



Thermal degradation of polylactide/aluminium diethylphosphinate

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ABSTRACT

Direct pyrolysis mass spectrometry analyses of polylactide, PLA, reveal two dominating decomposition pathways; chain homolysis and trans-esterification reactions under the experimental conditions yielding mainly low mass fragments and cyclic oligomers. The main pyrolysis products of aluminium diethylphosphinate, ALPi, are determined to be the dimeric four coordinate compounds possessing Al—O—P linkages. Thermal stability of polylactide in the presence of ALPi is decreased due to the attack of phosphinates groups on carbonyl groups. Eventually, extensive fragmentation of PLA takes place and generation of four coordinate dimeric compounds involving Al—O—P linkages is suppressed. On the other hand, strong evidence for generation of polyphosphinates is detected. Collision induced dissociation experiments are used to confirm the proposed structures.

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1. Introduction

Poly lactide (PLA), because of its biodegradability and biocompatibility, has received significant attention for its medical, pharmaceutical applications. Furthermore, being derived from renewable sources it has also been considered as one of the most promising biopolymers for new application areas, such as electronics, automotive and household applications. However, its poor thermal stability, poor flame retardance characteristics and high sensitivity to heat and moisture restrict its applications.

Thermal degradation of PLA has been studied in details in the literature [1–8]. It has been determined that thermal decomposition mainly occurs in the temperature range 300–400 °C by a complex mechanism involving intra and intermolecular trans-esterification reactions, homolytic chain scissions and cis-elimination reactions yielding mainly gaseous products of cyclic oligomers, lactide, acetaldehyde, carbon monoxide and carbon dioxide.

In recent years, flame retardancy of PLA has also received noticeable interest of several scientists. The phosphorous containing flame retardants with good performance and low toxicity were the most commonly used [9–20]. Their flame-retardant mechanisms depend strongly on the nature of both the matrix polymer and the phosphorus compound. Condensed-phase mechanism involving

surface obstruction by phosphorus-containing acid catalyzed char formation and gas-phase mechanism involving flame inhibition and dilution of flammable gases are the two widely accepted mechanisms. However, up to now, to our knowledge, no study focusing on the effect of phosphorous compounds on thermal degradation characteristics, mainly the product distribution of PLA appeared in the literature.

Recently, it has been determined that by incorporation of ALPi, the fire retardancy of PLA is improved and fire risks are reduced as a consequence of increase in the lowest oxygen index, and lower peak heat release and peak mass loss rates [20]. However, TGA results indicated decrease in thermal stability of PLA in the presence of ALPi. In the current study, we investigated the effects of aluminium diethylphosphinate, ALPi, a specially designed phosphorous-based flame retardant for polyesters, on thermal degradation characteristics of PLA via direct pyrolysis mass spectrometry. Collision induced dissociation experiments were also acquired to provide fragmentation pathways to generate informative, structurally significant product ions to elucidate the structures of the pyrolysis products of both PLA and ALPi.

2. Experimental

Poly lactide, with Mn ~190,000, was provided by Cargill Dow. Aluminium diethylphosphinate, (ALPi) was purchased from Clariant (Germany) with the trade name Exolit OP 1240. Among the several PLA/ALPi composites involving various wt% ALPi prepared by melt-compounding, the composite involving 20 wt % ALPi with best fire retardancy, was selected as the sample for thermal analyses. The

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preparation of the samples was described in a recent publication in detail [20].

Direct pyrolysis mass spectrometry (DP-MS) analyses were performed on a 5973 HP quadrupole mass spectrometry system coupled to a JHP SIS direct insertion probe pyrolysis system. Seventy electron volt EI mass spectra, at a rate of 2 scan s^{-1} , were recorded. 0.01 mg samples in flared glass sample vials were heated to 450°C at a rate of $10^\circ\text{C min}^{-1}$. Collision induced dissociation experiments were performed by Waters Micromass Quattro Micro GC triple quadrupole Mass Spectrometer coupled to a direct insertion probe, using argon as the collision gas and 65, 40, 30 and 20 eV EI ionization. The daughter spectra of the precursor ions were recorded while pyrolyzing (0.010 mg) samples in quartz sample vials at the temperatures at which the yield of the selected precursor ion was maximized. Relationships between the various ions were established by product-ion spectra on fragment ions formed in-source and by precursor-ion spectra. All experiments were repeated at least twice to ensure reproducibility.

3. Results and discussions

3.1. Thermal degradation of pure PLA

The total ion current, (TIC), the variation of total ion yield as a function of temperature, curve of neat PLA, and the pyrolysis mass spectrum recorded at the peak maximum, at 368°C is presented in Fig. 1a. The base peak is at $m/z=56$ Da due to CH_3CHCO , the common fragment of lactide and its oligomers produced mainly during ionization. The mass spectrum recorded at 363°C is similar to the ones given in the literature and is dominated by the known homologous series of peaks at $m/z=72x-88$ for $x=2-12$; due to fragments generated by elimination of the neutral molecules CO_2 and acetaldehyde during ionization of the cyclic oligomers, whose molecular ions, produced even with the soft ionization techniques, are not stable (Fig. 11b). Thus, these peaks are associated with fragments with general formula $(\text{C}_2\text{H}_4\text{CO}_2)_x\text{C}_2\text{H}_4\text{CO}$ for $x=0-10$. The reaction mechanism, for generation of cyclic oligomers by inter and/or intra trans-esterification reactions, is given in Scheme 1a.

The second, much less pronounced series of peaks with $m/z=72x+73$ for $x=2-12$ are associated with fragments produced by cis-elimination reactions with general formula $(\text{C}_2\text{H}_4\text{CO}_2)_x\text{H}$ ($m/z=73, 145, 217$ and 289 Da for $x=1-4$) (Scheme 1b). A third series of fragments have the general formula $(\text{C}_2\text{H}_4\text{CO}_2)_x\text{C}_2\text{H}_4$

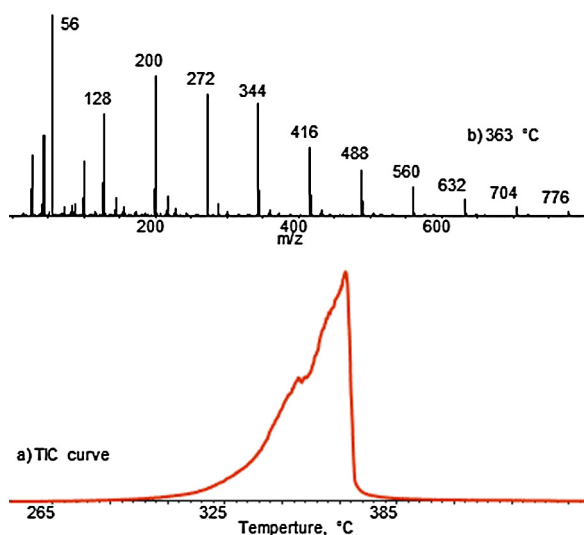
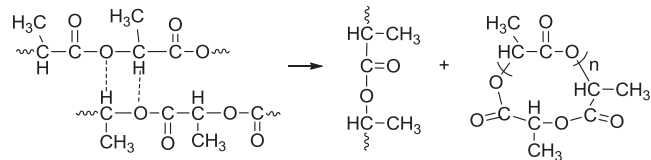
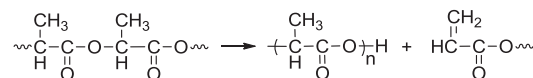


Fig. 1. (a) The TIC curve and (b) the mass spectrum at 363°C recorded during the pyrolysis of PLA.

a. Trans-esterification



b. cis-elimination



Scheme 1. Thermal degradation of PLA by (a) inter and intra trans-esterification reactions and (b) cis-elimination reactions.

($m/z=100, 172, 244$ and 316 Da for $x=1-4$), most probably generated by homolysis reactions.

Single ion evolution profiles of some of the representative fragments of PLA, such as C_2H_4 and/or CO (28 Da), $\text{C}_2\text{H}_3\text{O}$ (43 Da), $\text{C}_2\text{H}_4\text{O}$ and/or CO_2 (44 Da), $\text{C}_2\text{H}_4\text{OH}$ and/or CO_2H (45 Da), $\text{C}_2\text{H}_4\text{CO}_2$ (56 Da), $(\text{C}_2\text{H}_4\text{CO}_2)_x\text{H}$ (145 and 217 Da for $x=1$ and 2), $(\text{C}_2\text{H}_4\text{CO}_2)_x\text{C}_2\text{H}_4\text{CO}$ (128, 200, and 488 Da for $x=1, 2$ and 6 respectively) and $\text{C}_2\text{H}_4\text{CO}_2\text{C}_2\text{H}_4$ 100 Da are depicted in Fig. 2.

Small, but noticeable differences are detected in the single ion pyrograms of thermal degradation products of PLA contrary to the results of Kopinke et al. [3]. The trends in the evolution profiles revealed that thermal degradation of PLA starts by

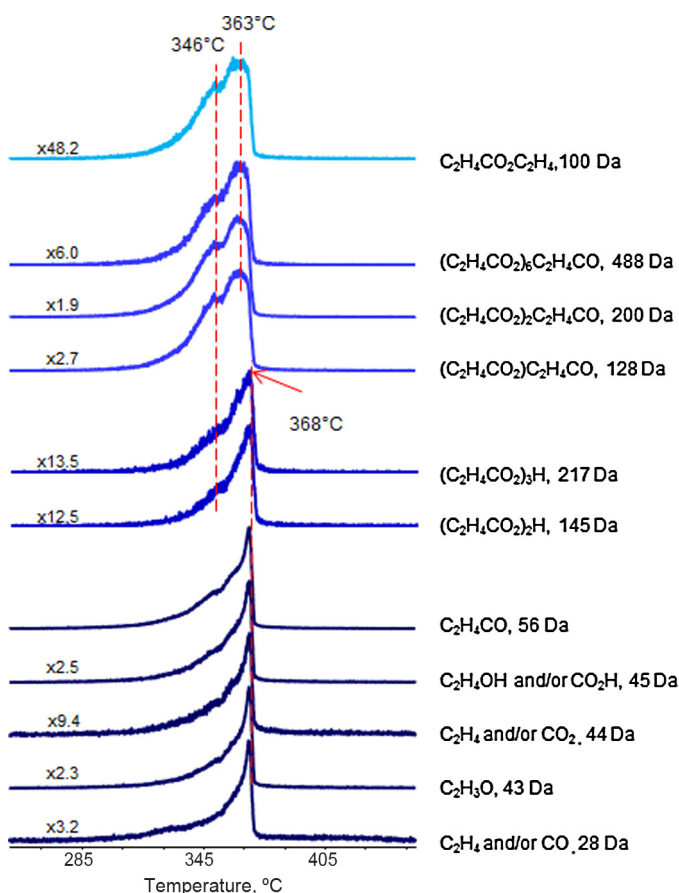


Fig. 2. Single ion evolution profiles of some selected fragments detected during the pyrolysis of PLA.

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