# Laser Ablation and the Production of Polymer Films

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**The formation of high-quality thin films of polytetrafluoroethylene (PTFE) is important in many applications ranging from material reinforcement to molecular electronics. Laser ablation, a technique widely used to deposit a variety of inorganic materials, can also be used as a simple and highly versatile method for forming thin polymer films. The data presented show that PTFE films can be produced on various supports by the evaporation of a solid PTFE target with a pulsed ultraviolet laser. The composition of the ablation plume suggests that PTFE ablation and subsequent film formation occur by way of a laser-induced pyrolitic decomposition with subsequent repolymerization. The polymer films produced by this method are composed of amorphous and highly crystalline regions, the latter being predominantly in a chain-folded configuration with the molecular axis aligned parallel to the substrate surface.**

The deposition of thin inorganic films by laser ablation has undergone explosive growth and development in the past 5 years. It can provide monolayer compositional control for the growth of oriented thin films with distinctive morphologies or properties (*1, 2*). Thus, it would be valuable to extend this technique to polymers, which would also provide a simple tool for mechanistic studies of polymer degradation and the kinetics of decomposition. This is an area of increasing importance both in evaluating the feasibility of polymer recycling and in understanding the impact of degradation products on the environment. The potential of laser ablation in the production of polymer films is illustrated here for the deposition of PTFE films. We chose PTFE because the production of thin PTFE films has been hampered by the inability of conventional coating techniques to process insoluble materials.

Although the details of the laser-target interaction, plasma formation, and evolution are complex, a qualitative description is simple. Upon absorbing ultraviolet (UV) light, organic molecules are excited into high-energy electronic states that may decay through direct bond dissociation, ablative photo decomposition (3), or rapid conversion of photon energy into vibrational energy to produce heat (4). For producing polymer films, the plume cannot be composed merely of molecular fragments resulting from random cleavage but rather must be composed of monomer. In situ measurements of the plume composition described below show that in the ablation of PTFE the monomer (TFE) is produced upon UV irradiation. PTFE films produced by laser ablation are stoichiometric, and, although the crystalline regions represent 50% of the film, they exhibit a high degree of local orientation. We propose that PTFE ablation is a thermally driven process; absorption induces local heating, leading to chain cleavage and a depolymerization reaction. The unzipping of the polymer chain leads to monomer that repolymerizes on a nearby surface.

In order to gain some understanding of the complex ablation process, we first addressed the laser-target interaction through study of the plume composition in the range 0 to 200 atomic mass units (amu) with a quadrupole mass spectrometer (QMS). The experimental configuration has been described (*2, 5*). The mass distributions of the species generated by laser ablation and thermal decomposition are compared in Fig. 1. The similarities between the spectra are remarkable. The peaks at 50, 100, and 150 amu correspond, respectively, to difluorocarbene ($CF_2$), a very stable species at elevated temperatures, its dimer tetrafluoroethylene ($C_2F_4$), and its trimer ($C_3F_6$). The remaining peaks can be identified as due to fluorine extraction or addition from these species. The peaks at 19, 31, 69, 81, 119, and 131 amu correspond to F, CF, $CF_3$, $C_2F_3$, $C_2F_5$, and $C_3F_5$, respectively. Although PTFE pyrolitically decomposes to monomer (6), TFE interactions in a plasma at elevated temperatures lead to the numerous species shown in Fig. 1. Mass spectra collected throughout 30 min of continuous ablation show that the abundances of $CF_2$ and TFE in the plume are independent of ablation time. The preservation of the plume composition throughout the ablation process suggests that, in contrast to some previous observations (*7, 8*), we are ablating PTFE, that is, material is being removed from the target without degradation or compositional changes to the target.

After deposition (9), the films were characterized by x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), and transmission electron microscopy (TEM). The C1*s* region of an ablated PTFE film with an F/C ratio of 2 is shown in Fig. 2. The only spectral feature, centered at 291 eV on the binding energy scale, is attributed to a carbon atom attached to two fluorine atoms. The $CF_3$, CF, CFH, and CH structural features were not observed. As in the ablation of ceramics, the film composition is strongly dependent on laser fluence, laser wavelength, substrate temperature, substrate-to-target distance, and background gas. The XRD patterns of PTFE films deposited at 320°C (*10*) correspond to the standard helical configuration with $a = 5.66$ Å and $c = 19.5$ Å and with 15 $CF_2$ units per helical turn (*11, 12*). The degree of crystallinity of the films was estimated to be ~50% from differential scanning calorimetry data, and the melting temperature was 323°C.

The more typical features observed in the TEM micrographs (*13*) of the crystalline regions of the laser-ablated films in Fig. 3 include "shish kebabs" (labeled 1), curvilinear rodlike structure (labeled 2), and smaller curved structure (labeled 3). The electron diffraction (ED) pattern for the shish kebab region identified is shown in the inset in the correct orientation relative to the image. The crystallinity of the shish kebab is evidenced by the sharp ED pattern in the inset. For the shish kebab structure identified, the lamellae (kebab) are about 150 to 450 nm long and 50 to 130 nm wide, slightly thicker than previously observed

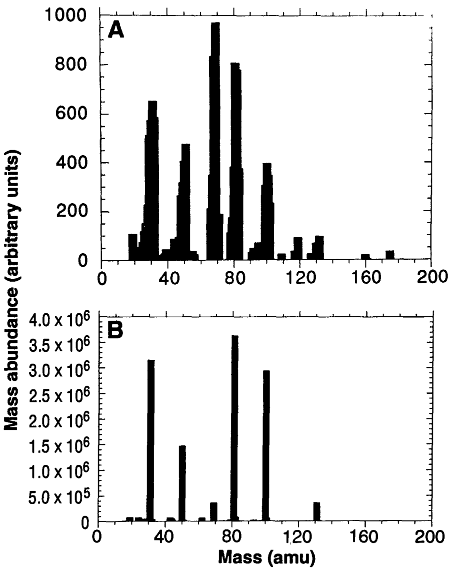

**Fig. 1.** (**A**) Mass distribution of species generated by laser ablation of PTFE. A pulsed laser beam (266 nm) was directed onto a PTFE target maintained at $10^{-7}$ torr. The plume was collected through a 3-mm-diameter pinhole 12 cm away from the target onto the QMS. (**B**) Mass distribution of the thermal decomposition products of PTFE pyrolyzed at 600°C in a He atmosphere.

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(*14–16*). The curvilinear rodlike features are about 200 to 300 nm wide and up to a few micrometers long. The ED pattern of shish kebabs and rods shows three strong reflections (*hk*0) at 0.49, 0.24, and 0.16 nm corresponding to the (100), (200), and (300) reflections, respectively, of the room-temperature polymorph of PTFE (*11, 12, 14*), in agreement with the XRD results described above. The absence of the strong (110) and (210) reflections (observed in unoriented samples and samples with fiber texture) indicates that the $a^*c^*$ plane lies in the plane of the substrate. Along $c^*$ the reflection identified is the diffuse arc at 0.13 nm corresponding to the (0015), (*hkℓ*) reflection (*12*). As shown by the ED pattern, shish kebab chains are normal to the lamellae with the long axes of the molecule positioned along $c^*$ parallel to the substrate surface. The chains in the curvilinear rods are normal to the length of the rod with $c^*$ parallel to the substrate.

The extraordinary similarities between the mass distribution of the species in the ablation plume and those observed in the pyrolitic decomposition of PTFE suggest that, in the range of fluences where stoichiometric films are produced, ablation of PTFE is consistent with a thermally driven mechanism. The UV pulses absorbed by the polymer provide an efficient thermal source. Temperature jumps greater than 1000°C (*2*) are achieved in nanoseconds and are maintained for the thermal relaxation time of the volume heated by the laser ($\sim$50 μs). As shown in (*6*), the pyrolitic decomposition of PTFE leads to monomer formation through the rapid unzipping of the PTFE chains. If we use the unzipping rate constant for pyrolitic decomposition (*6*) at 1000°C, we estimate that $10^4$ monomer units can depolymerize in the thermal relaxation time. However, in order to initiate the unzipping of the polymer chain, it is necessary to have first created a radical in the chain. Because thermal initiation by chain scission typically occurs in much too long a time scale, the more likely process would be either thermal initiation at chain ends, which can occur on the microsecond time scale, or photo-induced initiation.

Once the monomer is produced, the repolymerization reaction also requires the presence of the appropriate initiating species. We suggest that, if a fraction of the $CF_3$ and $C_2F_5$ readily available in the plume is in a radical form, these components may assist as efficient initiators in the repolymerization of the monomer.

The morphology of films produced by laser ablation is unlike any previously reported for PTFE (*14–21*). The ED pattern (Fig. 3) is consistent with a folded-chain packing configuration. Chains are parallel to the substrate surface and to the central core of the structure for the shish kebabs and are oriented normal to the length of the rod and along the substrate plane for curvilinear rodlike structures. Chains in a folded configuration have been observed for PTFE (*14–16*) and other polymers (*22*). If the lamellae consisted of a single folded chain, one would estimate the upper limit for the molecular weight to be $\sim 1 \times 10^6$ in a square platelet, in good agreement with PTFE grown by other methods (*21*).

The direct growth of a chain-folded morphology is interesting because, in general, PTFE polymerizes into an extended chain structure that can reorganize into a chain-folded structure upon subsequent melting. An unchanged melting temperature (345°C), measured for extended-chain PTFE after annealing to 320°C, suggests that the structures here are not the result of an annealing process. Because shish kebabs and rodlike features are also observed in lower temperature processes where polymerization occurs from the gas phase (*17*), it appears likely that their formation may reflect the details of polymerization kinetics.

**Fig. 2.** The C1*s* region of an ablated PTFE film. We carried out the XPS analyses using monochromatized Al Kα radiation at 1487 eV. A 1-mm spot size was used to obtain information from the largest possible sample area. We determined film stoichiometry from the ratio of the overall intensity of the C1*s* to F1*s* binding energies.

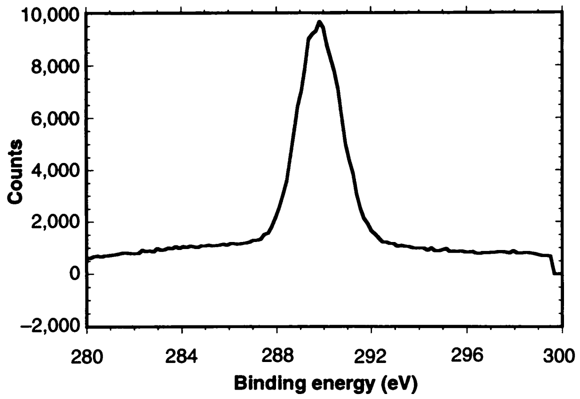
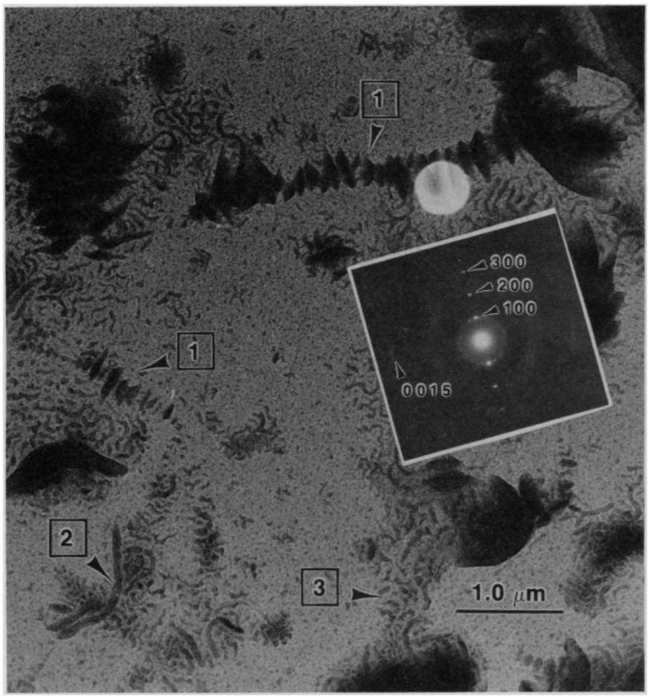


**Fig. 3.** A TEM micrograph of laser-ablated PTFE. Features include the following: 1, shish kebab; 2, curvilinear rodlike structure; and 3, smaller curved structure. The inset shows an ED pattern for the shish kebab region.



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9. Films were produced with a fluence of 1.5 J/cm$^2$ in an Ar atmosphere of 250 mtorr. The substrate temperature was maintained at 320°C throughout the deposition process.
10. The XRD diffraction patterns were collected in the symmetrical reflection mode with an automated Philips diffractometer (fixed time mode, reflected beam monochromator, Cu K$_\alpha$ radiation) from thin PTFE films deposited on single-crystal quartz. The crystal was cut so that there was zero scattering from the substrate.
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# Identification of Complex Aromatic Molecules in Individual Interplanetary Dust Particles

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**Seventeen stratospherically collected particles—eight of which are classified as interplanetary dust particles (IDPs), seven of which are classified as probable terrestrial contaminants, and two of which have uncertain origins—were studied with a microprobe two-step laser mass spectrometer. Many polycyclic aromatic hydrocarbons (PAHs) and their alkylated derivatives were identified in two of the eight IDPs. The PAHs observed include a high-mass envelope not found in meteorites or terrestrial contaminants and prominent odd-mass peaks suggestive of nitrogen-containing functional groups attached to aromatic chromophores. In addition, the complexity of the IDP mass spectra has no precedence in previous studies of meteorite samples or their acid residues. Extensive checks were performed to demonstrate that the PAH signals are not caused by terrestrial contaminants.**

Interplanetary dust particles consist of several distinctive types of primitive solar system materials that have similarities to and differences from meteorites (*1*). These particles have been proposed as the best vehicle for carrying potential organic matter to the primordial Earth's surface (*2*), but because of the technological difficulties associated with analysis of small particles (typically ≤20 μm in diameter), only recently has it become possible to investigate the carbon chemistry of IDPs. Measurements made with a microprobe two-step laser mass spectrometer ($\mu$L$^2$MS) (*3, 4*) show the presence of a rich mixture of nonvolatile, high-mass PAHs in two IDPs.

Several carbon-rich IDPs have been identified (*5, 6*), some with a carbon content greater than carbonaceous chondritic meteorites (*7–9*), but no definitive measurements of specific organic molecules have been reported. Allamandola, Sandford, and Wopenka (*10*) have suggested that PAHs are present on the basis of Raman spectra and deuterium enrichments of individual IDPs; Wopenka reported that some particles show C–C vibrations characteristic of amorphous carbons and coals (*11*); and Swan, Walker, Wopenka, and Freeman (*12*) found infrared bands at 3.4 μm characteristic of C–H stretches. Previous mass spectrometric studies of individual IDPs also have provided evidence for organics. Time-of-flight secondary-ionization mass spectrometry studies of a thinly sliced section of an IDP showed a faint signal with a high-mass envelope between 500 and 700 atomic mass units (amu) (*13*), although spectral interferences from silver ion attachment, fragmentation, and nonselective ionization prevented identification of the components of this envelope. Clusters of peaks separated by 14 amu indicate, however, the presence of methylene (CH$_2$) units or the replacement of H by CH$_3$. This evidence, like that of the vibrational spectroscopy, suggests that the carbon in IDPs is at least partially organic.

Laser microprobe studies have been performed on IDPs as small as 10 μm (*14, 15*). The laser microprobe technique differs from the use of the $\mu$L$^2$MS in that the desorption and ionization are accomplished in the same step, thereby eliminating selectivity and promoting fragmentation. Trace amounts of organic material used in collection and curation (silicone oil, hexane, and freon) created serious interferences in the first studies (*14*), but later work that included background correction (*16*) minimized this problem. Nevertheless, no specific molecular information was obtained.

Our experimental procedure was as follows. Dust particles 2 to 50 μm in diameter were collected from the stratosphere (altitude, 20 km) on "flags" mounted on the wings of the National Aeronautics and Space Administration's (NASA's) high-altitude ER-2 aircraft. The particle impact collector, which consisted of a surface coated with a thin film of viscous silicone oil, was examined postflight in a clean room, and particles were removed for further analysis (*17, 18*) (Table 1).

Elemental abundances were determined with a scanning electron microscope equipped with an energy dispersive x-ray detector (SEM-EDX). Particles denoted "chondritic" have Si, Mg, or Fe as the dominant element, contain Al (amounts less than that of Mg), as well as S, Ca, Cr, and Ni in variable proportions, and do not contain large proportions of K, Ti, or other elements not normally seen in the x-ray spectra of meteorite standards. Previous studies (*19–22*) have proven that many chondritic stratospheric particles are IDPs; by extrapolation, all chondritic particles are so classified. We also distinguished between probable terrestrial contaminants (TCs) (on the basis of, for example, their size or sporadic, large abundances on certain collectors) and particles for which other evidence suggests an extraterrestrial source and whose origin is thus uncertain.

The particles were crushed between quartz plates with apparatus at Washington University, and the material adhering to one of the plates was transferred to a KBr crystal mount for microscopic Fourier transform infrared spectroscopy (micro-FTIR) absorption measurements (*23*), micro-Raman scattering studies (*10*), or both. Material from the companion plate was transferred to a gold foil, and isotopic measurements were made with a modified Cameca IMS-3F ion probe (*22*). The SEM-EDX and ion microprobe results are presented elsewhere (*24, 25*). The relevant dust fragments were relocated on the KBr mounts and remeasured by micro-FTIR spectrosco-

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