

FISSION FRAGMENT IONIZATION MASS SPECTROMETRY OF POLYETHERS *

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ABSTRACT

The complete fission fragment ionization mass spectra of three polyether oligomer samples have been measured and spectra in the molecular weight region only have been measured for two other samples with known number average molecular weights. The samples consist of methoxypolyethylene glycols with nominal average molecular weights of 750 and 2000 and lauryloxypolyethylene glycol with nominal average molecular weight of 1200. The spectra consist of a series of quasi-molecular ions, four series of ions produced by identified fragmentation processes, and low mass fragment ions produced by unidentified processes. The quasi-molecular ion series are used to obtain average molecular weights for the samples. The agreement between the known number average molecular weights and the corresponding values derived from the mass spectra was excellent. The relative amount of quasi-molecular ions declines with increasing average molecular weight of the polymer sample. More fragmentation is observed with Li^+ adducts of the polymers than with Na^+ adducts.

INTRODUCTION

In this paper, we report a mass spectrometric examination of five polyether oligomer samples. This was done using our fission fragment ionization (^{252}Cf) mass spectrometer and the results are interesting from both a scientific and a practical point of view. We undertook our study to provide practical analytical information about certain polymer samples. However, the results of the study include information about fragmentation properties and mechanisms in fission fragment ionization mass spectrometry which is of value equal to that of the analytical results. No reports of the fission fragment ionization mass spectrometry of this class of compounds have been published.

* Dedicated to the memory of H.M. Rosenstock.

Mass spectrometric studies of oligomers have, in the past, been made primarily for providing information about molecular weight distributions, structural features, and purities. Several such studies of polyethers have been reported in the past several years. Otsuki and Shiraishi [1] give the field desorption spectra of several poly(oxyethylene)alkylphenyl ethers. The alkylphenyl groups included range from hexylphenyl to tridecylphenyl ($C_6H_{13}C_6H_4$ to $C_{13}H_{27}C_6H_4$). The number of monomer groups present ranges from 3 to 16 and thus the total molecular weight range encompassed is from 354 to 1118. The spectra reported contain only molecule ions (M^{++}) and the spectrum of a given sample thus comprises a representation of the molecular weight distribution and impurity content of the sample. Wood and Sun [2] present the field desorption spectrum of polyethylene glycol (PEG 1000) and the ionization is effected by the addition to the molecules of Ca^{2+} ions added to the sample in the form of CaI_2 . The reported spectrum consists only of the cationized quasi-molecular ions. Molecules with molecular weights up to 1338 are included. Lai et al. [3] give the molecular weight distributions of polyethylene glycol samples determined by electrohydrodynamic ionization mass spectrometry. The molecular weight ranges of the samples measured are 380–420, 570–630, 950–1050, and 1300–1600. The ions formed are quasi-molecular ions produced by cationization (addition of Li^+ or Na^+). A tendency toward multiple cationization in large molecules is observed. Matsuo et al. [4] report the field desorption spectra of polystyrene with m/z values up to 10 000 and of polypropylene glycol up to about 2000. Enhanced intensities are observed under cationizing conditions. It is reported [5] that spectra of large polypropylene glycol molecules have been observed with field desorption in a large double focusing deflection-type mass spectrometer. The highest mass ion observed had m/z 7400. De Stefano et al. have investigated the auto-oxidation decomposition products [6] and the rabbit urinary metabolites [7] of penta-oxyethyleneglycol monodecyl ether, $C_{10}H_{21}(OCH_2CH_2)_5OH$, a common non-ionic surfactant. Electron ionization and isobutane chemical ionization were used with appropriate derivatization of the compounds involved. As would be expected, electron ionization produced large amounts of fragmentation, but significant quasi-molecular ion intensities were produced by chemical ionization. Lattimer and Hansen [8] have determined molecular weight distributions of three polyglycol oligomers (polyethylene glycol, polypropylene glycol, and polytetrahydrofuran) using field desorption mass spectrometry. Whitney and Jaeger [9] have studied the electron ionization-induced fragmentation of pyridyl macrocyclic polyethers (crown ethers).

Californium-252 fission fragment ionization mass spectrometry [10–12] is a technique whereby molecular entities are desorbed and ionized directly from a solid surface by the passage of an energetic fission fragment from the

californium through a surface coated with the compound to be studied. Interest in the method stems largely from the ability of the method to produce significant yields of quasi-molecular ions of compounds which are large, involatile, and/or thermally unstable.

EXPERIMENTAL

The spectra were obtained with the Rockefeller University fission fragment ionization mass spectrometer [12,13]. The ion accelerating voltage was 10 kV and 6 kV was applied to the first ion accelerating grid. The electrostatic particle guide was maintained 12 V negative with respect to ground. The width of the time bins in the flight time measurements was 5.0 or 6.25 ns. Ion intensities were obtained by summing the counts in three bins across the tops of the peaks. The ion collection rate depends on the volatility of the sample and for this work the rate ranged from 200 to 1000 ions s^{-1} . For some measurements, a more intense ^{252}Cf source was used, which gave a count rate of 5000 ions s^{-1} . Results obtained using the two sources were completely compatible. We collected $0.5\text{--}1.0 \times 10^6$ ions per spectrum and thus the acquisition time per spectrum ranged from 30 to 180 min. The flight time to ion mass conversions were made using the two-constant equation described in ref. 12. The constants were evaluated using two known masses in a given spectrum, which might be those of the ubiquitous H^+ and Na^+ ions for a preliminary calibration, to be followed by a final calibration using, for example, Na^+ and an ion known to be a quasi-molecular ion. We give in Fig. 1 the portion of the spectrum of methoxypolyethylene glycol 750 with NaCl between flight times of 65 and 70 μs (m/z 840–975). One observes the good peak shape and the unit mass resolution indicated by the separation between the major peaks and their ^{13}C satellites.

18-Crown-6 cyclic polyether was obtained from PCR, Inc. (Gainesville, Florida). Methoxypolyethylene glycol of nominal molecular weight 750 (MPEG 750) was obtained from Matheson, Coleman and Bell (Norwood, OH). Lauryloxypolyethylene glycol (LPEG 1200) of nominal molecular weight 1200 was obtained from Aldrich Chemical Co. (Milwaukee, WI). Methoxypolyethylene glycol nominal molecular weight 2000 (MPEG 2000) was a product of Union Carbide Corp. (New York, NY). All of these samples were provided by Dr. T.P. King of this university and were used without further treatment. The molecular weights cited are the nominal values attributed to the samples by the manufacturers. We have no independent measurements of these quantities for these samples. Samples of methoxypolyethylene glycol with authentic number average molecular weights of 755 and 2021 (determined by the hydroxyl number method) were kindly

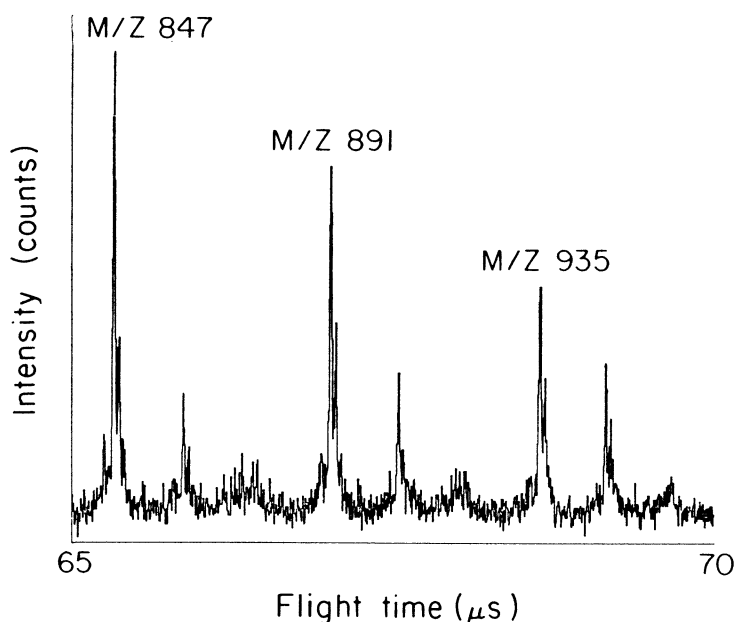


Fig. 1. A portion of the molecular ion region of the spectrum of PEG 750 + NaCl. Full scale intensity = 250 counts.

provided for us by Dr. Ron Thursack of the South Charleston Polymer Characterization Group, Union Carbide Corp.

The ionization involved in producing our spectra was accomplished by the addition of Li^+ or Na^+ ions and these ions were provided by adding LiCl or NaCl to the samples. Isotopically separated $^6\text{LiCl}$ and $^7\text{LiCl}$ were used. These lithium salts were obtained from the Oak Ridge National Laboratories. Their isotopic purities were greater than 99% [14]. The NaCl used was Baker (Phillipsburg, NJ) Reagent Grade. To prepare samples for measurement, solutions of the polyethylene glycols with concentrations of approximately 0.2 mg ml^{-1} were prepared in either methanol or acetone. To these was added enough LiCl or NaCl to provide about 4 g atoms of the metal ion per g mole of the glycol, i.e. the metal ion was present in appreciable excess. The solutions were then electrosprayed onto aluminum-coated polyester foils. The volume of solution sprayed was such that 10–30 μg of solute was deposited on the foil. The foil was then inserted into the mass spectrometer and the spectrum taken.

Because of their considerable length, detailed spectra of the compounds studied in this work are not included in this paper. We shall, however, provide complete spectra to readers who write us for them.

RESULTS AND DISCUSSION

18-Crown-6 Polyether (C₁₂H₂₄O₆)

As an introductory exercise to provide experience with polyethers, we measured the spectrum of 18-Crown-6 cyclic ether with added ⁷LiCl. We mention that we have made no effort to determine the spectra of this compound or of any of the other polyethers with alkali metals absent. First, we have found it largely impossible to prepare samples with adventitious alkali ions (especially sodium) absent and second, since ethers are neutral, inert compounds, prior experience suggested that the production of useful spectra would be enhanced by the ready availability of alkali ions for addition to the ether molecules. The spectrum of this compound is particularly simple, consisting of the (M + Li)⁺ peak at *m/z* 271 plus ¹³C satellites and an (M - 2 + Li)⁺ ion at *m/z* 269 with intensity about 5% that of the *m/z* 271 peak. In the region below *m/z* 100, ions to be attributed to LiCl appeared (Li⁺, Li₂OH⁺, LiCH₂O⁺, and Li₃Cl₂⁺), but none of the extensive fragmentation at low mass that we have observed with other compounds in the past. The ready addition of Li⁺ to this crown ether is in keeping with the known abilities of this class of compound to complex with alkali ions and the lack of fragmentation may be attributed to the cyclic structure of the compound.

Methoxypolyethylene glycol [CH₃O(CH₂CH₂O)_nH] of nominal M.W. 750 (MPEG 750)

Spectra of this compound were taken with added ⁶LiCl, ⁷LiCl, and NaCl. The samples used with added LiCl also contained Na⁺ impurity. The spectra obtained are unlike that obtained with 18-Crown-6, for the MPEG 750 spectra exhibit a large amount of fragmentation. However, they also exhibit meaningful intensities of quasi-molecular ions and thus the behavior of MPEG 750 is in keeping with that which we have postulated as obtaining generally with fission fragment ionization, namely a bimodal kind of ionization which combines extensive fragmentation with persistent quasi-molecular ion formation [12].

Our spectrum of MPEG 750 with added ⁶LiCl contains about 350 peaks and no ion has a relative intensity (RI) greater than 2% of the total ionization (intensities of H⁺, Li⁺, and Na⁺ omitted from this consideration). The three most intense ions in the spectrum are those with *m/z* 29.034 (RI = 1.9% of total ionization), *m/z* 45.038 (RI = 1.3%), and *m/z* 41.039 (RI = 1.2%). These masses correspond, with little error, to the atomic compositions C₂H₅⁺, C₂H₅O⁺, and C₃H₅⁺. One can conceive of ways in which

$\text{C}_2\text{H}_5\text{O}^+$ might be formed from a methoxypolyether, but the production of the other two ions would require extensive rearrangements. Similar difficulties with other low mass ions were encountered and we have not achieved an understanding of the processes producing ions with m/z values of less than approximately 200. These ions comprise 16% of the total ionization.

Many of the ions with m/z greater than 200 form series the elements of which are separated by 44 mass units, which is the mass of the $\text{C}_2\text{H}_4\text{O}$ monomer unit of polyethers. We give in Table 1 the m/z values and intensities of one of these series and in Fig. 2 we plot the intensities against the mass numbers. The bell shape of the plot in Fig. 2 is compatible with a molecular weight distribution and the mass numbers for the several peaks correspond to those for lithiated polymer molecules, i.e. quasi-molecular ions with formula $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}^6\text{Li}^+$. We include in Table 1 the values of n for the several ions. We assume the validity of this formula for one of the ions (that for which $n = 11$) and we use the m/z value corresponding to this formula to calibrate our mass scale. The m/z values for the other ions in Table 1 are experimental values obtained using this calibration. The average deviation of the experimental m/z values with $n = 8-19$ (the relatively intense peaks) from the values calculated from the several formulas is 26

TABLE 1

First quasi-molecular ion series $\text{MPEG 750} + {}^6\text{LiCl} [\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}^6\text{Li}^+]$

m/z	n	Intensity
258.129	5	101
302.229	6	84
346.313	7	87
390.238	8	190
434.262	9	261
478.295	10	366
522 ^a	11	469
566.366	12	500
610.339	13	553
654.345	14	572
698.469	15	493
742.465	16	371
786.549	17	289
830.479	18	210
874.564	19	190
918.566	20	106
		$\Sigma I = 4842$

^a Mass assumed to be 522.328 and used to calibrate mass scale.

mmu. As a minimum, this agreement indicates that the ions are all of the same type and we take them to be quasi-molecular ions. Then the average molecular weight of the polymer sample can be calculated from the data of Table 1 and the value for the number average m/z value is 613, which corresponds to a number average molecular weight for the polymer of 607. This value is to be compared with the nominal value of 750.

Five other series with $\Delta M = 44$ have been identified in the MPEG 750 + $^6\text{LiCl}$ spectrum and these can be initially characterized according to the mass differences with respect to the lithiated quasi-molecular ions series (QM) given in Table 1. The masses of the five series are QM - 2 (or QM - 46), QM - 16, QM - 18, QM - 32, and QM + 17. The mass numbers of the first four series are even, whereas those of the last are odd. Another difference of importance is that the intensity distribution of the last series is bell-shaped like that shown in Fig. 2, but the distributions of the other four series show a general decrease in intensity between their lower and upper limits (from about m/z 200 to about 800). The intensity distribution for the QM - 2 or QM - 46 series is given in Fig. 3 as an example. To obtain more information about the identity of the ions in the several series, a spectrum was taken of MPEG 750 with $^7\text{LiCl}$ added. The spectrum was the same as

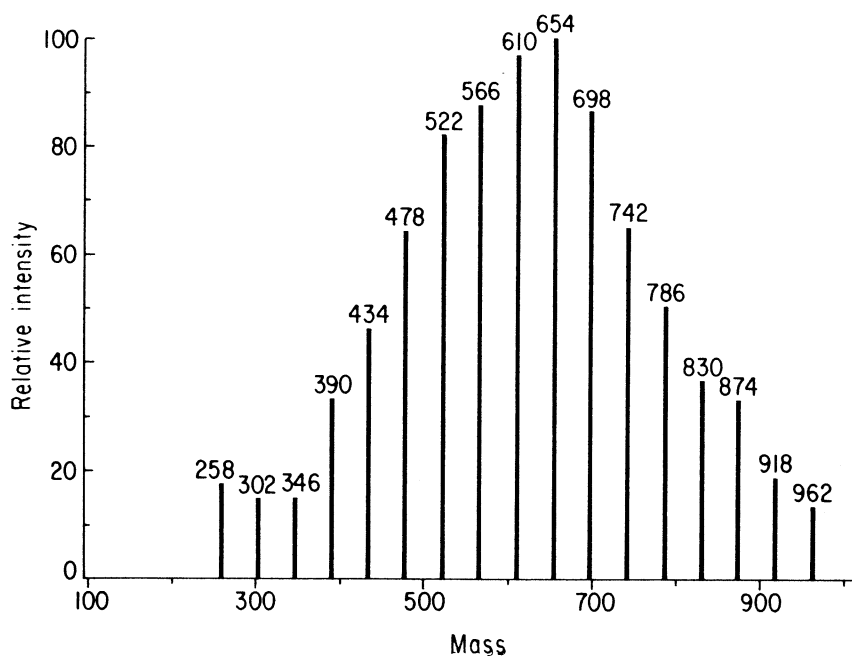


Fig. 2. Relative intensities vs. mass for $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}^6\text{Li}^+$ ions, PEG 750 + $^6\text{LiCl}$. Full scale intensity = 572 counts.

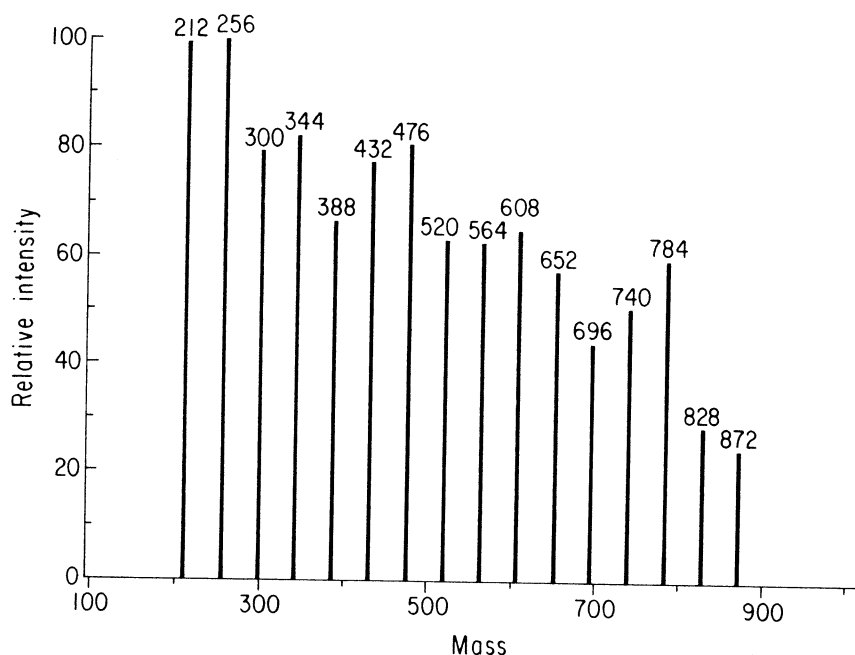


Fig. 3. Relative intensities vs. mass for the QM-2 or QM-46 series, PEG 750 + $^6\text{LiCl}$. Full scale intensity = 210 counts.

that with added $^6\text{LiCl}$ except that the masses of all the series except the QM + 17 series shifted upward by one mass unit and one concludes that Li is incorporated in the ions of the series with moving mass.

As we have stated, we find it difficult to exclude sodium from our samples and in our MPEG 750 spectra with both $^6\text{LiCl}$ and $^7\text{LiCl}$ added, the Na^+ intensity was of about the same magnitude as the Li^+ intensity. Taking this into account, all of the experimental aspects of the QM + 17 series can be accounted for by the postulate that this series is a quasi-molecular ion series formed by the addition of Na^+ to the polyethylene glycol. We give in Table 2 the m/z values, values of n , and the intensities observed. The experimental m/z values tabulated deviate from the values calculated for the atomic compositions $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{HNa}^+$ by an average of 58 mmu. The mass and intensity values given in Table 2 permit a second calculation of the number average m/z value and the value obtained is 667. The corresponding average M.W. is 644.

We summarize our findings about the four other ion series obtained in the MPEG 750 + LiCl spectra in Table 3 (data given refer specifically to the $^6\text{LiCl}$ spectrum, as an example). Since all of the ions in these series contain lithium, the ions might be produced by the addition of Li^+ to molecules

TABLE 2

Second quasi-molecular ion series MPEG 750 + $^6\text{LiCl}$ [$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H Na}^+$]

m/z	n	Intensity
451.251	9	99
495.277	10	111
539.303	11	138
583.329	12	129
627.355	13	162
671.381	14	150
715.407	15	150
759.433	16	142
803.459	17	128
847.485	18	71
891.511	19	64
935.537	20	39
		$\Sigma I = 1383$

present in the sample as impurities or they might be fragment ions produced from the molecules whose molecular weight distribution and QM ions are given in Tables 1 and 2. The difference in the intensity distributions shown in Figs. 2 and 3 is great enough to suggest that both do not represent molecular weight distributions. Thus, the number average molecular weight of the distribution in Fig. 3 is 457, which seems improbably low. Furthermore, the total ion intensity for the QM ions included in Tables 1 and 2 is 6225 counts and the total ion intensity of the series ions included in Table 3 is 8272 counts and if the series ions come from impurity molecules, one must conclude that the sample studied contained more impurities than nominal material. This is not compatible with our experience with the material and it

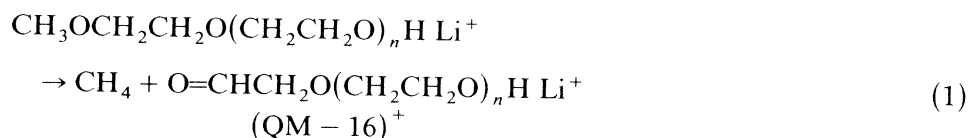
TABLE 3

Fragmentation series observed in MPEG 750 + $^6\text{LiCl}$ spectrum

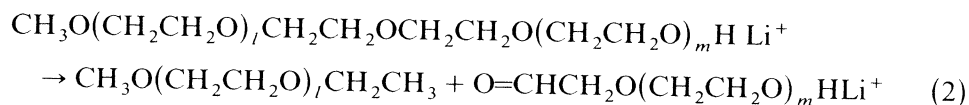
Series	Mass range covered	Number of peaks	Summed intensity
QM-2 or QM-46	212-872	16	2179
QM-16	154-770	15	2265
QM-18	152-768	14	2053
QM-32	182-754	13	1775
			$\Sigma I = 8272$

is also chemically unlikely. Thus, we suggest that the ions comprising the series given in Table 3 are produced by fragmentation.

We had hoped that the experimental masses of the ions in the series in Table 3 could be determined accurately enough to enable us to identify unequivocally the atomic groups lost from QM to produce the four series, but this hope was not realized. The experimental masses for the ions in the QM - 16 series, for example, are compatible with the postulate that the ions are formed by the loss of either O or C + 4H from QM, but it cannot distinguish between these two processes. However, we suggest some fragmentation reactions based on chemical experience. Thus, for the QM - 16 we write

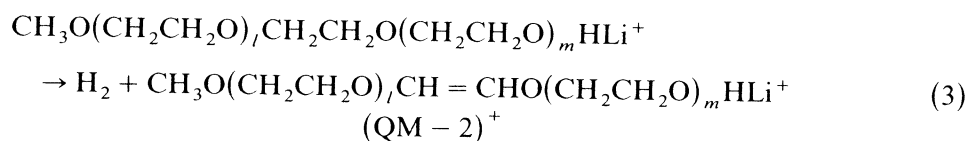


or, more generally

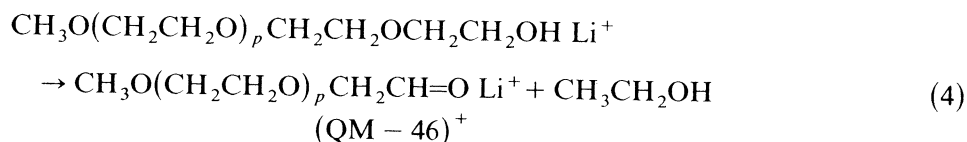


The loss of an O atom from QM would also produce the QM - 16 series, but it is difficult to see how, chemically, this could be accomplished. We presume that fragmentation such as that represented in Eqs. (1) and (2) is promoted by the Li^+ ion and we point out that, in Eqs. (1) and (2), the attachment of the Li^+ is represented as occurring at the end of the molecule only for convenience. It is reasonable to think that, in actuality, the attachment can occur at different places along the length of the molecule.

The series designated as QM - 2 or QM - 46 is written in this equivocal manner because two chemically reasonable reactions can be written to produce the observed mass series. These are



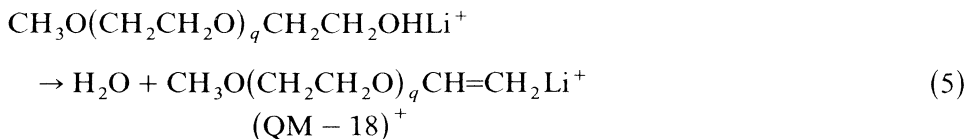
and



Loss of H_2 from ions is a common reaction and reaction (4) is the analog of

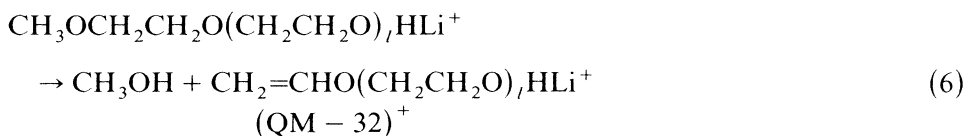
reactions (1) and (2). Of course, analogs of (4) can occur with the chain breaks at different places along the length of the molecule.

The 18 mass units lost to produce the QM – 18 series could be C + 4H + 2H formed by reactions (1) and (2) and (3) and (4) in sequence, or it could be H₂O produced by



In analogs of reaction (5), the fragmentation can occur at different places along the length of the molecule.

The 32 mass units lost to produce the QM – 32 series could be either 2O or C + 4H + O. The exact mass values obtained for this series make it unlikely that the 32 mass units lost corresponds to 2C + 6H. We have difficulty conceiving of reactions whereby two O atoms are lost, but for the loss of CH₃OH and its polymeric analogs we can easily write



Reaction (6) is the analog of reaction (5) and reactions (1)–(6) exhibit an interesting correspondence of loss of groups from each end of the chain. This behavior offers the possibility of deducing information about polymer structure from these fragmentation series.

We call attention to three other points concerning the MPEG 750 spectra with lithium. The summed intensities given in Table 3 show that the four fragmentation series have approximately the same probability of occurrence. Second, the total intensities given in Tables 1–3 enable one to calculate the QM ratio, *R*, defined as the ratio of the total intensity of QM to the sum of the QM intensities plus the fragment series intensities ($R = \Sigma \text{QM}^+ / (\Sigma \text{QM}^+ + \Sigma \text{F}^+)$). For the ⁶Li spectrum, the value of *R* is 0.37 (0.43 if the Na QM intensities are included). The corresponding ratios for the ⁷Li spectrum are 0.40 and 0.44. The average values for the lithium spectra (which we shall use later) are 0.39 and 0.44. Finally, the QM ions in the ⁷Li MPEG 750 spectrum can be used to provide a value for the number average *m/z* and the value obtained is 604. The corresponding number average molecular weight is 597.

As a complement to our spectra of MPEG 750 with added LiCl, we obtained a spectrum of this compound with added NaCl. The general features of the Na spectrum are identical with those of the Li spectra, but interesting quantitative differences exist. We give in Table 4 the quasi-molec-

TABLE 4

Quasi-molecular ion series MPEG 750 + NaCl [$\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H Na}^+$]

m/z	n	Intensity
275.159	5	81
319.219	6	82
363.252	7	93
407.179	8	102
451.267	9	289
495.274	10	433
539.315	11	643
583.333	12	772
627.379	13	839
671.321	14	913
715.406	15	866
759 ^a	16	782
803.505	17	619
847.535	18	556
891.546	19	436
935.573	20	308
979.678	21	198
1023.658	22	130
		$\Sigma I = 8142$

^a Mass assumed to be 759.435 and used to calibrate mass scale.

ular ion series. The average deviation of the experimental m/z values from those calculated for the assumed atomic compositions is 23 mmu for the ions with m/z values between 451 and 935. The number average m/z value for the ions in Table 4 is 687, which corresponds to a number average weight of 664. The four values obtained for the number average molecular weight for this compound are 607 (^6Li), 644 (Na impurity), 597 (^7Li), and 664 (added Na). The average value is 628 and the relative standard deviation is 2.5%. This value is lower than the nominal value of 750.

Fragmentation is observed as with the lithiated samples and the most intense ion in the spectrum (other than the Na^+ ion) is that with m/z 45.042 ($\text{C}_2\text{H}_5\text{O}^+$). The four fragmentation series found in the lithiated samples are also found with added sodium and a summary of the fragmentation is given in Table 5. The QM ratio, R , for the spectrum is 0.50. This is to be compared with the corresponding value of 0.39 found with the lithiated MPEG 750 spectra. Kebarle [15] gives enthalpies of association of alkali ions with H_2O and the enthalpy change in the association of Li^+ with H_2O is $-34 \text{ kcal mol}^{-1}$, whereas that for the association of Na^+ with H_2O is $-24 \text{ kcal mol}^{-1}$. The enthalpy change for the association of Li^+ with four H_2O

TABLE 5

Fragmentation series observed in MPEG 750 + NaCl spectrum

Series	Mass range covered	Number of peaks	Summed intensity
QM-2 or QM-46	185-845	16	2496
QM-16	215-787	14	1802
QM-18	213-741	13	2223
QM-32	199-639	11	1618
			$\Sigma I = 8139$

molecules is $-97 \text{ kcal mol}^{-1}$ and the corresponding value for Na^+ is $-74 \text{ kcal mol}^{-1}$. One expects that the enthalpy of association of Li^+ with polyethylene glycol will similarly be greater than that for the association of Na^+ and if the association occurs in the gas phase under low enough density conditions that the energy released is not removed by collisions, more fragmentation will result from Li^+ addition than from Na^+ addition. The fact that we observe this kind of difference in fragmentation suggests that, indeed, the alkali ion addition occurring in fission fragment ionization mass spectrometry occurs in the gas phase. From a practical point of view, these results indicate that some control over the amount of fragmentation occurring may be exercised by an appropriate choice of additive ion.

Because the number average molecular weights derived from our mass spectrometric measurements of the MPEG 750 sample deviated appreciably from the nominal value stated by the supplier of the sample, methoxypolyethylene glycol samples with authentic, experimentally determined number average molecular weights were obtained from an established polymer characterization laboratory (see Experimental section). We determined the number average molecular weights of these samples using our mass spectrometric method. For the sample with authentic number average molecular weight 755, we made measurements with added $^7\text{Li}^+$, Na^+ , and Cs^+ ions. The molecular weight values obtained were 771, 725, and 771, respectively, the average of which is 756. This agreement indicates that the mass spectrometric method is not subject to systematic errors.

Lauryloxypolyethylene glycol [$\text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$] of nominal *M.W.* 1200 (LPEG 1200)

Spectra of this compound were taken with added $^6\text{LiCl}$, $^7\text{LiCl}$, and NaCl . The results obtained are completely analogous with those obtained with MPEG 750. A quasi-molecular ion series can be identified and we list the

TABLE 6

Quasi-molecular ion series LPEG 1200 + $^7\text{LiCl}$ [$\text{C}_{12}\text{H}_{25}\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H } ^7\text{Li}^+$]

m/z	n	Intensity
545.3	8	111
589	9	
633.3	10	169
677.4	11	71
721.3	12	82
765.5	13	143
809.5	14	172
853.5	15	167
897.5	16	176
941.6	17	221
985.6	18	213
1029.6	19	199
1073.7	20	177
1117.5	21	158
1161.7	22	144
1205.9	23	169
1249.8	24	149
1293.9	25	125
1338.0	26	123
1382.0	27	111
1426.1	28	84
1469.9	29	44
		$\Sigma I = 3008$

ions formed with $^7\text{LiCl}$ in Table 6. The number average m/z value resulting from these data is 1009, which corresponds to a number average molecular weight for the polymer sample of 1002. We give in Table 7 the four

TABLE 7

Fragmentation series observed in LPEG 1200 + $^7\text{LiCl}$ spectrum

Series	Mass range covered	Number of peaks	Summed intensity
QM-2 or QM-46	235-1424	28	3146
QM-170	155-1432	29	4845
QM-18	307-1232	21	2035
QM-186	139-1195	22	4780
			$\Sigma I = 14806$

fragmentation series observed in LPEG 1200 + $^7\text{LiCl}$. Two of the series are identical with those observed with MPEG 750 (QM – 2 or QM – 46 and QM – 18) and two are different but completely analogous. The losses of CH_4 and CH_3OH in the methoxy-containing MPEG 750 are replaced by losses of $\text{C}_{12}\text{H}_{26}$ and $\text{C}_{12}\text{H}_{25}\text{OH}$ in the lauryloxy-containing LPEG 1200. This behavior provides strong confirmation of the occurrence of reactions (1), (2) and (6) in MPEG 750 and analogously in LPEG 1200. The behavior with added $^6\text{LiCl}$ and NaCl is completely analogous. The number average molecular weights obtained with these two added salts are 938 and 982. Thus, the average of the three molecular weights obtained for our sample of LPEG 1200 is 974 with a relative standard deviation of 2%.

The values of the QM ratio, R , obtained on LPEG 1200 are 0.17, 0.16, and 0.28 for the spectra obtained with added $^6\text{LiCl}$, $^7\text{LiCl}$, and NaCl , respectively. These values are slightly less than half the values found with MPEG 750, which indicates that the amount of fragmentation increases as the length of the chain increases. However, with LPEG 1200 as with MPEG 750, the amount of fragmentation is greater in the spectra with added lithium ion than in that with added sodium ion.

Methoxypolyethylene glycol of nominal M.W. 2000 (MPEG 2000)

A spectrum of this compound was taken with added NaCl . A weak quasi-molecular ion series was identified, although the form of the distribution was not good. We list the ions and intensities in Table 8. The number

TABLE 8

Quasi-molecular ion series MPEG 2000 + NaCl

m/z	n	Intensity
1507	33	46
1551	34	47
1595	35	36
1639	36	41
1683	37	43
1727	38	
1771	39	36
1815	40	40
1859	41	34
1903	42	36
1947	43	32
1991	44	33
		$\Sigma I = 424$

average m/z value of this distribution is 1734, which corresponds to an average molecular weight of 1711, appreciably below the nominal value of 2000. Because of this difference, we again mass spectrometrically measured the number average molecular weight of a sample with a known molecular weight experimentally determined by the established polymer characterization laboratory. The mass spectrometric measurement was made with added Na^+ ions and the number average molecular weight obtained was 2025. The authentic value obtained using the hydroxyl number method was 2021. The form of the distribution of the QM ions in this measurement was approximately Gaussian and quite acceptable. The same four series which are observed with the other polymer samples are also observed with MPEG 2000 and are summarized in Table 9. The value of the QM ratio, R , for this polymer is 0.028, which shows that the fragmentation in MPEG 2000 is about 10 times more extensive than that in our polymer with nominal molecular weight 1200, which in turn is greater than that in our polymer with nominal molecular weight 750. This decrease of the relative intensity of QM with chain length is reminiscent of the decrease in the molecule-ion intensity observed in normal alkanes with electron ionization and this similarity may reflect the fact that high-energy processes seem to be involved in part in fission fragment ionization. In any event, our results indicate that fission fragment ionization will not be very useful for obtaining molecular weight distributions for polyethers with molecular weights much larger than 2000. However, it is clear that, for polyethers up to this size, useful information about molecular weight distributions and polymer identities (especially end-group identities) can easily be obtained with this method. One expects that information will also be obtainable for other types of polymers and the size of the polymers which can be measured effectively will depend inversely on their volatility (polarity).

TABLE 9

Fragmentation series observed in MPEG 2000 + NaCl spectrum

Series	Mass range covered	Number of peaks	Summed intensity
QM-2 or QM-46	317-1945	34	2752
QM-16	215-1931	38	3939
QM-18	213-1929	35	3757
QM-32	199-1959	38	4309
			$\Sigma I = 14757$

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