

Surface analysis of bulk polymers using single- and multiple-photon ionization

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The surface analysis by laser ionization (SALI) technique has been applied to the chemical analysis of bulk solid polymer surfaces. Surface material was removed by a pulsed rare-gas ion probe beam at ~ 7 keV and sputtered neutral molecules were photoionized by pulsed coherent radiation at 118 nm (10.5 eV) or 248 nm (5.0 eV). Photoions were then extracted into a reflecting time-of-flight mass spectrometer. The ion beam dose during analysis was kept below significant damage levels ($< 10^{13}$ primary ions/cm²), indicative of the very high sensitivity. The single-photon ionization (118 nm) resulted in much more extensive and representative mass spectra than for the multiphoton ionization, reflecting the fact that it is a relatively "soft" ionization technique. Very distinct and readily interpretable mass spectra are shown for poly(tetrafluoroethylene), the polyamide nylon 66, and poly(ethylene-glycol)-monostearate. Where comparison secondary ion mass spectra are available, these SALI spectra with one-photon ionization compare quite favorably.

I. INTRODUCTION

Investigations of bulk organic polymers have been primarily undertaken using x-ray photoelectron spectroscopy.¹ While the method has produced many successful results, it is limited by relatively poor spatial resolution, large sampling depths (~ 50 Å), and often by ambiguities in the assignment of chemical shifts associated with C, N, and O bonding. Furthermore, with significant chemical shift information, complete structural information can still be very difficult to extract due to the great variety of chemical structures possible with several simple bonds. Recently these difficulties are being addressed by the use of mass spectrometric techniques such as secondary ion mass spectrometry (SIMS) (see, e.g., Refs. 2 and 3) and, to a lesser extent, laser desorption mass spectrometry (LDMS).⁴ These methods provide characteristic fragment spectra of oligomers and bulk polymers which can be used to examine molecular structure. However, proper interpretation of these mass spectra requires some understanding of both the desorption and ionization which is more difficult when both steps are simultaneously induced, and the coupling of desorption and ionization can place limitations on the nature of the measured spectra.

The approach taken in this work is to decouple the ionization and desorption steps, using the technique of surface analysis by laser ionization (SALI).⁵ This method, developed at SRI International, uses a surface probe beam for desorption, typically a rare-gas ion beam for sputtering, followed by nonselective untuned laser radiation for ionization. Photoions are detected by reflecting time-of-flight mass spectrometry. Decoupling of the ionization and desorption steps allows more flexibility, control, and quantitation in the analysis, and enables clearer investigations of the desorption and ionization processes themselves. A further advantage of the method is that matrix effects are greatly reduced relative to SIMS analysis; this is because desorbed or sputtered neutrals are detected rather than the secondary ions, which typically being much less probable than neutral molecules, have

yields that are much more sensitive to variations in the local chemical environment.

Nonresonant multiphoton ionization (MPI) has been used for ionization in studies of inorganic samples. At high intensities this usually results in ionization of all species in the laser focal region which permits reliable elemental quantitation. However, the situation is different with the analysis of complex molecular systems.

Mass spectroscopic analysis of nonvolatile organic materials is often constrained by fragmentation that occurs during both the desorption and ionization processes. This fragmentation may be extensive when using multiphoton ionization for the detection of desorbed neutrals (whether or not there is an intermediate resonance at the laser frequency) especially under high sensitivity conditions where fairly high intensity laser fields must be used. Because the molecular ion that is formed typically absorbs single photons (to fragmenting states by a bound-bound electronic transition) more strongly than the neutral molecule absorbing into the ionization continuum (a bound-free electronic transition), it is difficult to limit fragmentation while efficiency is being sought; for low primary beam doses (low degree of damage) and/or small amounts of sample, efficiency is an important issue. Exemplary of this difficulty, the branching ratio between parent and fragment molecules generally changes dramatically with laser intensity making quantitation and even spectral assignment very difficult.

Using vacuum ultraviolet (VUV) single-photon ionization these fragmentation processes are greatly reduced as demonstrated in the following examples. Single-photon ionization using a VUV source is generally considered as a "soft" ionization method because efficient ionization can occur with relatively low light intensities so that multiple-photon absorption is unlikely, and only modest amounts of excess internal energy can be deposited in the resulting photoion. (The larger the molecule, the longer internal energy can remain in the molecule without causing fragmentation thus making this type of ionization increasingly soft with increas-

ing mass.) Furthermore, single-photon ionization cross sections are much more uniform from molecule to molecule relative to MPI,⁶ resulting in more quantitative detection probabilities. Thus when there may be a wide range of molecules to be detected, as is the case for polymer surface analysis, the single-photon ionization approach has distinct advantages over MPI.

Mass spectra in this paper were obtained by photoionization of sputtered neutral molecules from bulk polymer surfaces under low-dose sputtering conditions. "Low-dose" irradiation here means $< 10^{13}$ incident ions/cm² during the course of the measurement. Bulk polymers are much more difficult to analyze by mass spectrometry than dispersed samples due to the extensive intertwining of the molecules and the resulting difficulty in removing significant sized fragments from the surface. Nevertheless, the bulk structural polymer case is the case of primary practical as well as scientific importance and therefore most in need of attention.

II. EXPERIMENTAL DETAILS

The SALI experimental technique is described in detail in Ref. 5. For these studies, a pulsed Ar⁺ or Xe⁺ beam from a duoplasmatron ion gun was incident at 60° from normal for sputtering. The range of ion beam parameters used in this work was 0.5 to 2.0 μ A dc current at 5–7 keV with ~ 7 - μ s pulse widths. Experiments were run at 10 Hz with a delay between the ion gun and the light source allowing for the flight time of the neutral molecules from the sample surface to the ionization zone located ~ 1 mm above the sample. The reflecting time-of-flight mass spectrometer is arranged so that secondary ions are electrostatically rejected while photoions are analyzed⁵; alternatively, time-of-flight SIMS spectra can be recorded with minor adjustment in the mass spectrometer voltages.⁷ The signal from a dual microchannel plate assembly passed through a variable VHF attenuator and a fast linear amplifier before being recorded in analog fashion by a 100-MHz transient digitizer.

The VUV (118-nm, 10.49-eV) radiation was obtained by third-harmonic generation of the third-harmonic output of a Nd:YAG laser (355 nm) in Xe phase matched with Ar⁸; this was found to be optimized with ~ 15 -Torr Xe in 160-Torr Ar for our laser with 20-mJ input into a 50-cm focal length input lens. This arrangement gave 10-ns pulses of $\sim 1.3 \times 10^{12}$ photons/pulse corresponding to 220 W which was focused into the UHV chamber by a LiF lens which also served as a window. By directing the collinear light beams off the center axis of the lens, the "fundamental" at 355 nm was dispersed by ~ 3 mm from the VUV beam at the sample position which was sufficient so that only the 118-nm light contributed to the signal given the experimental geometry. The 248-nm radiation was generated by an excimer laser operating on KrF.

One of the major problems encountered when studying insulating materials using ion bombardment is sample charging. This problem is often controlled by electron beam neutralization.⁹ However, at electron energies above ~ 20 eV these electrons may contribute significantly to sample damage as well as to desorption. In this work, because a low-

energy electron source was not available, samples were covered with a 90% transmission tungsten mesh which reduced charge buildup on the sample surface. All bulk samples studied in this work were introduced into the UHV chamber without any pretreatment.

III. RESULTS AND DISCUSSION

A. Poly(tetrafluoro-ethylene) (Teflon)

The low molecular weight, simple structure of the CF₂CF₂ repeat unit, and relative ease of sputtering makes poly(tetrafluoro-ethylene) (PTFE) a good candidate for a first investigation. Characteristic fragmentation patterns of this bulk polymer previously have been obtained by SIMS and LDMS.^{2,4,9}

Figure 1 displays spectra taken from 10 000 Ar⁺ ion and laser pulses using single-photon ionization with 118-nm laser radiation ($\sim 3 \times 10^3$ W/cm²). Figure 2 shows spectra taken with 248-nm radiation ($\sim 10^8$ W/cm²) with ion beam conditions identical to those for Fig. 1. Both spectra show some characteristic low-mass fragment peaks which help to

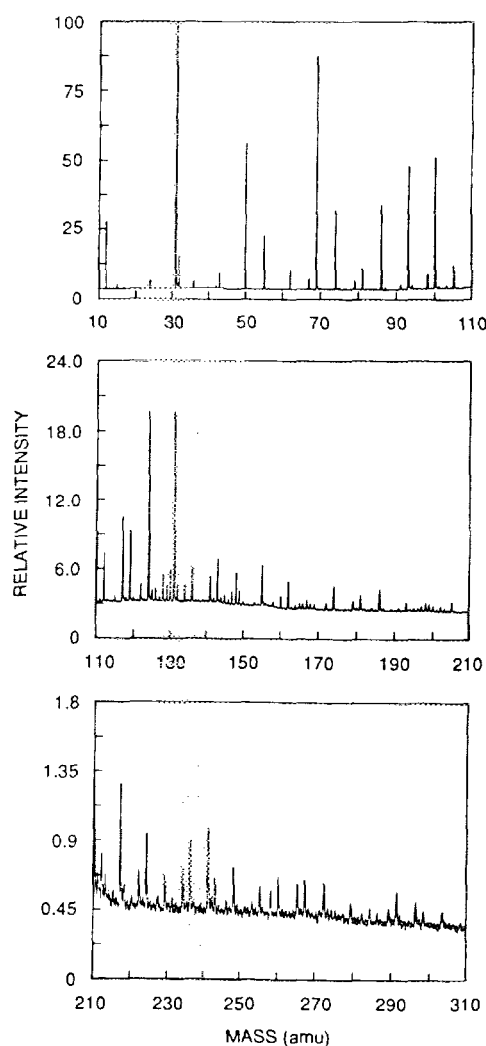


FIG. 1. SALI mass spectrum of untreated PTFE taken with 10 000 pulses of Ar⁺ bombardment at 7 keV and 118-nm radiation for single-photon ionization at $\sim 3 \times 10^3$ W/cm².

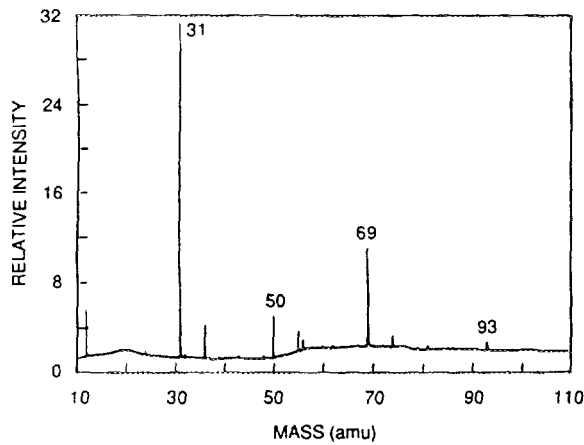


FIG. 2. SALI mass spectrum of untreated PTFE taken with 10 000 pulses of Ar^+ bombardment at 7 keV and 248-nm radiation for multiphoton ionization at $\sim 10^8 \text{ W/cm}^2$.

serve as a fingerprint for this material, for example, $m/e = 31$ (CF), 50 (CF_2), 69 (CF_3), and 93 (C_3F_3).

The relative intensities of mass peaks in the two spectra are clearly quite different; intensities of fragment peaks decrease faster with mass in the MPI spectrum, thus showing that fragmentation during the multiphoton ionization process is decreasing the abundance of high-mass fragments. Various laser powers at 248-nm were used, none giving any better high-mass results than shown. For the spectrum taken with 248-nm radiation, for masses not plotted, only low signal peaks at 117, 119, 124, and 131 amu were found. The C_2F_4^+ fragment at $m/e = 100$, the polymer repeat unit, is not present in the MPI spectrum at all, whereas with 118-nm photoionization it is one of the prominent peaks. The spectrum in Fig. 2 was taken with low laser power but sufficient to give adequate signal-to-noise ratios; increasing the laser power by a factor of 4 gave mostly C^+ and CF^+ fragments. In contrast, Fig. 1 shows a fairly intense long progression of fragments corresponding to C_xF_y , giving a much superior and unambiguous "fingerprinting" of the bulk polymer. In addition, high-mass fragments beyond $m/e = 400$ (not shown in the figure) can be easily detected using 118-nm ionizing radiation for this amount of signal accumulation. The SIMS^{2,9} and LDMS⁴ spectra of PTFE are similar to that found in Fig. 1 though there are significant differences, including a trend to higher masses in the SALI data.

The neutral C and CF_2 species have ionization potentials higher than the photon energy (10.49 eV); the appearance of these mass peaks in Fig. 1 is likely due to photofragmentation of larger species, probably aided by significant internal excitation from the sputtering process. This indicates that fragmentation can still occur at 118 nm, although it clearly is much less extensive than for the MPI process. An alternative mechanism to produce the C and CF_2 ions is photoionization of those neutral C and CF_2 moieties having sufficient internal (metastable electronic and/or vibrational) excitation caused by the sputtering process to make the ionization continuum energetically accessible.

B. Polyamide nylon 66

For polymers of more complex molecular structure, the need to obtain structural information using mass spectra increases. At the same time this information has been particularly difficult to obtain for bulk material. The SALI technique together with single-photon ionization promises to make a significant contribution in this area. As an example, Fig. 3 shows the SALI spectrum of the random copolymer nylon 66 taken with 1000 pulses of Xe^+ bombardment at 7 keV and 118-nm radiation for ionization.

The low mass range of the spectrum ($m/e < 100$) is dominated by small fragments, containing C, H, N, and O. Only large fragments of the polymer chain give definite structural information. The rather intense and distinct higher mass peaks appear at $m/e = 368$ and 353 which are greater in mass than the polymer repeat unit ($m/e = 226$). These features can easily be related to the structure of this particular polymer formed from the diamine (monomer subunit $M_1 = 114$ amu, see Fig. 3) and the dicarboxylic acid (corresponding monomer subunit $M_2 = 112$ amu). While the repeat unit ($M = M_1 + M_2 = 226$ amu) is not seen in the

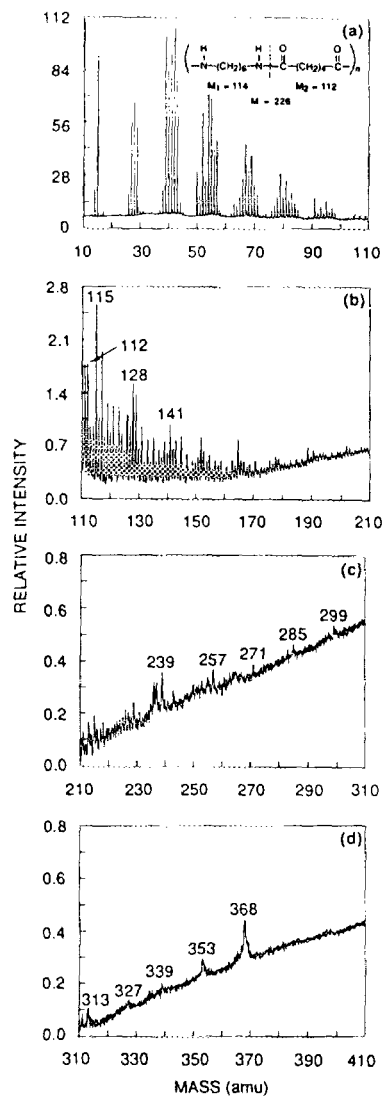


FIG. 3. SALI mass spectrum of untreated nylon 66 using 1000 pulses of Xe^+ bombardment and 118-nm radiation for one-photon ionization at $\sim 3 \times 10^3 \text{ W/cm}^2$. Particularly noteworthy mass peaks are discussed in the text. The slope of the base line is due to rf pickup by the particular amplifier used here.

spectrum, for example, the peak at 239 amu can be assigned to $M + CO-NH$, and in particular, the three highest mass peaks at 339, 353, and 368 amu show evidence for preferential cleavage of the N-C bonds leading to fragments of MM_2H , MM_2NH , and $HNMM_2NH$, respectively. These last three assignments give definite structural information and also provide some insight into the sputtering process for this material. Some other noteworthy mass peaks include m/e 115 (M_1H) and m/e 128 (M_2NH_2). These assignments clearly reveal the structure of nylon 66.

Spectra obtained using 248-nm laser light at several intensities were unsuccessful, giving only small fragment peaks at ~ 80 amu and below. Unlike the partial success for the Teflon with this wavelength, no satisfactory spectrum could be obtained in the sense that no significant structural information could be discerned.

A SIMS spectrum has been reported for nylon 66 previously.¹⁰ While there is some similarity between the positive ion SIMS spectrum and the SALI spectrum there is in general much less similarity between the two than found for PTFE. The SALI spectrum appears more easily interpretable especially with the "triplet" of peaks at 339, 353, and 368 amu. Further study comparing SALI and SIMS spectra should provide insight into the sputtering process *per se* for this material and the ion formation process during sputtering.

C. Poly(ethylene-glycol)-monostearate

This bulk sample contains the polymer chain poly(ethylene-glycol) (PEG) (monomer unit at $m/e = 44$ amu, with ~ 130 repeat units on average) terminated on one side by a stearate group. The spectrum shown in Fig. 4 was taken with 1000 pulses of Ar^+ ion bombardment and 118-nm radiation for ionization.

Low-mass fragments ($m/e \leq 100$ amu) are mainly due to fragmentation of the aliphatic hydrocarbon chains $(CH_2)_n$, which tend to overlap the PEG repeat unit at $m/e = 44$ and related fragments. Notable mass peaks at $m/e = 60$ and 73, assigned to MO^+ and $M(CH_2)_2H^+$ respectively, are indicative of the polymer chain. There are some significant differences in the spectrum relative to bulk PEG (without the monostearate), not shown, suggesting high end group segregation or high end group sputter yields.

Most of the peaks in the intermediate mass range ($m/e = 110-250$ amu) can be assigned to $(CH_2)_n^+$ and $(CH_2)_nOH^+$ fragments of the stearate. The stearic acid parent mass appears at $m/e = 284$ amu; it is not known yet if there may be some segregation of stearic acid contaminant in this sample which would also obscure the signature from the PEG. The intense peak at 256 amu can be assigned to $CH_3(CH_2)_{16}OH^+$ which may be due to a rearrangement or perhaps represents a contaminant itself. A signal is observed at 311 amu corresponding to the monomer plus the stearate end group. Higher mass fragments can probably be detected with more signal averaging although the limitation in observing higher masses, as with most other bulk polymer samples, is a decreasing sputter yield rather than a loss in detection sensitivity or photofragmentation, now that one-photon ionization is employed.

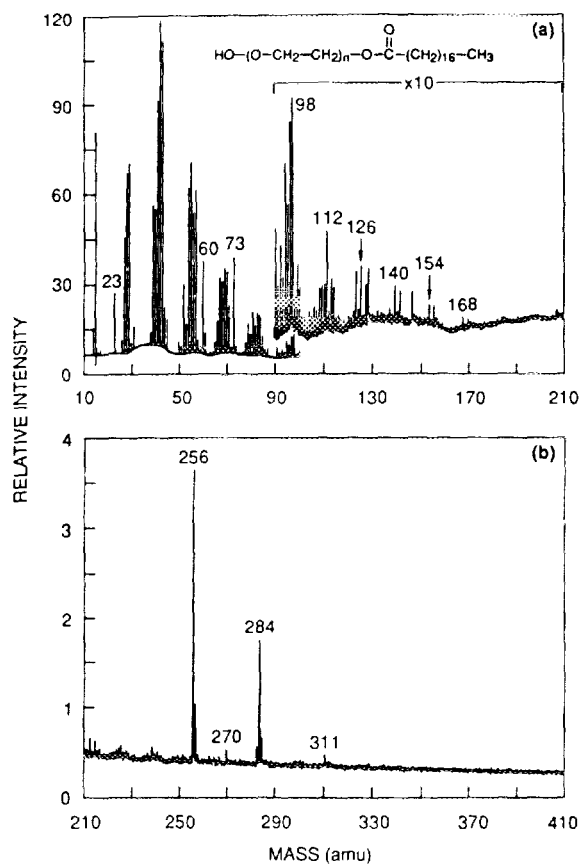


FIG. 4. SALI spectrum of poly(ethylene-glycol)-monostearate using 1000 pulses of Ar^+ bombardment and 118-nm radiation for one-photon ionization at $\sim 3 \times 10^3$ W/cm². See text for discussion.

Similar to the nylon case, and for most other bulk polymer systems we have investigated, no valuable spectra could be obtained using 248 nm, measuring at several power densities. Only low-mass fragments $< \sim 80$ amu were observed, revealing essentially no structural information.

IV. CONCLUSIONS

Mass spectra have been generated from insulating untreated bulk polymers by rare-gas ion sputtering and laser postionization of sputtered neutrals using near UV (248 nm, 5.0 eV) and VUV (118 nm, 10.5 eV) radiation. Multiphoton ionization at 248 nm leads to fragmentation that strongly depends on the laser power used. However, usually no operating laser power at 248 nm could be found providing structurally informative spectra due to extensive fragmentation. Using VUV radiation at 118 nm, produced at fairly high intensities by straightforward frequency tripling in a Xe-Ar mixture, this fragmentation is greatly reduced leading to much more extensive and interpretable spectra.

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