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Electrospray ionization mass spectrometric study of oligomeric linear polysulfides: characterization of repeat units, end groups and fragmentation pathways

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Electrospray ionization mass spectrometry is shown to offer excellent characterization of linear oligomeric polysulfides $H(SC_2H_4OCH_2OC_2H_4S)_nH$ with $n = 1$–24. Analysis of the mass spectra reveals the presence of individual oligomers, the presence in certain oligomers of repeat units containing additional oxyalkylene groups (and in some cases a monosulfide link rather than disulfide) and the presence of end groups such as epoxy. The attachment of polyacrylates during cure can also be detected. Assignments of individual peaks can be confirmed by collision-induced decomposition and precursor ion experiments: the fragmentation pathways are relatively few except for linear polysulfides of complex structure. The best signal-to-noise conditions are achieved with low-to-medium cone voltages and a mobile phase of acetone containing 0.5% KI. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Polysulfide oligomers, which constitute an important class of prepolymer with wide industrial applications, particularly as sealants[1,2], have proved difficult to characterize by such mass spectrometric methods as matrix-assisted laser desorption ionization (MALDI)—presumably owing to the failure to identify a suitable matrix[3,4]—and fast atom bombardment (FAB), which yield species of only very low molecular mass (see below).

In a preliminary communication[5], we have demonstrated the effectiveness of electrospray ionization (ESI) in producing cations in the form of ammonium ion adducts from a range of commercially significant linear polysulfides (LPs) $H(SC_2H_4OCH_2OC_2H_4S)_nH$ ($0 < n \leq 24$). It was also possible[5] to gain information about the structures of individually selected ions by submitting them to collision with argon gas followed by mass spectral characterization of the product ions (so-called collision-induced or collision-activated decomposition[6,7] (CID) or MS/MS).

In the present paper we present a comprehensive account of the application of ESI to the characterization of LPs, enlarging the range of LPs covered both by ESI and CID and focusing on such features as (1) identification and retention of the end groups, (2) variation in the mer unit, (3) improvement of spectral quality by variation of the mobile phase utilized, (4) the application of precursor-ion experiments to facilitate identification of the parentage of detected ions, and (5) the effect of variation of the cone voltage (c.v.) on ion abundances.

We have also sought to reduce the complexity of the spectra in order to strengthen spectral assignments and characterization of ion-decomposition pathways by utilizing LP formulations considered to be of exceptional simplicity and purity.

This study adds to the increasing library of detailed structural information on natural and synthetic polymers produced by ESI studies, including peptides[8], proteins[9], oligonucleotides[9], polyglycols[10,11], polyamidoamine starburst polymers[12], poly(methyl methacrylate)[13,14] and nitrated polyethers[15]. A general review of the application of newer methods of mass spectrometry to synthetic polymers has become available recently[16].

EXPERIMENTAL

Materials

Commercially available LPs, sold under the name Thiokol LPs, were obtained from Morton International Ltd; their general size characteristics are summarized in *Table 1*. Other LPs were also obtained from Morton, and are as follows:

(1) *Model LP-A*. This was considered to be an exceptionally pure LP, i.e. free from materials with variant mers, with an approximate relative molecular mass of ~2600.

(2) *ZL-2264*. This has the formula $H(SC_2H_4OC_2H_4OC_2H_4S)_nH$, i.e. the oxymethylene unit in a normal LP is replaced by oxyethylene.

(3) *ELP-3*. This has the formula $\overline{OCH_2C}\,HCH_2(SC_2H_4OCH_2OC_2H_4S)_n CH_2\,\overline{CHCH_2O}$, i.e. the terminal

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Table 1 Size characteristics of linear polysulfides
$H(SC_2H_4OCH_2OC_2H_4S)_nH$

Trade name	RMM (nominal)	Branching agent (mol%)[a]	n
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
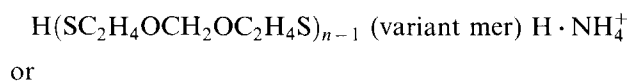
thiol groups are replaced by oxirane units, with $RMM \sim 1000$.

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 (c.v.) was set at $\sim$55 V for the THF/MeOH mobile phase and $\sim$100 V for the acetone/KI phase except during experiments conducted to ascertain the effect of changing the c.v. on the ESI spectrum. LPs at a concentration of $0.5 \mu g \mu l^{-1}$ were dissolved in a solvent compatible with the mobile phase. For most experiments this was a 1:1 (v/v) mixture of tetrahydrofuran (THF) and methanol (MeOH) in the presence of 0.5% aqueous ammonium chloride. A number of experiments were conducted using acetone as the mobile phase containing potassium iodide ($0.5 \, mg \, ml^{-1}$) and yet others with 1:1 THF/MeOH containing 0.5% trifluoroacetic acid (TFA), and also THF/DMF with KI and NH_4Cl, the latter with little success.

Mass spectra were scanned 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. In CID experiments, polysulfide ions of selected m/z passed at a translational energy of 20 eV from the first quadrupole mass analyser into the radio frequency—only hexapole collision cell containing argon at an indicated pressure of 3.8×10^{-3} mbar. 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.
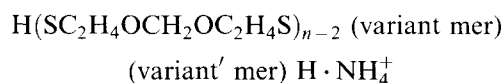
RESULTS AND DISCUSSION

ESI spectra. All LPs studied gave singly charged positive ions of the type $[M + NH_4]^+$ when the THF/MeOH/aq. NH_4Cl mobile phase was used. Those from LP-1400C, LP-980C and LP-12C shown in *Figure 1* are quite typical of the LPs listed in *Table 1*, and the general similarity between different LPs is also evident from this figure. These complex spectra can be rationalized by postulating the coexistence of several series of oligomers within a single type of LP; each member of each series differs in mass from its neighbours in the
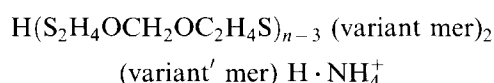
same series by 166 Da, which corresponds to the most common repeat unit $(SC_2H_4OCH_2OC_2H_4S)$. These various different series are identified by letters (A, B, C, ...) in *Figure 1*, and the assignments of individual peaks within each series for LP-980C are summarized in *Table 2*. Three new series have been identified since our preliminary communication[5], and the situation can be summarized thus: all series have the general formula

$$H(SC_2H_4OCH_2OC_2H_4S)_{n-1} \text{ (variant mer) } H \cdot NH_4^+$$

or

$$H(SC_2H_4OCH_2OC_2H_4S)_{n-2} \text{ (variant mer)}$$
$$\text{(variant' mer) } H \cdot NH_4^+$$

or

$$H(S_2H_4OCH_2OC_2H_4S)_{n-3} \text{ (variant mer)}_2$$
$$\text{(variant' mer) } H \cdot NH_4^+$$

(series A shows no variant mer). The designations of individual series, which are displayed for the most part by all LPs, are as follows:

Series B: variant = $(C_2H_4OCH_2OC_2H_4S)$

Series C: variant = $(SC_2H_4OC_2H_4OCH_2OC_2H_4S)$

Series D: variant = $(SC_2H_4OCH_2OCH_2OC_2H_4S)$

Series E: variant = $(SC_2H_4OC_2H_4OCH_2OC_2H_4S)$, variant' = $(SC_2H_4OC_2H_4OCH_2OC_2H_4S)$

Series F: variant = $(SC_2H_4OC_2H_4OCH_2OC_2H_4S)$, variant' = $(SC_2H_4OCH_2OCH_2OC_2H_4S)$

Series G: variant = $(SC_2H_4OC_2H_4OCH_2OC_2H_4S)$, variant' = $(C_2H_4OCH_2OC_2H_4S)$

Series H: variant = $(SC_2H_4OC_2H_4OCH_2OC_2H_4S)_2$, variant' = $(SC_2H_4OCH_2OCH_2OC_2H_4S)$

Series I: variant = $(C_2H_4OC_2H_4OCH_2OC_2H_4S)$ $(SC_2H_4OC_2H_4OCH_2OC_2H_4S)$

Series J: variant = $(SC_2H_4OCH_2OCH_2OC_2H_4S)_2$

Series K: variant = $(SC_2H_4OC_2H_4OCH_2OC_2H_4S)$ $(SC_2H_4OC_2H_4OC_2H_4OCH_2OC_2H_4S)$

It should, however, be noted that:

(1) the location of the variant mer(s) within the linear sequence is random;

(2) when there are several variants, these may be distributed between several mers or be located (at least partially) within a single mer.

Accordingly, the designations given above refer to only one of several possible distributions of variants.

The situation as regards the presence of particular series within the various LPs investigated is summarized in *Table 3*; one series is very prominent in all the LPs, namely series C with an extra oxyethylene link in one mer unit, while series B (lacking a single S atom) and series E (with an extra oxyethylene link in *two* mer units) are the only other mers to show any prominence in several LPs. Series featuring three variants in the structure are either absent or barely detectable.

As expected, model LP-A shows a very simple ESI spectrum (*Figure 2*), featuring only one significant series in addition to the expected series A, namely series B, i.e.
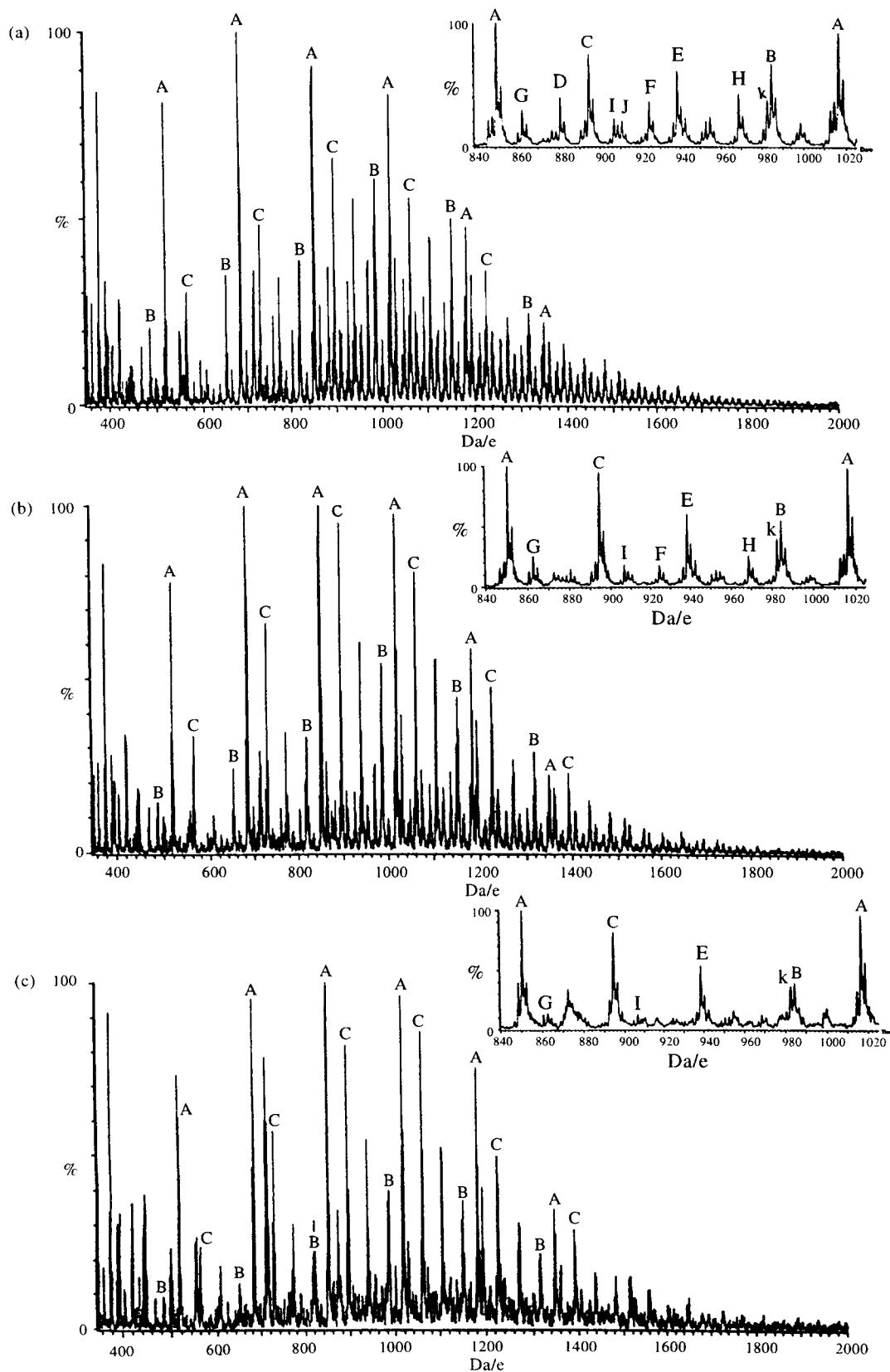
Figure 1 ESI spectra of (a) LP-1400C, (b) LP-980C and (c) LP-12C; mobile phase THF/MeOH containing 0.5% aqueous NH_4Cl. Assignments of ions are given in *Table 2* (mass range 350–2000 Da). Insets: expansion of spectra in m/z range 840–1020 to reveal greater detail

with a single –S– link replacing –S–S–. A summary of the spectral peaks and associated assignments is given in *Table 4*.

ELP-3 which contains terminal epoxy groups (see 'Materials' in the Experimental section), produces an

ESI spectrum (*Figure 3*) displaying the usual series A–K with 166 Da separation but with different masses because of the end groups (the replacement of the thiol hydrogen by epoxy at each end increases the *RMM* by 112 over the LP analogue). For brevity, only assignments of series A

Table 2 Assignments of principal peaks in the ESI spectrum of LP-980C ('extra' groups are indicated in bold)

Series A $H(SC_2H_4OCH_2OC_2H_4S)_nH \cdot NH_4^+$

n	m/z
9	1514.7
8	1348.7
7	1182.6
6	1016.5
5	850.5
4	684.5
3	518.4

Series B $H(SC_2H_4OCH_2OC_2H_4S)_n(C_2H_4OCH_2OC_2H_4S)H \cdot NH_4^+$
(i.e. one –S–S– link replaced randomly by –S–)

n	m/z
9	1648.3
8	1482.8
7	1316.6
6	1150.7
5	984.5
4	818.6
3	652.6
2	486.6

Series C
$H(SC_2H_4OCH_2OC_2H_4S)_n(SC_2H_4OC_2H_4OCH_2OC_2H_4S)H \cdot NH_4^+$
(i.e. one mer unit contains an extra oxyethylene link)

n	m/z
9	1724.9
8	1558.9
7	1392.6
6	1226.6
5	1060.5
4	894.5
3	728.4
2	562.4
1	396.4

Series D
$H(SC_2H_4OCH_2OC_2H_4S)_n(SC_2H_4OCH_2OCH_2OC_2H_4S)H \cdot NH_4^+$
(i.e. one mer unit contains extra oxymethylene link). This series, while clearly apparent with some LPs (see *Table 3*), is not apparent in LP-980C

Series E
$H(SC_2H_4OCH_2OC_2H_4S)_n(SC_2H_4OC_2H_4OCH_2OC_2H_4S)_2H \cdot NH_4^+$
(i.e. *two* mer units contain an extra oxyethylene unit)

n	m/z
7	1602.6
6	1436.8
5	1270.7
4	1104.7
3	938.4
2	772.6
1	606.6

Series F $H(SC_2H_4OCH_2OC_2H_4S)_n(SC_2H_4OC_2H_4OCH_2OC_2H_4S)$
$(SC_2H_4OCH_2OCH_2OC_2H_4S)H \cdot NH_4^+$
(i.e. one mer unit contains an extra oxyethylene unit and one contains an extra oxymethylene unit). This series, while clearly apparent with some LPs (see *Table 3*), is only just visible in LP-980C

Series G $H(SC_2H_4OCH_2OC_2H_4S)_n(SC_2H_4OC_2H_4OCH_2OC_2H_4S)$
$(C_2H_4OCH_2OC_2H_4S)H \cdot NH_4^+$
(i.e. one mer unit contains an extra oxyethylene unit while another has an –S– link replacing –S–S–)

n	m/z
8	1692.9
7	1526.8
6	1361.7
5	1194.6
4	1028.6
3	862.6
2	696.6

Series H $H(SC_2H_4OCH_2OC_2H_4S)_n(SC_2H_4OC_2H_4OCH_2OC_2H_4S)_2$
$(SC_2H_4OCH_2OCH_2OC_2H_4S)H \cdot NH_4^+$
(i.e. *two* mer units contain an extra oxyethylene unit while one contains an extra oxymethylene unit)

n	m/z
6	1632.9
5	1466.8
4	1301.8
3	1134.5
2	968.6
1	802.6
0	636.6

Series I $H(SC_2H_4OCH_2OC_2H_4S)_n(C_2H_4OC_2H_4OCH_2OC_2H_4S)$
$(SC_2H_4OC_2H_4OCH_2OC_2H_4S)H \cdot NH_4^+$
(i.e. one mer unit contains an extra oxyethylene unit while one contains an extra oxyethylene unit and either it or another mer unit, has an –S– link instead of an –S–S– link). This series while clearly apparent is of only weak intensity

n	m/z
7	1570.8
6	1405.7
5	1238.7
4	1072.6
3	906.5
2	740.5

Series J
$H(SC_2H_4OCH_2OC_2H_4S)_n(SC_2H_4OCH_2OCH_2OC_2H_4S)_2H \cdot NH_4^+$
(i.e. two mer units contain an extra oxymethylene unit). This series, while clearly apparent with some LPs (see *Table 3*), is not apparent in LP-980C

Series K $H(SC_2H_4OCH_2OC_2H_4S)_n(SC_2H_4OC_2H_4OCH_2OC_2H_4S)_2$
$(SC_2H_4OC_2H_4OCH_2OC_2H_4S)H \cdot NH_4^+$
(i.e. three extra oxyethylene groups are present, possibly in three separate mers or with two extra in a single mer and one in another mer)

n	m/z
8	1812.8
7	1646.8
6	1480.7
5	1314.7
4	1148.6
3	982.6
2	817.6
1	650.6

are given (in *Table 5*). The CID behaviour of ELP-3 is discussed below.

The behaviour of LP ZL-2264 closely mirrored that of LP-A; while the *RMM* of the mer unit $(SC_2H_4OC_2H_4OC_2H_4S)$ is 180 Da, giving a larger peak-to-peak separation in each series, variant mers are once again visualized in the ESI spectrum (*Figure 4*), although these now refer solely to the presence of one or two monosulfide links at the expense of disulfide links. The assignments of individual peaks are given in *Table 6*.

Variation of the composition of the mobile phase. All data in the preliminary communication referred to a mobile phase consisting of a 50/50 THF/MeOH mixture containing 0.5% aqueous NH_4Cl as an electrolyte to charge neutral LP molecules by forming 1:1 ion–molecule adducts, $[M \cdot NH_4]^+$. Changing the mobile phase to an acetone solution of potassium iodide $(0.5\,mg\,ml^{-1})$ resulted in two main effects, namely:

(1) The level of baseline noise in the spectra was considerably reduced (*Figure 4*).

Table 3 Level of appearance of series A to K in individual LPs

Series	A	B	C	D	E	F	G	H	I	J	K
LP-1400C	s	s	s	w	m	w	w	w	w	x	x
LP-3	s	s	s	x	s	x	m	w	m	x	s
LP-33	s	s	s	m	s	w	w	m	w	w	w
LP-977C	s	m	s	w	w	w	w	x	w	x	w
LP-980C	s	m	s	x	m	w	w	w	w	x	w
LP-32C	s	m	s	x	m	x	w	x	x	x	m
LP-12C	s	m	s	x	m	x	w	x	w	x	w
LP-541C	s	m	m	w	w	w	x	w	w	x	w
LP-31C	m	w	m	x	w	x	x	x	x	x	w
ELP-3	s	w	s	w	m	w	w	w	w	x	w
Model A	s	m	w	x	x	x	x	x	x	x	x

s, strong; m, moderate; w, weak; x, little sign
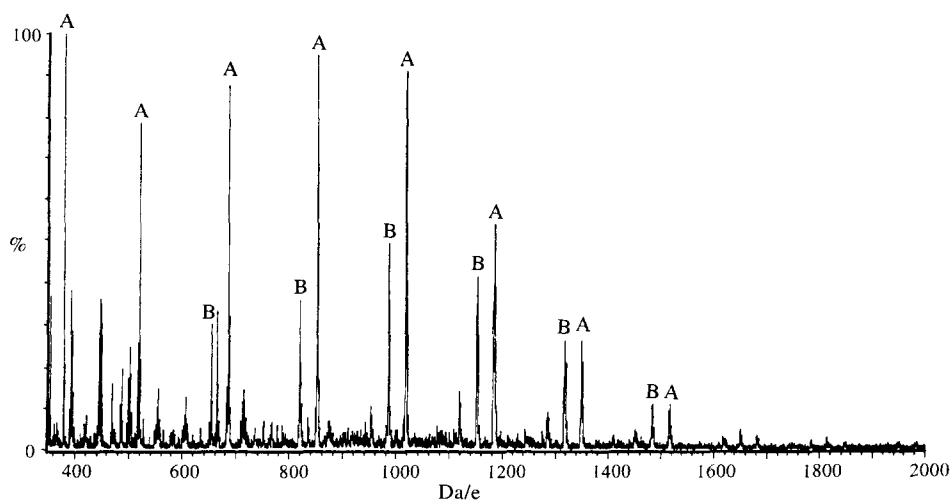
Figure 2 ESI spectrum of model LP-A; mobile phase THF/MeOH containing 0.5% aqueous NH_4Cl. Assignments of ions are given in *Table 4*

Table 4 ESI spectral peaks and associated assignments in the spectra of model LP, LP-A

Series A $H(SC_2H_4OCH_2OC_2H_4S)_nH \cdot NH_4^+$

n	m/z
10	1680.2
9	1514.0
8	1348.0
7	1182.1
6	1016.2
5	850.3
4	684.3
3	518.4
2	352.5

Series B $H(SC_2H_4OCH_2OC_2H_4S)_n(C_2H_4OCH_2OC_2H_4S)H \cdot NH_4^+$
(i.e. one $-S-S-$ link replaced randomly by $-S-$)

| n	m/z
9	1648.1
8	1482.3
7	1316.3
6	1150.4
5	984.3
4	818.4
3	652.4
2	486.5

(2) The K^+ ion adducts of the LP did not undergo dissociation with argon under CID conditions. The ready decomposition of NH_4^+ ion adducts is associated with initial loss of NH_3 leading to the H^+ ion

Table 5 Assignments of principal peaks in series A of the ESI spectrum of ELP-3

Series A

$OCH_2C HCH_2(SC_2H_4OCH_2OC_2H_4S)_nCH_2 CHCH_2O \cdot NH_4^+$

n	m/z
9	1626.7
8	1460.7
7	1294.6
6	1128.5
5	962.5
4	796.5
3	630.6
2	464.6

adduct, which then fragments on collision with argon.

Variation in the c.v. The CID of precursor ions produced in the ESI source was investigated without precursor ion mass analysis by studying the effect of increasing the c.v., all other conditions remaining constant. At low c.v. (e.g. 20 V), little CID is expected to occur so that the spectrum shown in *Figure 5a* is largely of precursor ions formed in the source. As the c.v. is increased, more CID occurs, leading to a reduction in the abundance of higher mass ions and a corresponding increase in the abundance of lower mass fragment ions. This is illustrated in *Figures*
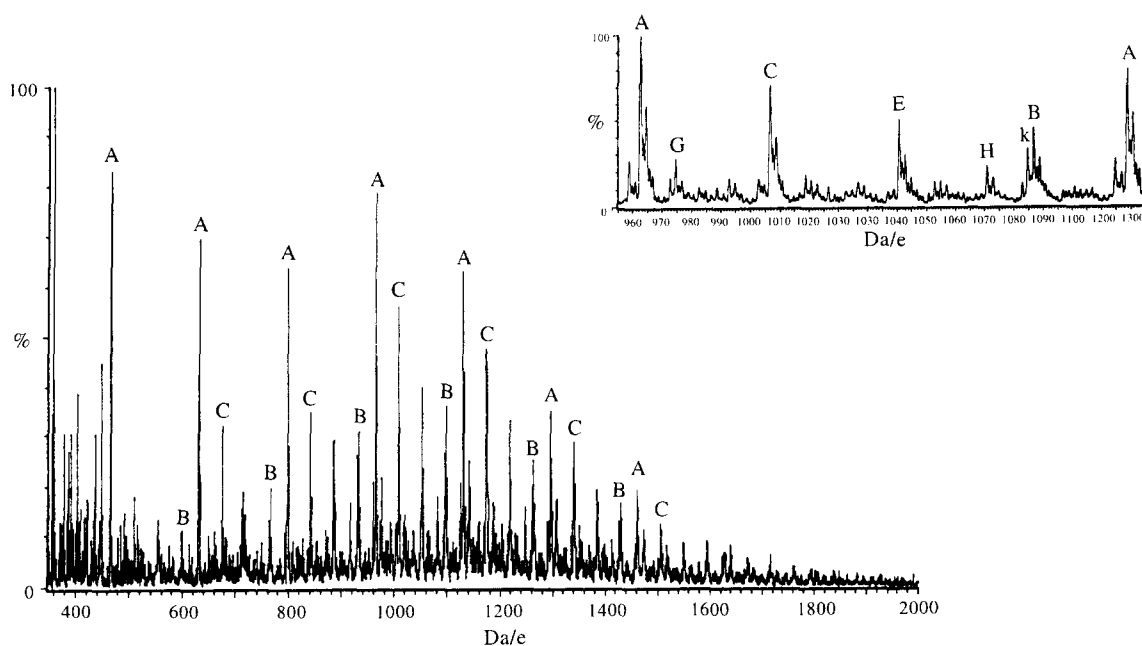
Figure 3 ESI spectrum of ELP-3; mobile phase THF/MeOH containing 0.5% NH_4Cl. Inset: expansion of spectrum in m/z range 960–1130 to reveal greater detail. Assignments of A series ions are given in *Table 5*

Table 6 ESI spectral peaks and associated assignments in the spectra of ZL-2264

Series A $H(SC_2H_4OC_2H_4OC_2H_4S)_nH \cdot NH_4^+$

n	m/z
10	1820.1
9	1640.2
8	1460.2
7	1280.3
6	1100.2
5	920.3
4	740.2
3	560.5
2	380.4

Series C $H(SC_2H_4OC_2H_4OCH_4S)_n(SC_2H_4OC_2H_4OC_2H_4)H \cdot NH_4^+$
(i.e. one –S–S– link replaced randomly by –S–)

n	m/z
10	1968.0
9	1788.7
8	1608.4
7	1428.2
6	1248.3
5	1068.3
4	888.3
3	708.4
2	528.4

Series Q $H(SC_2H_4OC_2H_4OC_2H_4S)_n(SC_2H_4OC_2OC_2H_4)_2H \cdot NH_4^+$
(i.e. two –S–S– links have been replaced randomly by –S–)

n	m/z
9	1936.1
8	1756.4
7	1576.3
6	1396.5
5	1216.5

5b and *5c* in which the ions of m/z 137, 167, 211 and 243 emerge as the dominant ions at high c.v. These ions are assigned the structures $(C_2H_4SSC_2H_4O)H^+$, $(SC_2H_4-OCH_2OC_2H_4S)H^+$, $(SC_2H_4OCH_2OC_2H_4SC_2H_4O)H^+$ and $(SC_2H_4OCH_2OC_2H_4SSC_2H_4O)H^+$, respectively.

Under the relatively mild CID conditions employed, ions of the monomer and terminal species are relatively stable and account for the major species giving rise to the spectra.

Generally similar behaviour was exhibited when the c.v. was increased from 20 to 180 V with a solution of ELP-3 in the THF/MeOH/NH$_4$Cl: all the high-mass peaks up to 1128.1 disappeared on going from c.v. 20 to 60 V, and the intense m/z peaks at 281.3 and 298.3 found at c.v. 20 V gave way at c.v. 60 V to new peaks at 149.3, 223.3 and 243.2. At c.v. 90 V the 223.3 peak was about four times as abundant as any other ion: this is attributed to the terminal species

$$\overline{OCH_2C}\,HCH_2SC_2H_4OCH_2OC_2H_4S^+.$$ The peaks at 281.3 and 298.3 detected at low c.v. are assigned to

$$\overline{OCH_2C}HCH_2SC_2H_4OCH_2OC_2H_4SCH_2\overline{CHCH_2}OH^+$$

and $\overline{OCH_2C}\,HCH_2SC_2H_4OCH_2OC_2H_4SCH_2\overline{CHCH_2}O \cdot NH_4^+$, respectively. The peak at 149.3 is attributed to

$$\overline{OCH_2C}\,HCH_2SC_2H_4OCH_3 \cdot H^+.$$

CID and precursor-ion experiments. The ESI spectra of LPs give rise to a number of long, well-defined series (see *Figure 1*) differing in m/z value within a given series by 166 Da. Identification of the origin of each individual series, and the nature of the differences between parallel series, can be partially effected by inspection of the mass differences between the members of parallel series. This method of assignment can be confirmed by determining the fragmentation patterns of one or two representative ions from each series in question on CID with argon in a collision cell, and some examples of this approach were illustrated in our preliminary communication[5]. Additional information may be obtained from a precursor ion scan in which all precursors of a chosen product ion are identified by scanning the first quadrupole mass
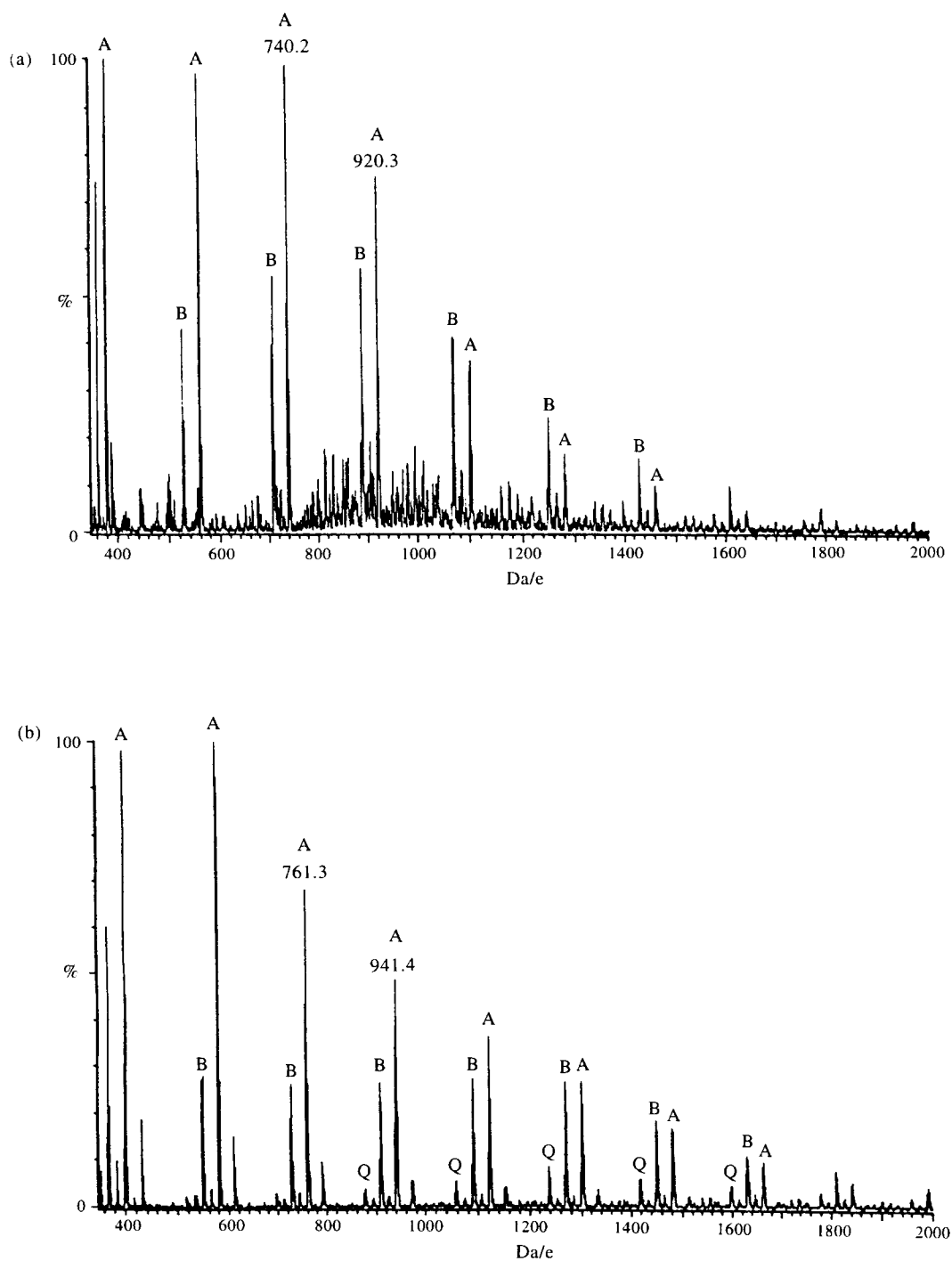
Figure 4 ESI spectrum of ZL-2264; effect of mobile phase on spectral quality. Mobile phase: (a) THF/MeOH containing aqueous NH₄Cl; (b) acetone containing KI

analyser while holding the second quadrupole mass analyser constant to transmit the ion of chosen m/z.

In *Figure 6* is illustrated the CID spectrum of the ion m/z 684.2 taken from series A in the ESI spectrum of LP-1400 (mobile phase THF/MeOH/0.5% aqueous NH₄Cl). The product ions result from the fragmentations
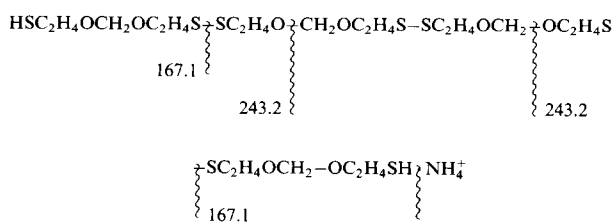
The simplicity of this CID spectrum accords with the high symmetry of the precursor ion. By contrast, the mass 652.4 ion from series B produces a more complex CID spectrum attributable to the fragmentations
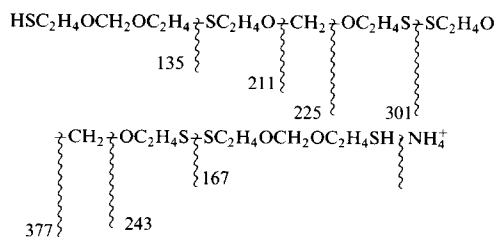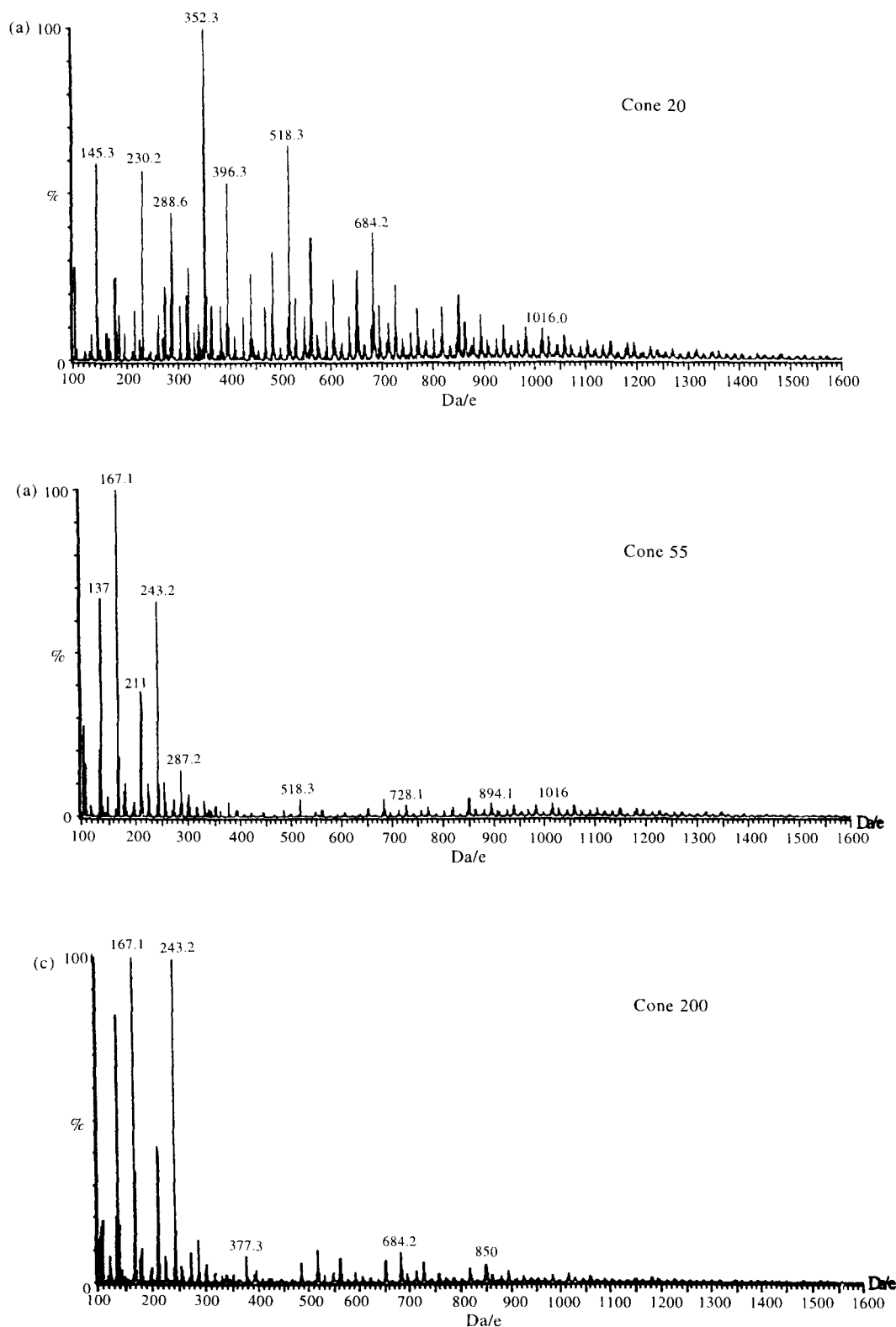
Figure 5 Effect of varying cone voltage on electrospray mass spectrum of LP-1400C in a mobile phase of THF/MeOH containing 0.5% aqueous NH₄Cl (mass range 100–1600 Da). (Each spectrum is normalized to its base peak)

A summary of the ions observed during CID of ions from all the series A–H is given in *Table 7*. These series show the following:

(1) The cleavage sites are relatively few and are repeated between different series, with –S–S– and –C–O– fission being particularly prominent, although –C–S– cleavage is also found.

(2) The series F, G and H, which feature more than one type of structural variant, give rather complex CID spectra indicating the presence of isomers which differ in the location of the variant (one or more CH₂O or C₂H₄O groups, and one fewer S atom) in the polymer chain. While the CID spectral assignments made in *Table 7* account for virtually all the ions detected, the data cannot allow positional
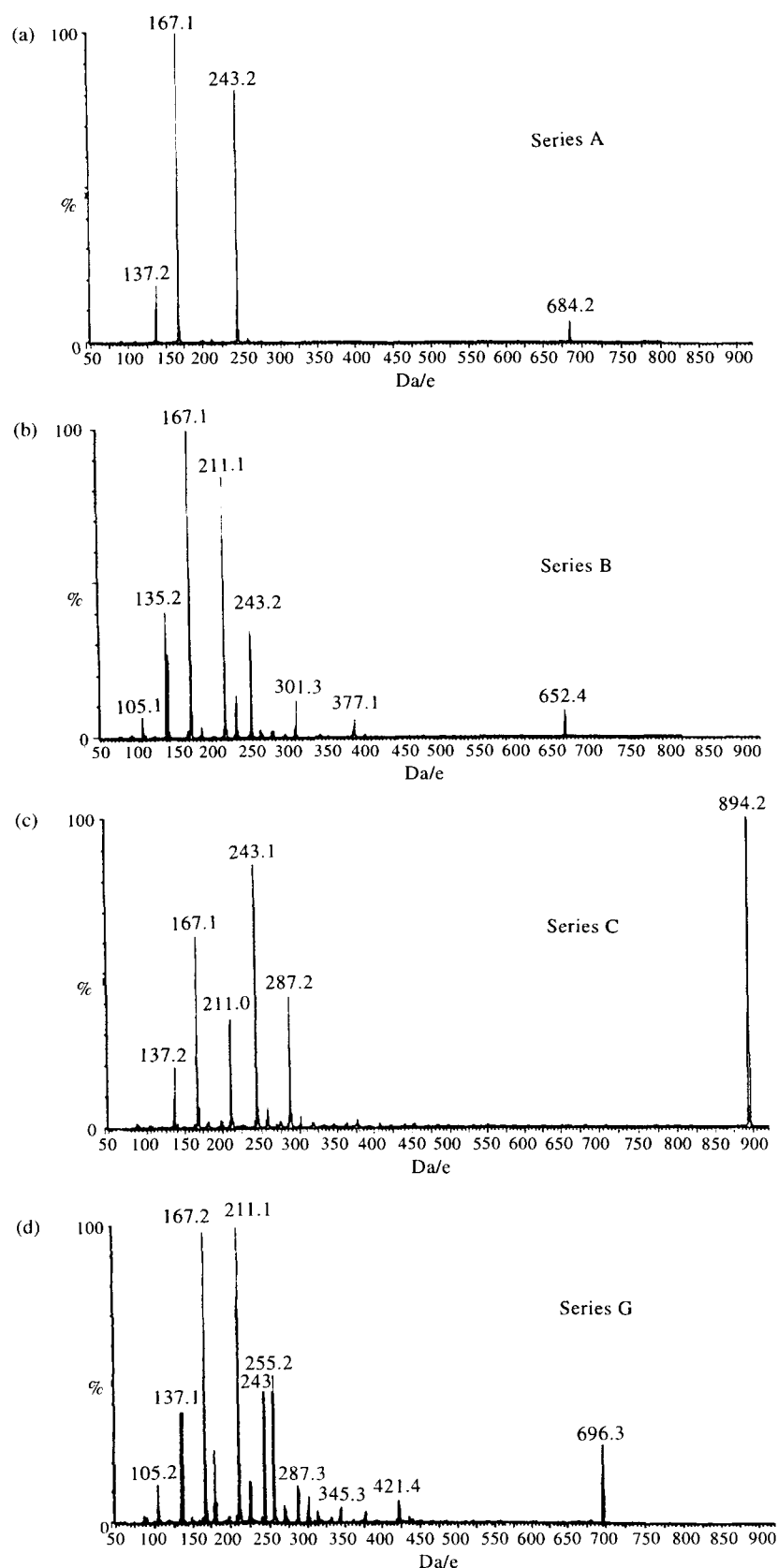
Figure 6 CID spectra of ions selected from the spectrum of LP-1400C: (a) ion at m/z 684.2 peak in series A; (b) ion at m/z 652.4 peak in series B; (c) ion at m/z 894.2 peak in series C; (d) ion at m/z 696.3 peak in series G. CID (20 eV) with argon gas, 3.8×10^{-3} mbar

discrimination within a single mer unit, e.g. a $HSC_2H_4OCH_2OC_2H_4OC_2H_4S$ unit will contribute to the mass of a fragment ion in the same way as a $HSC_2H_4OC_2H_4OCH_2OC_2H_4S$ unit. The occurrence

of several variant mers within an LP sample is rare: *Figure 1* shows that the major species present correspond to the ideal LP (series A) or with a single variant within the chain (series B–D).

Table 7 Summary chart of ion fragmentation observed in CID of selected ions from LP-1400 (all fragments refer to the NH_4^+-loss species)

Series	Selected ion	Fragmentation
A	684.2	See text
B	652.4	See text
C	894.2	

$HSC_2H_4OCH_2OC_2H_4S \cdot SC_2H_4O \cdot CH_2OC_2H_4SSC_2H_4OCH_2OC_2H_4SSC_2H_4O \cdot CH_2 \cdot OC_2H_4S \cdot SC_2H_4O\mathbf{C_2H_4}OCH_2OC_2H_4SH \cdot NH_4^+$

167   243   287   301   211

D   714.1

$HSC_2H_4O\mathbf{CH_2}OCH_2OC_2H_4S \cdot SC_2H_4O \cdot CH_2OC_2H_4SSC_2H_4OCH_2 \cdot OC_2H_4S \cdot SC_2H_4OCH_2OC_2H_4SH \cdot NH_4^+$

197   273   243   167

E   772.4

$HSC_2H_4\mathbf{OC_2H_4}OCH_2OC_2H_4S \cdot SC_2H_4O \cdot \mathbf{C_2H_4O} \cdot CH_2OC_2H_4SSC_2H_4OCH_2 \cdot OC_2H_4S \cdot S \cdot CC_2H_4OCH_2OC_2H_4SH \cdot NH_4^-$

211   287   331   243   135   167

F   758.3

$HSC_2H_4OCH_2OCH_2OC_2H_4S \cdot SC_2H_4O \cdot \mathbf{C_2H_4O} \cdot CH_2OC_2H_4SSC_2H_4OCH_2 \cdot OC_2H_4S \cdot S \cdot C_2H_4OCH_2OC_2H_4SH \cdot NH_4^+$

197   273   317   243   135   167

or

$HSC_2H_4\mathbf{OC_2H_4}OCH_2OC_2H_4S \cdot SC_2H_4O \cdot \mathbf{CH_2O} \cdot CH_2OC_2H_4SSC_2H_4OCH_2 \cdot OC_2H_4S \cdot S \cdot C_2H_4OCH_2OC_2H_4SH \cdot NH_4^+$

211   287   317   243   135   167

G   696.5

$HSC_2H_4OCH_2OC_2H_4S \cdot SC_2H_4O \cdot CH_2 \cdot OC_2H_4 \cdot S \cdot C_2H_4OCH_2 \cdot OC_2H_4S \cdot S \cdot C_2H_4OCH_2O\mathbf{C_2H_4}OC_2H_4SH \cdot NH_4^-$

167   243   301   345   287   179   211   421

+

$HSC_2H_4OCH_2OC_2H_4SSC_2H_4OCH_2OC_2H_4SSC_2H_4O \cdot CH_2 \cdot OC_2H_4SC_2H_4OCH_2O\mathbf{C_2H_4}OC_2H_4SH \cdot NH_4^+$

255   269

+

$HSC_2H_4OCH_2OC_2H_4SC_2H_4O \cdot CH_2 \cdot OC_2H_4SSC_2H_4O \cdot CH_2OC_2H_4SSC_2H_4OCH_2O\mathbf{C_2H_4}OC_2H_4SH \cdot NH_4^+$

211   225   377

H   802.4

$HSC_2H_4OCH_2OC_2H_4S \cdot SC_2H_4O \cdot CH_2O\mathbf{CH_2}OC_2H_4SSC_2H_4 \cdot OCH_2OC_2H_4S \cdot SC_2H_4OCH_2O\mathbf{C_2H_4}OC_2H_4OC_2H_4SH \cdot NH_4^+$

167   243   255   361

+

$HSC_2H_4\mathbf{OC_2H_4}OCH_2OC_2H_4S \cdot SC_2H_4O \cdot CH_2O \cdot C_2H_4SSC_2H_4O \cdot CH_2OC_2H_4SSC_2H_4O\mathbf{C_2H_4}OCH_2OCH_2OC_2H_4SH \cdot NH_4^+$
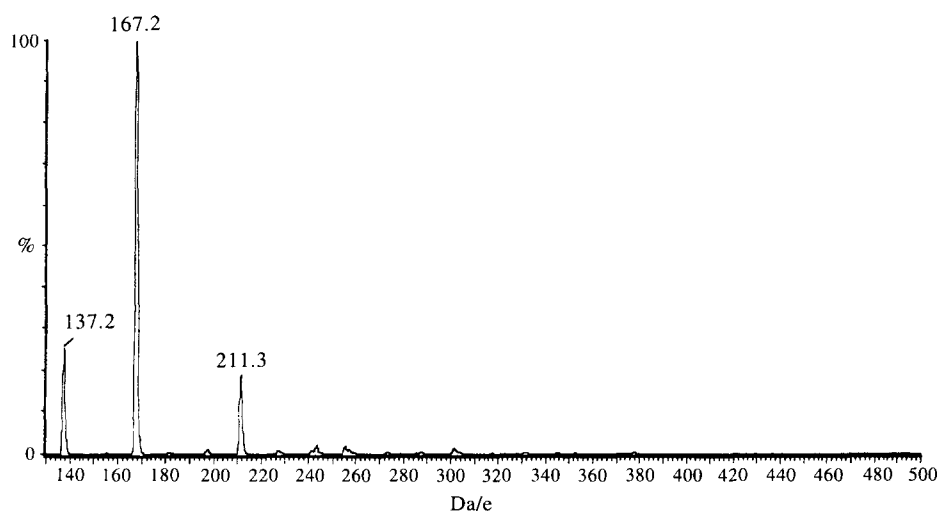
211   287   317   331

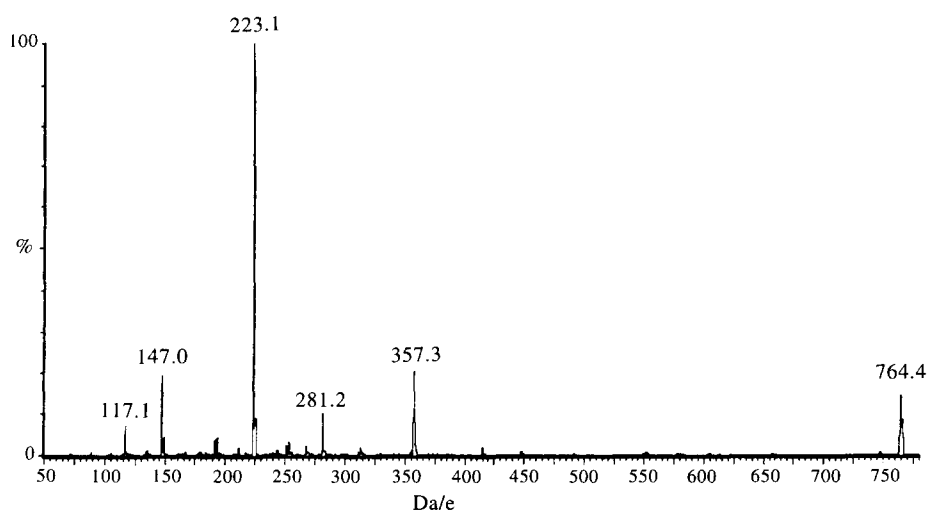**Figure 7** Precursor-ion spectrum of ion with m/z 137.2 derived from the CID of LP-1400C

Figure 8 CID spectrum of m/z 764.4 ion from ELP-3

(3) Fragment ions do not show the presence of an extra proton originating from the NH_4^+ group, but rather terminate in an -SH group.

Precursor-ion experiments (see above) were carried out on selected fragment ions obtained by CID of LP-1400. Thus, *Figure 7* reveals that the ion with m/z 137.2 originates from the 167.2 fragment, which has itself been detected in the various series A–H following CID. The production of the m/z 137.2 ion from $HSC_2H_4OCH_2OC_2H_4S^+$ (m/z 167.1) signifies the loss of 30 Da which can be due only to elimination of formaldehyde:
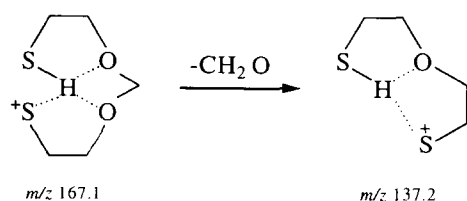
This elimination parallels that of C_2H_4O units from protonated macrocyclic polyether lactones under electron impact conditions[17].

Table 8 Scheme for the fragmentation of ELP-3 on CID

Ion m/z	Assignment
764.4 (parent)	
357.3	$O-CH_2-CHCH_2SC_2H_4OCH_2OC_2H_4SSC_2H_4OCH_2OC_2H_4^+$
281.2	
223.1 (base peak)	$O-CH_2-CHCH_2SC_2H_4OCH_2OC_2H_4S^+$
147.0	$O-CH_2-CHCH_2SC_2H_4OCH_2^+$
117.1	$O-CH_2-CHCH_2SC_2H_4^+$

CID experiments carried out on ELP-3 (*Figure 8*) indicated fragmentation to involve few pathways: fragmentation involves complete retention of the terminal epoxy group in all species detected (*Table 8*).

Fast atom bombardment. FAB experiments were carried out on LP 1400 by ways of comparison (*Figure 9*): such species as m/z 243, 167 and 137, which were ubiquitous in the CID/ESI spectra of various LPs, are
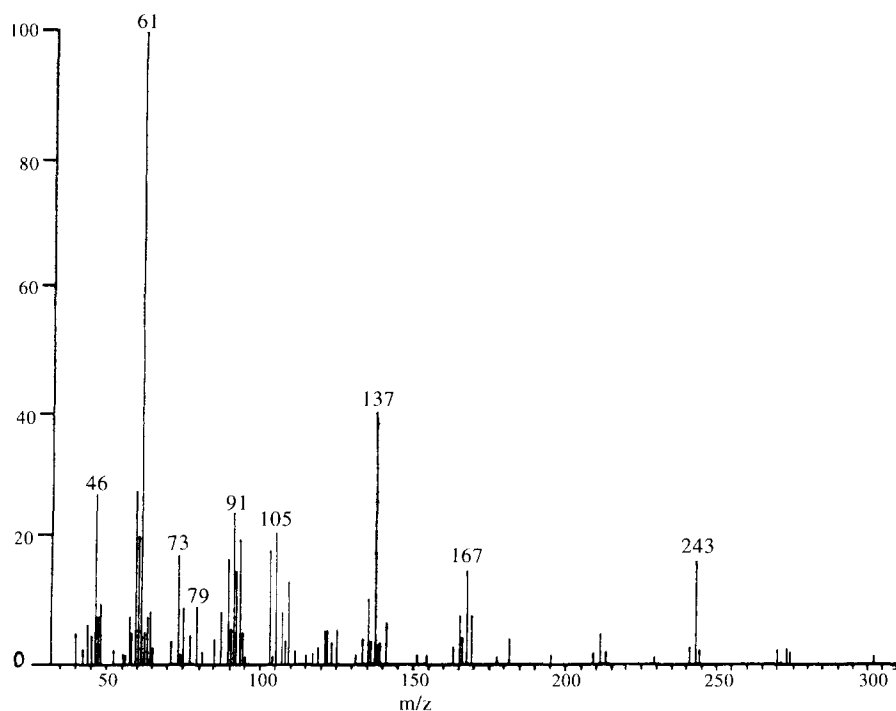
Figure 9 Positive-ion FAB spectrum of LP-1400C in 3-nitrobenzyl alcohol matrix
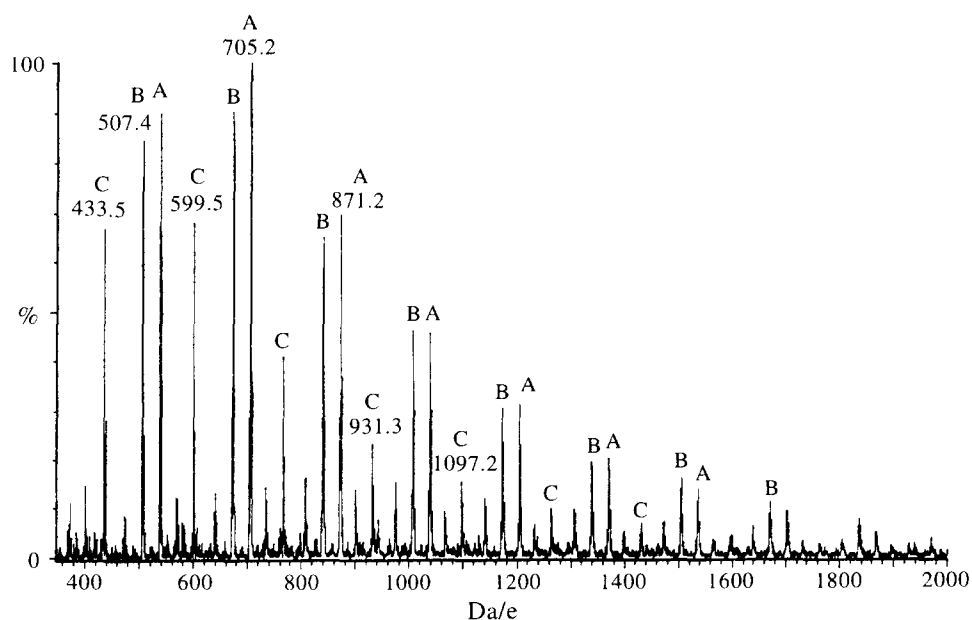

Figure 10 ESI spectrum of a reaction mixture of LP-A with hexane-1,6-diol diacrylate. Series C refers to the monoadduct of LP with the diester. Mobile phase: acetone containing KI

prominent; the small fragment ions m/z 91 and 61 are assigned respectively to $HSC_2H_4OCH_2^+$ and $HSC_2H_4^+$.

ESI spectra of reaction systems. To investigate the possibilities of monitoring extents of reaction of LPs undergoing curing, we reacted LP model A with hexane-1,6-diol diacrylate (HDDA) and ran an ESI spectrum (*Figure 10*) on the product without separation. A new series of peaks (series C) appeared in the spectrum, attributable to the monoadduct of HDDA ($RMM = 226$) with the LP, i.e. $RSCH_2CH_2CO_2C_6H_{12}O_2CCH=CH_2$.

General comments. It is clear from the various ESI spectra portrayed in this paper, particularly those in

Figure 1, that while the technique provides very accurate mass information at $RMM < 2000$, it gives a heavy bias towards the detection of low-mass oligomers at the expense of those of higher mass, thus even when, as in LP-12C, the average RMM is ~4000, no peaks appear at $m/z > 2500$, and the ion abundances at $m/z > 1800$ do not reflect the abundances of oligomers present. This does not seem due to lower solubility of the higher mass oligomer because changing the solvent to THF/ DMF offered no advantage. At this stage we can only conclude that LP ions of higher mass have (1) a greater tendency to fragment before detection, (2) (less probably) transfer their charge to lower mass material or (3) fail to be transmitted or detected. That higher mass

species derived from synthetic linear polymers *can* be detected by ESI has been demonstrated in the study of polystyrenes[18]. High-mass dendrimers (m/z up to 5154 for singly charged ions) have also been detected by ESI[19].

ESI spectra offer a very direct insight into the presence of variant mers and of the end groups. Some of these features can be detected in LP oligomers by ^{1}H and ^{13}C n.m.r. spectroscopy but, even then, the location of an anomalous group within the chain cannot be defined as precisely as it can be from CID spectra. Infrared spectra of LPs offer only general information about the functional groups present and cannot be used to observe the presence of additional groups such as CH_2O or C_2H_4O.

CONCLUSIONS

ESI has proved to be a most useful addition to the armoury of mass spectroscopic techniques applicable to the characterization of oligomeric materials, in this case LPs. The individual spectra are well resolved, enabling conclusions to be reached about the distribution of mers within a given formulation, about the presence of variant mers (usually associated with additional oxymethylene or oxyethylene units or a monosulfide linkage, or some combination of these), about the identity of end groups and about the nature and extent of simple reactions of LPs with acrylate esters. The most informative spectra are those obtained at a c.v. of 100 eV, using a mobile phase of acetone containing 0.5% KI, although this system does *not* lend itself to CID or precursor-ion experiments, when THF/MeOH/0.5% aqueous NH_4Cl is superior.

The CID spectra of ions derived from LPs reveal relatively simple fragmentation pathways, depending on the complexity of the LP structure.

ACKNOWLEDGEMENTS

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