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# Three-dimensional microfabrication using two-photon activated chemistry

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## ABSTRACT

Photochemical reactions which can be activated by the simultaneous absorption of two photons provide a means for single-step fabrication of complex three-dimensional microstructures. These types of structures are needed for a wide range of applications, including microfluidics, electrooptics, and micro-electromechanical systems (MEMS). We have shown that chromophores can be engineered to have both large two-photon absorptivities as well as an efficient means for activating chemical processes, such as radical polymerization, subsequent to the photoexcitation. Chromophores designed following this strategy two-photon-activate the radical polymerization of acrylates at lower incident laser powers than conventional UV initiators. Efficient two-photon photopolymer resins based on these chromophores were used in the fabrication of complex microarchitectures, such as photonic bandgap structures and tapered waveguides. We have devised a strategy which allows this approach to be extended to other chemical systems.

**Keywords:** Microfabrication, two-photon absorption, photopolymerization, micro-electromechanical systems (MEMS), photonic bandgap.

## 1. INTRODUCTION

Two-photon excitation provides a means for activating chemical or physical processes with high spatial resolution in three dimensions and has enabled the development of 3D fluorescence imaging, 3D optical data storage, and 3D lithographic microfabrication.<sup>1,2</sup> Each of these applications takes advantage of the fact that the two-photon absorption probability depends quadratically on intensity, and therefore under tight-focusing conditions, the absorption is confined at the focus to a volume of order  $\lambda^3$ , where  $\lambda$  is the laser wavelength. Any subsequent process, such as fluorescence or a photo-induced chemical reaction, is also localized in this small volume. For instance, two-photon excitation can initiate conventional reactions such as side-group deprotection, radical generation, and polymerization, through energy transfer or electron transfer. However, the efficiency of such processes depends critically on the strength of the chromophore's two-photon absorptivity.

We have developed a wide array of chromophores which hold great promise for optical data storage, 3D microfabrication, and 3D fluorescence imaging. These materials are based on donor- $\pi$ -donor (D- $\pi$ -D), donor-acceptor-donor, or acceptor-donor-acceptor structural motifs. The magnitude of the two-photon absorption cross section,  $\delta$ , and the position of the two-photon absorption maximum can be controlled by varying the length of the conjugated bridge and by varying the strength of the donor/acceptor groups. In this way, chromophores have been developed which exhibit strong two-photon absorption in the range of 500 - 975 nm, in some cases as high as  $4400 \times 10^{-50} \text{ cm}^4 \text{ s/photon-molecule}$ . Experimental and theoretical work has shown that for these systems, the large absorption cross sections are correlated with a symmetric re-distribution of charge from donor groups to acceptor groups upon excitation.<sup>3,4</sup>

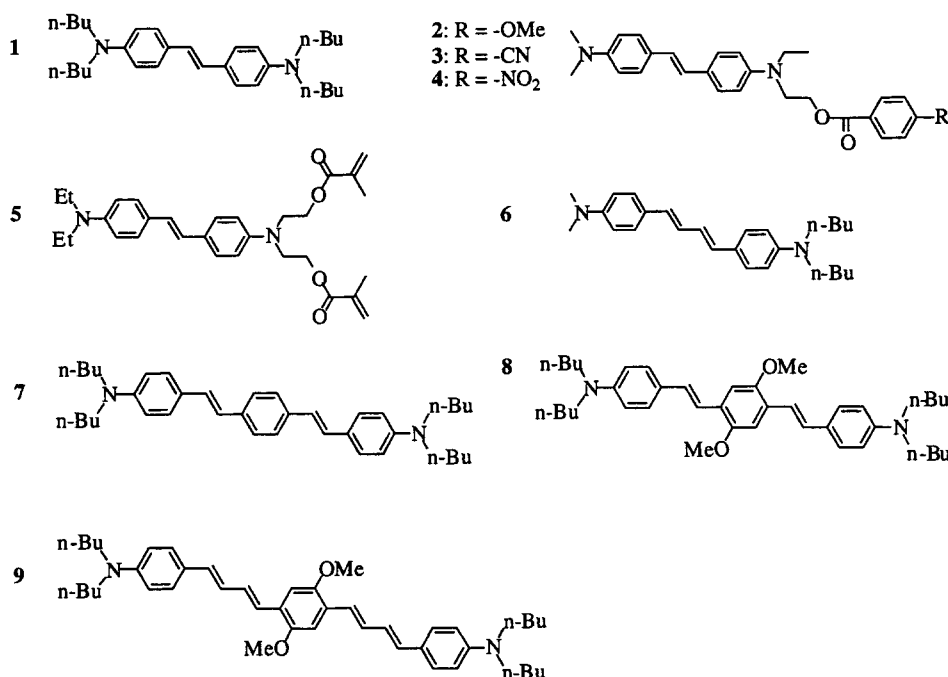
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We recently reported that D- $\pi$ -D molecules can be used to photochemically activate the polymerization of acrylates, and that this process can be initiated by both one- and two-photon excitation.<sup>5</sup> Since the two-photon absorptivity of D- $\pi$ -D molecules is large, photopolymer resins based on these chromophores offer higher sensitivity and lower initiation thresholds under two-photon excitation conditions than systems based on conventional UV initiators. Photopolymer resins based on D- $\pi$ -D chromophores have been developed and utilized for the production of complex microstructures. From this work we have devised a general strategy for designing efficient two-photon initiators for a variety of photochemical systems.

## 2. TWO-PHOTON-ACTIVATED PHOTOCHEMISTRY USING D- $\pi$ -D CHROMOPHORES

We noted<sup>5</sup> that molecules having the general structural motif D- $\pi$ -D are sufficiently electron rich that subsequent to one- or two-photon photoexcitation, they could transfer an electron even to relatively weak acceptors, and this process could be used to activate various chemical reactions, including polymerization. For example, 4,4'-bis(*N,N*-di-*n*-butylamino)-*E*-stilbene (**1**, see Table 1) has a ground-state oxidation potential of -35 mV (relative to ferrocenium/ferrocene) and an energy of 3.1 eV for the first one-photon-allowed excited state, S<sub>1</sub>, which together provide a large driving force for a photoinduced electron-transfer (ET) reaction. This driving force is also accessible via two-photon excitation into the higher-lying state S<sub>2</sub> followed by rapid non-radiative decay to S<sub>1</sub>. Since  $\delta$  is large for this class of molecules, two-photon-induced ET should be efficient.



Efficient ET from photoexcited **1** to various electron acceptors was evidenced by 1) steady-state fluorescence quenching, 2) fluorescence lifetime shortening, and 3) the appearance of electronic absorption bands due to the radical cation of **1**, which has  $\lambda_{\text{max}} = 620$  nm. Relatively large bimolecular quenching rate constants,  $k_Q$ , were obtained for photoinduced intermolecular charge transfer reactions of **1** with C<sub>60</sub> in toluene ( $k_Q = 8.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) and with acrylates in acetonitrile ( $k_Q \approx 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  and  $6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for two commercial triacrylates, Sartomer SR9008 and Sartomer SR454, respectively). Additionally, we synthesized covalently linked chromophore-acceptor systems wherein one or more of the amine-bound alkyl groups of **1** was replaced with an electron acceptor (**2** - **5**). For these systems, the fluorescence is quenched by fast intramolecular ET. Whereas the fluorescence lifetime,  $\tau_n$ , of **1** in acetonitrile is 1.5 ns,  $\tau_n$  for **2**, **3**, and **4** is 90 ps, < 10 ps, and 35 ps, respectively. The steady-state fluorescence intensity of **5** in acetonitrile is reduced by a factor of 33 relative to **1**. Table 1 lists the quenching rate constants obtained by steady-state and time-resolved fluorescence for several D- $\pi$ -D dyes quenched by SR9008 in acetonitrile.

**Table 1.** One- ( $\lambda_{\max}^{(1)}$ ) and two-photon ( $\lambda_{\max}^{(2)}$ ) absorption maximum (in nm), peak two-photon absorption cross section ( $\delta$ , in  $10^{-50}$  cm<sup>4</sup> s/photon-molecule), oxidation potential ( $E_{D^+/D}$ , in mV vs. ferrocenium/ferrocene in THF/0.1 M [Bu<sub>4</sub>N]<sup>+</sup>[PF<sub>6</sub>]<sup>-</sup>), and bimolecular quenching rate constants ( $k_Q$ , in  $10^8$  M<sup>-1</sup> s<sup>-1</sup>) for D- $\pi$ -D chromophores.<sup>3, 4</sup> The two-photon absorption cross sections were measured with ns-laser pulses using an apparatus similar to that described by Xu *et al.*<sup>6</sup> The quenching rate constants were determined in acetonitrile with SR9008 as the quencher using steady-state and time-resolved fluorescence measurements.

Compound	$\lambda_{\max}^{(1)}$	$\lambda_{\max}^{(2)}$	$\delta$	$E_{D^+/D}$	$k_Q$ (steady-state)	$k_Q$ (time-resolved)
1	374	600	210	-35	290	122
6	390	645	260	-80*	145	109
7	410	730	995	90	3.4	7
8	425	730	900	-10	3.7	2.2
9	448	775	1250	-45	3.7	--

\* two electron oxidation observed.

We reasoned that the radical ions formed by electron transfer from photoexcited **1** to an acrylate, or subsequent radical products, could initiate the polymerization of acrylates.<sup>7</sup> Indeed, polymerization of neat acrylate monomers (methylacrylate, methylmethacrylate and various tri- and penta-acrylates) was found to proceed via a radical mechanism under both one- and two-photon excitation of **1**. Following a treatment given by Odian,<sup>7</sup> the polymerization rate under steady-state conditions for one-photon excitation,  $\tilde{R}_p^{(1)}$  (the rate of monomer consumption), can be expressed in the form:

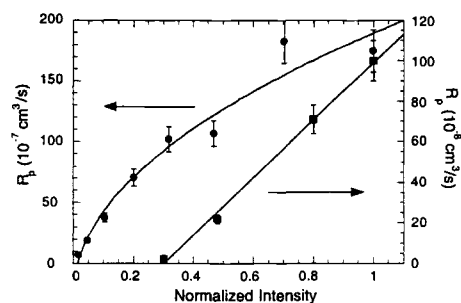
$$\text{One-photon induced polymerization} \quad \tilde{R}_p^{(1)} = k_p [M] \left\{ \frac{\phi \sigma [C]}{2k_t} \right\}^{\frac{1}{2}} \sqrt{I}. \quad (1)$$

Here,  $k_p$  is a rate constant for polymer propagation,  $M$  is the monomer concentration [moles/L],  $\phi$  is the quantum efficiency for photogeneration of a radical,  $\sigma$  is the one-photon absorption cross section of the photoinitiator [cm<sup>2</sup>/molecule] at concentration  $C$  [moles/L],  $k_t$  is the termination rate, and  $I$  is the incident intensity or photon flux [photons cm<sup>-2</sup> s<sup>-1</sup>]. We have extended the treatment to the case of TPIP, for which the TPIP rate,  $\tilde{R}_p^{(2)}$ , has the form:

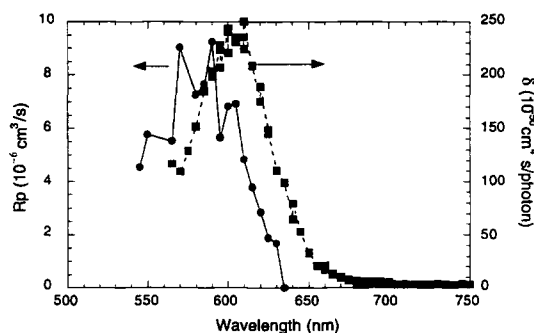
$$\text{Two-photon induced polymerization} \quad \tilde{R}_p^{(2)} = k_p [M] \left\{ \frac{\phi \delta [C]}{4k_t} \right\}^{\frac{1}{2}} I. \quad (2)$$

A comparison of (1) and (2) reveals that for one-photon initiated polymerization the polymerization rate is expected to be proportional to the square root of the light intensity, whereas under two-photon excitation the polymerization rate should be linearly proportional to the intensity.

Using a dose-array type experiment, we measured the rate at which polymer features grew,  $R_p$  [cm<sup>3</sup>/s], when a triacrylate monomer was photopolymerized by **1** under either one- or two-photon excitation. Assuming that the growth rate,  $R_p$ , is proportional to the polymerization rate,  $\tilde{R}_p$ , the intensity dependence of the growth rate provides an indication of whether the photopolymerization is initiated by a one- or two-photon process. For excitation into S<sub>1</sub> at 355 nm, we found that  $R_p$  depended on  $I^{1/2}$ , as expected for one-photon initiated polymerization. In contrast, laser excitation into S<sub>2</sub> at 600 nm led to a linear dependence of  $R_p$  on  $I$ , as predicted for TPIP (Figure 1). Furthermore, for excitation across the two-photon absorption band the wavelength dependence of  $R_p$  was found to be similar to the two-photon excitation spectrum (Figure 2). D- $\pi$ -D chromophores with extended conjugated bridges (**6-9**) were also found to initiate the polymerization of a wide range of acrylates under both one- and two-photon excitation.



**Figure 1.** Intensity dependence of the polymerization growth rate,  $R_p$ , of a triacrylate monomer photoinitiated by **1**, with one-photon excitation at 355 nm (●) and two-photon excitation at 600 nm (■). Dose array experiments were performed in which cross-linked polymer volumes were grown by irradiating a monomer solution of Sartomer SR9008 as a function of intensity and exposure time. After exposure, the unpolymerized solution was washed away using tetrahydrofuran. The volume of the polymerized features was obtained from scanning electron microscopy images.  $R_p$  was calculated from the gradient of volume versus time for each intensity. 8-ns, 10-Hz pulses from a frequency-tripled Nd:YAG laser were used for single-photon excitation. A 5-ns pulsed dye laser operating at 20 Hz was used for two-photon excitation.



**Figure 2.** Polymerization action spectrum for triacrylate monomer Sartomer SR9008 photoinitiated by **1** (●) and two-photon absorption spectrum of **1** in toluene (■). The polymerization growth rate  $R_p$  was measured (see Figure 1) at a constant intensity as a function of wavelength using 5-ns pulses at 10 Hz from an optical parametric oscillator laser. The two-photon absorption spectrum was recorded by the two-photon excited fluorescence method (as described by Xu *et al.*<sup>6</sup>) using 4-ps laser pulses from a synchronously-pumped dye laser.<sup>3,4</sup>

### 3. SENSITIVITY

Nonlinear photopolymer resins can be formulated in quite a general way by incorporating D- $\pi$ -D initiators at low weight percent into liquid or semi-solid blends of cross-linkable acrylate monomers. We examined the TPIP sensitivity of liquid resins based on SR9008 which contained either the D- $\pi$ -D chromophore **1** or **6** or one of the following conventional UV radical generators<sup>7</sup> as the photoinitiator: benzil, benzophenone, *bis*(*N,N*-dimethylamino)benzil, isopropyl-thioxanthone, 1-[4-(methylthio)phenyl]-2-methyl-2-morpholinopropan-1-one (MP), 4,4'-*bis*(*N,N*-dimethylamino)benzophenone (DABP). The TPIP threshold energies,  $E_{th}$ , and  $R_p$  were measured under excitation at 600 nm with 5-ns pulses and a radial spot size of 225  $\mu\text{m}$  (see Table 2). The most photosensitive UV initiators were MP and DABP, for which  $E_{th} = 1.0$  mJ. Compounds **1** and **6** had higher two-photon photosensitivity, with  $E_{th} = 0.3$  mJ, and  $R_p$  of **1** exceeding that of MP by a factor of ten. In general, the two-photon photosensitivity depends on both  $\delta$  and the overall chemical efficiency of initiation. We determined that the values of  $\delta$  at 600 nm are less than  $10 \times 10^{-50}$   $\text{cm}^4$  s/photon for the UV photoinitiators. These data indicate that the enhanced  $\delta$  of D- $\pi$ -D molecules contributes significantly to the improvement of the two-photon photosensitivity.

**Table 2.** Threshold energies for the polymerization of triacrylate monomer (Sartomer SR9008) using D- $\pi$ -D chromophores and some UV initiators. All measurements were performed using 600-nm 5-ns pulses at 20 Hz collimated to a radial spot size of 225  $\mu$ m, except in the case of **8**, for which the laser wavelength was 730 nm. The monomethylether hydroquinone (MEHQ) inhibitor was removed from the monomer using a caustic soda wash.

Photoinitiator	$E_{th}$ / mJ
<b>1</b>	0.3
<b>6</b>	0.3
<b>8</b>	0.2
MP	1.0
benzil	1.8
<i>bis(N,N-dimethylamino)benzil</i>	>2.3
benzophenone	>4.8
DABP	1.0
isopropyl-thioxanthone	>1.0

Similarly, we compared the TPIP sensitivity of a range of semi-solid photopolymer resins exposed with femtosecond pulses at 730 - 800 nm. The resins were comprised of a polymer binder, a cross-linkable acrylate monomer, and either the D- $\pi$ -D chromophore **8** or **9** or the UV radical generators MP, benzil, or DABP as the photoinitiator. Films of these resins were exposed to highly focused laser pulses ( $\approx 0.35$   $\mu$ m radial spot size, 150 fs, 76 MHz) at 730 nm (800 nm in the case of **9**). These wavelengths are near the two-photon absorption peak of the D- $\pi$ -D initiators. The threshold power for writing ( $P_{th}$ ) was 200  $\mu$ W for **8** at 730 nm and 300  $\mu$ W for **9** at 800 nm. In both cases, damage was observed at powers greater than 10 mW. The dynamic power range for polymerization is then 50 and 33 for **8** and **9**, respectively. In the absence of initiator, no writing occurred at powers below the damage threshold. The films in which the photoinitiator was MP, benzil, or DABP were found to have much smaller dynamic ranges, varying from  $\sim 1.4$  to 4 at 730 nm. Thus, replacement of a conventional UV initiator by a D- $\pi$ -D chromophore, which is designed for large two-photon absorptivity, has resulted in photopolymers with an order-of-magnitude improvement in TPIP photosensitivity.

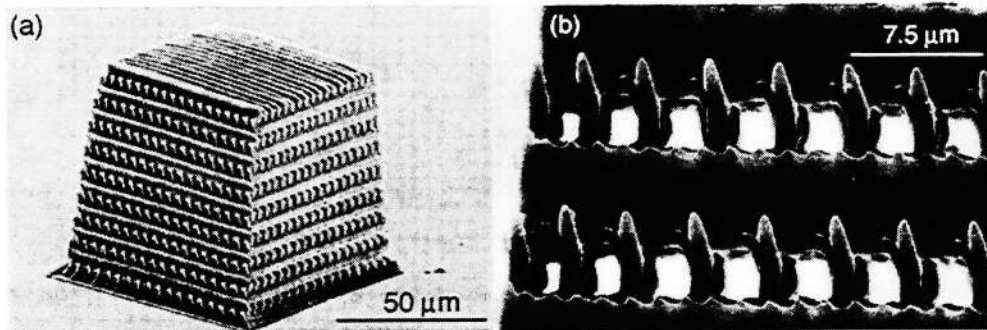
#### 4. D- $\pi$ -D PHOTOPOLYMER RESINS FOR 3D MICROLITHOGRAPHY

TPIP has also been utilized for 3D lithographic microfabrication (3DLM).<sup>1, 2, 5, 8, 9</sup> In this process, a pattern is impressed into a photopolymer by translating the focus of an intense laser beam within the material. The localized photoexcitation crosslinks the photopolymer resin thereby reducing the solubility of the exposed material. The desired 3D structure is obtained by dissolving away the unexposed material. This technology is promising in that complex 3D microstructures, which would be either difficult or time-consuming to fabricate by any other technique, can be produced in a single step. Previously, this approach has been of limited use since the available initiators were weak two-photon absorbers, and therefore high-power excitation sources were required for TPIP. However, the enhanced two-photon sensitivity of D- $\pi$ -D initiators offers a means for preparing high-sensitivity TPIP resins, which could allow 3DLM to become a more accessible technique. Photopolymer resins of the type envisioned for efficient 3DLM could also be useful for certain types of 3D optical data storage.<sup>5, 10, 11</sup>

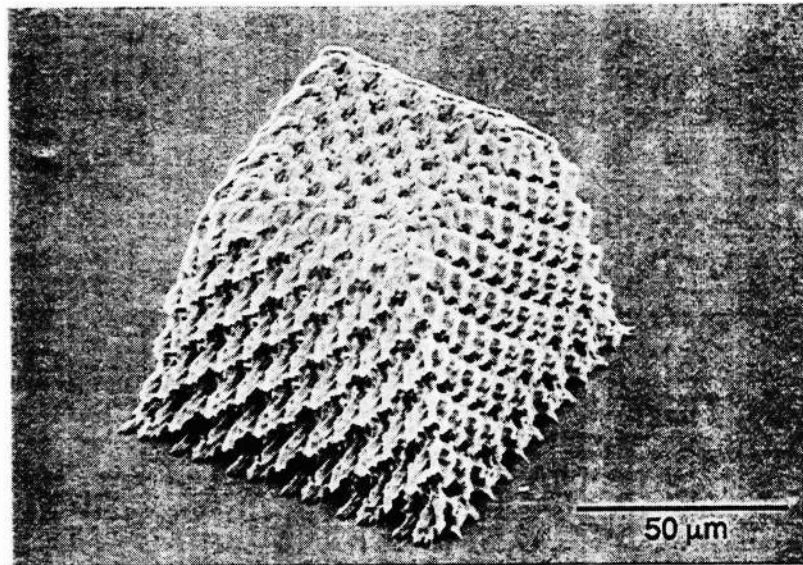
To illustrate the utility of our two-photon photopolymer systems, we used the 3DLM approach to produce a variety of potentially interesting 3D structures in a semi-solid acrylate film of the type described above. 3D periodic structures are needed for photonic bandgap (PBG) materials, which have unique optical properties.<sup>12, 13</sup> These structures are difficult to fabricate on micron or submicron length scales as needed for applications in the IR and visible spectral regions.<sup>14</sup> Figures 3a and 3b show scanning electron microscope (SEM) images of a "stack-of-logs" structure that, given a sufficiently high refractive index, should exhibit PBG properties in the IR spectral region. High-refractive-index structures, based for example on refractory ceramics, could be fabricated by using the polymer structure as a preform.<sup>14</sup> Other structures of arbitrary pattern

and periodicity down to  $\sim 1 \mu\text{m}$  length scales can be readily obtained with this photopolymer system. For example, Figure 4 shows a microstructure which was fabricated to have the same structure as the diamond lattice.

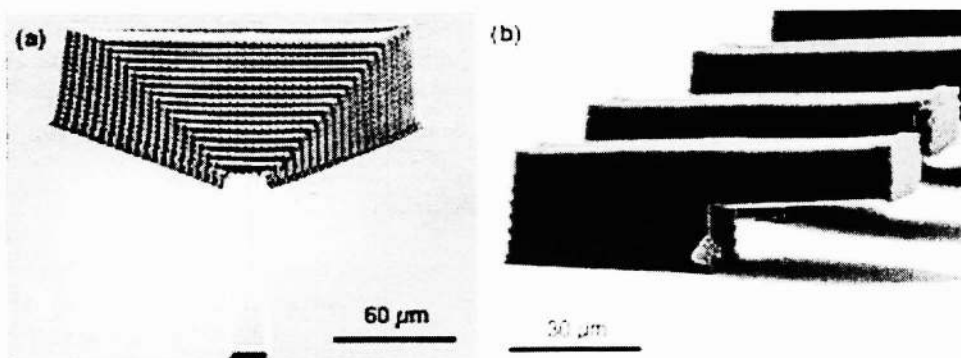
Two-photon 3DLM could also find application in the production of tapered optical waveguides, such as those in Figure 5a. For the example shown, the waveguide cross section varies along the length from a  $100 \mu\text{m} \times 100 \mu\text{m}$  square aperture to a  $2 \mu\text{m} \times 10 \mu\text{m}$  rectangular aperture. Tapered optical-waveguides have the potential to reduce optical loss in the coupling of waveguide components with disparate cross sections.<sup>15</sup> Microelectro-mechanical systems (MEMS) are often produced using 2D lithography, and 3D structures are built up by an iteration of processing steps.<sup>16</sup> As an example of MEMS structures easily fabricated with a single development step, we produced the array of polymeric cantilevers shown in Figure 5b. Recently, we have used 3DLM to fabricate high-aspect ratio 2D-gratings of the type shown in Figure 6. These gratings were found to strongly diffract a HeNe laser beam.



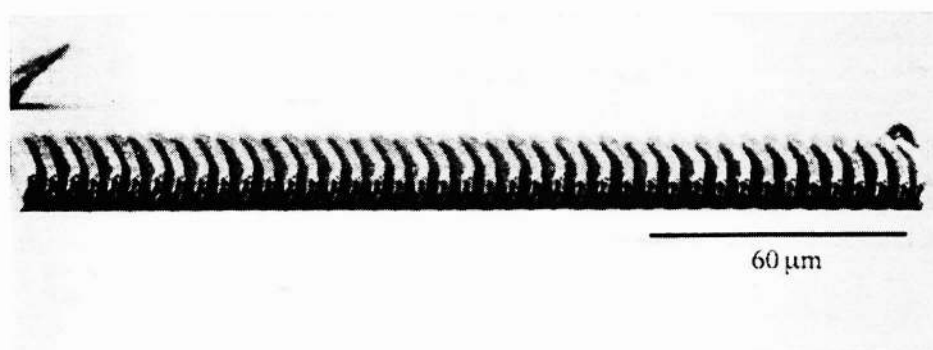
**Figure 3.** (a) SEM images of a "stack-of-logs" photonic bandgap-type microstructure. (b) Close-up side-view of the structure shown in (a).



**Figure 4.** SEM image of a microstructure having the same internal connectivity as the diamond lattice.



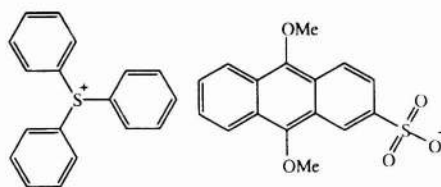
**Figure 5.** SEM images of microstructures fabricated by two-photon induced polymerization of a trifunctional acrylate: (a) Tapered waveguide; (b) Cantilever microstructures.



**Figure 6.** SEM image of a high-aspect-ratio 2D grating fabricated by two-photon induced polymerization of a trifunctional acrylate.

## 5. FUTURE DIRECTIONS: NEW HIGH-SENSITIVITY TWO-PHOTON INITIATORS

We believe that any route to more photosensitive two-photon initiators should involve the design and synthesis of molecules possessing: 1) a chromophoric group with a large  $\delta$ , such as a D- $\pi$ -D structure; 2) a chemical functionality that has a high efficiency of initiation, such as those in UV initiators; and 3) a mechanism by which excitation of the chromophore leads to activation of the chemical functionality, such as an electron-transfer process. Along these lines, we are investigating a number of candidates which could be efficient radical generators and photoacid generators (PAG's) under two-photon excitation. PAG initiators would be useful for 3D photoprocessing a variety of materials, such as polymerizable epoxides and side-chain functionalized polymers.



10

We have examined the salt triphenylsulfonium 9,10-dimethoxyanthracenesulfonate TPS-DMAS (**10**) as a prototype two-photon PAG. Following two-photon excitation, DMAS is thought to transfer an electron to TPS, which then fragments generating a proton.<sup>17</sup> We have used TPS-DMAS to two-photon-activate the acid-catalyzed polymerization of epoxides in a photopolymer resin consisting of 1 wt.% TPS-DMAS and 99 wt.% Epon SU-8 (Shell), a cross-linkable epoxide monomer. For this system, the polymerization threshold power at 740 nm was found to be high ( $\sim 2.1$  mW, for  $\approx 0.35$   $\mu\text{m}$  radial spot size, 150 fs pulses, 76 MHz repetition rate) and close to the damage threshold of 5.1 mW. Since the usable power range for



TPIP is narrow, repeated attempts at microfabrication frequently yielded damaged structures, and microstructures could not be generated reliably with this system. In accord with the scheme outlined above, we believe that a more efficient PAG can be produced by replacing DMAS by a D- $\pi$ -D anion, which offers large two-photon absorptivity and strong reducing power in the excited state. Efforts are currently underway in this direction.

## 6. CONCLUSION

This work demonstrates that symmetric, donor-substituted conjugated chromophores designed to have large  $\delta$  and strong electron-donating properties are effective as two-photon-excitabile charge-transfer agents and are able to initiate the polymerization of acrylate monomers. The results described here open a path toward the design of chromophores with even higher efficiency for the activation of radical polymerization. These systems would offer lower polymerization thresholds, higher polymerization rates, and wider dynamic write ranges, all of which are critical in 3D lithographic microfabrication, where rapid fabrication and low-power writing are essential. Moreover, these principles can be applied equally well in the design of properly functionalized two-photon absorbers, which are engineered to activate other chemical processes, thereby making efficient 3D lithographic microfabrication possible with other materials systems.

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