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GPC/MALDI TOF ANALYSIS OF POLYMERIC COMPOUNDS

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SUMMARY

A method for the analysis of polymers is described, which couples Gel Permeation Chromatography (GPC) with Matrix Assisted Laser Desorption Ionization (MALDI) Mass Spectrometry by means of an automated eluent collection/deposition module designed specifically for this application. A synthetic polymer soluble in THF was mixed post-column with a suitable matrix solution and deposited onto a MALDI target plate. Subsequent MS analysis was performed on a Waters® Micromass® MALDI Time of Flight (TOF) Mass Spectrometer.

INTRODUCTION

Matrix assisted laser desorption ionization (MALDI) mass spectrometry is one of the most powerful tools for mass analysis of complex mixtures, and is therefore highly suitable for MS analysis of bulk polymers. The technique is used to: (i) determine aparent average molecular weight; (ii) measure the mass of the end groups, which is important to the performance properties of the polymer; (iii) monitor polymerisation reactions by characterizing the chemical structure of the products, and (iv) measure rate of polymerisation.

However, MALDI MS has limitations, in terms of dynamic range, for the accurate determination of mass distribution of polymers with high polydispersity. Samples of polydispersity greater than 1.3 (most commercial polymers) typically produce distorted mass spectra, or give no signal at all.

We can now demonstrate a targeted approach, comprising an automated process for GPC sample preparation and eluent collection/deposition with MALDI mass spectrometry, which has significant advantages over traditional off-line techniques. With prior separation by GPC, each fraction (or location on the deposited track) examined by MALDI MS has narrow polydispersity, and produces an accurate spectrum. The system benefits from a range of unique software capabilities, which combine individual spectra to produce a truly representative composite and relate MALDI data to samples deposited on a chromatographic time base.

This system also has significant advantages where ion series from materials with different chemical identities but similar molecular weights overlap, since spectral simplification is achieved when the sample is fractionated by GPC prior to MALDI MS analysis.

This work demonstrates the suitability of the technique for the analysis of synthetic polymers, which invariably prove difficult to analyse by MALDI TOF MS alone.

METHODS

A Waters Alliance™ 2790 HPLC system equipped with a 2487 UV Detector was used for the GPC experiment. The GPC column was a Pgel, 5µ mixed D from Polymer Laboratories. All tubings were of stainless steel. Post UV detection was carried out at 254 nm. A Valco® T-piece was used to reduce the flow rate from 1 mL/min to 800 µL/min and a second Valco T piece was inserted in the eluent stream to allow the addition of the matrix solution. The sample plus matrix was deposited onto a target plate using the Waters LC MALDIprep™ spraying unit.

For the GPC experiments an isocratic elution of 15 min at a flow rate of 1 mL/min, with THF as the mobile phase, was performed. 0.1 mg of sample dissolved in THF was injected. A fresh matrix solution of 10 mg/mL Dithranol and 0.1 mg/mL Na-TFA in THF was added with a syringe pump operated at a flow rate of 10 µL/min.

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The LC MALDIprep was triggered by a contact closure from the LC system to start spraying onto the MALDI target. The spraying device was operated at 140°C and a gas pressure of 20 psi. The track deposition velocity was set to 2.5 mm/min.

MASS ANALYSIS

Mass analysis was performed on a Waters Micromass MALDI TOF mass spectrometer operated in reflectron mode. The chromatographic time axis and movement of the LC MALDIprep stage were time coordinated. Data were acquired automatically over a mass range of 800 - 5000. No Lockmass correction was used.

RESULTS

The UV chromatogram (fig. 1) displays a broad intense signal at 7.5 min and a sharp signal at 9.5 min. The Base Peak Intensity (BPI) chromatogram, (fig. 2) shows three compounds eluting from the column. The mass spectra were combined (fig. 3) and show different average molecular weights. The eluting times correspond with the size of the polymers according to the principle of GPC analysis. A close up of the mass peaks (fig. 4) identifies two ion series with a mass difference of 16 amu and a repeating unit of 104 amu. The isotopic distribution reveals the loss of bromine, as there is no characteristic isotope distribution (50.5% 79Br and 49.5% 81Br) present. Spectra were analysed with Polymerix software (Sierra Analytics) to confirm the chemical composition of the polymer. The two ion series contain both the sodiated and potassiated species of Polymer 1 (fig. 6). An additional advantage of using a mass analyzer is the ability to identify, in combination with the chromatographic separation, the compounds differing in only 0.5 amu.

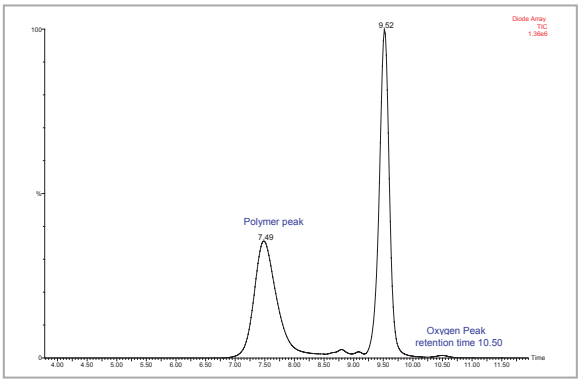

Figure 1: UV chromatogram at 254 nm.

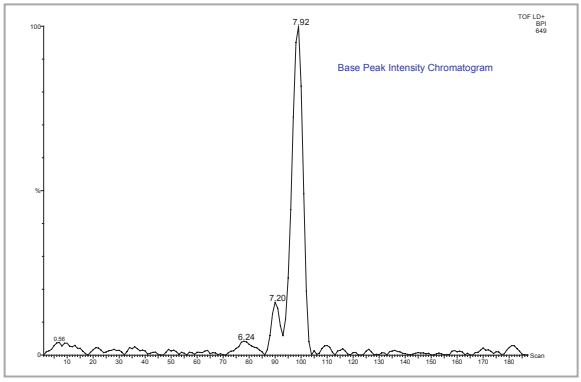

Figure 2: BPI chromatogram.

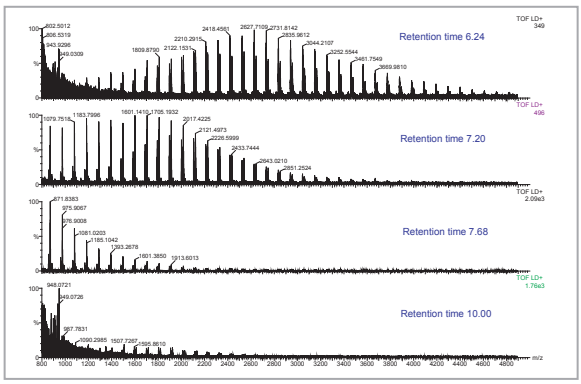

Figure 3: Combined mass spectra from eluting fractions revealing the different molecular weights and compounds.

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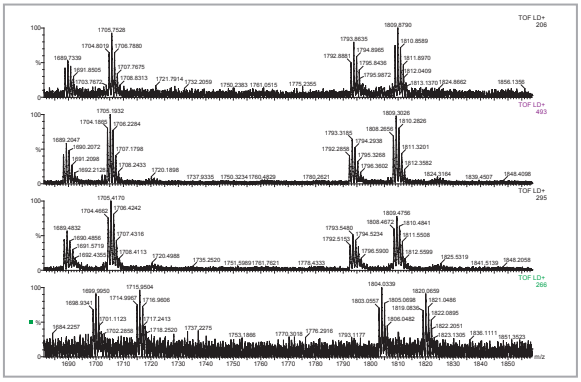

Figure 4: Differences in the molecular weight: m/z 1689.74 is the M+Na and m/z 1705.75 is the M+K series of RV 125. Ion series in the bottom spectrum were identified as RV 74, a minor compound.

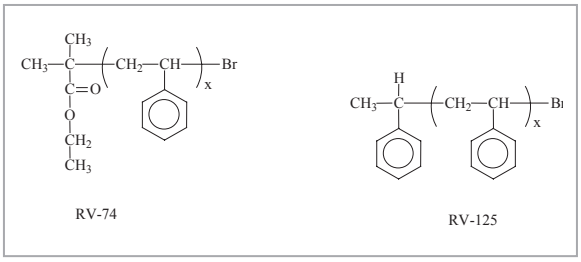

Figure 5: Chemical structure of Polymer 1 (RV-125) and RV 74. The presence of Bromine at the end of the chain was not proven by the analysis.

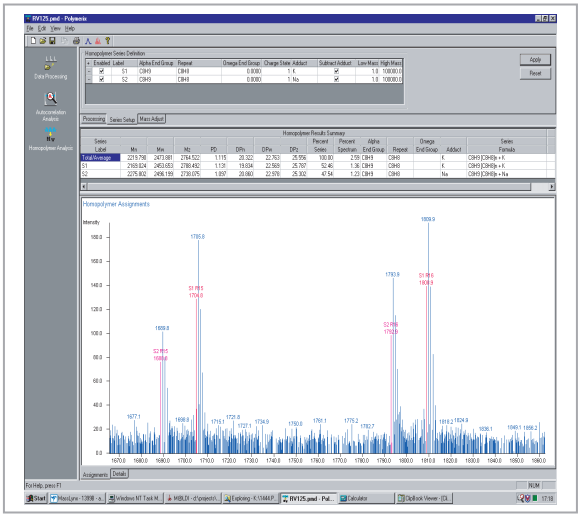

Figure 6: Homopolymer assignments with Polymerix software from Sierra Analytics; S1 is the sodiated polymer and S2 is the potassiated polymer.

DISCUSSION

This new Waters system for GPC/MALDI, comprising an automated process for GPC sample preparation and eluent collection/deposition, combined with MALDI mass spectrometry has been used successfully for the characterization of synthetic polymers. The chromatographic separation has revealed the presence of three different compounds. Complementary data from MALDI MS analysis have shown the molecular weight of the compounds with respect to the elution time.

In order to be able to observe individual ions with MALDI TOF MS it is crucial to have a narrow polydispersity (Mw/Mn<1.3). With the on-line collection of fractions of the sample after GPC separation, this is ensured. Shifts in the most intense peaks on MALDI MS can be identified as varying ionization efficiencies that can be correlated to the chemical nature and/or the sample preparation method.

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