laser trapping:[2]

$$F_r \approx \frac{1}{2}\varepsilon_m \alpha \nabla E^2 \qquad (1)$$

in which E is the electric field strength and α is the polarizability, given by $\alpha = 3V(\varepsilon_p - \varepsilon_m)/(\varepsilon_p + 2\varepsilon_m)$, where V and ε_p are the volume and dielectric constant of the small trapped object, respectively, and ε_m is the dielectric constant of the surrounding medium. Equation 1 indicates that a particle with a larger polarizability experiences a stronger trapping force. The polarizability of a particle increases monotonically with V and ε_p, and therefore, a stronger trapping force is exerted on polymer chains with a higher degree of polymerization (molecular weight). The dielectric constant generally depends on the wavelength of the light: ε_p increases with decreasing wavelength under nonresonant conditions (i.e., no absorption). Hence, using a trapping laser with a shorter wavelength should generate a stronger trapping force.

Equation 1 also predicts that a steeper electric-field gradient of the light provides a stronger force for the same trapping target. A simple way to realize a optical-field gradient steep enough to achieve the laser trapping of small particles is by tightly focusing a laser beam using a microscope objective with a high numerical aperture. As the minimum spot size of a laser beam is determined by the diffraction limit of the light, using a laser beam with a shorter wavelength produces a smaller focusing spot, leading to stiffer optical trapping. However, although the use of a shorter-wavelength laser permits stiffer optical trapping, focusing a laser beam at a short wavelength can often damage the trapping target via photoabsorption. To avoid this, we employed an NIR laser as the trapping light source.

From eq 1, the estimated minimum particle sizes trapped by the radiation force from a focused NIR laser beam at room temperature are 10−20 nm for organic compounds. We reported previously that nonresonant NIR laser irradiation can induce the production of an assembly (μm-sized particle) of polymer chains with 5−10 nm radius of gyration by radiation pressure in solution.[14−16] This means that not only terminated product polymer chains but also large intermediate oligomers and their aggregates can be trapped, or at least that their translational diffusion can be suppressed by NIR irradiation.

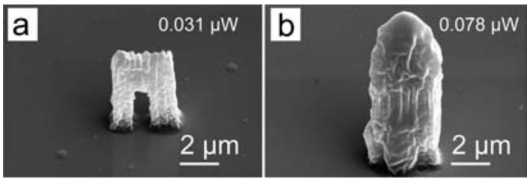

Figure 4. (a) Microstructure resembling the "Arch of Triumph" produced by simultaneous irradiation with UV and NIR lasers. (b) Microstructure produced by UV irradiation only. The two structures (a and b) were produced via the same procedure with the same blueprint. Applied UV powers are shown in the figures.

It should be noted that the size of the microstructure produced with a large power of the UV laser light under NIR light is much smaller than that without NIR light (Figure 2c). This small microstructure may be related to the efficient termination reaction of the polymerization process. As discussed above, termination reactions such as chain recombination and disproportionation occur between the intermediate polymer chains undergoing propagation. Hence, the high local concentration of the chains under propagation leads to effective termination, giving densely polymerized products. In other words, NIR laser irradiation accelerates the production of the microstructure when the UV light weakly initiates polymerization and, through effective termination, can suppress the production of large and obscure structures.

As already described, simultaneous irradiation with UV and NIR lasers at separate positions decreased the efficiency of local polymerization (Figure 3). These results indicate that precise 3D overlap of the two laser beams is indispensable for efficient solidification. In the present work, we used amorphous films of fluorescent dyes on coverslips with thicknesses of several micrometers for precise overlapping of the two focal spots. Focusing with the UV and NIR lasers produced two fluorescence spots on the fluorescence amorphous film. It should be noted that the film was photoexcited via the two-photon absorption of the NIR light because of the very high concentration of the dye. By adjusting the external optics, we carefully overlapped the two fluorescence spots three-dimensionally to an accuracy of less than several tens of nanometers in the XY plane and <200 nm in the Z direction. To control the locations of the two focal points relative to the surface of the coverslips, we introduced red light (632.8 nm) from a He−Ne laser as a guide. The red beam was focused at the same Z location as the UV and NIR lasers by adjusting the external optics. This enabled us to focus the two invisible lasers (UV and NIR) precisely at the interface between the coverslip and acrylate solution.

The confinement of polymerization and solidification by radiation pressure prominently produced a perforated structure (Figure 4a,b), indicating that 3D one-photon polymerization and solidification with submicrometer resolution can be achieved by radiation pressure. As demonstrated by an elegant approach using two-photon excitation,[17] inducing the initial processes (photoabsorption and successive photochemical reactions) within a small volume has been an area of interest in photochemical microfabrication research. Herein we demonstrate that laser trapping enables polymerization to be confined to the nanometer-sized domain. Our approach can be applicable to any photopolymerization, including visible-initiating systems.

As our method confines reactants with high molecular weights (e.g., oligomers) using radiation pressure, this can be applicable to photochemical reactions involving intermediates with sizes of

~10 nm. Proteins and DNAs will be candidate molecular systems, as their trapping, manipulation, and alignment in solution with radiation pressure have been well-studied.[21,22] An important future target for research on the use of radiation pressure will be its application to the control of chemical reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, transient absorption spectra of the photoinitiator used in the present work, scanning electron micrographs of the polymeric microstructures obtained in the control experiments, the principle and results of temperature measurement using FCS, and complete ref 17b. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ NOTE ADDED AFTER ASAP PUBLICATION

This article was published ASAP on August 30, 2011. Equation 1 has been corrected. The corrected version was posted on September 14, 2011.