

Laser ablation of aryltriazene photopolymer films: Effects of polymer structure on ablation properties

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Abstract

Laser ablation of a homologous series of four tailor-made UV-sensitive aryltriazene polymers with an increasing content of photodecomposable chromophore units has been studied with a XeCl excimer laser (emission wavelength 308 nm). Irradiation induces a photolytic cleavage of the aryltriazene chromophores which then leads to a fragmentation of the polymer main chain. Resulting effects of different chromophore densities on the ablation parameters of thin films were investigated by profilometry analysis of the ablated spots. No relevant influence of the chromophore density was found for the threshold fluence of laser ablation ($\sim 25 \text{ mJ/cm}^2$) of the four polymers for single-pulse experiments. In the same way, ablation depths per pulse at a given laser fluence and with the same film thickness showed no significant differences. Remarkable differences were found for the resulting surface morphology of ablated spots at laser fluences near the ablation threshold. Homogeneous ablation resulting in a flat and smooth bottom surface of the ablated pits were observed mainly for laser fluences above the range of two times the ablation threshold ($> \sim 50 \text{ mJ/cm}^2$). Investigating the ablation behaviour of such triazene-based photopolymers allows to derive photophysical key parameters necessary for the optimization of application processes where the designed polymers are used as sacrificial absorbing release layers in advanced laser-induced forward transfer (LIFT) applications.

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1. Introduction

Laser-induced forward transfer (LIFT) has been applied as the first direct-writing technique for the deposition of defined patterns of various materials, such as metals, ceramic powders and even organic materials with micrometer resolution [1–3]. For LIFT applications a pulsed laser is used to induce the mass transfer from a source layer towards a receiver substrate which is placed in close proximity. Due to the high thermal load on the entire layer of transfer material induced by direct absorption of laser radiation, mainly robust and heat-resisting materials could be directly transferred. Attempts to apply conventional LIFT conditions for pixel deposition of more heat-sensitive materials, such as organic dyes, electroluminescent polymers, biomaterials,

or even living cells proved to be limited by their proneness to heat damage or direct laser exposure [4]. In order to avoid direct irradiation of sensitive organic transfer materials, more complex donor systems were developed with an additional dynamic release layer (DRL) [5,6]. The incident laser energy is absorbed by the sacrificial DRL which then decomposes and propels the overlying transfer material towards the receiver. Therefore, sensitive transfer materials are protected by the DRL from incident high-intensity radiation. Polymers, used as such sacrificial light-to-heat conversion layers are increasingly finding applications, and various DRL-based LIFT applications were reported, e.g. for high-resolution full-colour printing (cf. [1]), the transfer of single molecules [7] as well as biologic cellular systems [8–12], for the release of prefabricated parts in the assembly of microelectromechanical systems [13], or the structured transfer of semiconducting polymers used in organic light-emitting diodes [14,15]. One of the common issues of these sacrificial light-to-heat conversion layers, predominantly used

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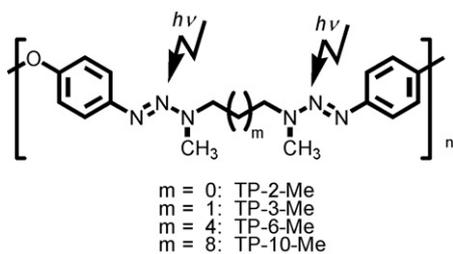


Fig. 1. Structure formula of the studied photopolymers. Two photodecomposable aryltriazene chromophores per repeating unit are covalently incorporated into the polymer main chain, joined by an alkyl bridge.

with IR-lasers, is the intrinsically high thermal load on sensitive materials to be transferred [16].

To prevent defects from overheating and radiation-induced damages [16], we developed an advanced LIFT process applying a thin film of a UV-sensitive photopolymer as the absorbing sacrificial DRL. Photodecomposable aryltriazene (Ar–N=N–N–) chromophore units are covalently integrated into the main chain of the tailor-made polymer, as shown in the structure formula in Fig. 1. Exposure to UV-irradiation causes photolytic cleavage of the triazene chromophores with evolution of elementary nitrogen, as depicted in Fig. 2 [17]. Simultaneously, two instable radical fragments, a phenyl σ -radical and a secondary aminyl radical are formed which then undergo further disproportionation reactions [18]. Cleavage of the bridging aryltriazene chromophores in the polymer backbone leads to a photo-triggered fragmentation of the polymer main chain. Upon pulsed laser irradiation aryltriazene polymers can therefore be efficiently ablated at very low laser fluences, with ablation thresholds in the range of 20–25 mJ/cm² [18]. This class of photopolymers proved also to be particularly well suited for DRL-based LIFT systems because they decompose integrally into volatile and gaseous fragments. By ablative laser decomposition of the polymer film, a photo-induced pressure jet is generated [19] which then propels an overlaying film of pure transfer material towards the receiver substrate.

The broad scope of advanced LIFT applications based on these sacrificial photopolymer DRLs was demonstrated recently: Assisted by a 100 nm thick aryltriazene polymer film, living mammalian neuroblast cells were successfully forward-deposited onto a bio-receiver substrate with a pulsed ArF excimer laser [20]. In a similar manner, pixel arrays of sensitive multi-spectral nanocrystal quantum dots (NCQD) were smoothly transferred with good resolution [21]. The

photo-DRL-based LIFT process was also applied with a pulsed XeCl excimer laser for the fabrication of organic light-emitting diodes (OLED) by microdeposition of well-resolved and clear-cut bilayer pixels of an electroluminescent polymer (MEH-PPV) together with an aluminium cathode [22]. For such advanced LIFT applications a photopolymer suitable as DRL has to fulfil a complex profile of properties: Key characteristics are not only photosensitivity and a high absorption in the range of the specific photosensitive laser emission wavelength, but also a clean photocleavage and efficient ablation without carbonization or debris formation. For thin-film applications, polymers have to provide excellent film-forming properties as well as sufficient solubility for the processing steps. We improved a versatile synthesis strategy that opens access to various aryltriazene polymers with different structural elements incorporated in the main chain and as side-chain substituents [23]. Specific modifications of the polymer substructures based on rational structure-property relationships allow to adapt physical and macroscopic properties of the polymer films to the individual demands of the LIFT application. Therefore, we are investigating in detail the influences of varied structural parameters on the functionality of photopolymer films.

In this study we report on effects of the length of the alkyl chain between the two triazene chromophore units on the ablation behaviour of the polymers. The length of that alkyl spacer chain determines the sequence density of photocleavable chromophore moieties along the polymer main chain, acting as laser-triggered predetermined breaking-points in the polymer backbone. As shown in Fig. 1, a series of four homologous aryltriazene polymers TP-2-Me to TP-10-Me, with each a C₂-, C₃-, C₆- or a C₁₀-alkyl spacer chain was investigated and the ablation behaviour of thin polymer films was characterized, as well as the influence on the surface morphology of ablated films.

2. Experimental

Aryltriazene polymers TP-2-Me, TP-3-Me and TP-10-Me were synthesized according to the improved general protocol published for TP-6-Me [23]. Number- and mass-average molar masses and polydispersity were all in the same range as given for the reference polymer TP-6-Me. Thin polymer films were prepared by spin-coating polymer solutions (in a 1:1 w/w mixture of cyclohexanone and chlorobenzene) onto quartz substrates (Suprasil 2) in a laminar flow hood, as described for TP-6-Me [23]. Film thicknesses and surface roughness

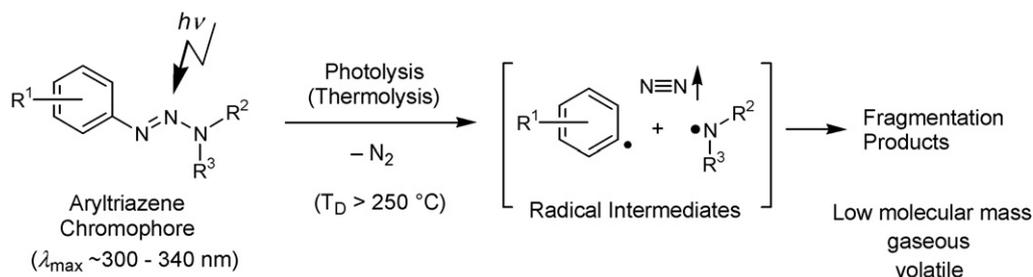


Fig. 2. Pathway of the photolytic cleavage of an aryltriazene chromophore with release of molecular N₂ and formation of two radical fragments. The decomposition process can also be thermally triggered at temperatures above about 250 °C.

measurements were performed on a profilometer (Ambios XP-1, tip radius 2.5 μm), with a stylus force of 0.05 mg. Micrographs were taken by an optical microscope (Zeiss Axioplan) coupled with a digital camera system (Leica DC500). Ablation experiments were performed with a XeCl excimer laser (Compex, Lambda Physik, $\lambda = 308$ nm, $\tau = 30$ ns), and the fluence was controlled by an attenuator plate. A homogeneous part of the beam was imaged by a quartz lens onto the polymer film surface (magnification 0.25), and the geometry of the ablated spots defined by a rectangular mask (aperture 2 mm), yielding a spot size of 500 $\mu\text{m} \times 500 \mu\text{m}$. Pulse energies at each fluence were measured by a pyroelectric energy meter (Moletron J4-09 or Gentec QE 50), and averaged over 100 pulses. Variation of the single-pulse energies were typically in the range of $\pm 10\%$. Films coated on quartz substrates were mounted on a translation stage perpendicular to the laser beam and irradiated with the film side oriented towards the incident laser. A matrix of ablation spots was created on each film sample supported by a computer-controlled system that allowed variation of the pulse energy and the number of pulses. A matrix of 13×10 rectangular spots were ablated per experiment, with 13 increasing values for the laser fluence in the range from 20 to 180 mJ/cm^2 , and 10 spots for each fluence value, with six spots each for single-pulse ablation, and one for two-, three-, four-, and five-pulse experiments. Linear decadic absorption coefficients α of polymer films at the laser emission wavelength were determined by dividing the absorbance at 308 nm (measured with a Cary-50 spectrophotometer) by the film thickness (measured by profilometry) and were found to be 94,300, 96,800, 89,600, 85,400 cm^{-1} for the four polymers TP-2-Me to TP-10-Me.

3. Results and discussions

The most relevant key parameter of photopolymers designed for DRL applications in LIFT processes is their fast and clean decomposition upon laser irradiation. A low ablation threshold fluence and high ablation rates per laser pulse are essential in order to minimize the incident laser energy for the transfer process. For that reason, suitable polymers have to provide a high absorption coefficient α within the wavelength range of the laser

radiation, and therefore an content of incorporated chromophore units as high as possible. On the other hand, physical properties of the polymers relevant for the practical processing, like solubility, brittleness, wettability and especially thin-film-forming properties, depend on the molecular structure, as well as the resulting photofragmentation behaviour. In order to investigate the effects of the chromophore density on the photodecomposition properties, a homologous series of four aryltriazene photopolymers TP-2-Me to TP-10-Me was synthesized and their ablation behaviour characterized. Fortunately, all four polymers were sufficiently soluble in the same solvent system (chlorobenzene/cyclohexanone, 1:1), and homogeneously smooth, crack-free films with thickness between ~ 100 and ~ 500 nm could be uniformly prepared by spin-coating. The average roughness of the film surfaces were typically below 5 nm, which corresponds to the roughness of the substrate surfaces.

3.1. Single-pulse ablation

Micrographs of details of the ablation matrix in films of TP-2-Me and TP-10-Me are shown in Fig. 3 as examples that demonstrate the high surface quality of the photopolymer films. Laterally well-defined ablation spots with clear-cut structures and sharp edges were created for all four polymers, and no carbonization or deposition of ablation debris was detected. However, we observed some differences in patterns and surface roughness of the remaining polymer layer within the ablated spots for TP-2-Me. In Fig. 4, a compilation of profilometer traces of ablation spots created by single-pulse irradiation with increasing laser fluences is shown for films of TP-2-Me and TP-10-Me. Corresponding profilometer traces of ablated spots of TP-3-Me and TP-6-Me (not shown) reveal nearly identical shapes for the single-pulse ablation as presented for TP-10-Me in Fig. 4(b). Above the ablation onset at a threshold fluence in the range of 23–25 mJ/cm^2 , removal of material takes place and spots with a well-defined pot-type geometry are formed. However, a remarkable difference was observed for TP-2-Me, the polymer with the shortest alkyl spacer, and therefore with the highest number of chromophores along the polymer main chain. This polymer proved to be the most photosensitive within this homologous series and showed already at a laser

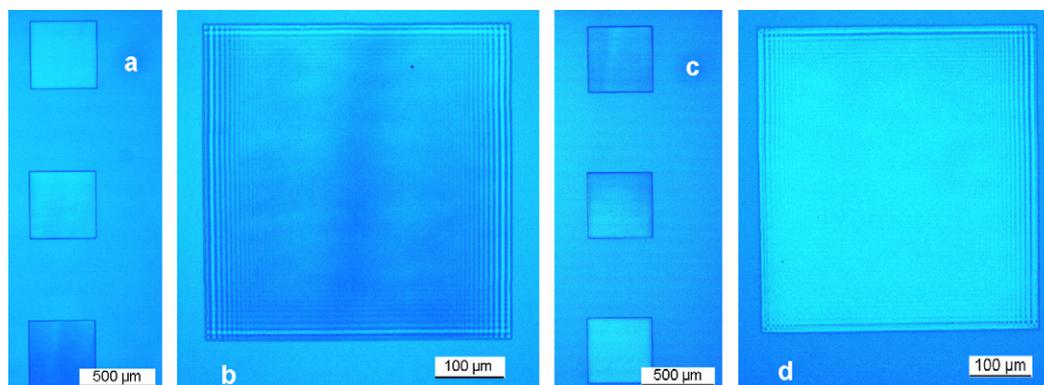


Fig. 3. Microscope pictures of spots ablated by a single pulse in films of TP-2-Me (a and b) and TP-10-Me (c and d), with laser fluences of 181, 154 and 125 mJ/cm^2 [from top to down in (a) and (c)]. Spots ablated with 125 mJ/cm^2 are shown for both polymers in the pictures (b) and (d) with higher magnification.

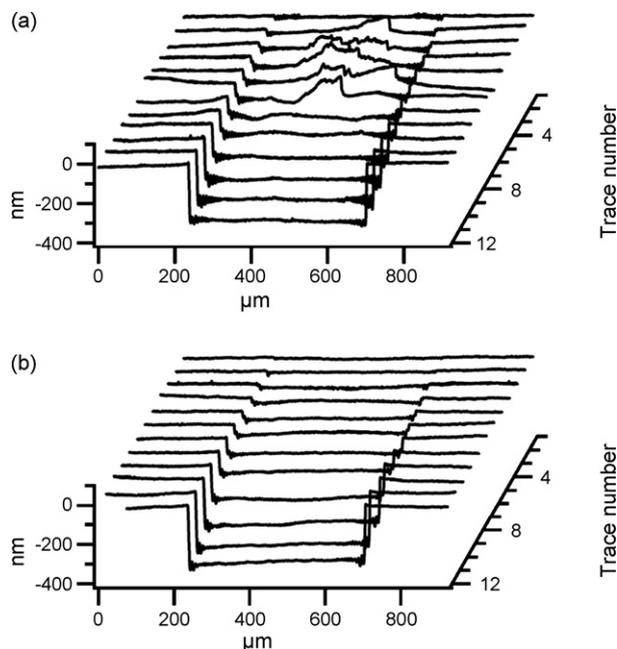


Fig. 4. Profilometry traces of ablated spots created by a single pulse in films of TP-2-Me (a) and TP-10-Me (b) at 12 increasing laser fluences (20, 24, 28, 32, 36, 40, 49, 61, 87, 125, 154, and 181 mJ/cm^2 , corresponding to traces 1–12, respectively).

fluence of 20 mJ/cm^2 a clearly detectable roughening of the film surface as a first indicator for the onset of the ablative photodecomposition. A significant surface swelling with uncontrolled formation of protruding structures can then be seen in Fig. 4(a) for higher laser energies just above the ablation threshold. Again a more regular ablation behaviour of TP-2-Me, as observed for the other polymers, was observed only for fluence values above $\sim 60 \text{ mJ}/\text{cm}^2$. We attribute this different behaviour to a possibly slightly different photodecomposition mechanism of TP-2-Me. After simultaneous photolysis of two adjacent triazene chromophore units, two molecules of N_2 together with a 1,2-diaminylethyl radical fragment (Fig. 5) are formed. In general, 1,4-diradical species were found to be predestined to undergo spontaneously a subsequent homolytic cleavage of the central C–C-single-bond, which leads to the formation of two neutral molecules [24], as depicted in Fig. 5. Exclusively the polymer with the C_2 -alkyl bridge can undergo this type of subsequent 1,4-fragmentation reaction which additionally will generate two neutral and easily volatile low-molecular-mass fragments of methylimine.

In general, photolytic decomposition reactions of aryltriazene chromophores in the solid state can be triggered even at much smaller irradiation energies, far below fluences necessary for ablation. Only photo-induced degradation processes with-

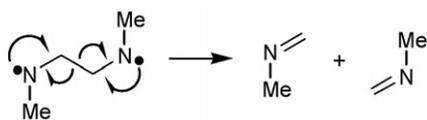


Fig. 5. Subsequent cleavage step of the remaining bisaminyl-1,4-diradical fragment of TP-2-Me after initial photodecomposition of the adjacent chromophore units.

out any volume ablation take place within the polymer film when the applied irradiation energy is below the ablation threshold [23]. Nevertheless, one molecule of elemental N_2 is liberated for each photocleaved triazene chromophore moiety which then can lead to the formation of bubbles within the irradiated polymer film. If the applied fluence is below the ablation threshold, remaining reactive radical fragments of the photodecomposition process are not ejected and can therefore undergo recombination reactions leading to a cross-linked polymer matrix. At low ablation fluences, the intensity of the incident laser radiation is only sufficient for the removal of a certain top-layer thickness and is exponentially decreasing within the polymer film. After a certain thickness of the superficial layer has been ablated, the remaining energy of the laser drops below the critical ablation threshold and is therefore only sufficient to induce non-ablative photolysis reactions within the polymer layer below. The formed gaseous fragmentation products then expand and lift up the overlying polymer matrix, inducing a foamy and rough surface structure. Polymers TP-3-Me to TP-10-Me with longer alkyl spacer moieties form a relatively smaller amount of easily volatile fragmentation products, and evolve therefore less decomposition pressure within the underlying polymer film, resulting in smoother surfaces of the ablated spots. Nevertheless, ablation depths per pulse were found to be nearly equal for all four polymers in single-pulse experiments.

3.2. Multi-pulse ablation

A typical diagram of the ablation depths depending on the laser fluence and the number of applied subsequent laser pulses is shown in Fig. 6 for a 420 nm thick film of TP-6-Me. Polymer films with a thickness $>300 \text{ nm}$ were investigated in order to investigate also the ablation characteristics in multi-pulse experiments. Within the chosen range of laser fluences, complete ablation of the polymer films could only be reached by irradiation with more than one pulse. Upon irradiation with two subsequent pulses with a fluence of 125 mJ/cm^2 , the 420 nm thick film was apparently completely ablated.

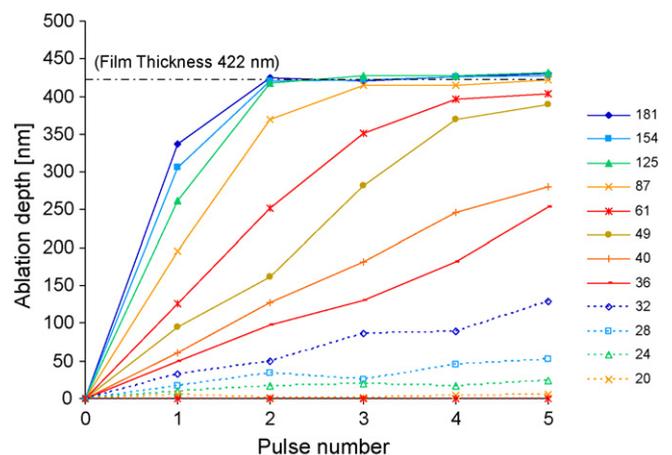


Fig. 6. Ablation depths per pulse and the number of pulses at 12 increasing laser fluences (values in mJ/cm^2) for a 420 nm thick film of TP-6-Me.

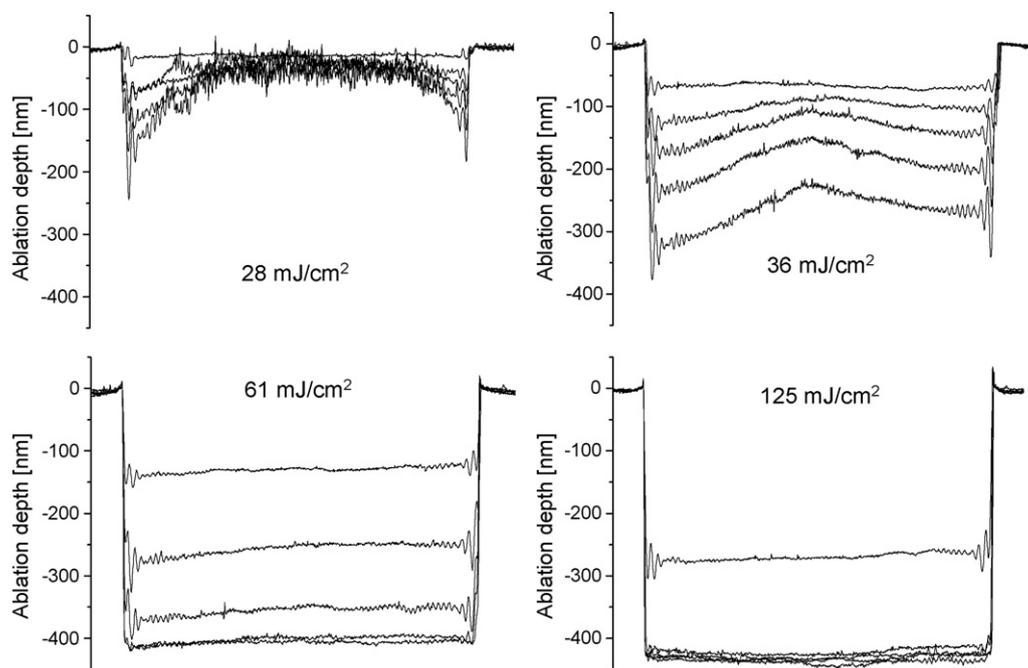


Fig. 7. Compilation of profilometry traces of ablation spots, each created with one to five pulses at four increasing laser fluences of 28, 36, 61 and 125 mJ/cm². The horizontal width of the ablation spots is 500 μm.

At laser fluences of above ~ 35 mJ/cm², a roughly linear increase of the ablation depth with increasing number of pulses was found. However, profilometer analysis of the surface of the corresponding ablation spots reveal significant differences in the ablation behaviour for multi-pulse experiments at various laser fluences. Corresponding typical profilometry traces of a 420 nm thick film of TP-6-Me are compiled in Fig. 7 for four fluences, and each for one to five subsequent laser pulses (ablation from top to down). The profiles correspond to the data presented in Fig. 6. With the first pulse at 28 mJ/cm² a homogeneous ablation with a depth of ~ 20 nm and a flat spot surface is achieved. A second pulse with the same laser energy leads to an inhomogeneously curved and rough surface, similar to the irregular ablation patterns of TP-2-Me with single-pulse irradiation at low fluence values (see Fig. 4). Obviously, the ablation properties of the remaining polymer surface have changed during exposure to the first laser pulse, and predominantly a swelling and expanding of the partially ablated polymer is observed for subsequent pulses. Since during the first pulse free radical species were generated by photolysis of the triazene chromophores in the underlying irradiated polymer film, recombination of non-ejected radical fragments will lead to a layer of photochemically modified, cross-linked and gas-expanded polymer as the remaining crater bottom. We recently demonstrated that solid-state photodecomposition of thin polymer films of TP-6-Me with continuous-wave UV irradiation at low energies leads to the loss of the characteristic triazene absorption bands and a slow cross-linking reaction of the polymer film surface [23]. Therefore, photolytic cleavage of the triazene chromophores decreases the absorption coefficient α of the film locally, and the remaining polymer film is less easily ablatable as before. A thin “skin” layer on top of the partly ablated crater is formed that allows

penetration of incident laser photons into the adjacent underlying film volume, but the volatile photodecomposition fragments are enclosed by the overlying skin which then gets expanded. At a laser fluence of 36 mJ/cm² more bonds are simultaneously cleaved, and more of the formed polymer fragments are ejected out of the crater which obviously favours a more uniform ablation process. Nevertheless, a curved and rough surface profile is generated for subsequent multi-pulse ablation steps. A more complete and uniform ablation of the film was observed for five pulses at a fluence of 61 mJ/cm². The remaining surface in the ablation crater is here much smoother and shows no curved bottom shape anymore. A nearly flat shape of the crater bottom is also found for two subsequent pulses at a laser fluence of 61 mJ/cm² leading to an ablation depth of about 270 nm. A similar profilogram for the material removal was achieved for the first pulse at 125 mJ/cm². From that laser fluence onward, the whole film thickness of about 420 nm seems to be ablated just by the second pulse, whereas at a fluence of 61 mJ/cm² the absorbed laser energy even after five pulses is apparently not sufficient to ablate the polymer film without a residual thin layer.

4. Summary and conclusions

Ablation characteristics of four homologous tailor-made aryltriazene photopolymers were compared with respect to the effect of the chromophore density on the surface morphology of the ablated spots. Whereas photophysical parameters as a low threshold fluence of less than about 25 mJ/cm² for the ablation onset as well as ablation rates per pulse were found to be nearly equal for thin films of the four polymers, significant differences were found for the shape of the crater bottoms. Photodecomposition of films of TP-2-Me with the highest relative content of

chromophore units in the polymer main chain leads to an uncontrolled expansion of the film surface at fluences below $\sim 85 \text{ mJ/cm}^2$. Similar effects were observed for fluences in the range between the ablation threshold and about 60 mJ/cm^2 when ablation spots were created by more than one laser pulse. Studying the ablation behaviour of the individual polymers at different irradiation conditions allows us to define optimum process parameters for the tailored application of such aryltriazene polymer films as photo-triggered DRL for LIFT processes. Experiments for the more detailed study of the influence of photothermal effects and heat diffusion processes are currently under investigation.

Acknowledgement

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