

F₂ excimer laser (157 nm) ablation of polymers: relation of neutral and ionic fragment detection and absorption

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Abstract. The ablation products of various polymers (triazene polymers, polyimides and glycidyl azide polymer) with 157 nm F₂ laser irradiation were studied with time-of-flight mass spectroscopy, ion probe and white-light interferometry. In contrast to the ablation with longer UV wavelengths, 157 nm irradiation results in non-preferential bond-breaking and a much more pronounced fragmentation into fragments with masses <50 amu. This result suggests a photochemical ablation process that occurs at any bond in the molecule. In addition, ions have been detected at very low fluence similar to the threshold of neutral detection, which is below 30 mJcm⁻² for the triazene polymers and Kapton. The observation of ions from the onset of ablation suggests a 2-photon ablation mechanism and possibly involves an excited neutral as an intermediate step. The low thresholds were verified by ion probe measurements of the ablation plume and white-light interferometry of the ablated target surface.

1. Introduction

Laser ablation of polymers has been extensively studied with various methods in the last decades, but the ablation mechanism is still controversial. In order to better understand the mechanism, it is important to know the product distribution and the kinetic energy of the products. One of the most commonly used methods for identifying the ablation products is time-of-flight mass spectroscopy (TOF-MS), and particles ranging from single atoms to large polymer fragments have been found. The kinetic energies of many fragments follow a Maxwell-Boltzmann distribution, indicating a photothermal ablation process. Particles with much higher kinetic energies have also been detected, suggesting a photochemical decomposition process, especially for UV wavelengths.

The ablation behavior of polyimides (Kapton HN, PMDA) and triazene polymers (TP6, TP8) (Figure 1) has previously been studied at various UV wavelengths (193 nm, 248 nm, 266 nm, 308 nm) and published by Lippert [1-7] and Hauer [8]. The shorter wavelengths (248 nm and 193 nm) are absorbed in the aromatic system, but the energy is transferred to the bonds with the lowest binding energies (N-N: 1.7 eV, C-N: 3.2 eV, C-O: 3.7 eV), resulting in specific large fragments. As an example, triazene polymers preferentially decompose into large neutral fragments, such as 76/77 amu

(phenyl group), 142 amu (aliphatic diamine group) and 168 amu (biphenylether) as well as the smaller N_2 fragment.

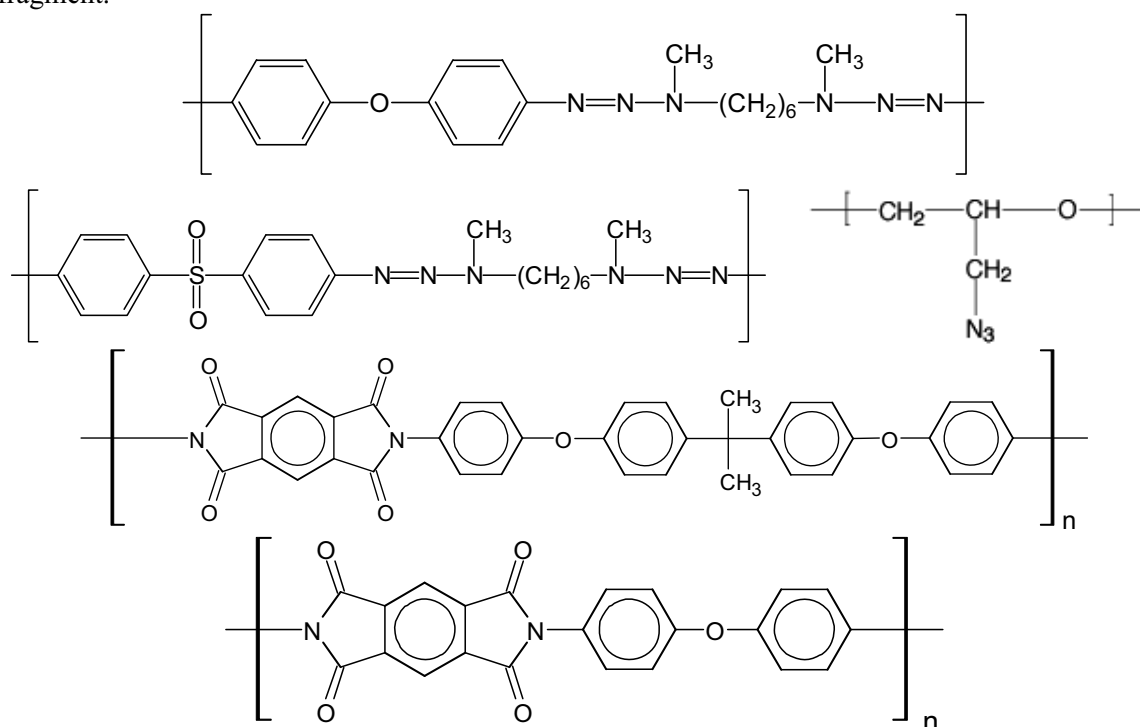


Figure 1: Structural formulas of TP6, TP8, GAP, PMDA and Kapton HN.

VUV wavelengths such as 157 nm (F_2 laser) are increasingly important for practical applications such as micromachining and nano-structuring, as they provide excellent spatial resolution and low ablation thresholds for organic and inorganic materials [9,10]. Due to the high photon energy of 7.9 eV, the ablation mechanism is likely to be more photochemical than photothermal, as is the case with UV wavelengths, and the formation of ions and excited neutrals is much more probable.

In this paper we describe experimental studies of the ablation of various polymers (triazene polymers, polyimides and glycidyl azide polymer) with 157 nm F_2 laser irradiation. At this wavelength, the polymers reveal quite different behavior than for irradiation with the UV wavelengths 248 nm (KrF) and 308 nm (XeCl). Due to the high photon energy of 7.9 eV, the formation of ions and excited species is much more probable.

2. Experimental

TOF-MS measurements were carried out in a UHV setup (Figure 2), which was evacuated to $\sim 5 \cdot 10^{-9}$ Torr ($7 \cdot 10^{-9}$ mbar) by a cryo pump. The samples were mounted on a manipulator in a distance of 14 cm from the ionizer grid of the TOF-MS, the total distance to the detector was 30.5 cm. As the F_2 laser, a Lambda Physik LPF200 with a pulse width of 20 ns was operated at 1 Hz and focused by a lens ($f=35$ cm) onto a spot behind the sample surface. The fluence was adjusted by reducing the incident pulse energy by varying the number of sapphire disks in the N_2 -purged beam delivery tube. The non-uniform beam intensity profile results in a fluence-dependent beam spot size on the sample surface, as the ablation threshold is not reached for the outer regions if the fluence is reduced.

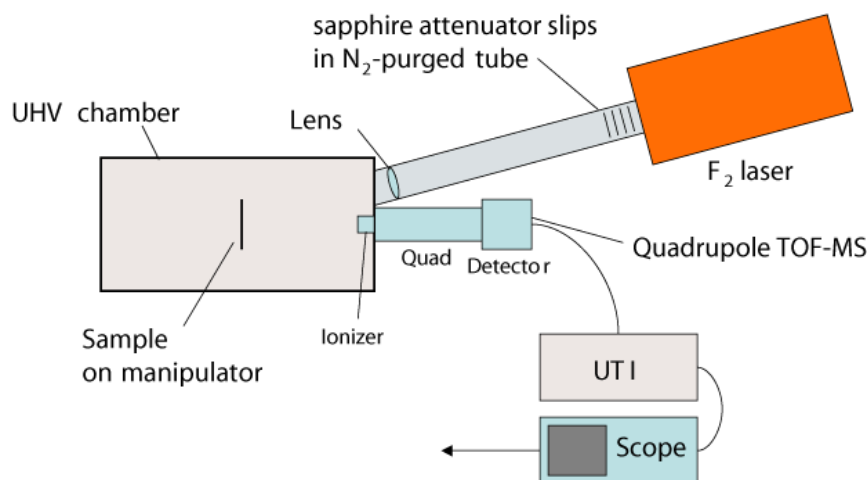


Figure 2: Test setup for TOF-MS experiments

For the detection of neutral fragments, the ionizer and an acceleration voltage of 15 V were used. In the case of ion detection, no ionizer was necessary. The UTI 100C quadrupole mass spectrometer was adjusted to the appropriate mass/charge ratio and the voltage signal corresponding to the actual particle flow was amplified and then recorded with a LeCroy 500 MHz oscilloscope. For each measurement, 100 pulses were recorded and averaged.

Ion probe measurements were performed with a 3 mm Pt-Rh collector with grid, biased at -64V to collect positive ions and located along the surface normal 13-14 mm from the target. A Wyko white-light interferometer was used to characterize the ablation spots with a size of about $350 \times 170 \mu\text{m}^2$.

The absorption of the polymers was measured in a UV-Vis-NIR Spectrophotometer (Varian Cary 500) and a VUV absorption spectrophotometer (Acton Research Co., Model VUVMS-502). Due to the high absorptivity, thin polymer samples of 50-100 nm thickness have been prepared on sapphire substrates by spin coating.

3. Results and Discussion

3.1 Mass Spectrometry

3.1.1. Neutral Fragment Distribution. The ablation of TP6, TP8, GAP and polyimide yields only small fragments, most of them consisting of not more than five atoms. Most fragments are hydrocarbons and nitrogen compounds, predominantly found around 15 and 28 amu. At masses >50 amu, virtually no fragments were detected.

In the case of the triazene polymers the main fragments are 14 amu (N, CH_2), 15 amu (NH, CH_3), 26 amu (CN, C_2H_2), 27 amu (CHN) and 28 amu (N_2) (Figure 3). This is in contrast to earlier studies at longer UV wavelengths [1] and can be explained with the high photon energy that is sufficient to break up the aromatic system. The decomposition into smallest fragments indicates that bond breakage occurs at any position in the molecule.

The standard photolysis decomposition mechanism of GAP is known to be the formation of a nitrene group ($\text{R}=\text{N}\cdot$) and nitrogen, where in a second step various products with masses from 16 to 42 amu (CH_4 , NH_3 , HCN, CO, C_2H_4 , CH_2O , HCCO, CH_2CO) are formed by intra- and intermolecular reactions of the nitrene [11]. When irradiated with 157 nm, the main products are 15 amu (HN, CH_3), 16 amu (O), 17 amu (NH_3), 28 amu (N_2 , CO) and 30 amu (CH_2O , N_2H_2) (Figure 4, left). Fragments that might be formed by secondary reactions, such as CH_4 , NH_2 , OH, C_2H_4 and NO, are not considered to be significant.

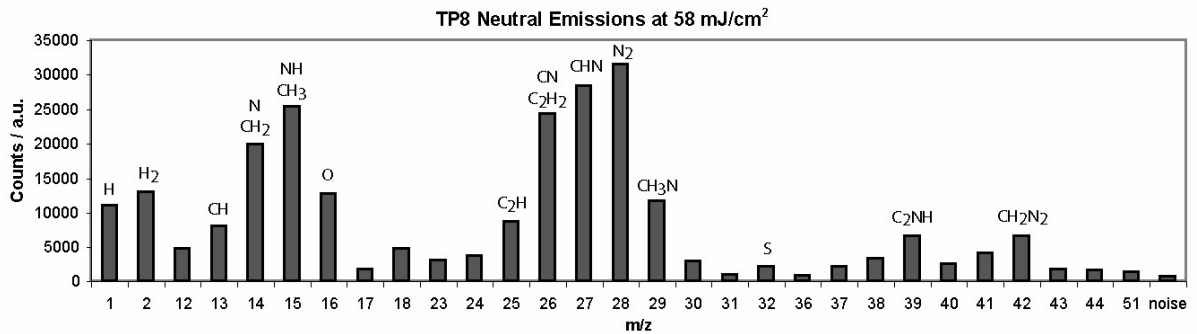


Figure 3: Neutral fragments from TP8 ablation

The predominant fragment of Kapton is 28 amu (CO), followed by 26 amu (CN, C₂H₂) and 27 amu (C₂H₃) (Figure 4, right). PMDA ablation yields similar fragments, but with an even larger fraction of CO.

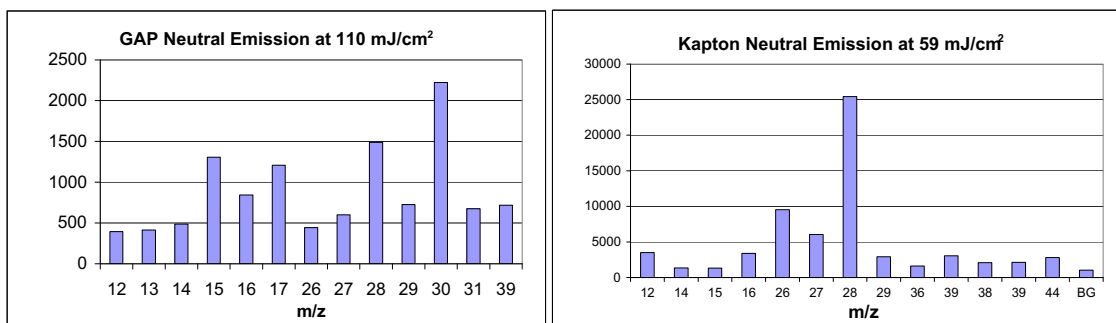


Figure 4: Neutral ablation fragments of GAP (left) and Kapton HN (right)

3.1.2. *Threshold for Neutrals.* The threshold for neutrals was defined by fitting the integrated and averaged 28 amu signal versus the fluence (Figure 5), which corresponds to N₂ in the case of TP6 and TP8, and CO in the case of Kapton. GAP may decompose into both N₂ and CO fragments, but the majority is expected to result from N₂.

For all polymers the ablation threshold is very low (Figure 5), between 20 and 30 mJcm⁻² for the triazine polymers and Kapton. Only the PMDA with about 42 mJcm⁻² and GAP with 80-90 mJcm⁻² yielded higher thresholds.

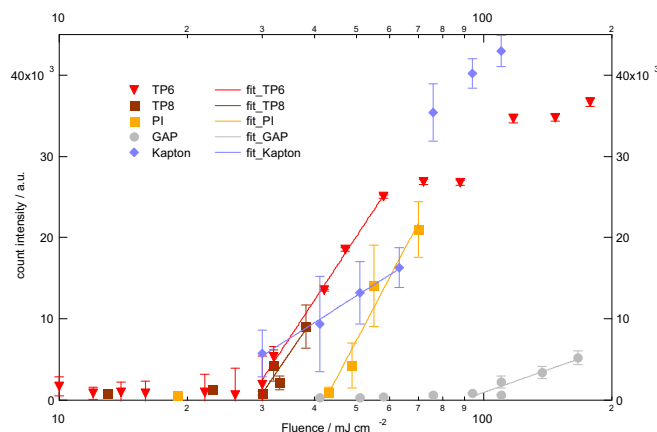


Figure 5: Neutral fragment counts with 28 amu as a function of the laser fluence

The large difference between the two very similar PI materials is quite surprising as well as the fact that the polymer GAP, containing the group with the lowest bond energy (< 1.3 eV), reveals the highest threshold in the range of $80 - 90$ mJcm⁻². This is clearly not related to the absorption coefficients at 157 nm, where GAP shows the highest absorption (Figure 7, below). The ablation threshold at longer wavelengths is normally directly related to the absorption coefficient and inversely to the bond energy.

3.1.3. *Threshold for Ions.* N₂⁺ ions were found at very low fluences of < 35 mJcm⁻² for TP6 and about 40 mJcm⁻² for GAP, which is different to mass spectrometric experiments performed with 248 and 308 nm irradiation. In these experiments, N₂ neutrals and ions are simultaneously formed even at the lowest fluences, despite the high ionization energy of 15.56 eV ($^2\Sigma_g^+$). This means that two photons of 7.9 eV are necessary for ionization from the ground state. This direct ionization from neutral N₂ can only occur during ablation and not in the gaseous phase, as the absorption of 157 nm by nitrogen gas is very low. An alternative path is the formation of excited N₂^{*} neutrals (6.149 eV, $A^3\Sigma_u^+$) during the ablation, which are metastable with a lifetime of 1-2 s and require 9.4 eV for ionization. Two photons are still required, but the absorptivity of excited neutrals is different.

In the case of GAP the threshold fluence for ion formation is a factor of two below that of neutral formation. A possible explanation in the case of GAP is the presence of a resonance hybrid of several Lewis/Kekulé structures of the azide group [12] (Figure 6), which might facilitate the formation of ions.

Modelling results suggest that photoionization dominates the ion formation at 157 nm. These experiments performed with Kapton are in good agreement with the calculations based on a 2-photon mechanism, and may explain the comparable neutral and ionization thresholds observed in our experiments.

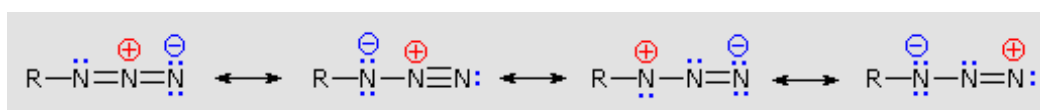


Figure 6: Resonance canonical structures of azide [12]

3.2. Ion Probe Measurements

In order to verify the extremely low threshold for the formation of ions, measurements with an ion probe were performed for TP6, GAP and Kapton. The thresholds were determined by fitting the ion probe signal versus 5-7 data points in the low fluence range, resulting in values of 14.5 ± 2.0 , 18.5 ± 1.0 and 28 ± 4 mJcm⁻², respectively (Figure 7).

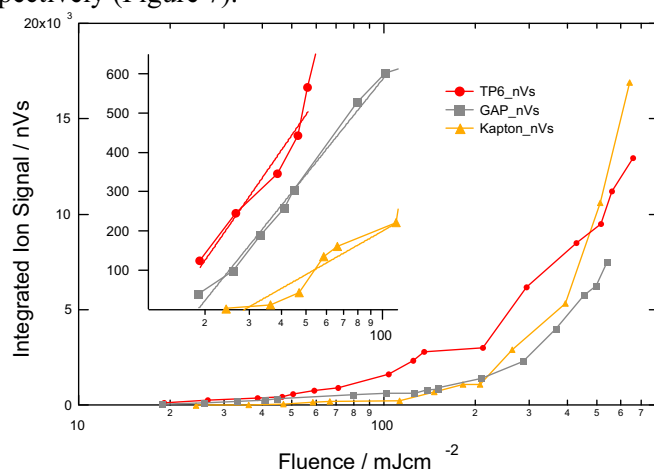


Figure 7: Integrated ion signal of the ion probe as a function of fluence

3.3. Ablation Threshold

The threshold for material removal was determined by measuring the ablation depth versus the fluence by interferometry. These values are 20, 21 and 30 mJcm⁻² for TP6, GAP and Kapton and thus similar to the results obtained from MS and ion probe measurements.

3.4. Absorption

In order to better understand the different ablation thresholds for the tested polymers, the absorptivity was determined for TP6, GAP and PMDA (Figure 8). At longer UV wavelengths, only the triazene polymers designed for 308 nm ablation exhibit a high absorptivity of about 80,000 cm⁻¹, while those of GAP and PMDA are at least one order of magnitude lower. Below 200 nm, the absorptivities of PMDA and GAP increase to >60,000 cm⁻¹ and about 160,000 cm⁻¹, respectively, for 157 nm. At this wavelength, the TP6 is only slightly more absorbing than the polyimide.

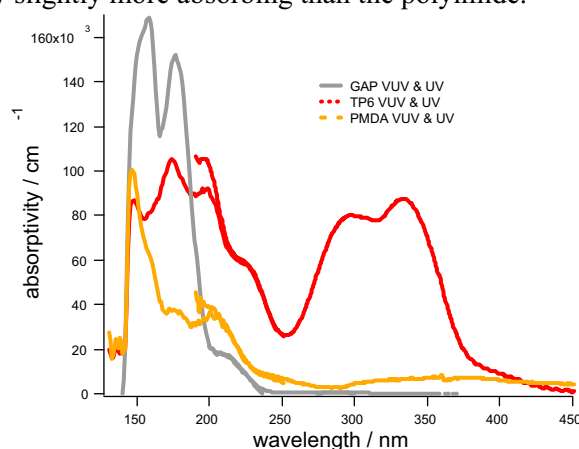


Figure 8: Absorptivity of TP6, GAP and PMDA

4. Conclusion

In Table 1, the results are summarized for comparison. In the case of Kapton HN, all methods provide very similar thresholds (both neutral and ionization) in the range of 20-30 mJcm⁻². For TP6, the numbers obtained with different methods are all around 30 mJcm⁻², except for the ion probe, which is about half this value, although this may be related to the sensitivities of the different measurements. Furthermore, the determination of the fluence in the MS experiments incorporates significant errors, as the spot size varies with the fluence. The only result that cannot be explained at the moment is the observation of ions at much lower fluences than neutrals in the case of GAP.

Thresholds / mJcm ⁻²	TP6	TP8	GAP	PMDA	Kapton HN
MS Neutrals	28	28	80-90	42	20-25
MS Ions	<35		40		
Ion Probe Signal	14.5		18.5		28
Whitelight Interferometry	30		21		20
Absorptivity / cm ⁻¹	80,000		160,000	60,000	
Weakest Bond / eV	1.7	1.7	<1.3	3.2	3.2

Table 1: Threshold and absorptivity data of polymers

The ablation behavior of triazene polymers, an azide polymer and two polyimides at the VUV irradiation wavelength of 157 nm is substantially different from UV laser ablation with 248 nm and 308 nm wavelength. The high photon energy results in pronounced fragmentation of the ablation products, including the aromatic system; a feature that is not observed for 248 and 308 nm irradiation. The high photon energy (7.9 eV) most likely leads to an effective 2-photon absorption mechanism that

yields a substantial amount of ions at low fluence (~ 30 mJ), which for longer wavelength irradiation is only observed for fluence in the Jcm^{-2} range. These ionic species include a considerable fraction of ionized N_2 , which cannot be formed by single photons at 157 nm since its first ionization potential is >15 eV. Ablation properties such as the ablation rate and threshold also differ significantly at 157 nm compared to irradiation at longer wavelength although for GAP the behavior is particularly different. Of the polymers investigated, GAP reveals the highest absorption at 157 nm and contains the azide bond with the lowest binding energy, but it is also characterized by the highest threshold fluence and lowest ablation rates. The most striking feature of GAP ablation is the observation of ions at fluences lower than that necessary for the detection of neutrals. This remarkable feature cannot be readily explained, but may be related to GAP structure that contains an azide group in the side chain which can exist in several different canonical forms. If the absorption of 157 nm irradiation were favored by one of these forms and efficient N_2^+ ion formation is facilitated, this might explain the pronounced formation of ionic products compared to neutrals.

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