

**SURFACE ANALYSIS OF RUBBERS AND PLASTICS USING  
SECONDARY NEUTRAL MASS SPECTROMETRY\***

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**"SURFACE ANALYSIS OF RUBBERS AND PLASTICS USING  
SECONDARY NEUTRAL MASS SPECTROMETRY"**

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# SURFACE ANALYSIS OF RUBBERS AND PLASTICS USING SECONDARY NEUTRAL MASS SPECTROMETRY\*

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## ABSTRACT

Rubber and plastics are complex mixtures of long-chain polymers, smaller organic additives used as plasticizers, mildicides, fungicides, colorants, etc., and inorganic additives such as carbon and silica. Surface analysis of such materials is at once difficult and important. The difficulty lies in the need to identify specific carbon molecules on a very similar organic surface. The importance arises from the dramatic effect that the distribution and concentration of additives have on the physical properties of polymeric materials.

Recently we have had some success in applying laser desorption/laser postionization mass spectrometry in measuring the surface concentration and distribution of both additives and the polymer molecules themselves. The key has been to use the photoionization properties of the analyte of interest to augment mass spectrometric information.

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## INTRODUCTION

Modern materials, such as plastic and rubber, consist of a heterogeneous mixture of a wide assortment of compounds. The interaction, migration, and morphology of the components of these

complex materials determine not only their performance and aging characteristics, but also the ability of these materials to be safely and cheaply recycled or scrapped. Analysis of these materials is extremely difficult because of the similarity of the components used, and because it is important to measure minority species that may be present only in certain phases. In recent years the invention and optimization Matrix Assisted Laser Desorption Ionization (MALDI)<sup>1-8</sup> and Electrospray Ionization instruments for bulk analysis of polymers, and of Time of Flight Secondary Ion Mass Spectrometers (TO-SIMS) for analysis of polymer surfaces<sup>9-102</sup> have made significant strides toward analysis of these complex materials.

While powerful, the potential for TOF-SIMS to become a routine, quantitative surface analytical tool for polymer and rubber analysis is limited because the ion signal reflects not only the amount of various analytes in a given sample but also the product of ionization and desorption yields.<sup>77</sup> Quantitation is complicated further, because the ionization and desorption yields are strongly matrix and surface condition dependent.<sup>14,48,73</sup> For the past several years we have examined secondary neutral mass spectrometry as a method that allows separate optimization of desorption and ionization conditions with some success.<sup>103-120</sup> In this technique, an independent laser source is used to intercept and photoionize the desorbing surface flux. A variety of laser postionization methods have been tried in an attempt to find an ionization laser that is at once efficient, non-selective and non-fragmenting. Among these sources are intense multiphoton methods, femtosecond lasers<sup>106,110,121-124</sup> and Vacuum Ultra Violet (VUV) single-photon ionization sources.<sup>103-105,111-114,118-120,124-126</sup> It is the intention of this paper to convince the reader of the efficacy of VUV single-photon ionization as an effective tool for surface analysis.

## EXPERIMENTAL

Two separate laser postionization apparatuses have been used in this study. Each apparatus used has been described in detail elsewhere.<sup>103,106,108,119,127</sup> Samples are placed into an ultrahigh vacuum chamber and analyzed via time-of-flight mass spectrometry. A schematic diagram of one of the

instruments is shown in Figure 1. It has three major parts: the desorption source, the photoionization lasers, and the time-of-flight (TOF) mass analyzer. We describe each in turn.

In our instruments, either of two desorption source types may be used for molecular analysis; ion beams or lasers. Two ion guns are available for surface analysis and sample cleaning. The first is a Colutron 101 Q ion source that delivers 5 keV  $\text{Ar}^+$  ions into a millimeter spot on the surface. The second is an IonOptika liquid Ga ion gun that delivers 20 keV  $\text{Ga}^+$  ions into a submicron spot. The  $\text{Ga}^+$  beam can be rastered on the surface to produce an image.

The analyses in this paper were obtained via laser desorption, and here many choices are available. The desorption laser need not be powerful, but must be pulsed and preferably should be stable both pulse-to-pulse and over long periods. Three different desorption lasers were used in this work. A Laser Science, Inc.  $\text{N}_2$  laser (model VSL-337ND) operating at 337 nm was used for analyzing fullerenes, self-assembled monolayers, and Tinuvin 234. The fifth harmonic of a Continuum Nd:YAG laser (model #661-20), at a wavelength of 213 nm, and a KrF excimer (Questek, model 2650) were used for analyzing a polyurethane/polycarbonate laminate. Each desorption laser source was focused onto the sample surface using an all-reflecting Schwarzschild microscope. 108

The Schwarzschild microscope consists of two concentric spherical mirrors – a 3.8-cm-diameter convex mirror with a 5.08-cm-radius of curvature and a 17.8-cm-diameter concave mirror with a 14.7-cm-radius of curvature. The microscope has a magnification of 19 and a working distance of 8.13-cm. The working distance is sufficient to allow introduction of ion extraction optics without obscuration of the 0.47 numerical aperture of the microscope. The microscope is arranged so that one of the conjugate planes of the system (object) is the front surface of the sample. The second conjugate plane (image), is located 81.3-cm from the sample and outside the vacuum chamber of the instrument. This is accomplished using a third plane mirror installed at a  $45^\circ$  angle to the principal axis of the Schwarzschild microscope. Each spherical mirror has a hole drilled through its central obstructed field (the smallest being 1.5 cm in the convex optic) to allow photoions to travel through the microscope objective and into the TOF mass spectrometer. The

all-reflecting nature of this microscope objective ensures achromatism. Using dichroic optics it is possible to use the microscope for sample viewing and laser desorption at the same time. This magnified optical view of the sample surface, imaged on a CCD camera and displayed on a TV monitor, is critical in finding and analyzing the microscopic grains. Presently, the optical resolution of the instrument is  $\sim 1 \mu\text{m}$ .

The second major component of the laser postionization apparatus is the photoionization laser. Three different lasers were used. The first was the third harmonic of the tripled Nd:YAG described above, at a wavelength of 355 nm. Typically approximately 20 mJ in a 6 ns pulse were delivered into a  $3 \text{ mm}^2$  volume immediately above the target surface. The second was the 193 nm ArF output of the Questek excimer described above. In this case the 3 mJ, 20 ns pulse was focused into a volume roughly  $3 \text{ mm}^2$  position just above the surface.

The final ionization source utilized in this work was a VUV source capable of producing 118 nm photons. The technique for 118 nm production has been described before.<sup>113</sup> Briefly, 118 nm radiation was produced by frequency tripling the third harmonic of a Nd<sup>3+</sup>:YAG laser (355-nm). The 355 nm beam was focused with a nominally 25-cm focal-length lens into a gas cell containing 65 Torr of a nonlinear medium composed of  $\sim 1:10$  Xe/Ar mixture. The large difference between the refractive index of the MgF<sub>2</sub> lens at the YAG third harmonic ( $n = 1.385$  at 355 nm) and ninth harmonic ( $n = 1.67$  at 118 nm) wavelengths caused separation of the ultraviolet and vacuum ultraviolet beams. Therefore, focusing off-axis allowed the spatial separation of the 118 and 355 nm beams in the photoionization region of the mass spectrometer. A 355-nm mirror was placed inside the vacuum chamber to divert the less dispersed light into a beam dump outside the vacuum chamber for monitoring the 355 nm radiation. Although the spot size was not measured, we calculated the ultraviolet radiation to be focused to a 40 micron diameter spot and the intensity of the generated VUV radiation to be approximately 100 nJ ( $10^{10}$  photons/pulse) assuming a  $10^{-5}$  efficiency for conversion.

The final part of the instrument is the TOF mass spectrometer. In simpler instruments this consists of a pair of charged grids to accelerate ions into a linear drift region, after which they strike a microchannel



plate and generate the analytical signal.<sup>103,119</sup> In the instrument of Figure 1, the TOF begins with the extraction optics. Prior to photoionization, but after desorption, voltages on the extraction optics are adjusted to reject direct ions (those formed during the desorption event). Immediately following photoionization, pulsed voltages on the extraction optics push the photoions into the TOF mass analyzer. The extraction optics are carefully designed to efficiently extract from the large photoionization volume and yet allow for high mass resolution ( $m/\Delta m > 1000$ ). This mass resolution is achieved through a combination of pulsed draw-out compression and the use of an ion mirror (reflectron). In combination these two reduce the mass dispersion caused by the energy spread in extracted photoions. This energy spread is induced both by the broad energy distribution of desorbed species and by the large extraction volume.

Each measurement cycle consists of the following sequence: (1) a desorption laser, focused on a polymer surface or standard, produces a cloud of neutral atoms, ions and molecules; (2) a voltage pulse is applied to an extraction electrode to electrostatically suppress the ions; (3) a photoionization laser beam intersects the cloud of neutral species above the sample, generating photoions; (4) a positive 2000 V target pulse extracts and accelerates these photoions; (5) the photoions are mass-analyzed in a reflectron-type time-of-flight mass spectrometer with 4 m long flight path; (6) data are collected in an ion counting mode, in which the signal produced by a single photoion is converted to a normalized voltage pulse (500 mV, 5 ns) and digitized in a 200 MHz transient recorder.

## RESULTS and DISCUSSION

Rubber and plastics are complex mixtures of long-chain polymers, smaller organic additives used as plasticizers, mildicides, fungicides, colorants, etc., and inorganic additives such as carbon and silica. Often simpler models are used to test analytical capabilities. Figures 2 through 4 demonstrate the use of two such model systems, fullerenes and self-assembled monolayers (SAMs). Figure 2 compares the multiphoton ionization of laser desorbed  $C_{60}$  with that of one photon ionized laser desorbed  $C_{60}$ .

Figure 2 compares the multiphoton ionization of laser desorbed  $C_{60}$  with single photon ionization. When light interacts with desorbed neutral  $C_{60}$  molecules in the gas phase three major processes can occur: direct ionization, dissociation into neutral and ionic fragments, and delayed ionization. In the case of 355 nm multiphoton ionization, all of these processes can occur only after absorption of more than one photon. Delayed ionization is responsible for the substantial broadening of the  $C_{60}^+$  primary ion peak and has been attributed to a process similar to thermionic emission.<sup>114,128,129</sup> The absorbed electronic energy is rapidly internally converted into ro-vibronic energy. Delayed thermionic emission leads to the broad molecular feature. Dissociation leads to even-numbered ion fragments in the range  $C_{60}^+$  to  $C_{32}^+$ . In contrast, direct ionization becomes the preferred channel as the photoionization laser wavelength is decreased. At photon energies above the ionization potential direct ionization can occur following the absorption of a single photon. At 118 nm the primary ion mass peak is the only channel.

Figures 3 and 4 show spectra from self-assembled thiol monolayer samples. Substrates were prepared from silicon wafers that were coated first with a binder layer of chromium and then with a 20 nm overlayer of gold. The gold surfaces were then immersed overnight in solutions of alkanethiols or dialkyl disulfides. Figure 3 shows the 337 nm laser desorption/118 nm photoionization mass spectrum of a  $C_{14}H_{29}SH$  self-assembled monolayer on a gold surface. The major photoion produced was the disulfide dimer of the adsorbed species,  $(C_{14}H_{29}S)_2^+$ , rather than the thiol itself. Multiphoton ionization and direct ion (i.e. one laser to both desorb and ionize simultaneously) spectra showed only the thiol accompanied by many smaller fragment peaks. Single-photon spectra taken of the thiol in the gas phase and of multilayer samples showed only the monomeric thiol, demonstrating the dimers were produced only when the thiol was directly attached to the gold surface and was irradiated with the desorbing laser pulse.<sup>104,105,126</sup>

Figure 4 shows the single-photon ionization spectrum of a monolayer formed by depositing exposing the gold surface to a solution of dialkyl disulfides, in this case  $(C_{14}H_{29}S)_2$  and  $(C_{12}H_{29}S)_2$ . As in the thiol case, only disulfides are seen in the neutral flux after laser desorption when single-photon ionization is used, but in this case a new asymmetric disulfide is produced, namely  $C_{12}H_{29}SS C_{14}H_{29}$ . This indicates that disulfides adsorb dissociatively on gold to form thiolates, and that the thiolates desorb

dissociatively to form disulfides, since the mixed dimer would be absent if the disulfides remained intact on the surface of the substrate. The explanation lies in the fact that the energy difference between one S-S bond and two Au-S bonds is only a few kcal/mol<sup>130,131</sup>, so that the energy required to break the S-S bond during adsorption of a disulfide is compensated by the energy released in forming the two Au-S bonds. Similarly, the formation a S-S disulfide bond compensates for the breaking of two Au-S bonds during desorption. Such behavior can only be seen using single photon techniques.

Figures 5-7 demonstrate the utility of 118 nm photoionization for samples that are closer to commercial test cases. Figure 5 is the 337 nm laser desorption/118 nm photoionization time of flight spectrum of a polystyrene sample with a UV stabilizer added (1% Tinuvin 234). The primary mass peak of the additive is clearly visible in the mass spectrum, in addition to the two major polystyrene fragments, styrene and toluene, produced by unzipping and fragmenting the polymer backbone. Multiphoton ionization fragmented the additive and made detection much more difficult by 1) distributing the ion signal among many mass channels, thus reducing the signal-to-noise ratio, and 2) generating isobaric interferences with the polymer fragments. In this case the polymer was simple and depolymerized rapidly when irradiated with the desorption laser to give fragments well separated from the additive peaks. Thus single-photon ionization, which is a relatively non-selective technique for organic molecules, can be used to advantage. In cases where isobaric interference with the polymer is a problem it is sometimes possible to use resonantly enhanced multiphoton ionization to get good results.<sup>113</sup>

A more complicated polymer system is shown in Figures 6 and 7. The sample is a laminate of a thermoplastic polyurethane (TPU) based on a C<sub>4</sub>-adipate and methylene diphenylisocyanate and a polycarbonate (PC) based on bisphenol-A. Distinguishing between the two polymers is difficult using an in-situ microprobe technique such as laser-desorption MS, owing to the structural similarity of the two polymer backbones and the presence of processing aids and mold release agents. Figure 6 shows laser desorption mass spectra taken from ~1 micron spots on each side of the laminate interface. At a photoionization wavelength of 193 nm (6.4 eV), nearly all ionization events are two-photon and result in severe fragmentation of the desorbed neutrals, which are themselves backbone fragments produced by the

desorption laser and exit the surface vibrationally hot. There are only a few peaks unique to the TPU spectrum, i.e. strong peaks which are either weak or absent in the PC spectrum, while the PC spectrum has no unique peaks. This was typical of all spectra in which the ionization step was multiphoton, regardless of the choice of ionizing laser.

In comparison, Figure 7 shows that the single-photon PC and TPU spectra are much cleaner and easier to distinguish from each other. The low mass region ( $m/z < 60$ ) of the TPU spectrum arises from the  $C_4$ -adipate portion of the backbone, which was present but indistinguishable from the fragmented PC spectrum in the multiphoton case. The higher mass regions of each spectra contain many peaks unique to each polymer, with the PC spectrum extending out to  $m/z$  720 (not shown).

This paper has of course largely ignored the difficulty and importance of choosing a desorption method that well matches the analytical problem of interest. For example, different fragment patterns are observed in the PC and TPU spectra depending on the choice of desorbing laser wavelength. Even when efficient, non-selective and non-fragmenting photoionization methods are used, surface analysis of polymers will remain a challenging problem due to the difficulties in understanding and optimizing desorption methods.

## CONCLUSIONS

Postionization of secondary neutrals produced either by ion or laser desorption can greatly increase the information content present in the mass spectra of polymers and rubbers in three ways. First, because the dominant portion of the desorbing flux is neutral, postionization can lead allow measurement of molecular constituents either at lower concentration levels or with less surface damage. This is particularly true for laser desorption/postionization where the threshold desorption laser intensity for neutral emission is generally significantly smaller than for secondary ion emission. Second, photoionization laser colors may be optimized to identify certain molecular components such as aromatic groups while maintaining for those molecules a high useful yield. Alternatively, by using VUV light

sources, nonselective photoionization gives the promise of easily quantifiable spectra. Finally, postionization allows separate optimization of the ionization source and the desorption source. The desorption method (ions or lasers) and its optimization is crucial to the successful analysis of molecular samples. Often desorption of intact surface molecules can be accomplished only under very restrictive conditions. Using a separate ionization source allows significantly more freedom in the choice of desorption conditions.

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## FIGURES

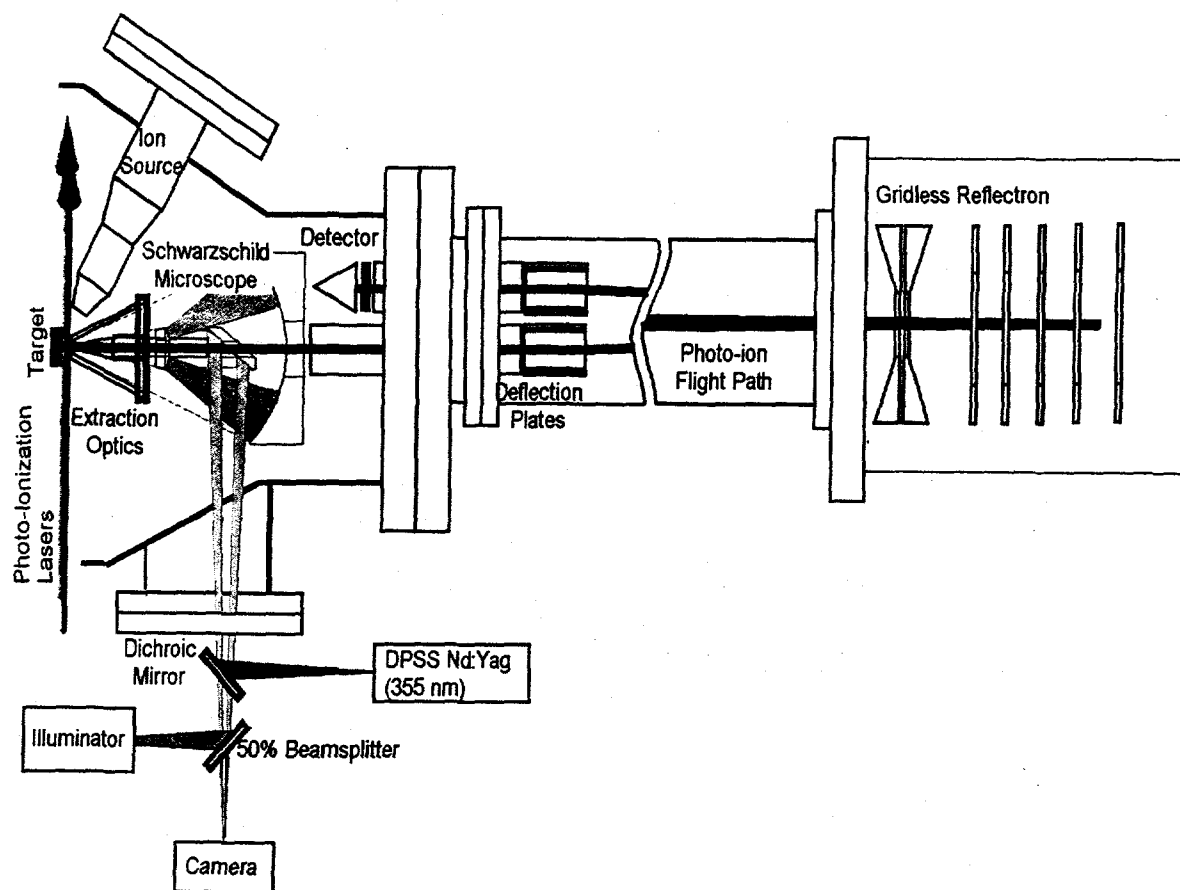


Figure 1. Shown is a schematic diagram of the RIMS apparatus. There are two desorption sources shown – a diode pumped solid state Nd:YAG laser and an ion source (either a fine focussed Ga ion gun or a 5 keV Ar<sup>+</sup> source). When using laser desorption, the laser was brought onto the target through a Schwarzschild microscope that also allowed sample viewing using a dichroic mirror. Material atomized from the target was photoionized using any of several lasers. The photoions are then pulse-extracted into a time of flight (TOF) mass spectrometer whose reflectron was used to improve the mass resolution ( $m/\Delta m > 1000$ ).

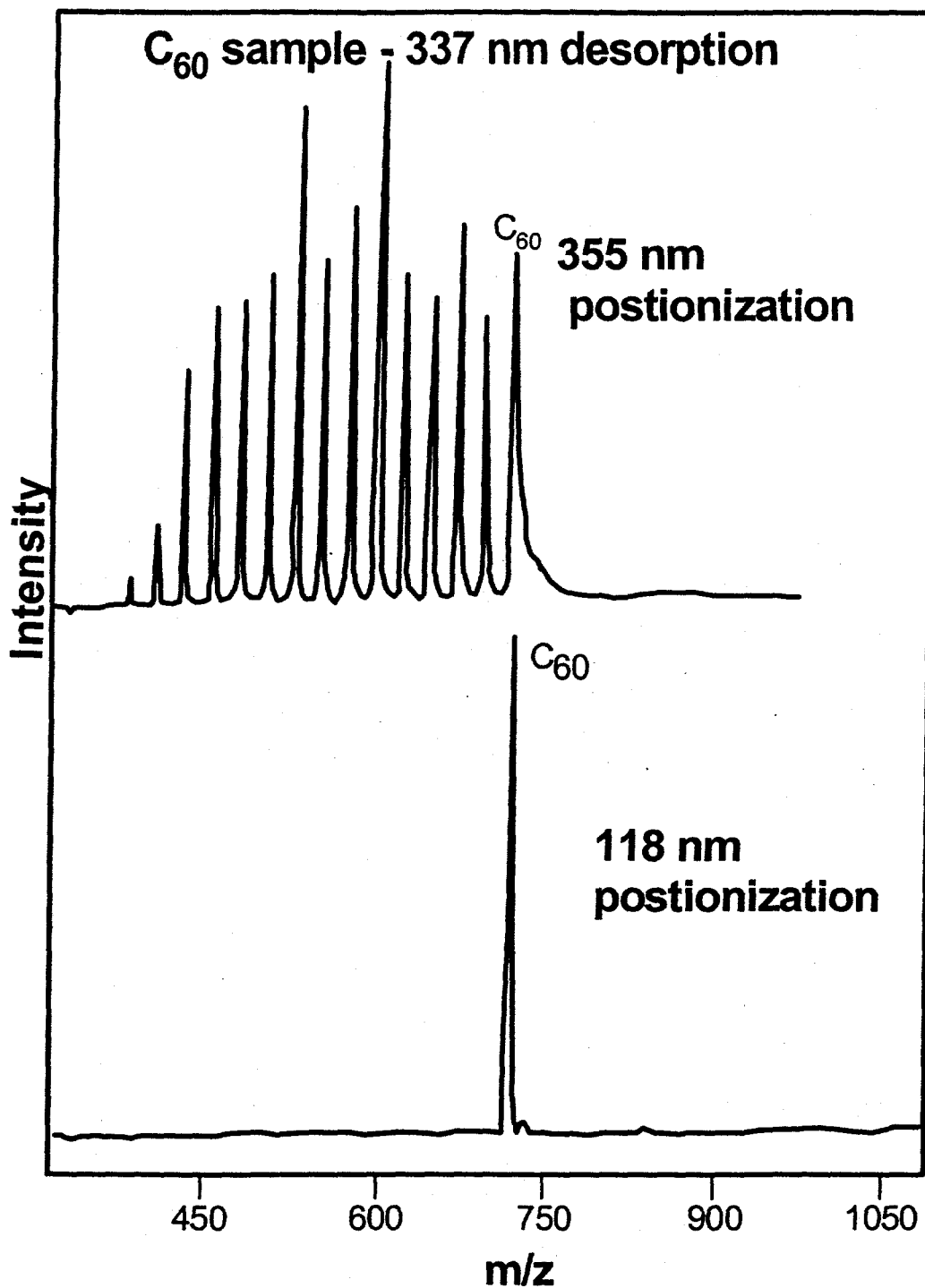


Figure 2. Laser Desorption/laser ionization Time of Flight spectra of a  $C_{60}$  sample deposited on a steel target holder as a toluene solution and allowed to dry. The top spectrum was obtained using a 355 nm photoionization laser. Note the significant fragmentation of  $C_{60}$  by consecutive  $C_2$  loss. Also note the significant broadening of the  $C_{60}^+$  primary ion peak. The lower spectrum was obtained with 118 nm photoionization and shows no fragmentation at all.

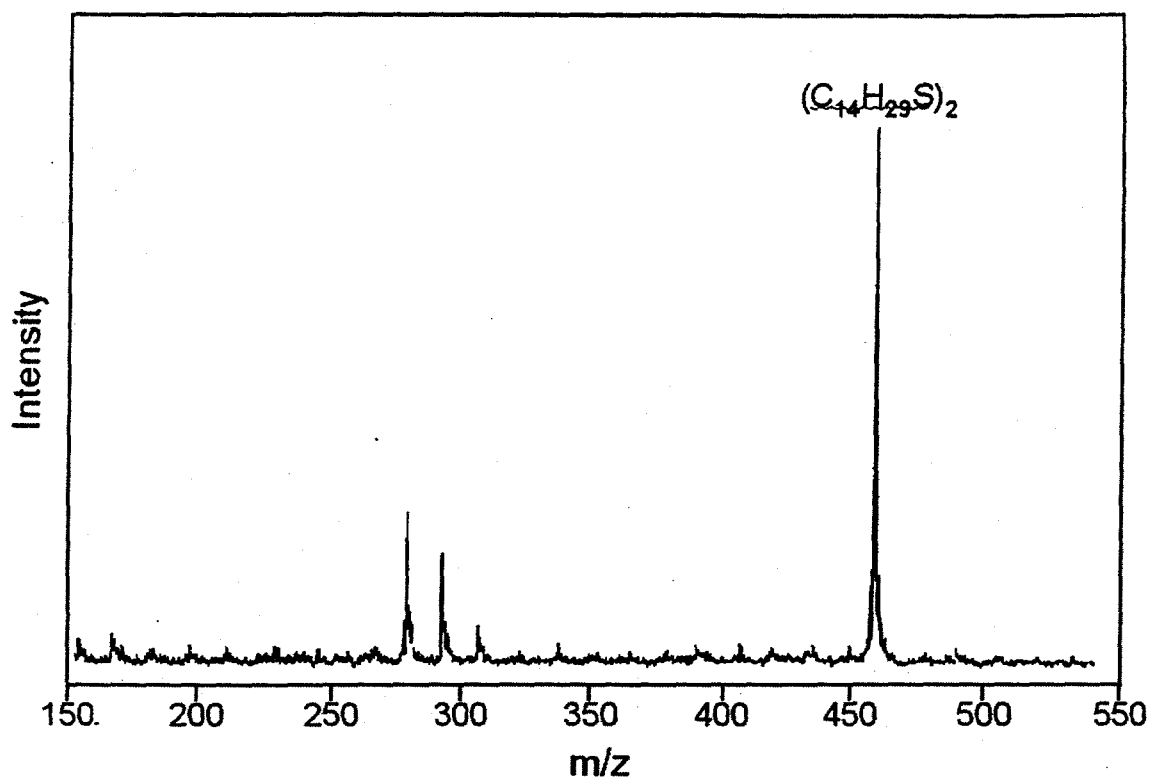


Figure 3. 337 nm laser desorption/118 nm photoionization time of flight spectrum of a  $C_{14}H_{29}SH$  self assembled monolayer on a gold surface. Note the lack of monomeric desorption. Almost all the desorption products are dimers.

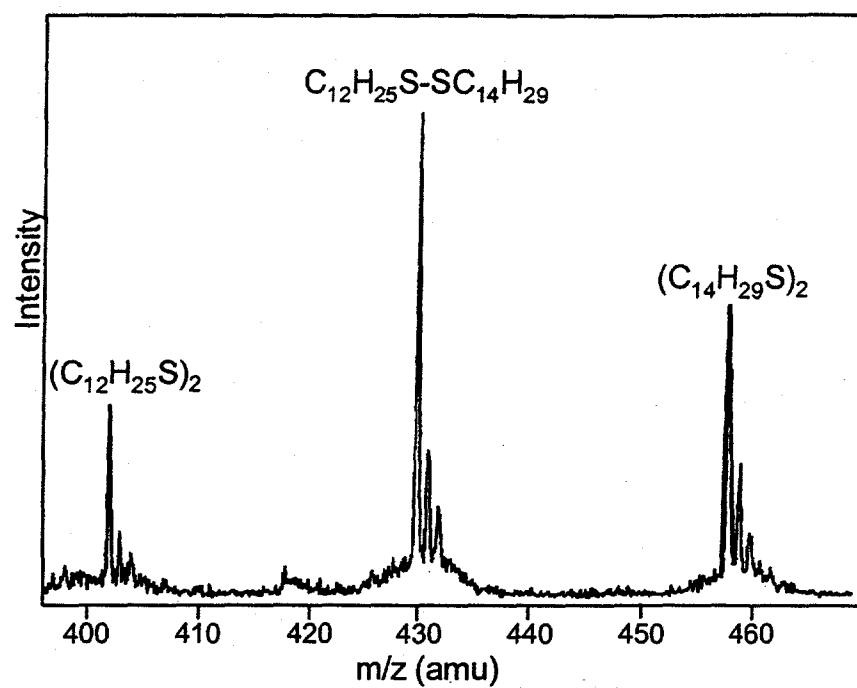


Figure 4. 337 nm laser desorption/118 nm photoionization time of flight spectrum of a mixed  $(C_{12}H_{25}S)_2$  and  $(C_{14}H_{29}S)_2$  self assembled monolayer on a gold surface. Note the randomization of the desorbing products.

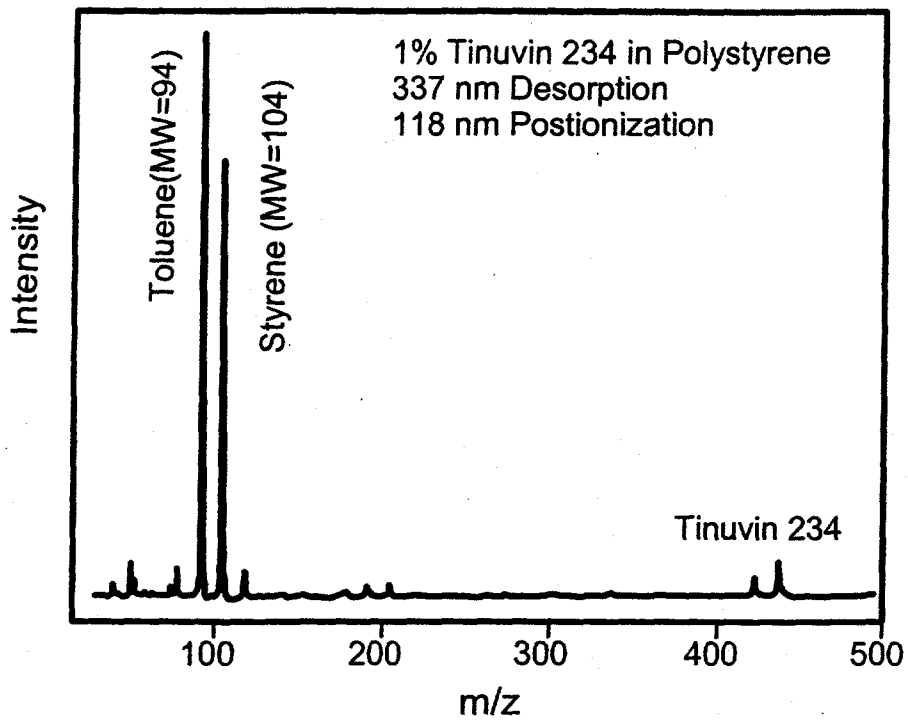


Figure 5. 337 nm laser desorption/118 nm photoionization time of flight spectrum of a polystyrene sample with a UV stabilizer added (1% Tinuvin 234).

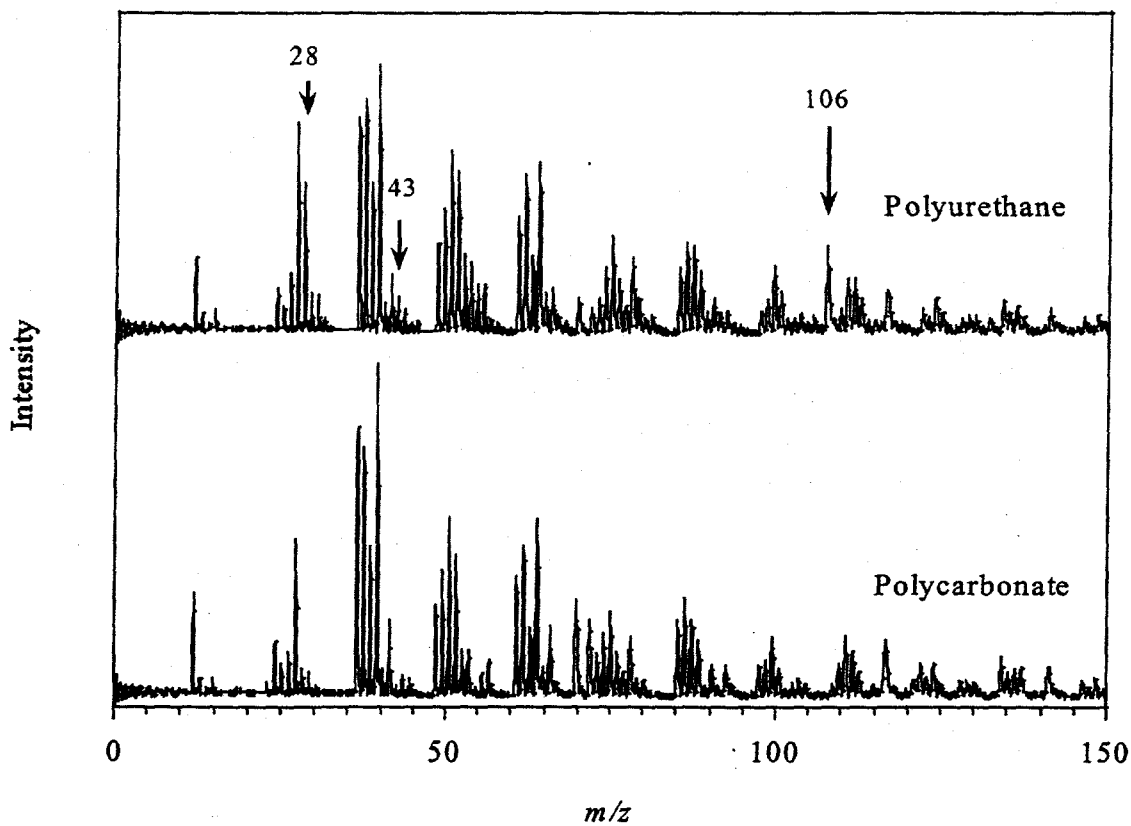


Figure 6. Comparison of thermoplastic polyurethane and polycarbonate laser desorption / multiphoton ionization mass spectra. The desorbing laser wavelength was 213 nm and the ionizing laser wavelength was 193 nm. Peaks unique to the polyurethane spectrum (i.e. having no strong counterpart in the PC spectrum) are  $m/z$  28 (CO), 43 (HNCO), and 106 (benzaldehyde).

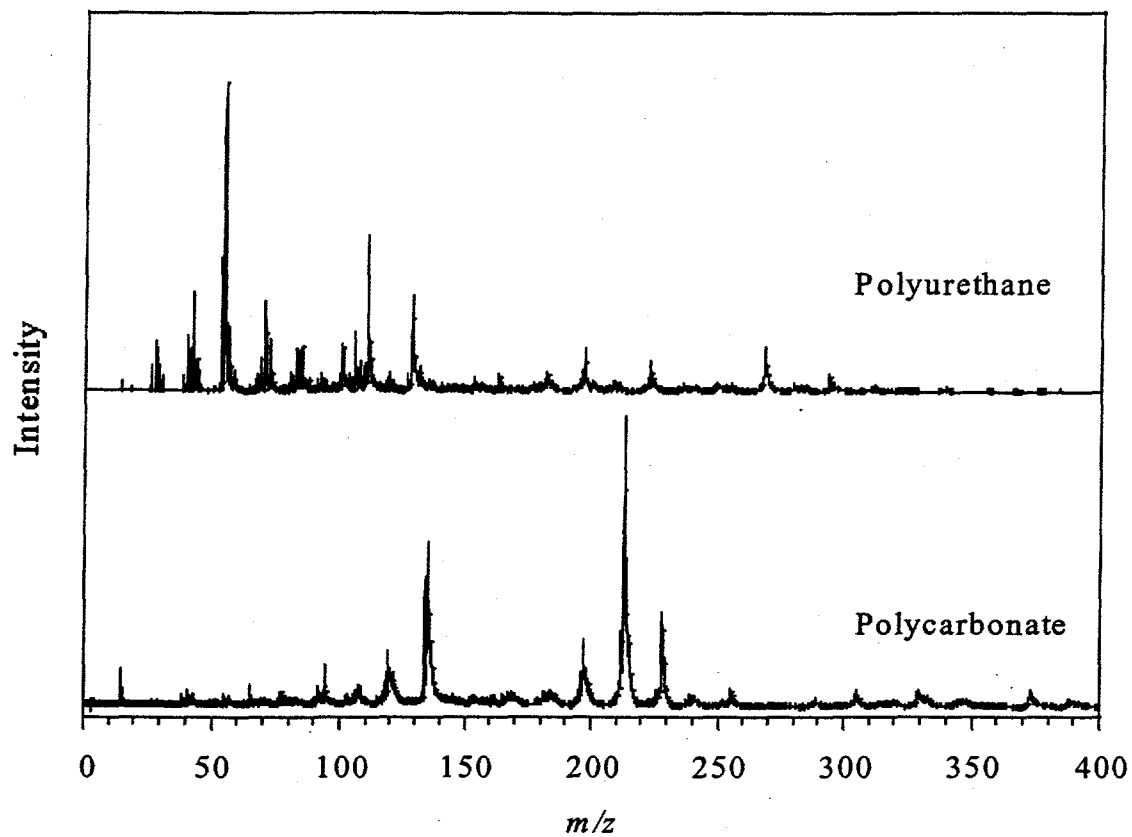


Figure 7. Comparison of thermoplastic polyurethane and polycarbonate laser desorption / single-photon ionization mass spectra. The desorbing laser wavelength was 248 nm and the ionizing laser wavelength was 118 nm.