

## Improvement of Spatial Resolution in Nano-Stereolithography Using Radical Quencher

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**Abstract:** The improvement of spatial resolution is a fundamental issue in the two-photon, polymerization-based, laser writing. In this study, a voxel tuning method using a radical quencher was proposed to increase the resolution, and the quenching effect according to the amount of radical quencher was experimentally investigated. Employing the proposed method, the lateral resolution of the line patterns was improved almost to 100 nm. However, a shortcoming of the quenching effect was the low mechanical strength of polymerized structures due to their short chain lengths. Nano-indentation tests were conducted to evaluate quantitatively the relationship between mechanical strength and the mixture ratio of the radical quencher into the resins. The elastic modulus was dramatically reduced from an average value of 3.015 to 2.078 GPa when 5 wt% of radical quencher was mixed into the resin. Three-dimensional woodpile structures were fabricated to compare the strength between the resin containing radical quencher and the original resin.

**Keywords:** radical quencher, two-photon polymerization, three-dimensional microstructures.

### Introduction

During the past ten years, there has been a rapid progress in nano/microfabrication for the creation of two-dimensional (2D) and three-dimensional (3D) nano/microstructures. Numerous works have been conducted to improve the resolution, efficiency, and productivity of related processes. Among them, photolithography, wherein light is irradiated selectively using a photomask on a substrate, is considered one of the most successful processes, and has played an important role in microfabrication since its invention. However, it is known that the resolution of features fabricated using photolithographic methods is limited by the optical diffraction. In addition, expensive photomasks are essentially required. To overcome these obstacles, diverse alternative processes have been developed, including soft-lithographic approaches,<sup>1</sup> imprinting methods,<sup>2</sup> and direct writing methods using an electron-beam or laser. However, most of the developed processes focus on 2D patterning, and do not allow the creation of perfect 3D microstructures.

Two-photon polymerization (TPP) has attracted increasing interest due to its intrinsic 3D processing capability, and is considered as a promising technology with unique merits in relation to nanofabrication.<sup>3-15</sup> In particular, TPP provides a convenient and effective method for the fabrication of neo-conceptive 3D optoelectronic products such as 3D photonic crystals, 3D optoelectronic diodes, 3D optoelectronic semiconductors, 3D bio-chips, and many others. Two-photon absorption (TPA) is a popular multiple photon excitation method for a photochemical change; when a molecule is under a high intensive electromagnetic field come from a femtosecond (fs) pulse lasers, one photon is absorbed by a molecule, and the second photon must be almost simultaneously absorbed by the same molecule within the lifetime (approximately  $10^{-15}$  sec) of a virtual intermediate state to cause a photochemical change. TPP employs this TPA feature to initiate photopolymerization, making it possible to obtain patterns with a high resolution down to nanoscale under the diffraction limits of the incident laser beam.

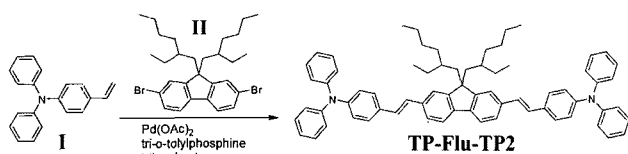
Improving the spatial resolution of the TPP process poses a challenge. In a previous work, the lateral resolution of a voxel (volumetric pixel: a photopolymerized unit of pattern) was reduced to roughly 120 nm by controlling the level of the

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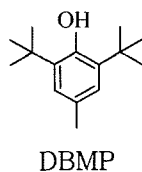
laser dose to the critical optimum.<sup>4</sup> However, it is difficult to achieve less than 100 nm resolution through control of the laser dose alone. In the present work, a novel means of improving the precision of TPP using a radical quenching effect is proposed. The radical quencher can play an important role in inhibiting polymer chains from growing longer. Therefore, the spatial resolution of the voxel can be improved by reducing the chain length and/or molecular weight of the polymers in the low radical-concentrated area of an activated domain via TPA.

## Experimental

**Materials.** In this work, we have used the SCR500 resin for photopolymerizable oligomers containing photoinitiators, which is mixed with a TPA chromophore (photosensitizer) in 0.1 wt%. The resin, SCR500, is a mixture of urethane acrylate monomer, oligomer, and a photoinitiator (2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butanal-1-hydroxy-chlorohexylphenylketone), and is supplied by Japan Rubber Company. The two-photon absorbing chromophore (TP-Flu-TP2) with long alkyl chain was synthesized using palladium catalyzed coupling reaction designed by Heck from compound-I and II. The compound-I was obtained from Vilsmeier-Haack formylation of triphenylamine followed by Wittig reaction, and the 2,7-dibromofluorene was reacted with excess amount of ethylhexylbromide to give compound-II.<sup>16</sup> The resulting two-photon chromophore, TP-Flu-TP2 was extensively purified before use as a light sensitizer/photoinitiator in two-photon photopolymerization. The optical transparency of a chromophore at the wavelength of operation is crucial for successful 3D microfabrication with TPP. The absorption and emission maximum wavelengths were observed at 411 and 472 nm, respectively. TPA cross-section of the sensitizer showed 954 GM (1 GM =  $10^{-50}$  cm<sup>4</sup> · sec/photon) at 740 nm with a 80 fs pulse laser.<sup>11</sup>



The radical quencher used in this study for improvement of the spatial resolution is 2,6-di-*tert*-butyl-4-methylphenol (DBMP) with a molecular weight of 220.35 g/mol.<sup>17,18</sup>



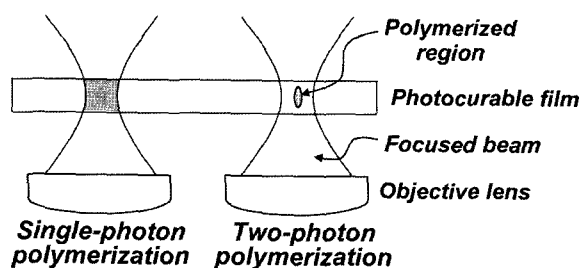
**Laser Setup for TPP.** To fabricate 3D patterns with nano-scale resolution, a nano-stereolithography method based on a fs-laser system, developed in an earlier study, was utilized. A Ti:Sapphire mode-locked laser was used as a light source. It provided a wavelength of 780 nm and a pulse width of less than 100 fs at a repetition rate of 80 MHz. The beam was scanned on the focal plane using a two-galvano-mirrors set with a resolution of approximate 1.2 nm per step, and along the vertical axis using a piezoelectric stage. The laser was closely focused into a volume of photocurable resin with an objective lens having a high numerical aperture (NA  $1.4 \times 100$ , immersion oil used). A Galvano-shutter combined with a pin-holed plate was applied to achieve short exposing duration of less than 1 ms. The shutter, scanner, and piezoelectric stage were controlled using a developed control program. A detailed explanation of the system is available in our previous research reports.<sup>7-15</sup>

**Nano Indentation Test.** In order to measure the mechanical properties of solidified resins, a nano-indenter (model: Nano Indenter XP, MTS) was utilized. The type of indenter tip was Berkovich diamond tip with the roundness of 40 nm. The continuous stiffness measurement (CSM) mode was used with the following measurement conditions: depth limit of 2,500 nm, surface approach velocity of 10 nm/s, and load range of 16 to 25 mN.

## Theoretical Study

**Mechanism of TPP.** TPP has two sequential steps: first, upon irradiation of an intensive laser beam with a wavelength of infrared light, a two-photon absorption material absorbs two photons simultaneously, in order to be the electrically excited states, located higher than the single photon excited states. These excited molecules turn down to the lowest excitation states by releasing energy for the duration of  $10^{-6}$  sec, and then return to the ground state, emitting ultraviolet/vis light. The light energy is transferred to an initiator inside the photopolymerizable resin and consequently the initiator generates radicals. These radicals may proceed in three different pathways: (i) to decay to the initial ground state with the emission of light or heat; (ii) to be quenched by quenching agents such as oxygen existing in the resin<sup>19</sup>; (iii) to react with the monomers in the resin to initiate polymerization. We are interested in the last pathway. The Ti:Sapphire laser is widely used for inducing TPA, because it produces ultrahigh peak power with a very short pulse width of approximately 100 fs or less. Furthermore, it is very useful for TPP because it has a central wavelength of approximately 800 nm, which is close to half the wavelength of the polymerization of various UV-curable resins. This enables easy control of the threshold energy for photopolymerization.

The probability of TPP to occur is not constant inside the entire focus area, but increases depending on the intensity of the beam according to the following eq. (1)<sup>6</sup>,

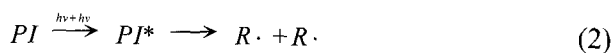


**Figure 1.** Comparison of single-photon polymerization (SPP) and two-photon polymerization (TPP). The polymerized region in TPP is confined in the local area of a focused plane.

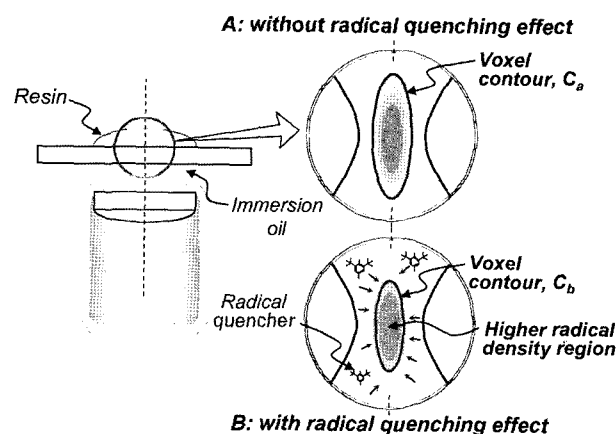
$$\frac{\partial \rho}{\partial t} = (\rho_0 - \rho) \sigma_2 I^2 \quad (1)$$

where  $\rho$ ,  $\rho_0$ ,  $\sigma_2$ , and  $I$  denote the radical density, initial radical density, two-photon absorption cross-section, and beam intensity, respectively. When a laser beam is closely focused into a volume of photocurable resin, a focused spot with high photon density is formed locally with the total number of photons at every cross-section being constant. This means that the linear response of the materials to the light intensity based on single-photon absorption (SPA) does not have an optical sectioning capability. If the material response is proportional to the square of the photon density, the integrated material response is enhanced greatly at the focal point. The two-photon transition rate is extremely small in general, and hence a high spatial resolution can be obtained under the limit of diffraction of a light in the TPP process.<sup>5</sup> Figure 1 provides the comparison of polymerized regions by SPA and TPA.

**Control of TPA by Radical Quenching Effect.** Photo-initiators ( $PI$ ) reach to the excited state ( $PI^*$ ) by absorption of the light coming from TPA chromophores followed by decomposition to radicals. These initiating species trigger a chain reaction with monomers and oligomers, finally producing long-chained polymers. Radical quenchers ( $Q$ ) block the growth of polymer chains by terminating chain radicals. The quenched radicals ( $RQ\cdot$ ) are then deactivated by irradiation or release of heat. The quenching process is expressed in eqs. (2) to (4), where  $\nu$  is the incident light energy.



As shown in the inserts 'A' and 'B' in Figure 2, the border of the beam focal area, in which the density of radicals is distributed depending on the intensity of the focused beam. The high beam intensity in the focal area yields the high



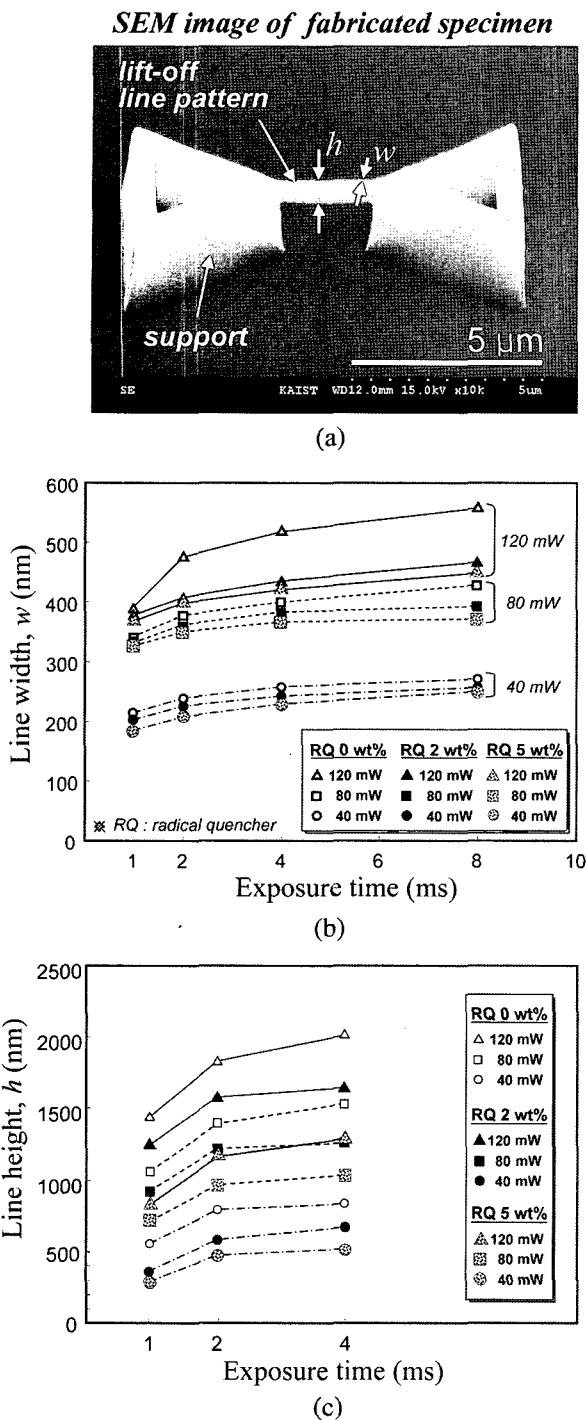
**Figure 2.** Schematic illustration of radical quenching mechanism. In case the radical quencher is mixed into the original resin, the voxel size ( $C_b$ ) is reduced comparing to the case of the original resin only used ( $C_a$ ).

density of the radicals. In the surroundings far from the center of the focal area, the radical density decreases continuously due to the lower intensity of the laser beam. However, the polymerization may occur within some extents of the radical density. When radical quenchers are used (see insert 'B' in Figure 2), the growth of polymer chains is inhibited by the quenching effect in the region of low radical density. And, only around the center of the beam focus, the intensity of the laser is sufficiently high enough to generate numerous radicals which lead the polymer-chain growth. Therefore, it is apparent that the voxel tuning by the employment of radical quencher provides an effective means of improving the spatial resolution for TPP fabrication.

## Results and Discussion

**Radical Quenching Effect Depending on the Mixing Ratio of Radical Quencher.** In order to investigate the quenching effect quantitatively, we have designed the 3D structure shown in Figure 3(a); the lift-off line is supported by triangular pillars at both ends of the line. The specimens have been fabricated under three different laser powers (40, 80, and 120 mW) and a fixed exposing duration of 1 ms per voxel. The resins used in the tests were one original resin and two resins including the radical quencher (DBMP) in the ratio of 2 and 5 wt%. Their heights and widths ( $h$  and  $w$ ) were measured and are plotted with respect to the exposure time in Figures 3(b) and 3(c), respectively. The spatial resolution of voxels with quenchers improved significantly both in width and height comparing with the original resin used cases. Furthermore, with increased amount of quenchers, the improvement becomes larger. Under the fabrication conditions of laser power of 40 mW and exposure time of 1 ms with the resin including 5 wt% quenchers, the line width and the height were reduced by as much as 18 and 43%, respec-

tively, compared to the case of the resin without quenchers was used (see Figure 3(b, c)).

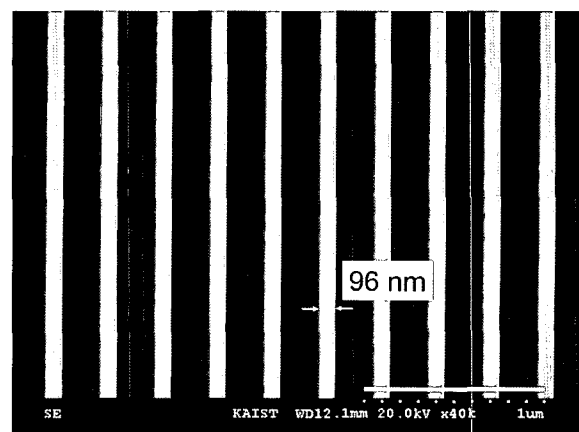


**Figure 3.** (a) SEM image of fabricated lift-off line pattern:  $h$  and  $w$  are the height and width of line pattern, respectively. (b) and (c) the variation of line width and height according to laser doses (laser power from 40 to 120 mW and exposing time from 1 to 8 ms). There three cases: no radical quencher, radical quencher of 2 and 5 wt%, respectively.

Also, when the radical quencher was used, the change of line-height is larger than that of the line-width, because the density of radicals induced by TPA is distributed much longer along the beam axis (vertical height direction shown in Figure 2); therefore, a low aspect ratio of voxels can be created by the quenching effect. In case of the resin mixed with 5 wt% radical quencher, the aspect ratio (width/height) of a line fabricated under a laser power of 40 mW and an exposure time of 1 ms was reduced considerably to 1:1.7, compared to the original resin case (aspect ratio, 1:2.5). This low aspect ratio of a voxel is advantageous in the fabrication of 3D microstructures by means of accumulating layers. The experimental results indicate that the voxel tuning method with radical quenchers is an effective way to reduce the voxel size. Therefore, TPP in conjunction with the radical quenching method can provide many advantages for precise 3D direct laser-writing.

In order to determine the limit of a resolution using resins incorporated with a radical quencher, we have attempted to fabricate line patterns. A line-width of about 96 nm was achieved using the resin containing 5 wt% quenchers with threshold conditions of 20 mW laser power and 1 ms exposure, as shown in Figure 4. This suggests that more precise TPP fabrication can be realized by optimizing the fabrication conditions, and around 100 nm should not be the final objective of a resolution. However, in our present optical laser system, when the laser beam strays from the center of the condensing lens even slightly, TPP does not take place at all. In addition, some difficulties were encountered in the fabrication of uniform patterns using the quenchers under the threshold condition for polymerization.

**Evaluation of the Variation of Mechanical Strength by Quenching Effect.** In general, the mechanical strength of photopolymers is proportional to the molecular weight which is increased depending on the chain length. The radical quencher restricts the growth of polymer chains, and as a



**Figure 4.** SEM image of sub-100 nm line pattern created using the radical quencher of 5 wt% under the fabrication conditions; laser power of 20 mW and exposure time of 1 ms.

result, reduces the conversion rate of monomers leading to low molecular weight of the polymers. The kinetic chain length of the polymer ( $\nu$ ) can be expressed as the following eq. (5)<sup>20</sup>;

$$\nu = \frac{k_p[M]}{2(fk_d k_t [I])^{1/2}} \quad (5)$$

where  $k_p$ ,  $f$ ,  $k_d$ ,  $k_t$ ,  $[M]$ , and  $[I]$  are a chain growth rate constant, initiator efficiency, an initiator dissociation rate constant, a termination rate constant, the concentration of monomers, and the concentration of initiators, respectively. When the radical quencher is used in photopolymerization,  $k_p$  is decreased and  $k_t$  is increased; therefore, the use of a radical quencher can adversely affect mechanical strength due to the low molecular weight caused by short chain length as well as low conversion.

For an explicit investigation of the relationship between the quenching effect and the variation of mechanical strength of polymers, nano-indentation tests have been conducted. In Figures 5(a) and 5(b), the experimental results of the nano-indentation test on polymerized specimens, which were fabricated using several resins with the quencher mixing ratios of 0, 1, 3, and 5 wt%, are plotted with respect to the elastic

**Table I. Average Values of Elastic Modulus and Hardness**

wt%	Elastic Modulus (GPa)	Hardness (GPa)
0	3.015	0.148
1	2.474	0.125
3	2.224	0.103
5	2.078	0.098

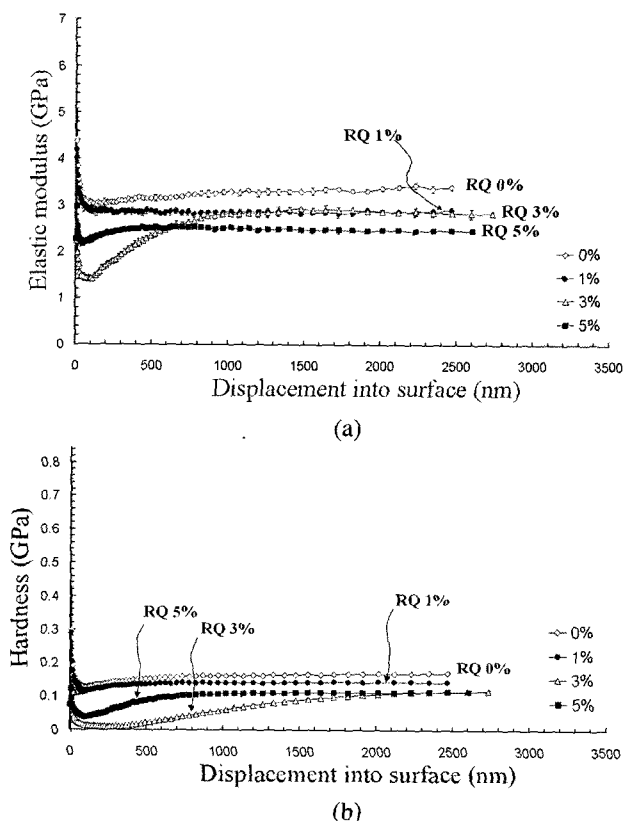
modulus and hardness. In both plots, poor data at the beginning point to 500 nm arose from initial instability such as poor arrangement of the indenter on the sample surface. The converged range from 2,000 to 2,500 nm gives reliable data, as summarized in Table I. With increased mixing amount of quencher in the resin, the elastic modulus and hardness of the polymerized structure decrease. Specifically, the elastic modulus of the resin with radical quenchers of 5 wt% is 2.078 GPa, which constitutes a reduction of roughly 31% relative to that of the original resin case.

We have fabricated a 3D woodpile using resins containing 2 wt% radical quenchers in order to evaluate the practical problems of poor strength. The elastic modulus of the 2 wt% radical quencher included resin may be presumed to be in the range of 2.474 to 2.224 GPa based on the Table I; therefore, its strength becomes weak in the degree of about 22% compared to that of the original resin. SEM images of the woodpile structures fabricated with resin incorporating quenchers of 2 wt% and the original resin are shown in Figures 6(a) and 6(b), respectively. There are numerous spaces inside and at the lateral side of the 3D woodpile structure. Consequently, when ethanol is used to wash away the un-solidified, liquid-state resin, surface tension is generated by evaporation of ethanol from the inside and lateral region of the woodpile, resulting in deformation of the structure. As shown in Figure 6(a), 33% shrinkage took place in the top of the woodpile fabricated with the resin having quenchers due to a reduction of the elastic modulus; the bottom of the woodpile could not be shrunken, because it was attached strongly on the surface of a glass plate. On the other hand, only 12% shrinkage occurred in the case of the original resin was used.

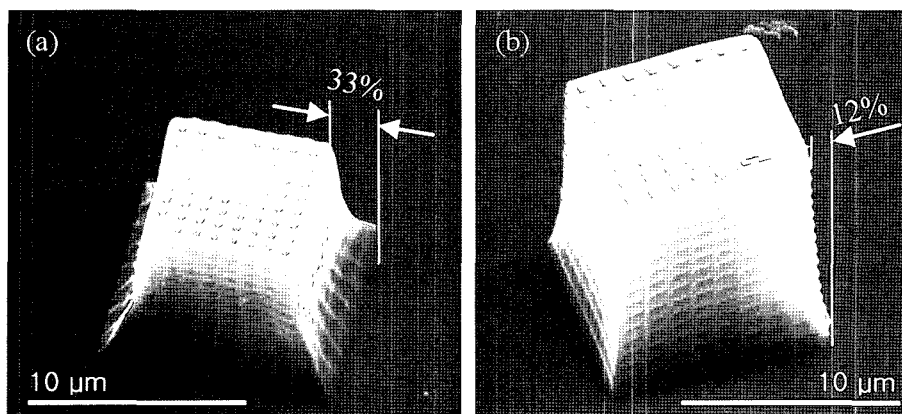
Accordingly, when we employ the quenching effect in 3D nanofabrication for the purpose of attaining better a spatial resolution, the polymer strength should be considered. One of practical solutions for increasing the strength is the change of the backbone of a polymer network, such as the structure of an oligomer, because the physical properties of a solidified polymer are strongly determined by the backbone of the polymer network.

## Conclusions

In this work, we have evaluated the merits and demerits of radical quenching in relation to improving the spatial reso-



**Figure 5.** Variation of elastic modulus and hardness depending on the amount of the radical quencher in the resin from 0 to 5 wt%.



**Figure 6.** SEM images of fabricated 3D woodpile structures in case of (a) the radical quencher (2 wt%) mixed resin and (b) the original resin. The shrinkage amount of (a) is larger than that of (b).

lution of TPP. The radical quenchers mainly acting on the area surrounding the focal plane with weak beam intensity prevent monomer radicals from growing into a long-chained polymer network. As a result of the quenching effect, the aspect ratio as well as the size of the voxel is decreased considerably by increasing the concentration of radical quenchers. In this work, the smallest line-width near 100 nm has been achieved. However, when the quenching effect is utilized, the mechanical strength of the polymerized structure is inevitably reduced, because of the smaller molecular weight of the polymerized structures. Therefore, enhancement of mechanical strength when employing radical quenchers in 3D nanofabrication remains a challenging task for a future work.

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## References

- (1) Y. Xia and G. M. Whitesides, *Angew. Chem. Int. Ed.*, **37**, 550 (1998).
- (2) S. Y. Chou, C. Keimel, and J. Gu, *Nature*, **417**, 835 (2002).
- (3) S. Maruo and S. Kawata, *J. Microelectromech. Syst.*, **7**, 411 (1998).
- (4) S. Kawata, H. B. Sun, T. Tanaka, and K. Takada, *Nature*, **412**, 697 (2001).
- (5) H. B. Sun, T. Tanaka, and S. Kawata, *Appl. Phys. Lett.*, **80**, 3673 (2002).
- (6) J. Serbin, A. Egbert, A. Ostendorf, and B. N. Chichkov, *Opt. Lett.*, **28**, 301 (2003).
- (7) S. H. Park, T. W. Lim, D. Y. Yang, H. J. Kong, R. H. Kim, and K.-S. Lee, *Bull. Korean Chem. Soc.*, **25**, 1119 (2004).
- (8) S. H. Park, T. W. Lim, D. Y. Yang, H. J. Kong, and K.-S. Lee, *Polymer(Korea)*, **28**, 305 (2004).
- (9) S. H. Park, T. W. Lim, D. Y. Yang, H. J. Kong, and K.-S. Lee, *Macromol. Res.*, **14**, 245 (2006).
- (10) S. H. Park, S. H. Lee, D. Y. Yang, H. J. Kong, and K.-S. Lee, *Appl. Phys. Lett.*, **87**, 154108 (2005).
- (11) K.-S. Lee, D. Y. Yang, S. H. Park, and R. H. Kim, *Polym. Adv. Technol.*, **17**, 72, (2006).
- (12) T. W. Lim, S. H. Park, D. Y. Yang, and K.-S. Lee, *Polymer(Korea)*, **29**, 418 (2005).
- (13) T. W. Lim, S. H. Park, D. Y. Yang, S. W. Yi, H. J. Kong, and K.-S. Lee, *J. Mech. Sci. Technol.*, **19**, 1989 (2005).
- (14) S. H. Park, T. W. Lim, D. Y. Yang, S. W. Yi, H. J. Kong, and K.-S. Lee, *J. Nonlinear Opt. Phys. Mater.*, **14**, 331 (2005).
- (15) S. H. Park, T. W. Lim, D. Y. Yang, S. W. Yi, and H. J. Kong, *Sens. Mater.*, **17**, 65 (2005).
- (16) H. K. Yang and K.-S. Lee, unpublished results 2006.
- (17) C. D. Cook, *J. Org. Chem.*, **18**, 261 (1953).
- (18) O. Breda, M. R. Ganapathi, S. Naumov, W. Naumann, and R. Hermann, *J. Phys. Chem. A*, **105**, 3757 (2001).
- (19) V. K. Varadan, *et al.*, *Microstereolithography and other fabrication techniques for 3D MEMS*, John Wiley & Sons, Chichester, 2001.
- (20) S. C. Kim, *et al.*, *Polymer Engineering I*, Heechoongkak, Seoul, 1994.