

Emission of neutral molecules during UV laser ablation of a photolabile triazeno polymer

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Abstract. The neutral products of irradiating a photolabile triazeno-polymer with a pulsed laser at 248 nm (KrF excimer) were studied with time-of-flight (TOF) mass spectrometry. At fluences below 1.3 J/cm^2 , N_2 is by far the most intense neutral product. Phenyl radical (mass 76) production was also observed. The leading edge of the N_2 TOF signal shows a shoulder corresponding to kinetic energies of about 1.1 eV, followed by a long tail that lasts hundreds of microseconds. The tail is attributed to delayed emission of reaction products from the polymer. The kinetic energy of the fast peak is attributed to direct ejection of products from surface sites undergoing exothermic decomposition. The fluence dependence of the N_2 signal is highly nonlinear and is shown to fit an Arrhenius equation.

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The decomposition mechanisms involved in the laser ablation of polymers (e.g., photothermal vs. photochemical processes) are often controversial, despite extensive study [1]. The identity and kinetic energy of decomposition products provide important clues as to these mechanisms [2]. Mass spectrometry has revealed ionic and neutral species with masses ranging from small degradation fragments [3, 4], to the monomer (from unzipping reactions) [5, 6], to carbon clusters [7], and to polymer fragments with molecular weights as high as 2500 [8, 9]. For several polymers (e.g., polystyrene, Teflon, and polymethyl methacrylate), Maxwell-Boltzmann time-of-flight (TOF) distributions are obtained with effective temperatures consistent with photothermal decomposition [10–12]. In other work, much higher temperatures are inferred [13, 14].

In this work, we study a photolabile polymer with excellent properties as a resist for high-resolution microlithography [15, 16]. We show that the principle products (chiefly N_2) from this triazeno-polymer have components that are much more energetic than expected for thermal products. Furthermore, the fluence dependence of the emissions is a strongly

nonlinear function of fluence, again suggestive of a nonthermal decomposition mechanism. Nevertheless, an Arrhenius description (used previously for UV-laser-induced products from PTFE [5]) yields a good description of the emission intensities. We tentatively conclude that the decomposition process itself is photothermal under the conditions of this work.

1 Experiment and curve fitting

Synthesis of the polymer is described elsewhere [17]. The chemical structure of the polymer is diagramed in Fig. 1. Its average molecular weight is about 71 000 g/mole, corresponding to about 190 monomer units (n in Fig. 1). The decomposition process is exothermic with an enthalpy change of -624 J/g [18]. Although the absorption coefficient at 248 nm is high ($\sim 66 000 \text{ cm}^{-1}$), the absorption peaks at con-

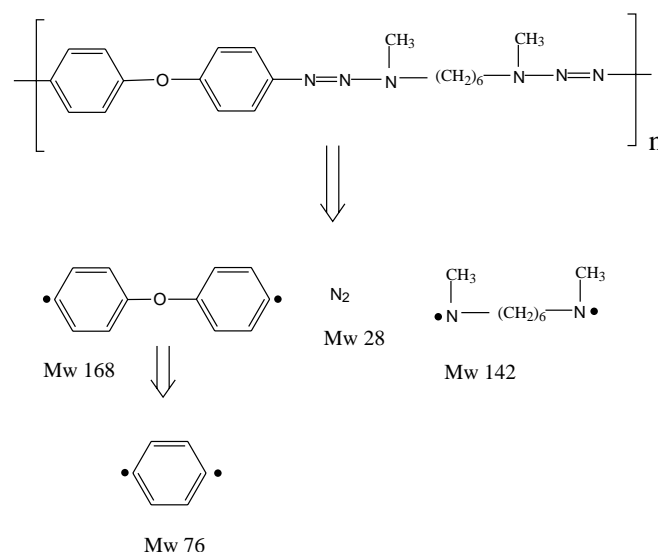


Fig. 1. Chemical structure and a possible decomposition scheme for the triazeno-polymer

siderably longer wavelengths (310–350 nm). Cast polymer films were irradiated at 248 nm at a pulse repetition rate of 1 Hz to avoid accumulative heating. The emissions were detected with a quadrupole mass spectrometer (UTI 100C) mounted with the ionizer 30 cm from the sample. Time-resolved quadrupole mass spectroscopy was used to simultaneously measure both the charge-to-mass ratio (m/z) and the TOF distributions of the emitted species. Curve-fitting techniques were employed to test various models of the emission process.

Nitrogen molecules emitted from the polymer had both highly energetic components (short TOF) and very slow components consistent with emission long after the laser pulse. The overlap between the fast and slow components, and the fact that a large majority of the total counts reside in the slow component, make it particularly important to describe the leading edge of the slow component accurately in order to characterize the fast component. To carry this out a number of models were tested by curve fitting the acquired TOF curves.

The model employed below assumed that the emission intensity of the slow component $S(t')$, was controlled by a thermally activated process: $S(t') \sim S_0 \exp(-E_a/kT)$, where E_a is an activation energy, k is the Boltzmann constant, and T is the surface temperature. We assume that the laser heats the surface uniformly to a temperature T_{RT} (room temperature) plus ΔT to a surface layer of depth a . Under these conditions, the surface temperature after the laser pulse varies as:

$$T = T_{RT} + \Delta T \operatorname{erf}\left(\frac{a}{2\sqrt{\kappa t}}\right) = T_{RT} + \Delta T \operatorname{erf}\left(\frac{\alpha}{2\sqrt{t}}\right), \quad (1)$$

where κ is the thermal diffusivity, t is the time since the laser pulse, and $\alpha = a/2\sqrt{\kappa}$, the actual fit parameter employed in modeling. The resulting $S(t')$ was convoluted with a Maxwell-Boltzmann velocity distribution by nonlinear curve fitting techniques [19] as discussed in previous work [20]. Although the physical model (and the number of parameters) may seem unnecessarily complex, the resulting equations displayed physical behavior (i.e., the intensity of the slow component in the model fell below the experimental total intensities) when fits to the slow tail were extrapolated back into the fast/slow overlap region. This is not the case with several simpler models, including those based on linear, Beer's law absorption.

The fast component was then described by assuming that the emitted N_2 had a Gaussian energy distribution with amplitude A , most probable energy E_0 , and standard deviation σ , where all particles are emitted during the laser pulse (a Δ function in time). This distribution is readily transformed to yield a particle density at the ionizer as a function of time.

2 Results and discussion

Photo-decomposition of the polymer yields significant amounts of volatile N_2 (28 amu) phenyl radicals (76 amu), presumably by the reaction pathways shown in Fig. 1. Other lowmolecular-weight species are also expected (e.g., various CH fragments), but in most cases it is not clear whether these other fragments were created during ablation or are cracking fragments created by electron impact ionization. No intact repetition units were found among the ablation fragments,

consistent with the photolabile character of the triazeno units ($R - N^1 = N^2 - N^3 <$), of which two are found in each repetition unit [21, 22]. Both N_2 and the phenyl radical show very stable parent molecular ions. In contrast, aliphatic compounds like the aliphatic amino fragment ($m/z = 142$) undergo extensive fragmentation in the ionizer.

By far the most intense neutral signal is due to N_2 . A typical N_2 TOF curve is shown in Fig. 2. Only the first 500 μ s of data are shown, where the great majority of the detected signals can be attributed to N_2 emitted directly from the sample, as opposed to molecules bouncing off the chamber walls. (This was verified by performing identical TOF measurements after blocking the direct path between the sample and the ionizer.)

At fluences below 400 mJ/cm^2 , the N_2 TOF signals consistently showed a distinctive shoulder on the fast leading edge, followed by a broad peak and long tail. The particles in the shoulder move extremely fast, with mean kinetic energies (from curve fitting to a Gaussian energy distribution) of 1.1 ± 0.1 eV. This is well above typical thermal energies and presumably reflects the concerted ejection of decomposition fragments, where reaction fragments leave the parent molecule without colliding with other particles. Similar TOF curves have been observed during the IR-induced, exothermic decomposition of molecular cyclotrimethylene-trinitramine (RDX), an energetic compound used in explosives and rocket propellants [23]; both fast and slow product components were observed when RDX single crystals were exposed to UV laser irradiation (248 nm) [24].

The broad, slow peak in the N_2 TOF distribution is much broader than Maxwell-Boltzmann distributions with similar peak TOFs. Nevertheless, the peak TOF does shift to shorter times with increasing fluence. This shift is often associated with thermal emission, where higher fluences produce higher surface temperatures and thus faster particles. In such cases, long emission tails are often associated with emission *after* the laser pulse [20, 25]. This delayed emission may be due either to thermal decomposition after the laser pulse, as the surface gradually cools, or to the diffusion of volatile species (produced in the bulk of the polymer) to the surface. At fluences above 300 mJ/cm^2 , the estimated total N_2

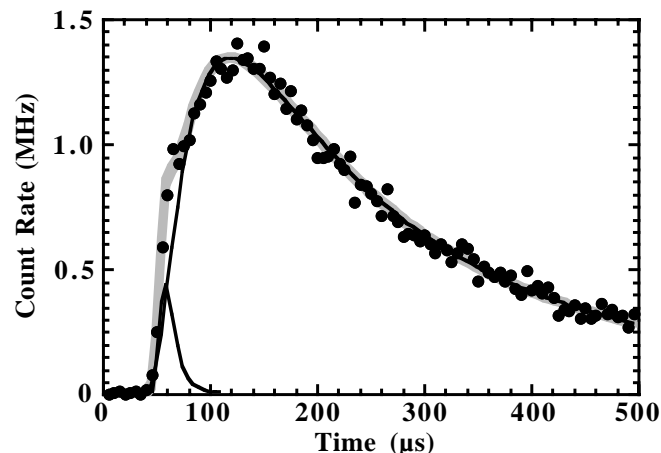


Fig. 2. Time-of-flight signal for N_2 at 310 mJ/cm^2 . A curve fit to the data using a Gaussian energy distribution for the shoulder and a thermally activated emission for the slow peak is shown by the *light, broad line*; the individual fast and slow components are shown as *dark lines*

yield per laser pulse exceeds 10^{15} molecules/cm². At this particle density, collisions among the emitted N₂ molecules are expected to modify the original (as emitted) velocity distribution [26].

The N₂ intensities depend strongly on fluence, as shown in Fig. 3 (log-log plot). The intensity rises sharply in approximately power law fashion as the signal rises above the background. Finally, at still higher fluences, the intensity rolls over, growing more slowly with increasing fluence. The slope of the power-law portion is ~ 8 . Although we could suggest that this corresponds to an eight-photon process (i.e., multiphoton), this is not reasonable. Furthermore, it is inconsistent with a simple photodecomposition mechanism, where the product intensity is proportional to the laser fluence.

Alternatively, thermally activated processes are typically described by an Arrhenius relation. Given a simple expression for the surface temperature as a function of fluence, appropriate Arrhenius-like expressions are formed [5]. For a single-photon photothermal process, where all absorbed light goes into heat, and neglecting thermal diffusion, the temperature rise ΔT is proportional to the fluence. This temperature rise is readily incorporated into an Arrhenius-like description with activation energy E_a , where E_a is determined by fitting the Arrhenius expression to the data. A more stringent test of the thermal decomposition hypothesis is obtained if we fix E_a to the known activation of thermal decomposition for this material ($E_a \sim 2.1$ eV). The result of such a fitting procedure is shown in Fig. 4. Although one might argue that the data systematically depart from the model at the lower fluences, the fluence range adequately treated by an Arrhenius expression is significantly greater than the power-law region of Fig. 3. Figure 4 also shows the intensities of the fast N₂ component, normalized to the total peak intensities at a single point. These data points fall directly on the Arrhenius equation fit. Our conclusion is that a thermal-activation model describes the intensity vs. fluence data quite adequately.

The slow decay of the N₂ and phenyl emissions after the laser pulse requires emission after the laser pulse. (Although collisions can slow particles as well as speed them up, the net effect in TOF measurements is to shift the peak TOF to shorter times [26]. Collisions cannot explain the long tails.) The duration of this emission can be estimated from the source function used to describe the slow tails. The fast molecules were excluded from the analysis by considering

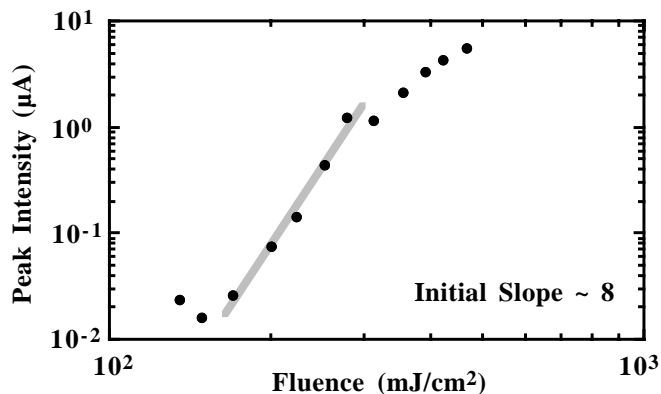


Fig. 3. Log-log plot of the N₂ (28 amu) signal intensity as a function of laser fluence

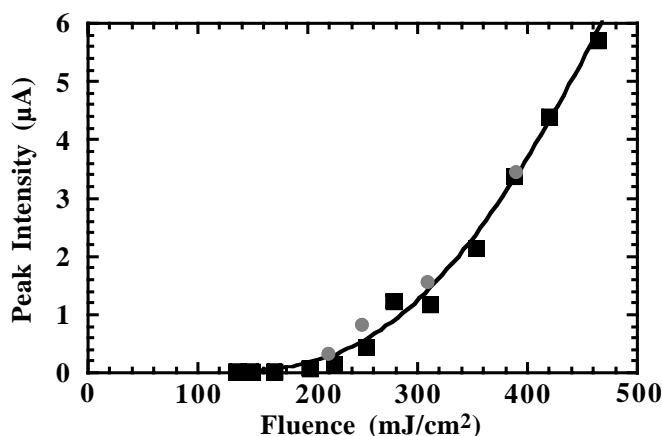


Fig. 4. Linear plot of the signal intensities for the N₂ (28 amu) signal intensity as a function of laser fluence. The dark line shows a least-squares fit of the data to a thermal model for emission, assuming an activation energy of 2.1 eV (the activation energy for thermal decomposition of the polymer). The gray dots indicate the N₂ fast peak intensity determined from curve fits to the TOF data

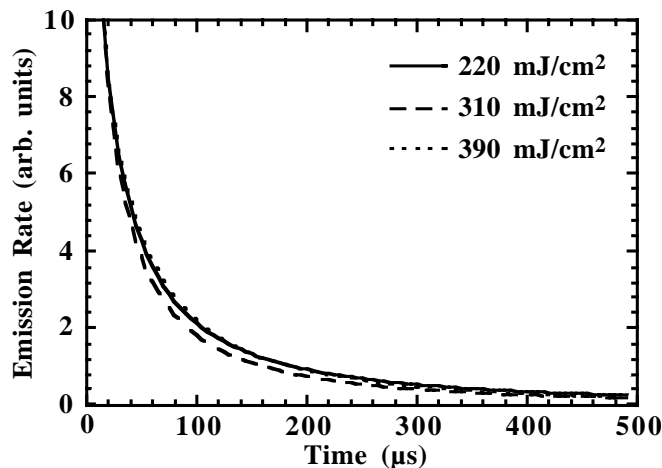


Fig. 5. Plots of the source functions determined from fitting a thermally activated model for emission intensity to the N₂ TOF data, all normalized to the same initial intensity

only those particles arriving at least 80 μs after the laser pulse. The source functions corresponding to the N₂ measurements at three fluences are shown in Fig. 5, all normalized to unit intensity at time $t = 0$. The source functions for N₂ are all very similar to each other and to the low-fluence source functions for the phenyl radical. This tail is in fact entirely consistent with the proposed thermal decomposition rate decaying because of cooling of the surface, as given by (1).

3 Conclusion

Mass-selected TOF measurements during the UV-laser-induced (248 nm) decomposition of a photolabile polymer show fast neutral particles which are most likely to be due to particles emitted directly from the surface by a concerted, exothermic chemical reaction. At this point, TOF measurements cannot distinguish whether this reaction is initiated directly by photon absorption (photochemical dissociation) or by thermal excitation. Importantly, the intensities of both the

fast N₂ component and the total N₂ intensity follow a just an Arrhenius relation where the temperature is predicted from the total laser energy deposited. We therefore propose that photothermal processes dominate the rates of formation of these products. The fast N₂ component may then be attributed to a thermally induced exothermic decomposition where the products come off prior to equilibrating with the surface. Gradual surface cooling would account for the slow tail in the emission that follows the laser pulse. Nevertheless, this polymer is known to photodecompose at low fluences [14], suggesting that photochemical processes contribute to the observed emission.

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