

## ***Spectroscopic Investigations***

### **Mixtures of Cyclic Oligomers of Poly(Lactic Acid) Analyzed by Negative Chemical Ionization and Thermospray Mass Spectrometry**

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#### SUMMARY

An investigation of the distribution of the cyclic oligomers of poly(lactic acid), formed both by pyrolysis of the polymer and by equilibration with a catalyst, has been performed by Negative Chemical Ionization and Thermospray Mass Spectrometry.

The results indicate that the two methods can be used to obtain information on the relative amounts of the oligomers present in the mixture.

#### INTRODUCTION

Cyclic oligomers are often formed in the course of polymerization or by heating polyesters above their melting temperatures (1-3).

Current methods of studying these oligomers are based on gas, liquid and size exclusion chromatography, combined with some structural identification method.

These techniques are indeed powerful, but sometimes low volatility or thermal instability of samples, low solubility in suitable organic solvents, low resolution problems in liquid chromatography make highly desirable alternative and rapid methods of detection and identification for mixtures of oligomers.

Mass Spectrometry (MS) is particularly suitable to the detection of these materials since they are volatile under high vacuum at relatively mild temperatures, at which polymers remain undecomposed and therefore undetected (4,5).

Electron impact mass spectra of aliphatic cyclic esters do not show molecular ions, so that soft ionization techniques must be used for their detection (6).

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In the present article an attempt is made to show that negative chemical ionization (NCI) and thermospray (TSP) mass spectrometry can be conveniently used to identify poly(lactic acid) oligomers and also to estimate their distribution.

## EXPERIMENTAL

### Materials

Poly(lactic acid) was a pure sample obtained from Polysciences, Inc. GPC analysis showed, however, that the polymer sample contained synthetic oligomers. In order to remove the synthetic oligomers, the polymer was dissolved in chloroform, reprecipitated in petroleum ether, and analyzed by GPC.

The poly(lactic acid) was dried "in vacuo" at 60 °C for 24 hours.

The inherent viscosity ( $\eta_{inh} = \ln \eta_r / c$ ;  $c = 0.5$  g/dl), measured in a Desreux-Bishoff suspended-level viscometer, using chloroform as solvent, is:  $\eta_{inh} = 1.23$ . The temperature was maintained at  $30 \pm 0.01$  °C.

The polymer decomposition temperature (PDT), obtained with a Perkin-Elmer TGS/2 apparatus in a nitrogen atmosphere (60 ml/min) at a heating rate of 10 °C/min, as indicated by the maximum in the differential thermogravimetric curve, is 365 °C.

The mixture of cyclic oligomers (indicated in the following as "mixture I") was prepared as follows. In a glass tube, having a side arm to collect the boiling fraction, were placed 3.0 g of poly(lactic acid) and 0.03 g (1% weight) of magnesium chloride hexahydrate, as a catalyst. A nitrogen stream was bubbled into the mixture; the tube was then evacuated at a pressure of about 0.1 mm Hg, sealed and heated in a silicon bath to about 270 °C over a period of 2 hours. The distilled mixture was then analyzed by NCI and TSP mass spectrometry.

### Mass Spectrometry

A double focusing Kratos MS 50 S equipped with the standard chemical ionization source and a DS 55 data system was used to obtain mass spectra.

The instrument was scanned from  $m/z$  1000 to  $m/z$  20, with a scan rate of 10 s/decade.

Perfluorokerosene (PFK) was used for computer calibration; the ion source was maintained at 200 °C.

Negative chemical ionization mass spectra were obtained using ammonia (99.998%) as reagent gas (gas purchased from Matheson Gas products).

Thermospray MS was carried out using a Kratos MS 25RF mass spectrometer equipped with a Kratos thermospray LCMS interface (7). The interface was operated at a vaporizer temperature of 193 °C and at a source temperature of 200 °C. Samples were introduced directly into the interface, mobile phase consisting of 0.1 M ammonium acetate water solution.

## RESULTS AND DISCUSSION

In figure 1 is reported the ammonia NCI mass spectrum of mixture I at a probe temperature of 220 °C. Molecular ions corresponding to the cyclic oligomers  $M_2^- - M_7^-$  are seen at  $m/z$  144, 216, 288, 360, 432 and 504. Carboxylate ions are also seen at  $(M+17)^-$  ( $m/z$  161, 233, 305 and 377).

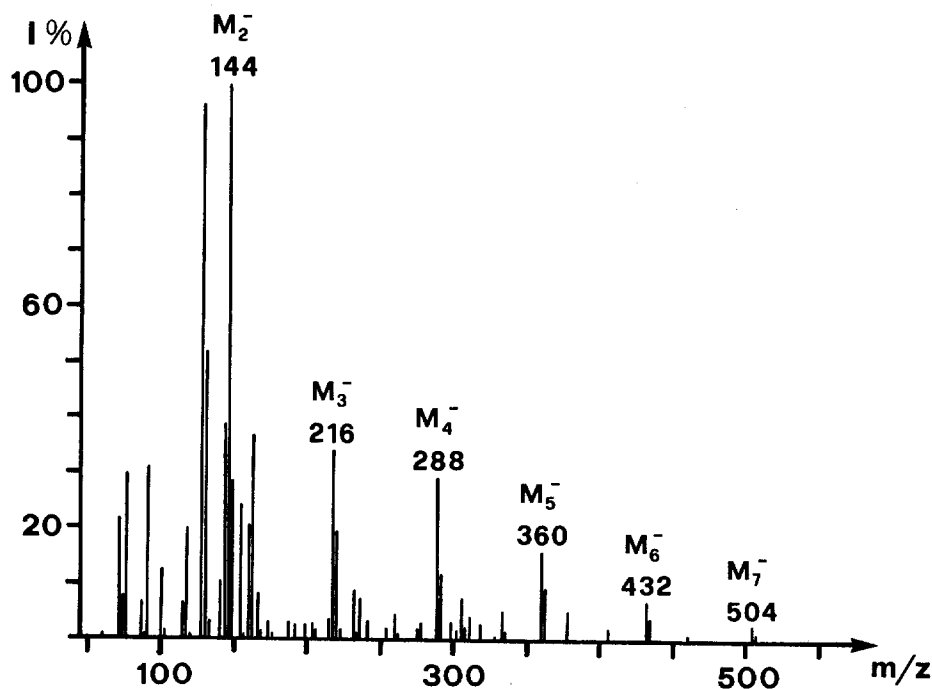


Fig. 1 - Ammonia NCI mass spectrum of mixture I at 220 °C.

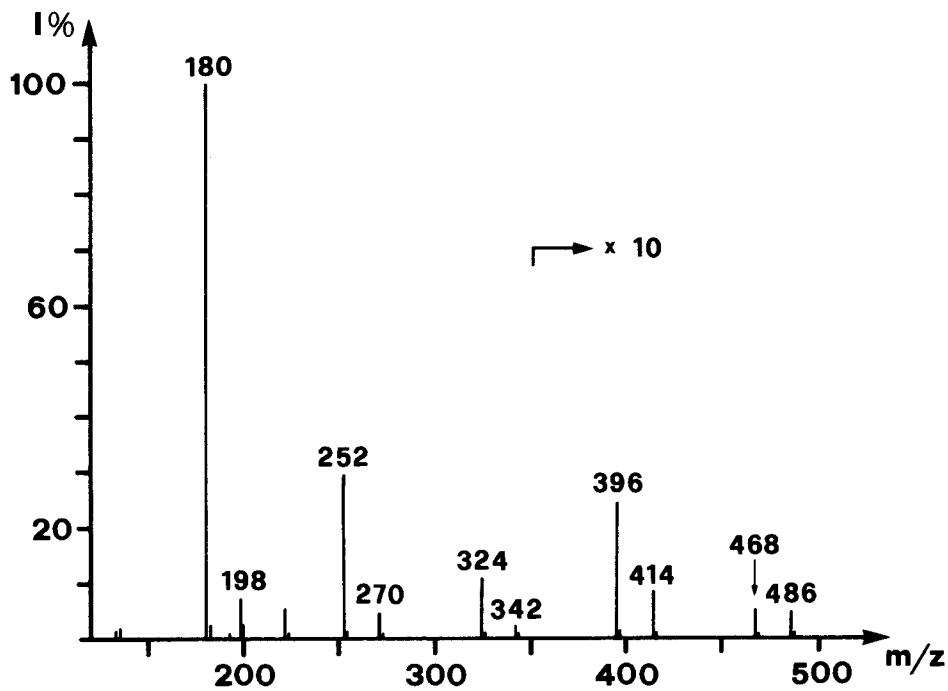


Fig. 2 - Thermospray mass spectrum of mixture I.

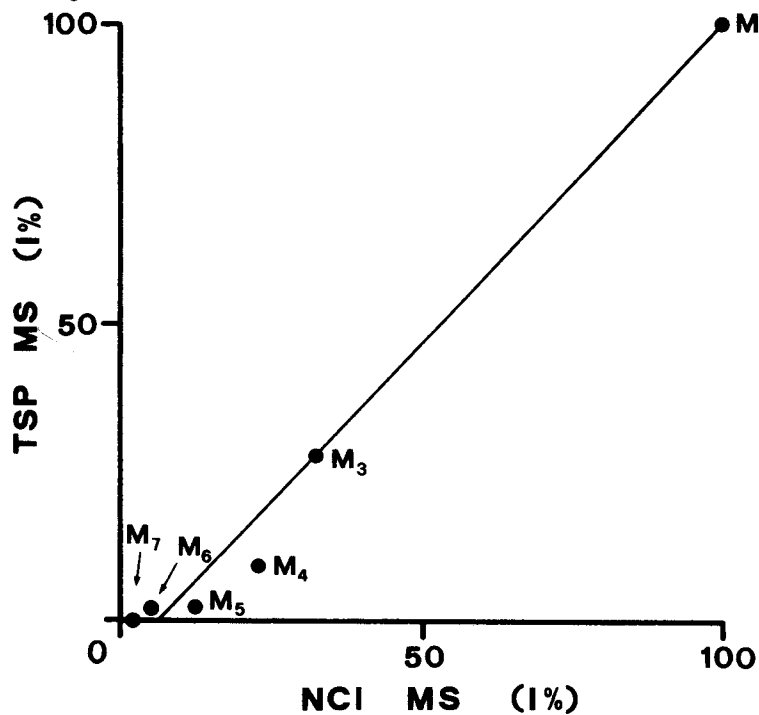


Fig. 3 - Correlation between NCI and TSP data.

The thermospray-filament off mass spectrum of mixture I in water solution containing ammonium acetate (0.1 M), injected directly into the thermospray interface (thermospray interface: 193 °C), is reported in figure 2. Molecular ions corresponding to the cyclic oligomers  $M_2^-$  -  $M_6^-$  appear as  $(M+H_2O+NH_4^+)$  ions at  $m/z$  180, 252, 324, 396 and 468. This interpretation is confirmed by the presence in the TSP mass spectrum of the peaks corresponding to ions of the type  $(M+2H_2O+NH_4^+)$  at  $m/z$  198, 270, 342, 414 and 486. The absence of the protonated molecular ions is not surprising (8), since they are also absent in the positive ammonia CI mass spectrum of the pyrolysis products of poly(lactic acid).

In order to estimate the reliability of the cyclic products distribution obtained by NCI and TSP, in figure 3 the peak intensities of the molecular ions in the two respective mass spectra are reported. A fair correlation is obtained between the two sets of data, indicating that in this case the MS method, besides providing identification, yields also information on the relative amounts of oligomers present in the mixture.

In figure 4 is reported the ammonia NCI mass spectrum of poly(lactic acid) pyrolyzed in the mass spectrometer at a probe temperature of 360 °C (heating rate of 10 °C/min). The polyester pyrolysis yields a series of cyclic oligomers

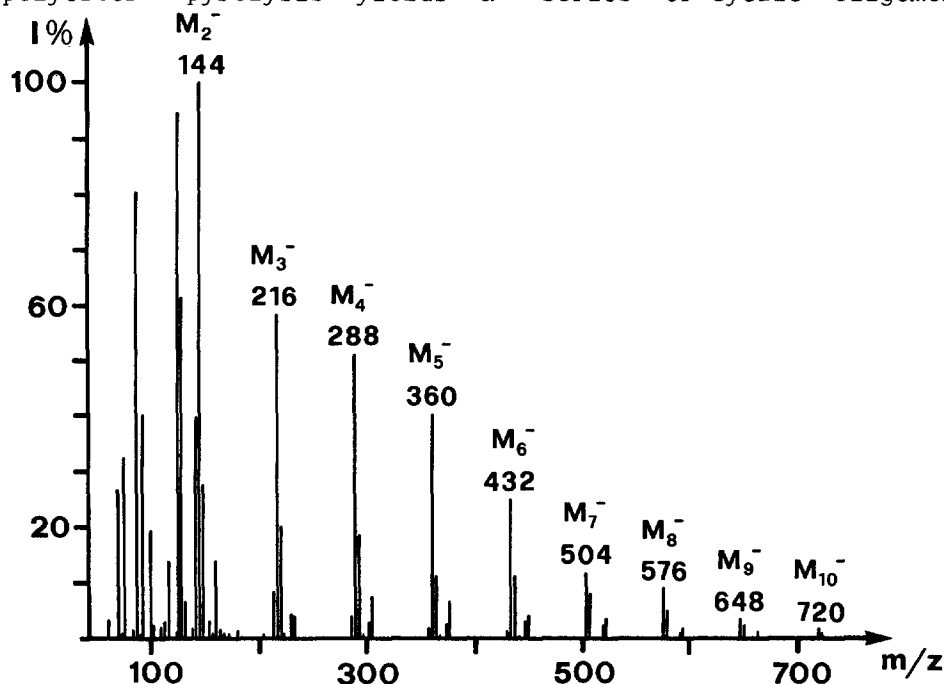


Fig.4- Ammonia NCI mass spectrum of poly(lactic acid) at 360 °C

$M_2$  - $M_{10}$  which appear at  $m/z$  144, 216, 288, 360, 432, 504, 576, 648 and 720, with decreasing intensity.

The distribution of cyclic oligomers obtained in this experiment (figure 4) appears different from that observed for mixture I (figures 1 and 2).

This might be explained by the fact that the distribution of cyclic oligomers generated in the Direct Pyrolysis-Mass Spectrometry experiment is kinetically controlled, since the reaction products are not allowed to equilibrate but are removed from the hot zone as they are formed (5). On the contrary, in the case of mixture I the reaction products were allowed to equilibrate for some time in the reaction vessel, and therefore the distribution is closer to thermodynamic equilibrium (2).

Summarizing our results, NCI and TSP mass spectrometry appear suitable methods for the rapid analysis of mixtures of cyclic oligomers of poly(lactic acid). The present work, as well as others of similar nature (4-6), illustrates the capabilities of MS in the analysis of polymer systems and their oligomers distribution.

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