
Temperature-Programmed Pyrolysis Hyphenated with Metastable Atom Bombardment Ionization Mass Spectrometry (TPPy/MAB-MS) for the Identification of Additives in Polymers

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Thermoanalytical techniques are currently used for the analysis of additives contained in polymers that cannot be easily dissolved, extracted, or hydrolyzed. With these techniques, the polymers are heated to liberate the additives trapped in the polymer matrix. If the polymer is heated slowly, up to its thermal degradation, the technique is called temperature-programmed pyrolysis (TPPy). For TPPy experiments, mass spectrometry is generally used as the detection method. The ionization sources commonly used in mass spectrometry, such as CI and EI, can cause fragmentation during the ionization process. Fragmentation decreases the sensitivity of the molecular ions and increases the risks of interferences with the compounds coming from the matrix. An energy-tunable ionization technique, called metastable atom bombardment (MAB), is proposed for TPPy/MS experiments. With this ionization source, the energy of ionization depends on the metastable gas used. With low-energy metastable gases such as Xe or N₂, fragmentation is reduced compared to CI, whereas with medium-energy metastable gases such as Ar or Kr, the fragmentation is similar to that observed with CI. TPPy/MAB-MS was performed on an unknown polyurethane-based car paint. The detection of molecular ions and characteristic fragments with MAB(N₂) led to the identification of two light stabilizers: *Bis*(1,2,2,6,6-pentamethyl-4-piperidinyl)sebacate (BPPS) and 2-(2H-benzotriazol-2-yl)-4,6-di-*tert*-pentylphenol (PTPP). Using MAB(Ar) to simulate CI, the molecular ion and one of the two characteristic fragments of BPPS were not detected, thus confirming the advantage of using MAB(N₂) ionization for TPPy/MS experiments. (J Am Soc Mass Spectrom 2004, 15, 1315–1319) © 2004 American Society for Mass Spectrometry

A large variety of additives are used in polymer processing to obtain compounds with the desired properties. These additives can modify the color (pigments and dyestuffs), improve or modify the mechanical properties (fillers and reinforcements), provide resistance to heat and aging (antioxidants and stabilizers), provide resistance to light degradation (UV stabilizers), improve flame resistance (flame retardants), improve processing characteristics (recycling additive), and improve the performance (anti-static/conductive additives, plasticizers, blowing agents, lu-

bricants, mold release agents, surfactants, preservatives) of the polymers [1]. The identification of additives accounts for a great part of the reformulation process often needed to reproduce, recycle or environmentally discard unknown polymers.

The techniques actually used for the analysis of additives in polymers are extensively reviewed by J. C. J. Bart [2, 3]. The additives can be liberated by extraction, dissolution, or hydrolysis of the polymer and analyzed using conventional methods (e.g., HPLC, GC, MS). However, for some insoluble or cross-linked polymers, these approaches are difficult to apply and other techniques must be used. When the matrix does not interfere, non-destructive in-polymer spectroscopic techniques such as diffuse-reflectance near infrared spectroscopy [4] can be employed. In other cases, thermoanalytical techniques that consist of liberating the

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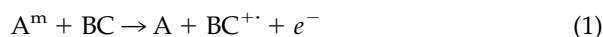
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additives by heating the polymer are needed. Information about the additives can be obtained rapidly using flash pyrolysis hyphenated with mass spectrometry (Py/MS) or gas chromatography (Py/GC, Py/GC/MS). Using Py/MS, all the compounds generated during the pyrolysis of the polymer are emitted at the same time and the small amounts of additives can be masked by the interferences coming from the matrix [3]. The chromatographic separation allowed by Py/GC or Py/GC/MS is a good way of separating the additives from the interferences and thus increasing the selectivity and sensitivity of the technique [5]. To identify additives with high molecular weight that cannot be analyzed using GC owing to their low volatility, temperature-programmed pyrolysis (TPPy) in combination with mass spectrometry (TPPy/MS) can be employed. TPPy consists of gradually heating the polymers to perform selective desorption of the organic additives at temperatures often below the polymer's decomposition temperature [3]. For TPPy/MS, the thermal degradation of the polymer is generally performed directly inside the mass spectrometer's ionization chamber and the high vacuum favors the analysis of high molecular weight compounds.

The extent of fragmentation is decisive in identifying additives in polymers for three reasons: (1) More structural information about the original molecule is contained in large fragments, (2) the dispersion of the additive in many fragments decreases the sensitivity, and (3) the fragmentation of the compounds coming from the matrix increases the risk of interference with the additives analyzed. Two factors influence the extent of the fragmentation: The pyrolysis temperature and the ionization source used for mass spectrometry detection. A pyrolysis temperature kept at the minimum reduces the risks of thermal degradation of the additives as well as of the matrix. On the other side, the conventional ionization sources used in mass spectrometry (EI, CI) generally cause fragmentation of the molecules during the ionization process, and sometimes the molecular ions of the additives are not observed.

A recently introduced ionization technique allowing better control of the ionization energy is proposed for TPPy/MS analysis of additives in polymers. This technique, called metastable atom bombardment (MAB) [6], is based on Penning ionization [7]: An electrophilic reaction of a metastable species with an analyte. Eq 1 represents this process:

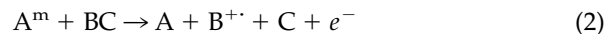


The metastable species (A^m) attacks a molecular orbital of the analyte (BC) from which an electron is transferred into a vacant orbital of A^m . Simultaneously, an electron (e^-) from the outer shell of A^m is ejected into a continuum state. The highest amount of excess energy that is imparted to the analyte ($BC^{+\cdot}$) upon ionization equals the difference between the energy of A^m and the ion-

Table 1. Energy and lifetime of the metastable states of the gases used for metastable atom bombardment ionization [7–9]

Gas	Metastable state	Energy (eV)	Lifetime (s)
He	1S_0	20.62	2.0×10^{-2}
	3S_1	19.82	9.0×10^3
He	3P_0	16.72	4.3×10^2
	3P_2	16.62	2.4×10^1
Ar	3P_0	11.72	4.5×10^1
	3P_2	11.55	5.6×10^1
Kr	3P_0	10.56	4.9×10^{-1}
	3P_2	9.92	8.5×10^1
Xe	3P_0	9.45	7.8×10^{-2}
	3P_2	8.32	1.5×10^2
N ₂	$E^3\Sigma_g^+$	11.88	2×10^{-4}
	$w^1\Delta_u$	9.02	$1-5 \times 10^{-4}$
	$a^1\Pi_g$	8.67	$1.0-1.5 \times 10^{-4}$
	$a'^1\Sigma_u^-$	8.52	1.4
	$W^3\Delta_u$	7.32	17
	$A^3\Sigma_u^+$	6.17	1.0–2.6

ization potential of BC. If this excess energy is sufficient, dissociative Penning ionization can also occur as described by eq 2:



Thus, by using a metastable gas that has an energy close to the ionization potential of the analyte, the internal energy of the analyte ion formed is small and fragmentation is essentially absent. However, if the energy difference is large, the reaction shown in eq 2 is favored and extensive fragmentation can result. Table 1 shows the excitation energy and the lifetime of the metastable species of the gases used for MAB ionization [7–9]. During the excitation process, each gas generates more than one metastable state. For each rare-gas, it is the metastable state with the weaker energy that is the most populated [7]. Therefore, with these gases, ionization is performed using a quasi-monoenergetic metastable atom beam. Using N₂ as the ionization gas, the global ionization energy is located between the ionization energies of Xe and Kr. Piperidine was analyzed with the different MAB gases to observe the variation in fragmentation [10]. Using He or Ne, an extent of fragmentation greater than or equal to EI (70 eV) is observed. When gases providing intermediate internal energies such as Ar and Kr are used, the fragmentation observed with MAB is comparable to that of CI mostly involving rearrangement ions. Finally, the low energy mode of the MAB source (Xe, N₂) yields mainly molecular ions. The MAB ionization technique has already been used to analyze flame retardants [11], dioxins and furans [12], bacteria [13], and explosives [14].

Experimental

Polymer Studied

The polymer for which the additives were analyzed was a polyurethane-based clear coating for the car industry

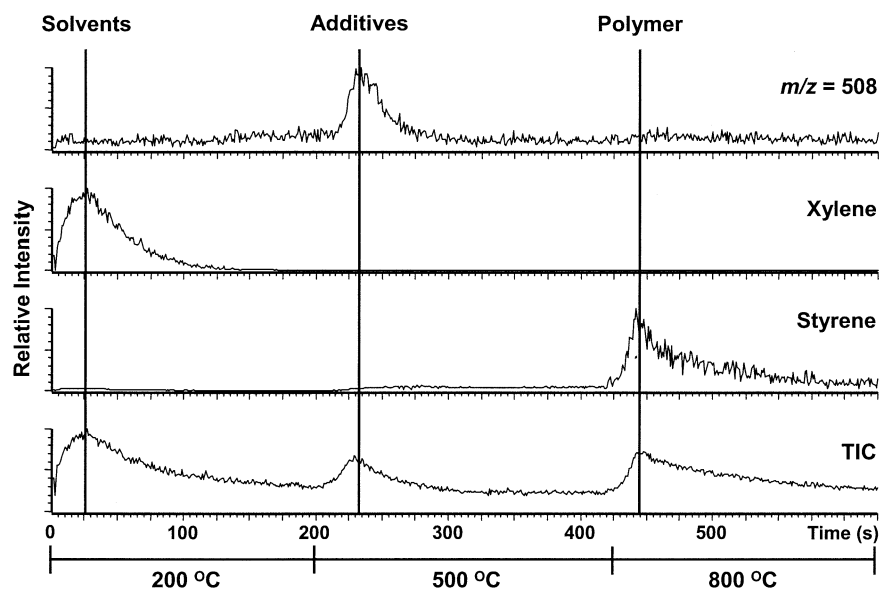


Figure 1. TPPy/MAB-MS ion chromatogram of the unknown car paint studied using N_2 as ionization gas.

collected in a car repair shop just after its application. The polymer matrix was made of isocyanurate, the cyclic trimer of 1,6-hexamethylenediisocyanate (HDI), reacted with a hydroxyl-functional polyacrylate resin.

TPPy/MAB-MS Analysis

TPPy/MAB-MS experiments were conducted using a Py/MAB-ToF mass spectrometer (Dephy Technologies Inc., Montreal, Canada) optimized for thermo-analytical mass spectrometry [15]. N_2 was used as the MAB ionization gas at a pressure of 85 mBar. The discharge work current was 12 mA, and the temperature of the source was 150 °C. The orthogonal-acceleration reflectron-based time-of-flight mass analyzer was operated at a push-out rate of 25–50 kHz, which ensures good sensitivity and a rapid acquisition rate compatible with pyrolysis experiments. The instrument has a mass range of 3000 Da. The pyrolyzer used was a Pyroprobe 2000 (CDS Analytical, Oxford, PA). With this apparatus, the maximum temperature allowed was 1400 °C, and the permitted heating rate ranged from 0.01 to 20 $K\ ms^{-1}$. The solid probe consisted of a quartz tube placed inside an electronically controlled, platinum heating coil. All the temperatures mentioned in this article are nominal instrument temperatures that correspond to the temperatures of the heating coil provided by the manufacturer. The temperature at the level of the sample is thus unknown and probably much lower than the nominal temperature set. For a nominal instrument temperature of 600 °C, Funazukuri et al. [16] measured a sample temperature of only 275 °C.

Previous TPPy/MAB-MS experiments have been carried out on the car paint studied to identify the isocyanates generated during its thermal degradation

[17]. A temperature program, consisting of three consecutive temperature levels (200 °C for 200 s, 500 °C for 225 s, and 800 °C for 200 s), was used. At 200 °C, the solvents trapped in the polymer (toluene, xylene and trimethylbenzene) were emitted, and at 800 °C, the polyurethane matrix had decomposed to generate various isocyanates and styrene. To identify the additives, new experiments focusing on the 500 °C level were performed using the same temperature program. To increase the sensitivity of the additives, the weight of the pyrolyzed samples was increased to approximately 0.5 mg.

Additive Identification Validation

A pure additive, identified during the TPPy/MAB-MS experiments, was analyzed using an AutoSpec-ToF mass spectrometer (Micromass, Manchester, UK) to confirm its fragmentation pattern. The mass spectrometer was equipped with a MAB ionization source (Dephy Technologies Inc., Montreal, Canada) operated under the same conditions as during the TPPy/MAB-MS experiments. This apparatus was also used for the exact-mass measurement used to validate the fragmentation mechanism.

Results and Discussion

TPPy/MAB-MS

The TPPy/MAB(N_2)-MS ion chromatogram is shown in Figure 1. As expected, owing to the temperature program, the emission of organic compounds was separated into three steps: the solvents, the additives, and the polymer matrix. Figure 2a shows the mass spectra of the

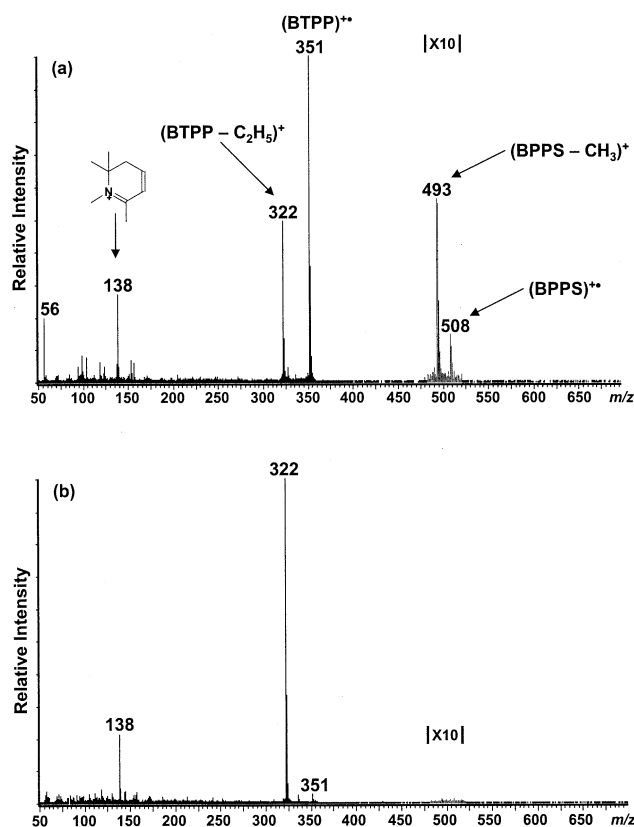
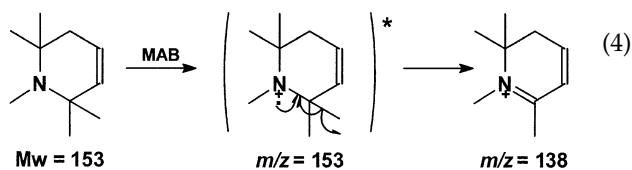
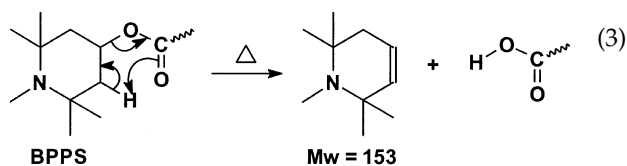


Figure 2. Mass spectrum obtained during the TPPy/MAB-MS analysis of the car paint at 500 °C. (a) MAB(N₂); (b) MAB(Ar).

car paint obtained at 500 °C using N₂ as ionization gas. The higher m/z ratio detected was 508, which corresponds to the molecular ion of *Bis*(1,2,2,6,6-pentamethyl-4-piperidiny)sebacate (BPPS) (Figure 3), a light stabilizer used in the coating industry. Two characteristic fragments of this compound were also detected at $m/z = 138$ and 493. The loss of the methyl group to generate the ion at $m/z = 493$ comes from an α -cleavage of the molecular ion similar to that observed for 1,2-dimethylpiperidine [18]. For the formation of the ion at $m/z = 138$, a two-step mechanism is proposed in eqs 3 and 4.



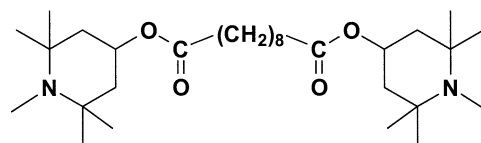
The molecule with a molecular weight (Mw) of 153 was probably generated during the thermal degradation of the additive according to eq 3. Following MAB ionization, the major fragmentation pathway proposed is shown in eq 4. The ion at $m/z = 153$ loses a methyl group during α -cleavage to generate the ion at $m/z = 138$. This low-energy cleavage is favored by the energy stabilization gained by the appearance of electronic resonance between the two double bonds.

The dominant ion at $m/z = 351$ corresponds to the molecular ion of an other light stabilizer named 2-(2H-benzotriazol-2-yl)-4,6-di-*tert*-pentylphenol (BTTP) (Figure 3). The fragment at $m/z = 322$ corresponds to the loss of an ethyl radical from one of the two di-*tert*-pentyl groups attached to the phenol. The loss of ethyl groups was favored over the loss of methyl groups during this fragmentation process according to the “loss of the largest alkyl group” rule [18].

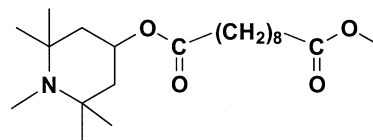
The TPPy/MAB-MS experiment was repeated using Ar as ionization gas to simulate CI. As shown in Figure 2b, under these conditions, for BPPS, only the fragment at $m/z = 138$ was observed. Detection of only this fragment was not sufficient to identify this additive.

Additive Identification Validation

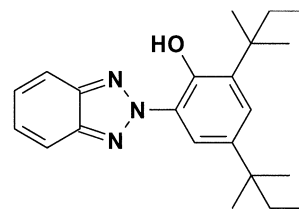
To validate the identification of BPPS, Tinuvin292 (Ciba Specialty Chemicals), a light stabilizer consisting of an almost pure mixture of BPPS and methyl(1,2,2,6,6-pentamethyl-4-piperidiny)sebacate (MPPS) (Figure 3),



Bis(1,2,2,6,6-pentamethyl-4-piperidiny)sebacate (BPPS)



Methyl(1,2,2,6,6-pentamethyl-4-piperidiny)sebacate (MPPS)



2-(2H-benzotriazol-2-yl)-4,6-di-*tert*-pentylphenol (BTTP)

Figure 3. Light stabilizers used in car paint.

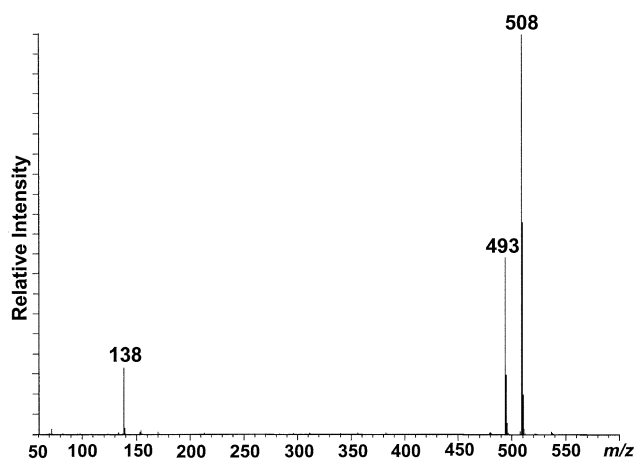


Figure 4. Mass spectrum of Bis(1,2,2,6,6-pentamethyl-4-piperidinyl)sebacate (BPPS) using N_2 as MAB ionization gas.

was analyzed. The solid probe was heated to 150 °C to evaporate the MPPS. Then, the temperature of the probe was raised to 350 °C to detect the BPPS. As shown in Figure 4, the fragments detected during the analysis of the BPPS contained in the Tinuvin292 are the same as the fragments observed during the TPPy/MAB(N_2)-MS experiment. To reinforce the fragmentation mechanism proposed for BPPS, an exact-mass measurement was performed on the fragment at $m/z = 138$. A difference of -5.7 ± 5.0 ppm between the measured mass and the calculated mass confirmed the empirical formula of the compound proposed for the ion detected at $m/z = 138$ ($C_9H_{16}N$). No other empirical formula is closer than 54.3 ppm from the exact-mass measured.

Conclusion

The MAB ionization source was used during TPPy/MS experiments for the analysis of a polyurethane-based car paint. With a low-energy MAB gas (N_2), molecular ions and characteristic fragments of BPPS and BTPP, two light stabilizers, were observed. Detection of the molecular ion of BPPS, necessary for the identification of this additive, was not possible using a medium-energy MAB gas (Ar) that simulates the fragmentation occurring during CI. These results confirmed the advantage of using MAB(N_2) compared to CI or other medium- or high-energy ionization techniques to identify additives in polymers. According to the supplier's recommendations, the concentration of BPPS and BTPP in the paint, based on solid weight, must be between 0.5 and 3%. Additives at low concentration can thus be identified using TPPy/MAB-MS. After the molecular ion of the additives was identified using MAB (N_2), if the structural information on the mass spectrum is not sufficient for structural elucidation, complementary information can be obtained by using a more energetic MAB gas, that increases the fragmentation, such as Ar.

Acknowledgments

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