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Direct Observation of Excimer-Laser Photoablation Products from Polymers by Picosecond-UV-Laser Mass Spectroscopy

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Abstract. Excimer laser (248 nm, 15 ns) photoablation products from the polymers PMMA and polystyrene are directly observed using picosecond uv laser (290 nm, 1 ps) ionization time-of-flight mass spectroscopy. Species heavier than the monomer masses are detected, which cannot be attributed to simple direct fragments of the polymer chains, but rather show the importance of fast chemistry and/or photochemistry during the ablation process.

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Since the first demonstration of the photoetching of polymers by excimer-laser radiation [1, 2], the ability to produce sharp structures with submicrometer accuracy and well-defined depth has stimulated a series of investigations of this process. It is now well established that this process works for a series of polymers and tissue material and for a range of laser wavelengths between 193 and 351 nm. The key feature seems to be the energy absorbed per unit volume. In almost all cases, a threshold fluence is observed on the order of between ten and several hundred mJ/cm^2. The relative contributions of thermal and photochemical processes for the ablation of material were demonstrated using calorimetric and acoustic studies [3, 4].

Several models have been designed to describe the ablative photodecomposition by far-ultraviolet radiation [5]. The ablation is attributed to the increase in volume that accompanies the photolysis of the polymer species. It is not yet clear, how much, in addition to thermal effects, photochemical and chemical effects are influencing the process. The peak stress induced in the absorbed volume can be as high as 10^7 Pa (≈ 100 atm) [6] resulting in up to supersonic material ejection velocities. Several investigations have been performed to detect the species which are involved in the ablation process by using emission spectroscopy [7] and laser induced fluorescence [8] for small fragments like C_2 and CN, and conventional gas chromatography and/or electron impact (EI) mass spectroscopy to detect other volatile species [9, 10, 15, 18]. Using vuv laser mass spectroscopy, for the case of polystyrene the ablation of the monomer after 193 nm irradiation was detected [11].

We shall describe the direct observation of excimer-laser (248 nm) photoablation products from the polymers PMMA and polystyrene using picosecond (ps) laser mass spectroscopy [12–14]. By this technique, the abundance of the parent molecular ion P^+ in the mass spectrum can be enhanced dramatically. In most cases, it becomes the dominating ion in the mass spectrum, and in a few cases [13] even the parent ion P^+ alone is observed. Since with EI mass spectroscopy the extensive fragmentation [15] may cause problems for the analysis, especially when a mixture of unknown compounds is to be analyzed, we used ps laser mass spectroscopy in order to find answers for: a) is the monomer always ablated?, b) are heavy species with $m/e \geqq$ monomer mass ablated?, c) what is the time evolution of the ablated masses?

The experimental setup has been described in detail in [12, 14, 16]. The main part is a differentially pumped time-of-flight (TOF) laser ionization mass spectrometer. Polymer samples were introduced into the ionization region of the TOF mass analyzer about 5 mm below the axis of the ion optics electrodes. The samples were irradiated with light from an excimer

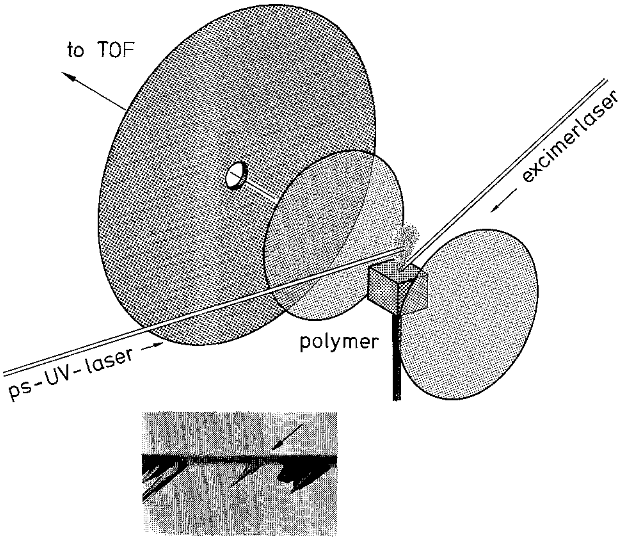

Fig. 1. Schematic view of the experimental setup. The polymer sample is irradiated by the excimer laser and the ablated material is ionized after a variable delay (2...80 µs) using ps-uv-laser excitation. Starting with flat polymer surfaces, after a few excimer laser shots, a hole is generated into the substrate surface due to the ablated material (≈1000 Å/shot). A microscopic view of a PMMA sample showing a series of holes from which the detected material has been ablated is given in the insert, with the direction of the excimer laser beam indicated for one hole

laser (248 nm, several tens to a few hundred mJ/cm^2) under 45° and the ablated material was ionized after a variable delay (2–80 µs) using ps-UV-laser excitation (≈1 ps, 290 nm). This is shown schematically in Fig. 1. Starting with flat polymer surfaces, after a few excimer laser shots a hole was generated into the substrate surface due to the ablated material (≈1000 Å/shot), see insert of Fig. 1. The TOF mass spectra shown in the following are *single-shot* recordings and the typical spectra for different polymers, delay times and intensities were selected for presentation here (ps pulse energy ≈5...50 µJ, 290 nm, $f\approx 250...400$ mm).

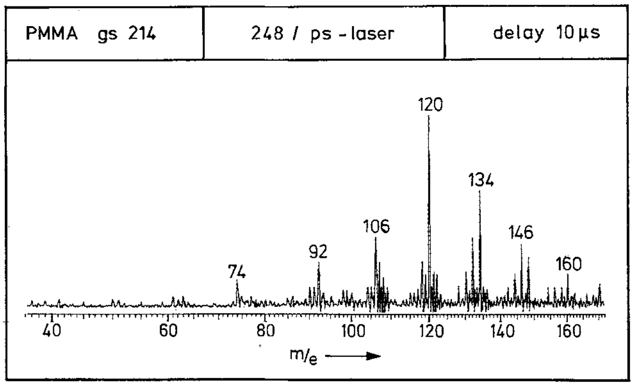

Fig. 2. The ps-uv-laser (1 ps, 290 nm), TOF mass spectrum after the excimer laser (15 ns, 248 nm) photoablation from PMMA (delay 10 µs, distance ≈5 mm). The monomer mass $m/e=100$ has low abundance

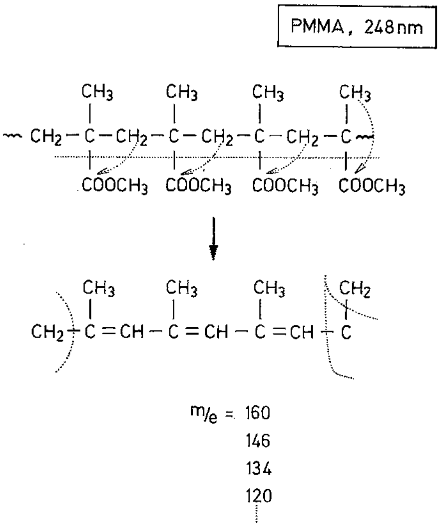

Fig. 3. The mass peaks observed in the range ($92\leq m/e\leq 160$) for ablation of PMMA at 248 nm may be tentatively assigned to $CH_2\text{-}C(CH_3)=CH\text{-}C(CH_3)=CH\text{-}C(CH_3)=CH\text{-}C\text{-}CH_2$ and fragments of it. This is shown schematically

PMMA

The ps-UV-laser ionization TOF mass spectrum ($m/e=37$ to 172) for PMMA (extra purity kind, Röhm GS 214) ablation products at 248 nm is shown in Fig. 2. Masses larger than the monomer mass ($m/e=100$) are clearly detected with $m/e=120$ being the dominating ion in the TOF mass spectrum. The monomer mass is practically *not* observed under our ablation conditions. This was confirmed by taking the ps UV laser TOF mass spectrum of MMA (methylmethacrylate) separately, where the $m/e=100$ mass peak was clearly detected. In addition, several typical fragment ions of MMA are absent in the spectrum obtained from PMMA ablation products also for higher ps-laser intensities up to tenfold compared to the intensity used in Fig. 2. The low relative abundance of the monomer MMA at 248 nm is in agreement with [19], where less than 1% of the polymer appeared as MMA. None of our observed mass peaks with $m/e\geq 74$ in the photoablation mass spectrum of PMMA are due to fragment peaks of the monomer MMA, and the peaks for $m/e\geq 100$ cannot be identified as a simple fragment of the polymer chain, but rather have to be attributed to a fast chemical and/or photochemical reaction during the ablation process. The species

$$CH_2\text{-}C(CH_3)= \\ =CH\text{-}C(CH_3)=CH\text{-}C(CH_3)=CH\text{-}C\text{-}CH_2$$

and fragments of it is one possibility for a tentative assignment of the mass peaks ($92\leq m/e\leq 160$). This is schematically shown in Fig. 3. The peak at $m/e=74$

can be due to $[CH_3COOCH_3]^+$. By repeated optical inspection of the PMMA samples under a microscope (insert Fig. 1) we confirmed that the excimer laser fluence was kept within the range suitable for ablation.

Polystyrene

The ps uv laser ionization TOF mass spectra for polystyrene ablation products at 248 nm are shown in Fig. 4. Different from the case of PMMA, the mass spectrum strongly depends on the delay time between the ablation excimer laser pulse and the ps uv ionization laser pulse. The delay was varied between 3.5 and 80 µs. For long delay times, the monomer at $m/e=104$ is dominating the TOF mass spectrum. Towards shorter delay times, ions with masses larger than the monomer mass are detected. For a delay of $\Delta t=3.5$ µs, the TOF mass spectrum shows two distributions, one centered around the monomer mass $m/e=104$ and one centered around $m/e=181$, which may be attributed to a stilbenelike structure. The distance between the irradiated point on the polystyrene sample and the point of ionization was about $d=7$ mm in this case. Therefore, the TOF mass spectrum obtained for a delay of $\Delta t=3.5$ µs is due to neutral species ablated with supersonic velocities (2000 m/s) from the polymer sample, whereas the TOF mass spectra at long delay time are attributed to thermal elimination conditions. When comparing the results obtained for PMMA ($\Delta t=10$ µs) and polystyrene, the thermal component seems to be stronger in the case of polystyrene than in the case of PMMA. Indication for this is already given by optical inspection of the two samples after the ablation, where the polystyrene polymer sample shows some glassy surface like after melting. Also the TOF mass spectrum shows some similarity with the pyrolysis mass spectrum, which is not the case for the PMMA sample [17].

The ps uv laser mass spectra for ablation products at 248 nm from two different plexiglas samples are compared in Fig. 5. The spectrum of an airplane window sample (Boeing 747, LH), top, is somewhat similar to the spectrum of PMMA GS 214 (like Fig. 2). The differences observed in the relative peak heights may be due to the airplane window constituents, e.g., plasticizers and uv stabilizers, which are not found in the extra purity PMMA sample.

In summary, we directly observed excimer laser photoablation products from the polymers PMMA and polystyrene at 248 nm using ps-uv-laser mass spectroscopy. Masses larger than the monomer mass are detected with high relative abundance. Many of these masses *cannot* be attributed to simple direct fragments of the polymer chain (for example $m/e=120$ for PMMA, $m/e=181$ for polystyrene), but rather

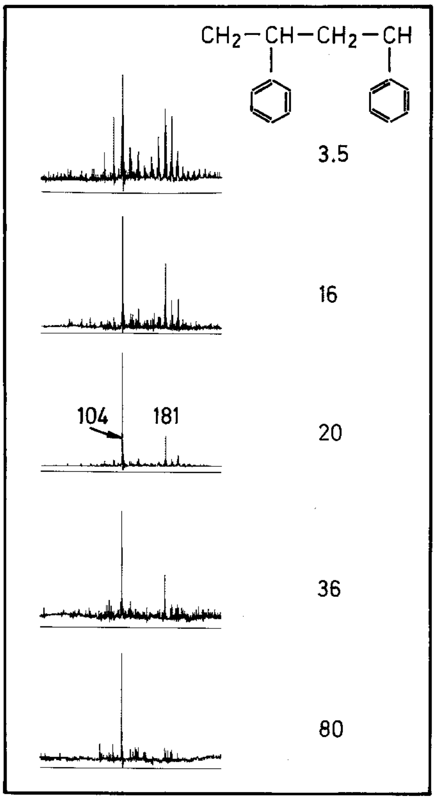

Fig. 4. The ps-uv-laser (1 ps, 290 nm) TOF mass spectra after the excimer laser (15 ns, 248 nm) photoablation from polystyrene (delay 3.5...80 µs, distance ≈7 mm). The monomer mass $m/e=104$ has high abundance

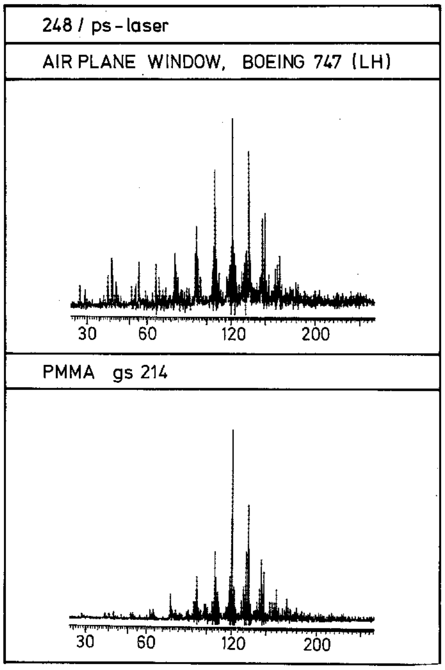

Fig. 5. The ps-uv-laser mass spectra of two PMMA samples: airplane window (Boeing 747, LH), top and plexiglas gs 214, bottom, compare Fig. 2

show the importance of fast chemistry and/or photochemistry during the ablation process. Since for some polymers (Kapton, Teflon) we could separately detect abundant ionic products ablated together with the neutrals, the influence of ionic species has to be taken into account for a complete understanding of the photoablation process. In the case of PMMA, the monomer has only very small abundance at 248 nm, whereas for polystyrene the monomer was clearly observed, especially for material ejected with thermal velocities.

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