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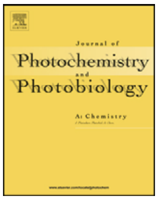

Two-photon polymerization of a diacrylate using fluorene photoinitiators–sensitizers

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ABSTRACT

Two-photon polymerization (TPP) of a diacrylate (monomer) using two different fluorene molecules as photoinitiators–sensitizers is reported. The fluorene molecules contain e⁻ donating (triphenylamine) or e⁻ withdrawing (phthalimide) edge substituents. An amine co-initiator is also used lowering the polymerization threshold. The dependence of the polymerization properties (threshold, polymerization rate, lateral and axial resolution) on the type of resin, the writing power and speed as well as on the NA of the focusing lens is studied in detail. The fluorene with triphenylamine substituent exhibits favorable properties as TPP photoinitiator–sensitizer compared to the fluorene with phtalimide one, although its two-photon absorption cross-section is smaller. Polymerization of the pure monomer or monomer-amine composite (i.e. without fluorene) is also reported.

1. Introduction

Two-photon polymerization (TPP) is widely considered as one of the most important techniques for the realization of three-dimensional micro-optical components and micro-nanodevices required in optical and electronics industry [1–11]. It is also an appropriate technique for fabrication of biocompatible microstructures for medicine delivery and medical examination [12] as well as for the fabrication of conductive micro-nanowires [13,14]. Unique advantages of TPP compared with other techniques are: (i) direct laser induced microfabrication without the use of a mask and (ii) high resolution reaching a sub-diffraction limit of less than 100 nm. Takada et al. and Park et al. have achieved resolution of polymerized structures as high as 65 and 95 nm respectively by introducing radical quenchers inside the resin [15,16]. Additionally, Xing et al. achieved a resolution of 80 nm using a very efficient TPP initiator [17]. Some groups have prepared micromachines like rotators and springs driven by laser tweezers [18,19]. Recently, Wang et al. have achieved remote operation of micromachines by introducing magnetic nanoparticles into resins [20]. In TPP, 3D structures are fabricated in a negative-type resin in which the polymerized pattern (irradiated pattern) survives the developing process. However, Zhou et al. and Kuebler et al. have used two-photon photoacid generation together with a positive-tone resist, in which the irradiated pattern is washed away during development [21,22]. This opens up new prospects for the use of two-photon absorption processes as a tool for the fabrication of masks with <100 nm resolution to be used in microelectronics.

Resins used for TPP generally consist of a two-photon absorbing (TPA) sensitizer, an initiator and a monomer. In order to obtain low polymerization thresholds and enhanced polymerization rate, high TPA and initiating efficiency are needed. In some cases, the TPA sensitizer also plays the role of initiator (type I photoinitiator). Among many organic chromophores, fluorenes have gained an increased scientific interest since the fluorene moiety provides high overlap of π-orbitals. Fluorenes have shown attractive TPA properties combining enhanced TPA and high fluorescence quantum yield [23–25]. However, they have been poorly studied in TPP as TPA sensitizers–photoinitiators [26,27].

In this work, we report on the TPP of a diacrylate using two different fluorene molecules as TPA sensitizers and initiators. The dependence of the TPP properties on the type of the resin, writing power and speed as well as on the NA of the focusing lens is studied in details. An amine co-initiator is also used lowering the polymerization threshold. The two fluorene molecules contain e⁻ donating (triphenylamine) or e⁻ withdrawing (phthalimide) edge substituents. The fluorene with triphenylamine substituent exhibits favorable properties as TPP sensitizer compared to the fluorene with phtalimide one, although its TPA cross-section is smaller and its fluorescence quantum yield is higher. Polymerization of the pure monomer or monomer–co-initiator is also reported.

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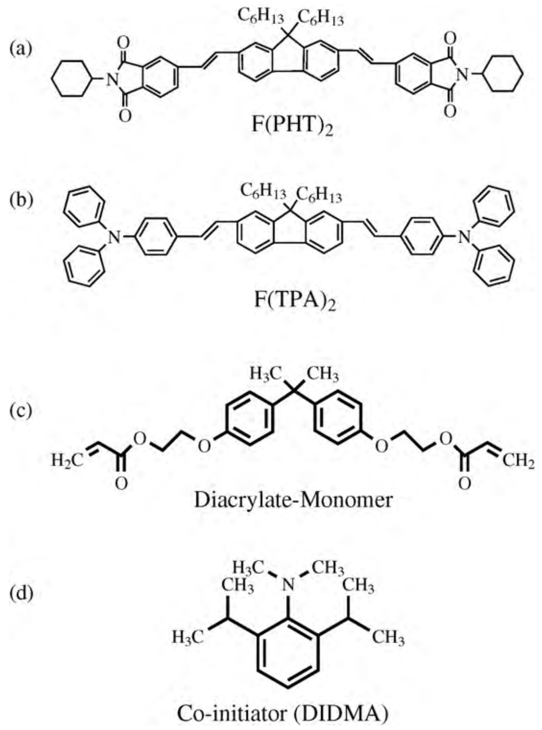

Fig. 1. Chemical structures and abbreviations of (a and b) the two fluorenes, (c) the diacrylate monomer and (d) the co-initiator.

2. Experimental

The two fluorene molecules have been synthesized as reported recently [28,29] and their structures are shown in Fig. 1(a) and (b) together with their abbreviations. They consist of a fluorene central core while the edge substituents are phthalimide F(PHT)$_2$ and triphenylamine F(TPA)$_2$. Bisphenol A ethoxylate diacrylate (Aldrich) was used as the polymerizing monomer (Fig. 1c). It contains two functional groups at both ends, being a bifunctional monomer. It generates an insoluble cross-linked network by free radical polymerization [30]. 2,6-Diisopropyl-*N*,*N*-dimethylaniline, DIDMA (Aldrich), was used as a co-initiator (Fig. 1d) [31]. For the preparation of the two-component resins (monomer with fluorene dye), a suitable amount of the fluorene dye was initially dissolved in THF and was then mixed with the viscous solution of the monomer. The mixture was stirred until THF was evaporated. The concentration of the fluorenes was 0.12 wt.%. Especially, F(TPA)$_2$ was also studied at a concentration of 0.05 wt.%. For the three-component resins (monomer with fluorene dye and DIDMA), DIDMA was mixed with the monomer at a concentration of 0.5 wt.%. Then, the fluorene in THF was added and the mixture was stirred until the solvent was evaporated. In a test experiment, two additional resins consisting of only the monomer or the monomer with DIDMA were also used for TPP. All types of resins are summarized in Table 1.

For TPP, a mode locked Ti:Sapphire laser emitting 80 fs pulses (80 MHz repetition rate) at 800 nm was used as the laser source. The laser beam was expanded using a 5-fold telescope in order to uniformly illuminate the back aperture of the objective lens, used for the focusing of the beam inside the sample. Thus, an almost homogeneous excitation profile at the sample is achieved. A fast shutter was used to control the irradiation of the photopolymerizable resin. The resin was casted on a horizontal microscope cover slip which was placed on a 2-axis DC motor stage connected to a controller. The objective lens was moved across the axis of the laser beam with another DC motor linear stage in order to realize the 3D structures. Two different objective lenses with NA of 1.25 and 0.85 were used, focusing the beam to a radius of ~390 and ~570 nm respectively. The fabricated structures were continuously observed during the writing procedure using an incandescent bulb and a CCD camera connected to a monitor. The lamp with a UV filter was placed over the cover slip containing the resin. The filter was used to reject the UV light of the lamp in order to avoid further polymerization of the resins. The light of the lamp, after passing through the resin, was collected with the same objective lens used for the TPP and was directed towards the CCD camera by means of a dichroic mirror. After the polymerization, the structures were developed by removing the unpolymerized material in a mixture of ethanol and acetone.

3. Results and discussion

The TPA properties of the two fluorene dyes have been studied using a two-photon excited fluorescence technique under femtosecond pulsed excitation and have already been published in the past [32,33]. Their TPA cross-sections, at 800 nm, have been found 835 and 234 GM for F(PHT)$_2$ and F(TPA)$_2$ respectively (in THF solutions). Their fluorescence quantum yields (Q.Y.) are 0.36 for F(PHT)$_2$ and 0.65 for F(TPA)$_2$.

In this work, different types of resins (abbreviated as R_1–R_7 in Table 1) have been tested in order to define the optimum polymerization conditions and properties. The TPP and damage thresholds for different resins and NA of the focusing lens are also summarized in Table 1. The TPP threshold is defined as the lowest power that can produce stiff polymerized structures, capable of surviving the development process, at a writing speed of 10 μm/s. The power has been measured before the objective lens.

The TPP threshold values for resins R_1, R_2 and R_4, R_5 indicate that there is an approximately 45% reduction of the polymerization threshold when F(TPA)$_2$ dye is used (R_2, R_5) instead of F(PHT)$_2$ (R_1, R_4). The reduction occurs independently of NA and of the use of DIDMA as a co-initiator. This result seems to be in contrast to the TPA cross-section values of the dyes since F(TPA)$_2$ has a smaller TPA cross-section than F(PHT)$_2$. Additionally, F(TPA)$_2$ has a higher Q.Y. than F(PHT)$_2$. According to Xing et al. high Q.Y. leads to low polymerization rate because radiative deactivation tends to decrease the active population which generates radicals and initiates polymerization [34]. However, F(TPA)$_2$ is more efficient as a

Table 1
Resins used in this study together with their TPP and damage thresholds.

Resin	TPP threshold (mW)		Damage threshold (mW)
	0.85 NA	1.25 NA	
R_1: monomer/F(PHT)$_2$ 0.12 wt.%	5.6	3.6	45
R_2: monomer/F(TPA)$_2$ 0.12 wt.%	3.2	1.8	
R_3: monomer/F(TPA)$_2$ 0.05 wt.%	5.0		
R_4: monomer/F(PHT)$_2$ 0.12 wt.%/DIDMA 0.5 wt.%	3.9	2.5	45
R_5: monomer/F(TPA)$_2$ 0.12 wt.%/DIDMA 0.5 wt.%	2.1	1.4	
R_6: monomer	32.5		55
R_7: monomer/DIDMA 0.5 wt.%	24		45

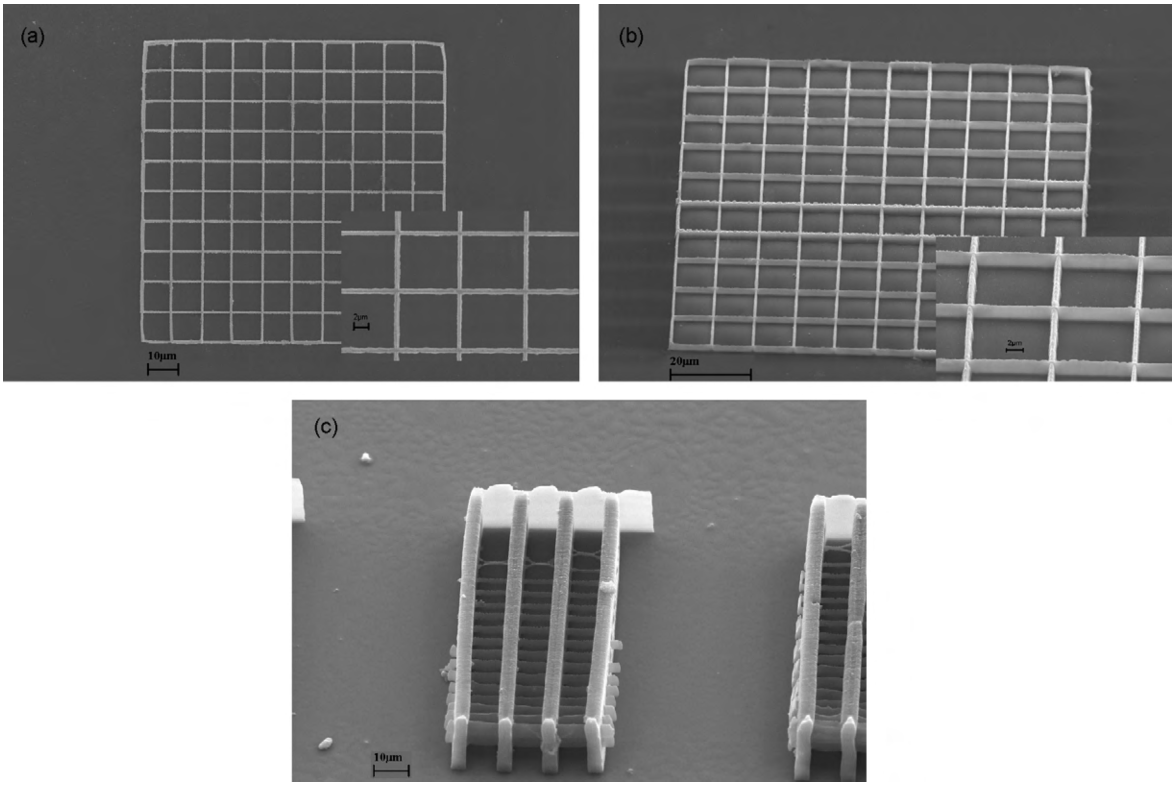

Fig. 2. (a and b) SEM images of a 3D lattice fabricated using resin R_4 under a plane view and at 45° (writing power: 6 mW, writing speed: 10 μm/s). (c) SEM image of single polymerized lines used to measure the lateral and axial resolution. The writing speed is 50 μm/s and the laser power increases from the upper towards the lower line. The perpendicular thick polymerized walls support the single horizontal lines.

TPP initiator than $F(PHT)_2$. In order to explain this result, we have to consider that the rate of the free radical polymerization depends not only on the TPA efficiency and Q.Y. of the dyes but also on the radical generation quantum yield and the initiation efficiency of the generated radicals.

It is well known, after the work of Cumpston et al. [2], that in order to initiate radical polymerization after TPA, electron transfer from the photoexcited molecule to the initiator or polymerizing monomer is needed. For this reason, electron-rich molecules capable of transferring electrons even to weak acceptors should be used. Thus, conjugated molecules having strong electron donating substituents are favorable in TPP. The transfer of electrons to the initiator or monomer generates active species and initiates the polymerization. In our case, $F(TPA)_2$ contains substituents with strong electron donating efficiency while $F(PHT)_2$ contains electron acceptors. Therefore, the electron-rich substituents of $F(TPA)_2$ render this molecule more chemically active, compensating the fact that it has smaller TPA cross-section and higher Q.Y. than $F(PHT)_2$.

Additionally, by increasing the NA of the focusing lens from 0.85 to 1.25 there is an average 35% reduction of the polymerization threshold in all resins tested (R_1, R_2, R_4 and R_5). This is plausibly attributed to the tighter focusing of the laser beam inside the resin under 1.25 NA than under 0.85 NA.

Furthermore, the threshold decreases by approximately 32% in resins having DIDMA as co-initiator (R_4, R_5) compared to resins without DIDMA (R_1, R_2). This occurs for both types of fluorene molecules. Thus, although the fluorenes can initiate TPP without the use of a co-initiator, the presence of a co-initiator lowers the threshold. The lowest threshold equal to 1.4 mW (which corresponds to 0.018 nJ pulse energy and 0.067 J/cm^2 laser fluence) is achieved using resin R_5 and a 1.25 NA lens.

Finally, by reducing the concentration of the dye $F(TPA)_2$ from 0.12 wt.% (R_2) to 0.05 wt.% (R_3) the TPP threshold increases from 3.2 to 5.0 mW (NA = 0.85) indicating that the threshold is inversely proportional to the concentration of the photosensitizer dye. Studies with higher concentration could probably further reduce the threshold but could not been performed because of aggregation in the resin.

In a test experiment, the pure monomer or the monomer–DIDMA composite was used as polymerizing resins (R_6, R_7). Polymerization of the pure monomer (R_6) was achieved at relatively high laser power. The threshold for this polymerization was 32.5 mW. The polymerization threshold decreased to 25 mW when DIDMA was added (R_7). In any case, the structures fabricated with R_6 and R_7 were not stiff and suffered from shrinkage. An experiment in which resins R_6 and R_7 were irradiated by a continuous wave laser beam with the same wavelength and power as the femtosecond pulsed beam was also realized without observing any polymerization. Polymerization of a pure monomer (but with sufficiently lower threshold) was recently reported by Xue et al. although they have not made experiments on a monomer–co-initiator composite [35]. In our case, TPA of the pure monomer or monomer/DIDMA composite is unlikely to occur and the observed polymerization could be attributed to an accumulation thermal effect induced by the high repetition rate of the laser beam.

Fig. 2 shows SEM images of polymerized structures fabricated with resin R_4 (i.e. containing monomer, $F(PHT)_2$ and DIDMA). The Fig. 2(a) and (b) show a 3D polymerized lattice at a plane view and under 45° angle view. The lattice was fabricated using 6 mW (measured before the objective lens) at 10 μm/s writing speed and 1.25 NA focusing. For the investigation of the TPP threshold and rate as well as the axial and lateral resolution, single polymerization lines were fabricated. The lines were not fixed on the glass substrate but were standing in air so that both the lateral and axial resolution, i.e. width and height of the polymerized lines, could be measured from SEM images. The lines were supported by a series

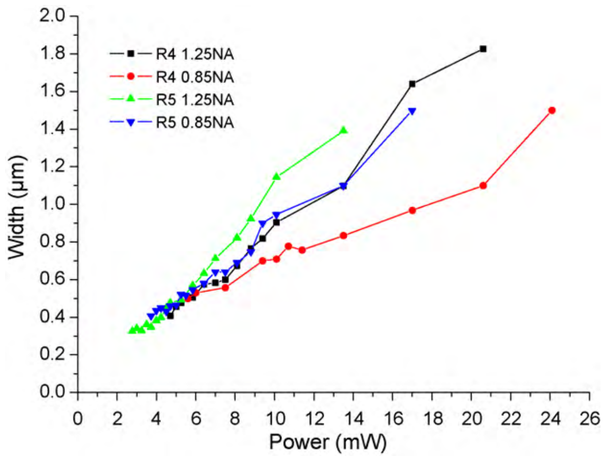

Fig. 3. Width of polymerized lines for R_4 and R_5 versus laser power for 1.25 and 0.85 NA. The writing speed is 50 μm/s.

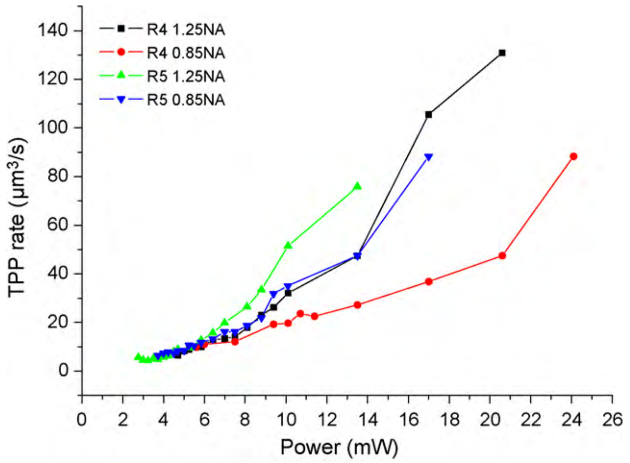

Fig. 4. TPP rate for resins R_4 and R_5 versus laser power under 1.25 NA and 0.85 NA focusing. The writing speed is 50 μm/s.

of perpendicular thick polymerized walls. A typical structure fabricated for this study is shown in Fig. 2(c) using resin R_4. In this figure, the horizontal single lines have been fabricated using the same writing speed (50 μm/s) but the laser power was increased from the upper towards the lower line. At the upper side of the image, where the irradiation power is low (below threshold), the polymerized lines were not stiff enough to withstand shrinkage and they have collapsed onto each other.

The lateral and axial resolution of TPP i.e. the width and height of the single polymerized lines have been measured as a function of laser power with different NA focusing. The writing speed was 50 μm/s. Fig. 3 shows the width of the polymerized lines as a function of writing power and NA for resins R_4 and R_5. It is obvious that the width is reduced as the power decreases. Furthermore, it is also clear that the TPP threshold is lower using high NA focusing than using low one. Specifically, the thresholds are 3.7 mW (R_5) and 5.6 mW (R_4) for 0.85 NA and 2.8 mW (R_5) and 4.7 mW (R_4) for 1.25 NA (speed 50 μm/s). The reduction of the TPP threshold under high NA leads to a better resolution as long as the power is at a low level. However, when the writing power is at a high level, better resolution is achieved under low NA. This can be explained through the threshold effect described in details in Ref. [36]. It is known that the irradiance distribution at the focal point is spatially wider with low NA focusing than with high one. However, TPP resolution is not only dependent on the spatial distribution of irradiance but also on the TPP threshold. If the TPP threshold is close to the peak of the irradiance profile, the active polymerizing area becomes very narrow and the TPP resolution surpasses the diffraction limit. At high power level, this is achieved in our case for 0.85 NA leading to an improved resolution compared to that of 1.25 NA as shown in Fig. 3. The smallest structures that survived the development process in these experiments, i.e. at a speed of 50 μm/s, were fabricated with R_5 and had a lateral resolution of 0.33 and 0.41 μm in the case of 1.25 and 0.85 NA focusing respectively.

The TPP rate, R_{TPP}, has been calculated using the equation $R_{\mathrm{TPP}} = \pi \cdot \left(d/2\right)^2 \cdot v_w$ where d is the width of the polymerized line and v_w is the writing speed [37]. The dependence of the polymerization rate on laser power for R_4 and R_5 is shown in Fig. 4 for low and high NA. The writing speed was 50 μm/s. The polymerization rates are larger for R_5 than for R_4 under the same laser power. In a typical power of ~8 mW and 1.25 NA, the R_{TPP} for R_4 and R_5 are 17.8 and 26.5 μm³/s respectively. These values become 12.2 and 17.8 μm³/s respectively with the same power (8 mW) but under 0.85 NA focusing. These results are comparable to those published recently [34].

In Fig. 5(a) the widths of the polymerized lines obtained using resins R_4 and R_5 under 1.25 NA focusing and 50 μm/s writing speed are compared. Since R_5 has a lower TPP threshold than R_4 (2.8 mW compared to 4.7 mW), there is a smaller width in resin R_5 at low power level [9]. However, at high power level, smaller width is achieved with R_4 than with R_5. This is explained since in R_4 the threshold level is closer to the peak of the irradiance and therefore the active area of the laser beam in which the intensity exceeds the threshold is more restricted than in R_5 (this is shown schematically

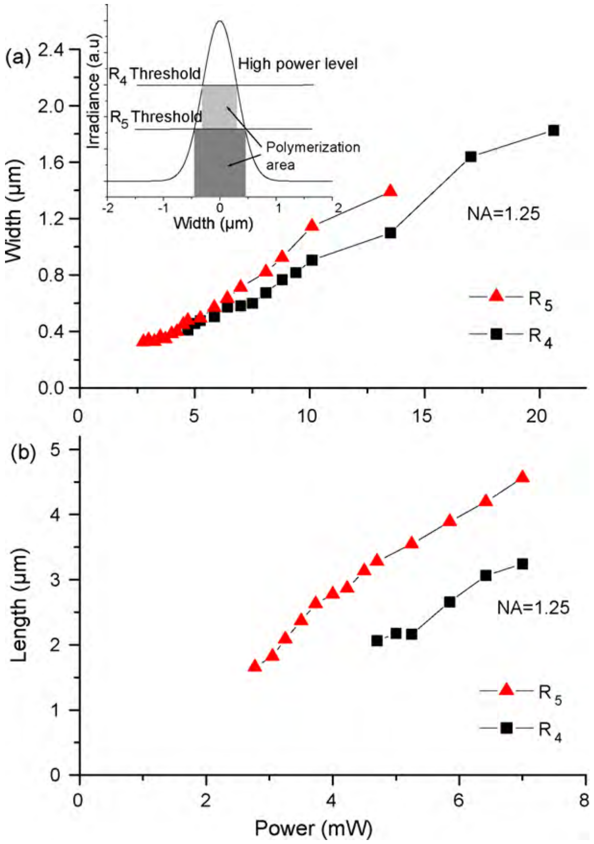

Fig. 5. (a) Width and (b) length of the polymerized lines for resins R_4 and R_5 versus laser power under 1.25 NA focusing. The writing speed is 50 μm/s. The inset in (a) shows schematically the polymerization areas (grey areas) at high writing power level for resins R_4 and R_5 having different thresholds. It is obvious that the polymerization area is narrower in the case of R_4.

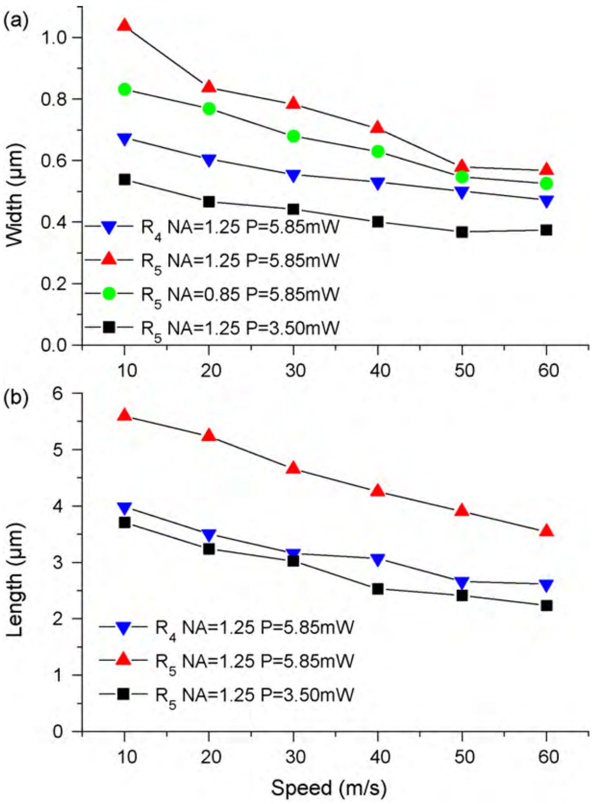

Fig. 6. (a) Width and (b) length of polymerized lines versus writing speed for various writing parameters and resins.

in the inset of Fig. 5(a)).

Fig. 5b shows the length of the lines under 1.25 NA focusing as a function of writing power for resins R_4 and R_5. As mentioned previously, the threshold is lower using resin R_5 than using R_4, and this also leads to a smaller length at low power level. Again, at high power level, smaller length is achieved with R_4 than with R_5. As it was expected, the axial resolution is worse than the lateral one i.e. the length is larger than the width of the polymerized lines. The ratio of axial to lateral resolution is 4.2 and 5 for R_5 and R_4 respectively at a writing power near threshold. Comparing the data in Fig. 5(a) and (b), it is also concluded that the length of the lines is more sensitive to the change of the laser power in agreement with previous theoretical results [38]. For example, when the power increases from 3 to 5.85 mW, the width and length increase by 1.67 and 2.13 times respectively. However, the difference in sensitivities is not as high as it was predicted theoretically for a TPP process [38]. As it is known, the final size of a TPP microstructure depends not only on the laser focal spot but also on the diffusion of the radicals [39]. The high repetition rate of the femtosecond laser may induce increased thermal effects inside the resin enhancing the diffusion of free radicals. This can cause deviations of the axial and lateral size of the structure from the theoretically predicted values.

Finally, in Fig. 6(a) and (b) the TPP width and length are shown as a function of writing speed for different powers and NA. As the speed increases, the exposure time decreases and the number of generated radicals is reduced. Therefore, both dimensions of the polymerized lines decrease. In Fig. 6(a), the smallest width at all speeds is achieved with R_5 at 1.25 NA as far as the writing power is at the low level of 3.5 mW. This power is capable for TPP under high NA but not under low one. At high power (5.85 mW) and 1.25 NA, smaller width is achieved using R_4 at all speeds. Finally, using resin R_5 and writing power of 5.85 mW, smaller width is obtained under 0.85 NA than under 1.25 NA at all speeds, because of the threshold effect [36]. Similar conclusions are also entailed from Fig. 6(b) concerning the dependence of the length on speed, power and type of resin.

4. Conclusions

In this work, two-photon polymerization of a diacrylate using two fluorene molecules as sensitizers–photoinitiators and an amine as co-initiator was reported. The fluorene having e^- donating edge substituents (triphenylamine) exhibited better TPP properties than the one having e^- withdrawing substituents (phthalimide). This occurs despite the fact that the former has smaller TPA cross-section and higher Q.Y. than the latter. The polymerization properties were studied in details as a function of writing power and speed as well as NA focusing and type of resin. High spatial resolution was achieved using laser power close to threshold and high NA focusing. TPP threshold as low as 1.4 mW (which corresponds to 0.018 nJ pulse energy and 0.067 J/cm^2 laser fluence), lateral resolution of 0.33 μm and TPP rate of 26.5 μm^3/s (at 8 mW) have been reported for resin R_5.

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