



BISTRIAZENE POLYURETHANES: SYNTHESIS, CHARACTERIZATION AND PHOTOBHAVIOR♦

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Abstract: Two new bistriazene diols, 1,1'[4,4'-diphenyl]-3,3'-di(β -hydroxyethyl methyl)-bistriazene (**TDF**) and 1,1'[4,4'-diphenylsulphone]-3,3'-di(β -hydroxyethyl methyl)-bistriazene (**TSO**) were synthesized via an electrophilic N-N coupling between a quaternary ammonium salt and N-methyl-monoethanol amine. These monomers were used as co-partners in polyaddition with 2,4-tolylene diisocyanate (2,4- and 2,6-TDI isomer mixture, 80:20 v/v) or 4,4' methylene diisocyanate, respectively, in order to obtain new hard type polyurethanes. The photosensitivity of monomers and polymers was evaluated by UV irradiation, in methanol or DMF solution and as thin films following the disappearance of the π - π^* absorption band from the UV spectra corresponding to the triazene chromophore. As a novel trend, the bistriazene polyurethanes were structured by laser irradiation ($\lambda = 308$ nm) in order to evaluate their ability to deliver efficient materials in microlithography.

Keywords: *bistriazene diol, polyurethane, photosensitivity, UV irradiation, laser ablation*

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INTRODUCTION

Recent progresses in the design of polymers with photosensitive structures in the main backbone or as pendant groups provide a number of unique tailor-made properties for an ever-increasing number of applications in microlithography or as photoresist [1-3]. Structure dimensions, resolution, and sensitivity to the irradiation process are the dominating aspects that qualify the performance of photoresist systems. Much attention was paid to the polymers with triazene chromophores ($>N=N=N-$), whose architecture may be conveniently adapted to the requirements of photosensitive materials such as thermostability, high photosensitivity, optical and good coating properties. So far, the literature provide information regarding various classes of triazene-sensitized polymers (polyesters, polyethers, poly(methyl methacrylates), polysulfides, or polytriazenes) [4-7] that may be structured with high resolution upon UV/laser irradiation. For our group, a novel tendency was the synthesis of triazene polyurethanes in order to combine the sensitivity of the triazene structure with the unlimited architectural variability offered by polyurethane chemistry [8, 9]. This outcome in a wide field of possibilities for tailoring special properties that yields new materials for microlithography.

Taking into account the latest developments in the ablation area, the generation of new highly sensitive polyurethanes, with an elevated content of triazene units in the main or side chains seems to be a very promising technique to produce systems for microlithographic applications [10]. Consequently, the present paper describes the structure and properties of new hard polyurethanes with triazene linkages as well as their photochemical behaviour under UV/laser irradiation.

EXPERIMENTAL

The bistriazene diols 1,1'[4,4'-diphenyl]-3,3'-di(β -hydroxyethyl methyl)-bistriazene (**TDF**) and 1,1'[4,4'-diphenylsulphone]-3,3'-di(β -hydroxyethyl methyl)-bistriazene (**TSO**) were synthesized in a two steps procedure, as shown in Scheme 1. As an example, is described the synthetic pathway used to obtain the TDF monomer. A stirred solution of 4,4'-diamino-diphenyl (10 g, 0.054 mol) in HCl 10 wt. % (84 mL) was cooled to 0 °C and diazotized with an aqueous solution of sodium nitrite (7.5 g, 0.1 mol). The reaction mixture was drop wise added to a solution of N-methyl-aminoethanol (8.15 g, 0.1 mol) and sodium carbonate (9.1 g, 0.085 mol) in 250 mL water at 0 °C over 1 h. Then, 10 g sodium chloride was added and the resulting mixture was extracted three times with Et₂O. The organic layers were dried onto Na₂SO₄ and concentrated under reduced pressure. After removal of the solvent, the monomer was separated as a brown crystalline solid (8.85 g; yield 81 %).

The hard type polyurethanes (**PUH-TDF** and **PUH-TSO**) were obtained by polyaddition carried out 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) (PUH-TDF) or 4,4' methylene bis(phenylisocyanate) (PUH-TSO). The reactions were performed under purified nitrogen at 65 °C for 15 h. The triazene

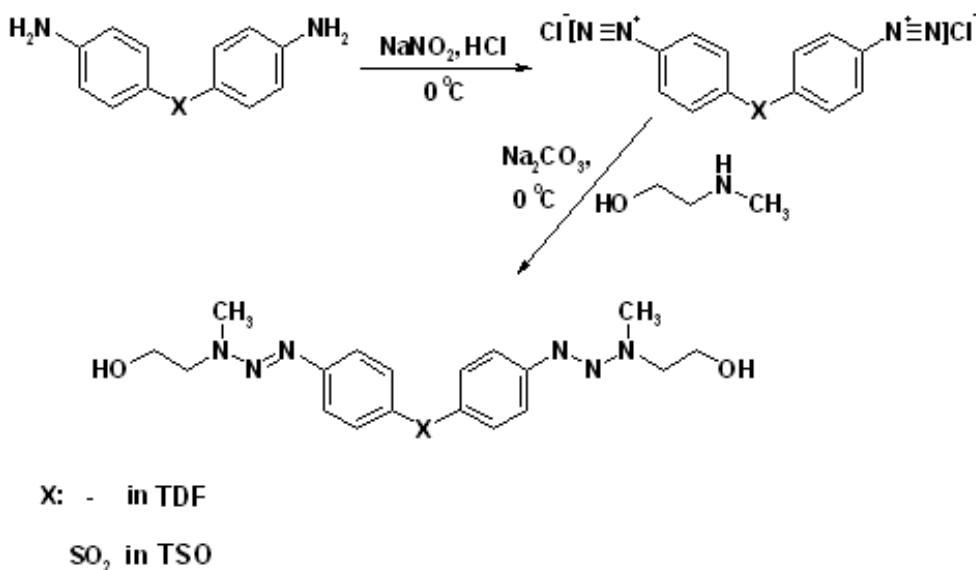
polyurethanes were precipitated in methanol and dried for 48 h at 60 °C under reduced pressure.

CHARACTERIZATION

The polymers structures were verified by $^1\text{H-NMR}$, IR and UV spectroscopy using a Bruker 400 MHz spectrometer, a Specord M80 and Specord M42 spectrophotometer, respectively. The thermal stability of the polyurethanes was analysed through thermogravimetry using a derivatograph (MOM Budapest). TG and TGA curves were recorded between 20 and 600 °C with a heating rate of 12 °C·min $^{-1}$ in air. UV irradiations were performed in DMF solutions 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 – 1.0. For the irradiation at 308 nm a Complex 205 XeCl excimer laser from Lambda Physik ($\tau = 30$ ns) was used. The samples for the laser ablation experiments were prepared by solvent casting from a 15 wt. % DMF solution on glass substrates.

RESULTS AND DISCUSSIONS

The synthesis of bistriazene monomers was performed *via* an *N-N* electrophilic coupling between an aryldiazonium salt and a secondary amine (N-methyl-monoethanol amine), similar to those described in the literature [4]. The bistriazene diols were obtained in good yields, their structures being verified using $^1\text{H-NMR}$ and IR spectroscopy, combined with elemental analysis (Table 1). The synthetic procedure used to obtain triazene derivatives is outlined in Scheme 1.



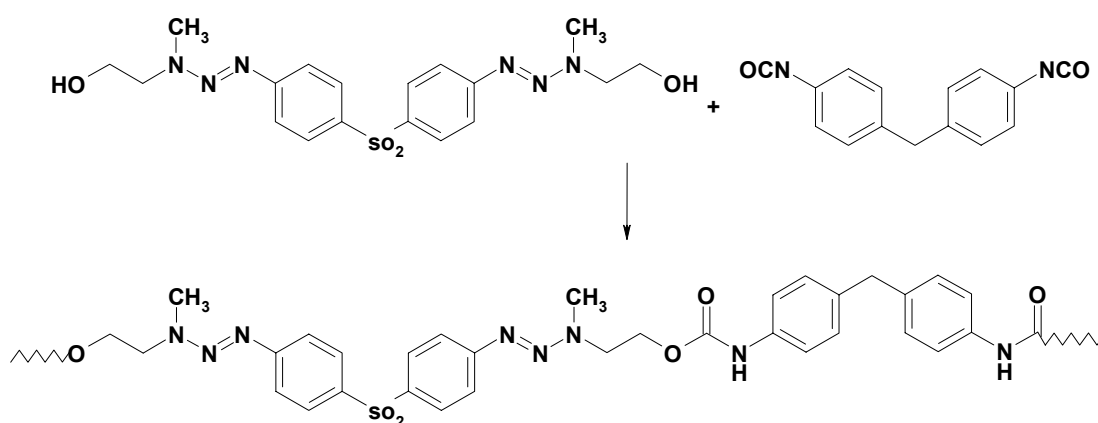
Scheme 1. Synthesis of bistriazene monomers (TDF, TSO)

Table 1. $^1\text{H-NMR}$ and elemental analysis data for triazene derivatives

Sample		TDF	TSO	PUH-TDF	PUH-TSO
Calculated (%)	C	60.67	51.42	61.13	59.10
	H	6.74	5.71	5.66	5.07
	N	23.59	20	21.13	16.71
Experimental (%)	C	60.48	51.50	60.97	59.06
	H	6.71	5.83	5.70	5.09
	N	23.65	19.85	21.16	16.69
$-\text{CH}_2-\text{CH}_2-\text{N}$ (ppm)		3.89	3.95	4.45 and 4.1	4.37 and 4.1
$\text{N}-\text{CH}_3$ (ppm)		3.35	3.34	3.67	3.23
Aromatic protons (ppm)		7.57 and 7.48	7.95 and 7.39	7.4 – 7.9	7.05 – 7.85
OH (ppm)		2,84	2,9		
$\text{NH}-\text{COO}$ (ppm)				9.6	9.5
$\text{Ph}-\text{CH}_3$ (ppm)				2.09	
$\text{Ph}-\text{CH}_2-\text{Ph}$ (ppm)					3.67

In the IR spectra of bistriazene monomers are evidenced strong absorption bands at $3350\text{--}3390\text{ cm}^{-1}$ assigned to the OH bond vibration, at about 2900 cm^{-1} the bands due to the vibrations of the CH_2 groups, while between 1550 and 1600 cm^{-1} is presented the vibration band attributed to the aromatic rings. The characteristic IR absorption band of the triazene group appeared around 1360 cm^{-1} , whereas the C-O vibration band is detected at 1240 , 1200 and 1100 cm^{-1} .

The synthesized polyurethanes include only hard segments generated by the reaction between toluene diisocyanate or 4,4'-methylene bis-diisocyanate and one of the above bistriazene diols (Scheme 2). The purified polymers were characterized by IR, $^1\text{H-NMR}$, and UV spectroscopy and also by TGA techniques.

**Scheme 2.** Synthesis of bistriazene polyurethane PUH-TSO

As in the case of monomers, the structure of bistriazene polyurethanes was confirmed by elemental and spectral methods. Infrared analyses offer important information regarding the molecular structure of the polymers (Figure 1).

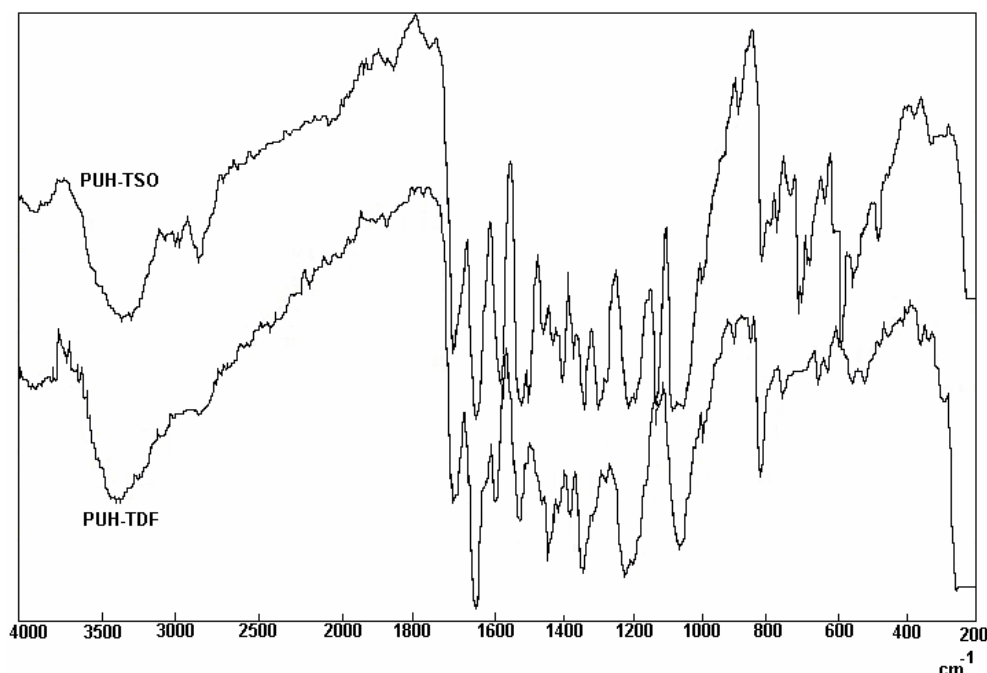


Figure 1. Infrared spectra for polyurethanes PUH-TDF and PUH-TSO

The synthesized polyurethanes present in the high wavenumber region a sharp band around 3340 cm^{-1} which can be assigned to the NH stretching vibration, while the peaks noticed around $1655\text{--}1670\text{ cm}^{-1}$ are due to the amide I stretching vibration. Other important absorption peaks observed in the IR spectra are assigned to the aromatic rings (1600 and 820 cm^{-1}), to the amide II deformation (1540 cm^{-1}), to the triazene units (1360 cm^{-1}) and to the C-O-C vibration (1220 cm^{-1} and 1100 cm^{-1}). An essential feature of these polyurethanes is their solubility in organic solvents (DMF, DMAc, DMSO) and the ability to form homogeneous, transparent, but brittle brown films by solvent casting with subsequent drying at moderate temperatures.

The influence of chromophore structure and position on thermal stability in polyurethanes was followed by thermogravimetric analysis. The temperature of different weight losses, initial and final decomposition temperature was determined from the original TGA curves, the investigations revealing a two-step decomposition process (Table 2). As can be observed, the thermal stability of bistriazene polyurethanes is relatively reduced, comparatively with elastomeric polyurethanes, as an outcome of the increased amount of triazene units in the polymeric chain. In agreement with the literature data, the concentration of photolabile chromophore represents the restrictive element for a better thermal stability of the bistriazene polyurethanes against further variety of polyurethanes. Technically, the weight loss observed in the first stage of the process is attributed to the triazene unit decomposition with releasing of small volatile molecules, such as nitrogen, succeeded by thermal disintegration of polymeric backbone.

Table 2. Thermal behaviour of bistriazene polyurethanes

Sample	Stage I			T_{10} (°C)	Stage II			T_{10} (°C)	Stage III		
	T_i-T_f (°C)	T_{max} (°C)	Weight loss (%)		T_i-T_f (°C)	T_{max} (°C)	Weight loss (%)		T_i-T_f (°C)	T_{max} (°C)	Weight loss (%)
PUH-TDF	90-175	140	16	150	175-240	205	8	150	240-360	325	15
PUH-TSO	110-190	150	12	175	190-255	220	11	175	280-430	375	18

To investigate the photolability of the triazene structure, the progress of the photodecomposition reaction of the monomers and polymers by an exhaustive irradiation with a high-pressure mercury lamp was monitored via UV/vis spectroscopy. As reported above [7], depending on the substituent nature attached to the aromatic ring in the vicinity of the triazene structure, bistriazene monomers TDF and TSO present in their UV/vis spectra absorption peaks centered at different wavelengths (table 3). The changes appeared in the UV absorption spectrum of TSO monomer in methanol solution, exposed to direct UV light is displayed in figure 2. Following the UV/vis absorption of the triazene chromophore as a function of irradiation time, it was noticed that after distinct irradiation intervals a gradual decrease of the absorptions band corresponding to the triazene group from 342 nm is a clear indicator for the irreversible photodecomposition of this chromophore. Monitoring of the photobehaviour of the triazene chromophore it is possible to evaluate the rate and the degree of photocleavage induced in the triazene units.

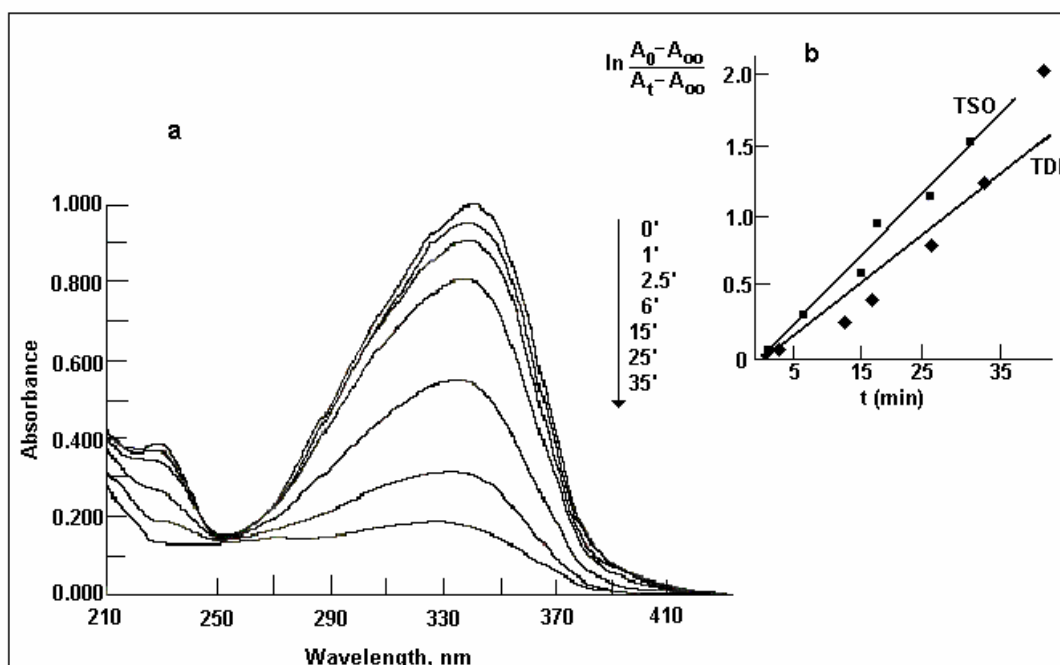


Figure 2. Changes in the UV-vis absorption spectra of TSO bistriazene diol in methanol solution upon UV light exposure (a) and kinetic representation of the photolysis processes for studied monomers (b)

The kinetic evaluation (Table 3) may be expressed by a first-order rate equation:

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

where, A_0 , A_t and A_∞ are the values of the absorbance at the time 0, t and ∞ , respectively, whereas k is rate constant. In order to compare the rate constant values of the different compounds, the logarithm of the reduced absorption is plotted against the time, the triazene monomers following a first order kinetic. A suggestive illustration of the calculated rate value for bistriazene monomers is represented in Figure 2 (b). As can be seen, the major importance on the monomers photobehaviour is attributed to the substituents attached to the triazene units and to the influence provoked by extensive conjugation. The results depicted in Figure 2 (b) indicated that the TSO monomer presents a higher photosensitivity relative to TDF diol, as it has the maximum value of the plot gradient.

Table 3. Physical and photolysis data of the bistriazene monomers and polymers

Sample	λ_{\max} (nm)		$k \cdot 10^{-4} \text{ (s}^{-1}\text{)}$		Time (min)	
	Solution	Film	Solution	Film	Solution	Film
TDF	360		5.3		50	
TSO	342		6.8		35	
PUH-TDF	355	352	9.26	11.3	42	9
PUH-TSO	344	342	2.5	5.7	51	12

Investigation of the triazene polyurethanes photosensitivity was performed by UV/vis spectroscopic assessment of structural changes caused by irradiation in thin films and solutions. It was found a similar behaviour as for monomers (Figure 3, b), the only difference consisting in the smaller values obtained for the rate constants. Such result achieved in the case of polymeric chains could be ascribed to the conformational restrictions determined by the coupling of structural factors and the favoured recombination of the formed radicals in the solvent cage. In Figure 3 (a) are presented the spectral changes observed for bistriazene polyurethane PUH-TSO in DMF solution with the irradiation time, whereas part b illustrates the differences between the kinetic plots of both hard polyurethanes, also in solution.

The examination of the ablation properties for the hard bistriazene polyurethanes was performed using a pulsed XeCl excimer laser at 308 nm. The polymeric films were spin-coated on quartz substrates and the tightly polyurethane areas were irradiated through a mask, establishing the effects of laser beam on the triazene photolabile units. In addition, it has to be mentioned that some difficulties related to the film deposition may be due to inhomogeneities within the sample of polymers and can be minimized by an improved sample preparation procedure.

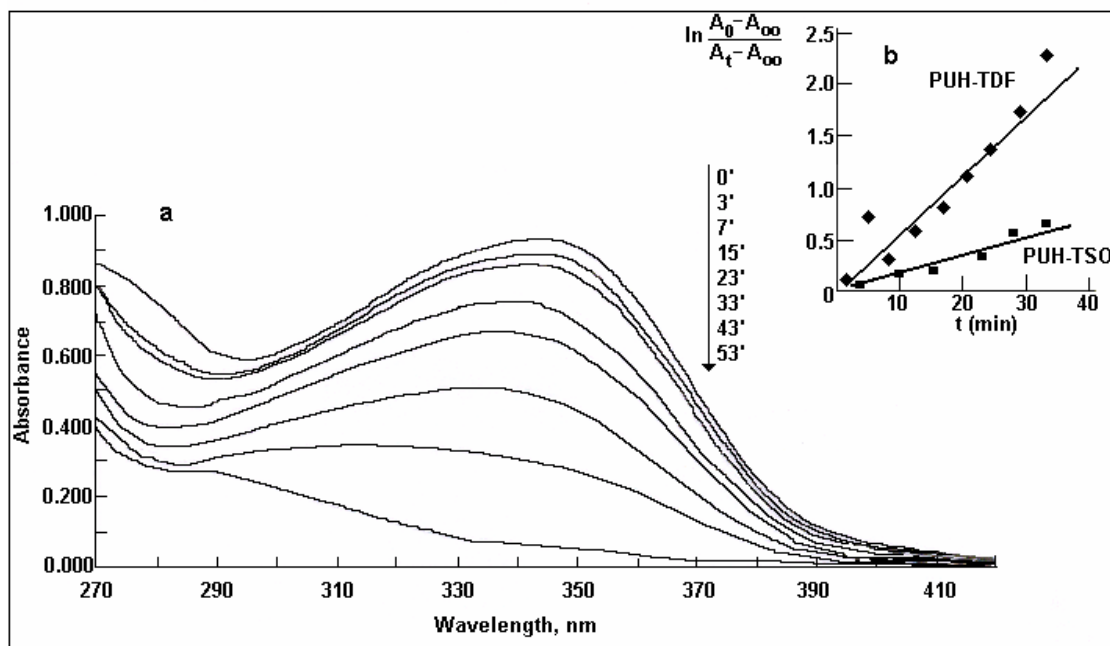


Figure 3. Changes in UV-vis absorption spectra of PUH-TSO polymer in DMF solution with the irradiation time (a) and kinetic representation of the photolysis processes for studied the polyurethanes (b)

The description of the ablation phenomenon is accomplished by a linear relation, which can connect the ablation parameters:

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

where, $d(F)$ is the ablated depth per pulse, F is the laser fluence, F_{th} represent the threshold fluence and α_{eff} is the effective ablation coefficient.

Structuring of polymeric samples *via* excimer laser is achieved by photoinduced and thermal decomposition leading to an ejection of fragments. A certain amount is removed completely and is observed the absence of any redeposited material, the so-called “debris” (Figure 4).

The absence of redeposition is a consequence of the regular cleavage at the triazene units in the polymer main chain. Photodecomposition leads to a release of gaseous fragments of quite defined low molar mass. These gaseous products, in particular nitrogen, are acting as a driving gas at least in the initial stages of the ablation, thereby removing other polymer fragments from the surface.

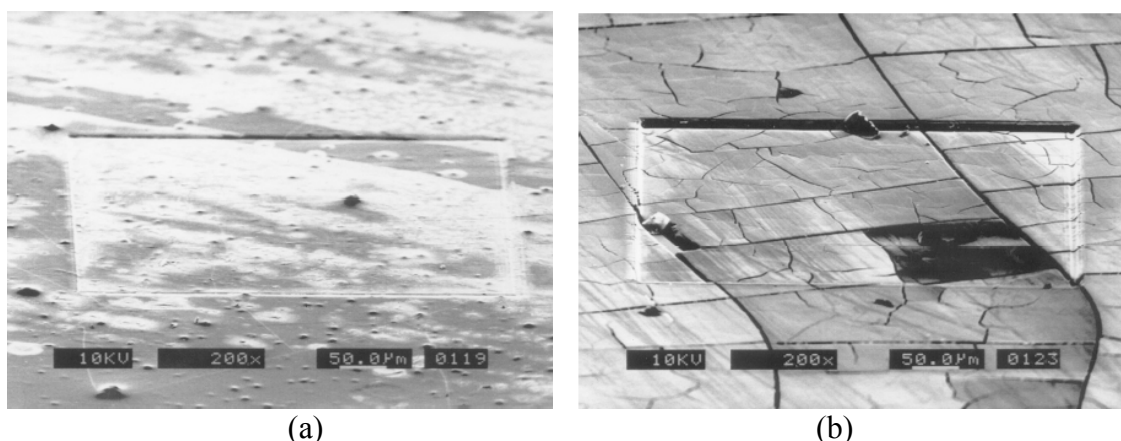


Figure 4. SEM micrographs of the ablation holes (308 nm) in PUH-TDF after 2 pulses at 1700 mJ cm^{-2} (a) and PUH-TSO after 4 pulses at 4400 mJ cm^{-2} (b) evidencing the resolution and the well defined patterning of the polymeric surface

CONCLUSIONS

New bistriazene diols with photolabile units included in the structure were synthesized and characterized. These monomers were further employed in the preparation of hard type polyurethanes in order to design highly photosensitive polymers. The photobehaviour of the monomers and polymers exposed to UV irradiation, generated by a conventional radiation from a high-pressure mercury lamp, evidenced certain differences between the triazene structures determined by the extended conjugation over the bistriazene systems. It has been found that the substituent attached to the aromatic ring connected with the triazene linkage has a remarkable importance in the further photosensitivity of the triazene monomers and polymers.

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