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The influence of laser power on the observed MALDI-TOF mass spectra of poly(diethyl 3-hydroxyglutarate), an AB_2 hyperbranched aliphatic polyester; Mn from MALDI-TOF MS?, Caveat Emptor

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Summary

Oligomers of poly(diethyl 3-hydroxyglutarate), an aliphatic hyperbranched polyester, have been prepared via a titanium(IV) butoxide catalysed step growth condensation process. The characterisation of the products depends on MALDI-TOF mass spectrometry; this study establishes that the incident laser power has a marked effect on the distribution of peak intensities in the spectra observed for these systems. High laser powers can initiate scissions in the polymer structure, whilst at lower incident laser power it is very difficult to define what constitutes a "representative spectrum".

Introduction

Soft ionisation mass spectroscopic techniques have rapidly become accepted as powerful tools for the characterisation of synthetic and natural polymers. So far most studies have been concerned with well understood linear polymers and well defined monodisperse systems such as dendrimers and, for relatively low molecular weight samples, the technique is successful. Flory predicted that AB_2 hyperbranched polymers should have polydispersities tending to infinity at high conversion (1), but we expected that, for the materials produced in this study at relatively low conversion and molecular weight, relatively narrow distributions might be expected which might be amenable to analysis by this technique (2). It has been reported (3,4) that MALDI-TOF spectra of linear polymers are highly dependent on the laser power incident on the sample, therefore the study reported here was undertaken to assess the effect of laser power on the spectra of these hyperbranched aliphatic polyesters since the technique was one of a very small array of analytical methods available giving, in principle, unambiguous molecular weight distribution information.

MALDI-TOF mass spectrometry is a technique which allows the desorption and mass analysis of intact polymer molecules each carrying one positive charge. Since the integrated peak intensity depends on the number of ions of a specific mass arriving at the detector the number average molecular weight can be calculated if a) all the sequences of molecular ions can be identified, b) there is minimal fragmentation

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and c) if representative sample of the whole polymer distribution is desorbed into the gas phase and analysed. The matrix is required to preferentially absorb the laser power hence allowing matrix/cation/polymer collisions in the gas phase which allow the polymer molecules to acquire a charge, usually a proton or an alkali metal cation. The charged species are detected and their masses are calculated, knowing the instrument dimensions, from the time difference between the laser pulse initiation and their arrival at the detector. The resulting mass spectra are comprised of a distribution of charged oligomer signals, from which the mass distribution may be calculated.

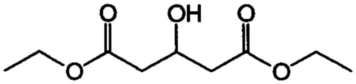
Experimental

The neat AB_2 monomer, diethyl 3-hydroxyglutarate, was placed in a glass reaction vessel attached to a vacuum/nitrogen line and fitted with an efficient overhead stirrer driven by a high torque motor through an Edwards vacuum seal. Titanium (IV) butoxide was added. The reaction vessel was placed in an oil-bath at 80°C and the temperature was increased to between 100 and 125°C, the reacting mixture was held at a predetermined temperature for a set time (usually between 2.5 and 6.0 hours) and a vacuum (10mmHg) was applied during the final 30 minutes to aid removal of the condensate. The resulting viscous yellow oil was dissolved in chloroform and the resulting solution was washed several times with water to remove the catalyst. After drying, the solvent was removed on a rotary evaporator at water pump pressure to yield a viscous, hyperbranched polymer.

MALDI-TOF MS were recorded using a Kratos Kompact IV spectrometer in the reflectron mode, operating with irradiation from a nitrogen laser at 337nm. Samples were prepared in a matrix of 2,5-dihydroxybenzoic acid by first depositing the matrix, 0.5μl of a 10^{-1}mol dm^{-3} in 40:60/water:acetonitrile , followed by 0.5μl of a 10^{-3}mol dm^{-3} solution of the polymer in acetone. Spectra were averaged over 100 laser pulses whilst scanning across the spectrum.

Results and discussion

In the presence of titanium(IV) butoxide the AB_2 monomer, diethyl 3-hydroxyglutarate (see below), undergoes condensation polymerisation with the



elimination of ethanol to give a hyperbranched polymer, the structure of the product is complicated by the intervention of side reactions including cyclisation and alkoxide exchange between the catalyst and polymer ethyl ester groups and the detailed structural characterisation of the series of materials produced in this work will be described elsewhere (5). The viscous liquid was subjected to MALDI-TOF analysis in an attempt to gain an insight into the process of producing representative MALDI-TOF mass spectra. In most samples, not only were the sodium adduct peaks of the simple condensation polymerisation products and the reaction byproducts observed, but the potassium adducts were present as a minor series also. These cation adducts are obtained as a result of the presence of "adventitious" impurities in the matrix, 2,5-dihydroxybenzoic acid, DHB.

Two systematic investigations (3,4) into the influence of the laser power on the MALDI mass spectra of polymers have been published. Both groups reported that for linear polymers, the spectrum obtained at the threshold laser power (that power where a spectrum is first observed) are the most representative of the polymer distribution. A slight increase in power giving a skewed distribution which is shifted to lower mass. It has been suggested (4) that this is due to degradation (scissions) of the polymer by the laser. In an attempt to investigate the dependence of laser power on the quality and nature of the observed MALDI-TOF mass spectra for these hyperbranched poly(diethyl 3-hydroxyglutarate)s, a series of spectra were collected and carefully compared. The power of the laser was varied from 36%-56% of the available power scale on the instrument and the collected spectra were averaged over 100 shots, where one shot is defined as one pulse of laser irradiation. Three examples of the many spectra recorded are reproduced below.

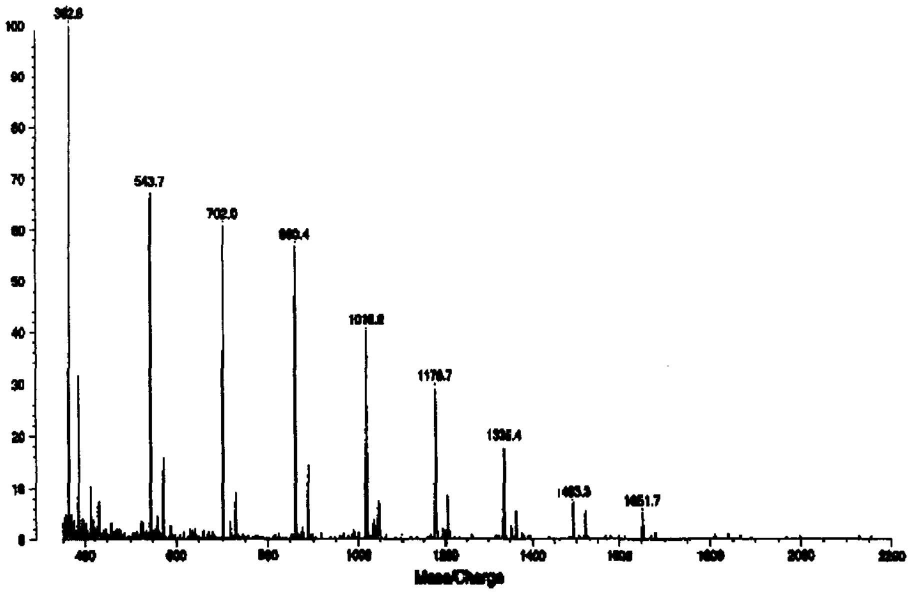


Figure 1. Spectrum obtained at threshold laser power (36%)

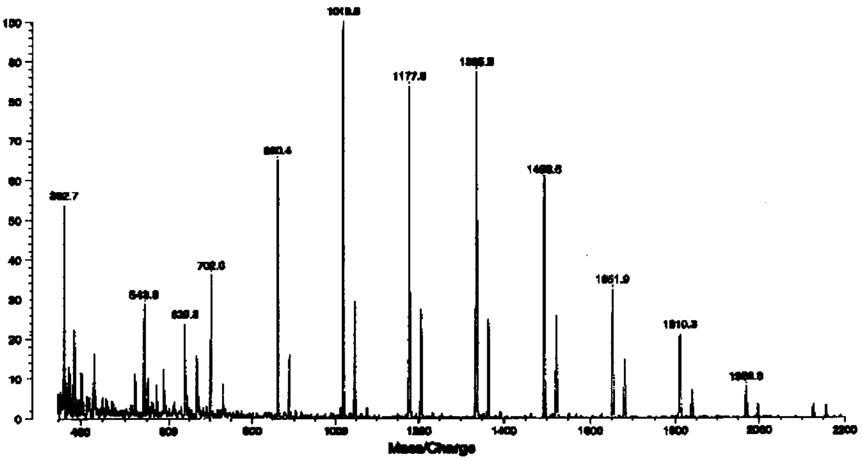


Figure 2 Spectrum obtained at laser power (44%)

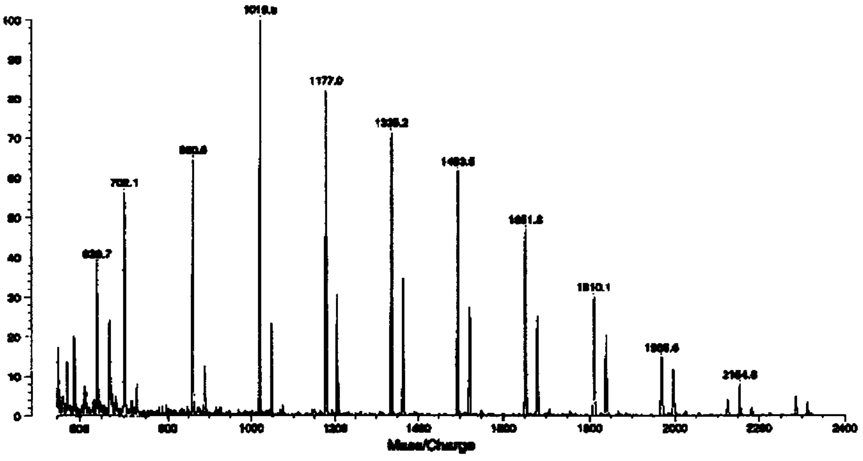


Figure 3 Spectrum obtained at laser power (47%)

On inspection of the spectra, Figures 1, 2 and 3, it is clear that the recorded spectrum is a function of laser power and there is probably only a small "laser power window" where "representative spectra" of the analyte can be obtained. At relatively low power, i.e. the threshold power, the distribution resembles the expected Flory number distribution, with low mass peaks most intense but with higher mass peaks of very low intensity and no peaks above m/e 1700. When higher laser powers are used (44 and 47%) the distribution changes and peaks at significantly higher m/e (>2000) are observed with a peak in the distribution; however, even in the small power range of 44 to 47% the observed distribution changes and is clearly a sensitive function of the incident laser power. The observation that the larger oligomers are present at higher powers, is as intuitively expected but if the sample actually does have a Flory number average distribution it is difficult to understand why the lower mass part of the distribution is less evident in the spectra recorded at higher incident laser power, possibly the lower mass species are degraded at the higher powers. If higher power simply resulted in a uniform fragmentation of all species we might expect to see relatively more, certainly not less, low mass peaks.

In the above spectra, the major mass series are due to the simple hyperbranched oligomers of poly(diethyl 3-hydroxyglutarate), whilst minor series can be attributed to alkoxide exchange between the catalyst and the polymer and there are peaks due to cyclisation reactions (5). It can easily be seen that the spectra are highly dependent on the power of the laser and that detailed interpretation of "one off" spectra are to be treated with considerable reserve.

Conclusions

MALDI-TOF MS is a powerful tool for the investigation of polymer structure and molecular weight distribution; however, it is still in the early stages of development and users need to be aware that several issues relating to the recording conditions need to be addressed before secure interpretations of recorded data can be made. For example, what is the definition of "optimum" laser power?, is it that which gives the strongest signals at the highest m/e or that which gives the "correct" distribution? The factors determining the form of the distribution observed in MALDI-TOF MS of polymers are clearly much more complex than might be expected from some published studies. The data reported above relates to one simple class of AB_2 polymer and a comprehensive analysis of this system will be published elsewhere (5); however, these observations appear to be fairly general in all of several other hyperbranched systems we have studied. We, and several other groups, have had very encouraging results from this mass measuring technique for narrow distribution low molecular weight linear polymers but it is important to realise that there is clearly much to learn in the application of this comparatively new technique to more complex systems. The instrument developers and specialist mass spectroscopists are making good progress in improving the measuring technology but routine users with access to "off the shelf" instruments would be well advised to treat the data from "one off" spectra with considerable caution and avoid reliance on detailed interpretation.

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