

Synthesis and characterisation of new hard polyurethanes with triazene pendants

Emil C. Buruiana^{a,*}, Violeta Melinte^a, Tinca Buruiana^a, Thomas Lippert^b, Hiroshi Yoshikawa^c, Hiroshi Mashuhara^c

^a Petru Poni Institute of Macromolecular Chemistry, 700487 Iasi, Romania

^b Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

^c Department of Applied Physics, Osaka University, Suita, Osaka 565 0871, Japan

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Abstract

Three new hard type polyurethanes based on 2,4-toluene diisocyanate (2,4-TDI) and different triazene diols, namely 1-phenyl-3,3'-di(2-hydroxyethyl) triazene (PT-D), 1-naphthyl-3,3'-di(2-hydroxyethyl) triazene (NT-D) and 1-(4-nitro)-phenyl-3,3'-di(2-hydroxyethyl) triazene (NOT-D) were synthesized and characterized. The photosensitivity of these polymers was evaluated by UV irradiation, in DMF solution and as films by following the disappearance of the π - π^* absorption band corresponding to the triazene group. The polyurethane containing the NOT-D monomer revealed no decrease of its absorption bands even during prolonged irradiation, but could be structured with high quality using 308 nm laser irradiation. The ablation results revealed that the etching depth could be controlled by varying the laser fluence and number of laser pulses.

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Keywords: Hard triazene polyurethanes; Photosensitivity; UV irradiation; Laser ablation

1. Introduction

Over the past decade, polymeric systems with light-controlled surface topology have been the subject of intense research, due to their unique and unexpected properties that allow various applications in the field of photoresists, imaging materials and microoptical elements [1–7]. Significant progress has been recently made in sensitizing the polymers for ablation through the incorporation of photochemically active chromophores into the polymer main or side chain as a route to tailored high-performance new photopolymers. On this line, the triazene-polymers were intensively investigated owing to the high photosensitivity of the triazene groups ($-\text{N}=\text{N}=\text{N}<$) and its spontaneous fragmentation into gaseous products upon exposure to excimer lasers, which would reduce or eliminate the problem of redeposited material in the

ablation process [8–10]. It has been demonstrated that the presence of triazene chromophores in the polymer backbone leads to photosensible materials in which structural and optical properties can be manipulated by UV/laser irradiation [11–14]. The triazene moiety has been widely studied prior 1950 [15], but its versatility in organic synthesis has been greatly expanded during the past 30 years [16]. The idea of introducing photosensitive breaking points of triazene type into a polymer structure is relatively new [17] and polymers such as polyesters, polyethers, polytriazenes or polysulfides with additional triazene moieties have been reported [18–21]. A novel approach is the synthesis of triazene polyurethanes in order to combine the sensitivity of the triazene structure with the particular properties of the polyurethanes. This outcome results in a wide field of possibilities for tailoring special properties that yields new materials for microlithography.

Polyurethanes have attracted much attention in the last few years due to the ease of processing and especially to

* Corresponding author. Tel.: +40 2 3221 7454; fax: +40 2 3221 1299.
E-mail address: emilbur@icmpp.tuiasi.ro (E.C. Buruiana).

the unlimited architectural versatility for optimizing their properties [22–25]. The combination of the excellent mechanical characteristics of polyurethanes with the photoactive triazene group has recently been described and some correlations between the triazene molecular structure and the polymer properties were found [26,27]. These polyurethanes include photolabile groups in the hard segment beside the soft segment ones in order to achieve flexible photosensitive materials.

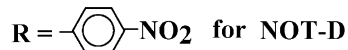
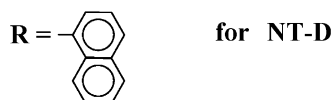
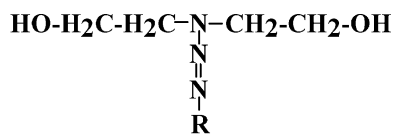
As a continuation of our effort to attain a better understanding of the effect of the triazene chromophore on the polymer properties, in this paper we report the synthesis of new hard polyurethanes with triazene units in the side chain and the photochemical behavior of this type of polymers under UV irradiation. We also show data about the laser ablation of one selected polymer, i.e. a nitro-triazene polyurethane.

2. Experimental

2.1. Synthetic procedures

The general structure of the triazene monomers employed in our study, i.e. 1-phenyl-3,3'-di(2-hydroxyethyl) triazene (PT-D), 1-naphthyl-3,3'-di(2-hydroxyethyl) triazene (NT-D) and 1-(4-nitro)-phenyl-3,3'-di(2-hydroxyethyl) triazene (NOT-D) is shown in Scheme 1, while the detailed synthesis procedure has been reported previously [26,27].

The hard type polyurethanes (PU-P, PU-N, PU-NO) were obtained by a polyaddition performed in dry DMF starting from 5 g triazene diols and a corresponding stoichiometric amount of toluene diisocyanate (2,4- and 2,6-TDI isomer mixture, 80:20 v/v). The reactions were carried out under purified nitrogen at 65 °C for 15 h. The triazene polyurethanes were precipitated in methanol and dried for 48 h at 60 °C under reduced pressure.



Scheme 1. Chemical structures of the triazene monomers.

2.2. Equipment

The polymers structures were verified by ¹H NMR, IR and UV spectroscopy using a Bruker 400 MHz spectrometer, a Specord M80 and Specord M42 spectrophotometer, respectively. Gel permeation chromatography (GPC) measurements were performed with a Polymer laboratories MD-950 apparatus equipped with an evaporative mass detector and two PL gel 5 μm columns. The sample for measurement was 1.0 g dL⁻¹ solution in DMF and the flow rate of the carrier solvent was 1 mL min⁻¹. The average molecular weight was calculated on the basis of the molecular weight versus retention volume curve of monodisperse polystyrene standard. The thermal stability of the polyurethanes was analyzed by thermogravimetry using a derivatograph (MOM Budapest). TG and TGA curves were recorded between 20 °C and 600 °C with a heating rate of 12 °C min⁻¹ in air. UV irradiations were performed in DMF and for thin films, using a 500 W high-pressure mercury lamp without wavelength selection, at room temperature. The initial absorbance of the samples in the absorption band maximum was kept between 0.9 to 1.0. For the irradiation at 308 nm a Complex 205 XeCl excimer laser from Lambda Physik (τ = 30 ns) was used. The samples for the laser ablation experiments were prepared by solvent casting from a 15 wt.% DMF solution on glass substrates.

2.3. Measurements

PU-P, ¹H NMR (DMSO-d₆, δ ppm): 8.8 and 9.6 (m, NH-COO); 7.4, 6.8 and 6.55 (m, aromatic protons from TDI); 7.34, 7.15 and 7.05 (m, aromatic protons from the triazene sequence); 4.36 (m, NHCOO-CH₂-CH₂); 4.1 (m, NHCOO-CH₂-CH₂-N-); 2.19 and 2.1 (s, Ph-CH₃).

UV (DMF), λ_{max}: 294 nm and 307 nm.

PU-N, ¹H NMR (DMSO-d₆, δ ppm): 8.5 (m, NH-COO); 7.9–6.8 (m, aromatic protons from TDI and from naphthalene ring); 4.47 (m, NHCOO-CH₂-CH₂); 4.2 (m, NHCOO-CH₂-CH₂-N-); 2.22 and 2.1 (s, Ph-CH₃).

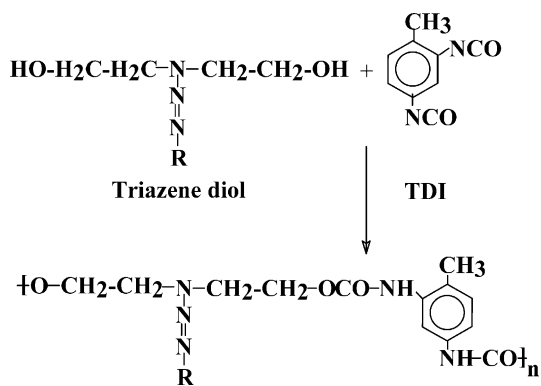
UV (DMF), λ_{max}: 345 nm.

PU-NO, ¹H NMR (DMSO-d₆, δ ppm): 9 and 9.5 (m, NH-COO); 8.2 (m, aromatic protons from the triazene sequence in *ortho* position relatively to the nitro group); 7.62 (m, aromatic protons from the triazene sequence in *meta* position relatively to the nitro group); 7.15 and 6.4 (m, aromatic protons from TDI); 4.42 (m, NHCOO-CH₂-CH₂); 3.81 (m, NHCOO-CH₂-CH₂-N-); 2.22 and 2.1 (s, Ph-CH₃).

UV (DMF), λ_{max}: 370 nm.

3. Results and discussions

Starting from the data obtained on a series of polyetherurethane ionomers [26,27], we extended this study on hard polyurethanes with triazene functionalities introduced by means of 1-phenyl-3,3'-di(2-hydroxyethyl) triazene, 1-naphthyl-3,3'-di(2-hydroxyethyl) triazene and 1-(4-



Scheme 2. General synthesis pathway for hard type triazene polyurethanes.

nitro)-phenyl-3,3'-di(2-hydroxyethyl) triazene. The resulting polyurethanes contain only hard segments generated by the reaction between toluene diisocyanate (2,4- and 2,6-TDI) and one of the triazene diols (Scheme 2). The reaction was carried out in DMF solution at a given temperature in order to obtain the polyurethanes in high yields and with the desired properties. The purified polymers were characterized by IR, $^1\text{H-NMR}$, and UV spectroscopy, elemental analysis (Table 1), GPC and TGA techniques.

Infrared analysis provides information about the molecular structure of the materials (Fig. 1). The synthesized polyurethanes reveal in the high wavenumber region a sharp band around 3340 cm^{-1} which can be assigned to the NH stretching vibration while the broad peak around 1720 cm^{-1} is due to the C=O stretching vibration of the urethane groups. Other important absorption peaks observed in the IR spectra are assigned to the amide I stretching vibration ($1655\text{--}1670\text{ cm}^{-1}$), to the aromatic rings (1600 and 1450 cm^{-1}), to the amide II deformation (1540 cm^{-1}), to the triazene units ($1375\text{--}1400\text{ cm}^{-1}$) and to the O–C–O vibration (1230 cm^{-1} and 1065 cm^{-1}). All polymers present a high solubility in common polyurethane solvents such as DMF, DMSO, DMAc and have film-forming properties. Consequently, homogeneous, transparent, but brittle brown films were prepared by solvent casting with subsequent drying at moderate temperatures. The molecular weights of the triazene polyurethanes were determined by GPC and were below 10,000.

Table 1
Elemental analysis data and the triazene amount for the studied polyurethanes

Polymer		Elemental analysis			Triazene content (%) ^a
		C (%)	H (%)	N (%)	
PU-P	Calculated	59.5	5.48	18.27	31.07
	Found	59.50	5.41	18.24	
PU-N	Calculated	63.74	5.31	16.16	39.03
	Found	63.69	5.28	16.11	
PU-NO	Calculated	53.27	4.67	19.62	38.31
	Found	53.23	4.62	19.58	

^a Calculated.

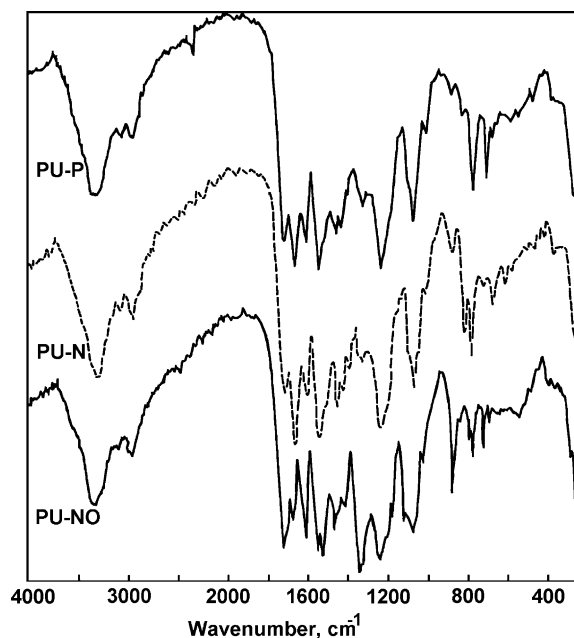


Fig. 1. Infrared spectra of the triazene polyurethanes.

The thermal stability of the polymers was examined by thermogravimetric analysis (TGA). These investigations revealed a two-step decomposition process (Table 2). The polymer degradation started relatively early ($<100\text{ }^\circ\text{C}$) indicating a poor thermostability of this kind of polymers compared to the polyetherurethanes studied previously [26,27]. The initial decomposition temperature for all polymers is below $100\text{ }^\circ\text{C}$ and the weight loss in the first step is correlated to the release of nitrogen gas and aromatic fragments that are the main products of the disintegration of the triazene side chains. This process continues with the complete degradation of the polymeric main chain.

Since these polyurethanes contain a significant proportion of triazene units in the side chain it is important to analyse their photobehavior under UV light illumination. Decrease in the chromophore concentration with irradiation time was monitored firstly in solution. Fig. 2 illustrates the UV absorp-

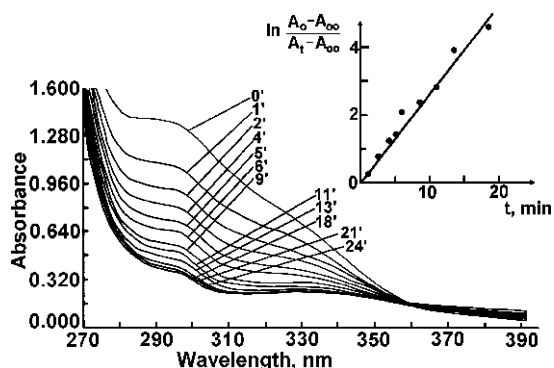


Fig. 2. UV-vis spectrum of the phenyl triazene polyurethane (PU-P) in DMF solution monitoring the vanishing of the UV absorption maximum of the triazene linkage after different irradiation periods and the kinetic evaluation of its photolysis (inset) at 298 K.

Table 2
Thermal behavior of the hard triazene polyurethanes

Sample	Stage I			$T_{10\%}$ (°C)	Stage II		
	$T_1 - T_f$ (°C)	T_{max} (°C)	Weight loss (%)		$T_1 - T_f$ (°C)	T_{max} (°C)	Weight loss (%)
PU-P	80–180	130	22	130	180–320	235	26
PU-N	90–200	155	31	140	200–330	242	22
PU-NO	90–190	145	24	140	210–320	275	22

tion spectral changes for PU-P in DMF solution. It is clearly visible that the absorption maximum, assigned to the triazene group, which is centered at 296 nm decreases gradually with irradiation time. This shows that the triazene unit decomposes irreversibly upon irradiation. Such spectral changes are reflected in the photolysis rate values, for which the rate constant k was determined according to Eq. (1)

$$k = \ln \frac{A_0 - A_\infty}{A_t - A_\infty} \times \frac{1}{t} \quad (1)$$

where A_0 , A_t and A_∞ are the values of the absorbance at the time 0, t and ∞ , respectively. In the case of PU-P the rate constant is $k = 2.1 \times 10^{-3} \text{ s}^{-1}$ and the photodecomposition of the triazene groups is accomplished in 23 min for the given irradiation conditions. The rate constant of the polymers is obtained from plotting the logarithm of the reduced absorption against the time and a first-order kinetic (Fig. 2, inset) was observed for the PU-P solution. The polyurethane with the naphthyl-triazene units (PU-N) presented a similar photobehavior under identical conditions, but with a pronounced slower rate constant ($k = 9.6 \times 10^{-5} \text{ s}^{-1}$) which is almost one hundred times slower than for PU-P. To evaluate a possible application of these polymers in microlithography PU-N was also studied in thin films. The photolytic degradation of the PU-N in film proceeds with a rate constant of $k = 3.3 \times 10^{-4} \text{ s}^{-1}$, and the photolysis is completed in 51 min compared to the 113 min in solution. The photodecomposition rate of PU-N in film and solution is shown in Fig. 3 (inset).

It is noteworthy to mention that the molecular weight decrease of other types of triazene polymers with the triazene unit in the main chain is much slower in film as compared

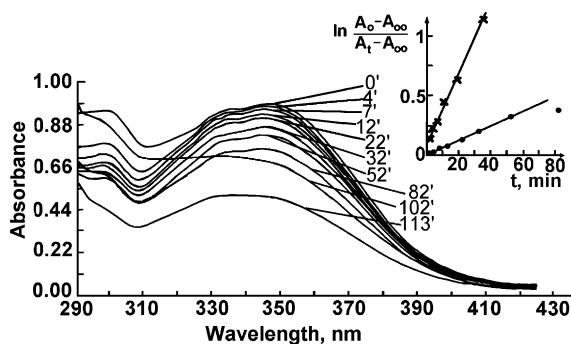


Fig. 3. Changes in the UV spectra of the triazene polymer PU-N in DMF solution with the irradiation time in film and kinetic evaluation of the photolysis (inset) in DMF solution (●) and in film state (×).

to solution [28]. In the case of the side chain triazene polymers of this study a different behavior may be present. This is quite surprising, as a pronounced cross-linking is expected but may not be observed in the UV-vis spectra, as only the triazene group is monitored.

On the other hand, the polymer with the naphthyl substituent anchored to the triazene linkage (PU-N) presented a higher stability in solution and as film compared to the phenyl-substituted triazene polyurethane (PU-P). This is probably due to an extensive conjugation between the triazene unit and the naphthyl ring. The lower photodecomposition rate in solution is possibly due to the “cage effect” of the solvent, which may favour the recombination of the formed radicals and, less likely, an enhancement of their lifetime.

The polymer with the *p*-nitro-phenyl triazene moieties (PU-NO) showed different photoresponse to the above-mentioned polymers so that no change in the absorption spectra even for a prolonged UV irradiation was noticed. This is most probably due to the higher stability of the polymer induced by the *p*-nitro substituent attached to the phenyl ring of the triazene unit. The observation is supported by previous studies [29] that showed an increase of the photochemical stability with electron-withdrawing substituents on the phenyl ring for the structurally closely related 1-aryl-3,3-dialkyl-triazenes. The high stability of the PU-NO to low-intensity UV irradiation could even be beneficial for laser structuring applications where no modification of the polymer under ambient conditions is desired. Therefore, PU-NO was selected for a detailed study on the laser ablation, i.e. laser structuring behavior. Other reason for selecting this polymer is the soft surface of the PU-P and PU-N polymers that render the structuring analysis more difficult. The ablation rate of the films based on PU-NO was obtained by determining the ablation depths as a function of pulse number (Fig. 4).

For all fluences the total ablated depth at a given fluence increases linearly with the number of pulses, indicating that no incubation behavior is present as expected for highly absorbing polymers ($\alpha_{lin} > 8000 \text{ cm}^{-1}$). The slope of these plots of ablation depths versus pulse number is used to obtain the single pulse ablation rate at a given fluence. These values are then plotted against the logarithm of the fluence (Fig. 5). In the low fluence range a linear relation is observed which can be used [30] to analyse the ablation parameter according to Eq. (2)

$$d(F) = \frac{1}{\alpha_{eff}} \ln \left(\frac{F}{F_{th}} \right) \quad (2)$$

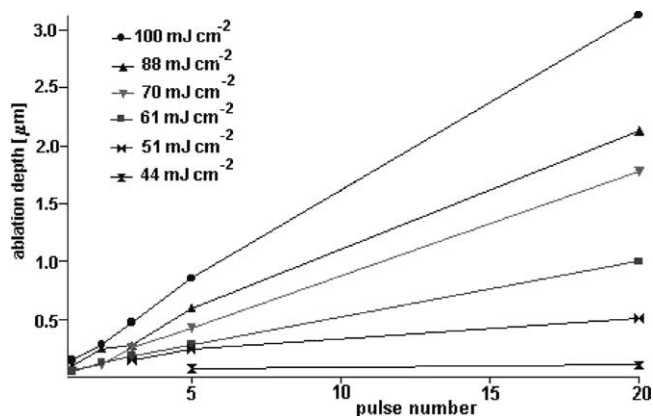


Fig. 4. Plots of the etch depth vs. pulse number for PU-NO at different fluences.

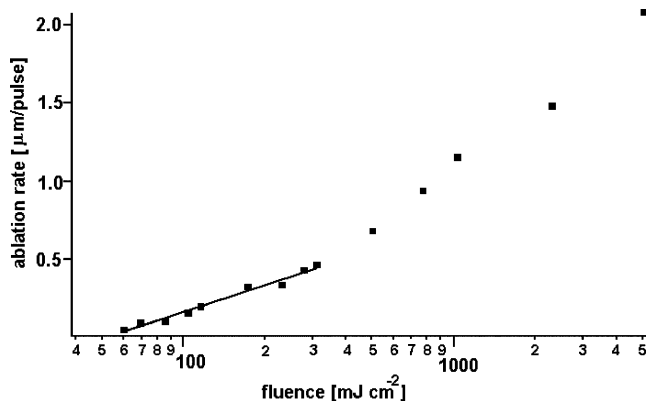


Fig. 5. Ablation rate as a function of the laser fluence for 308 nm irradiation of the *p*-nitro triazene polyurethane.

where $d(F)$ is the ablated depth per pulse, F is the laser fluence and F_{th} represents the threshold fluence.

In the case of PU-NO a threshold fluence of $52 \pm 3 \text{ mJ cm}^{-2}$ and an effective absorption coefficient for ablation, α_{eff} of $4.0 (\pm 0.2) \times 10^4 \text{ cm}^{-1}$, is obtained.

Microscopical and profilometric analyses of the polymer film after irradiation at fluences above and below the ab-

lation threshold reveal interesting features (Fig. 6). At fluences below the ablation threshold (e.g. at $F = 33 \text{ mJ cm}^{-2}$), a surface swelling is detected, which may be attributed to the decomposition of the triazene group. This decomposition yields gaseous species that results in a volume increase and therefore a swelling (shown in the profilometer trace in Fig. 6a for one pulse). At fluences around the threshold of ablation ($F = 51 \text{ mJ cm}^{-2}$), the triazene polyurethane is already etched without pronounced redeposition of the ablation products (shown in the optical micrograph in Fig. 6b for 20 pulses). If much higher fluences and pulse numbers are applied, the polymer surface and the surrounding of the crater appears strongly modified. At a fluence of 280 mJ cm^{-2} and five pulses, a clean ablation without a pronounced surface contamination (Fig. 7a) is observed, while for a higher number of pulses, e.g. 20, the surface becomes black and carbonized (Fig. 7b). At even higher fluences (5.1 J cm^{-2}), the number of pulses necessary for attaining the carbonization is only five, indicating that the amount of carbonization is directly proportional to the laser fluence. A comparable behaviour has also been observed for the 308 nm ablation of Kapton [31], but which is absent for other triazene polymers [10].

A detailed analysis and comparison of the ablation parameter α_{eff} , F_{th} , $d(100 \text{ mJ cm}^{-2})$ and of various material parameter (λ_{max} , α_{lin} at 308 nm and at λ_{max}) for PU-NO with other triazene polymers from literature [32] is shown in Table 3. The comparison shows clearly pronounced differences, i.e. that PU-NO present in all ablation relevant parameter inferior values. The threshold is much higher and the ablation rate is lower, with additional problems originating from the surface modification. It is also noteworthy that similar α_{eff} for all triazene polymers, including PU-NO, are obtained, even with opposite trends compared to the linear absorption coefficient. The other polymers showed a decrease while PU-NO reveals an increase of the α_{eff} compared to α_{lin} . This enhancement corresponds to a lower laser penetration depth during ablation compared to the values expected from α_{lin} . Analogous values of α_{eff} may suggest that related species or at least species with a similar absorption coefficient in the gaseous ablation product or remaining film are formed. Possible candidates

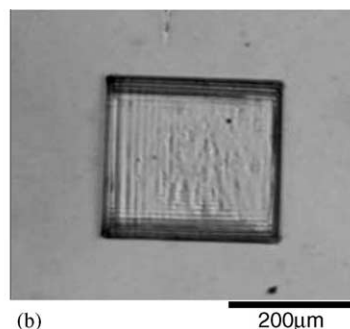
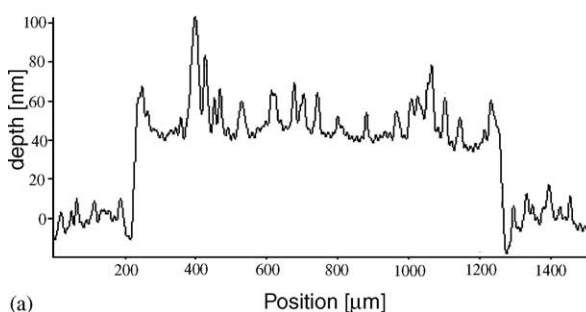


Fig. 6. (a) Profilometer trace of the triazene polymer (PU-NO) after one pulse with 33 mJ cm^{-2} ; (b) optical micrograph of the film surface after 20 pulses with 51 mJ cm^{-2} .

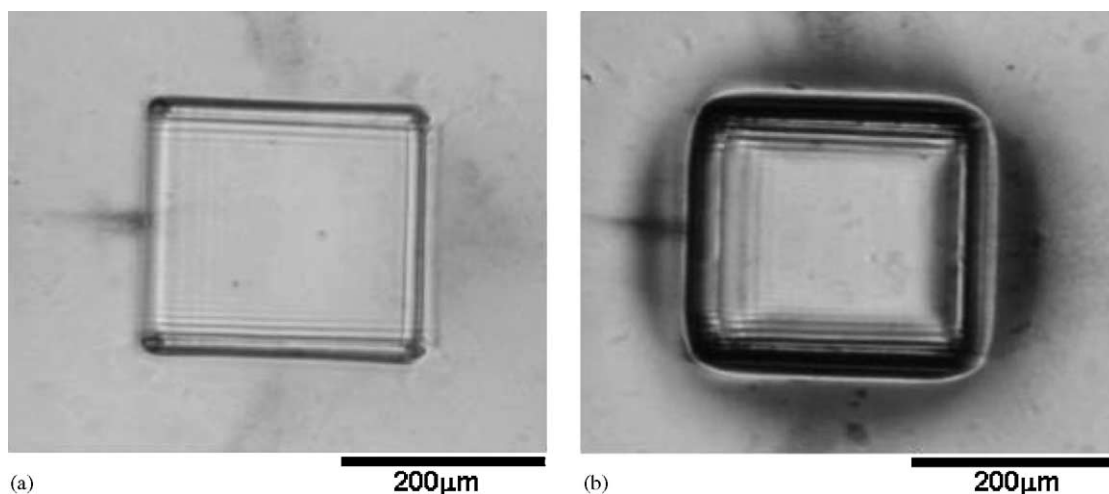


Fig. 7. Optical micrographs of the triazene polyurethane (PU-NO) irradiated at 280 mJ cm^{-2} : (a) after 5 pulses; (b) after 20 pulses.

Table 3

Ablation and material parameter of PU-NO and other triazene containing polymers [32]

Parameter	PU-NO	Other triazene containing polymers ^a
Linear absorption coefficient, α_{lin} , at 308 nm/(cm^{-1})	10400	69000–100000
Absorption maximum, λ_{max} /(nm)	371	310–360
Linear absorption coefficient, α_{lin} , at λ_{max} /(nm)	25000	70000–160000
Effective absorption coefficient, α_{eff} /(cm^{-1})	40000	50000–56000
Threshold fluence, F_{th} /(mJ cm^{-1})	52	27–31
Ablation rate for 100 mJ cm^{-2} , $d(100 \text{ mJ cm}^{-2})$ /(nm)	160	230–260

^a All with the triazene group in the polymer main chain.

for this are aromatic radical species that are most probably formed during the ablation of all triazene polymers. The marked difference between PU-NO and the other triazene-polymers with a very similar ablation behavior is not clear right now, but it may be due to the low absorption coefficient at the laser irradiation wavelength of 308 nm or the fact that the triazene group is placed in the side chain. This may cause in a release of the triazene fragment and the remaining of the main polymeric chain at least partially intact. The radical decomposition mechanism may even induce a cross-linking of the ablated polymer that is not any more photoactive, resulting in higher threshold fluence, lower ablation rates and surface modification. All of these trends are observed for PU-NO, suggesting that the location of the triazene group has an important influence on the ablation properties.

4. Conclusions

Three new hard type polyurethanes with triazene moieties incorporated in the side chain of the polymeric backbone were synthesized and characterized. These polymers showed a significant photosensitivity and a poor thermal stability due to the high triazene content. The photosensitivity of the polyurethanes is studied under UV irradiation and a

higher sensitivity in films than in solution is observed. This is probably due to the “cage effect” in solution, which results in the recombination of the radicals created inside the solvent cage. The polymer with the *p*-nitro triazene moieties is much more stable under UV irradiation compared to the polyurethanes with phenyl and naphthyl units, but can still be structured by laser ablation. Laser ablation at fluences below the threshold of ablation causes a permanent swelling of the surface while with intermediate fluence high resolution structuring can be achieved. Very high fluences result in a pronounced carbonization of the polymer surface. A comparison of the ablation parameter of PU-NO with other triazene polymers suggests that the location of the triazene unit, i.e. side chain or main chain of the polymer, may have a pronounced effect on the ablation parameters. An alternative reason may be the relatively low linear absorption coefficient of PU-NO.

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