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Rapid analysis of polyester and polyethylene blends by ion mobility – mass spectrometry

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In this work ion mobility–mass spectrometry (IM-MS) coupled to an atmospheric solid analysis probe (ASAP) was used for the characterization of polymer blends involving biodegradable polymers (poly(lactic acid) (PLA), poly(butylene succinate) (PBS)) and poly(ethylene) (PE). Interestingly both PLA and PBS yielded by ASAP ionization ion series corresponding to cyclic oligomers that are nearly identical to those obtained by conventional Py-GC-CI/MS. However from the drift-time vs m/z plot of a PLA/PE blend, the ion series of both polymers can be readily identified, as the PLA ions are significantly more compact than the PE ions. From this 2D plot specific mass spectra can be extracted which are almost identical to those of each polymer alone. This work highlights the potential of ASAP-IM-MS to achieve a very fast analysis of complex polymer blends. It was demonstrated that coupling gas phase ion separations (IM) with direct and weakly-discriminant ionization techniques (ASAP) significantly enhances the dynamic range of accessible concentrations and polymer polarities, opening the road to carry out more complex “materiomics” studies.

KEYWORDS

Polymer blends, poly(lactic acid), poly(butylene succinate), poly(ethylene), ASAP, ion mobility, mass spectrometry, atmospheric pressure pyrolysis, materiomics

INTRODUCTION

Polyesters are an important class of polymers used in the textile and plastic industry. Recently, biodegradable polyesters such as poly(lactic acid) (PLA) and poly(butylene succinate) (PBS), mainly used for plastic bag and food packaging applications, are experiencing growing interest from an environmental point of view. PLA is of particular interest as the lactic acid used in its production may be synthesized from renewable resources (corn starch). Moreover, the biodegradability of PLA permits its use in medical applications such as suture threads or stents. In order to expand the range of applications of such biodegradable plastics, blends are developed with other synthetic polymers such as polyethylene (PE). In this context, the structural characterization of polymers and polymer blends is essential to establish structure property relationships for future polymer design or quality control.

PLA thermal decomposition was reported by pyrolysis mass spectrometry (Py-MS) with electron ionization (EI) by I. C. McNeill et al. They obtained two main series of fragment ions, m/z 72n, referred as α, corresponding to cyclic oligomers of PLA and m/z 72n–88, referred as β, as well as several low m/z ions. They proposed a main degradation process pathway by non-radical backbiting ester interchange reaction involving OH chain ends leading to cyclic fragments. The cyclic fragments ions detected as distribution α rapidly eliminated CO2 and acetaldehyde molecules generating the fragment ion distribution β. F. D. Kopinke et al also reported similar fragment ion distributions by Py-GC-MS with EI, sometimes coupled with gas chromatography (Py-GC-MSS). Garozzo et al obtained similar results by Py-MS with Chemical Ionization (CI). They observed mainly the protonated version of distribution α, and the β one in a lesser extent. More recently, Arrieta et al. have developed a quantitative method to analyze pyrolysis residues of PLA by Py-GC-MS with EI. Contrary to others studies, they observed only the fragment series β. Other works have reported the characterization of PLA by electrospray MS. However, this ionization strategy cannot be envisioned to study PLA blend with polyolefin such as PE. In fact, polyolefin are particularly difficult to analyze by MS due to their aliphatic nature. They have no organic function allowing cation attachment and are generally too large for classical EI. Therefore, such as PLA the classical way reported to study polyolefin involves a step of pyrolysis before MS analysis. In particular, Lattimer described the pyrolysis...
residue of PE and their formation mechanisms. He reported three fragment distributions, corresponding to alkenes with \( m/z \) 14n (referred as A), alkanes with \( m/z \) 14n+2 (referred as B) and dialkenes with \( m/z \) 14n–2 (referred as C). Blazso reported similar results.9 Rizzarelli, reported the structural characterization of PBS by tandem mass spectrometry after matrix assisted laser desorption/ionization (MALDI-MS/MS).12 The author observed that the main fragmentation pathway of polymer sodium adducts consists in a β hydrogen transfer bond. This fragmentation pathway permits the formation of two fragment ions, one having a carboxylic end group while the other is terminated with a \( CH_2=CH(CH_2)_nOCO \) group. The β hydrogen rearrangement mechanism has been reported in thermal degradation of poly(propylene succinate)13 or in mass spectrometry dissociation study of similar polyester sodium adducts by MALDI-MS/MS.14 In addition and as already reported for PLA, cyclic fragment ions obtained by backbiting ester interchange were also observed by Py-GC-MS15 or thermo gravimetric studies.16

These works have shown that Py-MS seems to be a convenient strategy for polyester and polyolefin analysis. In a previous work we demonstrated that the Atmospheric Solid Analysis Probe (ASAP), is an efficient ionization probe for the MS analysis of polymers17 and in particular polypropylene (PP).18 This ionization probe, recently developed by McEwen, consists of a glass capillary tube onto which a liquid or solid sample was deposited. A heated gas flow (up to 650°C) was used for thermal desorption or atmospheric pressure pyrolysis (AP-Py) of compounds. A plasma was generated by a corona discharge, which allowed ionization to occur.19 The ASAP probe does not require sample preparation and allows a large range of compounds of differing polarity to be ionized.19,21 This source is a solvent free method in which ionization is initiated by a plasma, such as in other analogous approaches.22-25 Several works have in particular shown the interest of such approach for the analysis of polymers and/or additives.20, 26, 27 The resulting ions were similar to those obtained after atmospheric pressure pyrolysis. In the case of PP, the obtained pyrolysis residue ions were similar to those obtained by Lattimer with classical Py-MS.28 The coupling of ASAP with ion mobility-mass spectrometry (IM-MS) is an interesting tool for the characterization of mixtures such as polymer and additives and is expected to be of particular interest for the analysis of polymer blends. Indeed, we have shown that the ions of pyrolysis residues can be easily distinguished from additives ions as they often present very different conformation and are therefore separated in the drift time vs \( m/z \) plot. The coupling of a source allowing the ionization of a wide range of compounds with a universal separation technique such as ion mobility-mass spectrometry permits to envision efficient “materiomics” studies.29 In the same way to biological “omics” approaches, materiomics could consist in a comprehensive study of material structure and composition to understand its macroscopic characteristics and behavior.

In this work, we explore ASAP-IM-MS ability to carry out comprehensive studies of material composition and structure. This methodology was extended to the characterization of polymer and polymer blends involving biodegradable polymers (PLA, PBS) and PE. The molecular structures of the three studied polymers are given in Scheme 1.

![Scheme 1. Molecular structure of (a) poly(lactic acid), (b) poly(butylene succinate) and (c) poly(ethylene)](image)

**EXPERIMENTAL SECTION**

**Samples:** Two samples of poly(l-lactic acid) with weight average molecular weights (\( M_w \)) of 10 kDa (TOTAL, Feluy, Belgium) and 76 kDa (Synterra PLLA1010, Synbra, Etten Leur, Netherlands) equivalent to polystyrene (PS) were used. Two PBS (Mw<100 kDa eq. PS) from Showa Denko K, K (Minato-ku, TKY, Japan) and coming from different batch were referred as PBS 1 and PBS 2. Two polymer home-made blends, PLA (125 kDa eq. PS) / PBS (<100 kDa eq. PS) (50/50, w/w) and PLA (75 kDa eq. PS) / PE (103 kDa) (30/70, w/w) were obtained by compounding in a lab twin-screw extruder. The corresponding PE was from TOTAL.

**Mass spectrometry:** Data acquisitions were performed using a SYNAPT G2 HDMS fitted with an ASAP source (Waters Corp., Manchester, UK). This instrument is a hybrid quadrupole/time-of-flight mass spectrometer, which incorporates a travelling wave (T-Wave)-based mobility separation device. The instrument and the T-Wave device have been described in detail elsewhere.30, 31 The samples were heated to their melting point in a glass bottle. ASAP capillary tube was dipped in the melt polymer before cooling at room temperature. ASAP was conditioned to experimental temperature during 1 h before experiments. Finally the capillary tube was fixed to the ASAP probe holder and introduced in the ionization source. ASAP mass spectra were acquired in positive ion mode over the \( m/z \) 50-2000 range during 5 min and 1 min for MS and MS/MS spectra respectively. Note that a blank was recorded during 1 min before each sample introduction. A nitrogen flow of 1200 L h\(^{-1}\) heated at 650°C was used for thermal desorption. The ASAP source was heated at 140°C. The corona discharge voltage was 4 kV and sampling cone voltage was 20 V. Trap and transfer collision gas flow were set at 2.0 mL min\(^{-1}\) (0.02 mbar for Ar cell pressure). For IM/MS experiment, Helium cell gas flow was set at 180 mL min\(^{-1}\) and IMS gas flow (N\(_2\)) was set at 70 mL min\(^{-1}\) (3.0 mbar for IMS cell pressure). TWIMS travelling wave height and velocity were set respectively at 40 V and 700 m s\(^{-1}\). Argon was used as target gas in the trap cell for MS/MS experiments. The collision...
energy reported in the manuscript is in laboratory reference frame. Data acquisition and mass spectra treatment were provided by MassLynx (version 4.1). DriftScope (version 2.1) software was used for the treatment of m/z vs drift-time maps. Note that the peak at m/z 277.0777 observed on mass spectrum is a background ion of the ASAP source, it corresponds to a fragment ion (loss of H\textsuperscript{+}) of triphenylphosphine oxide (C\textsubscript{18}H\textsubscript{14}OP), present as flame retardant. This background ion is used as internal standard for accurate mass measurement in MS mode.

**RESULT AND DISCUSSION**

**Polyesters**

In the first part of this study we focus on the characterization of polyester PLA and PBS. The ASAP-MS spectra obtained for both PLA samples are given Figure 1.

![Figure 1. ASAP-MS spectra of PLA (a) 10 and (b) 76 kDa equivalent to Polystyrene (PS).](image1)

Firstly, we can note that a mass spectrum was easily obtained for each sample independently of its molecular weight. These mass spectra were recorded with a 5 min acquisition time using standard experimental conditions. We can observe in Figure 1 that the two PLA samples gave similar spectra with a main distribution of peaks with m/z 72.02\(n\)\(+1\), with \(n\) the number of repeating unit for each oligomers. Similarly to Garozzo works, this distribution corresponded to protonated cyclic oligomers [M+H]\textsuperscript{+} issued from atmospheric pyrolysis of the samples, previously referred protonated \(\alpha\) distribution.

The ASAP-MS spectrum obtained for the PBS 1 sample was given Figure 2.

![Figure 2. ASAP-MS spectrum of PBS 1 showing one main distribution of PBS oligomers (labelled with a black circle).](image2)

The ASAP-MS spectrum of PBS shows a series of ions with mass difference of 172.07 Da between two consecutive peaks, corresponding to butylene succinate repeating unit molecular weight. As already observed for PLA, this series, annotated with black circle, probably corresponds to protonated cyclic fragments [M+H]\textsuperscript{+} with m/z 172.07\(n\)+1 formed by a backbending ester interchange reaction.\textsuperscript{2,4,15,16}

The ASAP-MS spectrum obtained for the PBS 2 sample was given Figure 3.

![Figure 3. ASAP-MS spectrum of PBS 2 showing three ion distributions labelled with black circles (expected PBS pyrolysis products), white circles (PBS+C\textsubscript{2}H\textsubscript{4}) and black squares (PBS+C\textsubscript{4}H\textsubscript{8}).](image3)

The ASAP-MS spectrum of PBS shows three series of ions with mass difference of 172.07 Da between two consecutive peaks, corresponding to butylene succinate repeating unit molecular weight. As already observed for PBS 1 the major series, already annotated with black circle, probably corresponds to protonated cyclic fragments [M+H]\textsuperscript{+}. The two additional distributions, labeled with white circles and black squares, corresponded respectively to +28.03 Da (C\textsubscript{2}H\textsubscript{4}) and +56.06 Da (C\textsubscript{4}H\textsubscript{8}) mass shifts compared to the major distribution. These propositions were supported by accurate mass measurements given Table 1.
bond cleavage (β hydrogen transfer mechanism) leading to fragment ions with carboxylic acid and CH₂⁻.

Table 1. Accurate mass measurement of ions detected on the PBS 2 ASAP-MS mass spectrum.

<table>
<thead>
<tr>
<th>Experimental m/z</th>
<th>Chemical formula</th>
<th>Theoretical m/z</th>
<th>Δ (m/z) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>173.0813</td>
<td>[(C₅H₇O₂)₄-H⁺]</td>
<td>173.0808</td>
<td>+2.9</td>
</tr>
<tr>
<td>201.1125</td>
<td>[(C₅H₆O₂)₃-H⁺]</td>
<td>201.1121</td>
<td>+2.0</td>
</tr>
<tr>
<td>345.1557</td>
<td>[(C₅H₇O₂)₃-H⁺]</td>
<td>345.1544</td>
<td>+3.8</td>
</tr>
<tr>
<td>373.1871</td>
<td>[(C₅H₇O₂)₃(H₂O₂)₃-H⁺]</td>
<td>373.1857</td>
<td>+3.8</td>
</tr>
<tr>
<td>401.2178</td>
<td>[(C₅H₆O₂)₂-H⁺]</td>
<td>401.2170</td>
<td>+2.0</td>
</tr>
<tr>
<td>517.2308</td>
<td>[(C₅H₇O₂)₂(H₂O)₃-H⁺]</td>
<td>517.2280</td>
<td>+5.4</td>
</tr>
<tr>
<td>545.2593</td>
<td>[(C₅H₇O₂)₂(H₂O)₅-H⁺]</td>
<td>545.2593</td>
<td>+4.8</td>
</tr>
<tr>
<td>573.2906</td>
<td>[(C₅H₇O₂)₃(H₂O)₂-H⁺]</td>
<td>573.2906</td>
<td>+3.8</td>
</tr>
<tr>
<td>689.3015</td>
<td>[(C₅H₇O₂)₄-H⁺]</td>
<td>689.3015</td>
<td>+4.2</td>
</tr>
<tr>
<td>717.3328</td>
<td>[(C₅H₇O₂)₃(H₂O)₃-H⁺]</td>
<td>717.3328</td>
<td>+4.7</td>
</tr>
<tr>
<td>745.3669</td>
<td>[(C₅H₇O₂)₄(H₂O)₂-H⁺]</td>
<td>745.3664</td>
<td>+3.8</td>
</tr>
</tbody>
</table>

The non-expected additional distributions detected on PBS 2 ASAP-MS spectrum could be in accordance with a copolymeric species presenting repeating unit with a mass difference of +28.03 Da compared to the butylene succinate one. This copolymer could come from the presence of additional monomers in the polymer synthesis. In fact, PBS are generally prepared by polycondensation using technical grade succinic acid and 1,4-butanediol as monomer. The presence of adipic acid and/or 1,6-hexanediol during the PBS 2 synthesis could not be excluded. The chemical formula and molecular weight of the possible monomers were summarized in Table 2.

Table 2. Structure and molecular weight of the possible monomers.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Chemical formula</th>
<th>Monoisotopic mass (Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Succinic acid</td>
<td>HOOC-(CH₂)₃-COOH</td>
<td>118.0266</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>HOOC-(CH₆)₃-COOH</td>
<td>146.0579</td>
</tr>
<tr>
<td>1,4-butanediol</td>
<td>HO-(CH₂)₃-OH</td>
<td>90.0681</td>
</tr>
<tr>
<td>1,6-hexanediol</td>
<td>HO-(CH₅)₂-OH</td>
<td>118.0994</td>
</tr>
</tbody>
</table>

However, the presence of peak at m/z 201.11 (corresponding to protonated 1-mer plus C₃H₆) on the MS spectrum (Figure 3) and the absence of peak at m/z 229.14 (corresponding to protonated 1-mer plus C₄H₈) indicated that only one additional monomer (adipic acid or 1,6-hexanediol) was present. Overall this result is consistent with a copolymer involving normal PBS repeating unit noted as A (172.07 Da) and an unexpected repeating unit noted as B (200.11 Da). Tandem mass spectrometry experiments were carried out to identify the non expected B repeating unit. The ions detected at m/z 745.36 [A₃B₂-H⁺], 713.33 [A₃B₁-H⁺] and 689.30 [A₂H⁺] were selected in the quadrupole and submitted to collisional activation in the trap cell, the corresponding spectra were given Figure 4.

The tandem mass spectrum of the expected 4-mer PBS (cyclic oligomer containing four repeating unit) is given Figure 4(a). It should be noted that as the precursor ion is a cyclic species, the obtained fragment ions result from the cleavage of at least two covalent bonds. As previously observed for polyester the main fragmentation occurred via (CO)O-CH₂ bond cleavage (β hydrogen transfer mechanism) leading to fragment ions with carboxylic acid and CH₂=CH(CH₂)₂OCO-terminations. In fact, Figure 4(a) shows three main fragment ions at m/z 517.23, 345.15 and 173.08 corresponding formally to repeating unit neutral losses (172.07 Da). This fragmentation was followed by water molecule elimination as supported by the ions detected at m/z 155.07, 327.14 and 499.22 in a lesser extent. Another β hydrogen transfer mechanism could lead to species with two CH₂=CH(CH₂)₂OCO- terminations, detected at m/z 571.27, 399.20 and 227.13. Their complementary ions, terminated with two acidic functions, were detected in a lesser extent at m/z 635.25, 463.18, 291.11 and 119.03. These ions could consecutively lose a water molecule to give fragment ions detected at m/z 445.17, 273.10 and 101.02. This fragmentation pathway is depicted in Figure 5.
Figure 5 Proposed fragmentation pathways for the protonated expected cyclic 4-mer PBS pyrolysis product. * corresponds to low intensity ions.

![Diagram of fragmentation pathways](image)

The tandem mass spectra of 4-mer cyclic PBS containing one and two impurity monomers at $m/z$ 717.33 [A$_3$B$_1$+H]$^+$ and 745.36 [A$_2$B$_2$+H]$^+$ respectively were given Figure 4(b) and Figure 4(c). These MS/MS spectra were substantially similar to the spectrum of the expected 4-mer PBS (Figure 4(a)) and could be explained by the same fragmentation pathway.

Nevertheless, we can note that the expanded views of the [A$_3$B$_1$+H]$^+$ and [A$_2$B$_2$+H]$^+$ MS/MS spectra show a fragment ion at $m/z$ 147.07 corresponding to protonated adipic acid molecule. This ion confirms the presence of adipate as repeating unit in these two oligomers. Moreover it supports the presence of adipic acid rather than 1,6-hexanediol as “non expected” monomer during the polymer synthesis. Thus, we can say that the sample referred as PBS2 is a poly(butylene succinate adipate) (PBSA) copolymer with a succinic acid/adipic acid ratio of about 3.6 according to the relative signal intensities in Figure 3. Interestingly the MS/MS spectra of the copolymer ions show ion series that can confirm the presence of the two different repeating units A and B. For instance, the ions at $m/z$ 201.11 and 401.23 (Figure 4c) present 1 and 2 B repeating unit respectively. The presence of this $m/z$ ion 401.22 suggests that two B units can be present consecutively in the polymer.

**Polyester blends**

In this part, we will focus on polymer blends based on the previously studied polyester (PLA, PBS) and also a PE.

The ASAP-IMMS results for PLA/PBS blend were reported Figure 6 as a two dimensional plot with mass spectrometry data ($m/z$) on x-axis and ion mobility data (drift time in ms) on y-axis.

![ASAP-IMMS result of PLA/PBS blend and the corresponding mass spectrum of polymer blend](image)

We can see in Figure 6(a) that two main areas appeared on the drift time vs $m/z$ plot of the PLA/PBS blend. The ions of the upper area having higher drift time, corresponded to molecule having more expanded conformation than the cyclic ions of PLA and PBS that appeared in the other area. The comparison of Figure 6(a) with ASAP-IMMS results of PLA sample (data not shown) indicates that these previous ions corresponded to additives (or impurity) from PLA. We can note that ions coming from PLA and PBS polymers were on the same area of the drift time vs $m/z$ plot due to the similar conformation of cyclic pyrolysis residue ions of these two polyesters. The extracted mass spectrum of the PLA and PBS pyrolysis residue given Figure 6(b) shows the distribution of cyclic PLA ions $m/z$ 72.02$n+1$ noted as #, and the expected distributions of PBS ions $m/z$ 172.07$n+1$ (black circle). We can note that additional distributions previously annotated with white circle and black squares were not detected in this sample. Moreover we observe a large difference in PLA and PBS ions intensity probably coming from difference in pyrolysis efficiency. In fact, the PLA used in this blend has a molecular weight significantly higher than the PBS one, $M_w$=125 kDa eq. PS for PLA vs $M_w$<100 kDa eq. PS for PBS. This molecular weight difference could explain a variance in pyrolysis efficiency.
Figure 7(a) shows the ASAP-MS spectrum obtained for PLA-PE blend. We can note that only one distribution of ion corresponding to protonated PLA cyclic oligomers is observed. The absence of PE ions on the spectrum could be explained by a large difference in ionization efficiency between polar PLA and aliphatic PE. It should be noted that even when expanding the mass spectra, ions that can be attributed to the PE overlap with other background ions and will be most likely not considered during the analysis of an unknown sample. In fact, although the ASAP source is able to ionize very non-polar compounds such as alkanes, these species are discriminated when they are present in mixtures with more polar species.

However, ASAP-IM/MS results given Figure 7(b) clearly show two distinct areas whose extracted spectra were given as insert. The comparison of Figure 1 with the lower insert spectrum allows PLA to be clearly identified. Moreover the spectrum given as higher insert exhibits different ions series with difference of 14 m/z unit between consecutive peaks, it could correspond to PE pyrolysis residue ions. An additional peak detected at m/z 855.86 and already observed on Figure 6(a) could be attributed to an additive or impurity present in the PLA sample. It was demonstrated that using ion mobility as gas phase ion separations technique, hyphenated with a weakly-discriminant ionization technique (ASAP) significantly increases the dynamic range of accessible concentrations and polymer polarities, for mass spectrometry studies.

Expands of the PE mass spectrum (Figure 8) showed areas presenting mass difference of 14 m/z unit, they correspond to the overlapped isotopic patterns of PE pyrolysis residues. We could note that the PE spectrum obtained by ASAP is particularly complex. The most intense ions, detected at m/z 390.43, 404.45 and 418.45 on the expand spectrum could be attributed to molecular ions [M]⁺ of dialkene Mw = 14n−2, previously noted as series C by Lattimer.⁸ We can also note the presence of oxidized species detected for example at m/z 421.4392 corresponding to [C20H37O]⁺ while 421.4777 corresponds to [C30H61]⁺. This oxidized species are most likely due to the presence of traces of oxygen that can react with the radical ions produced during the ionization process.²²

The result obtained in Figure 7 is due to several factors. First, the additional separation afforded by the ion mobility yielded direct spectra cleanup. In this particular case, the gas phase conformation of the PE and PLA ions is very different allowing their differentiation in the drift time dimension. Second, the 2D plot uses a log scale for the intensity axis allowing low abundance species to be highlighted. One can consider plotting the mass spectrum with a log scale but this will lead to an increase of the background ions.
CONCLUSION

This work shows that ASAP-IMMS combination technique is powerful for the analysis of polyester and polyester blend. Indeed, contrary to classically used electrospray or MALDI ionization source, ASAP ionization technique does not require any sample preparation and allows to analyze polymers and polymer blends over a wide range of polarities, in a few minutes. In addition, these polymers could be easily analyzed for a wide range of molecular weights. ASAP can yield relatively large pyrolysis product that can be used to further investigate more complex systems such as copolymers. Indeed, this ionization technique, combined with tandem mass spectrometry experiments has also allowed us to quickly detect and identify impurities in the monomers used for the synthesis of one of the PBS sample. It should be noted however that information on average molecular weights and end-groups, might be lost during pyrolysis. Moreover, in favorable case such as PLA/PE blend, the use of ion mobility permits to improve dynamic range for mass spectrometry studies. It will be particularly useful in the case of polymers (or polymer blends) that are difficult to solubilize or analyze by other techniques. Finally, ASAP-IM-MS seems to be a technique of choice for comprehensive studies of materials and to carry out materiomics studies.

ACKNOWLEDGEMENT

The authors thank the Region Haute-Normandie, the Labex SynOrg (ANR-11-LABX-0029) and the European Regional Development Fund (ERDF 31708) for financial support.

Notes and references