

Analysis of Photoablation Products Resulting from Polymer Materials by Supersonic Beam/Multiphoton Ionization/Time-of-Flight Mass Spectrometry

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Photoablation products arising from polymer materials were examined by supersonic beam spectrometry, and the results are compared with those obtained by thermal decomposition. The high selectivity provided by supersonic beam spectrometry allows detection of minor species, e.g., styrene occurred from poly(α -methylstyrene) by cleavage of a methyl group and by proton rearrangement. Because ablation techniques involve high temperatures, thermally stable materials such as poly(*p*-methylstyrene) can be examined. The latter material is difficult to examine by thermal decomposition, even at 350 °C. It is also possible to differentiate between isomer ablation products, e.g., α -methylstyrene and *p*-methylstyrene. The instrumental setup described herein was used to examine several authentic samples, such as ABS resin (acrylonitrile-butadiene-styrene) and O-ring (SBR, styrene-butadiene rubber), as well as polystyrene foam. As a result, a styrene segment could be confirmed to be present in these materials. However, no evidence was found for its presence in a glue sample that was suspected to contain styrene on the basis of conventional mass spectrometry. The latter finding confirms the high degree of selectivity of the technique.

In order to improve thermal and mechanical characteristics of a polymer, a functional group is frequently introduced into the monomer, and its position is carefully optimized to improve the physical performance of the material. For example, poly(*p*-methylstyrene) has a higher glass-transition temperature; it is more thermally stable and more resistant to mechanical impact than polystyrene. In addition, two different monomers are frequently copolymerized in order to improve the characteristics of a polymer. For example, styrene is copolymerized with α -methylstyrene to improve thermal stability but can also be copolymerized with butadiene to form SBR or with acrylonitrile and butadiene to form ABS resins, which are more resistant to mechanical impact than is ordinary polystyrene. It is frequently necessary to examine the composition of a polymer, as well as its isomeric structure. Currently, gas chromatography combined with mass spectrometry is the technique of choice and is used in conjunction with thermal decomposition of the polymer. These techniques take advantage of the high selectivity of gas chromatography and the high sensitivity of mass spectrometry. These techniques alone, however, sometimes give insufficient informa-

tion for complete polymer characterization. Alternatively, infrared absorption and nuclear resonance spectrometry are used for structural analysis of polymers, but they are not effective in trace analysis, e.g., in detection of additive, impurities, initiator, or inhibitor remaining in the polymer.

Recently, laser ablation has been recognized as an important technique for vaporizing neutral species from a solid surface. This technique allows direct sampling without pretreatment of the polymer. Electron and ion beams are also used for vaporization of the solid sample including polymers,¹ but it is difficult (though not impossible) to apply them to electrically insulated materials. Numerous research groups have investigated the mechanism of laser ablation, including velocity distributions and spatial density profiles of the plume.²⁻⁷ Polymers, rubber vulcanizers, and biological substances can be successfully analyzed by this method.⁸⁻¹⁴ The chemical species produced by laser ablation would be expected to be different from those produced by thermal decomposition, since the temperature and the time period for sample heating are 10 000 K⁵ and nanoseconds, respectively, considerably different from the parameters for thermal decomposition.

The species produced by laser ablation can be measured by single-photon (VUV) or multiphoton (UV) ionization/time-of-flight mass spectrometry.¹²⁻¹⁴ However, wavelength-fixed lasers, such as harmonic emission of a Nd-YAG laser or an excimer laser, appear to be in more common use. Such lasers provide poor wavelength selectivity. Since the characteristics of a polymer can change considerably with slight modification of chemical structure, a more selective analytical method would be highly desirable, in

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order to obtain more precise data for structural analysis of the polymer. It is possible to use a tunable laser source for this purpose, but the absorption spectrum measured at room or elevated temperature is rather broad, thus making it difficult to differentiate between closely related, isomeric chemical species.

Supersonic jet expansion into a vacuum cools a molecule to several degrees kelvin, thus providing a narrow spectral feature in an optical spectrum. Such a technique has seldom been applied to a polymer sample. Thermally decomposed products resulting from polystyrene, its derivatives, and polycarbonate have been measured by both laser-induced fluorescence spectrometry and multiphoton ionization/mass spectrometry.¹⁵ On the other hand, laser-ablated products of polystyrene have first been measured by laser-induced fluorescence spectrometry.¹⁶ Lubman and Lustig have reported the multiphoton ionization mass spectra for laser-ablated products measured by using a wavelength-fixed Nd-YAG (266 nm) laser.¹⁷ However, the full advantage of supersonic jet spectrometry, i.e., the wavelength selectivity, has not yet been demonstrated.

In this study, we report an analysis of polymers by laser ablation/supersonic beam/multiphoton ionization/mass spectrometry using a tunable laser. In this technique, the chemical species photoablated from a polymer surface are mixed with argon and are then entrained in a supersonic jet, which is expanded into a vacuum for molecular cooling, which allows narrow spectral features to be obtained.^{18–22} The molecules are then ionized by multiphoton ionization using a tunable dye laser and measured by means of a time-of-flight mass spectrometer. Polystyrene is used as the experimental starting material to compare this laser ablation technique with thermal decomposition procedures. The present instrumental technique is applied to thermally stable poly(*p*-methylstyrene) to demonstrate the advantage of the laser ablation technique. The detection of minor chemical species produced by laser ablation and isomer selectivity are also demonstrated by taking advantage of the high selectivity given by supersonic beam/resonance-enhanced multiphoton ionization spectrometry. We have also applied the present method to commercially produced materials such as ABS resin, an O-ring made of SBR, and a sample of polystyrene foam which is ordinarily used as a thermal insulator or mechanical damper. We have also examined a glue sample (Henry Glue A) which was suspected of containing styrene, as evidenced by conventional mass spectrometry.

EXPERIMENTAL SECTION

Apparatus. The supersonic jet spectrometer developed in this study has been reported in detail elsewhere and thus is only briefly described herein.^{16,23} A block diagram of the instrument is shown in Figure 1. An interface (not shown in the figure) is mounted on a homemade pulsed nozzle. A rod sample is inserted just below the nozzle throat and is rotated (1/30–6 rpm) and

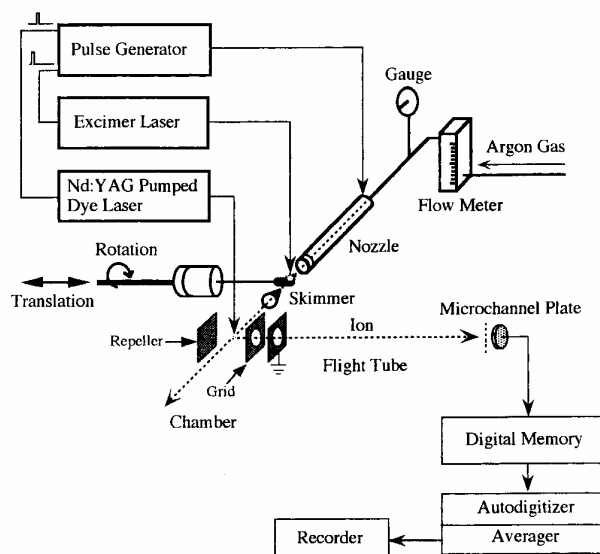


Figure 1. Experimental apparatus for laser ablation/supersonic beam/multiphoton ionization/time-of-flight mass spectrometry.

translated (0.1–0.5 mm/min) by a motor (Oriental Motor, SS21L). Photoablated products are mixed with a sufficient amount of argon, which is injected through the nozzle into the throat, and are then allowed to expand into a vacuum chamber. A part of the jet is passed through a skimmer to form a molecular beam into the second chamber, which is maintained below 6×10^{-6} Torr during the experiment. Ions induced by multiphoton ionization are then extracted by a repeller and a grid into a flight tube maintained below 1×10^{-6} Torr. The mass resolution was 150–200, which is limited by a rather short (45 cm) flight tube. This tube length was chosen to improve the efficiency in ion detection. The conditions used in thermal decomposition are reported elsewhere.²³

An excimer laser (Lambda Physik, LPX205i, 308 nm) and a Nd-YAG laser-pumped dye laser (Quantel, YG581-C20, TDL50, UVX-2, Rhodamine 590/610) are used for laser ablation and multiphoton ionization, respectively. The ions that drift in the flight tube are detected by an assembly of three microchannel plates (Hamamatsu, F1094-32S). A mass spectrum is recorded by measuring the transient signal by a digital memory (Iwatsu, DM901), which is converted into a signal which is 100 times slower. This signal is recorded a second time by an autodigitizer (Autonics, S-210) and is accumulated 1024 times by an averager (Autonics, F610). When a conventional mass spectrometer was used, a glue sample was vaporized by using a pulse-heating probe. The sample was put on a tungsten filament, vaporized rapidly by joule heating, and directly introduced into a quadrupole mass spectrometer, which was operated in the electron impact mode.

Reagents. Styrene and polystyrene ($n = 1600$ – 1800) were obtained from Wako Pure Chemicals. Other monomers, such as α -methylstyrene and *p*-methylstyrene, were supplied by Tokyo Kasei. Poly(α -methylstyrene) was purchased from Polyscience. Authentic samples of O-ring and ABS resin were obtained from Japan Valqua Co. and Sanko Plastic Co., respectively. Henry Glue A (tarlike polymerized hydrocarbon) was a gift. This glue is frequently used as a floor tile adhesive.

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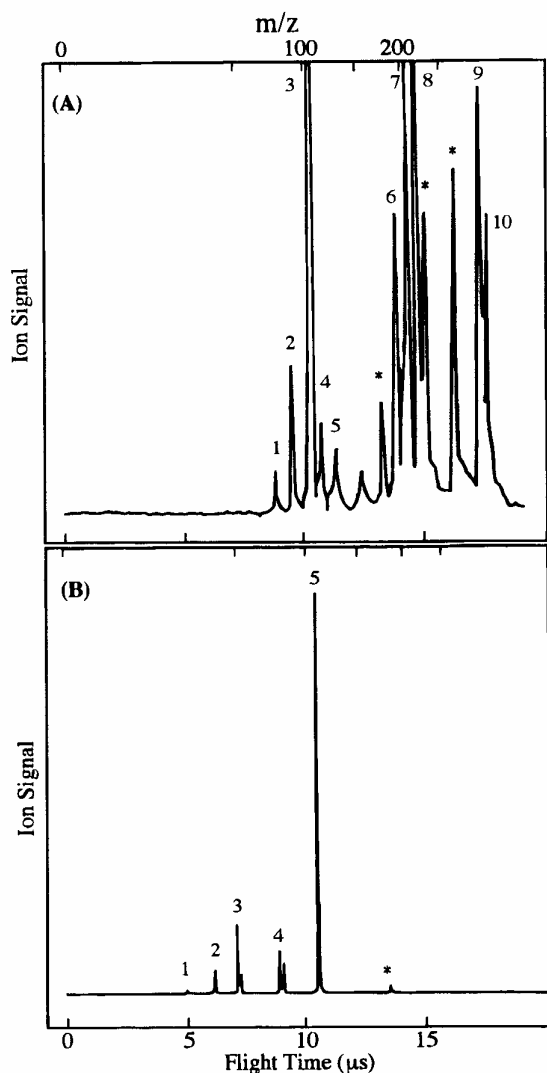


Figure 2. (A) Mass spectrum for thermally decomposed products resulting from polystyrene (cited from ref 14). (B) Mass spectrum for laser-ablated products resulting from polystyrene. The wavelength of the ionization laser ($100 \mu\text{J}$) was set at 287.63 nm , which corresponds to the 0–0 transition for styrene. An excimer laser ($200 \mu\text{J}$) was used for ablation of the polymer. The mass peaks marked by asterisks originate even when the ablation laser is not fired and, therefore, are assigned to peaks originating from impurities, e.g., pump oil.

RESULTS AND DISCUSSION

Comparison with Thermal Decomposition. Figure 2A shows a mass spectrum for the thermal decomposition products resulting from polystyrene, measured at 287.63 nm , which corresponds to the 0–0 transition for styrene.²² The most intense peak (3) had $M_w = 104.2$, corresponding to the molecular weight of styrene monomer. Other peaks, which appeared over the mass range of 200–330, correspond to dimers and trimers. Benzene and toluene were also observed, but their intensities were relatively small. Figure 2B shows a mass spectrum for laser-ablated products measured using the same apparatus under similar conditions. The largest peak at $M_w = 104.2$ corresponds to the monomer. Neither dimers nor trimers were observed in this study, even when the sensitivity of the instrument was further increased. This is in contrast to the thermal decomposition data.

Table 1. Possible Candidates for Thermal Decomposition and Laser Ablation Products Resulting from Polystyrene

thermal decomposition		laser ablation		chemical formula
peak no.	M_w	peak no.	M_w	
		1	26	C_2H_2^+
		2	39	C_3H_3^+
		3	52	C_4H_4^+
		4	78	C_6H_6^+
1	78			C_7H_8^+
2	92			C_8H_8^+
3	104	5	104	$\text{C}_9\text{H}_{10}^+$
4	118			$\text{C}_{10}\text{H}_{13}^+$
5	132			$\text{C}_{16}\text{H}_{16}^+$
6	208			$\text{C}_{17}\text{H}_{18}^+$
7	222			$\text{C}_{18}\text{H}_{15}^+$
8	236			$\text{C}_{24}\text{H}_{24}^+$
9	312			$\text{C}_{25}\text{H}_{26}^+$
10	326			

It is noted that the dimers and trimers are detected in a similar experiment using a CO_2 laser for laser ablation and a Nd–YAG laser (266 nm) for multiphoton ionization.¹⁷ So, we do not conclusively insist that such oligomers occur only in thermal decomposition, but we consider that they are less efficiently effected by laser ablation, at least under present experimental conditions, e.g., using a more photochemical UV laser for ablation instead of a more thermal CO_2 laser. The chemical formulas for possible candidates for each signal peak in Figure 2 are summarized in Table 1. It is noteworthy that a series of distinct fragments, C_nH_n ($n = 2, 3, \dots, 6, 8$), is observed for the laser-ablated product.

It is well-known that two types of processes are involved in polymer decomposition reactions: depolymerization (unzipping reaction) and random decomposition. The former occurs at lower temperatures and gives rise to dimers and trimers, while the latter occurs at higher temperature, giving rise to heavily dissociated fragments. In laser ablation, the temperature increases rapidly up to $10\,000 \text{ K}$,⁵ which is much higher than the temperature in thermal decomposition ($350 \text{ }^\circ\text{C}$). Thus the change in the mass spectrum may be attributed to effect of the temperature difference on decomposition of the polymer. Laser ablation allows determinations of the molecular weight of the monomer from the largest peak, giving the molecular ion, and of the chemical structure of the monomer from the fragment ions, indicating that it is suitable for identification of the monomer species. On the other hand, thermal decomposition is the preferred technique for investigations of dimers and trimers, thus providing information on overall polymer structure, e.g., to distinguish random, alternating (syngiotactic or isotactic), or block copolymers.

Detection of Minor Species. Figure 3 shows mass spectra for laser-ablated products resulting from poly(α -methylstyrene). The mass spectrum is measured under on-resonance and off-resonance conditions for a specific molecule. In Figure 3A, the products are ionized at 281.87 nm , which corresponds to one of the resonance lines observed in the fluorescence excitation spectrum for α -methylstyrene. The 0–0 transition of α -methylstyrene is very weak²² and, therefore, was not used in this study. A prominent mass peak at $11.4 \mu\text{s}$ is readily assignable to the molecular ion of α -methylstyrene. In Figure 3B, the laser wavelength is adjusted to 287.63 nm , corresponding to the 0–0 transition for styrene. In this spectrum, the styrene peak, which was barely observable in Figure 3A, is clearly seen, in addition to

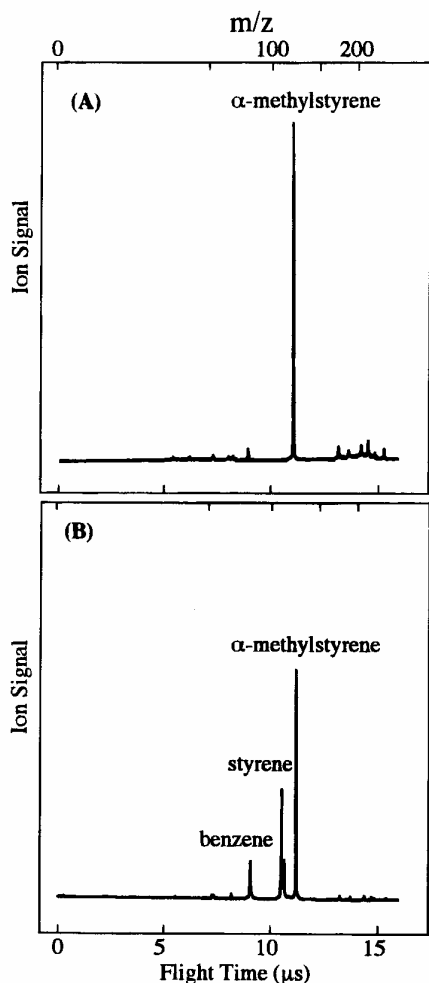


Figure 3. Mass spectra for laser-ablated products resulting from poly(α -methylstyrene). The wavelength of the ionization laser is adjusted to one of the resonance lines for (A) α -methylstyrene (285.65 nm, 60 μ J) and (B) styrene (287.63 nm, 60 μ J). The mass peaks seen above 11 μ s are derived from impurities.

peaks arising from α -methylstyrene and benzene by nonresonant multiphoton ionization. The methyl group of α -methylstyrene could be dissociated from the α -position by laser ablation, resulting in styrene after proton rearrangement. Since the dissociation energy of the C–C bond in a polymer chain is much smaller than that of the C–C bond in the α -position, a monomer of α -methylstyrene might be obtained as a major product; the heat of polymerization is rather low for poly(α -methylstyrene) (8.4 kcal mol⁻¹), and the polymer is easily decomposed to monomers.²⁴ It should be noted that the minor species of styrene produced by laser ablation can be clearly detected, indicating a high degree of selectivity in the present method, which is based on resonance-enhanced multiphoton ionization.

In Figures 2B and 3, a peak corresponding to benzene (C₆H₆) is observed even though the spectrum is measured under nonresonance conditions; this assignment was unfortunately not confirmed by resonance-enhanced multiphoton ionization spectrometry due to a limited tunable range of the dye laser. On the other hand, toluene and ethylbenzene are not observed from the laser-ablated products. These results suggest that benzene is

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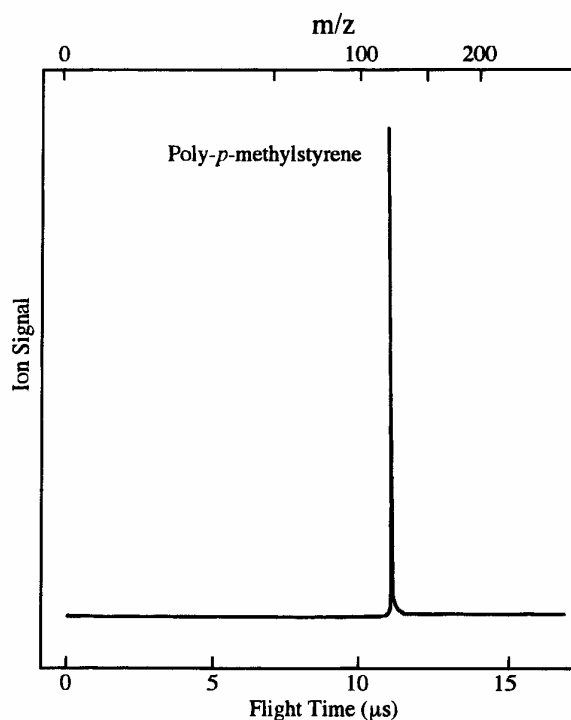


Figure 4. Mass spectrum for laser-ablated products resulting from poly(p -methylstyrene). The wavelength of the ionization laser (100 μ J) is adjusted to one of the resonance lines for p -methylstyrene (291.67 nm, 100 μ J).

easily formed by cleavage of the C–C bond between a polymer chain and formation of a benzene ring after rearrangement of a proton, and that toluene and ethylbenzene are formed with more difficulty due to more complicated rearrangements required in a short time period and under elevated temperature.

Applications to Thermally Stable Polymers. The characteristics of a polymer are drastically changed by slight modifications in the monomer structure. Poly(p -methylstyrene) is known to be more thermally stable than ordinary polystyrene. In an earlier study,¹⁵ based on thermal decomposition, no signal could be observed, even when this polymer was heated to 350 °C. Figure 4 shows a mass spectrum for photoablated products resulting from poly(p -methylstyrene). As demonstrated, this thermally stable polymer is readily decomposed by laser ablation, and the products can be measured with good sensitivity. Monomer fragmentation is not appreciable, implying a high degree of stability of the monomer itself. Differentiation of the isomers of α -methylstyrene and p -methylstyrene was also demonstrated by means of resonance-enhanced multiphoton ionization.

Application to Real Samples. Figure 5 shows mass spectra for authentic samples which are thought to contain a styrene segment. A sharp peak is observed at 10.7 μ s for (A) ABS resin, (B) O-ring, and (C) polystyrene foam. These peaks appeared at $M_w = 104.2$ and can be assigned to styrene. However, an analogous signal is not observed for the glue sample (Figure 5D). When a conventional mass spectrometer was used, many mass peaks appeared; a strong signal was observed especially at $M_w = 104.2$. On the basis of these data, styrene was suspected to be a major component of this sample. The present results suggest that the glue contains little or no styrene and that the observed signal in conventional mass spectrometry may be due to some other

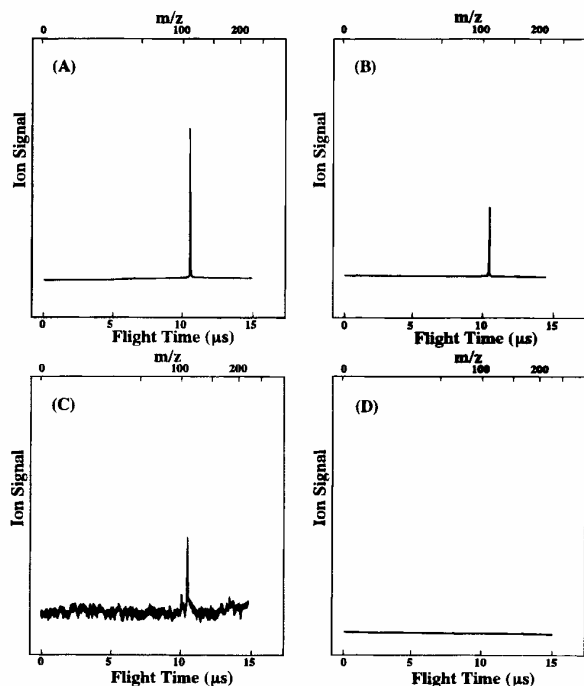


Figure 5. Mass spectrum for laser-ablated products resulting from (A) ABS resin, (B) O-ring, (C) polystyrene foam, and (D) glue. The wavelength of the ionization laser ($100\ \mu\text{J}$) is adjusted to 287.63 nm, which corresponds to the 0–0 transition for styrene.

Table 2. Relative Intensities of Styrene Peaks Resulting from Authentic Samples

sample	styrene content (%)	relative ionization signal intensity
polystyrene	100	1.0
ABS resin ^a	40–60	0.12
O-ring ^b	23.5	0.033
polystyrene foam	90–95	0.013

^a Acrylonitrile–butadiene–styrene resin. ^b Styrene-butadiene rubber (SBR).

unknown compound. The styrene content and the relative signal intensity for the above samples are summarized in Table 2. The ionization signal intensity is not necessarily proportional to the amount of styrene monomer, suggesting that the sensitivity also depends on the form of the polymer material.

CONCLUSIONS

Monomers and fragments derived from them are formed by laser ablation, indicating that this technique is suitable for

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investigations of monomer units contained in a polymer. On the other hand, dimers and trimers are more efficiently formed by thermal decomposition, suggesting that it is the preferred technique for investigations of polymer structure. Because of the sharp spectral features produced by supersonic beam/resonance-enhanced multiphoton ionization spectrometry, minor species such as styrene, which was produced from poly(α -methylstyrene), were detected. This spectral selectivity could also be used for differentiation of the isomers. A laser ablation technique is applicable to studies of thermally stable polymers such as poly(p -methylstyrene), which could not be effectively examined by thermal decomposition, even at 350 °C. Thus, the laser ablation technique will have more universal applications for analysis of polymers, especially for thermally resistive polymers, in the future. In this study, authentic samples such as ABS resin, O-rings, and even polystyrene foam were examined, and the presence of styrene segments could be verified for all samples. However, no signal peak for styrene was observed for a glue sample that was suspected to contain styrene on the basis of conventional mass spectrometry studies.

It is noted that isomer analysis is possible by infrared absorption spectrometry. However, it is quite difficult to identify the chemical species when neither the standard spectrum nor the standard sample is available. We have already performed a feasibility study to assign the chemical species by theoretical calculation of the molecular orbital and by fuzzy pattern recognition of the well-resolved spectral feature.^{25–27} Alternatively, gas chromatography can be used for isomer analysis. However, it is time consuming, and it cannot be applied, e.g., to continuously monitor the product yield for chemical species resulting from a thermally decomposed polymer with changing the furnace temperature. One of the problems encountered in more broad applications of supersonic beam/multiphoton ionization/mass spectrometry to practical samples is the narrow tunable range of the dye laser. This problem can be offset, to some extent, by using a multifrequency laser emission²⁸ or an optical parametric oscillator,^{29,30} which allows the tunable range to be extended and, hence, the characterization of numerous other types of polymers.

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