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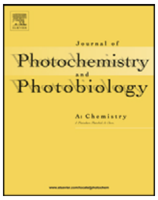

Two-photon polymerization of a diacrylate using fluorene photoinitiators–sensitizers

I. Fitilis[a], M. Fakis[a,*], I. Polyzos[a,b], V. Giannetas[a], P. Persephonis[a]

[a] *Department of Physics, University of Patras, 26504 Patras, Greece*
[b] *Department of Optometry and Vision Studies, Technological Educational Institute of Patras, Greece*

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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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* Corresponding author. Tel.: +30 2610 997 488.
E-mail address: fakis@upatras.gr (M. Fakis).

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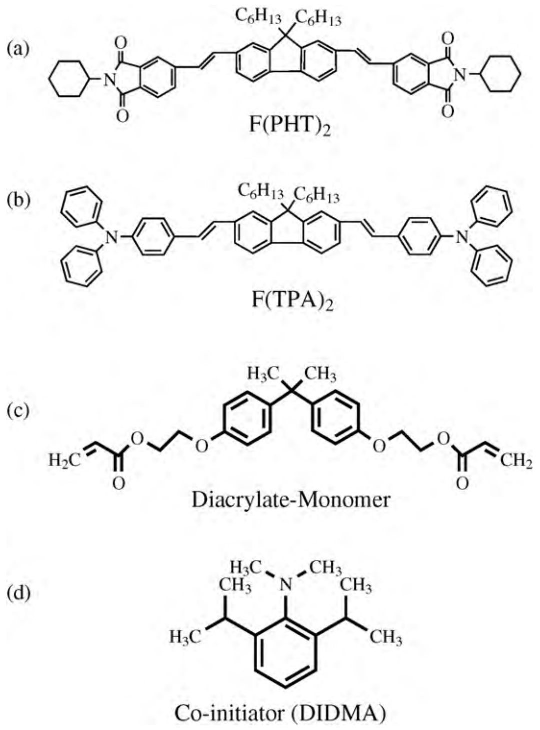

Fig. 1. Chemical structures and abbreviations of (a and b) the two fluorenes, (c) the diacrylate monomer and (d) the co-initiator.

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