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Collision-induced dissociation of polymer ions: Charge driven decomposition for sodium-cationized polylactides and isomeric end-group distinction

Julien De Winter[a,b], Olivier Coulembier[b], Philippe Dubois[b], Pascal Gerbaux[a,*]

[a] Mass Spectrometry Research Group, Centre Interdisciplinaire de Spectrométrie de Masse (CISMa), University of Mons, 20, Place du Parc, 7000 Mons, Belgium
[b] Center of Innovation and Research in Materials and Polymers (CIRMAP), Laboratory of Polymeric and Composite Materials, University of Mons, 20 Place du Parc, B-7000 Mons, Belgium

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ABSTRACT

Tandem mass spectrometry is increasingly applied to polymer ions in the context of in-depth structural characterization. In particular, the well-known collision-induced dissociation (CID) methodology is nowadays advantageously used to characterize end-groups and to distinguish isomeric polymer ions. When applied to sodium-cationized polyesters, CID was demonstrated to mainly involve charge remote fragmentation processes and consecutive as well as competitive dissociation pathways. In the present report, an experimental and theoretical study of collision induced dissociation of isomeric sodium cationized polylactide was investigated. The investigated polymers were designed to obtain oligomers only differentiated on the basis of regioisomeric end-groups, using ortho-, meta-, and para-methylbenzyl alcohols as initiators. The CID spectra revealed the presence of competitive charge driven and charge remote fragmentations. In particular, the charge induced fragmentations allowed the minute distinction between the three isomeric end-groups. The intermediacy of an ion/neutral complex was proposed to account for the observed decomposition and some theoretical calculations were performed to support the proposal.

1. Introduction

As extensively reviewed by Wesdemiotis et al. [1] tandem mass spectrometry is increasingly applied to polymer ions in the context of in-depth structural characterization. In particular, the well-known collision-induced dissociation (CID) methodology is nowadays advantageously used to characterize end-groups or in-chain substituents, to distinguish isomeric polymer ions and to determine macromolecular connectivities and architectures [1]. Polymer ions are mainly produced from the polymer samples using soft ionization methods, namely electrospray ionization (ESI) and matrix-assisted laser desorption/ionization (MALDI) [2]. Upon ESI and MALDI and depending on the functionalities present on the polymer chains, polymer molecules (M) are mainly ionized by protonation $[M+H]^+$ or metal ion (Me^+) attachment $[M+Me]^+$, in the positive ion mode, or by deprotonation $[M-H^+]^-$, in the negative ion mode. Whatever the ionization reaction, the vast majority of polymer ions are closed-shell species (even electron species), i.e. bearing no unpaired electron [3]. For the sake of information, it is interesting to remind that highly conjugated polymer chains, such as polythiophenes, are ionized upon MALDI by one electron removal affording radical cations (odd electron species) [4].

The ion decomposition reactions are basically classified into two different families of mechanisms. Indeed, ions can competitively dissociate either by homolytic bond cleavages or rearrangement reactions [5]. Based on the nature (odd or even electron species) of the decomposing ions, the kinetics of these competitive processes are highly dependent on the internal energy available to drive the decomposition [5]. As for a general rule, for closed-shell ions, activated by collisional activation at low kinetic energy (E_{lab} = 10–100 eV), rearrangement reactions that rely on concomitant bond cleavage and bond formation processes are often kinetically favoured [5].

The rearrangement reactions undergone by collisional-activated ions include charge-induced and charge-remote reactions. Charge-induced reactions are mainly observed starting from protonated molecules, whereas, upon deprotonation or metal ion attachment, most of the reactions are explained on the basis of a charge remote pathway [1]. In the case of charge-induced (charge-localized or charge-driven) mechanisms, the rearrangement process is occurring at the positive (protonated) charge site and the decomposition mechanism really involves the cationizing species. Such mechanism is also observed upon cationization by lithium ion [6]. At variance, upon, for instance, sodium cation attachment, the rearrangement reactions are occurring at locations

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[*] Corresponding author. Tel.: +32 65 37 33 42.
E-mail addresses: Pascal.Gerbaux@umons.ac.be, pascal.gerbaux@umh.ac.be (P. Gerbaux).

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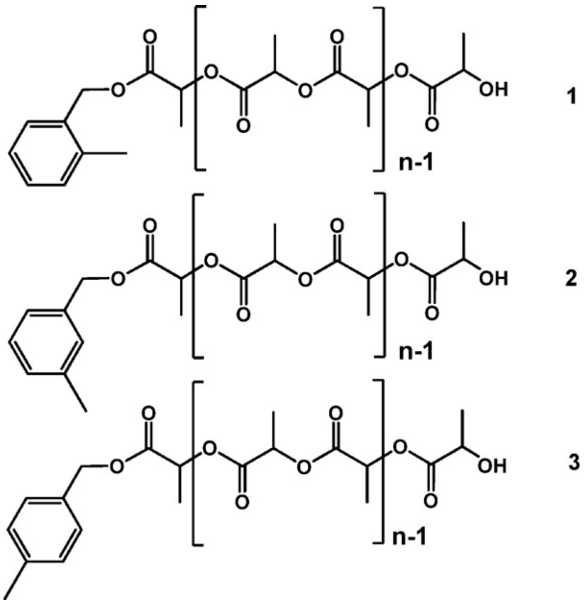


Scheme 1. Investigated polymers: α-ortho-methylbenzyl, ω-hydroxylpolylactide (**1**), α-meta-methylbenzyl, ω-hydroxylpolylactide (**2**) and α-para-methylbenzyl, ω-hydroxylpolylactide (**3**).

that are not directly bonded to the cationizing species. The so-called charge-remote decompositions present great similarity with thermal decompositions [1]. Basically, for cationized species, the difference between charge remote and charge driven pathways can be understood on the basis of the strength of the bond created between the cationizing particles and the neutral molecules. Indeed, upon protonation or Li^+ attachment, the electronic structure of the neutral molecule is definitively strongly modified since true covalent bonds are created. At variance, upon sodium ion attachment, the electronic structure of the neutral molecule is not extensively modified since the metal ion bonding to the neutral molecule is better considered as a complexation process.

In this context, we recently reported a joint theoretical and experimental investigation on the collision-induced dissociation reactions at low kinetic energy of sodium-cationized polylactides (PLA) [7]. In that paper, we demonstrated that, upon collisional activation, PLA. Na^+ systematically suffers from end-group specific dissociations. Those dissociations involve favourable six-membered ring transition states. Consecutive and competitive fragmentations were also highlighted and were shown to correspond to progressive fragmentations of the oligomer chain starting from both end-groups. Interestingly, in addition to those structurally indicative dissociations, we also demonstrated that collisionally excited PLA. Na^+ competitively suffer from two consecutive backbone cleavages leading to sodium-bound dimer and trimer cations that ultimately lead to the loss of a monomeric residue that corresponds to neutral acrylic acid. Such a decomposition is definitively not end-group specific [7b].

In the course of these studies, we investigated the CID behaviors of different end-group modified PLA. In particular, when studying the collision-induced decompositions undergone by sodium-cationized α-ortho-methylbenzyl, ω-hydroxyl poly(lactide), see Scheme 1, the loss of 5,6-bis(methylene)-1,3-cyclohexadiene (MW = 104 u) was observed competitively to the expected decomposition reactions. Whereas all the other reactions can definitively be considered as charge-remote processes, this interesting decomposition can only be explained on the basis of the intermediacy of an ion/neutral complex. Such a mechanism can be associated with a charge driven process from collisionaly excited sodium cationized PLA.

In the present paper, we would like to propose a mechanism to account for the observed decomposition reaction and we will apply this peculiar fragmentation in the context of isomeric end-group differentiation.

2. Experimental

2.1. Materials

All the products were commercially available except α-ortho (meta/para)-methylbenzyl, ω-hydroxylpolylactides that were prepared following the procedure described here after. L-Lactide monomer and initiators (methylbenzyl alcohol) were firstly dried by successive azeotropic distillations of toluene and then stored in glovebox (under N_2, $O_2 < 5$ ppm, $H_2O < 1$ ppm). Toluene and chloroform (solvent of polymerization; Labscan, 99%) were dried using an MBraun solvent purification system under N_2.

2.2. Syntheses

2.2.1. α-Ortho (meta/para)-methylbenzyl,ω-hydroxylpolylactide

In glovebox, 12 mg of initiator (1×10^{-4} mol; MW = 122.17 g mol^{-1}), and 39 mg of 1,8-diazobicyclo[5.4.0]undec-7-ene (2.5×10^{-5} mol; MW = 152.24 g mol^{-1}) were introduced in a vial and dissolved in 2 ml of chloroform. After complete homogenization of the solution, 144 mg of L-lactide (1×10^{-3} mol; 144.13 g mol^{-1}) were introduced into the vial. After 100 s at room temperature, the polymerization was stopped by addition of few milligrams of benzoic acid. After solvent evaporation, the as-obtained polymer samples were then characterized by single stage MS.

2.3. Mass spectrometry investigations

All experiments were performed on a Waters QToF2 mass spectrometer. The polymer solutions (1 mg mL^{-1} in acetonitrile/1 mg mL^{-1} NaI in acetonitrile: 9/1) were delivered to the ESI source by a Harvard Apparatus syringe pump at a flow rate of 5 μL/min. Typical ESI conditions were: capillary voltage, 3.1 kV; cone voltage, 30 V; source temperature, 80 °C; desolvation temperature, 120 °C. Dry nitrogen was used as the ESI gas. These ionization conditions led to the formation of abundant $[PLA+Na]^+$ cations for each polymer under investigation. The quadrupole was set to pass ions from 200 to 2000 Th and all ions were transmitted into the pusher region of the time-of-flight analyser for mass-analysis with 1 s integration time. Data were acquired in continuum mode until acceptable average data were obtained (typically 20 scans).

For the ESI-MSMS experiments, the ions of interest were mass-selected by the quadrupole mass filter. The precursor ion resolution

Table 1
Relevant thermochemical data for the ortho- (**4**), meta- (**5**) and para- (**6**) bis(methylene) cyclohexadiene isomers.

	4	5	6	Sodium acetate
ΔH_f (C_8H_8) (kJ mol^{-1})	233[b]	403[b]	203[a]	–
ΔH_f ($C_8H_9^+$) (kJ mol^{-1})	849[a]	855[a]	837[a]	–
PA (kJ mol^{-1})	914[c]	1078[c]	896[c]	960[d]
m/z 761/*m/z* 105[e]	2.9	0.1	13.7	–

[a] Ref. [9].

[b] From the relative energies calculated at the B3LYP//6-311++G(d,p) level of theory and the reported heat of formation of (**6**).

[c] Based on the ion and neutral heats of formation.

[d] From the relative energies of the neutral and protonated molecules calculated at the B3LYP//6-311++G(d,p) level of theory.

[e] Intensity ratio of the *m/z* 761 and *m/z* 105 signals in the corresponding CID spectra.

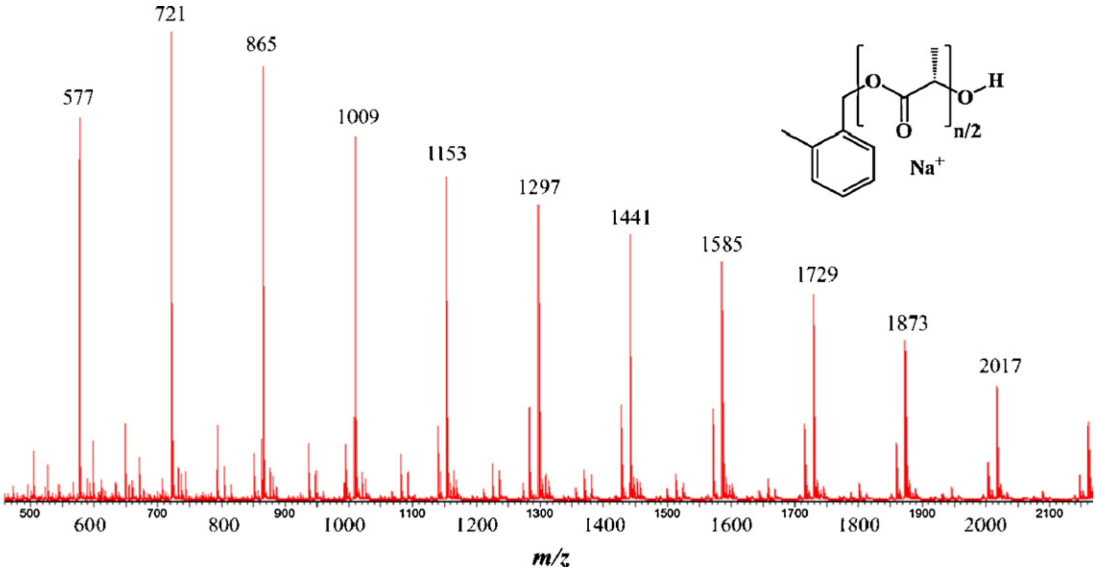


Fig. 1. ESI mass spectrum of α-ortho-methylbenzyl, ω-hydroxylpolylactide.

was adjusted to select only the monoisotopic signal. The selected ions were then submitted to collision against argon in the rf-only hexapole collision cell (pressure estimated at 0.9–1 mbar). The laboratory frame kinetic energy (E_{Lab}), typically at 50 eV, was selected to afford intense enough fragment ion signals (see presented spectra). All ions coming out of the hexapole cell, either the fragment or the undissociated precursor ions, were finally mass measured with the oa-ToF analyser. Data were acquired in continuum mode until acceptable average data were obtained.

2.4. Computational chemistry

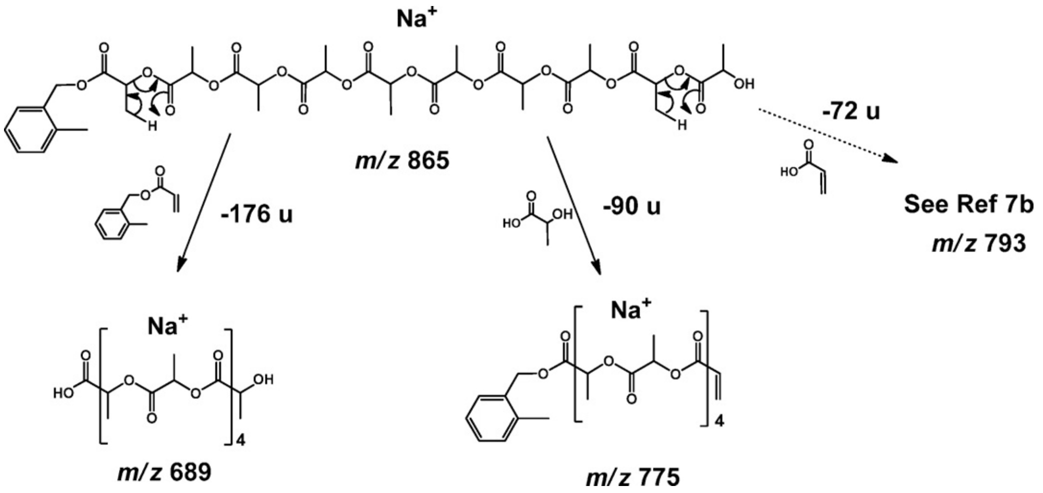
Quantum chemical calculations using density functional theory (DFT) were performed using the GaussianW 98 suite of programs [8]. Geometries were optimized by using the hybrid B3LYP functional in conjunction with the polarized double-zeta plus diffuse functions 6–311++G(d,p) basis set. Spin-unrestricted (UHF, UB3LYP) method was used for open-shell systems. Spin contamination in the UB3LYP calculation was small as judged from the $\langle S^2 \rangle$ operator expectation values that were 0.75–0.77. The optimized structures were subsequently characterized by harmonic vibrational analyses as local minima (all frequencies real) at the same level. The B3LYP/6-311++G(d,p) frequencies were scaled by 0.98 to evaluate the zero-point vibrational contributions (ZPE) to the relative energies.

2.4.1. Proton affinity (PA) calculations

The PAs of the ortho- (**4**) and meta- (**5**) bis(methylene)cyclohexadiene (C_8H_8) isomers were evaluated as follow. First, the relative energies between the neutral ortho-, meta- and para-C_8H_8 molecules were calculated at the B3LYP/6-311++G(d,p) level of theory. Based on the experimental heat of formation of neutral para-C_8H_8 [9], the relative energies were used to estimate the heats of formation of the ortho- and meta-isomers, see Table 1. The reported experimental heats of formation of H^+ (1530 kJ mol^{-1}) and of the $C_8H_9{}^+$ cations and the heats of formation of the neutrals were then used to estimate the corresponding proton affinities (Table 1).

3. Results and discussion

When subjected to ESI ionization under the experimental conditions defined in the experimental section, α-ortho-methylbenzyl, ω-hydroxylpolylactide molecules (α-ortho), see Scheme 1, are ion-



Scheme 2. CID fragmentations of sodium-cationized oligomers of α-ortho-methylbenzyl, ω-hydroxylpolylactide (**1**): end-group specific and unspecific charge remote processes.

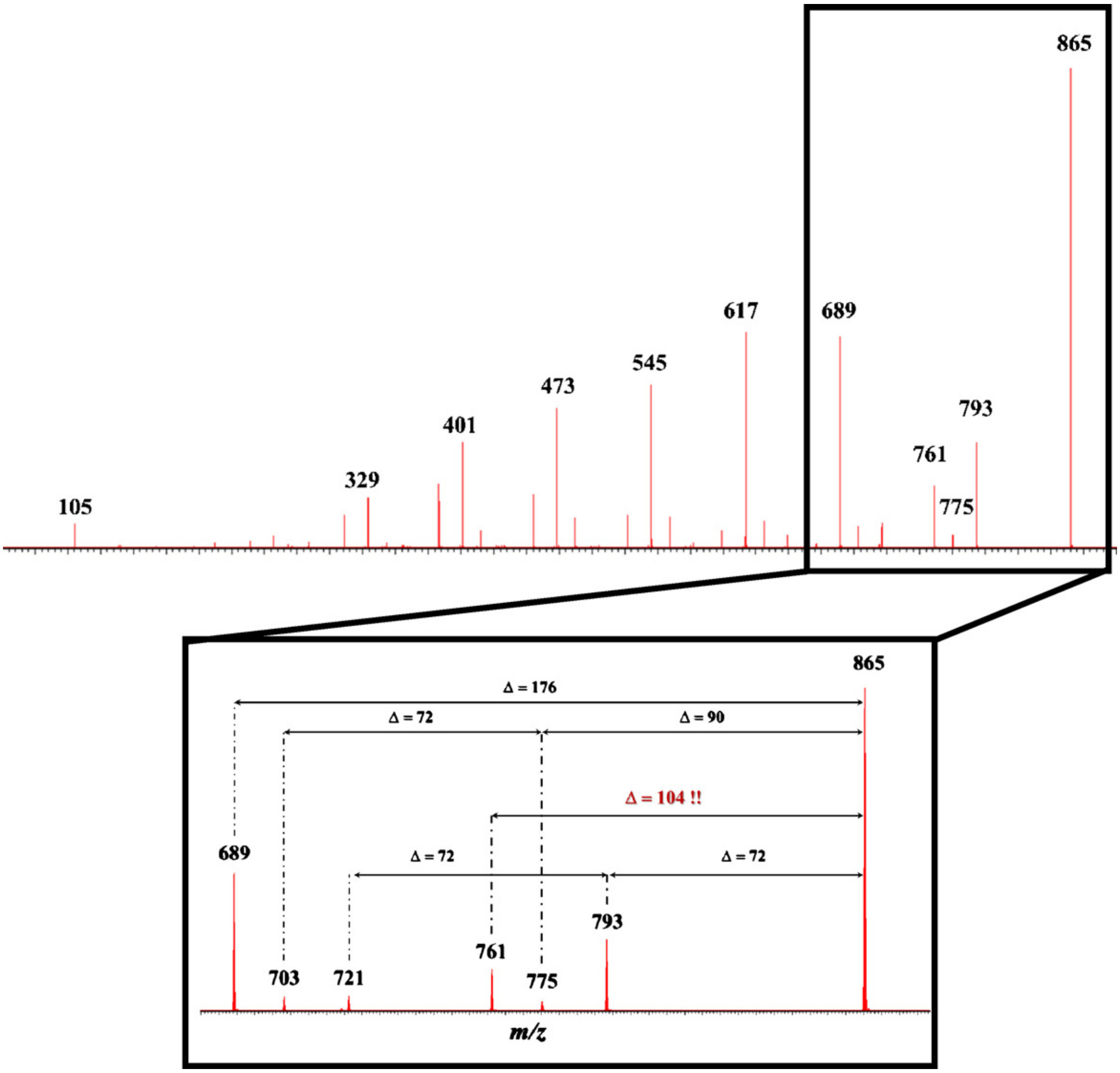
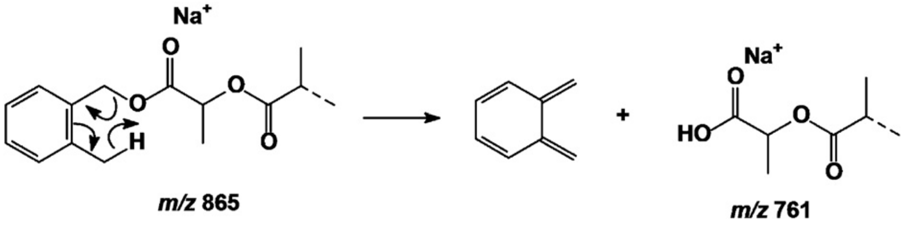


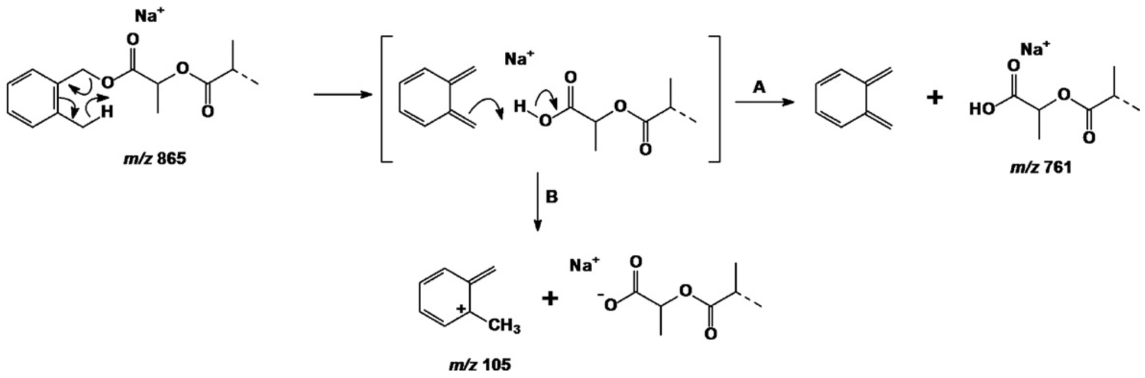
Fig. 2. CID mass spectrum of sodium cationized α-ortho-methylbenzyl, ω-hydroxylpolylactide (m/z 865, collision gas: Ar, collision energy: 50 eV).

ized by sodium cation attachment to afford abundant [α-ortho·Na]$^+$ cations as observed from the ESI full scan mass spectrum presented in Fig. 1. In this spectrum, the assignment of the ions constituting the main ion series to singly charged [α-ortho·Na]$^+$ cations is straightforward. As for an example of ion identification, the ions observed at m/z 865 correspond to sodium cationized poly(lactide) presenting a methylbenzyl (CH_3-Bz-) and a hydroxyl group as end-groups and constituted by 5 lactoyl repeating units.

The connectivity of the observed detected polymer ions is readily confirmed by CID experiments, see Scheme 2. Indeed, when subjected to CID against argon in the hexapole cell of a QToF instrument, the m/z 865 cations undergo the competitive and consecutive decompositions characteristic of the α-ortho-methylbenzyl, ω-hydroxylpolylactide connectivity [7]. As exemplified in Scheme 2, the expected end-group specific dissociations are the losses of 176 u and 90 u. The product ions of such decompositions are observed in the CID spectrum presented in Fig. 2 at respectively m/z 689 and 775. A consecutive 72 u loss from m/z 775 is also observed and the occurrence of such a consecutive decomposition was unambiguously demonstrated by a recent investigation on metastable decompositions [7a]. In agreement with our previous results [7b], the observation of the unspecific fragmentation (72 u loss) from the parent m/z 865 ions is also rationalized and the so produced cations are detected at m/z 793 in Fig. 2.



Scheme 3. CID fragmentations of sodium-cationized oligomers of α-ortho-methylbenzyl, ω-hydroxylpolylactide (**1**): loss of bis(methylene)cyclohexadiene following a charge remote mechanism.



Scheme 4. CID fragmentations of sodium-cationized oligomers of α-ortho-methylbenzyl, ω-hydroxylpolylactide (**1**): competitive productions of *m/z* 761 and *m/z* 105 cations and intermediacy of a sodium bound complex.

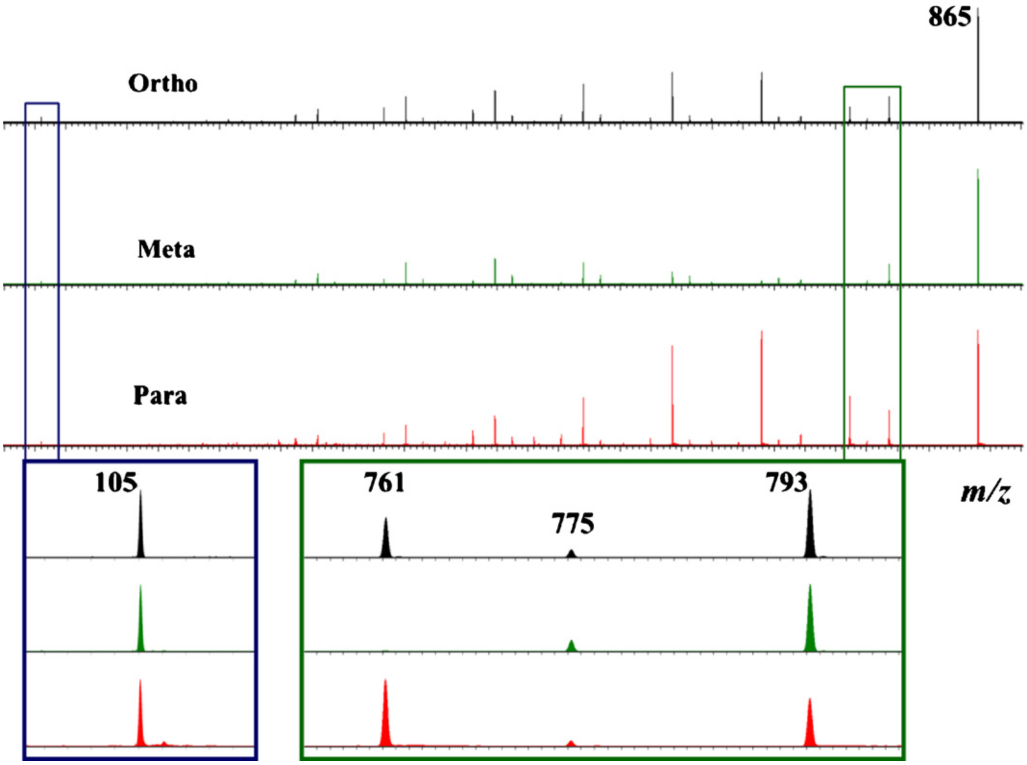
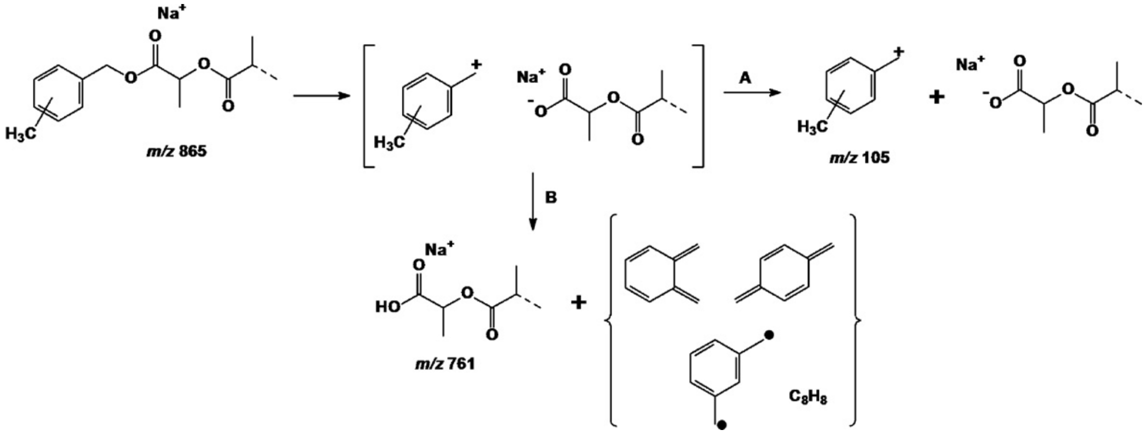
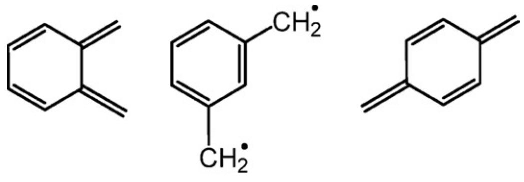


Fig. 3. CID mass spectrum of sodium cationized α-ortho, α-meta and α-para-methylbenzyl, ω-hydroxylpolylactide (*m/z* 865, collision gas: Ar, collision energy: 50 eV).



Scheme 5. CID fragmentations of sodium-cationized oligomers of α-methylbenzyl, ω-hydroxylpolylactide: competitive production of *m/z* 761 and *m/z* 105 cations and intermediacy of an ion/neutral complex.



4 5 6

Scheme 6. CID reactions of the isomeric sodium cationized oligomers: expelled C_8H_8 isomers.

Beside all those expected collision-induced decompositions, an additional fragmentation reaction occurs and corresponds to a 104 u loss that is readily identified as a C_8H_8 loss owing to the use of the high mass accuracy allowed on the QToF2 instrument. The so-produced cations are detected at *m/z* 761 in the CID spectrum presented in Fig. 2. Such a neutral loss is clearly associated to the methylbenzyl end-group. As for a decomposition mechanism, a rearrangement reaction involving the displacement of a hydrogen atom from the methyl group of the methylbenzyl end-group to the oxygen atom of the ester function could be proposed, as shown in Scheme 3. Such a charge remote decomposition process is in good agreement with the nature of the parent mass-selected cations, i.e. sodium cationized PLA.

However, a signal at *m/z* 105 is also clearly detected amongst the CID fragments in Fig. 2. Interestingly, such a process could be related to the 104 u loss, except that the production of protonated bis(methylene)cyclohexadiene (*m/z* 105) requires a proton transfer between neutral bis(methylene)cyclohexadiene and the sodium-cationized PLA prior to the decomposition. As for a mechanistic proposal, the intermediacy of a sodium bound complex associating neutral bis(cyclohexadiene) to PLA could be envisaged to account for the competitive productions of *m/z* 761 cations and *m/z* 105 cations, following respectively the losses of neutral C_8H_8 (route A) and of neutral sodium PLA carboxylate (route B), see Scheme 4. Based on such a mechanism, the charge driven nature of the process is clearly demonstrated.

As presented in Scheme 4, the production upon collisional activation of the intermediate ion/neutral complex is associated to an ortho-effect and is then *a priori* rather unlikely to occur starting from the meta and para methylbenzyl isomeric end-groups, see Scheme 1. As presented in Fig. 3, when subjected to CID, sodium cationized α-meta methylbenzyl, ω-hydroxylpolylactide does not expel 104 u since the signal at *m/z* 761 is not observed amongst the CID fragments. The absence of those fragment ions seems then in good agreement with the mechanism presented in Scheme 4 for the ortho isomer. Nevertheless, the signal at *m/z* 105 is clearly detected in the CID spectrum of sodium cationized α-meta methylbenzyl, ω-hydroxylpolylactide. In addition, the collisionally excited para isomeric ions competitively eliminate neutral C_8H_8 (*m/z* 761 in Fig. 3) and neutral sodium PLA carboxylate (*m/z* 105 in Fig. 3). On the basis of those experimental data, a new mechanism is proposed in Scheme 5 and involves an initial C–O bond cleavage in the dissociating ions leading to an ion/neutral complex associating (*o*-, *m*-, *p*-) methylbenzyl cation, on one hand, and sodium PLA carboxylate, on the other hand. The production of such an intermediate is not dependent on the position of the methyl substituent in the methylbenzyl end-groups. Based on this mechanism, the production of the *m/z* 105 ions starting from the three sodium-cationized isomeric PLA is definitively expected following route A in Scheme 5. As far as the C_8H_8 loss is concerned, a proton transfer reaction from the methylbenzyl cation to the sodium PLA carboxylate inside the complex is thus required as exemplified by route B in Scheme 5.

In order to get some theoretical insights on the observed competitive dissociations from the proposed intermediate, we selected a model ion/neutral complex associating protonated bis(methylene)cyclohexadiene (see Scheme 6 for the neutral counterparts) and sodium acetate to mimic the sodium PLA carboxylate. The proton affinities (PAs) of the three isomeric C_8H_8 molecules are not reported in the literature. The PA of neutral C_8H_8 molecules can be estimated on the basis of the heats of formation of the C_8H_8 and $C_8H_9^+$ species, see Table 1. Since the heat of formation of neutral C_8H_8 is only reported for the para molecule, theoretical calculations at the B3LYP//6-311++G(d,p) level of theory were undertaken to estimate the PAs of the ortho (**4**) and meta (**5**) bis(methylene)cyclohexadiene isomers, see experimental section for more details.

In Table 1, the PAs of the three C_8H_8 isomers relevant to the present discussion, namely the ortho-bis(methylene) cyclohexadiene (**4**), the meta-bis(methylene)cyclohexadiene (**5**) and the para-bis(methylene)cyclohexadiene (**6**), see Scheme 6, are presented together with the heats of formation of the neutral and the protonated molecules. The PA of sodium acetate was also calculated to amount to 960 kJ mol^{-1} at the B3LYP//6-311++G(d,p) level of theory.

As reported in Table 1, the PAs of the ortho-, meta- and para-bis(methylene)cyclohexadiene isomers amount to 914, 1078 and 896 kJ mol^{-1}, respectively. When compared to the PA of sodium acetate, i.e. 960 kJ mol^{-1}, the PA of the meta isomer is calculated to be about 120 kJ mol^{-1} higher. On the other hand, the PAs of the ortho and para isomers are respectively calculated to be 45 and 65 kJ mol^{-1} lower than the PA of the sodium carboxylate. As for a direct consequence, the competition between both the decomposition pathways from the proposed ion/neutral intermediates, namely the loss of 104 u and the production of *m/z* 105 cations (Scheme 5), is expected to be isomer-dependent. This competition can be correlated to the *m/z* 761/*m/z* 105 branching ratio in the corresponding CID spectra. In Fig. 3, the CID spectra of the three isomeric *m/z* 865 cations are presented. In all the spectra, beside the expected end-group specific and the non specific 72 u loss reactions (see Scheme 2), the signal at *m/z* 105, corresponding to protonated bis(methylene)cyclohexadiene is always detected. At variance, the signal at *m/z* 761, corresponding to the loss of neutral C_8H_8, is not significantly observed starting with the meta isomer. This is of course totally in keeping with the relative calculated PAs since the highest PA of meta-bis(methylene)cyclohexadiene renders the neutral C_8H_8 loss less competitive. Interestingly, the *m/z* 761/*m/z* 105 branching ratio is significantly different for both the ortho- and para-isomers, the *m/z* 761 signal being relatively higher for the para isomer. This is also in perfect agreement with the higher PA of ortho-bis(methylene)cyclohexadiene relative to para-bis(methylene)cyclohexadiene. Overall, these peculiar competitive CID reactions allow the distinction between the three isomeric end-groups, see Scheme 1.

4. Conclusions

In the present report, the capabilities of tandem mass spectrometry in the context of end-group identification for polymer ions were largely extended to the possibility to unambiguously differentiate regioisomeric end-groups. Upon CID experiments, sodium-cationized polylactides bearing α-ortho-methylbenzyl, α-meta-methylbenzyl or α-para-methylbenzyl as end-groups were shown to suffer from a charge driven decomposition reaction involving an ion/neutral complex associating protonated bis(methylene)cyclohexadiene ($C_8H_9^+$) and a sodium PLA carboxylate. Depending on the relative proton affinities, this intermediate can further evolve yielding protonated bis(methylene)cyclohexadiene molecule and/or protonated sodium PLA carboxylate as CID fragment ions. The branching ratio between the corresponding signals in the CID spectra was demonstrated to be isomeric end-group dependent.

Acknowledgments

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References

[1] C. Wesdemiotis, N. Solak, M.J. Polce, D.E. Dabney, K. Chalcharoen, B.C. Katzenmeyer, Mass Spectrom. Rev. 30 (2011) 523–559.
[2] See for instance S.M. Weidner, S. Trimpin, Anal. Chem. 82 (2010) 4811.
[3] See for instance H.J. Rader, W. Schrepp, Acta Polym. 49 (1998) 272.
[4] J. De Winter, G. Deshayes, F. Boon, O. Coulembier, P. Dubois, P. Gerbaux, J. Mass Spectrom. 46 (2011) 237.
[5] L. Sleno, D.A. Volmer, J. Mass Spectrom. 39 (2004) 1091.
[6] R.P. Lattimer, J. Am. Soc. Mass Spectrom. 3 (1992) 225.
[7] (a) J. De Winter, A.L. Goffin, O. Coulembier, P. Dubois, R. Flammang, P. Gerbaux, J. Mass Spectrom 15 (2009) 431;
(b) J. De Winter, V. Lemaur, P. Marsal, O. Coulembier, J. Cornil, P. Dubois, P. Gerbaux, J. Am. Soc. Mass Spectrom. 21 (2010) 1159.
[8] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuserai, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, B.B. Liu, A. Liashenko, P. Piskorz, A. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, M.W. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Reploge, J.A. Pople, Gaussian 98W, Gaussian, Inc., Pittsburgh, PA, 1998.
[9] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, Gas-phase ion and neutral thermochemistry, J. Phys. Chem. Ref. Data 17 (Suppl. 1) (1988).