Macromolecules **1996,** *29,* 7865−7871

Spatially Resolved in-Situ Analysis of Polymer Additives by Two-Step Laser Mass Spectrometry

Qiao Zhan,[†] Renato Zenobi,*,[†] Scott J. Wright,[‡] and Patrick R. R. Langridge-Smith[‡]

Department of Chemistry, Swiss Federal Institute of Technology (ETH), 8092 Zürich, Switzerland, and Department of Chemistry, King's Buildings, West Mains Road, The University of Edinburgh, Edinburgh EH9 3JJ, U.K.

Received April 12, 1996; Revised Manuscript Received August 16, 1996[⊗]

ABSTRACT: Two-step laser mass spectrometry has been employed for the direct in-situ analysis of a variety of additives in different polymers. Because of the high sensitivity and optical selectivity of this approach, mass spectra can be obtained directly from the polymer material. The effects of CO_2 laser irradiation (λ = 10.6 μm) on samples of poly(oxymethylene) (POM), poly(vinyl chloride) (PVC), polypropylene (PP), and poly(ethylene terephthalate) (PET) and the mechanism of additive desorption have been examined. Several hydroxyphenylbenzotriazole (Tinuvin) UV stabilizers as well as a phenolic antioxidant (Santo White) were successfully detected in typical industrial polymers. The detection limit for Santo White antioxidant in POM was found to be as low as 28 ppm. Finally, depth profiling by stepwise CO_2 laser ablation was carried out for a POM injection bar containing 0.1 wt % antioxidant. These spatially resolved measurements established that the near surface concentration of antioxidant was 40% lower than in the bulk.

Introduction

Polymers are among the most important materials used in today's world. Virtually all polymeric materials, both of synthetic and natural origin, undergo reactions with oxygen or degradation under sunlight. Oxidation can manifest itself in every stage of the life cycle of a polymer, e.g. during manufacturing and storage of the material or during processing and use. The UV component of sunlight, in the 290−400 nm wavelength range, leads to photochemical reactions in many polymers, which result in changes in their optical and mechanical properties. To improve their stability, additives protecting them against oxidation, UV radiation, weathering, etc. are widely used.[1,2]

Throughout the lifetime of the polymer, the additives will be depleted by photochemical reactions or by diffusion out of the host material, which can greatly influence the material properties. Normally, many different additives are used in a polymer formulation. UV stabilizers and antioxidants may be present in the polymer matrix at a level of only 1 wt % or less. Due to this low concentration and complex environment, sensitive and selective methods of chemical analysis are necessary to identify additives in a typical commercial polymer.

Because of the polarity and nonvolatilty of many UV stabilizers and antioxidants, gas chromatography is not commonly employed as an analysis method. However, other spectroscopic and liquid chromatographic methods are very powerful in identifying ingredients in compounded polymeric materials. High-pressure liquid chromatography (HPLC) or its combination with mass spectrometric detection (HPLC−MS) has been used for the analysis of additives in polymers.[3,4] Approximately 1 g of the polymer is necessary for extraction with solvents, typically acetone or acetonitrile, which may take 12 h or longer. Supercritical fluid extraction (SFE) offers a faster alternative for polymer extraction and SFE coupled with subsequent chromatographic separation is also employed for analysis of polymer additives.[5,6] However, in extraction-based analytical techniques, all information on the additive's spatial distribution within the polymer is lost.

As an alternative to extraction-based analytical methods, Lattimer and co-workers advocated the use mass spectrometric methods (FAB-MS, field ionization MS, pyrolysis−MS) for direct analysis of nonvolatile agents in polymer matrices.[7−10] Organic secondary ion mass spectrometry (SIMS) with[11,12] or without postionization[13] can be used for direct analysis of polymer surfaces. The drawbacks of FAB and SIMS are that they provide no selectivity for the detection of minor sample components. Also, these techniques deposit large amounts of energy at the sample surface and typically generate predominantly fragment ions of the polymer itself. Laser desorption (LD) and laser desorption/Fourier-transform ion cyclotron resonance (LD-FTICR) mass spectrometry have also been applied with considerable success to the detection of many classes of nonvolatile compounds including organic polymers.[14−19] Johlman et al. demonstrated that LD-FTICR could be used to identify polymer additives in polyethylene extracts. The spectra were found to contain intense quasimolecular ions (Na^+ and K^+ adducts) as well as fragments.[16−19]

Since its introduction by Hillenkamp[20,21] and Tanaka,[22] matrix-assisted laser desorption/ionization (MALDI) mass spectrometry has been widely used as a soft ionization technique that allows desorption and ionization of very large molecules, for example polymers.[22,23] However, this technique is employed neither as an *in-situ* analytical method nor as a selective method for detecting minor polymer constituents. This is due to the requirement that in MALDI the analyte must be well mixed with the matrix *prior* to analysis. Furthermore, the molecular weights of typical UV stabilizers and antioxidants are normally a few hundred mass units, a range that is often obscured by intense matrix peaks present in MALDI mass spectra.

---

* To whom correspondence should be addressed at: Analytical Chemistry Group, Department of Chemistry, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich, Switzerland. Tel: +41-1-632-4376. Fax: +41-1-632-1292. E-mail: ZENOBI@org.chem.ethz.ch.

[†] Swiss Federal Institute of Technology.

[‡] University of Edinburgh.

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1996.

S0024-9297(96)00547-5 CCC: $12.00

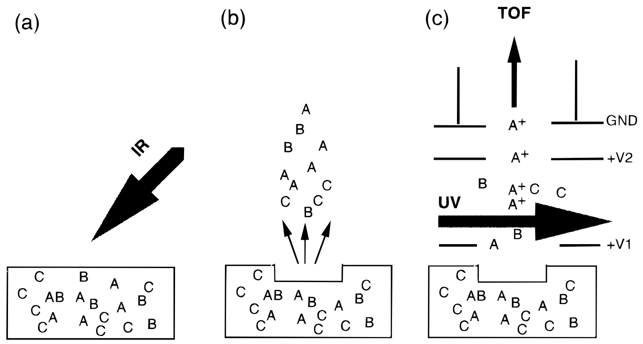


Figure 1. Principle of L2MS. A, B, and C are different additives. The polymer is irradiated by an IR laser pulse (a) and decomposes and is ejected from the bulk together with intact additives (b). Selective ionization is carried out by a UV laser with resonant two-photon ionization (c). Finally, the ions are mass-separated and recorded in a time-of-flight mass spectrometer.

Direct laser desorption/ionization mass spectrometry (LDMS) has proven to be quite useful for direct in-situ analyses,[24−26] but it suffers from ionization matrix effects. To circumvent this problem, a postionization step can be used. Lykke et al.[27,28] have used this approach to analyze vulcanizates in rubber and rubber extracts. They demonstrated that the use of different wavelengths for the postionization step provides important additional information about the chemical composition of the samples.

In the present study we have applied two-step laser mass spectrometry (L2MS) to the direct chemical analysis of additives in a range of polymers. It has been previously demonstrated that L2MS is a highly sensitive and optically selective method[29] which can serve as a very powerful tool for the direct detection of selected compounds in complex sample mixtures. This methodology decouples the desorption and the ionization step, allowing each process to be independently optimized. In brief, an infrared laser is used to irradiate the polymer and cause ablation, probably by a pyrolysis mechanism[30] (Figure 1a). During this ablation step the polymer is thermally decomposed and ejected from the bulk material, together with intact additives (Figure 1b). After a suitable time delay, the liberated molecules are intercepted by a pulse from a UV laser. This leads to soft ionization of the liberated species via a resonance-enhanced multiphoton ionization (REMPI) process. For common UV laser wavelengths, two photons are necessary to overcome the ionization potentials of the substances investigated here. If the first photon is resonantly absorbed by the molecule under study, a greatly enhanced ionization efficiency is found, providing a high degree of optical selectivity. The second photon then raises the energy of the excited molecules above the ionization threshold. Finally, a reflectron time-of-flight (TOF) mass spectrometer is used for mass separation of the ions produced (Figure 1c).

In order to analyze additives in a polymer sample with L2MS, it is necessary to desorb neutral species from bulk material. It was first reported in 1982 that with pulsed UV laser radiation, the surface of an organic polymer can be ablated to a depth ranging from 0.1 μm to several micrometers.[31] Nearly all organic polymers can be ablated by UV laser photodecomposition.[32−34] However, ionization of the ejected material often occurs simultaneously, which complicates mass spectrometric analysis of minority species such as additives. Infrared laser radiation, in contrast, excites vibrational states and can induce pyrolysis of polymers. Dyer et al. examined the irradiation of poly(ethylene terephthalate) (PET) films by radiation from a TEA CO_2 laser tuned to the 9R42 line ($\approx$9.2 μm).[35] They found that the PET film could be successfully ablated with 9.2 μm laser radiation. The major volatile ablation products found were carbon monoxide, carbon dioxide, methane, ethyne, ethene, benzene, ethanal, similar to products found in the purely thermal pyrolysis of PET.[30] In contrast, ablation of poly(ether ether ketone) (PEEK) with 9.2 μm laser light was found to be difficult.[30]

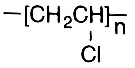
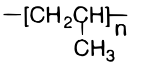
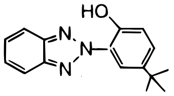
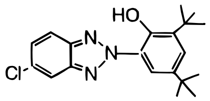
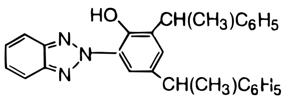
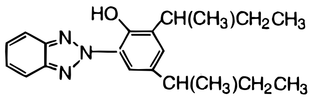
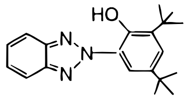
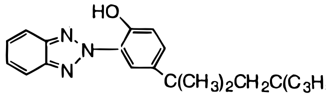
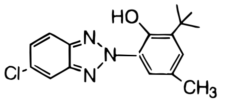
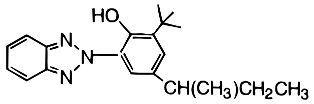
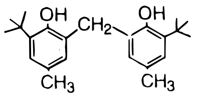
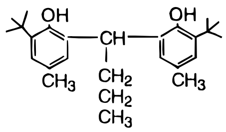
In this work, several complementary methods have been used to improve L2MS analysis of polymers and polymer additives. In preliminary studies, we found that for many polymers, no signals of polymer additives (dyes, antioxidants, UV stabilizers) could be detected by L2MS, although large craters were generated by IR laser irradiation of the polymer surface. We therefore studied the behavior of different polymers under 10.6 μm laser irradiation using IR spectroscopy and electron microscopy. We found that either laser-induced ablation or laser melting occurred for different polymers, depending on their IR absorption cross section. Information about the spatial resolution of IR laser ablation was also obtained from the electron microscopy studies. Direct in-situ detection of polymer additives as well as measurements of mass spectra for the pure additives were then carried out. Finally, stepwise CO_2 laser ablation was used to study the spatial distribution of an antioxidant in an injection-molded bar of poly(oxymethylene) (POM).

Experimental Section

Materials. Several different polymers were used in this study, most of them commercial polymers (PVC and PET sheets and a POM injection bar), although some samples did not contain additives and had to be mixed with UV stabilizers or antioxidants in the laboratory (e.g., POM powder, PP film). Pure POM powder, antioxidants, and a POM injection bar stabilized with $\approx$0.1 wt % of an antioxidant were obtained from DuPont (Geneva, Switzerland). A 100 μm thick PP film as well as the Tinuvin UV stabilizers were obtained from Ciba-Geigy (Marly, Switzerland). PVC and PET sheets were obtained from Notz Plastics A.G. (Brügg bei Biel, Switzerland). Little is known about the additives present in these two commercial polymers. The structures of the polymers and additives used in this study are shown in Table 1. Pyrene and coronene were used as internal mass standards for mass calibration and were obtained from Socochim SA (Lausanne, Switzerland).

Sample Preparation. Pure additives were dissolved in acetone and dosed onto a glass plate for L2MS experiments. Commercial polymers that contained the additives were used as received; the POM injection bars containing Santo White powder antioxidant were further machined into 1 mm thick sheets for depth profile experiments. Tinuvin UV stabilizers were added to several polymer samples in the laboratory using two different procedures: (i) POM powder was mixed with the UV stabilizer (0.1−0.3 wt %) and pressed under 400 atm into a 12 mm diameter by 4 mm thick pellet. This is a quick and easy sample preparation method, although it is not used in standard polymer processing. (ii) For the PVC and PET sheets and the PP film, pure UV stabilizers were spread onto the polymer surface and covered with an aluminum foil to form a sandwich. This sandwich was fixed between two aluminum plates and then kept in an oven at 100 °C in a nitrogen atmosphere for 12 h, allowing the UV stabilizer to diffuse into the polymer samples. The residual UV stabilizer was then washed away from the polymer surface with acetone, a simple and effective cleaning process also used by other researchers.[36] Due to their high solubility, the residual amount of additives on the surface was negligible.

Table 1. Structure of Polymers and Polymer Additives

Name	Structure	Name	Structure
Polyoxymethylene	$-[OCH_2]_n-$	Polyvinylchloride	 $-[CH_2CH(Cl)]_n-$
Polypropylene	 $-[CH_2CH(CH_3)]_n-$	Polyethylene terephthalate	$-[OCOC_6H_4COOC_2H_4]_n-$
Tinuvin™ PS (m/z = 267)		Tinuvin™ 327 (m/z = 357)	
Tinuvin™ 234 (m/z = 447)		Tinuvin™ 328 (m/z = 351)	
Tinuvin™ 320 (m/z = 323)		Tinuvin™ 329 (m/z = 323)	
Tinuvin™ 326 (m/z = 315)		Tinuvin™ 343 (m/z = 323)	
Lowinox 22 (m/z = 340)		Santo white powder (m/z = 382)	

IR Spectroscopy. PP and POM were also studied by IR spectroscopy. The 100 μm thick PP film was used directly, whereas 7 mg of POM powder were mixed with 159 mg of KBr and pressed into a pellet. The effective thickness of the POM was 40 μm, as calculated from the amount of material used to make the KBr pellet. The spectra were taken on a 5SXC FT-IR spectrometer (Nicolet Instrument Corp., Madison, WI).

Electron Microscopy. To study the surface appearance of the polymers after infrared laser irradiation, scanning electron microscopy was carried out using a S-700 electron microscope (Hitachi, Japan). The samples were vacuum coated with a 20 nm layer of Au–Pt alloy. The microscope was operated with 25 kV acceleration voltage, about 70 V emission voltage, and a current ≤1 μA. A standard copper photoresist stripe was used to calibrate the length scale.

L2MS System. For mass spectrometric analysis, a home-built L2MS system was used.[29] The polymer samples were cut to size, mounted onto the tip of the sample holder and directly introduced into the vacuum chamber through a rapid vacuum interlock. No extraction, purification, or preconcentration steps are required for the L2MS experiment. The beam of the CO_2 laser used for ablation (Alltech model 853 MS, Lübeck, Germany) was directed into the system by a set of mirrors and a ZnSe lens. The power density was regulated to ca. 6×10^6 W/cm^2, by two irises and by the size of the laser focus. The infrared laser (10.6 μm wavelength, ≤100 ns pulse width) was operated at 4 Hz repetition rate to avoid cumulative heating of the polymers. The ionization laser wavelength was 266 nm (fourth harmonic of a Nd: YAG laser, model Surelite II, Continuum). The UV laser power density was ca. 6×10^7 W/cm^2, and this UV laser pulse was delayed with respect to the CO_2 laser pulse by about 20 μs. Mass spectrometric analysis was achieved using a reflectron time-of-flight instrument (R. M. Jordan Co.) with a mass resolution of ≈1500 at $m/z = 300$. The total acceleration potential in the ion source of the time-of-flight mass spectrometer was about 5 kV. Ions were detected by a pair of microchannel plates in a Chevron configuration, and the data were collected with an acquisition rate of 100 MS/s on a digital oscilloscope (model 9350, Le Croy, Geneva, Switzerland). The spectra were then transferred to a PC for further data processing. Only positive ion spectra were acquired in these experiments. A two-point mass calibration was performed using pyrene ($m/z = 202$) and coronene ($m/z = 300$). For CO_2 laser depth profiling experiments, care was taken to keep all experimental conditions constant for successive experiments.

Results and Discussion

CO_2 Laser Ablation of Polymers. In the present study CO_2 laser ablation of POM, PVC, PP, and PET was carried out at a wavelength of 10.6 μm. The IR spectra of all polymers used in this study can be found in the literature or in handbooks.[37–40] As a result of different polymerization processes (e.g. isotactic and syndiotactic PP), the spectra of specific polymer formulations may appear quite different. We found that polymers absorbing strongly at 10.6 μm showed good laser ablation characteristics whereas weakly absorbing materials exhibited poor ablation. In order to illustrate this, infrared spectra for PP and POM are shown in Figure 2. The absorbance scales were normalized to a sample thickness of 100 μm, so that these two spectra are directly comparable. POM absorbs well at 10.6 μm, whereas PP has almost no absorption at this wavelength. The IR spectra of PVC and PET, obtained from the literature,[40] show strong IR absorption for PVC at 10.6 μm and weak absorption of PET at this wavelength.

Figure 3a,b shows electron micrographs of ablation craters in the POM and PVC samples at a laser radiant exposure of 7.6 J/cm^2. The elliptical shapes are due to the 45° angle of incidence of the focused desorption laser

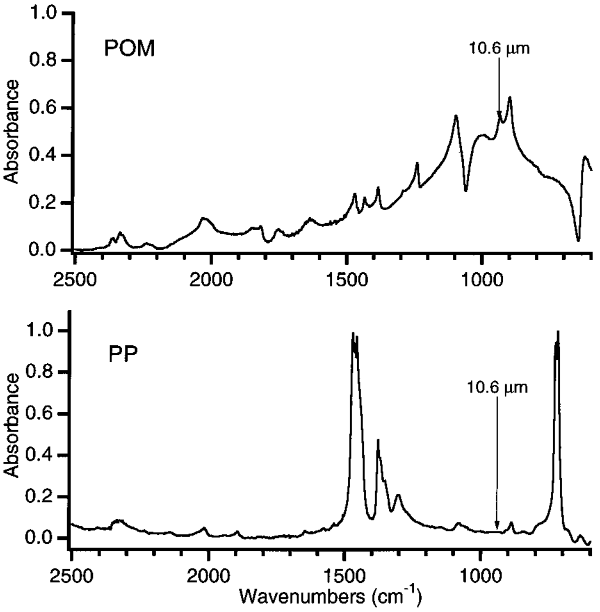


Figure 2. Infrared spectra of POM (top) and PP (bottom). The PP sample was a 100 μm thick film; the POM powder was pressed into a pellet with KBr. The spectra were normalized to an effective sample thickness of 100 μm. As shown in the picture, POM has a relatively strong absorption band at 10.6 μm while PP has almost no absorption.

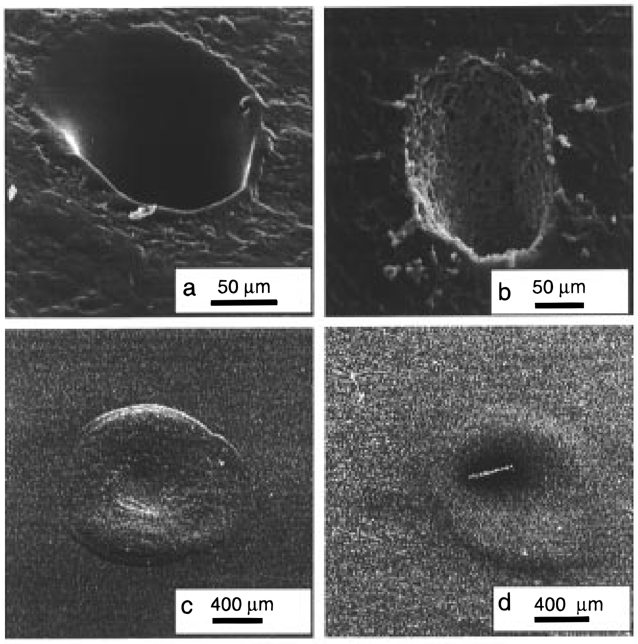


Figure 3. Electron micrographs of different polymer surfaces after irradiation with 10 shots from a pulsed CO_2 laser at 10.6 μm. POM (a) and PVC (b) show efficient ablation; PP (c) and PET (d) show only laser melting.

beam. Since POM and PVC strongly absorb the 10.6 μm laser light, efficient ablation is observed. The edges and the crater walls are well-defined. By optimizing the laser beam focus and the laser power density, a spatial resolution of 40 μm in diameter can be obtained, close to the theoretical diffraction limit for our IR optical system. The crater depth was not measured but is estimated to be several tens of micrometers in Figures 3a,b. During ablation the polymer is pyrolytically decomposed and fragments are ejected with high velocity within a short time after the laser pulse. Comparatively little energy will be directly deposited in the additives at 10.6 μm. We propose that, by analogy with the MALDI process, the laser only heats up the host polymer directly, whereas the guest molecules are still close to their initial temperature at the maximum desorption rate.[41] In addition, collisions in the plume can assist in the relaxation of the desorbed molecules, so that intact neutral additive molecules are obtained.

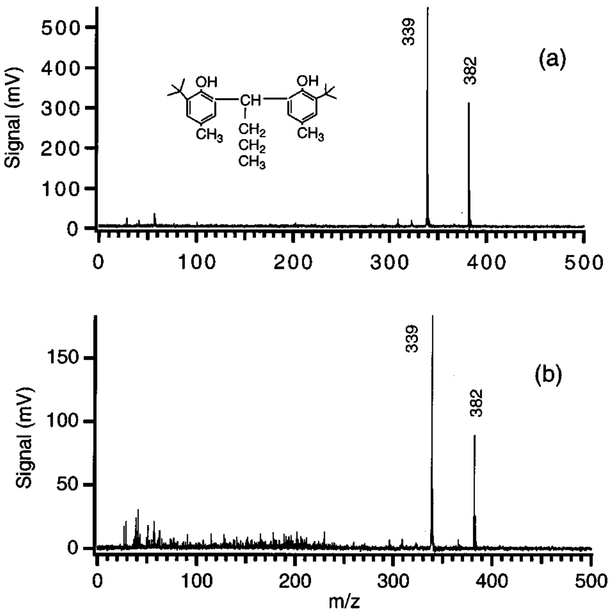


Figure 4. L2MS spectra of (a) a pure antioxidant, Santo White powder, and (b) in-situ L2MS spectrum of Santo White powder in a POM injection bar (40 shot average). 266 nm was used as a postionization wavelength.

If the laser radiation is only weakly absorbed by the polymer, as in the case of PP and PET, there is a large penetration depth, and the energy spreads over a large volume. Ablation is difficult and the laser power required is 5 times higher than that needed for ablation of POM and PVC. These polymers showed extensive melt flow when irradiated by the IR laser. Figure 3c,d shows the surfaces of PP and PET after 10.6 μm laser irradiation. Melted material seems to have flowed over from the exposed to the unexposed region. The foamlike region around the center hole on PP is probably due to internal vapor production. The 200 μm bright streak in the center in Figure 3d is probably a dust particle on the PET surface. Under our normal L2MS experimental conditions it proved difficult to observe additives directly from the PP and PET samples. However, the use of higher desorption laser power along with a considerable enlargement of the desorption spot can lead to some desorption of additives. In this way, it was possible to obtain L2MS data for additives in PP beads, although at lower spatial resolution.[42]

L2MS Studies of Polymer Additives. Table 1 shows the structures of all additives we investigated. Figure 4 shows the positive ion L2MS spectra of (a) pure Santo White antioxidant, and (b) of an antioxidant-stabilized POM injection bar. Signals characteristic of Santo White powder at $m/z = 382$ and 339 are very intense in both spectra, although the additive concentration in the polymer was only 0.1 wt %. The peak at $m/z = 382$ is the parent ion, while the $m/z = 339$ fragment $[M - 43]^+$ results from the loss of the C_3H_7 side chain, resulting in a planar fragment ion that is resonance stabilized. The spectrum in Figure 4b which was obtained from a freshly exposed interior surface of the injection bar is virtually identical to the spectrum for the pure additive. Neither greater fragmentation

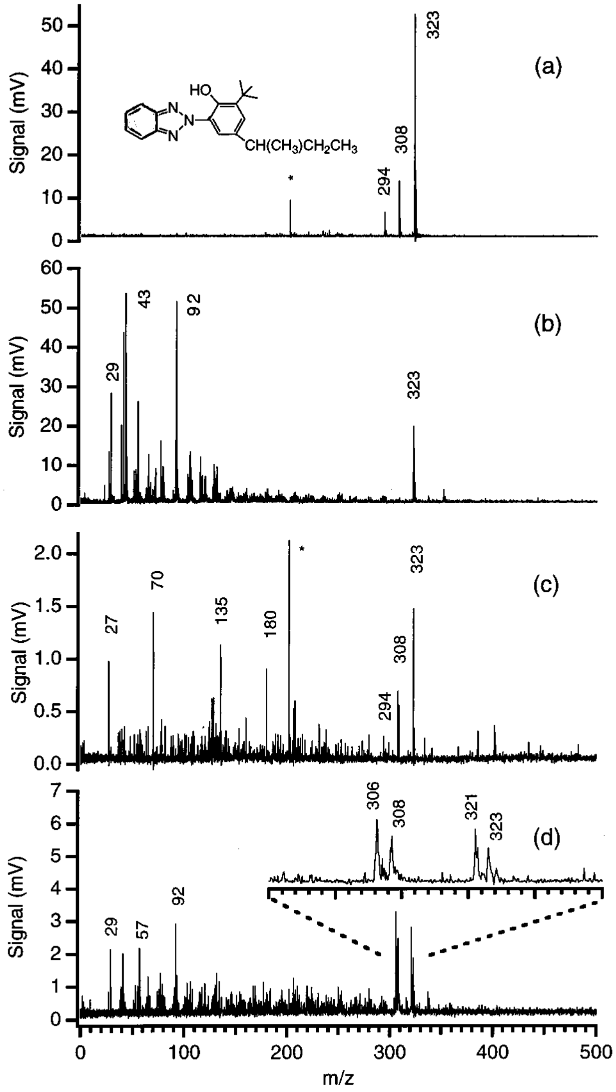


Figure 5. (a) L2MS spectrum of a pure UV stabilizer, Tinuvin 343, deposited onto a glass substrate from an acetone solution. (b) in-situ L2MS spectrum of Tinuvin 343 in a POM pellet (concentration 0.1 wt %). (c) in-situ L2MS spectrum of Tinuvin 343 diffused into a commercial PVC sheet. (d) L2MS analysis after CO_2 laser transfer from a 100 μm PP film to a glass backing plate. Peak assignments are given in the text.

nor significant contamination is observed; the weak signals in the low mass range are not related to Santo White antioxidant. The additive signals at $m/z = 382$ and 339 persisted with every shot. Given a known additive concentration in the polymer, and by measuring the ablated polymer volume, we calculate a detection limit of 28 ppm (S/N = 3, 40 shot average) for the Santo White antioxidant in this POM injection bar.

Figure 5 shows L2MS spectra of Tinuvin 343, obtained from the pure compound deposited on a glass plate (Figure 5a), and from different polymers (Figures 5 b−d). Pure Tinuvin 343 was deposited on a glass substrate and mass spectra were averaged over 40 shots (Figure 5a). The spectrum was very clean, dominated by an intense molecular ion peak at $m/z = 323$. The peaks at $m/z = 308$ and 294 are fragments resulting from the loss of CH_3 and CH_2CH_3 groups, and that at $m/z = 202$ is a mass standard, pyrene (asterisk), which is sometimes still present in the background gas of the chamber after calibration measurements.

The L2MS spectra of a number of other Tinuvin UV stabilizers as well as Lowinox 22 antioxidant were also recorded (spectra not shown, refer to Table1). We observed that fragmentation of the Tinuvin UV stabilizers always occurred on the aliphatic side chains, mostly by loss of methyl or ethyl radicals. Although the ionization potentials (IPs) for these compounds are unknown, they can be estimated by comparison with model compounds such as indole, 2,4-dimethylphenol, or 4-ethylphenol which have IPs of 7.76, 8, and 7.8 eV, respectively.[43] Hydroxyphenylbenzotriazole has a more extensive conjugated π-electron system and we therefore assume that its IP is less than 8 eV. The two-photon energy at $\lambda = 266$ nm is 9.32 eV. This yields ions with more than 1.32 eV excess energy, which, combined with some internal excitation (from laser desorption) should lead to fragmentation. At $\lambda = 193$ nm, the excess energy is over 4.8 eV and more extensive fragmentation was observed.[42] It is interesting to note that although Tinuvin 320, Tinuvin 329, and Tinuvin 343 have the same molecular weight (see Table 1), it was possible to distinguish between them by the fragmentation pattern observed in the L2MS spectra.[42]

Figure 5b shows an in-situ L2MS spectrum of Tinuvin 343 obtained directly from a POM pellet. The concentration of Tinuvin 343 was about 0.15 wt %. For a signal-to-noise ratio of 3, we estimate the detection limit to lie in the 10−100 ppm range. The uncertainty is due to the sample preparation process which does not allow control over the spatial distribution of the UV stabilizer in the POM pellet.

No signal was obtained with either the desorption laser or the ionization laser blocked, confirming that laser ablation liberates neutral additive species only. Quasimolecular ions which are typically obtained in MALDI (e.g. Na, K cationized or protonated species) are not observed in the L2MS spectra, facilitating spectral interpretation.

The molecular ion at $m/z = 323$ is clearly seen in Figure 5b but the $M - CH_3$ and $M - CH_2CH_3$ fragments are not observed. We believe that in the case of efficient polymer ablation, the additive molecules were collisionally cooled in the plume, reducing fragmentation induced by the UV ionization laser. The fragments in the low mass range, however, appear to be fundamentally different from those seen in Figure 5a. Since the repeating unit of POM is $[OCH_2]$, these peaks are not derived from the polymer itself. We interpret these signals as degradation products of the Tinuvin 343 (or fragments thereof) produced during preparation of the POM pellet. For example, the peak at $m/z = 92$ is interpreted as a fragment peak (either C_6H_4O or C_7H_8) based on a phenyl ring permitting REMPI detection; other aromatic and alkane fragments originating from such degradation products (C_2H_5, C_3H_7, and C_4H_9 at $m/z = 29$, 43, and 57) are also detected. From visual inspection of the sample surface, we speculate that during preparation of the POM pellet under 400 atm pressure, the sample melted. The temperature at that moment must be several hundred degrees Celsius, which might have induced some thermal degradation of the additives.[44]

Figure 5c shows a L2MS spectrum of Tinuvin 343 diffused into a commercial PVC sheet.[36] No other UV stabilizers had been added to this PVC sample by the manufacturer. Again, the molecular ion and the $M - CH_3$ and $M - CH_2CH_3$ fragments were observed. This sample of commercial PVC sheet was filler reinforced, and several new peaks of unknown origin were observed in the lower mass range ($m/z = 27$, 70, 135, 180). As shown in the electron micrograph in Figure 3b, the PVC sheet has a foamlike morphology, and the apparent polymer density is low. Laser ablation from this sample was less efficient than from POM, resulting in a lower detection sensitivity for the Tinuvin 343. Another possible reason for the lower detection sensitivity for Tinuvin 343 from PVC is the sample itself, prepared by additive diffusion into the PVC film rather than by pressing as in the case of POM.

As mentioned above, irradiation of PP and PET did not lead to any ablation, only laser melting was observed. It was very difficult to liberate additives by pulsed CO_2 laser irradiation ($\lambda = 10.6\ \mu$m) of these materials.[40] Therefore, a "laser transfer" experiment was carried out.[45] The PP film, stretched over a clean glass substrate, was attached to the tip of the sample holder. The sample holder was then exposed in vacuum to the CO_2 laser operated at a slightly elevated power density. This resulted in melting of the PP film and partial transfer of the material to the glass substrate. The sample holder was then retracted from the mass spectrometer and the polymer film removed, revealing the transferred material on the glass substrate. Finally, the glass plate was reintroduced into the mass spectrometer for L2MS analysis.

Using this approach, the additive signal could be detected with regular CO_2 laser desorption from glass. Figure 5d shows the result of such a laser transfer experiment for Tinuvin 343 diffused into a 100 μm PP film. Besides the molecular ion peak and the known fragments, low mass peaks similar to the data in Figure 5b were found. Additionally, peaks at $m/z = 306$ and 321 were observed (insert in Figure 5d). These peaks are two mass units below the molecular ion and $M - CH_3$ fragment signals. They are interpreted as the result of dehydrogenation of the isobutyl side chain of Tinuvin 343. A fairly stable structure could result from conjugation with the aromatic rings of Tinuvin 343. This dehydrogenation pathway seems to open up in conjunction with the laser transfer process, where a high temperature might persist for a relatively long time, facilitating dehydrogenation.[46] In spite of these added complications, the data in Figure 5d show that laser transfer makes additives from the host polymer available for regular L2MS detection by accumulating them, probably together with some polymer, on the backing plate. Although this method is only applicable to thin samples such as films and the spatial information is partially lost, the selective nature of the ionization process removes the requirement for any wet chemical separation procedures to be performed prior to mass spectral analysis. Furthermore, laser transfer might be an interesting option for detection of the transferred species with other analytical methods, for example optical spectroscopy.

Spatially Resolved L2MS by Stepwise Ablation. Depth profiling experiments have also been carried out to study the additive distribution perpendicular to the sample surface. The sample used was the POM injection bar containing Santo White powder. In this sample the antioxidant was well mixed and distributed in the polymer matrix. However, polymer processing such as injection and molding can change the additive distribution and result in concentration gradients, especially near the surface. Similarly, diffusion of the additive into the ambient air can lead to a depletion in the near-surface region.

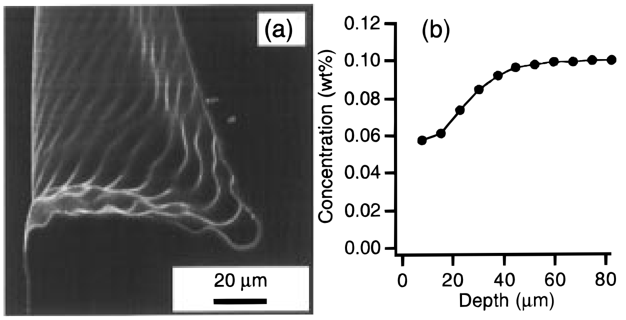


Figure 6. Spatial distribution of Santo White powder antioxidant in a POM injection bar near the surface. The concentration near the surface is 40% lower than in the bulk.

The depth profiling experiment was carried out in a stepwise fashion: 200 laser shots (using <1 J/cm^2 of laser energy density) were fired at the sample, and L2MS spectra were recorded simultaneously. After 200 laser shots, the experiment was paused and the L2MS data (200 shot average) were stored. Then the next 200 shots were accumulated, and so on. Figure 6a shows an electron micrograph of a cross section of the resulting ablation crater. During 200 shots the polymer was ablated by about 7 μm, as judged from the staircase-like structure. Since the desorption laser beam was focused at a 45° angle with respect to the sample surface, the resulting ablation crater assumes a tilted shape. Because the laser focus was located behind the surface of the polymer piece under study, the volume sampled in each profiling step was not constant. A calibration experiment was therefore carried out. The interior of the injection bar was analyzed in the same fashion after removing a layer of about 1 mm thick from the surface. Assuming that the additive concentration at any depth is homogeneous in the interior and equals 0.1 wt %, the resulting peak areas can be taken as a measure of the volume sampled.

The combined peak areas of the M and $M - C_3H_7$ signals in each L2MS spectrum were used as a measure of the additive concentration. The normalized additive signal versus depth was plotted to show the spatial distribution of the additive in the near-surface region of the injection bar (Figure 6b). Since the exterior surface turned out to be contaminated, the first point is omitted in the figure. We found that the additive concentration near the surface is 40% lower than that in the bulk. This may be a result of the polymer injection process: the melting points of POM and the antioxidant are 175 and 209 °C, respectively, whereas the mold temperature was only 90 °C. Therefore, during injection, the POM would have solidified first, and the additive concentration near the surface is expected to be lower than bulk. Furthermore, the sample was exposed to air for more than 1 year, so depletion of the antioxidant near the surface by diffusion processes is also possible.

Conclusions

The analysis of UV stabilizers and antioxidants both as pure compounds and in a variety of polymers has been successfully carried out using L2MS. This method shows considerable potential for direct in-situ chemical analysis of small concentrations of additives in a range of polymers. The effects of far infrared laser irradiation of the polymers and the desorption mechanism of additives from the host polymer have been studied. It was found that for strongly absorbing polymers, such as POM and PVC, laser-induced pyroablation decomposes the host matrix but liberates intact neutral additives. Hydroxyphenylbenzotriazole UV stabilizers and phenolic antioxidants were efficiently and selectively postionized with a UV laser pulse by two photon REMPI. The detection limit for Santo White powder antioxidant in a POM injection bar was found to be as low as 28 ppm.

Weakly absorbing polymers, such as PP and PET, showed only laser melting. Additives in these polymers are not easily detectable by L2MS. For this case detection of the additives after laser transfer from a polymer film to a substrate has been demonstrated, although thermal decomposition has been found to occur concomitantly. Depth profiling L2MS experiments were carried out for the first time and enabled the spatial distribution of an antioxidant within an injection-molded bar of POM to be determined with micrometer resolution. In this sample, the near-surface concentration of the antioxidant was found to be about 40% lower than that in the bulk.

Acknowledgment. We gratefully acknowledge financial support for this work by the Swiss National Science Foundation. We thank Dr. V. Dudler (Ciba-Geigy, Marly) Dr. J.-M. Philippoz (DuPont, Geneva), and Dr. M. J. Dale (University of Edinburgh) for providing samples and/or for helpful discussions. This collaborative study was made possible through a CIBA-ACE award and through a J. Beynon studentship award to S.J.W. P.R.R.L.S. would also like to thank CIBA for the award of a Senior Research Fellowship.

References and Notes

(1) Gächter, R., Müller, H., Eds. *Plastics Additives Handbook*; Hanser/Gardner Publications, Inc.: Cincinnati, OH, 1993.
(2) Rabek, J. F. *Photostabilization of Polymers, Principles and Applications*; Elsevier: London, 1990.
(3) Haney, M. A.; Dark, W. A. *J. Chromatogr. Sci.* **1980,** *18*, 655.
(4) Vargo, J. D.; Olson, K. L. *Anal. Chem.* **1985,** *57*, 672.
(5) Hawthorne, S. B. *Anal. Chem.* **1990,** *62*, 633A.
(6) Knowels, D. E.; Hoge, T. K. In *Applications of supercritical fluids in industrial analysis*; Dean, J. R., Ed.; Blackie: Glasgow, 1993; p 104.
(7) Lattimer, R. P.; Harris, R. E.; Rhee, C. K. *Anal. Chem.* **1986,** *58*, 3188.
(8) Lattimer, R. P.; Harris, R. E. *Rubber Chem. Technol.* **1989,** *62*, 548−567.
(9) Lattimer, R. *J. Anal. Appl. Pyrol.* **1993,** *26*, 65.
(10) Riley, T. L.; Prater, T. J.; Gerlock, J. L.; de Vries, J. E.; Schuetzle, D. *Anal. Chem.* **1984,** *56*, 2145.
(11) Schühle, U.; Pallis, J. B.; Becker, C. H. *J. Vac. Sci. Technol. A* **1988,** *6*, 936.
(12) Ervin, M. H.; Winograd, N. *Surf. Interface Anal.* **1994,** *21*, 298.
(13) Benninghoven, A. *Surf. Sci.* **1994,** *299/300*, 246.
(14) Hogan, J. D.; Laude, D. A., Jr. *Anal. Chem.* **1992,** *64*, 763.
(15) O'Malley, R. M.; Randazzo, M. E.; Weinzierl, J. E.; Fernandez, J. E.; Nuwaysir, L. M.; Castoro, J. A.; Wilkins, C. L. *Macromolecules* **1994,** *27*, 5107.
(16) Asamoto, B.; Young, J. R.; Citerin, R. J. *Anal. Chem.* **1990,** *62*, 61.
(17) Johlman, C. L.; Wilkins, C. L.; Hogan, J. D.; Donovan, T. L.; Laude, D. A. Jr.; Youssefi, M.-J. *Anal. Chem.* **1990,** *62*, 1167.
(18) Nuwaysir, L. M.; Willkins, C. L. *Anal. Chem.* **1988,** *60*, 279.
(19) Brown, R. S.; Wilkins, C. S. *Anal. Chem.* **1986,** *58*, 3396.
(20) Karas, M.; Hillenkamp, F. *Anal. Chem.* **1988,** *60*, 2299.
(21) Hillenkamp, F.; Karas, M.; Beavis, R. C.; Chait, B. T. *Anal. Chem.* **1991,** *63*, 1193A.
(22) Tanaka, K.; Waki, H.; Ido, Y.; Akita, S.; Yoshida, Y.; Yoshida, T. *Rapid Commun. Mass Spectrom.* **1988,** *2*, 151.
(23) Cotter, R. J.; Honovich, J. P.; Olthoff, J. K.; Lattimer, R. P. *Macromolecules* **1986,** *19*, 2996.
(24) Lattimer, R. P.; Harris, R. E. *Mass Spectrom. Rev.* **1985,** *4*, 369.
(25) Holm, R.; Karas, M.; Vogt, H. *Anal. Chem.* **1987,** *59*, 371.
(26) Blease, T. G.; Scrivens, J. H.; Monaghan, J. J.; Weil, D. *Proceedings of the 36th ASMS Conference on Mass Spectrometry and Allied Topics*, San Francisco; 1988; p 357.
(27) Lykke, K. R.; Parker, D. H.; Wurz, P.; Hunt, J. E.; Pellin, M.; Gruen, D. M.; Hemminger, J. C. *Anal. Chem.* **1992,** *64*, 2797.
(28) Lykke, K. R.; Wurz, P.; Parker, D. H.; Pellin, M. J. *Appl. Opt.* **1993,** *32*, 857.
(29) Voumard, P.; Zhan, Q.; Zenobi, R. *Rev. Sci. Instrum.* **1993,** *25*, 3393.
(30) Kelly, J. M., McArdle, C. B., de F. Maunder, M. J., Eds. *Photochemistry and Polymeric Systems*; Royal Society of Chemistry: Cambridge, U.K., 1993; p 54.
(31) Srinivasan, R.; Mayne-Banton, V. *Appl. Phys. Lett.* **1982,** *41*, 576.
(32) Srinivasan, R.; Baren, B. *Chem. Rev.* **1989,** *89*, 1303.
(33) Srinivasan, R.; Braren, B.; Casey, K. G. *J. Appl. Phys.* **1990,** *68*, 1842.
(34) Dickinson, J. T. J.; Shin, J.; Jiang, W.; Norton, M. G. *J. Appl. Phys.* **1993,** *74*, 4729.
(35) Dyer, P. E.; Oldershaw, G. A.; Sidhu, J. *Appl. Phys.* **1989,** *B 48*, 489−493.
(36) Dudler, V.; Muinos, C. In *Polymer Durability: Degradation, Stabilization, and Lifetime Prediction*; Clugh, R. L., Billingham, N. C., Gillen, K. T., Eds.; American Chemical Society: Washington, DC, 1996; p 441.
(37) Mucha, M. *Colloid Polym. Sci.* **1984,** *262*, 841.
(38) Haslam, J.; Willis, H. A.; Squirres, D. C. M. *Identification and analysis of plastics*, 2nd ed.; Heyden: London, 1980.
(39) Crompton, T. R. *The analysis of plastics*; Pergamon Press: Oxford, U.K., 1984.
(40) Hummel, D. O., Ed. *Atlas der Polymer und Kunststoffanalyse*; Carl Hanser Verlag: München, 1978.
(41) Vertes, A., Gijbels, R., Adams, F., Eds. *Laser Ionization Mass Analysis*; John Wiley & Sons: New York, 1993.
(42) Wright, S. J.; Dale, M. J.; Langridge-Smith, P. R. R.; Zhan, Q.; Zenobi, R. *Anal. Chem.*, in press.
(43) Lias, S. G., Bartmess, J. E., Liebmen, J. F., Holmes, J. L., Levin, R. D., Mallard, W. G., Eds. *Gas-phase Ion and Neutral Thermochemistry*; American Chemical Society: Washington, DC, 1988.
(44) A thermogravimetry experiment (Perkin-Elmer Sereis 7 thermal analysis system, 20 °C/min, ~8 mg sample) showed that thermal decomposition for Tinuvin 343 starts at 250 °C and is complete at 335 °C.
(45) Dale, M. J.; Zhan, Q.; Zenobi, R.; Costello, K.; Langridge-Smith, P. R. R. *Anal. Methods Instrum.* **1994,** *2*, 101.
(46) Chauvel, A.; Lefebvre, G. *Petrochemical Processes - Technical and Economic Characteristics*; Editions Technip: Paris, 1989.

MA960547R