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Ions derived from linear polysulfide oligomers using matrix-assisted laser desorption/ ionisation time-of-flight mass spectrometry

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Attempts to produce detectable levels of ions from oligomers of linear polysulfides (LPs) $H(SC_2H_4O-CH_2OC_2H_4S)_nH$ (n up to 24) by matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) mass spectrometry failed with all common matrix/cation combinations except 9-nitroanthracene containing silver trifluoroacetate. The latter matrix yielded a series of species assigned to $Ag(SC_2H_4OCH_2OC_2H_4S)_n$ representing the loss of *two* thiol hydrogen atoms, together with smaller quantities of other series $Ag(SC_2H_4O-CH_2OC_2H_4S)_n(C_2H_4OCH_2OC_2H_4S)$ and $Ag(SC_2H_4OCH_2OC_2H_4S)_n(SC_2H_4OC_2H_4OCH_2OC_2H_4S)$ when a conventional LP was utilised. Other LP structures were examined and these also gave argentated species; one LP (designated ZL-2264) gave a spectrum featuring silver isotope splitting of all of its peaks. At higher laser powers, or with high silver salt concentrations, or after extensive ageing of samples prior to laser irradiation, a totally new series of peaks emerged attributed to $[(Ag_2S)_nAg]^+$ with n reaching 11, i.e. containing 23 silver atoms. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Matrix-assisted laser desorption/ionisation (MALDI) is a recently developed ionisation technique which has been found to be extremely effective for the analysis of large biological molecules and, more recently, in the characterization of synthetic polymers[1]. Hitherto MALDI studies have largely been devoted to fairly standard synthetic polymers such as poly(methyl methacrylate)[2-5], poly(ethylene glycol)[2,3] and polystyrene[2,3].

Linear polysulfides (LPs), which constitute an important class of pre-polymer with wide industrial application particularly as sealants[6,7], have previously proved difficult to characterise by MALDI tme-of-flight (TOF) mass spectrometry, presumably owing to the failure to identify a suitable matrix. No LP spectra of this type have been published in the open literature, but Ludicky[8] of Morton Thiokol reported Fourier transform ion cyclotron resonance (FT-ICR) mass spectra of laser-desorbed commercial LPs in an internal report. The expected relative molecular mass distributions (RMMD) for LPs were not observed, with no series of peaks being observed above around 2000 Da, even for LPs of known molecular masses of above 4000. Ludicky has also reported[8] that his group has been unsuccessful in obtaining MALDI spectra of LPs.

In previous publications[9,10] we have demonstrated the effectiveness of electrospray ionisation (ESI) in producing cations in the form of potassium or ammonium ion adducts from a range of commercially significant linear LPs $H(SC_2H_4OCH_2OC_2H_4S)_nH$ ($1 < n < 24$). It was also possible[9,10] to gain information about the structures of individually selected ions by submitting them to collision with argon gas followed by mass spectral characterisation of the product ions (so-called collision-induced or -activated decomposition[11-13] (CID) or tandem mass spectrometry, MS/MS).

The significant advantages of using MALDI for the analysis of LPs would be: (i) once a suitable matrix system is found, sample preparation is quick and easy; (ii) MALDI instruments are quicker and significantly easier to operate than many mass spectrometric techniques, including ESI.

Here we describe results on MALDI-TOF mass spectrometry of several selected polysulfide oligomers.

EXPERIMENTAL

Materials

(i) Commercially available LP-2C sold under the name Thiokol® LPs, was obtained from Morton International Ltd. This has a molecular weight of *ca.* 4000 based on end-group analysis by titration with iodine.

(ii) Model A: this LP was considered to be an exceptionally pure product, i.e. free from material with variant mers, with an approximate relative molecular mass of *ca.* 2600.

(iii) ZL-2264: this LP had the formula $H(SC_2H_4OC_2H_4OC_2H_4S)_nH$, i.e. the oxymethylene unit in the repeat unit of a normal LP is replaced by oxyethylene.

(iv) ELP-3: this had the formula $OCH_2CHCH_2(SC_2H_4OCH_2OC_2H_4S)_nCH_2CHCH_2O$, i.e. the terminal thiol groups are replaced by oxirane units, and it was supplied as having a RMM *ca.* 1000.

THF was h.p.l.c.-grade (Fisons). All matrices and salts were purchased from Aldrich.

Mass spectrometry

All experiments were carried out on a Kratos Kompact III

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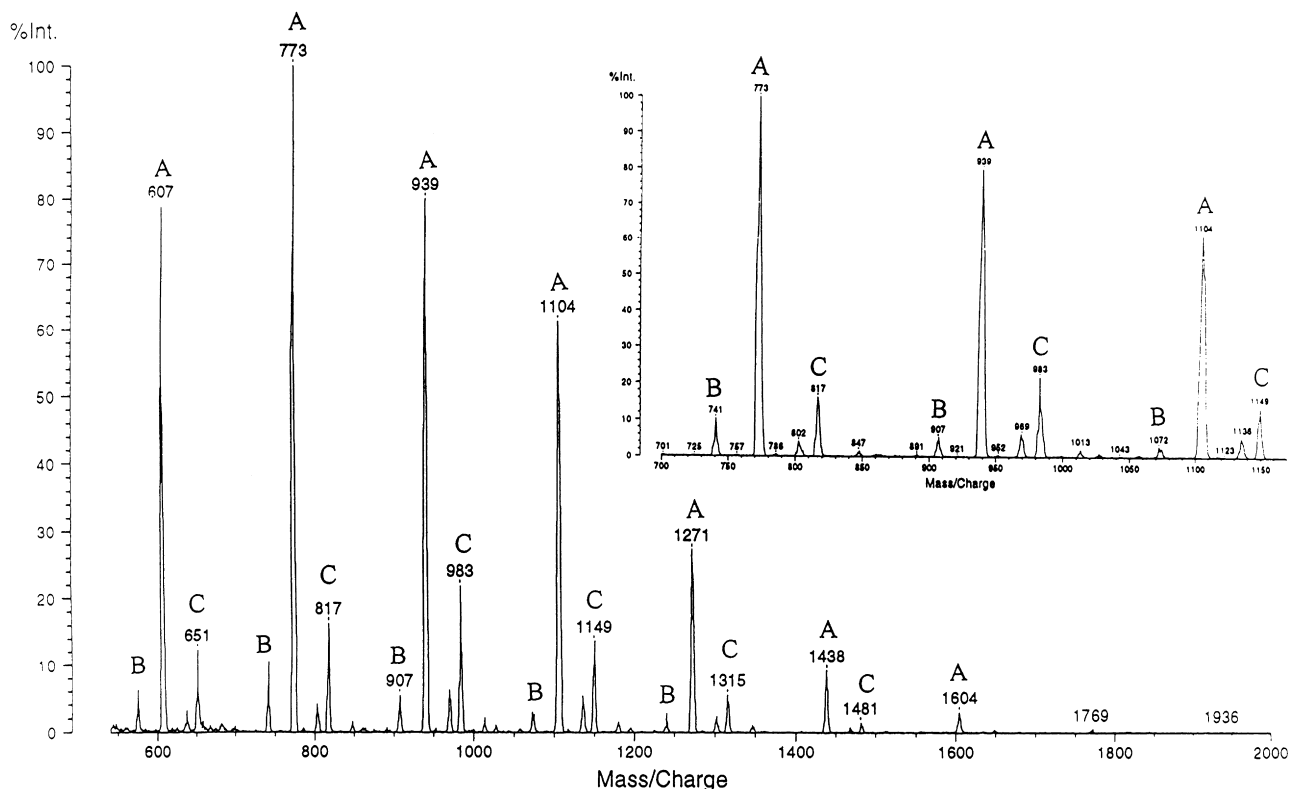
Figure 1 MALDI spectrum of LP-2C with 10 μl of silver trifluoracetate in 9-NA matrix. Inset: expansion of spectrum in m/z range 700–1160 to reveal greater detail

MALDI-TOF mass spectrometer. The instrument was fitted with a nitrogen laser of wavelength 337 nm with a 3 ns pulse duration, and an electron multiplier detector. The spectrometer was operated in the positive ion linear mode with an accelerating potential of 20 kV. It was calibrated with a sample of bovine insulin.

All polymer sample concentrations were approximately 3 mg/ml in THF. Various volumes of silver trifluoroacetate (10–200 μl) were used to dope the analyte solution (0.5 ml). Equal quantities of this solution and the matrix solution (0.1 M 9-nitroanthracene (9-NA) in THF) were mixed and the resulting solution left to stand for up to 4 h; 1 μl of this mixture was deposited onto the stainless steel sample slide and the solvent was allowed to evaporate.

Every sample was analysed at various laser powers and spectra were averaged over 200 laser shots. Analysis of the data acquired was carried out using software installed on the Kompact III instrument.

RESULTS AND DISCUSSION

A variety of matrices, salts and concentration levels was examined unsuccessfully before our first MALDI spectrum of an LP was obtained. Initial studies using the generally favoured 2,5-dihydroxybenzoic acid (DHB) and sinapinic acid as the matrix, either alone or with lithium, sodium or potassium chloride, gave no ions. Dithranol as matrix, in combination with silver trifluoroacetate, also gave no ions from LPs.

However, the use of 9-nitroanthracene in combination with silver trifluoroacetate gave the MALDI spectrum shown in *Figure 1* when LP-2C was used as the analyte.

The principal features of this spectrum are: (i) the presence of a series of major peaks (denoted Series A) separated by 166 amu, i.e. the mass of the repeat unit; (ii) a set of minor peaks, denoted Series B, each member of which is located 32 amu below the corresponding peak in Series A. This mass difference we attribute to the presence of *one* unit in the entire polymer chain with one less sulfur atom; (iii) a set of minor peaks, denoted Series C, of which each member is located 44 amu above the corresponding peak in Series A. This mass difference we attribute to the presence of *one* unit in the entire polymer chain with one extra oxyethylene link.

The RMMs of Series A do not, in contrast to series in the ESI spectra of LPs[9,10], correspond to the RMM of the LP itself, which would be $(166n + 2) + RMM$ of the cation. The resolution of the MALDI-TOF mass spectra of LPs, compared to those obtained by ESI with a high-performance quadrupole[9,10], was poor in so far as virtually no peaks from other series, suspected to be present, were visible.

The assignment of the peaks in *Figure 1* is less obvious compared to those found in the ESI spectra of LPs. The peak at $m/z = 607$ can be viewed, at first sight, as an 'argentated LP', i.e. $Ag(SC_2H_4OCH_2OC_2H_4S)_3H^+$ which has an RMM of $(3 \times 166) + 1 + 108 = 607$, and all the main peaks in the spectrum of LP-2C (*Figure 1*) can similarly be attributed to: Series A, $Ag(SC_2H_4OCH_2OC_2H_4S)_nH^+$; Series B, $Ag(SC_2H_4OCH_2OC_2H_4S)_n(C_2H_4OCH_2OC_2H_4S)H^+$; Series C, $Ag(SC_2H_4OCH_2OC_2H_4S)_n(SC_2H_4\mathbf{OC_2H_4OCH_2}OC_2H_4S)H^+$.

The expected isotopic splitting from ^{107}Ag and ^{109}Ag was not, however, discernable (see, however, the spectrum from ZL-2264, *Figure 3*). Consequently we cannot assert confidently that the above assignments are incontrovertible: the peaks *could* be due to ions based on a silver compound of the LP with *both* thiol hydrogen atoms lost or to a simple adduct of Ag^+ with the LP, with both hydrogen atoms remaining intact. The result for ZL-2264 given below (see *Figure 3*) clarified this situation, indicating that the
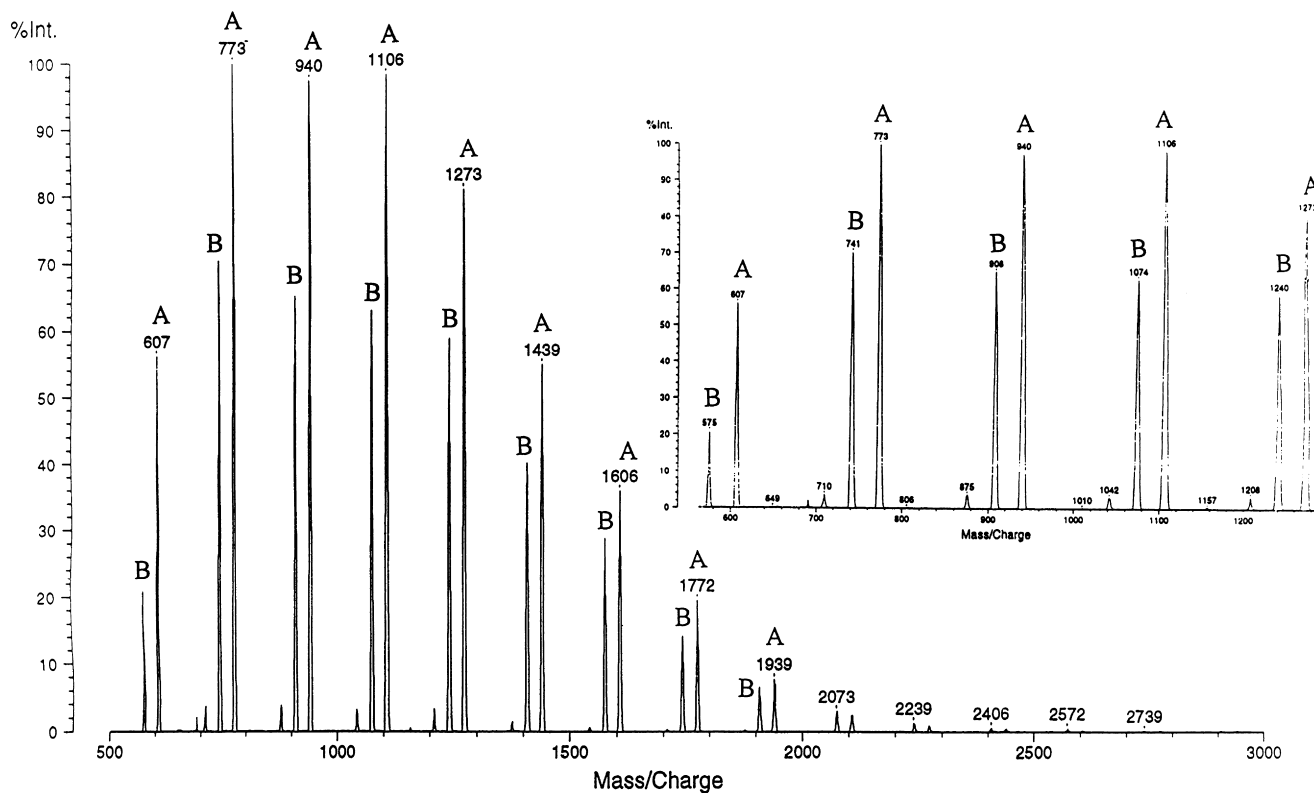
Figure 2 MALDI spectrum of LP Model A with 10 μl of silver trifluoracetate in 9-NA matrix. Inset: expansion of spectrum in m/z range 570–1280 to reveal greater detail
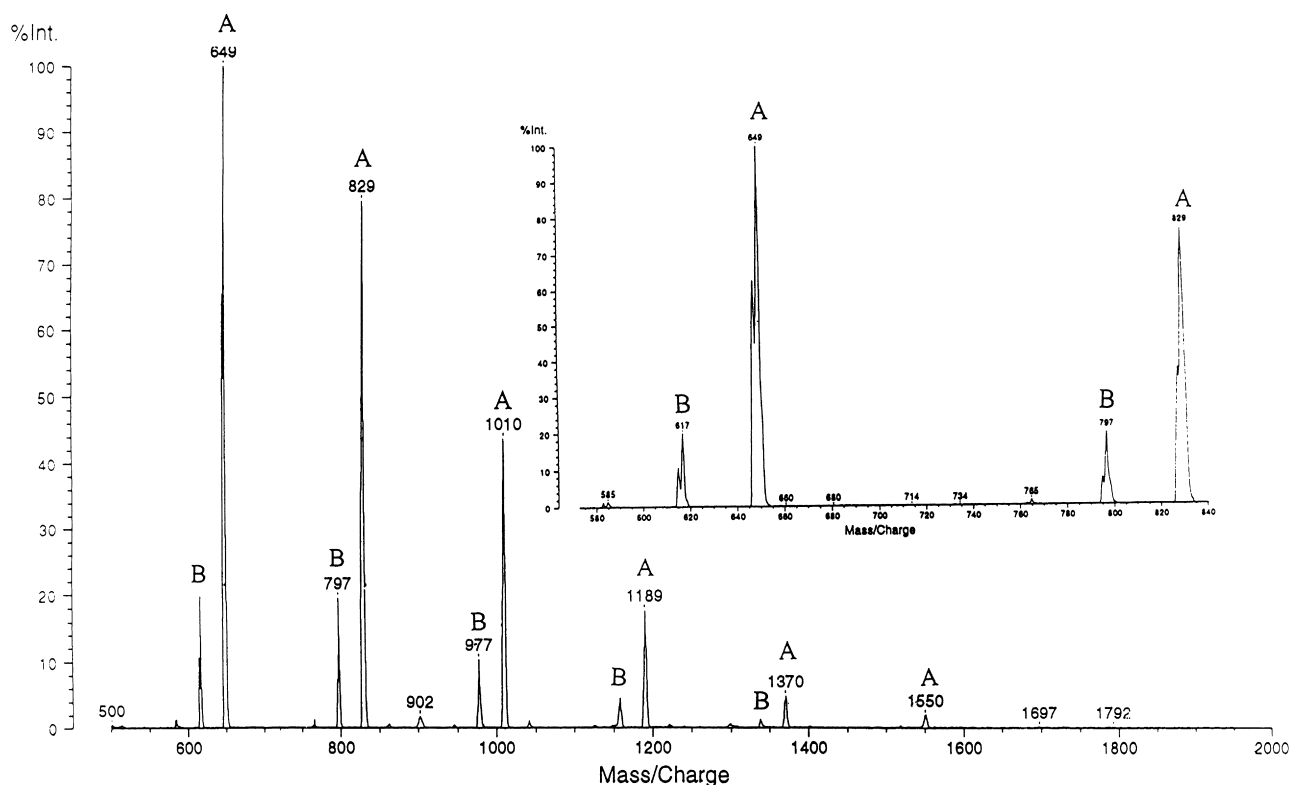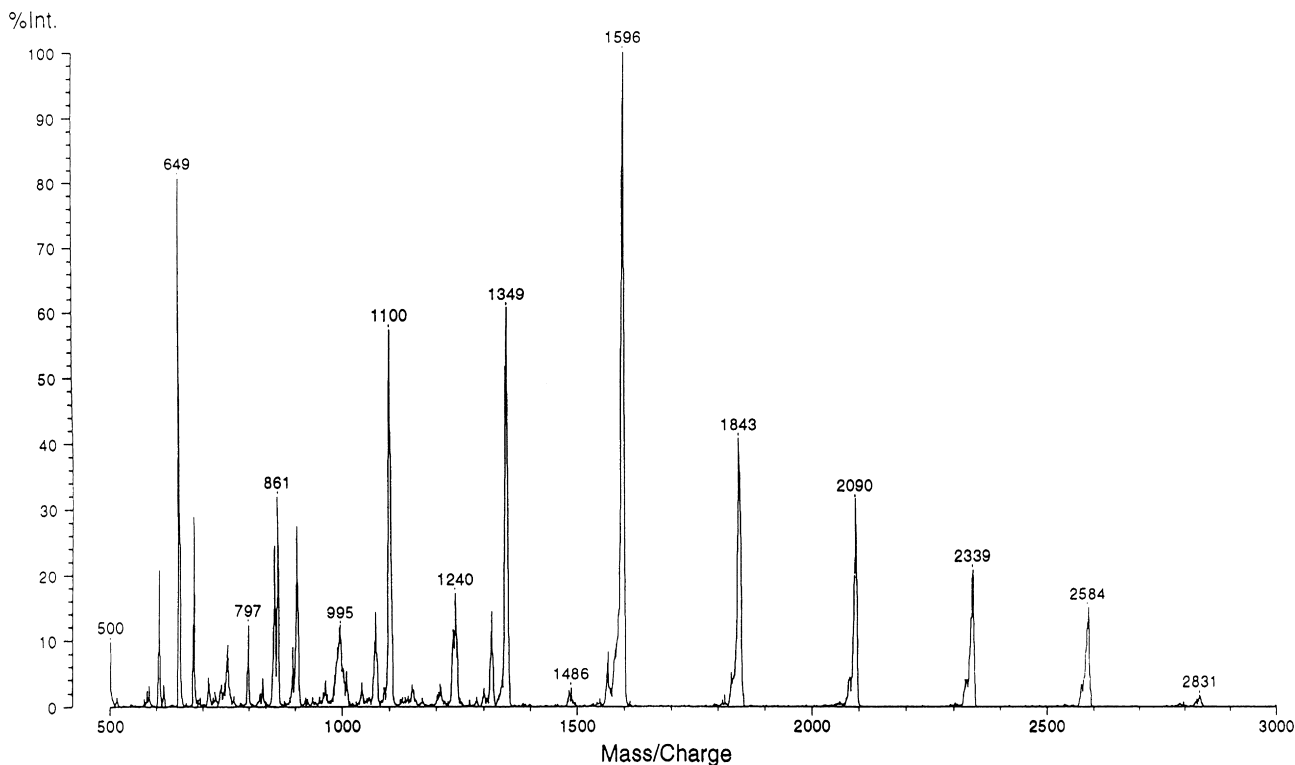

Figure 3 MALDI spectrum of LP ZL-2264 with 10 μl of silver trifluoracetate in 9-NA matrix. Inset: expansion of spectrum in m/z range 560–840 to reveal greater detail

assignment for the species derived from LP-2C, etc., should be to $Ag(SC_2H_4OCH_2OC_2H_4S)_n^+$.

The RMMD of LP-2C was not in accord with that expected. The average RMM of this polymer was ≈ 4000, but no peaks were observed in the spectrum above 2000 amu. Evidently low-mass oligomers were being detected at the expense of high-mass oligomers. Possible explanations for this are: (i) there was a bias for the detector

Figure 4 MALDI spectrum of LP ZL-2264 with 200 μl of silver trifluoracetate in 9-NA matrix

to favour the detection of low-mass oligomers, especially with the very polydisperse samples, as obtained with commercial LPs; (ii) the samples underwent fragmentation during ionisation, most likely at the weak disulfide linkage; (iii) only low-mass oligomers underwent desorption/ionisation into the gas phase. Fractionation of an LP sample using a g.p.c. column prior to MALDI-TOF analysis might lead to high-mass oligomers being detected using this technique, and hence the calculation of accurate molecular mass information for this class of polymers. This approach has been applied successfully by Montaudo *et al.*[14] for various polydisperse samples.

In view of the rather disappointing resolution of the spectrum obtained for LP-2C using MALDI, we decided to examine LPs with fewer impurities and LP variants in their formulation. An exceptionally simple form of LP, denoted Model A, gave the very clear MALDI spectrum shown in *Figure 2*, where Series A and B provide virtually the only peaks in the spectrum.

The LP denoted ZL-2264, which had the formal group in the repeat unit replaced by oxyethylene, also gave the very simple MALDI spectra illustrated in *Figure 3*. Peaks in these series were separated by the RMM of the repeat unit (180 amu), which are the analogues of Series A and B in the normally structured LPs.

The individual peaks showed a clear, but poorly resolved, doublet splitting of 2 amu, which supports strongly an assignment to the species $Ag(SC_2H_4OCH_2OC_2H_4S)_n^+$. The only silver isotopes of significant abundance are 107 (51.84%) and 109 (48.16%) which explains the existence of the doublet feature on the inset of *Figure 3*. The main peaks arising in this spectrum can therefore be assigned to a ^{109}Ag compound of the LP with *both* thiol hydrogen atoms lost, i.e. $^{109}Ag(SC_2H_4OCH_2OC_2H_4S)_n$, while the shoulder peak at 2 amu less can be attributed to $^{107}Ag(SC_2H_4\ OCH_2OC_2H_4S)_n$.

We also attempted to obtain MALDI spectra for ELP-3, an epoxy-terminated LP, and for heavily u.v.- and heat-degraded samples of Model A and other LP pre-polymers. No ions were observed in any of these cases, suggesting that MALDI is an inefficient technique for studying degradation reactions in LP-type polymers. The result for ELP-3 suggests that, in order for ions to be formed, thiol hydrogen atoms must be present in the LP. It also appears that any minor species obtained by a slight change in the LP structure yielded no observable ion peaks, which would explain why series D, E, F, etc., described in Ref. [10], clearly visible in the ESI spectra of LPs, were not visible in their MALDI spectra.

An unexpected observation was that, under certain experimental conditions, the MALDI spectra of LPs changed completely from the form shown in *Figures 1* and *2* to ones resembling that shown in *Figure 4*. This new-type spectrum consisted of a set of peaks separated not by the usual 166 amu associated with the LP repeat unit, but rather by 248 amu. That this figure has no relation to the LP repeat unit was confirmed by an experiment with ZL-2264 where the peak separation was, once again, 248 amu (see *Figure 4*). This phenomenon we attribute to the formation of mono-positively charged clusters of Ag_2S species, formed chemically either during the sample preparation or during the laser irradiation of the matrix sample once prepared.

Taking the most abundant peak in the spectrum, i.e. that at *m/z* 1596, we can see that this is not an integral number of Ag_2S units. The peak at *m/z* 649 *is* that present in the 'normal' MALDI spectra of ZL-2264 and is due to $^{109}Ag(SC_2H_4OC_2H_4OC_2H_4S)_3$; however, the next higher member is conspicuous by its absence. It seems that the main series has a formula of the type $[(Ag_2S)_n(X)]^+$, where X represents some other fragment derived from an LP or its silver adduct. While the peak at *m/z* 1100 is clearly a member of this series, the next lowest member should be at

Table 1 Predicted and observed masses of $(Ag_2S)_nAg^+$ clusters

	m/z calculated (Ag = 108)	m/z observed
$Ag(Ag_2S)^+$	356	
$Ag(Ag_2S)_2^+$	604	604
$Ag(Ag_2S)_3^+$	852	852
$Ag(Ag_2S)_4^+$	1100	1100
$Ag(Ag_2S)_5^+$	1348	1349
$Ag(Ag_2S)_6^+$	1596	1596
$Ag(Ag_2S)_7^+$	1844	1843
$Ag(Ag_2S)_8^+$	2092	2090
$Ag(Ag_2S)_9^+$	2340	2339
$Ag(Ag_2S)_{10}^+$	2588	2584
$Ag(Ag_2S)_{11}^+$	2836	2831

m/z 852, which is only of rather weak abundance, as is that of the next lowest member at m/z 604.

The peak at m/z 604 could be due to the cluster $Ag_5S_2^+$ or $Ag^+(Ag_2S)_2$ which has an RMM of 604, and the series in general is of the formula $(Ag_2S)_nAg^+$. Such a species would generate peaks at the predicted masses given in *Table 1* together with those observed.

Evidently the very strong Ag–S bond is the determining factor in producing these clusters from silver salts on reacting with the sulfur atoms of an LP. In accordance with this view, we found that the development of spectra like those in *Figure 4* were promoted by: (i) high levels of Ag salt in the matrix formulation, (ii) high laser powers, and (iii) when the analyte/silver samples were left for a relatively long time prior to laser irradiation. Thus experimental conditions must be carefully selected to preclude the occurrence of this type of cluster chemistry when dealing with sulfur-containing compounds using a silver-containing matrix. Such clustering processes have been well-established in fast atom bombardment mass spectral experiments with salts of uranyl ion[15,16] and of lanthanides[17–20].

CONCLUSIONS

We have been successful in obtaining mass spectra of LPs using MALDI-TOF mass spectrometry. The method of sample preparation was critical in obtaining a MALDI spectrum of reasonable quality. Well-tried matrices such as DHB and dithranol were unable to yield LP ions even when sodium, potassium or silver salts were added. The only matrix system that proved successful for LP samples was 9-nitroanthracene containing silver trifluoroacetate and, even then, the analyte/silver mixture had to be left to stand

for at least 4 h before a spectrum could be obtained. One possible explanation for this would be that the silver cation requires time to react with the thiol groups in the LP, which would imply the presence of preformed ions. We also encountered an interesting diversion in the formation of silver clusters $[Ag(Ag_2S)_n]^+$, with n reaching 11 (i.e. with 23 Ag atoms), under certain experimental conditions.

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