

Mass spectral characterization of oligomeric polysulfides by electrospray ionization combined with collision-induced decomposition

Andrea Mahon, Terence J. Kemp*, Armelle Buzy and Keith R. Jennings

Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

Polysulfide oligomers $\text{H}(\text{SC}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S})_n\text{H}$ with $n = 1-24$ can be characterized by electrospray ionization mass spectrometry. Samples prepared by the conventional method are shown to contain up to eight series of oligomers differing in structure by one of a small group of variants in one (or sometimes two) of the repeat units, e.g. with one less S atom or an additional CH_2O group. The composition of individual ions can be confirmed by collision-induced decomposition of cationized polysulfides, which yields unambiguous spectra of the fragmented ions.

(Keywords: polysulfide; electrospray; mass spectrometry)

Introduction

Attempts by two laboratories^{1,2} to obtain mass spectra of aliphatic linear polysulfide oligomers (LPs) $\text{H}(\text{SC}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S})_n\text{H}$ ($0 < n \leq 24$) by matrix-assisted laser desorption ionization (MALDI) have been unsuccessful hitherto, presumably owing to the lack of an ideal matrix. Fast atom bombardment (FAB) ionization yields species of only very low molecular mass². In view of the importance of this group of polymers in the construction, insulated glazing and aircraft industries^{3,4}, we have sought alternative means of characterizing these materials mass spectrometrically.

Electrospray ionization (ESI)⁵ has been used successfully to determine relative molecular masses (RMM) and structural information from a wide range of biomolecules such as peptides⁶, proteins⁷ and oligonucleotides⁷. The technique has recently been shown to be useful in characterizing a number of synthetic polymers including polyglycols⁸ and polyamidoamine starburst polymers⁹ and has been used in conjunction with size-exclusion chromatography^{10,11}. Since both ESI and FAB ionization are soft ionization techniques; structural information is normally obtained by the use of collision-induced decomposition (CID)¹² and studies of polyglycols have been reported in which ESI¹³ and FAB^{14,15} have been used. We report here our preliminary results on applying ESI and ESI/CID to LP samples.

Experimental

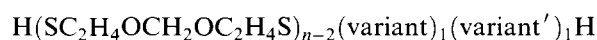
Materials. Linear polysulfides $\text{H}(\text{SC}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S})_n\text{H}$ were obtained from Morton International Ltd; their general size characteristics are set out in *Table 1*.

Mass spectrometry. The ESI/CID experiments were carried out in a Fisons' 'Quattro II' triple quadrupole mass spectrometer (VG Biotech, Altrincham, UK) equipped with an atmospheric pressure ionization (API) source operated in the nebulizer-assisted electrospray mode. The potential on the electrospray needle was set at 4 kV

and the extraction cone voltage was normally set at 55 V. Polysulfides at a concentration of $0.5 \mu\text{g}/\mu\text{l}$ were dissolved in a mixture of tetrahydrofuran and methanol (1:1 by volume) in the presence of 0.5% ammonium chloride. Aliquots of $20 \mu\text{l}$ were introduced into the ion source at a flow rate of $5 \mu\text{l min}^{-1}$. Mass spectra were acquired over the range m/z 3500–350 during a 10 s scan, and by operating the data system in the multichannel acquisition (MCA) mode, several scans were summed to produce the final spectrum. Calibration was carried out using a solution of sodium iodide. Polysulfide ions of selected m/z passed from the first quadrupole mass analyser into the r.f.-only quadrupole collision cell containing argon at 3.8×10^{-3} mbar at a translational energy of 20 eV. Fragment ion spectra were obtained by scanning the final quadrupole mass analyser over the m/z range from the mass of the precursor ion down to m/z 50 in 10 s using the MCA mode.

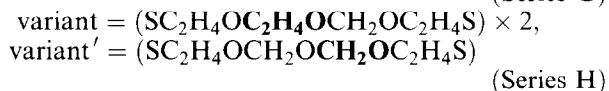
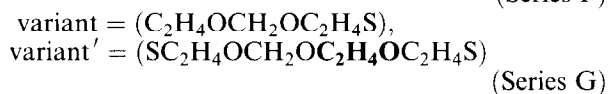
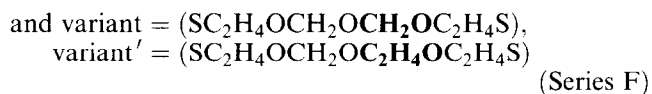
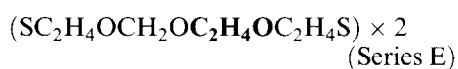
Results and discussion

ESI spectra. All LPs listed in *Table 1* form singly charged positive ions of the type $[\text{M} + \text{NH}_4]^+$ under the experimental conditions used. The spectrum given by LP-1400C shown in *Figure 1* is quite typical. The complex spectra given by all LPs can be rationalized by postulating the coexistence of several series of oligomers within a single LP sample, each differing from its nearest neighbours by 166 Daltons, which corresponds to the most common repeat unit ($\text{SC}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S}$). These various different series, as evidenced for LP-1400C, are summarized in *Table 2*, from which it can be seen that LP-1400C contains series of the following composition ('extra' groups are denoted in bold font):



where variant = $(\text{C}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S})$ (Series B)
 $(\text{SC}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{S})$ (Series C)
 $(\text{SC}_2\text{H}_4\text{OCH}_2\text{OCH}_2\text{OC}_2\text{H}_4\text{S})$ (Series D)

* To whom correspondence should be addressed



(Series H)

Table 1 Size characteristics of linear polysulfides $\text{H}(\text{SC}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S})_n\text{H}$

Trade name	RMM (nominal)	Branching agent ^a (mol %)	<i>n</i>
LP-1400C	1000	0	7
LP-3	1000	2.0	7
LP-33	1000	0.5	7
LP-977C	2600	2.0	16
LP-980C	2600	0.5	16
LP-32C	4000	0.5	24
LP-12C	4000	0.2	24
LP-541C	4000	0	24

^a 1,2,3-Trichloropropane

Table 2 Assignments of principal peaks in the ESI spectrum of LP-1400C ('extra' groups are denoted in bold font)

Series A		Series B	
$\text{H}(\text{SC}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S})_n\text{H.NH}_4^+$		$\text{H}(\text{SC}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S})_n(\text{C}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S})\text{H.NH}_4^+$	
<i>n</i>	<i>m/z</i>	<i>n</i>	<i>m/z</i>
9	1514.6	8	1482.6
8	1348.6	7	1316.6
7	1182.6	6	1150.7
6	1016.5	5	984.5
5	850.5	4	818.7
4	684.4	3	652.6
3	518.4	2	486.4

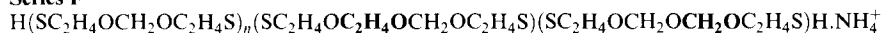
Series C	
$\text{H}(\text{SC}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S})_n(\text{SC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S})\text{H.NH}_4^+$	
<i>n</i>	<i>m/z</i>
7	1392.5
6	1226.6
5	1060.5
4	894.5
3	728.4
2	562.4

Series D	
$\text{H}(\text{SC}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S})_n(\text{SC}_2\text{H}_4\text{OCH}_2\text{OCH}_2\text{OC}_2\text{H}_4\text{S})\text{H.NH}_4^+$	
<i>n</i>	<i>m/z</i>
6	1212
5	1046
4	880
3	714
2	548

Series E	
$\text{H}(\text{SC}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S})_n(\text{SC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OCH}_2\text{OC}_2\text{H}_4\text{S})_2\text{H.NH}_4^+$	
<i>n</i>	<i>m/z</i>
6	1436
5	1270
4	1104
3	938.5
2	772.4
1	606.5
0	440.5

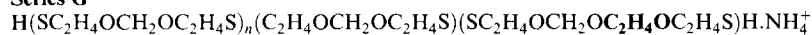
Table 2 Continued

Series F



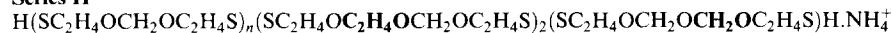
n	m/z
5	1256
4	1090
3	924
2	758
1	592
0	426

Series G



n	m/z
5	1194
4	1028
3	862
2	696
1	530

Series H



n	m/z
5	1467
4	1301
3	1135
2	968.6
1	802.6
0	636.5

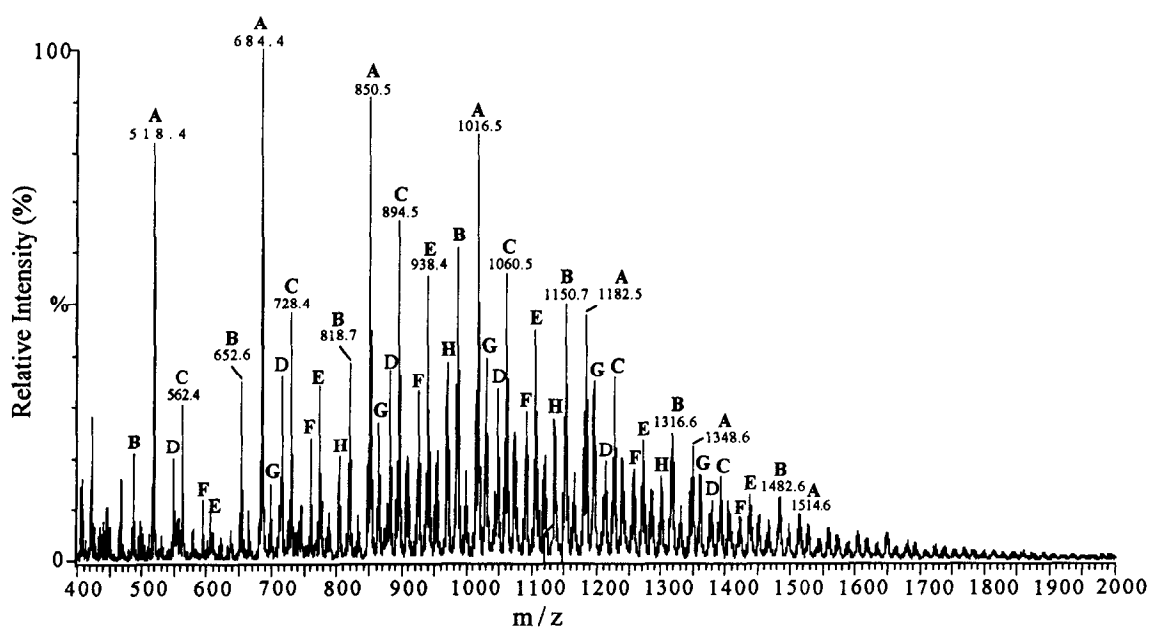


Figure 1 Electrospray mass spectrum of LP-1400C: mobile phase THF-McOH (50/50) containing 0.5% aqueous NH_4Cl . Assignments of ions are given in Table 2

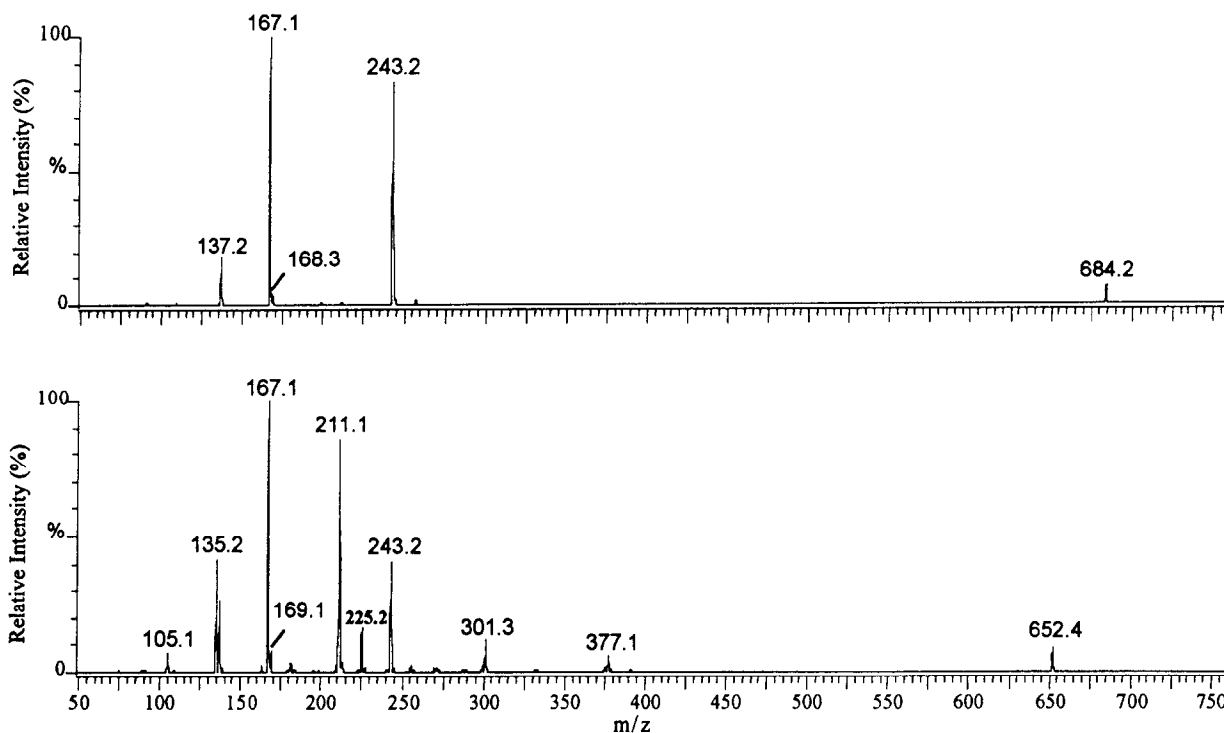


Figure 2 Collision-induced decomposition spectra of ions selected from electrospray mass spectrum of LP-1400C (see Figure 1). Collision gas, argon (pressure 3.8×10^{-3} mbar), collision energy 20 eV. Upper: ion mass 684.2 from Series A; lower: ion mass 652.4 from Series B

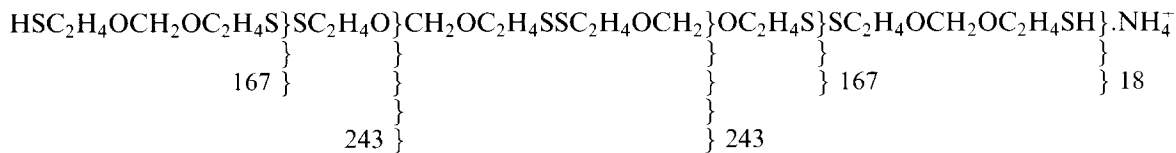
Similar types of complex distributions were observed in the ESI spectra given by all eight LPs listed in *Table 1*. This complexity results both from the coexistence of polymers having a range of *n* values within a given series and from the presence of several series of compounds that are based on ‘anomalous’ repeat units containing either fewer or additional S atoms, oxymethylene and oxyethylene units. This is not unexpected in view of the method of preparation of LPs³.

The relative intensities of peaks in the ESI spectra are not in accord with the expected relative abundances of the various components based on g.p.c. data for these LPs: even those with a nominal RMM of 4000 fail to give peaks at *m/z* values about 2000. Although this could suggest that

m/z of 166 Daltons would be reduced to 83 (doubly charged) or about 55 (triply charged) and these separations are not observed.

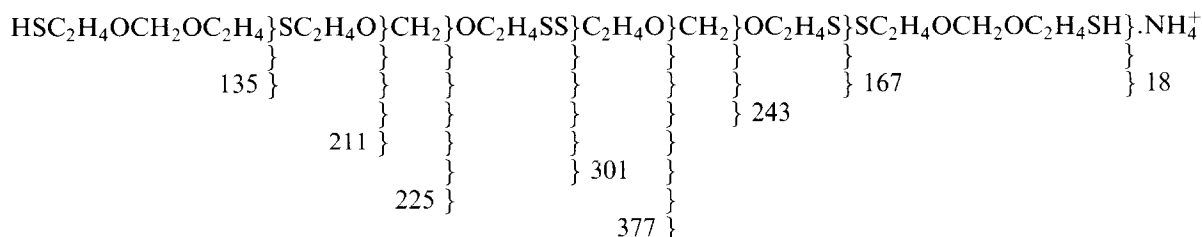
To confirm the assignments recorded in *Table 2*, where a degree of uncertainty attaches to species containing ‘anomalous’ repeat units, the CID spectra of selected ions of each series were recorded. These are exemplified by *Figure 2* for LP-1400C, the simplicity of the upper spectrum reflecting both the dominance of a particular mode of fragmentation and the symmetry of the precursor ion. The somewhat more complex lower spectrum is a consequence of the lower symmetry of the precursor ion.

Thus *Figure 2* (upper) shows the *m/z* 684.2 peak in Series A to fragment as follows:



ESI discriminates against ions of higher *m/z* values, it is also possible that the higher mass components are less soluble and so are not present in the sample that is ionized. The possibility that the ions of higher mass carry more than one charge can be ruled out since the separation in

whilst the 652.4 peak from Series B gives a more complex series of fragments due to the greater number of possibilities:



Conclusion

ESI is a powerful means of characterizing the highly complex mixtures which make up an LP, giving information on anomalous repeat units and on the RMM of individual components of lower mass, but because high mass components are not recorded, for reasons that are imperfectly understood, reliable information on lengths and average RMM values is not provided. We are planning to extend this work by carrying out a more detailed study of the ESI/CID spectra of a variety of LPs, including those terminated by different end-groups, together with an investigation of reaction pathways and alternative methods of introducing the samples, including the use of other solvent systems.

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