Polymer Vol. 38 No. 8, pp. 1957–1969, 1997

Printed in Great Britain
0032-3861/97/$17.00 + 0.00
PII: S0032-3861(96)00723-9

Mass spectral characterization of linear and cyclic forms of oligomeric nitrated polyethers by electrospray ionization: specific cationization effects in cyclic polyethers

Zachary Barton, Terence J. Kemp*, Armelle Buzy and Keith R. Jennings
Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

and Anthony V. Cunliffe
Defence Research Agency, Fort Halstead, Kent TN14 7BP, UK
(Received 2 July 1996)

Electrospray ionization mass spectrometry provides a highly detailed picture of the various species present in the high energy material poly(3-nitratomethyl-3-methyloxetane), also known as polynimmo. Polynimmo contains up to 18 cyclic oligomers in addition to the dominant tetramer, the highest species detected containing 22 repeat units. Linear oligomers from the tetramer up to species of mass 3200 Da are detected, affording the characterization of several new combinations of end groups X, Y in X–[nimmo]$_n$–Y. Various cations can be used to generate the cationized species, and highly specific cation–cyclic oligomer interactions are apparent in the adducts with Na^+, K^+, NH_4^+ and H^+: some of these can be rationalized through molecular modelling calculations. The cone voltage applied in the e.s.i. experiment is highly significant in influencing the relative abundances of high- and low-molecular mass ions and in the relative amounts of H^+ and NH_4^+ adducts in cationization experiments with NH_4Cl. Despite giving highly accurate relative molar masses of individual species within polynimmo, the e.s.i. technique fails to give accurate molecular mass distributions, especially as no doubly- or triply-charged ions are found. Crown copyright © 1997 Published by Elsevier Science Ltd.

(Keywords: electrospray ionization; poly(3-nitratomethyl-3-methyloxetane); cationization)

INTRODUCTION

Nitrated hydroxy polyethers have found application as binders in propellant formulations[1] and considerable attention has been paid to identifying their thermal degradation mechanisms. Such studies have concentrated on analysis of evolved gases during pyrolysis[2,3], thermogravimetric analysis[4,5], differential scanning calorimetry[5] and simultaneous mass and temperature change Fourier-transform infra-red (SMATCH/*FT*i.r.) spectroscopy[6].

The prepolymer of the binder poly(3-nitratomethyl-3-methyloxetane) (or polynimmo) is prepared by cationic polymerization of the monomer using BF_3 etherate and 1,4-butanediol. The resulting material is largely linear, with pendant nitrate ester groups and with end-groups (normally hydroxyl but also ethoxy as indicated by ^{13}C n.m.r. analysis). This viscous liquid is cured with the polyfunctional aliphatic isocyanate Desmodur N100 to give a rubbery material with a good mechanical strength.

Gel permeation chromatography (g.p.c.) of the prepolymer indicates an M_n value of 7500 with a polydispersity of 1.5. In view of the interest in this high energy material because of its use in the propellants and explosives sector, we have undertaken a mass spectrometric characterization of polynimmo using the soft ionization method of electrospray ionization (e.s.i.), which has been applied previously to complex mixtures of oligomers as found with the polysulfides[7]. Good precedents for the application of soft ionization methods to high energy molecules are provided by thermospray[8], fast atom bombardment[9] and e.s.i.[10] studies of arenediazonium salts, which feature the highly unstable ArN_2^+ ion as a gas phase species, and the application of e.s.i. liquid chromatography to a variety of explosives[11].

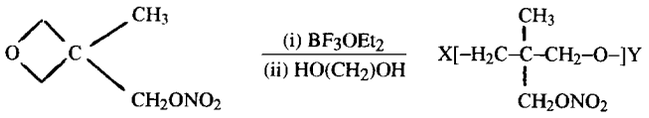
EXPERIMENTAL

Materials

Poly(3-nitratomethyl-3-methyloxetane) (polynimmo) was obtained as a prepolymer from DRA, the original source being ICI (Explosives Division). Gel permeation chromatography (g.p.c.) shows that its molecular weight distribution is centred at 7500 with a polydispersity of 1.5. It features a variety of end groups (see *Scheme 1*) consequent upon its preparation[12].

In *Scheme 1*, X and Y are end groups, e.g. H, OH, OC_2H_5, etc. Solvents (tetrahydrofuran, methanol, dimethylformamide) were of the highest grade available commercially and were dried prior to use.

* To whom correspondence should be addressed



Scheme 1

Mass spectrometry

The e.s.i./c.i.d. experiments were carried out in a Fisons' 'Quattro II' triple quadrupole mass spectrometer (VG Biotech, Altrincham, UK) equipped with an atmospheric pressure ionization (a.p.i.) source operated in the nebulizer-assisted electrospray mode. The potential on the electrospray needle was set at 3.5 kV and the extraction cone voltage was varied between 20 and 110 V. Oligomeric polynimmo at a concentration of 0.5 $\mu g\,\mu l^{-1}$ was dissolved in a mixture of tetrahydrofuran and methanol (1 : 1 by volume) in the presence of 0.5% ammonium chloride. Aliquots of 20 μl were introduced into the ion source at a flow rate of 5 $\mu l\,min^{-1}$. Mass spectra were acquired over the range m/z 3500–m/z 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.

The gel permeation chromatography (g.p.c.) system used in this work consisted of a dual piston high pressure liquid chromatography (h.p.l.c.) pump (ICI Instruments LC1110), an injection valve with a 20 μl sample loop (Rheodyne 7125), and a refractive index detector (ICI Instruments LC1240). The data were collected using a Polymer Laboratories (PL) data capture unit (DCU) and analysed using Pl Calibre g.p.c./s.e.c. software.

The g.p.c. eluent was THF with a flow rate of 1.0 ml min^{-1}. Toluene (0.2% wt) was used as an internal standard and flow marker in each sample. All samples were examined at equal concentrations (5 g dm^{-3}), except where stated otherwise. The column set consisted of a Pl 5 μm bead size guard column (50 × 7.5 mm) connected to a Pl 3 μm bead size Mixed-E column (300 × 7.5 mm). The system was calibrated with poly(propylene oxide) (PPO) standards.

RESULTS AND DISCUSSION

E.s.i. spectra of polynimmo

The electrospray ionization (e.s.i.) spectra of a solution of polynimmo at a concentration of 0.5 $\mu g\,\mu l^{-1}$ in THF–MeOH (1 : 1 by volume) with 0.5% NH_4Cl and recorded at different cone voltages are shown in *Figure 1*. These reveal the following features:

(i) At low cone voltage (20 V), the dominant feature in the spectrum is the series with $m/z = 606.6$, attributed to the NH_4^+ adduct of the cyclic tetramer. Also evident at this voltage are prominent peaks due to the NH_4^+ adducts of the cyclic pentamer ($m/z = 753.5$), hexamer ($m/z = 900.7$), heptamer ($m/z = 1047.8$) and octamer ($m/z = 1194.8$). At higher instrument gain it was possible to identify

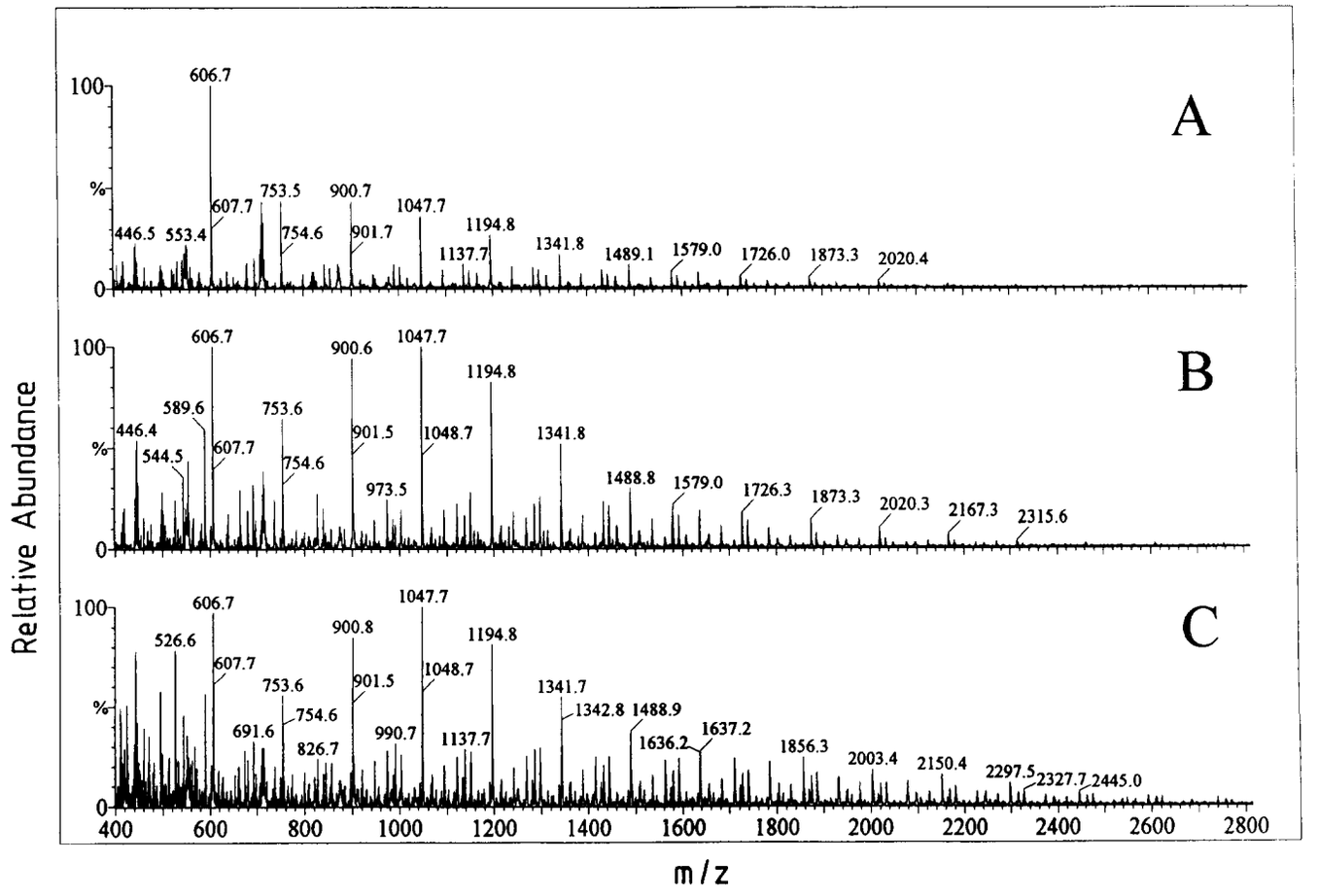


Figure 1 E.s.i. spectra of polynimmo in THF–MeOH (concentration 0.5 $\mu g\,ml^{-1}$) using NH_4Cl (0.5%) as cationizing agent at different cone voltages (cv). A: cv 20 V; B: cv 50 V; C: cv 100 V

Table 1 Species detected in e.s.i. spectrum of polynimmo

(a) Cyclic species (ammonium ion adduct)

Observed m/z	Assignment: number of repeat units	Calculated m/z
606.6	4	606.3
753.5	5	753.3
900.7	6	900.4
1047.8	7	1047.4
1194.8	8	1194.5
1341.7	9	1341.5
1488.9	10	1488.6
1636.2	11	1635.6
1783.1	12	1782.7
1930.2	13	1929.7
2076.8	14	2076.8
2224.9	15	2223.8
2370.7	16	2370.9
2517.8	17	2518.0
2665.9	18	2665.0
2813.6	19	2812.1
2960.3	20	2959.1
3106.7	21	3106.2
3254.8	22	3253.2

(b) Linear species

Observed m/z	Assignment	Observed m/z	Assignment
460.7	$HO[nimmo]_3H.H^+$	1279.6	$CH_3CH_2[nimmo]_8(CH_2)_4OH.H^+$
516.4	$CH_3CH_2O[nimmo]_3H.H^+$	1284.6	$HO(CH_2)_4O[nimmo]_8H.NH_4^+$
526.6	unassigned	1296.0	$CH_3CH_2O[nimmo]_8(CH_2)_4OH.H^+$
532.4	$HO(CH_2)_4[nimmo]_3H.H^+$	1296.9	$CH_3CH_2[nimmo]_8(CH_2)_4OH.NH_4^+$
544.5	$CH_3CH_2[nimmo]_3(CH_2)_4OH.H^+$	1313.2	$CH_3CH_2O[nimmo]_8(CH_2)_4OH.NH_4^+$
561.6	$CH_3CH_2[nimmo]_3(CH_2)_4OH.NH_4^+$	1342.5	$HO[nimmo]_9H.H^+$
607.4	$HO[nimmo]_4H.H^+$	1359.5	$HO[nimmo]_9H.NH_4^+$
626.6	$?[nimmo]_4?.H^+$	1361.9	$?[nimmo]_{10}?.NH_4^+$
652.5	$CH_3CH_2O[nimmo]_4H.H^+$	1370.7	$CH_3CH_2O[nimmo]_9H.H^+$
663.9	$CH_3CH_2O[nimmo]_4CH_2CH_3.H^+$	1387.7	$CH_3CH_2O[nimmo]_9H.NH_4^+$
679.7	$HO(CH_2)_4O[nimmo]_4H.H^+$	1414.6	$HO(CH_2)_4O[nimmo]_9H.H^+$
680.8	$CH_3CH_2O[nimmo]_4CH_2CH_3.NH_4^+$	1415.6	$CH_3CH_2O[nimmo]_9CH_2CH_3.NH_4^+$
691.4	$CH_3CH_2[nimmo]_4(CH_2)_4OH.H^+$	1426.6	$CH_3CH_2[nimmo]_9(CH_2)_4OH.H^+$
696.6	$HO(CH_2)_4O[nimmo]_4H.NH_4^+$	1431.8	$HO(CH_2)_4O[nimmo]_9H.NH_4^+$
754.6	$HO[nimmo]_5H.H^+$	1443.6	$CH_3CH_2[nimmo]_9(CH_2)_4OH.NH_4^+$
771.5	$HO[nimmo]_5H.NH_4^+$	1460.0	$CH_3CH_2O[nimmo]_9(CH_2)_4OH.NH_4^+$
773.5	$?[nimmo]_5?.NH_4^+$	1489.6	$HO[nimmo]_{10}H.H^+$
782.9	$CH_3CH_2O[nimmo]_5H.H^+$	1506.6	$HO[nimmo]_{10}H.NH_4^+$
799.2	$CH_3CH_2O[nimmo]_5H.NH_4^+$	1508.7	$?[nimmo]_{10}?.NH_4^+$
826.6	$HO(CH_2)_4O[nimmo]_5H.H^+$	1517.4	$CH_3CH_2O[nimmo]_{10}H.H^+$
838.6	$CH_3CH_2[nimmo]_5(CH_2)_4OH.H^+$	1534.7	$CH_3CH_2O[nimmo]_{10}H.NH_4^+$
843.6	$HO(CH_2)_4O[nimmo]_5H.NH_4^+$	1545.7	$CH_3CH_2O[nimmo]_{10}CH_2CH_3.H^+$
855.6	$CH_3CH_2O[nimmo]_5(CH_2)_4OH.H^+$	1561.9	$HO(CH_2)_4O[nimmo]_{10}H.H^+$
856.6	$CH_3CH_2[nimmo]_5(CH_2)_4OH.NH_4^+$	1563.0	$CH_3CH_2O[nimmo]_{10}CH_2CH_3.NH_4^+$
901.6	$HO[nimmo]_6H.H^+$	1574.0	$CH_3CH_2[nimmo]_{10}(CH_2)_4OH.H^+$
918.6	$HO[nimmo]_6H.NH_4^+$	1579.0	$HO(CH_2)_4O[nimmo]_{10}H.NH_4^+$
920.7	$?[nimmo]_6?NH_4^+$	1591.1	$CH_3CH_2[nimmo]_{10}(CH_2)_4OH.NH_4^+$
946.6	$CH_3CH_2O[nimmo]_6H.NH_4^+$	1607.6	$CH_3CH_2O[nimmo]_{10}(CH_2)_4OH.NH_4^+$
973.5	$HO(CH_2)_4O[nimmo]_6H.H^+$	1636.5	$HO[nimmo]_{11}H.H^+$
985.7	$CH_3CH_2[nimmo]_6(CH_2)_4OH.H^+$	1653.5	$HO[nimmo]_{11}H.NH_4^+$
990.7	$HO(CH_2)_4O[nimmo]_6H.NH_4^+$	1655.5	$?[nimmo]_{11}?.NH_4^+$
1002.7	$CH_3CH_2[nimmo]_6(CH_2)_4OH.NH_4^+$	1664.8	$CH_3CH_2O[nimmo]_{11}H.H^+$
1019.1	$CH_3CH_2O[nimmo]_6(CH_2)_4OH.NH_4^+$	1682.0	$CH_3CH_2O[nimmo]_{11}H.NH_4^+$
1048.4	$HO[nimmo]_7H.H^+$	1709.2	$HO(CH_2)_4[nimmo]_{11}H.H^+$
1065.7	$HO[nimmo]_7H.NH_4^+$	1710.6	$CH_3CH_2O[nimmo]_{11}CH_2CH_3.NH_4^+$
1067.7	$?[nimmo]_7NH_4^+$	1721.2	$CH_3CH_2[nimmo]_{11}(CH_2)_4OH.H^+$
1093.6	$CH_3CH_2O[nimmo]_7H.NH_4^+$	1726.0	$HO(CH_2)_4O[nimmo]_{11}H.NH_4^+$
1120.6	$HO(CH_2)_4O[nimmo]_7H.H^+$	1738.1	$CH_3CH_2[nimmo]_{11}(CH_2)_4OH.NH_4^+$
1121.6	$CH_3CH_2[nimmo]_7CH_2CH_3.NH_4^+$	1754.0	$CH_3CH_2O[nimmo]_{11}(CH_2)_4OH.NH_4^+$
1132.7	$CH_3CH_2[nimmo]_7(CH_2)_4OH.H^+$	1783.8	$HO[nimmo]_{12}H.H^+$
1137.7	$HO(CH_2)_4O[nimmo]_7H.NH_4^+$	1800.8	$HO[nimmo]_{12}H.NH_4^+$
1149.5	$CH_3CH_2[nimmo]_7(CH_2)_4OH.NH_4^+$	1802.8	$?[nimmo]_{12}?.NH_4^+$
1164.7	$CH_3CH_2O[nimmo]_7(CH_2)_4OH.NH_4^+$	1811.6	$CH_3CH_2O[nimmo]_{12}H.H^+$
1195.5	$HO[nimmo]_8H.H^+$	1829.1	$CH_3CH_2O[nimmo]_{12}H.NH_4^+$
1212.6	$HO[nimmo]_8H.NH_4^+$	1856.3	$HO(CH_2)_4[nimmo]_{12}H.H^+$
1214.6	$?[nimmo]_8?.NH_4^+$	1868.1	$CH_3CH_2[nimmo]_{12}(CH_2)_4OH.H^+$
1223.5	$CH_3CH_2O[nimmo]_8H.H^+$	1873.2	$HO(CH_2)_4O[nimmo]_{12}H.NH_4^+$
1240.5	$CH_3CH_2O[nimmo]_8H.NH_4^+$	1885.4	$CH_3CH_2[nimmo]_{12}(CH_2)_4OH.NH_4^+$
1267.6	$HO(CH_2)_4O[nimmo]_8H.H^+$	1902.1	$CH_3CH_2O[nimmo]_{12}(CH_2)_4OH.NH_4^+$
1268.1	$CH_3CH_2O[nimmo]_8CH_2CH_3.NH_4^+$		

peaks due to NH_4^+ adducts of a series of higher cyclic oligomers, with ions derived from rings containing up to 22 repeat units, being visible at a cone voltage of 110 V (*Table 1*).

(ii) Other prominent peaks in the e.s.i. spectrum at a cone voltage of 20 V are those at 1341.9 and 1489.1 which are attributable to linear oligomeric species (see below).

(iii) As the cone voltage is increased, the abundances of all peaks of $m/z > 800$ increase relative to the 606.6 base peak. This we attribute to selective decomposition of the cyclic tetramer in the e.s.i. experiment at higher cone voltages. A further effect of increasing the cone voltage is the appearance of peaks which are proton adducts; thus, at 20 V cone voltage, we observe a weak peak at $m/z = 990.8$ due to a linear hexamer (see *Table 1(b)*), while at 50 V we also find a peak at $m/z = 973.5$ due to loss of NH_3 from its ammonium ion adduct.

(iv) The presence of species with RMM > 2500 is not apparent in e.s.i., probably because of the reduced sensitivity of the instrumentation at $m/z > 2500$.

(v) The ^{13}C peaks are positioned at an m/z figure of 1 greater than the corresponding ^{12}C species, indicating that all the peaks are due to singly- (rather than multiply-) charged ions of polynimmo. In this respect, polynimmo differs from other polyethers such as poly(propylene glycol) which forms doubly- and triply-charged cations[13].

Cyclic oligomers. The principal discovery from these experiments is the identification of a long series of cyclic oligomeric forms of polynimmo. Previous work, particularly using ^1H and ^{13}C n.m.r., had identified the cyclic tetramer as a significant species in polynimmo[14], but no indication had been given of a range of higher cyclic oligomers. The situation as regards molecular mass distribution was also unexpected.

Polynimmo as supplied by ICI (Explosives Division) is known from g.p.c. to have a broad spread of RMMs centred around $\bar{M}_w = 7500$ (polydispersity 1.5) and, although the upper mass limit of the spectrometer for singly-charged ions is 4000, the e.s.i. data give no indication of any species with RMM >2500. Accordingly it was decided to chromatograph the polynimmo in an attempt to concentrate low- and high-molecular mass species into particular fractions for more detailed e.s.i. examination (see below). Chromatography would also afford discrimination between two possible assignments of heavier species, e.g. $[(\text{nimmo})_n NH_4]^+$ and the equally heavy $[(\text{nimmo})_{n/2}NH_4(\text{nimmo})_{n/2}]^+$.

Effect of increasing cone voltage. The effect of cone voltage on the relative abundances of high- and low-molecular mass species (particularly the tetramer) referred to above is intriguing. Loo *et al.*[15] have noted that the abundances of all ions derived from melittin, a 26-residue polypeptide, decline uniformly as the cone voltage is decreased below 170 V, and attribute this to collision processes which desolvate ions more efficiently at higher cone voltage. Unlike the polypeptide, polynimmo contains a wide range of different linear and cyclic species which may yield ions that are solvated to different degrees at a given cone voltage. Thus the relatively enhanced abundances of larger ions at higher cone voltage could be due to their greater relative ease of desolvation compared to the adducts of lower mass species. Similarly, the ammonium ion adducts of larger mass species may be relatively more stable than those of lower mass at higher cone voltages.

Another effect of cone voltage is apparent from *Figure 2* in the mass range 450–615 Da: as the cone voltage is increased, the relative abundance of the peak at 607.7 Da increases. Some contribution to the abundance at this mass is due to the ^{13}C isotope of the NH_4^+ adduct of the cyclic tetramer ($m/z = 606.6$), but the relative increase at higher cone voltage must signify the appearance of a new species. The effect of increasing cone voltage is even more marked for the peak at $m/z = 589.5$. We attribute the peaks at 589.5 and 607.7 to the presence of different ionic forms of the linear species

$$\underset{\text{I}}{\text{HO}-[\text{nimmo}]_4-\text{H}}$$

The ammonium ion adduct of this would have $m/z = 624.3$ and we find a very low intensity peak at 624.5. At high cone voltage, loss of NH_3 would be expected to occur to produce a protonated species of $m/z = 607.3$. Thus in *Figure 2* we attribute the peak at 606.7 in the spectrum taken at cone voltage 20 V to the ^{13}C satellite of the NH_4^+-ion adduct of the tetramer. At progressively higher cone voltages, the role of the protonated linear species IH^+ becomes increasingly significant. Likewise, the NH_4^+– adduct of the cyclic tetramer ($m/z = 606.7$) eliminates NH_3 at higher cone voltage to yield the protonated cyclic tetramer ($m/z = 589.5$).

Cationization using Na^+ and K^+. Various salts and solvent systems were utilized in an attempt to effect enhanced cationization of ions of higher mass. Alkali metal iodides in a 50/50 v/v mixture of dimethylformamide (DMF) and tetrahydrofuran (THF) proved to be the most revealing. Linear oligomers containing up to 23 repeat units were clearly apparent at 3500 Da towards the upper mass limit of the instrument. *Figure 3* shows the e.s.i. spectra of polynimmo using NaI (*Figure 3A*) and KI (*Figure 3B*). The nature of the cation strongly influences the relative stabilities of the ions formed from different cyclic oligomers; thus the peak at $m/z = 611.4$ (the Na^+ adduct of the cyclic tetramer) completely dominates *Figure 3A*, whereas there is no corresponding K^+ adduct of the cyclic tetramer in *Figure 3B* but instead there are relatively intense peaks due to the K^+ adducts of the cyclic heptamer ($m/z = 1068.2$), octamer ($m/z = 1215.3$), nonamer ($m/z = 1362.5$) and decamer ($m/z = 1509.3$). The exceptional stability of the Na^+ adduct of the cyclic tetramer prompted us to carry out molecular modelling calculations both of this species and of the Na^+ adduct with the cyclic pentamer. Both oligomers were initially modelled without Na^+ present by being subjected to simulated heating to 4000 K followed by cooling to 298 K to produce the lowest energy conformation. The Na^+ ion was then introduced and bonds added between the ion and the oxygen atoms in the oligomer ring; i.e., four bonds were created for the tetramer and five for the pentamer. The Na^+ to oxygen bond distance was estimated by averaging ten values of the same bond distance obtained from the Na^+ complexes of various 16–crown–4 ethers[16]. The Na^+ to oxygen bond distance

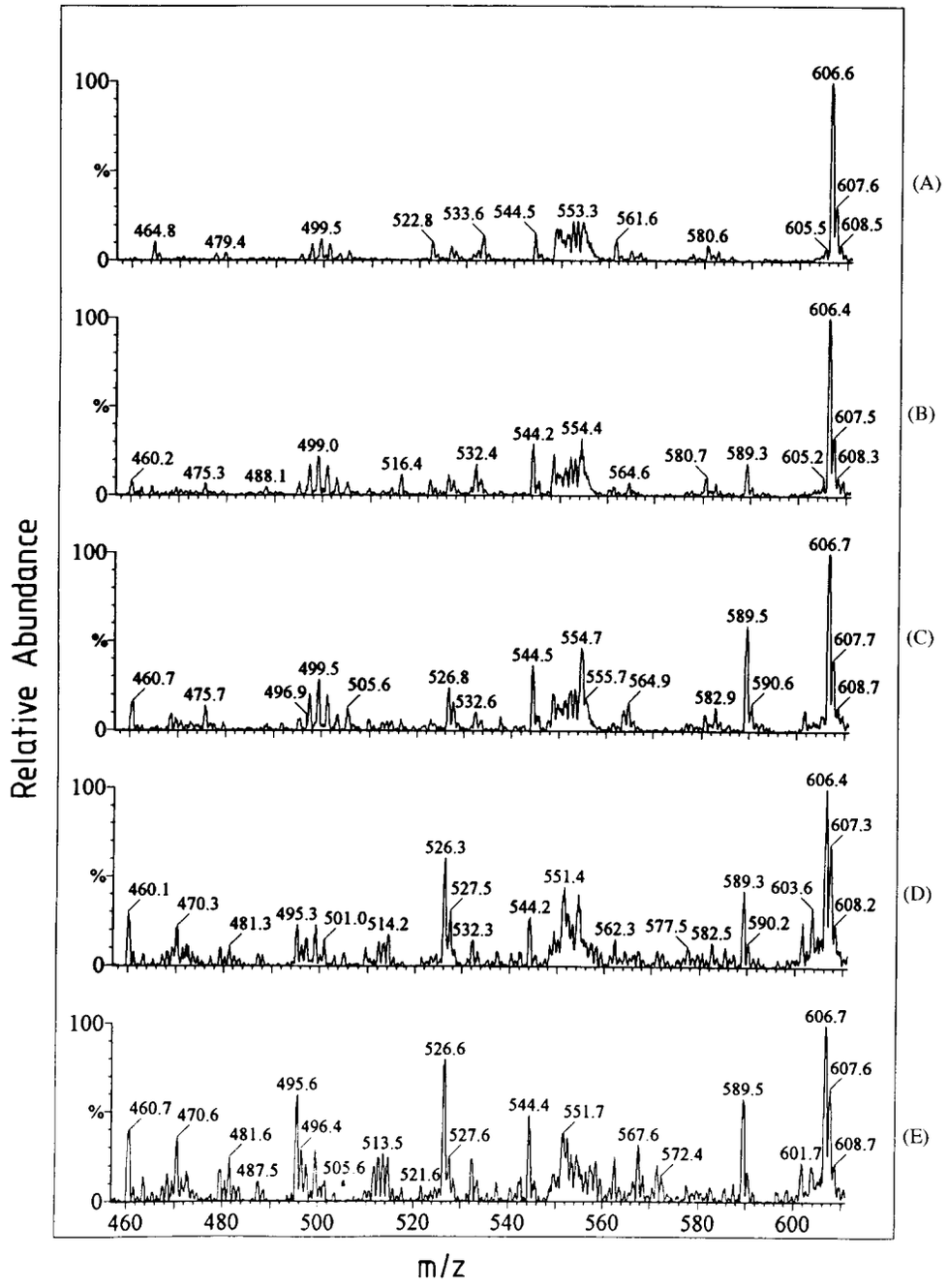


Figure 2 Effect of cone voltage on the appearance of low-mass species in the e.s.i. of polynimmo in THF–MeOH (concentration 1 μmol μl^{-1}) using NH_4Cl (0.5%) as cationizing agent. A: cv 20 V; B: cv 36 V; C: cv 50 V; D: cv 84 V; E: cv 110 V

is not fixed during the modelling process, but with the input of an experimentally obtained value for this bond distance the modelling process is considerably faster and more accurate. The oligometric adducts were then again subject to the simulated heating–cooling process outlined above. The resulting energy-minimized models for both tetramer and pentamer show that the Na^+ ion achieves its preferred six coordination by binding to all the ring oxygens and the appropriate number of oxygens in the nitrate ester side chains; *Figures 4* and *5* show the lowest energy conformations produced for the Na^+ complexes of the tetramer and pentamer respectively. *Table 2* shows the relative energy values obtained from the simulation.

This type of simulation produces energy values which are relative to an arbitrary zero; i.e., the energies of the conformers of a particular complex can be compared, but two structurally different complexes cannot. The behaviour of the polynimmo complexes mirrors that of the simple crown ether complexes in that pendant arms containing donor atoms offer increased levels of stabilization[17].

E.s.i. spectra of chromatographed polynimmo

Elution sequence. Our procedure for column chromatography of polynimmo using benzene–methanol (starting with pure benzene and gradually increasing the methanol content up to a maximum of 10% v/v) gave rise to 150–220 fractions which were characterized by ^{13}C n.m.r., g.p.c. and e.s.i. The early fractions gave predominantly tetramer, this giving way gradually to

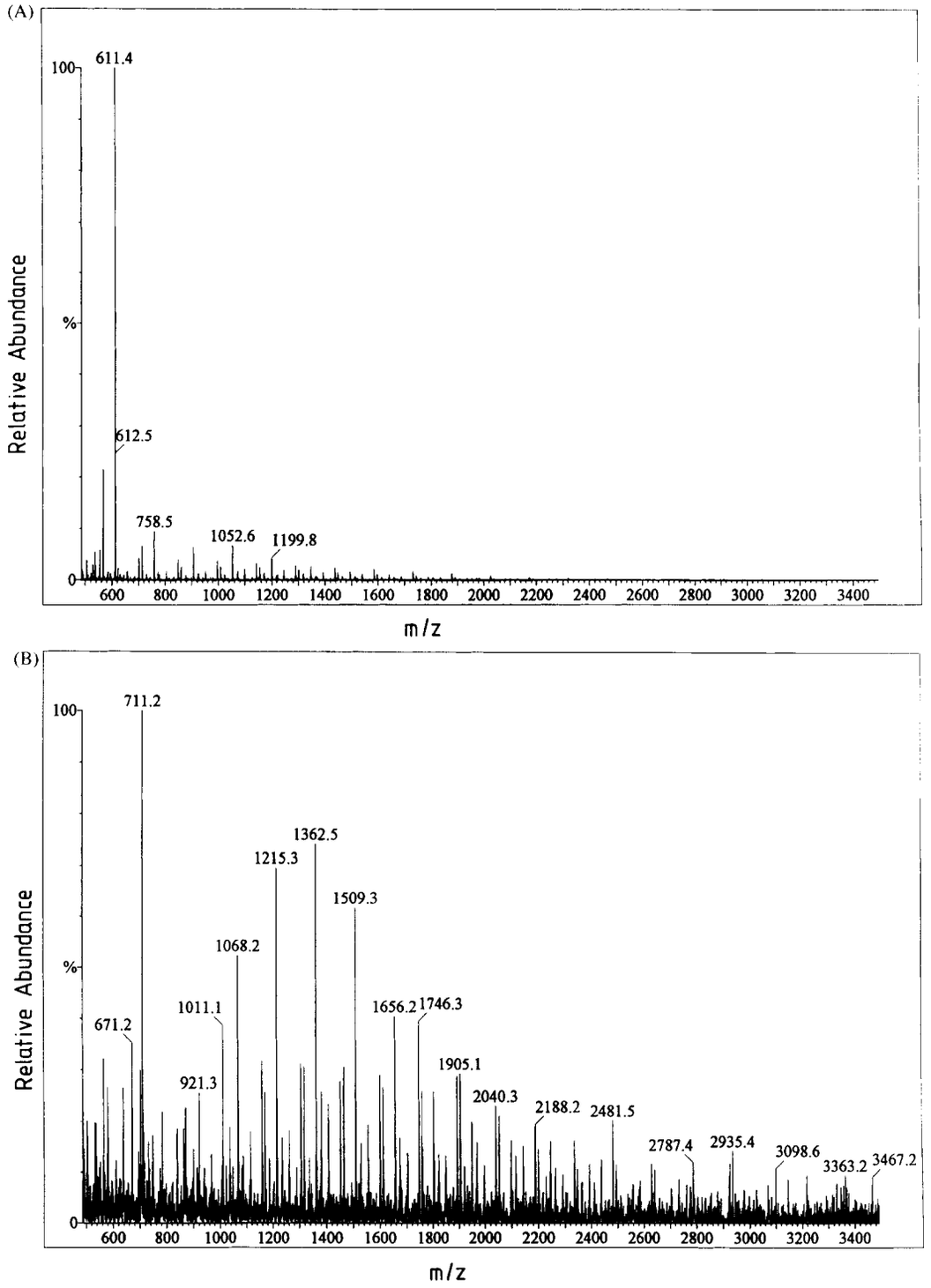


Figure 3 Effect of cation on ion abundances of cyclic oligomers in the e.s.i. of polynimmo in the presence of alkali metal iodides. A: polynimmo concentration 5 $\mu g\,\mu l^{-1}$ in THF–MeOH in the presence of NaI (0.005%), cv 36 V; B: polynimmo concentration 10 $\mu g\,\mu l^{-1}$ in THF–DMF in the presence of KI (2×10^{-3} mol dm^{-3})

higher cyclic oligomers (as determined by both g.p.c. and e.s.i.) whilst the late fractions gave mainly linear oligomers with RMM up to 3200 Da. This trend was mirrored in the e.s.i. spectrum of these fractions (*Figure 6A*), using NH_4Cl as cationizing agent; thus fraction 35 gave mainly the NH_4^+ tetramer ($m/z = 606.5$), fraction 50 gave NH_4^+ adducts of the tetramer and sizeable amounts of pentamer ($m/z = 753.4$) and hexamer ($m/z = 900.3$) with a minute quantity of heptamer (1047.4), fraction 55 gave mostly hexamer ($m/z = 900.3$) and fraction 65 mostly heptamer. Similarly fractions 75, 93, 117, 147 and 160 (*Figure 6B*) gave mainly octamer ($m/z = 1194.4$), nonamer ($m/z = 1341.5$), decamer ($m/z = 1488.3$), undecamer ($m/z = 1635.3$) and dodecamer ($m/z = 1782.4$) respectively. The e.s.i. spectra of fractions 147 and 160 also showed evidence for various linear species such as the H^+ and NH_4^+ adducts of the ethoxy-terminated oligomer of the pentamer (810.3, 827.4 Da) and hexamer (957.4, 974.4).

Table 2 Relative energies of Na^+ ion tetramer and pentamer polynimmo complexes

Structure	Energy ($kJ\,mol^{-1}$)
tetramer	178.6
tetramer + Na^+ (*cis*) (*Figure 4B*)	273.5
tetramer + Na^+ (*trans*) (*Figure 4A*)	202.7
pentamer	203.6
pentamer + Na^+ (*Figure 5A*)	398.2
pentamer + Na^+ (*Figure 5B*)	356.0

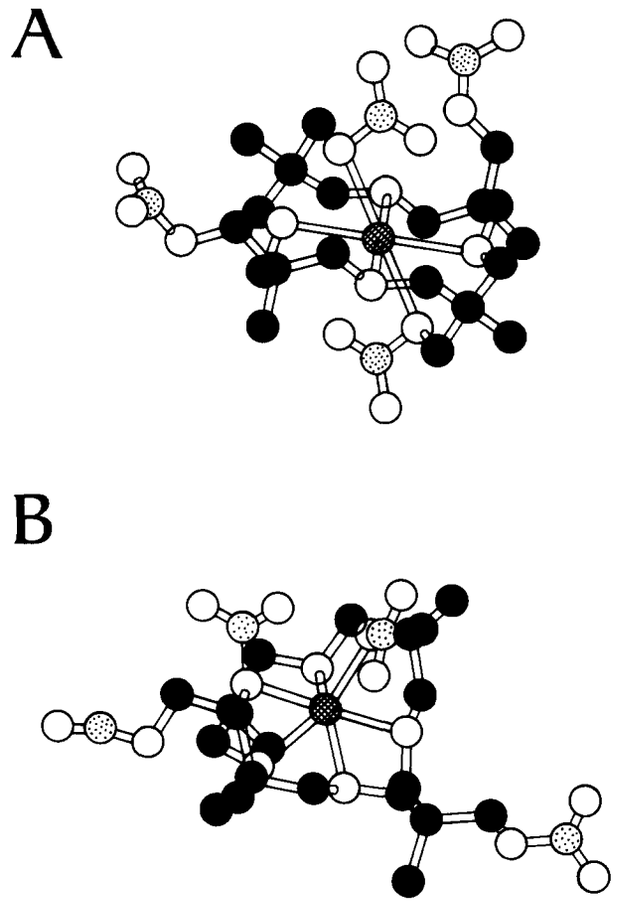


Figure 4 Energy-minimized structure and conformation of the Na^+ adduct of the cyclic tetramer of polynimmo. A: *trans*-form (energy = $202.7\,kJ\,mol^{-1}$); B: *cis*-form (energy = $273.5\,kJ\,mol^{-1}$). Open circles, oxygen; closed circles, carbon; dotted circles, nitrogen; hatched circles, sodium

In fraction 168 (*Figure 8*) there are peaks attributable to cyclic species of higher mass, and the assignments are given in *Table 1*. The heaviest ion observed is at $m/z = 2608.8$.

Cationization. The increased concentrations of individual cyclic species in the fractions obtained by column chromatography evidently provide more highly resolved e.s.i. spectra. The H^+ adducts of higher mass cyclic oligomers are now clearly visible, and the possibility that *in situ* reactions occur to produce the cyclic species seems very much less likely. Again, any assignment of higher mass species based on the formula $[(nimmo)_nNH_4]^+$ to conglomerates of lower mass cyclic species, e.g. $[(nimmo)_{n/2}(nimmo)_{n/2}NH_4]^+$, is also rendered much less credible. A better indication of the *relative* amounts of cyclic oligomers present can be

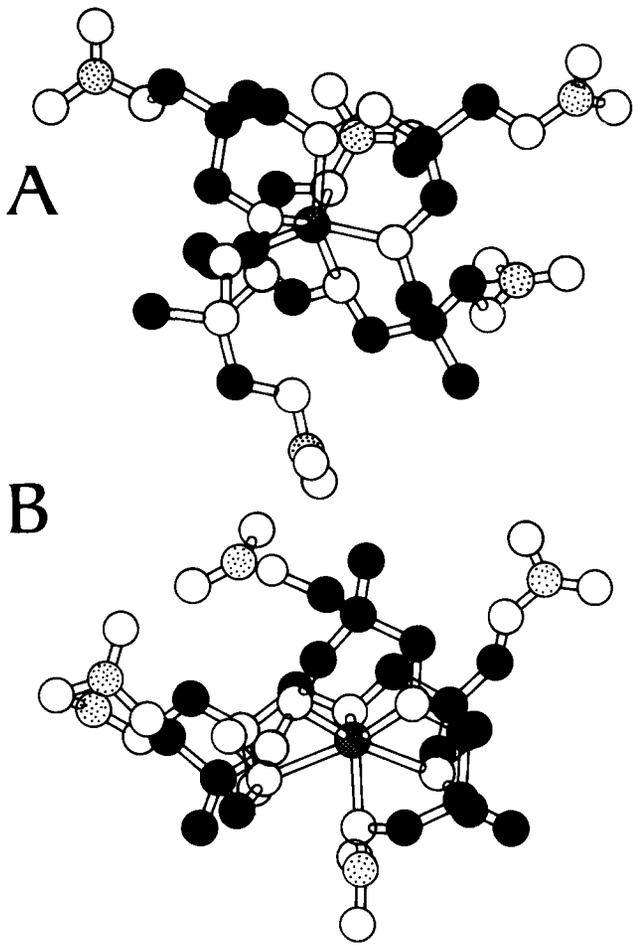


Figure 5 Energy-minimized structure and conformation of the Na^+ adduct of the cyclic pentamer of polynimmo. A: $398.2\,kJ\,mol^{-1}$; B: $356.0\,kJ\,mol^{-1}$. Open circles, oxygen; closed circles, carbon; dotted circles, nitrogen; hatched circles, sodium

obtained from the masses of individual fractions. The mass of isolated cyclic tetramer is approximately 20 times that of each of the pentamer, hexamer and septamer. The higher oligomers show a relatively decreasing concentration. Thus the relative ion intensities in the spectrum of unchromatographed polynimmo obtained using Na^+ for cationization gives the best approximation to the relative masses of cyclic oligomers present according to isolated weight. It has been clearly demonstrated, however, that the exact values and thus relative concentrations of the masses cannot be obtained without prior knowledge of the ion stabilities.

Comparison of e.s.i. with g.p.c. data. *Figures 7A* and *7B* show the g.p.c. chromatograms of the fractions obtained from the column chromatography of polynimmo which were all run using the low molecular weight column system (see 'Experimental' section) and equivalent concentrations of oligomeric material. Each chromatogram is labelled according to the fraction it represents.

The chromatograms of fractions 35 and 45 show a single peak with an $M_n = 700$. The e.s.i. spectra of the same fractions (*Figures 6A(A)* and *6A(B)*) show a single peak for the H^+ adduct of the cyclic tetramer at 589.4 Da. The accuracy of the e.s.i. results has already been demonstrated and thus the value of 700 obtained by g.p.c. seems to be high; however, the poly(propylene

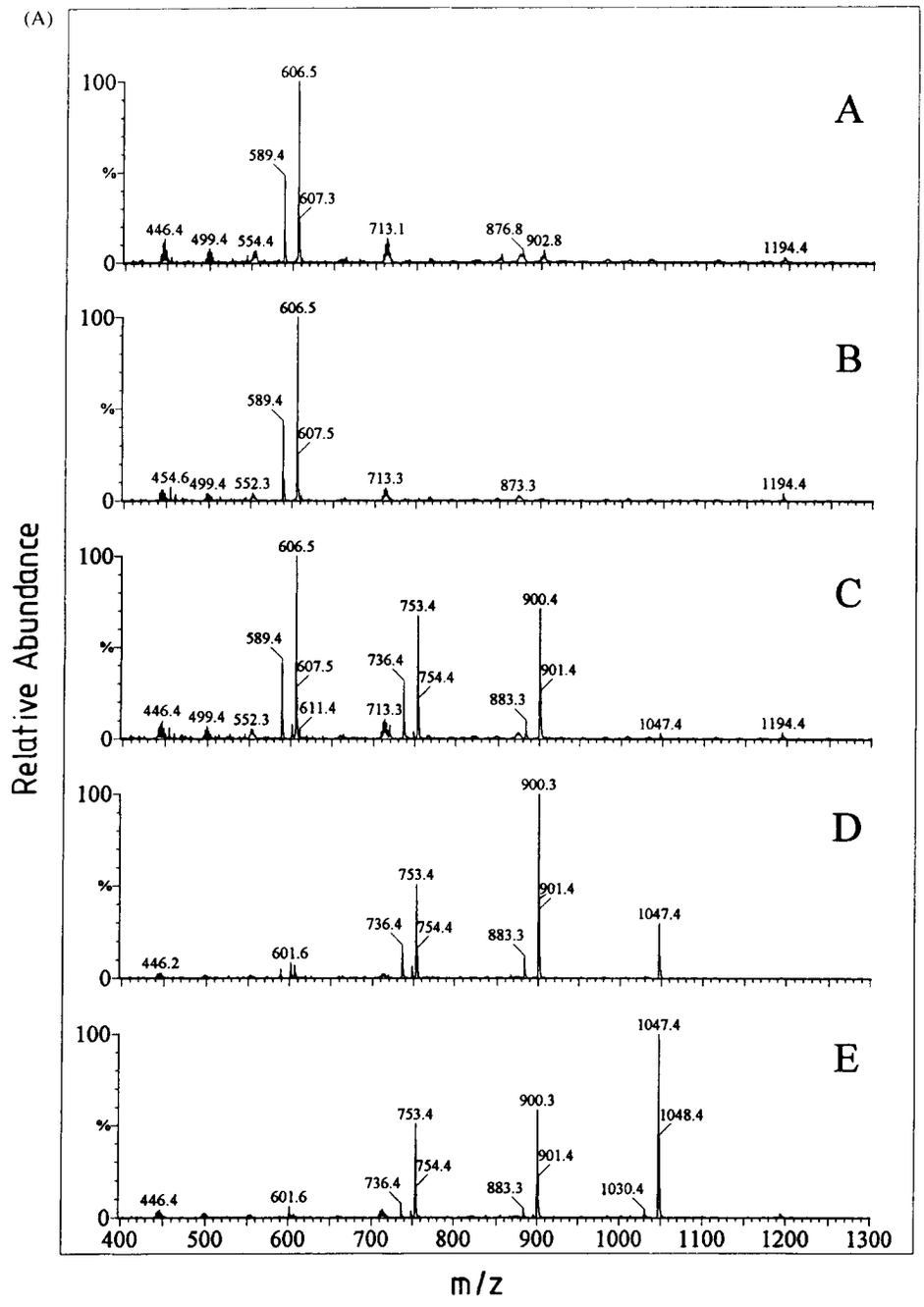


Figure 6 E.s.i. spectra of individual fractions from the column chromatography of polynimmo. E.s.i. solvent: THF–MeOH containing 0.5% NH_4Cl; polynimmo concentration 0.5 $\mu g\,\mu l^{-1}$. (A) A: fraction 35; B: fraction 45; C: fraction 50; D: fraction 55; E: fraction 60. (B) A: fraction 75; B: fraction 93; C: fraction 117; D: fraction 147; E: fraction 160

oxide) used to calibrate the g.p.c. equipment is substantially different in structure from the cyclic oligomers and thus some discrepancy is to be expected.

The chromatogram of fraction 50 shows three peaks in decreasing order of intensity. The g.p.c. peaks have M_n values of 700, 800 and 920 respectively. The e.s.i. spectrum in *Figure 6A(C)* of the same fraction also shows three peaks for the cyclic tetramer, pentamer and hexamer. Within experimental error, the $\bar{M}_n$ values of the three peaks obtained by g.p.c. correspond to these same three cyclic species. However, the g.p.c. chromatogram shows an intense peak for the cyclic tetramer and much weaker peaks for the cyclic pentamer and hexamer, whereas the e.s.i. spectra show intense ammonium adduct peaks for all the cyclic species, particularly the tetramer. Thus, the e.s.i. results appear to emphasize the concentrations of cyclic pentamer and hexamer relative to cyclic tetramer. This can be attributed to the differing stabilities of the ions in e.s.i., the cone voltage used during e.s.i. and the calibrant used for g.p.c. The latter two factors are thought to have a minimal influence here; the cone voltage was 36, which may have favoured the lower mass cyclic species and not the higher mass as here, and again, the calibrant used in g.p.c. would be expected to have little effect on the relative intensities of the cyclic species. The stability of the NH_4^+ adduct is thought to be the most influential factor here. E.s.i. spectra of unchromatographed polynimmo at a cone voltage of 36 show that even though the *concentration* of cyclic tetramer is approximately 20 times that of either

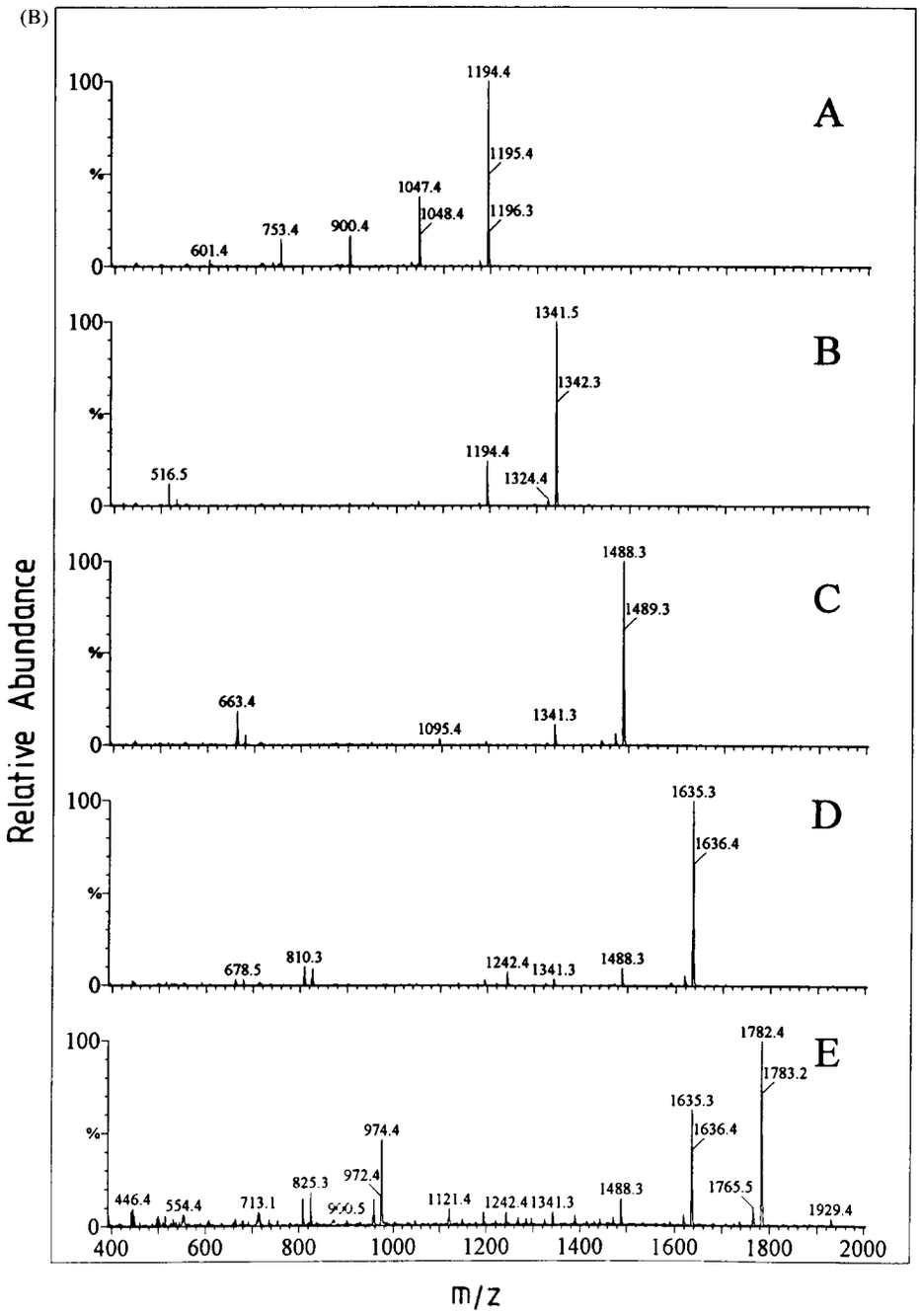


Figure 6 (*Continued*)

the pentamer or the hexamer, the abundance of the ion derived from it is only doubled. Thus the NH_4^+ adducts of the cyclic pentamer and hexamer are substantially more stable than that of the cyclic tetramer. This explains the apparently high concentrations of cyclic pentamer and hexamer present in the e.s.i. spectra. Similarly, the g.p.c. chromatogram for fraction 55 shows approximately equal concentrations of cyclic tetramer, pentamer and hexamer. The e.s.i. spectrum (*Figure 6A(D)*), however, shows no NH_4^+ adduct peak for the cyclic tetramer, but relatively strong peaks for the cyclic pentamer, hexamer and heptamer. By comparing the intensities of the peak in g.p.c. and e.s.i., it appears that the cyclic octamer and nonamer are the most stable ammonium ion adducts, while both higher and lower homologues are somewhat less stable.

Figure 7C shows the g.p.c. chromatograms of some of the later fractions obtained from column chromatography of polynimmo, each being labelled according to the fraction it represents. The chromatograms were all run using the low molecular weight column system (see 'Experimental') and equivalent concentrations of oligomeric material. The chromatogram of fraction 160 represents the cyclic dodecamer. This was the last cyclic oligomer that could be clearly identified from the eluted fractions by g.p.c. Subsequent fractions were too concentrated in linear oligomers for the individual characterization of cyclic oligomers. The g.p.c. chromatograms of the linear fractions show that a small degree of separation of the main polymer distribution is possible with the aid of column chromatography; however, no differences are apparent in the i.r. or n.m.r. spectra of these fractions.

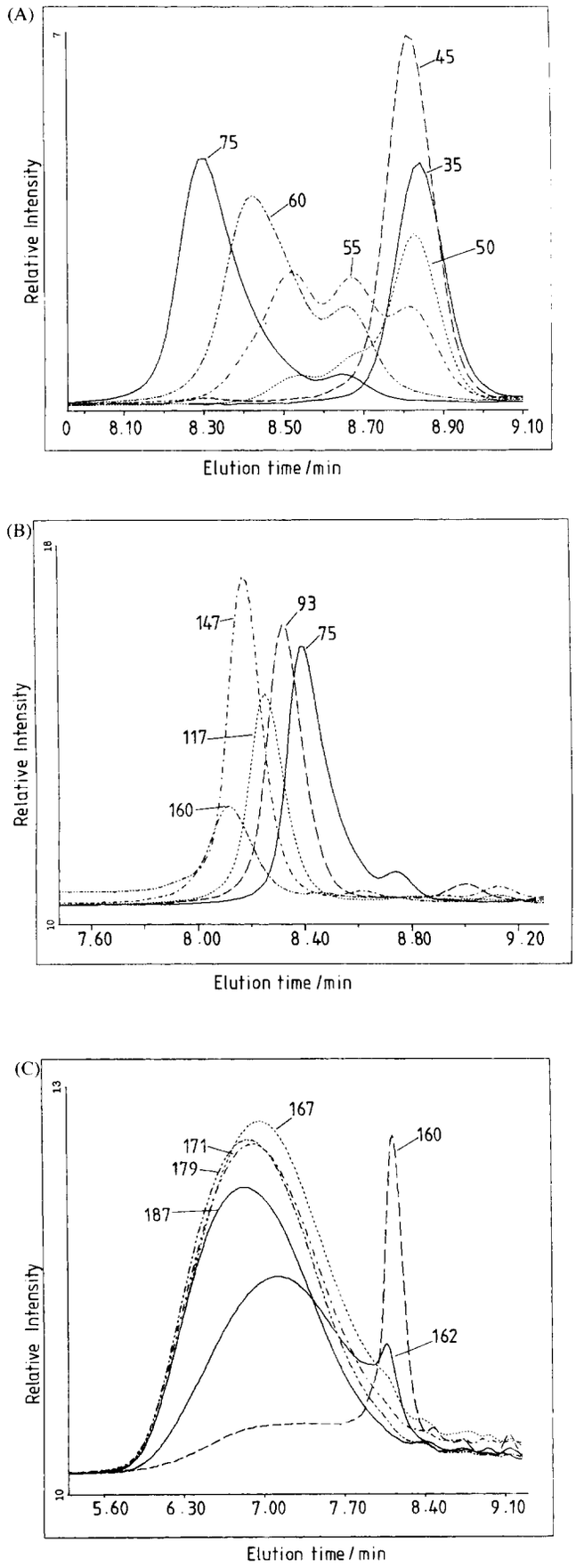


Figure 7 G.p.c. traces of early fractions from column chromatography of polynimmo. Numbers refer to sequence of fractions. A: early fractions (35–75); B: middle and later fractions (75–160); C: final fractions (160–180)

Figure 8 shows the e.s.i. spectrum of fraction 168 at a cone voltage of 50 V together with two separate enlargements of sections of the spectrum (*Figure 9*). Only cyclic oligomers of the nonamer and higher homologues are apparent in the spectrum, lower homologues having been eluted in the previous fractions. The removal of these relatively more highly concentrated cyclic oligomers from the linear oligomers facilitates the identification of the latter species. *Figure 8* features a series of singly-charged, predominantly linear oligomers with RMMs not exceeding 2800 Da. The g.p.c. chromatogram of the same fraction shows the main polymer distribution centring around 7500 Da. As shown previously, the main polymer distribution is simply undetectable under the experimental conditions used here; either the ions are not formed or they are not detected by the mass analyser. Fractions 162 to 170 all gave e.s.i. spectra similar to that for fraction 168 (*Figure 8*), but varying slightly as regards the relative intensities of the various linear oligomers. Different linear oligomers may have slightly different retention volumes in the toluene/methanol solvent system and thus will elute from the column at slightly different times. However, the e.s.i. spectrum shown is representative of the relative intensities of the low-mass oligomers present in unfractionated polynimmo. All subsequent fractions produced only very weak intensity ions.

The three different end groups known to exist in polynimmo have already been described. Linear oligomers with these end groups are apparent in the e.s.i. spectra (*Figure 8*). Four other different linear species are also visible in the spectra, and attempts to identify these end groups have been made by considering the materials used to prepare polynimmo.

Figure 9A shows a portion of the e.s.i. spectrum between 600 and 760 Da. The peaks are labelled with letters according to the scheme shown in *Table 3*. The H^+ adduct is considerably more stable than the NH_4^+ adduct for all the different types of linear tetramer. The spectrum (*Figure 9A*) clearly shows that, in this relatively low mass range, nearly all the peaks are due to H^+ adducts and only very low intensity peaks are visible for the NH_4^+ adducts. No peak is seen for the cyclic tetramer (606.3 Da) or the cyclic pentamer (753.3 Da) and the spectrum clearly shows that the peaks at 607.3 and 754.3 Da are not due to the ^{13}C isotopes of these cyclic species. Linear oligomers A to E are all visible in the spectrum (*Figure 9A*). The peak due to oligomer E is very weak, but is much stronger in the spectrum of unchromatographed polynimmo. Oligomer D is unassigned and is not visible in the spectrum of unchromatographed polynimmo. This oligomer is,

Table 3 Linear oligomers in polynimmo and their RMMs

Label[a]	Mass	Linear oligomer
A	$(147n) + 18$	$HO-[nimmo]_n-H$
B	$(147n) + 46$	$CH_3CH_2O-[nimmo]_n-H$
C	$(147n) + 90$	$HO(CH_2)_4O-[nimmo]_n-H$
D	$(147n) + 20$	$H-[nimmo]_n-F$
E	$(147n) + 74$	$CH_3CH_2O-[nimmo]_n-CH_2CH_3$
F	$(147n) + 102$	$CH_3CH_2-[nimmo]_n-(CH_2)_4OH$
G	$(147n) + 118$	$CH_3CH_2O-[nimmo]_n-(CH_2)_4OH$

[a] See *Figure 9*

[b] This might also be attributed to the cyclic series $[(nimmo)_nCH_2CCH_3(CH_2OH)CH_2O]$

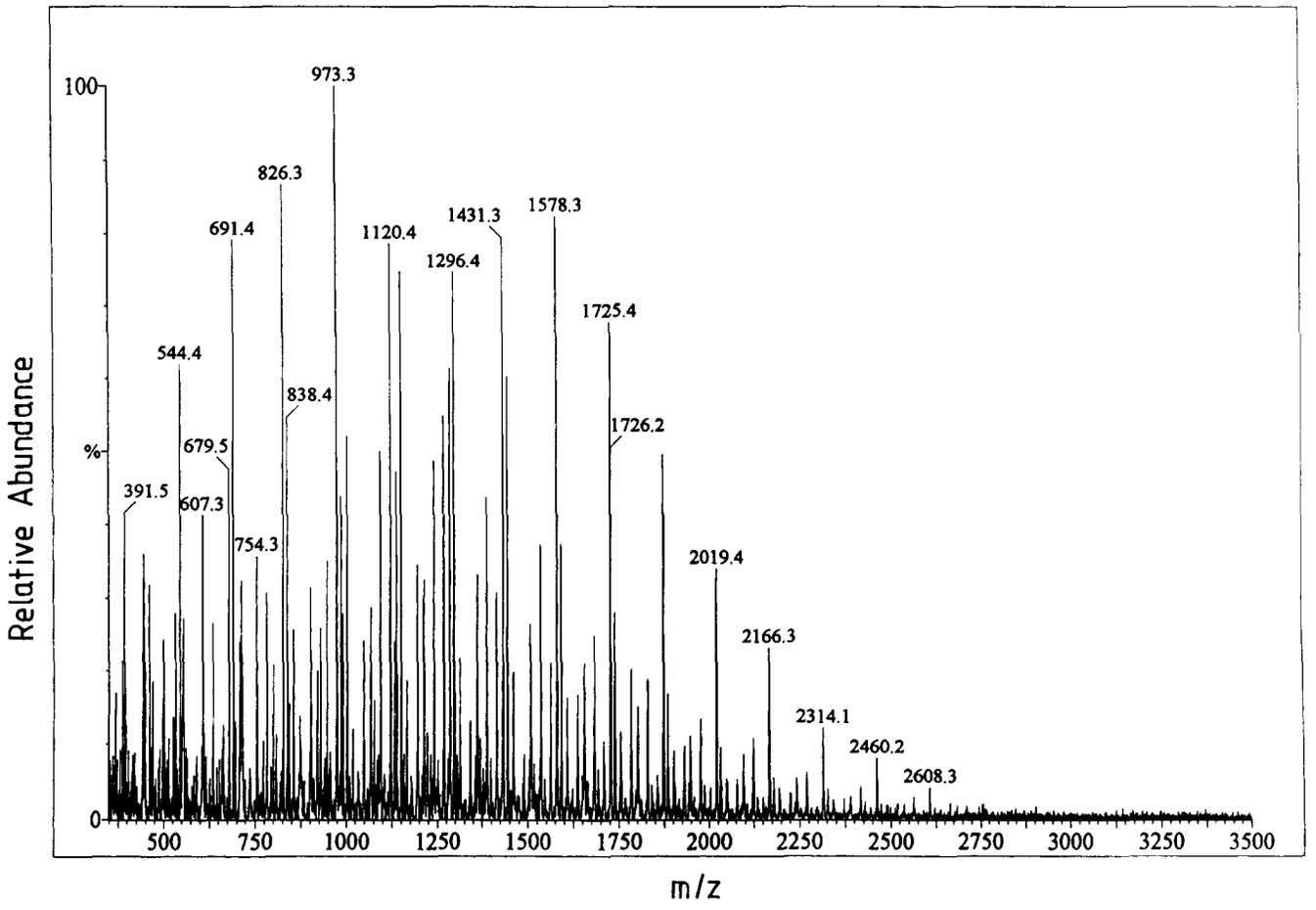
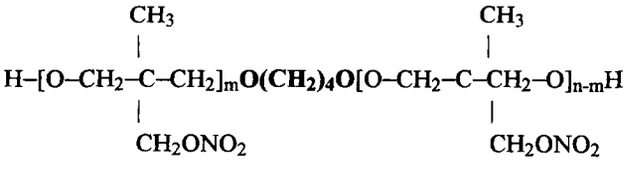


Figure 8 E.s.i. spectrum of fraction 168 from column chromatography of polynimmo (concentration 10 $\mu g\,\mu l^{-1}$). E.s.i. solvent system: THF–MeOH with 0.5% aqueous NH_4Cl

however, clearly visible in *Figure 9A*, particularly for the pentamer at 756.4 Da. The separation and thus the increased concentration of the low-mass linear oligomers in the sample of polynimmo makes the identification of relatively low concentration oligomers possible. The relative concentrations of the various linear oligomers present are difficult to calculate as they may have different stabilities with a particular ion. However, the stability of the H^+ adduct would not be expected to vary by a significant amount due to a change in end group. The H^+ ion most probably resides on an oxygen atom in the main chain and is relatively uninfluenced by the end group. Thus the e.s.i. spectrum of unchromatographed polynimmo shows that oligomers A, C, E and F are present in approximately equal concentrations and are roughly five times as concentrated as oligomers B, D and G. However, the peak for oligomer C is thought to be associated with two different species. The oligomer shown in *Scheme 2* is known to exist from n.m.r. measurements and has the same mass as oligomer C.



Scheme 2 Proposed structure of oligomer C

The relative concentrations of the two oligomers are thus impossible to calculate here.

The relative intensities of the H^+ ions for the various linear oligomers remain approximately constant as the mass increases, indicating that their relative concentrations also remain approximately constant.

Figure 9B shows a portion of the e.s.i. spectrum of fraction 158 (*Figure 8*) between 1770 and 1940 Da. The only peak in the spectrum due to an H^+ adduct is that at 1855.4 Da. This very low intensity peak is only visible because of the relatively high concentration of oligomer C. All other oligomers show only NH_4^+ adducts due to the low stability of the H^+ adduct for oligomers in this mass range. Cyclic oligomers of the nonamer and higher homologues were not separated from the linear oligomers, and the NH_4^+ adduct of the cyclic dodecamer is also visible at 1782.4 Da.

CONCLUSIONS

Polynimmo has been shown by electrospray ionization (e.s.i.) mass spectrometry to be a far more complex system than envisaged hitherto. Cyclic oligomers, while accounting for only *ca.* 5% of the total mass, are numerous and rings containing up to 22 repeat units have been characterized. The abundance of a particular cyclic ion in the e.s.i. spectra is largely determined by the stability of its ion adduct, which in turn depends on the size and nature of the cation involved. The size of the cone voltage is also influential, with high cone

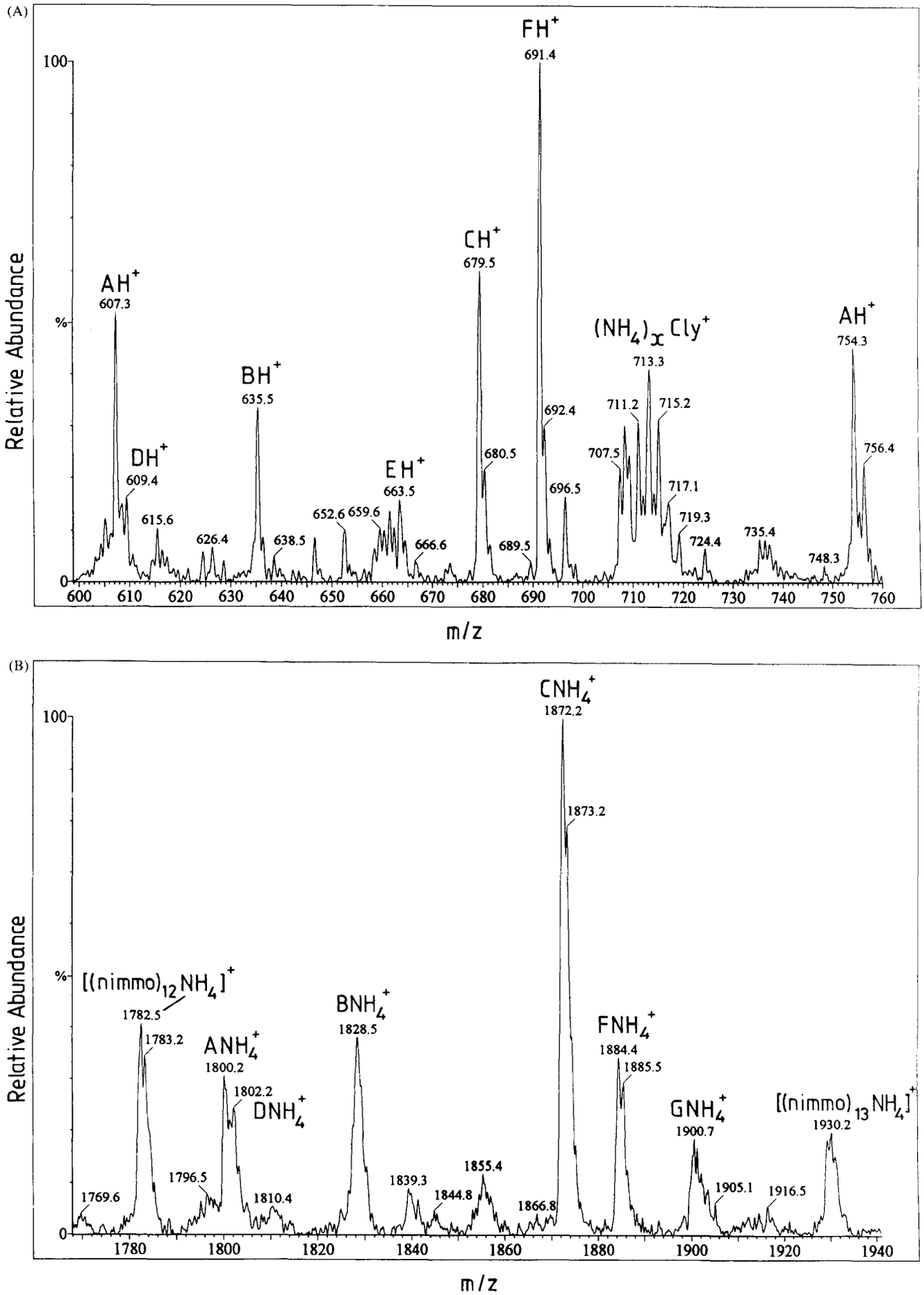


Figure 9 High resolution sections of e.s.i. spectrum of fraction 168 (see caption to *Figure 8*). A: m/z range 600–760; B: m/z range 1775–1940

voltages appearing to promote the appearance of larger cyclic ions at the expense of the highly visible tetramer.

A range of linear oligomers can also be detected by e.s.i., but the method fails to yield detectable multiply-charged ions under the experimental conditions used, which effectively reduces the mass range which can be accessed. Nevertheless, the spectra are well resolved, enabling identification to be made of the end groups involved.

Comparison of molecular weights of fractions at low mass gives reasonable agreement between g.p.c. and e.s.i., but at high mass, the low abundance of singly-charged polynimmo ions at MW *ca.* 3000–3500 indicates that, in the current state of instrumentation, e.s.i. does not give a true picture of molecular weight distribution.

ACKNOWLEDGEMENTS

We thank DRA for support of ZB via a studentship, EPSRC and MOD for financial support for AB and Dr D. M. Haddleton for access to his g.p.c. equipment. Professor P. Moore gave advice on the molecular modelling.

REFERENCES

1 Bunyan, P., Cunliffe, A. V., Davis, A. and Kirby, F. A. *Polym. Degrad. Stab.* 1993, **40**, 239
2 Bunyan, P., Cunliffe, A. V. and Davis, A. 'Proc. 16th International Pyrotechnics Seminar', June 1991, Jänköping, Sweden, p. 7
3 Farber, M., Harris, S. P. and Srivastava, R. D. Department of Navy Office of Naval Research, Arlington, Virginia, Report AD-A 168611, 1986
4 Chen, J. K. and Brill, R. B. *Thermochim. Acta* 1991, **181**, 71
5 Manser, G. C., Fletcher, R. W. and Knight, M. R. Final Report, Contract No. N00014-82-C-0800, Morton Thiokol Inc., Project JM101, 1985
6 Chen, J. K. and Brill, T. B. *Combust. Flame* 1991, **85**, 479
7 Mahon, A., Kemp, T. J., Buzy, A. and Jennings, K. R. *Polymer* 1996, **37**, 531
8 Schmelzeisen-Redeker, G., Röllgen, F. W., Wirtz, H. and Vögtle, F. *Org. Mass Spectrom.* 1985, **20**, 752
9 Ambroz, H. B., Jennings, K. R. and Kemp, T. J. *Org. Mass Spectrom.* 1988, **23**, 605
10 Broxton, T. J., Colton, R. and Traeger, J. C. *J. Mass Spectrom.* 1995, **30**, 319
11 Casetta, B. and Garofolo, F. *Org. Mass Spectrom.* 1994, **29**, 517
12 Colclough, M. E., Desai, H., Millar, R. W., Paul, N. W., Stewart, M. J. and Golding, P. *Polym. Adv. Technol.* 1993, **5**, 554
13 Barton, Z., Kemp, T. J., Buzy, A. and Jennings, K. R. *Polymer* 1995, **36**, 4927
14 Cunliffe, A. V., Desai, H. and Torry, S. A. unpublished results
15 Loo, J. A., Udseth, H. R. and Smith, R. D. *Rapid Commun. Mass Spectrom.* 1988, **2**, 207
16 Allen, F. H., Davies, J. E., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. and Watson, D. G. *J. Chem. Int. Comput. Sci.* 1991, **19**, 187
17 Lindoy, L. 'The Chemistry of Macrocyclic Ligand Complexes', Cambridge University Press, 1989, Chap. 4