

Generating Microstructures with Highly Variable Mechanical Performance using Two-Photon Lithography and Thiol-ene Photopolymerization

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Electronic Supplementary Information

Abstract In this study, we investigate the effect of the exposure dose on the mechanical property of the photoresins generated with acrylate self-polymerization and thiol-ene polymerization. The results indicate that the mechanical performance of the thiol-ene photoresin is highly depended on the exposure dose during the solidification process. With 350-fold exposure dose change, the stiffness of the thiol-ene photoresin reached more than 700-fold change compared to 14-fold of the acrylate photoresin. We developed a TPL photoresist based on our results and show the capability to fabricate microstructures with high resolution and variable mechanical performances using this method.

Keywords Thiol-ene; Two photo lithography; 3D printing; Photoresist

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INTRODUCTION

Two-photon lithography (TPL) has arisen tremendous attention as a powerful manufacturing technology over the past decade,^[1–3] due to its capability to generate microstructures with sub-micrometer resolution and virtually any geometry. The high precision and architectural versatility of TPL makes the method an ideal tool for the manufacture of precise micro-objects from various materials that could be used in photonics,^[4–6] bionics,^[7–9] basic cell biology study,^[10–12] and drug delivery.^[13,14]

Although TPL can create microstructures with complex and hierarchical geometries, the variation of the mechanical properties for every fabricated solid voxel is limited.^[15–17] This is simply because TPL is performed in a homogeneous photoresist, thus the composition of the fabricated voxels is almost identical. As a consequence, fabricating an object with variable mechanical performance at different area becomes a challenge for TPL.^[18] A solution for this problem is to endow the object with hollow-carved substructure,^[16,19] which leads to the change in the resulted mechanical performance (depends on the porosity and geometry of the hollow structure).^[17] However, this method usually requires carefully structure design with complicate calculation and simulation,

and may endow the fabricated objects with unexpected wettability, photonic and biological effects, which is not acceptable in many cases.^[18]

A more direct way is to control the mechanical property by the exposure dose during fabrication. TPL is based on the photoinduced polymerization of the monomers in the photoresist (normally acrylates). In this case, the exposure dose significantly affects the polymerization degree of the photoresist, which determines the crosslinking density as well as the mechanical property of the final photopolymer. Similar concepts have been proved to be feasible in 3D printing technology with digital light processing (DLP) devices, objects with variable mechanical performances were successfully fabricated.^[20,21] However, it was shown that, with an acrylate photoresist, the mechanical property of the objects can only change ~3-fold by directly controlling the light intensity, which greatly limits the potential of this concept.^[20]

Although acrylate self-polymerization is most common-used in TPL, other types of photochemistries are also included in some reports.^[22] One example is the thiol-ene photopolymerization, compared to acrylate polymerization, thiol-ene reaction exhibits better photoactivity and less oxygen sensitivity,^[23] thus is considered as a potential chemistry for TPL fabrication. In fact, thiol-ene photoresist has been investigated in some previous reports,^[24–27] however, the possibility of exposure dose-dependent mechanical performance control has not been investigated.

In this paper, we examined the mechanical performance of the photoresins fabricated using acrylate self-polymerization

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or thiol-ene polymerization under different exposure doses. We show that, the stiffness of the photoresin generated with thiol-ene polymerization exhibits linear relationship with the exposure dose. With 350 times of UV intensity (from 0.06 mW/cm² to 21 mW/cm², 60 s irradiation time), the stiffness (Young's modulus) of the cured photoresin shows more than 700-fold change compare to 14-fold of acrylate photoresin under same condition. Based on this result, we developed a TPL photoresist which allows to generate micro objects with variable mechanical property by the controlling the laser power and scanning speed.

EXPERIMENTAL

Materials

Pentaerythritol tetra(3-mercaptopropionate) (PETMP, 90%), pentaerythritol tetraacrylate (PTTA, 95%), pentaerythritol triacrylate (PETA, 98%), di(trimethylolpropane) tetraacrylate (Di-TMPTA, 98%), diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, 99%), trichlorovinylsilane (TCVS, 99%), 4-(dimethylamino)pyridine (DMAP 99%), triethylamine (TEA, 99%) and dichloromethane (DCM, 99.5%) were obtained from Macklin (China). Ethanol (99.5%), acetone (99.5%), acetophenone (AP, 99%), isopropyl alcohol (98%), and *n*-pentane (99%) were obtained from Aladdin (China).

The silicate glass plates used in the experiment were 7101 microscope slices of Sail Brand (China). The ultraviolet light source was the 365nm UV LED lamp (Highlight, Hangzhou, China). The intensity of ultraviolet power was measured by ultraviolet irradiator (Photoelectric Instrument Factory of Beijing Normal University, China).

Formation of Different Photoresists

PETMP-PTTA photoresist: 17.3 mg of TPO, 1 mL of PETMP and 0.73 mL of PTTA (the calculated molar ratio of mercapto groups and double bonds in the photoresist is 1:1 according to the purity, molecular weight and density of the reagents) were mixed and ultrasonicated for 30 min to form the thiol-ene photoresist.

PTTA photoresist: 17.3 mg of TPO in 1.73 mL of PTTA.

PETA photoresist: 17.3 mg of TPO in 1.73 mL of PETA.

Di-TMPTA photoresist: 17.3 mg of TPO in 1.73 mL of Di-TMPTA.

PETMP-PTTA photoresist for TPL processing: to form the optimized thiol-ene photoresist for TPL fabrication, 8.65 mg of TPO was mixed with 0.865 mL of AP, 1 mL of PETMP and 0.73 mL of PTTA. The mixture was ultrasonicated for 30 min to form a homogeneous solution.

Formation of Photoresin Slices

Photoresists were injected into a box formed using two glass slices separated with 500 μ m spacer. After exposing to 365 nm UV with pre-set intensity for 60 s and then washing with acetophenone and drying with N₂, photoresin slice with different cross-linking degrees could be obtained.

Pretreatment of Silicon Wafer

To enhance the adhere of the TPL-fabricated microstructures on the silicon substrate, C=C bonds were chemically modified onto the substrate. To do this, the silicon wafer surface was treated by O₂ plasma treatment (CPC-A plasma cleaner, CIF Instruments, 50 W, 30 s) to increase the density of surface

hydroxyl groups. A mixture of 200 μ L of TEA, 25 mg of DMAP, and 100 μ L of TCVS in 20 mL of DCM solvent was prepared. Then, the silicon wafer was immersed into the solution with gentle oscillation for 30 min and washed with ethanol to rinse away the excess TCVS.

TPL Fabrication of 3D Microstructures

Two-photon lithography was performed using a commercial workstation (Photonic Professional GT, Nanoscribe GmbH) equipped with a 780 nm femtosecond laser and objectives (25 $\times$, 0.8 NA, Zeiss, Plan Apochromat). In this system, the movement of the laser focus was controlled by a Galva-nometric scanner. The 3D structures were designed by SolidWorks. The photoresist was drop cast onto the silicon substrate and covered by a glass substrate, a 50 μ m tape was used as spacer. The 3D structures were then written on the silicon wafer by TPL. The laser power and the scan speed were set at 10%–50% (AOM=1.00, PowerScaling=1.00) and 400–20000 μ m·s⁻¹. The 3D structures with different mechanical properties could be obtained by adjusting laser power and scanning speed. After the direct-laser-writing process, the silicon substrate was developed with acetophenone, isopropyl alcohol, and *n*-pentane for 20, 5 and 3 min, respectively.

Scanning Electron Microscopy

Scanning electron microscope (SEM) images were obtained using a field emission scanning electron microscope (Zeiss Ultra Plus, Germany). The samples were sputtered with a gold layer by Hitachi E-1010 ion sputtering (Hitachi Ltd., Japan) for 10 s before measurement.

Raman Spectrometry Test

Raman characterizations were performed by an inVia confocal Raman microscopy (Renishaw Inc., UK) equipped with a 532 nm laser. Measurement conditions: the laser power was 5 mW, the continuous spectrum acquisition time was 10 s, and the spectral range was 3000–400 cm⁻¹. At least five points were taken from each sample and the average signal intensity was calculated to obtain the spectra.

X-ray Photoelectron Spectroscopy Analysis

X-ray photoelectron spectroscopy (XPS) spectra of the photoresist slices were obtained by a scanning XPS microprobe instrument (PHI-5000 VersaProbe, Ulvac-Phi, Japan, monochromated Al K α source, $h\nu$ =1486.6 eV).

Compression Modulus Test

Compression moduli of the cured photoresin slices were measured by Instron 5943 (Instron, a Division of Illinois Tool Works Inc) at room temperature. The cylinder-shaped photoresin slices (7 mm in diameter and 0.5 mm in height) were used for compression test and the crosshead speed was set at 6 mm/min. The compression modulus value was obtained from the fitting slope of the stress-strain curve.

Nanoindentation Test of Cured Photoresist Slices

Young's moduli of cured photoresin slices were measured using a Nanoindenter (Piuma, OPTICS 11, Amsterdam, Netherlands) and a contacting probe with a spherical indenter tip with a stiffness of 50 or 250 N/m and a diameter of 25 μ m. The loading velocity was 2 μ m/s. All measured Young's modulus data refer to the effective Young's modulus obtained by the software (Dateviewer V2) provided by Optics11.

Nanoindentation Test of 3D Microstructures

Young's moduli of 3D microstructures were measured by Nano Test (Micro Materials, UK) with a diamond Berkovich three-sided pyramid indenter. Indentations were made in the "load control" mode with 0.0025 mN/s loading rate, 0.0025 mN/s unloading rate, 10s dwell at a maximal load of 0.05 mN.

RESULTS AND DISCUSSION

The monomers used in this study are shown in Fig. 1(a). Acrylates are known to undergo self-polymerization under the stimulation of UV or heat. In our experiments, the acrylate

photoresist pentaerythritol tetraacrylate (PTTA, with 1 wt% diphenyl (2,4,6-trimethylbenzoyl)phosphine oxide (TPO) as photoinitiator) can easily form crosslinked homopolymer after 60 s illumination under 365 nm UV (Fig. 1b-i). Acrylate can also react with mercapto groups via the well-known thiol-ene photoclick chemistry, thus when curing a photoresist containing pentaerythritol tetra(3-mercaptopropionate) (PETMP) and PTTA (thiol-ene photoresist, 1 wt% TPO as photoinitiator) under UV, a crosslinked photoresin can be obtained (Fig. 1b-ii). XPS and Raman spectra were performed on PTTA and thiol-ene photoresins, the results are shown in Fig. 2 and Table 1. Thiol-ene photoresin exhibits clear S2p signal in XPS spectrum

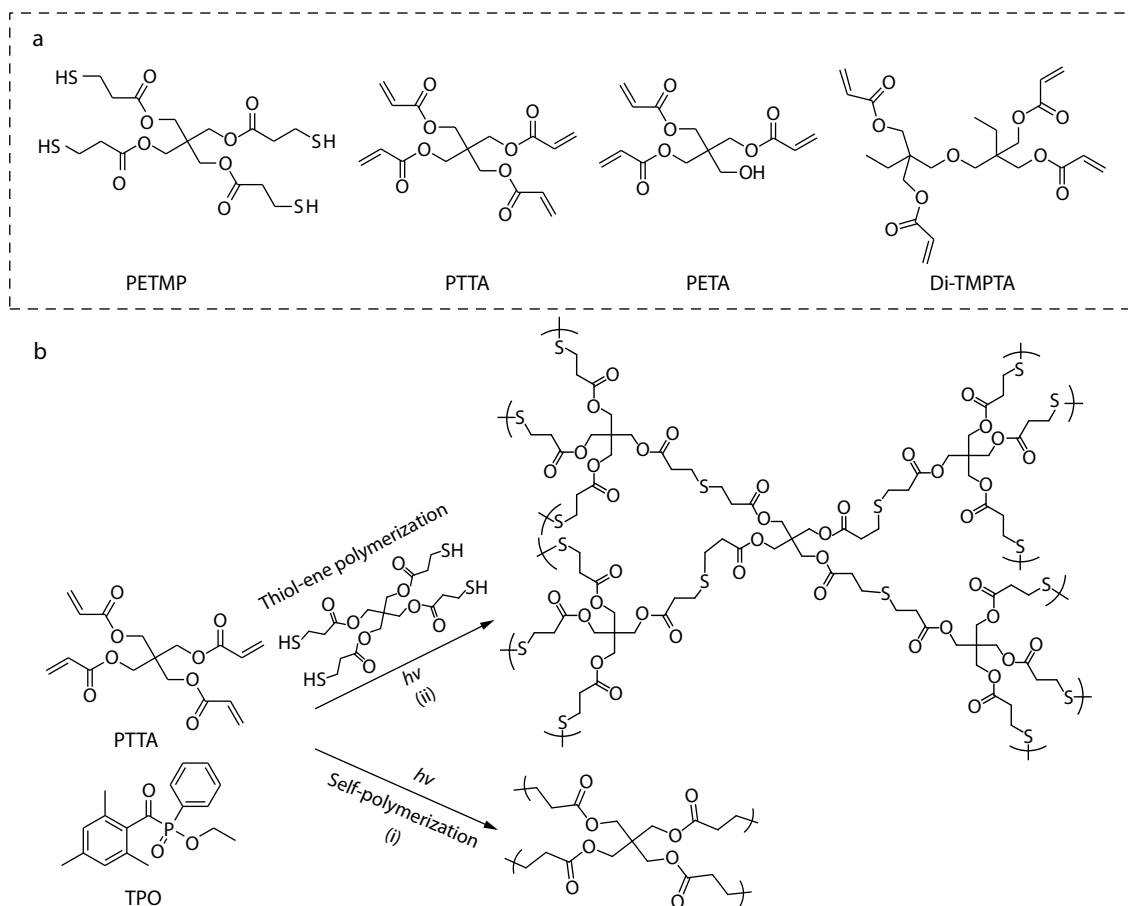


Fig. 1 (a) Chemical structure of the monomers used in this study; (b) Structure of the polymers obtained by acrylate self-polymerization or thiol-ene polymerization.

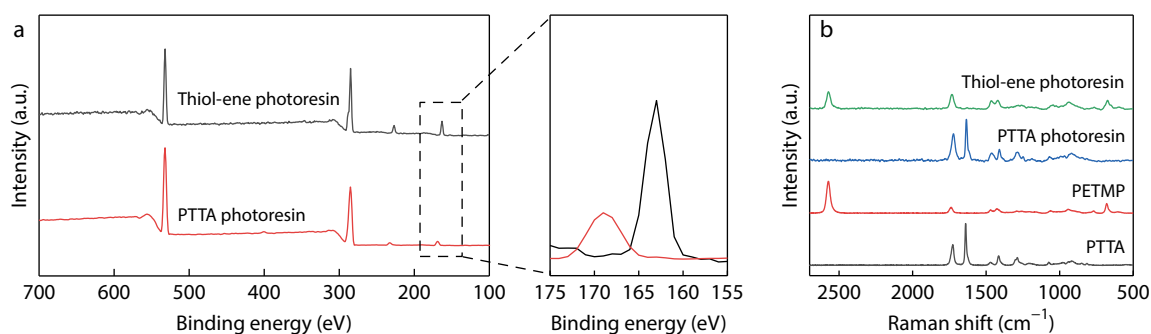


Fig. 2 (a) XPS (black: thiol-ene photoresin, red: PTTA photoresin) and (b) Raman spectra of the obtained photoresin slices.

Table 1 Atomic concentration (S, C and O only) of the photoresins.

Atomic concentration (%)	PTTA	Thiol-ene (0.4 mW)	Thiol-ene (21 mW)
S	0	5.82	5.87
C	66.22	66.29	65.63
O	33.78	27.89	28.5

(S% $\approx$ 5.8% as shown in Table 1), and shows characteristic bands of C—S bond ($\sim$ 676 cm^{-1}) and S—H ($\sim$ 2569 cm^{-1}) bond in the Raman spectrum, while such bands cannot be found in the corresponding spectra obtained from PTTA sample (S%=0%, Table 1). On the contrary, a band at 1634 cm^{-1} (characteristic band of the C=C bond) can be found on the Raman spectrum of the PTTA photoresin, indicating that some unreacted double bonds are left in the polymerized resin. However, such peak is almost missing in the Raman spectrum of the thiol-ene photoresin. The PTTA photoresin shows a Raman spectrum similar with the PTTA monomer, with weaker intensity at $\sim$ 1634 cm^{-1} due to the consumption of part of the double bonds during polymerization. The thiol-ene photoresin shows a spectrum which is the combination of the spectra from PTTA and PETMP, with the disappearance of the peak at $\sim$ 1634 cm^{-1} due to the thiol-ene reaction. This confirms the difference in the composition of the obtained photoresins.

Since the polymerization of the photoresists (either acrylate photoresist or thiol-ene photoresist) is highly controlled by light, we wonder if the mechanical property of the obtained photoresins can be well controlled by the exposure dose. To confirm this, PTTA photoresist and thiol-ene photoresist were exposed to UV light with different intensities (0.06, 0.4, 1.4, 4, 7.4, 11.4, 15.9 and 21 mW/cm^2) for 60 s, the obtained photoresin slices were analyzed with nanoindentation to investigate their stiffness (Young's modulus). As shown Table 2, the thiol-ene photoresist exhibits distinct performance to the acrylate photoresists. When the UV intensity is extremely low ($<0.06 \text{ mW}/\text{cm}^2$), the photoresists kept liquid state after illumination. Under 0.06 mW/cm^2 UV, the obtained thiol-ene photoresin shows a stiffness of 280 kPa, meaning that the resin is quite soft. On the contrary, the PTTA photoresin obtained with 0.06 mW/cm^2 UV exhibit a stiffness of 21 MPa, 75 times larger than that of the thiol-ene photoresin. When UV intensity gradually increases to 21 mW/cm^2 , the stiffness of the thiol-ene photoresin enhanced along with the UV intensity, and reached 197 MPa at 21 mW/cm^2 UV. While for PTTA photoresin, the stiffness of the solidified polymer slide changed very little when UV intensity increased from 0.06 mW/cm^2 to 0.4 mW/cm^2 . When UV intensity enhanced to 1.4 mW/cm^2 , the stiffness of the photoresin dra-

matically increased to 214.4 MPa, and then slowly increased to 305 MPa as UV intensity further increased to 21 mW/cm^2 . When UV intensity further increases, the obtained photoresins become fragile thus are not involved in the investigation. From Figs. 3(a-i) and 3(a-ii), it is clear that the stiffness of the thiol-ene photoresin shows linear dependence with the UV intensity, while the stiffness of the PTTA photoresin can hardly be controlled by the UV intensity. The maximum stiffness of the thiol-ene photoresin is lower than that of acrylate photoresin, this is probably because, unlike the linear polymerization reaction of acrylates, thiol-ene reaction is a coupling reaction (Fig. S1 in the electronic supplementary information, ESI). As a consequence, the thiol-ene polymerization will lead to polymer network with lower crosslinking density, and thus lower stiffness of the photoresin. The stiffness of the thiol-ene photoresin varied for more than 700 folds when UV intensity changes from 0.06 mW/cm^2 to 21 mW/cm^2 (350 folds), which is 50 times greater than that of PTTA photoresin (14 folds). This implies that, by using a thiol-ene photoresist, the mechanical performance of the printed object can be adjusted in a range much wider than the acrylate photoresist. To ensure that the composition of the thiol-ene photoresin obtained with different UV intensities are identical, XPS analysis was performed on the photoresin cured with 0.4 mW/cm^2 and 21 mW/cm^2 UV, respectively. The results (Fig. 3c and Table 1) indicate that the composition of the two photoresins is almost the same. Therefore, the stiffness change of the thiol-ene photoresin comes from the change in crosslinking density rather than composition.

To further confirm such conclusion, we performed similar test on other two acrylate photoresist, PETA and Di-TMPTA (Fig. 1), the results are similar (Table 1 and Figs. 3a-iii and 3a-iv), when UV intensity varies from 0.06 mW/cm^2 to 21 mW/cm^2 , PETA photoresin shows 75-fold stiffness change (5.62 MPa to 422.24 MPa) and Di-TMPTA shows 51-fold stiffness change (13.38 MPa to 689.28 MPa), much lower than that of thiol-ene photoresin.

The compression modulus of the photoresins were also analyzed by a universal testing machine, to verify the conclusion from nanoindentation tests. The results indicate a similar tendency, as shown in Fig. 4(a) and Table 3, when the UV intensity enhanced from 0.06 mW/cm^2 to 21 mW/cm^2 , the compression modulus of the thiol-ene photoresin gradually increased. While for the acrylate photoresins (PTTA, PETA and Di-TMPTA), the compression modulus increased dramatically when UV intensity increased from 0.06 mW/cm^2 to 1.4 mW/cm^2 , and then slowly increased as UV intensity further increased to 21 mW/cm^2 . The change of the compression mod-

Table 2 Stiffness (MPa) of the photoresins generated with different UV intensities.

UV intensity (mW/cm^2)	PTTA+PETMP	PTTA	PETA	Di-TMPTA
0.06	0.28 $\pm$ 0.02	21.1 $\pm$ 3.33	5.62 $\pm$ 0.19	13.3 $\pm$ 1.77
0.4	1.96 $\pm$ 0.04	24.98 $\pm$ 1.60	55.46 $\pm$ 8.59	181.4 $\pm$ 39.0
1.4	10.53 $\pm$ 0.56	214.40 $\pm$ 30.12	277.28 $\pm$ 19.41	292.32 $\pm$ 32.91
4	21.60 $\pm$ 4.50	223.50 $\pm$ 22.54	295.21 $\pm$ 20.48	430.45 $\pm$ 38.81
7.4	56.15 $\pm$ 2.73	239.64 $\pm$ 3.56	328.69 $\pm$ 41.79	504.70 $\pm$ 65.02
11.4	113.64 $\pm$ 8.27	256.63 $\pm$ 14.34	331.34 $\pm$ 20.22	629.52 $\pm$ 78.87
15.9	148.73 $\pm$ 13.45	296.08 $\pm$ 17.83	353.36 $\pm$ 18.27	618.92 $\pm$ 39.36
21	197.71 $\pm$ 22.30	305.08 $\pm$ 26.19	422.24 $\pm$ 49.01	689.28 $\pm$ 44.68

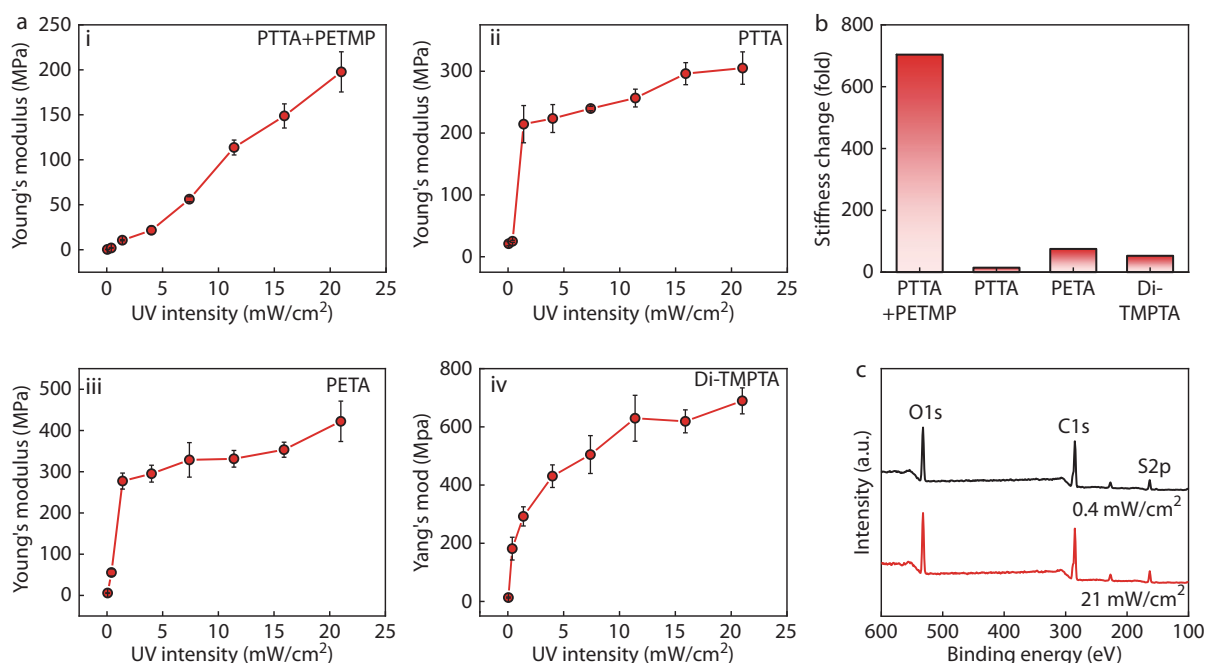


Fig. 3 (a) Stiffness of the photoresins generated with different UV intensities: (i) PTTA+PETMP (thiol-ene photoresist), (ii) PTTA, (iii) PETA, (iv) Di-TMPTA; (b) Stiffness change (fold) of the photoresin when UV intensity increased from 0.06 mW/cm² to 21 mW/cm²; (c) XPS spectra of the thiol-ene photoresin cured with 0.4 (black) and 21 (red) mW/cm² UV (365 nm).

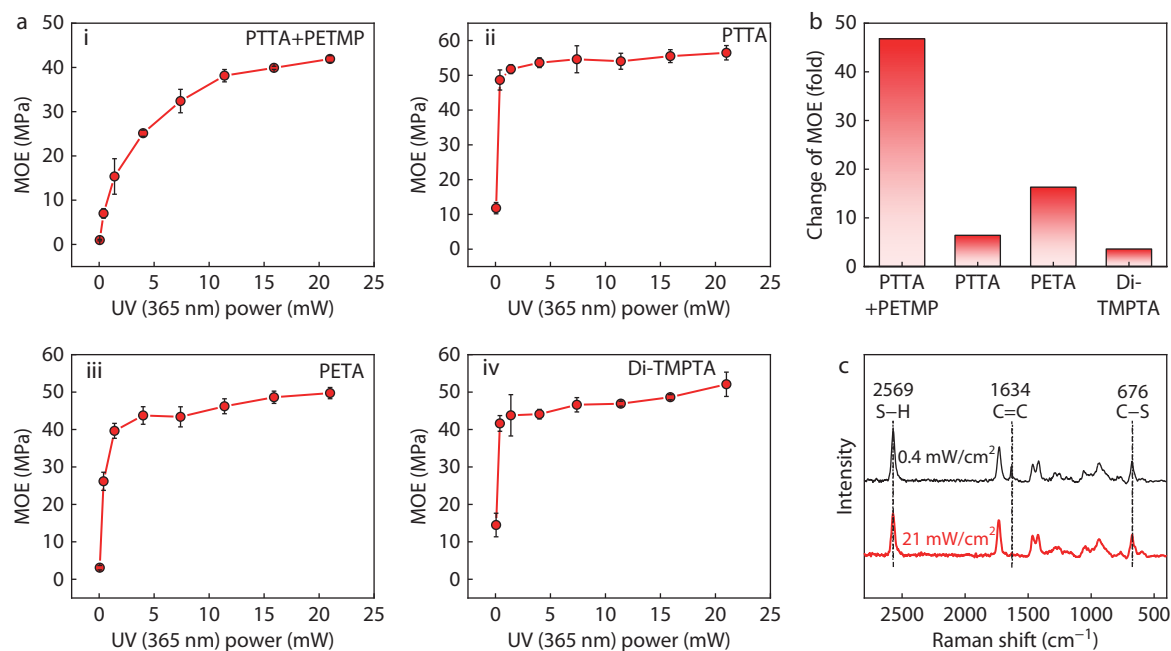


Fig. 4 (a) Compression modulus of the photoresins generated with different UV intensities: (i) PTTA+PETMP (thiol-ene photoresist), (ii) PTTA, (iii) PETA, (iv) Di-TMPTA; (b) Compression modulus change (fold) of the photoresin when UV intensity increased from 0.06 mW/cm² to 21 mW/cm²; (c) Raman spectra of the thiol-ene photoresin cured with 0.4 (black) and 21 (red) mW/cm².

ulus of the thiol-ene photoresin (43 folds when UV intensity changes from 0.06 mW/cm² to 21 mW/cm²) is much higher than that of the acrylate photoresins (4.8, 16 and 3.6 folds for PTTA, PETA and Di-TMPTA photoresins, respectively). This confirms the conclusion that the mechanical performance of the thiol-ene photoresin can be greatly changed with the exposure dose control. The reason for the high adjustability of the

thiol-ene photoresin is not clear yet, we performed Raman spectrometry on thiol-ene photoresins cured with 0.4 and 21 mW/cm² UV (Fig. 4c). It can be seen that, with lower exposure dose, the cured photoresin shows stronger peak at 2569 cm⁻¹ (S—H bond) and 1634 cm⁻¹ (C=C double bond), indicating a lower crosslinking density compared to that of higher exposure dose sample, which is probably the reason for the differ-

Table 3 Compression modulus (MPa) of the photoresins generated with different UV intensities.

UV intensity (mW/cm ²)	PTTA+PETMP	PTTA	PETA	Di-TMPTA
0.06	0.97±0.17	11.80±1.60	3.10±0.59	14.49±3.15
0.4	7.00±1.08	48.66±2.89	26.17±2.42	41.62±2.10
1.4	15.35±4.01	51.79±1.28	39.65±2.00	43.79±5.52
4	25.14±0.70	53.63±1.41	43.76±2.34	44.10±1.28
7.4	32.40±2.64	54.62±3.89	43.40±2.69	46.61±1.91
11.4	38.13±1.39	54.04±2.30	46.21±1.99	46.90±0.65
15.9	39.90±0.36	55.52±1.85	48.61±1.64	48.63±0.68
21	41.90±0.75	56.49±2.07	49.73±1.50	52.09±3.2

ence in the mechanical performances of different thiol-ene photoresins. The acrylate photoresins exhibit poorly adjustability probably because the polymerization reactivity of the acrylate photoresist is too high, a high conversion could be obtained even a trace of radicals was initially generated. In this case, the crosslinking density of the obtained photoresin is poorly adjustable by the exposure dose.

After confirming our hypothesis at macroscopic scale, we then tested if the thiol-ene photoresist can be fabricated by TPL. A commercial TPL system (Nanoscribe Photonic Professional GT) equipped with a 780 nm laser source was used in our experiment. As TPO shows reactivity under two-photon condition, the thiol-ene photoresist (PTTA+PETMP) was directly transferred to the TPL system for processing.^[28] In TPL fabrication, the exposure dose can be controlled either by varying the laser power or the scanning speed. To investigate the effect of these two parameters separately, we designed and fabricated a microcube array, each cube was generated with different processing parameters (Fig. 5a). However, as shown in Fig. 5(a), after development, microcubes with uni-

form shapes were not obtained under some conditions. This is probably because the mercapto group is highly reactive, thiol-ene reaction can occur with the stimulation from both light and heat. Therefore, the heat effect from the polymerization reaction may activate the surrounding mercapto groups (especially at the top of the laser focus, as proved by the increase of the microcube height under higher laser power), making the solidification of the photoresist uncontrollable. To overcome the problem, the composition of the photoresist was optimized, and we found that, by adding 33 vol% acetophenone into the photoresist, the above problem can be perfectly resolved. Microcube arrays were successfully fabricated (Fig. 5b). The resolution of the photoresist was tested by generating photoresin lines using different laser power and scanning speed. As shown in Fig. 5(c), with lower laser power and faster scanning speed, the width of the obtained photoresin become smaller. The narrowest lines that can be fabricated are approximately 800 nm. Such resolution is highly reproducible, as confirmed by repeatedly fabricating photoresin lines for 10 times and analyzing the width of the

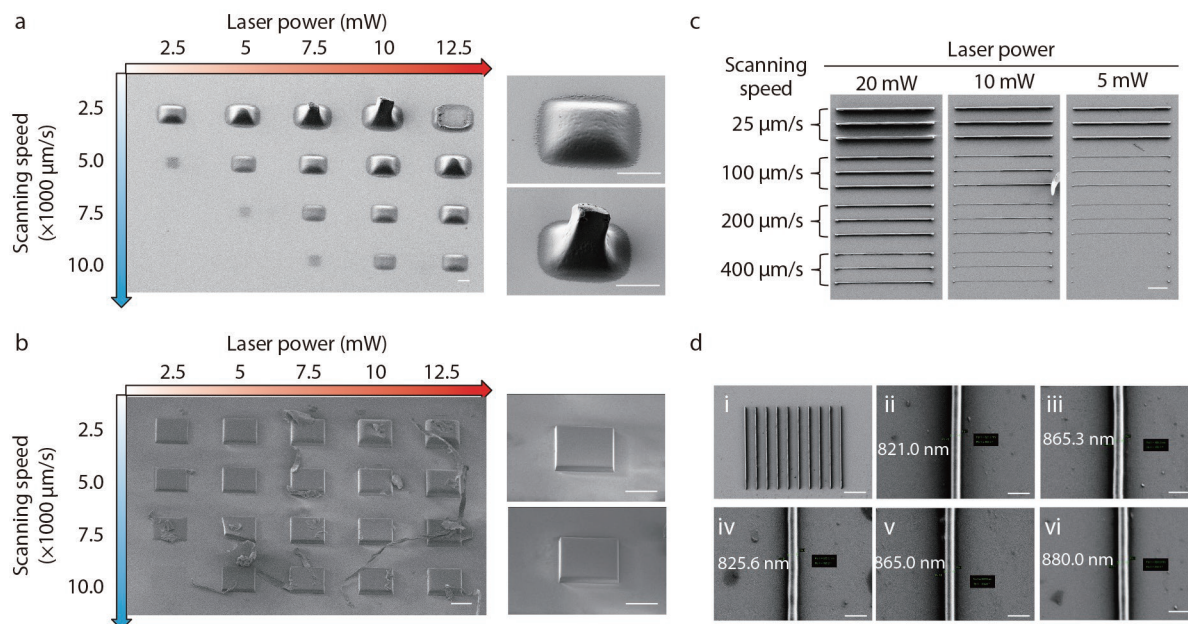


Fig. 5 TPL fabrication using thiol-ene photoresists. Microcube arrays were fabricated using photoresist containing (a) PETMP + PTTA, with 1 wt% TPO. The microcube at 12.5 mW/2500 μm parameter is missing, probably because in this case the height of the generated microcube is too high, making the structure unstable on the substrate; (b) PETMP+PTTA, with 33 vol% AP and 0.33 wt% TPO; (c) Resolution test by generating photoresin lines using different processing parameters; (d) Reproducibility test, by repeatedly generating photoresin lines with same processing parameters for 10 times. Scale bars: 20 μm for (a) and (c), 50 μm for (b), 20 μm for (d-i), 2 μm for (d-ii)–(d-vi).

obtained structures. The obtained photoresin lines exhibit an average width of 868 ± 27 nm, indicating that the fabrication results are highly reproducible.

To check whether the photoresin fabricated by TPL also shows exposure-dependent stiffness, microcubes fabricated with different processing parameters were analyzed with a nanoindenter. The results are shown in Table 4. When the laser scanning speed is fixed, the stiffness of the printed microcube increases gradually with the laser power. When the laser power is fixed, the stiffness of the printed microcube increases dramatically with the scanning speed. This is probably because, unlike UV exposure, in TPL processing, the time of exposure for every voxel is very limited, which greatly enhances the importance of irradiation time compared to light intensity. By slightly varying the laser power and scanning speed, the stiffness of the microcubes could be altered for more than 10 folds. This confirms the possibility to create micro objects with variable mechanical properties using the same thiol-ene photoresist.

Table 4 Stiffness of the TPL-fabricated microcube with different processing parameters.

Laser power (mW)	Scanning speed ($\mu\text{m/s}$)	Stiffness (MPa)
2.5	10000	15.55 ± 0.56
	7500	28.35 ± 1.02
7.5	10000	23.9 ± 1.50
	7500	150.65 ± 13.2
12.5	10000	28.45 ± 2.26
	7500	164.2 ± 9.47

By designing different models, diverse microstructures can be fabricated using the thiol-ene photoresist. As examples, we show some of the printed objects in Fig. 6. Microstructures with diverse geometries were successfully generated using the photoresist. This indicates the potential of our method to fabricate microstructures with desired 3D geometries and mechanical properties, which would be quite useful in the fabrication of microdevices or microscaffolds for mechanical and biological applications.

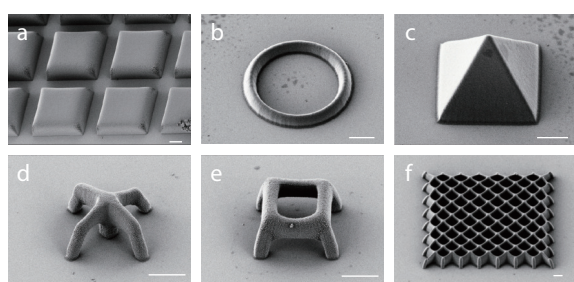


Fig. 6 2D and 3D microstructures fabrication by TPL using thiol-ene photoresist: (a) microcube array, (b) micro ring, (c) micro pyramid, (d) bionic spider structure, (e) square stool scaffold and (f) multi-grid scaffold. Scale bars: 10 μm .

CONCLUSIONS

In summary, we investigate the effect of exposure dose on the mechanical performance of the photoresins generated with acrylate self-polymerization and thiol-ene polymerization. We

show that the stiffness of the photoresin generated with thiol-ene polymerization can be well controlled by the exposure dose. With 350-fold exposure dose, the stiffness of the thiol-ene photoresin shows more than 700-fold changes. Using this result, we developed a thiol-ene photoresist for TPL, by which microstructures with high resolution and variable mechanical performances can be easily generated.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2802-5>.

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