

Supersonic Jet/Multiphoton Ionization Spectrometry of Chemical Species Resulting from Thermal Decomposition and Laser Ablation of Polymers

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Abstract. The chemical species resulting from thermal decomposition and laser ablation of polymers are measured by excitation/fluorescence and multiphoton ionization/mass spectrometries after supersonic jet expansion for rotational cooling to simply the optical spectrum. The signal of minor chemical species occurred is strongly enhanced by resonant excitation and multiphoton ionization, and even the isomer can be clearly differentiated. For example, p-cresol occurred by thermal decomposition of polycarbonate is detected selectively by mass-selected resonant multiphoton ionization spectrometry. Various chemical species occurred by laser ablation of even a polystyrene foam are also measured by this technique.

INTRODUCTION

Characteristics of the polymer are strongly affected by slight modification of the chemical structure of the constituents. Mass spectrometry is currently applied to chemical species resulting from thermal decomposition of the polymer, but there are many difficulties in this approach, due to poor selectivity, e.g. to differentiate isomers. In order to overcome this problem, mass spectrometry is sometimes combined with a separation technique such as gas chromatography. However, the retention time changes depending on the experimental conditions such as a temperature of the separation column, a flow rate of the carrier gas, etc. It is noted that many standard samples should be measured for each column for assignment of the

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chemical species.

In this study we use laser-induced fluorescence and multiphoton ionization spectrometries for measurements of chemical species resulting from polymers by thermal decomposition or laser ablation. Since room temperature spectrometry suffers from poor information due to a lack of sharp spectral feature, a vaporized sample diluted with an inert gas is expanded into a vacuum to cool the molecules to several kelvin. This supersonic jet technique provides us a spectrum consisting of sharp spectral feature, so that it is preferential to discriminate a specified component against a large amount of interferences. By this approach, even the isomer can readily be differentiated. Laser ablation used instead of thermal decomposition is useful for measurements of thermally stable polymers. The advantage of supersonic jet spectrometry in application to polymer analysis is discussed in this study.

EXPERIMENTAL

The instrument for supersonic jet spectrometry of thermally decomposed products was developed in our laboratory (1). The polymer sample was decomposed in a reservoir heated to a specified temperature. The thermally decomposed products were introduced into a pulsed nozzle through a stainless steel tube to expand them into a vacuum. A differential pump system was used to evacuate the first, second, and third chambers. In the first chamber, a laser beam was focused into the sample in the jet. A monochromator equipped with a photomultiplier was used for fluorescence measurements. After being passed through a skimmer, the sample molecule in the beam was multiphoton-ionized in the second chamber. The repulsive potential accelerated the ions into the third chamber for recording a mass spectrum by a time-of-flight mass spectrometer. An excimer-laser-pumped dye laser or a Nd:YAG-laser-pumped dye laser was used as a tunable light source. The signal of the mass spectrum was averaged 1024 or 2048 times to improve the signal-to-noise ratio.

For laser ablation, the excimer laser (308 nm) was weakly focused onto the polymer surface. In order to refresh the polymer surface, the sample rod placed under the nozzle throat was rotated and translated simultaneously. The ablated chemical species were mixed with a carrier gas of argon ejected into the nozzle throat and was succeedingly expanded into a vacuum to form a supersonic jet.

RESULTS AND DISCUSSION

The polymer can be thermally decomposed by raising the temperature slowly. So, the chemical species equilibrated at the reservoir temperature is measured; the nozzle is also heated to the temperature close to that of the reservoir. On the other hand, the temperature is quickly (probably in the nanosecond range) raised in a laser ablation process. So, the products formed might be quite different from those formed by thermal decomposition under equilibrated conditions.

Thermal Decomposition

When the mass spectrum was measured for thermally decomposed products resulting from polystyrene, a strong mass peak appeared at $M_w=104$, as shown in Fig. 1. This signal was strongly enhanced by adjusting the laser wavelength to 287.63 nm, which corresponds to the 0-0 transition of styrene. Thus a styrene monomer was apparently formed as a major component from polystyrene. However, many other products were also observed. Possible candidates are indicated in Fig. 2. Dimers and trimers are considered to be occurred efficiently by thermal decomposition. The mass spectrum was observed at which toluene was multiphoton-ionized

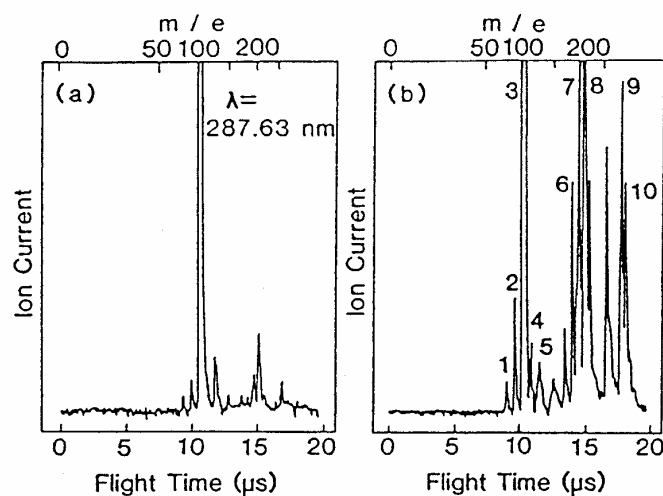


FIGURE 1. Mass spectra for thermally decomposed products from polystyrene measured at (a) on-resonance and (b) off-resonance conditions for styrene (cited from Ref. 1).

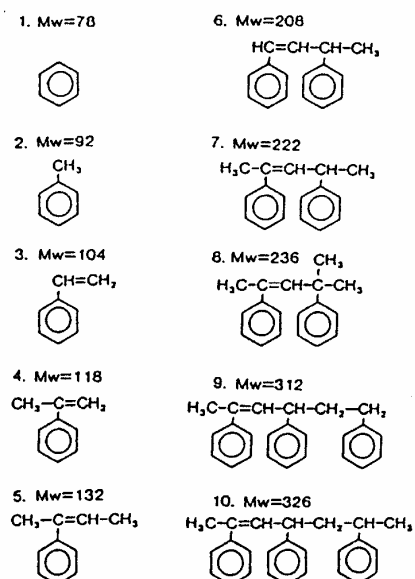


FIGURE 2. Possible candidates for thermally decomposed products from polystyrene (cited from Ref. 1).

under on-resonance and off-resonance conditions. The concentration of toluene formed by thermal decomposition of polystyrene was very small, but it was selectively detected by resonant multiphoton ionization.

A similar investigation was performed for poly-methylstyrenes (2). Styrene was clearly observed from poly- α -methylstyrene by resonant multiphoton ionization spectrometry. It was also possible to differentiate isomers; only α -methylstyrene could be observed even though the laser wavelength was also scanned in the region where β -methylstyrene could be observed.

The mass spectra for thermally decomposed products resulting from polycarbonate are shown in Fig. 3. Possible candidates are indicated in Fig. 4. The resonant multiphoton ionization

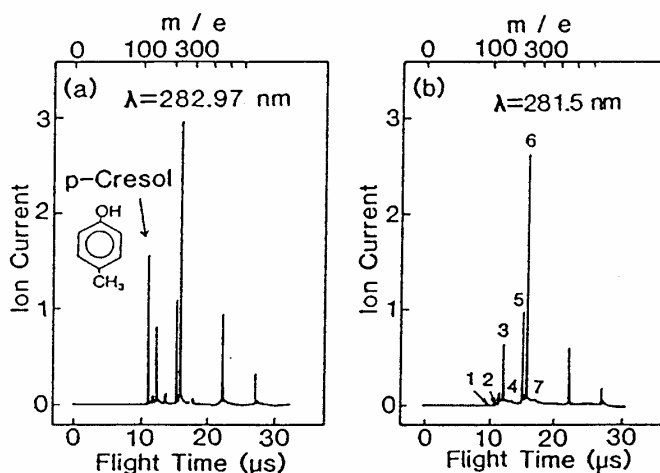


FIGURE 3. Mass spectra for thermally decomposed products from polycarbonate measured under (a) on-resonance and (b) off-resonance conditions for p-cresol (cited from Ref. 1).

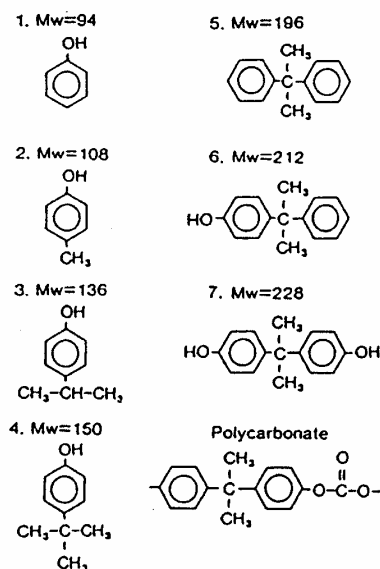


FIGURE 4. Possible candidates for thermally decomposed products from polycarbonate (cited from Ref. 1).

spectrum measured by monitoring a mass peak at $M_w=108$ were measured. A peak was observed at 282.97 nm, which corresponds to the 0-0 transition of *p*-cresol. Thus *p*-cresol is readily confirmed to be present in the thermally decomposed products from polycarbonate. It is noted that *tert*-butylphenol used as a termination reagent of the polymer chain reaction is also observed (number 4, $M_w=150$), which is characteristic to the "solvent method" used in polymerization. Thus the present method is useful not only for selective detection of the minor species but also for differentiation of the isomers.

Laser Ablation

The excitation and fluorescence spectra were measured for laser ablated products resulting from polystyrene (3). The signal arising from styrene was clearly observed. The fluorescence signal was measured by changing the time interval between laser ablation and laser ionization. The signal appeared only when they were synchronized within an error of 4 μ s, which indicated that the sample vaporized was well-localized within 2.4 mm in the 600-mm (1 ms) jet pulse. This fact means that the laser ablated products are mixed instantly with the diluent gas in the nozzle throat and are succeedingly expanded from the nozzle into a vacuum. The efficiency of laser ablation was improved by decreasing the distance between successive beam spots and by decreasing the beam spot size on the polymer surface. These results imply that the sample is vaporized through a thermal process and the monomer is efficiently formed by explosive ejection from the hot (partially melted) surface. It was possible to detect styrene from polystyrene and acrylonitrile-butadiene-styrene, but no signal could be observed from polycarbonate. Thus the constituent of the polymer can readily be examined by this laser ablation technique.

Multiphoton ionization spectrometry was used instead of fluorescence spectrometry for characterization of the chemical species. Figure 5 shows the mass spectrum measured for laser ablated products resulting from polystyrene. When only the ablation laser is fired, no signal is observed. On the other hand, when only the ionization laser is fired, a few signal peaks appeared, which probably originate from a pump oil. A strong signal appears when the ionization laser pulse is fired synchronously to the ablation laser. Thus neutral species formed by laser ablation are resonantly-ionized and detected. It was possible to detect styrene from laser ablated products resulting from poly- α -methylstyrene by adjusting the wavelength of the ionization laser to the 0-0 transition of styrene. It is noted that dimers and trimers are not observed in this case. This is in contrast to the result obtained by thermal decomposition. This implies that the dimers and trimers are easily decomposed in the laser ablation process due to a high temperature. Poly-*p*-methylstyrene was relatively thermally stable, and no monomer could be detected from thermally decomposed products. However, *p*-methylstyrene was apparently detected from the laser ablated products, indicating the advantage of the laser ablation technique. Several real samples were measured by using the present instrument. Styrene was detected from acrylonitrile-butadiene-styrene resin, styrene-butadiene rubber (*o*-ring), and polystyrene foam, but no signal was observed for a glue sample (Henry A) though this sample was suspected to contain styrene by conventional mass spectrometry. The relative signal intensities were 0.12, 0.033, and 0.013 for the above three samples, though the styrene contents

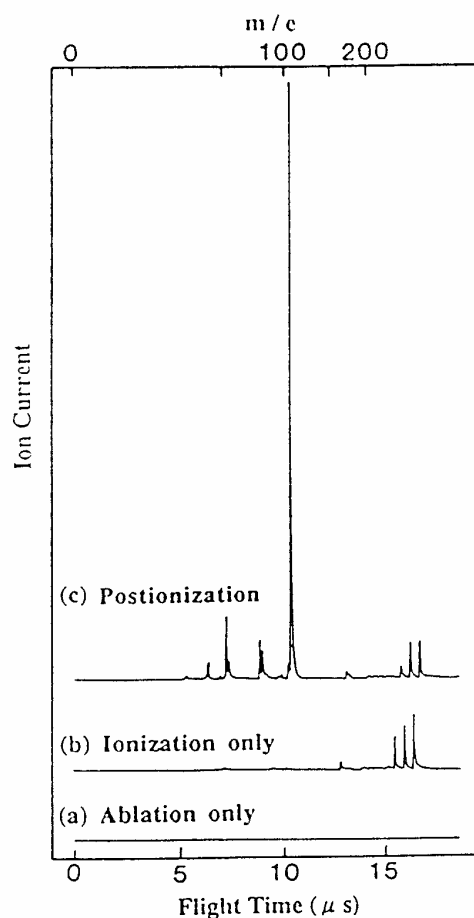


FIGURE 5. Mass spectra for laser ablated products.

were 40–60 %, 23.5 %, 90–95 %, respectively. Thus the signal intensity depends not only on the styrene content but also on the form of the sample.

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