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International Journal of Mass Spectrometry 188 (1999) 121–130

International Journal of Mass Spectrometry

Gas phase conformations of synthetic polymers: poly (methyl methacrylate) oligomers cationized by sodium ions

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Received 22 June 1998; accepted 12 November 1998

Abstract

Gas phase conformations of a series of poly(methyl methacrylate) (PMMA) oligomers cationized by sodium ions were investigated experimentally and theoretically. Ion chromatography and molecular mechanics methods were used to measure the cross sections of Na^+(PMMA)3 to Na^+(PMMA)11 (i.e. from the 3-mer to the 11-mer). Collision induced dissociation (CID) of Na^+(PMMA)10 is also reported. The dominant fragment peaks in the CID spectrum are solely in the low mass-to-charge range and correspond to the loss of 1–2 monomer units from each end of the oligomer. The fragments also retain the Na^+ ion indicating that the ion interacts with both ends of PMMA. Molecular modeling of the Na^+(PMMA) oligomers support this finding. The calculations show that the lowest energy structures are U-shaped with Na^+ bound to multiple carbonyl oxygen atoms near both ends of the oligomer. The cross sections of these structures agree with those obtained from the ion chromatography experiments. Ion chromatography and molecular dynamics simulations also show that the cross sections are independent of temperature between 300 and 600 K, further supporting the indication that the Na^+ ion strongly binds to both ends of the oligomer. A mechanism for the surprising CID results is suggested. (Int J Mass Spectrom 188 (1999) 121–130)

Keywords: Conformations; Polymethyl methacrylate; Collision induced dissociation

1. Introduction

The notion that the structure and behavior of macromolecules are closely related is well known. Shapes and sequences of proteins, nucleic acids, and other biopolymers have been shown to impact significantly synthesis and recognition abilities [1,2]. Like their biological counterparts, synthetic polymers also exhibit a structure–performance relationship, although considerably less attention has been paid to them. The molecular structure of polymers plays a major role in influencing physical and mechanical properties like thermal degradation, moulding processes, or impact resistance [3].

Matrix assisted laser desorption/ionization (MALDI) [4] mass spectrometry has been successful in characterizing the structures of synthetic polymers because of its ability to vaporize these molecules intact. Besides its popular use as a means of measuring molecular weight distributions [5–7], MALDI has been used to identify the chemical nature and structure of the repeat units and end

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Dedicated to Brian Green for his many innovative contributions to mass spectrometry instrument development and for his tireless help in teaching us how to take advantage of them.

1387-3806/99/$20.00
PII S1387-3806(98)14287-2

groups [8–10]. This is generally achieved by resolving individual oligomers or by analyzing collision induced dissociation (CID) fragments. Although mass spectrometry relies on the sample being ionized, the cationizing agent (usually an alkali ion) also plays an important role in polymer characterization. Several studies have shown that the molecular weight distributions of poly (ethylene terephthalate) [11], poly (methyl methacrylate) [12], and poly(styrene) [13] vary with the cation used for ionization. The variance is believed to be due to larger cations interacting less favorably with the small oligomers than with the large ones thus creating an apparent shift in the molecular weight distribution to higher molecular weights.

Although these methods provide valuable information on the primary structures of polymers, very few studies have investigated the tertiary structures, or conformations, of these industrially important molecules. Polymers can have many different conformations because of easy rotations about single bonds but relatively few of them are energetically favorable. We would like to identify these conformations and examine the factors influencing the preference of one conformer over another.

To achieve this, our group has combined mass spectrometry with "ion chromatography" (IC) [14ab] to probe the details of the conformations of macromolecules. The main principle behind IC is that isomers with different geometric shapes have different collision cross sections and hence different mobilities when drifting through a buffer gas in a weak electric field. Various computational methods are then used to generate proposed structures for these isomers. The cross sections of these model structures are calculated and compared to those obtained from the IC experiment.

This method has been successfully used to probe the major structural types of carbon clusters and determine how these structures changed as a function of size [15abcd]. It has also been used to obtain detailed structural information on more flexible systems like crown ethers [16] and poly (ethylene glycol) (PEG) oligomers [17ab]. In the PEG system it was found that the polymer completely enveloped the cationizing metal ion with multiple oxygen atoms coordinating to the ion. Significant effort was put into these systems to determine the parameters required to obtain accurate structural information of large molecular ions [18abcd].

In this article we will discuss our results concerning the gas phase conformations of poly (methyl methacrylate) (PMMA) oligomers cationized by Na^+. PMMA is a commercially important polymer with a variety of applications from automobile light fixtures to contact lenses to kitchen sinks. We are interested in determining the preferred PMMA oligomer conformations and how the cation influences that conformation. Ion chromatography and molecular mechanics were used to measure the cross sections of Na^+(PMMA)3 to Na^+(PMMA)11. (In this notation the postscripts 3 and 11 refer to the values of *n* in

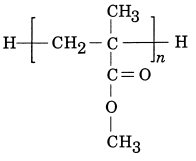


Diagram 1.

The Na^+ indicates that a sodium ion cationizes the oligomers.) CID was also applied to Na^+(PMMA)10 to provide additional structural information. Finally, a mechanism is suggested that accounts for both the relative intensity of metal ion formation and skeletal bond breaking in the CID spectrum.

2. Experimental

2.1. CID

The CID experiments were carried out on an Auto Spec 5000 orthogonal acceleration time of flight (oa-TOF) (Micromass, Manchester, UK) tandem mass spectrometer with a MALDI source [19,20]. PMMA samples were obtained from Polymer Laboratories and used without further purification. 10 mg/mL solutions of PMMA and the matrix, dithranol (1,8-dihydroxy-9[10H]-anthracenone), were prepared using 1,1,1,3,3,3-hexa-fluoro-iso-propanol (HFIP) as the solvent. Approximately 0.2 μL of NaI, dissolved in acetone, was applied

to the sample target and 0.5 μL of a 1:10 mixture of PMMA and dithranol applied on top of the salt.

Na^+(PMMA)*n* ions, formed in the MALDI source, were accelerated to 8 kV and mass selected with a double focusing sector mass spectrometer. The selected oligomer ions were then decelerated to 800 eV and focused into a collision cell containing Xe gas. The beam intensity was attenuated to approximately 70%. On average, this CID process corresponds to single conditions at this value of the attenuation of the ion beam. Ions exiting the cell were mass analyzed by the oa-TOF. Because of the pulsed nature of MALDI, a voltage pulse was applied to the oa-TOF and timed to coincide with the time that the packet of precursor and fragment ions was passing through the oa chamber. Fragment ions were detected by a microchannel plate detector and the data processed by OPUS software (Micromass, Manchester, UK).

2.2. Ion chromatography

The details of the IC experimental setup have been previously described [21] so only a brief outline will be given here. Approximately 50 μL of NaI, dissolved in methanol, was initially applied to the sample target. 100 μL of a 1:6 mixture of PMMA and dithranol, dissolved in HFIP, was applied on top of the salt and dried. Ions were formed in a specially designed MALDI ion source [18a], accelerated to 5 kV, and mass selected with a reverse geometry, sector mass spectrometer. The mass selected oligomer was then decelerated to a few electron volts and injected in 1–5 μs pulses into a variable temperature drift cell containing 2–3 Torr of He gas. (The temperature of the cell can be varied from 80 to 600 K.) The ions drift through the cell under the influence of a weak electric field, pass through a quadrupole mass filter and are detected using standard ion counting techniques. The time it takes for the ions to drift through the cell is measured to yield an arrival time distribution (ATD). Ions with different drift times appear as different peaks in the ATD. This drift time depends on the mobility of the ion which is inversely proportional to the ion's collision cross section [22]. A longer drift time corresponds to a smaller mobility and a larger cross section.

2.3. Molecular modeling

Because of the relatively large size of the ions, AMBER 4.0 molecular mechanics/dynamics programs [23] were used to generate proposed structures for M^+(PMMA)3 to M^+(PMMA)11 (M = Li, Na, K, Rb, and Cs). A series of annealings and energy minimizations [24] generated 100–150 low energy structures for each oligomer size. The angle averaged collision cross section of each structure was calculated using previously developed Monte Carlo techniques [15,18abcd]. These cross sections were then compared to those obtained from the ion chromatography experiments to check the validity of the theoretical structures. In addition, AMBER 4.0 was used to calculate approximate binding energies of the alkali ions to the oligomers and CID fragments. In these calculations, energies of minimized structures with the cation attached and remote from the annealed oligomer/fragment were obtained. The binding energies reported are the differences in these numbers.

3. Results/discussion

3.1. CID

Fig. 1 shows the CID spectrum of Na^+(PMMA)10 along with a fragmentation scheme of the two main series of peaks labeled A and B. The spectrum is dominated by fragments in the low mass range (*m*/*z* 100–250) which have the Na^+ ion still attached. The fragments appear to arise from the direct cleavage of each end of the oligomer as shown in the fragmentation scheme. These results point out two interesting aspects of the Na^+(PMMA) oligomer. They not only indicate that the Na^+ ion interacts with both ends of the oligomer, but suggest that the metal ion may bind exclusively with the ends of the oligomer. In contrast, a CID spectrum of Na^+(PEG)15 [25]

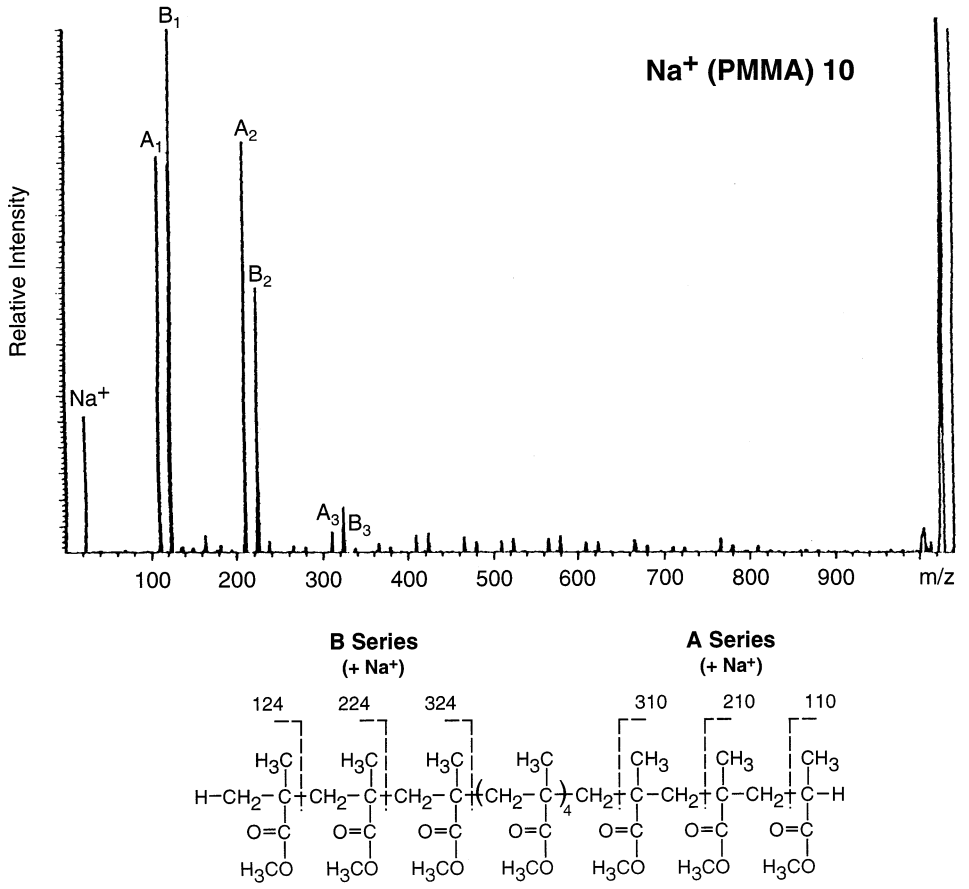


Fig. 1. CID spectrum of Na^+(PMMA)10 along with a fragmentation scheme for the two main series of peaks labeled A and B.

showed intense fragment peaks corresponding to the loss of 1–12 monomer units. As previously mentioned, molecular modeling of Na^+(PEG) oligomers indicated that the Na^+ ion is completely surrounded by the oligomer and coordinated to as many oligomer oxygen atoms as possible (up to 8 for Na^+) [18abcd]. With the losses of only 1–2 monomer units for Na^+(PMMA)10, the Na^+ ion appears to be preferentially bound to only the ends of the oligomer. This favored binding site appears to extend to larger oligomers. A CID study of the 30-mer [26] and 40-mer [25] both showed intense fragment peaks from each end of the oligomer exclusively in the low mass range, corresponding to the loss of only 1–6 monomer units. These results, along with those obtained for PMMA oligomers with different end group structures [25], suggest that the nature of the end groups on PMMA may have a substantial role in determining how well the cation binds to the oligomer (that could influence molecular weight distributions) and in determining the final conformation of the oligomer (that could affect the polymer's physical properties).

3.2. Molecular modeling

Molecular modeling of the Na^+(PMMA) oligomers corroborate the CID results. The lowest energy structures for each oligomer size (3- to 11-mer) have the same basic features. The oligomer is somewhat U-shaped with the Na^+ ion coordinated to multiple

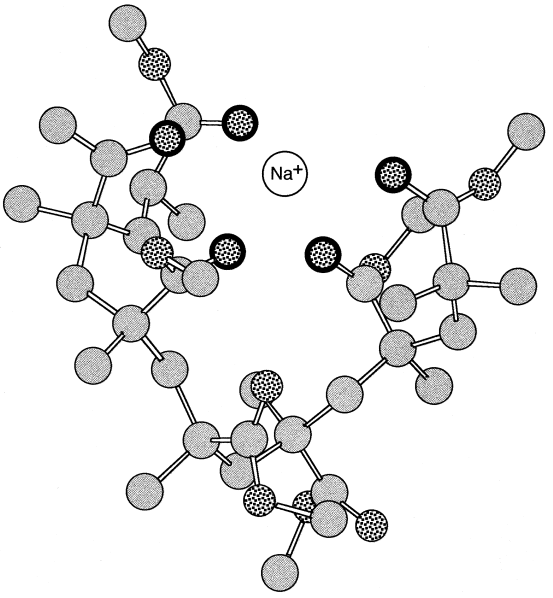


Fig. 2. Lowest energy structure of Na^+(PMMA)7 (see text). Carbon atoms are shown in gray and oxygen atoms are shown with dots (those that are less than 2.5 Å from the Na^+ ion are highlighted). Hydrogen atoms are omitted for clarity.

carbonyl oxygen atoms on both ends of the oligomer. This conformation is shown for the 7-mer in Fig. 2. In this case, the Na^+ ion coordinates to five oxygen atoms (three on one end of the oligomer and two on the other end). For the 9- and 11-mer, the Na^+ ion coordinated to six oxygen atoms (three on each end).

These calculations were repeated using Li^+, K^+, Rb^+, and Cs^+ as the cation. The structures were similar to the sodiated ones with six as the maximum number of carbonyl oxygen atoms coordinated to the alkali ion for the larger oligomer sizes. In each instance the metal ion binds to both ends of the oligomer and adjacent carbonyl oxygens.

3.3. Ion chromatography

To determine whether these theoretical structures are accurate models of the actual oligomers, ion chromatography experiments were employed. The arrival time distributions (ATDs) of Na^+(PMMA)5, Na^+(PMMA)7, and Na^+(PMMA)9 at 300 K are shown in Fig. 3. As can be seen in Fig. 3, the average

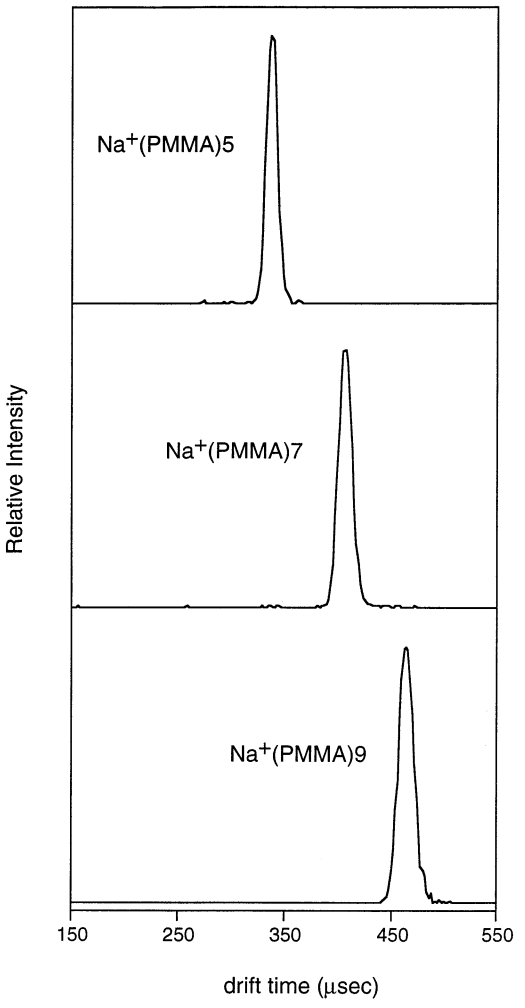


Fig. 3. Arrival time distributions (ATDs) of Na^+(PMMA)5, Na^+(PMMA)7, and Na^+(PMMA)9 at 300 K. The drift time increases as the oligomer size increases consistent with an increase in cross section. A single peak is observed for all oligomers at all temperatures studied.

drift time increases with increasing oligomer size consistent with an increase in cross section. For each oligomer, only one peak was observed in the ATD and it could be fitted with a theoretical transport model [22]. This indicates either one isomer exists or multiple isomers are present that have very similar cross sections. In studies on carbon clusters [15abcd], isomers with substantially different cross sections appeared as multiple peaks in the ATD.

The cross sections of the PMMA oligomers can be

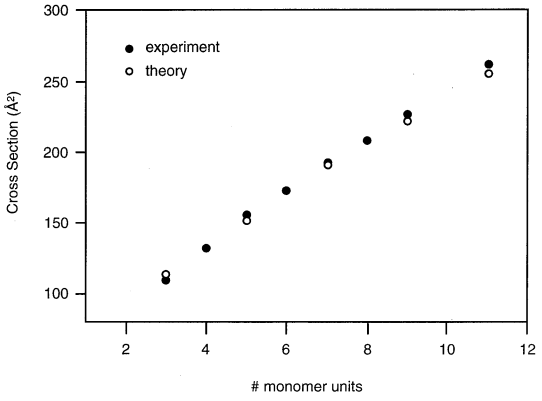


Fig. 4. Collision cross section vs. the number of monomer units for Na^+(PMMA)*n* at 300 K. The solid points are from the experimental ATDs. The open circles are from the theoretical structures calculated by molecular mechanics/dynamics.

determined from the ATDs. Fig. 4 shows the cross section as a function of the number of monomer units for Na^+(PMMA)3 to Na^+(PMMA)11 at 300 K. The cross section increases linearly with oligomer size, as is expected for ions that are structurally similar [15c]. Also shown in Fig. 4 are the cross sections of the calculated structures. The theoretical cross sections agree reasonably well with experiment (~2% difference) lending support to the validity of the calculated structures.

The experimental temperature dependence of the cross sections for Na^+(PMMA)5, Na^+(PMMA)7, and

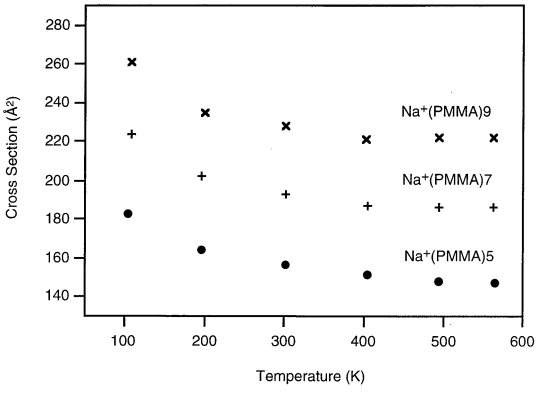


Fig. 5. Collision cross section vs. temperature for Na^+(PMMA)5 (closed circle), Na^+(PMMA)7 (plus sign), and Na^+(PMMA)9 (cross).

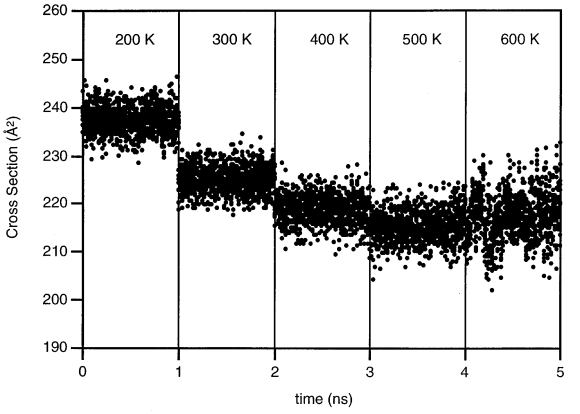


Fig. 6. Theoretical cross sections vs. temperature for the lowest energy structure of Na^+(PMMA)9 from molecular dynamics simulations. The average cross section remains essentially constant for temperatures above 300 K. The deviation in the cross sections increases at higher temperatures with a maximum deviation of 10–15 $Å^2$ at 600 K.

Na^+(PMMA)9 is shown in Fig. 5. The increase in cross section at temperatures below 200 K is due to the attractive part of the potential between the Na^+(PMMA) ion and the He collision gas and has been extensively studied [18abcd]. However, the cross sections are independent of temperature above 300 K. A study of similar sized Na^+(PEG) oligomers showed a slight increase in the cross section in the temperature range of 300–600 K [18ab]. This increase was attributed to the unraveling of the part of the oligomer that was not directly in contact with the Na^+ ion. The lack of dependence of the cross sections on temperature observed for Na^+(PMMA)*n* indicates that these oligomers cannot easily expand as the temperature increases. This result can be accounted for if both ends of the oligomer are strongly bound to Na^+. The ion can effectively act as an anchor and limit the amount of thermal motion the oligomers can undergo.

Molecular dynamics simulations of Na^+(PMMA)*n* are consistent with this interpretation. The simulations were run for 5 ns starting at 200 K and increasing to 600 K in 1 ns increments. Structures were saved every 0.5 ps and their cross section calculated. Fig. 6 shows the cross sections as a function of time and temperature for Na^+(PMMA)9. The spread in cross sections

Table 1
Comparison of CID intensities as a function of alkalating metal ion with metal ion binding energies for the 9-mer of PMMA

	Experiment[a]		M^+ binding energy (kcal/mol)[b]				
M^+	A_1^+/M^+	B_1^+/M^+	9-mer	B_1	A_1	A_3	A_5
Li	>10[c]	>10[c]	139	36	34		
Na	0.95	0.85	118	28	26	66	87
K	···	···	96	23	21		
Rb	0.059	0.11	92	21	19		
Cs	0.014	0.057	84	19	17		

[a] See Fig. 1 for definitions of the A and B ions. The ratios given are obtained from the intensities of the peaks in the CID spectrum in [26].
[b] Calculated using the AMBER 4.0 suite of programs [23].
[c] These numbers are estimates since Li^+ intensities could not be accurately measured.

at 200 K is primarily because of the statistical nature of the cross section calculations. The cross section of each structure is determined from averaging hundreds of random orientations about the oligomer's center of mass. The orientational sampling is continued until the cross section converges to 1%. At 600 K, a larger spread in cross section is observed that arises from the thermal expansion of the oligomer. However, the maximum variance in the cross sections at 600 K is only 10–15 $Å^2$. For a similar size Na^+(PEG) oligomer, the maximum variance was ~30 $Å^2$ at 600 K, indicating that the PEG oligomer is less constrained than PMMA even though eight oxygen atoms are coordinated to the Na^+ ion in the PEG system.

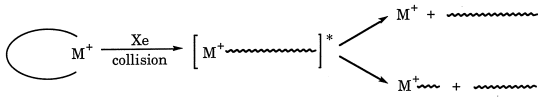
3.4. Modeling of CID fragments

It was previously observed that loss of metal ion became a competitive pathway to backbone fragmentation in the CID of various PMMA oligomers [26]. For the smaller oligomers, significant, but not dominant loss of Na^+ is observed (see Fig. 1 for the 10-mer CID data). However, loss of Rb^+ or Cs^+ is the dominant fragmentation pathway in the smaller size range [26] when these metal ions cationize PMMA. At larger oligomer sizes, like the 30-mer, Na^+ loss becomes negligible but Cs^+ loss is still the major fragmentation pathway [26]. This effect can be clearly seen in the data in Table 1 for the 9-mer of PMMA. (The 9-mer data are similar to the Na^+ cationized 10-mer data in Fig. 1 where loss of 1 or 2 monomer units dominates the backbone CID pattern). While Na^+ loss is approximately as likely as formation of A_1^+ or B_1^+ ions, loss of Rb^+ or Cs^+ totally dominate their CID spectra.

Two related questions arise. First, why do the heavier alkali ions detach from the PMMA oligomer and oligomer fragments much more readily than the lighter metal ions? Second, why do small oligomer fragments so strongly dominate the backbone fragmentation part of the spectrum? The answer to the first question appears to be related to the binding energy of the alkali ion to PMMA. For the parent 9-mer ion, Li^+ is bound by 139 kcal/mol, Cs^+ by only 84 kcal/mol (Table 1). Hence, once energized by collisions, Cs^+ loss is much more energetically feasible than Li^+ loss.

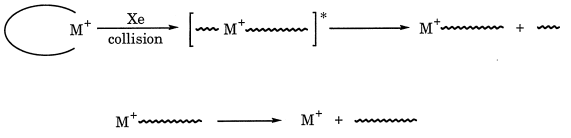
The data indicate that metal ion loss and backbone fragmentation are competitive processes, and any mechanism must allow for this fact. If we assume the stable M^+(PMMA)*n* oligomers have the quasicyclic structure indicated by the molecular mechanics and ion chromatography studies, then two possible general schemes can be put forth to explain the CID data.

First, upon collisional activation the cyclic structure can simply open up, leaving the metal ion attached to either end of the oligomer. From this configuration the metal ion can dissociate or backbone cleavage can occur. This possibility is shown in Scheme I.



Scheme I.

The second possibility is that collisional activation first severs the PMMA backbone of the quasicyclic species leaving the metal ion bound to two fragments of variable length. This species would then dissociate by loss of one of the PMMA neutral fragments. This possibility is shown in Scheme II.



Scheme II.

We will discuss Scheme II first. Two difficulties arise with this scheme. First, there is no facile way to lose the metal ion. In this scheme M^+ could be formed only in a sequential process where first a neutral fragment is lost and then M^+ dissociates from the remaining fragment. Although sequential processes can, and do, occur in CID studies, they usually do not result in major or dominant product pathways.

The second problem with Scheme II is in the formation of the metal cationized PMMA fragments. The data (Fig. 1) indicate a very strong preference for one or two MMA units attached to M^+. However, in a competitive loss scenerio the metal ion would almost certainly remain with the larger fragment because of energetic reasons. As shown in Table 1 for the A_n sequence ions, A_5 ions are 60 kcal/mol more stable than A_1 ions yet A_1 ions are favored in the CID spectrum by about a factor of 20. Hence, Scheme II is a very unlikely mechanism.

Scheme I shows more promise. Once the quasicyclic structure opens, competitive loss of M^+ or a backbone neutral fragment can occur, presumably based at least in part on the relative energetics of the two processes. One question still remains. Why do A_1, B_1, and A_2, B_2 ions dominate the CID pattern even though these are the least thermodynamically stable? The answer must be that the dissociation is charge induced, with the metal ion preferentially inducing backbone cleavage in close proximity to it. This kind of chemistry has been invoked to explain CID patterns of peptides cationized by alkali ions [27ab,28].

A second condition is also required for formation of energetically unfavored products. Once the fragmentation occurs, the products must permanently separate and not reform an ion–neutral complex with the large neutral fragment. If such a complex formed, the metal ion would be transferred and A_n, B_n fragments with large values of *n* observed. One possible mechanism that is consistent with the data is fragmentation from a M^+(PMMA)*n* complex that has highly excited backbone bending modes. When a small fragment is cleaved it leaves with high velocity in order to conserve angular momentum. (This same mechanism is at play in the childhood game of crack-the-whip.) The high bending excitation would be a natural consequence of the initial ring opening step upon collisional activation.

In summary, Scheme I appears to be able to explain the data given reasonable assumptions about the detailed mechanism, and Scheme II cannot explain the data. A more quantitative accounting of the various product distributions as a function of metal ion and oligomer size is not possible at this time due to lack of information on both thermodynamic and kinetic parameters for the various reaction channels.

4. Summary

Conformational information for Na^+(PMMA)*n* oligomers was obtained using ion chromatography and CID experiments and molecular mechanics/dynamics calculations. The CID experiments indicate that the Na^+ ion binds to both ends of the oligomer. Molecular mechanics calculations support this claim. The lowest energy structures for Na^+(PMMA)3 to Na^+(PMMA)11 have Na^+ bound to multiple carbonyl oxygen atoms near the two ends of the oligomer. A maximum of six oxygen atoms, three from each end of the oligomer, were observed to coordinate to the Na^+ ion. The cross sections of the theoretical structures are in good agreement with those obtained from ion chromatography experiments. IC experiments also show that the

cross sections are independent of temperature between 300 and 600 K giving further support that Na^+ binds strongly to both ends of the oligomer.

Molecular dynamics calculations were also carried out for $M^+ = Li^+$, K^+, Rb^+, and Cs^+. These metal ions exhibited binding to PMMA oligomers similar to Na^+, i.e. only to the end groups. Metal dependent binding energies increased in the order $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$. This information was used along with the CID product distributions to establish an overall mechanism for fragmentation of the collisionally activated M^+(PMMA)*n* oligomers.

One of the implications of this study is that the nature of the end groups on PMMA can have a significant influence on how well the cation binds to the oligomer. The quality of this binding can have a direct influence on molecular weight distributions measured by MALDI and how they vary with metal ion. They can also alter conformational preferences of the oligomers. Both of these factors can affect physical properties of the polymer. Additional studies on PMMA with different end groups are planned, as are extensions of these ideas to other types of polymers.

Acknowledgements

The support of the Air Force Office of Scientific Research under grant nos. F49620-96-1-0033 and F49620-96-1-0257 and in part the National Science Foundation under grant no. CHE-9729146 is gratefully acknowledged. The authors would like to thank Martin R. Green and Robert H. Bateman (Micromass UK Ltd.) for help with the MALDI-CID experiments. We also want to extend our thanks to Brian Green for his many contributions to mass spectrometry as a discipline and to our research groups in particular. Congratulations, Brian, on a great career.

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