Characterization of Poly(Ethylene Glycol) Esters Using Low Energy Collision-Induced Dissociation in Electrospray Ionization Mass Spectrometry

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A method of characterizing polyglycol esters, an important class of industrial polymer, has been developed using electrospray ionization ion trap mass spectrometry (ESI ITMS). The fragmentation behavior of polyglycol esters is found to be different from that of polyglycols whose functional end groups are linked to the polymer chain via ether bonds (i.e., polyglycol ethers). The fragmentation pattern of an oligomer ion generated by low-energy collision-induced dissociation is strongly dependent on the type of cation used for ionization. It is shown that structural information on the polymer chain and end groups is best obtained by examining the fragment ion spectra of oligomers ionized by ammonium, alkali, and transition metal ions. The application of this method is demonstrated in the analysis of two surfactants based on fatty acid methyl ester ethoxylates. (J Am Soc Mass Spectrom 2002, 13, 888–897) © 2002 American Society for Mass Spectrometry

Tandem mass spectrometry using either matrix-assisted laser desorption ionization (MALDI) or electrospray ionization (ESI) is being developed as a tool for polymer structural characterization [1–16]. We are particularly interested in characterizing functional polyglycols, including poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), and their copolymers [12–19]. Structural characterization of this type of polymer is important because polyglycols are widely used in industry with their properties strongly depending on not only molecular weights, but also structures and compositions. Recently, polyglycols have also been increasingly used in biotechnical and biomedical applications such as the development of slow releasing drugs [20, 21]. Traditionally, polyglycols were thought to be difficult to fragment in low-energy CID tandem MS. In our recent work, we demonstrated that lithium and transition metal ions could form adduct ions with polyglycol in ESI, and these adduct ions could readily undergo fragmentation [15, 16]. The resulting fragment ion spectra were very informative for the structural characterization of polyglycol. Our previous study was focused on alcohol ethoxylates whose end-groups are linked to polyglycol chains via ether-type C–O bonds (i.e., polyglycol ethers). The results generated therein were compared to earlier studies of the same type of polyglycols employing fast atom bombardment (FAB) MS/MS by Latimer and coworkers [22–25].

Poly(ethylene glycol) ester, especially fatty acid methyl ester ethoxylate (FAMEE), is another class of polyglycol which can be used as an alternative to alcohol ethoxylates in many industrial applications. With varying alkyl chain lengths in the fatty acid moiety, a wide range of hydrophilic lipophilic balance (HLB) values can be achieved to suit different applications [14]. They are extensively used as non-ionic bases for cosmetics and pharmaceuticals, non-ionic emulsifiers for vegetable and mineral oils, thickening agents for creams, anti-static agents for plastics, and non-ionic surfactants. Despite active MS study on alcohol ethoxylates [12–19, 22–62], the literature on ester ethoxylates is scarce [5, 16, 63].

In this work, we report a method of generating low energy CID mass spectra of PEG esters that can be used for structural characterization. We demonstrate herein that, with the proper choice of cationization reagents in ESI, the fragmentation behavior of these polymer ions can be altered to produce desired information. For example, the end group moieties can be lost as neutrals during fragmentation, providing mass information of the end groups. Under a different experimental condition, they can form product ions, offering the possibility for further tandem mass spectrometric analysis for direct structural elucidation. In addition, it is shown that in-source fragmentation can be purposely introduced to improve the quality of subsequent MS/MS spectra. Finally, the ESI CID MS/MS method is dem-

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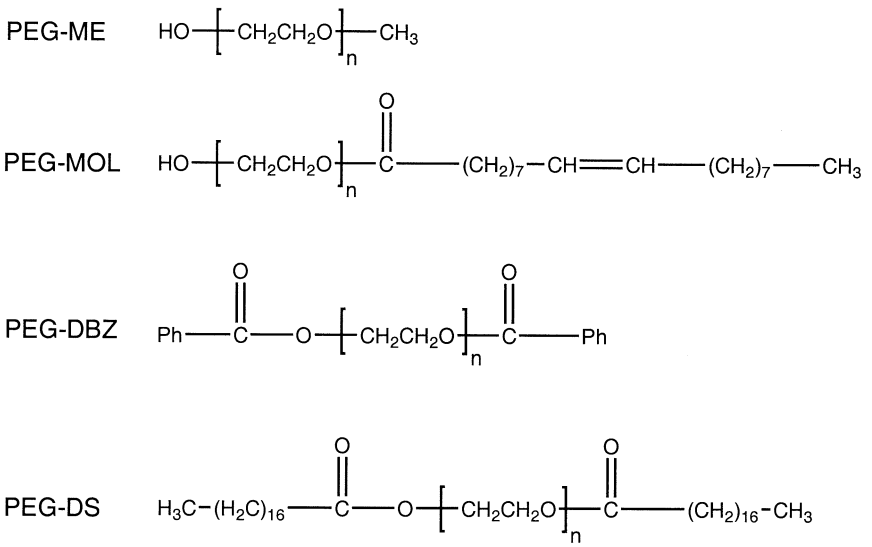


Scheme 1. Abbreviations and chemical structures of the PEG esters used in this study.

onstrated to be useful for characterizing two fatty acid methyl ester ethoxylates.

Experimenntal

Materials and Reagents

Poly(ethylene glycol) methyl ether (PEG-ME) (M_n ca. 550), poly(ethylene glycol) dibenzoate (PEG-DBZ) (M_n ca. 410), and poly(ethylene glycol) monooleate (PEG-MOL) (M_n ca. 460) were from Aldrich Chemical Co. (Milwaukee, WI). Poly(ethylene glycol) distearate (PEG-DS) (M_n ca. 930) was obtained from an industrial research partner (a small amount of this sample can be obtained from the authors). The structures of these samples are shown in Scheme **1**. All samples were analyzed without purification. Ammonium acetate, sodium chloride, lithium chloride, silver nitrate, cobalt chloride, and cupric nitrate were obtained from either Aldrich or Fisher and used as received. High performance liquid chromatograph (HPLC) grade methanol was obtained from Sigma (Milwaukee, WI). Distilled water was from a Milli-Q UV plus ultra-pure system (Millipore, Mississauga, ON).

ESI MS and MS/MS

All salts were dissolved in water at a concentration of 0.1 M. The analyte solution was prepared by mixing PEG stock solution, 10% (vol/vol) cationization reagent solution and appropriate amount of water/methanol (volume ratio 1:1) mixture to make the final PEG concentration of 100 μM.

All MS experiments were carried out in a Bruker/Agilent Esquire-LC Ion Trap LC/MS^n system. Sample solution was infused into the electrospray interface by a syringe pump (Cole-Parmer Instrument Co., Vernon Hills, IL) at a flow rate of 10 μl/min. Mass spectra were acquired over the mass range *m/z* 50–2200. Each spectrum was the result of an integration of the raw data for at least 1 min to ensure the correct isotope patterns were reflected. All data were reprocessed using the Igor Pro Software package (WaveMetrics, Lake Oswego, OR) without background subtraction.

Results and Discussion

Differentiation of PEG Ethers and PEG Esters

Despite the evident end group difference between PEG-ME and PEG-MOL, the ESI spectra (data not shown) of both samples show the typical PEG mass distributions with adjacent peaks separated by 44 Da, corresponding to the mass of the repeat unit, ethylene oxide. No detailed structural information with regard to their end groups can be revealed. However, the MS/MS spectra (Figure 1) depict totally different scenarios for the two samples. Figure 1a displays the characteristic

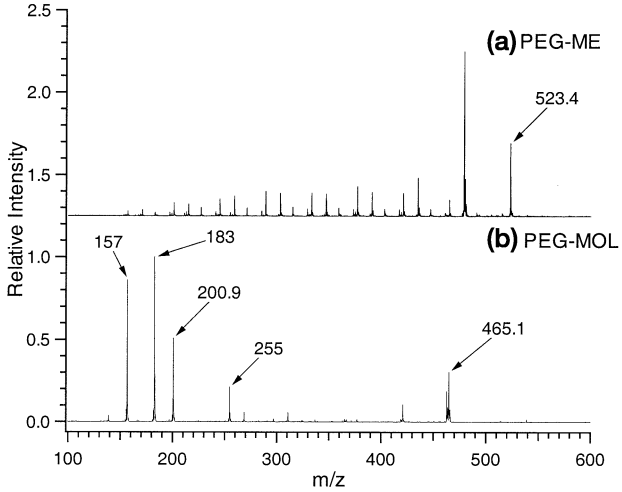


Figure 1. ESI MS/MS spectra of PEGs with Li^+: (**a**) PEG-ME, and (**b**) PEG-MOL.

fragmentation pattern of PEG ethers [15]. Briefly, consecutive losses of repeating units form the major product ion series. In the case of PEG-MOL (Figure 1b), as will be illustrated in detail in a later section, the major fragments are the results of the losses of end groups and their derivatives. Figure 1 illustrates that PEG ethers and PEG esters behave differently under low energy CID conditions. Thus, these two classes of PEGs can be readily differentiated by a simple MS/MS experiment.

End Group Elucidation for PEG Dibenzoate and Related Issues

A series of ESI mass spectra of PEG-DBZ (spectra not shown) were obtained using different cationization reagents, including Na^+, Li^+, NH_4^+, Ag^+, Co^{2+}, and Cu^{2+}. The trend of ionization efficiency with these cations, judged by the signal-to-noise (S/N) ratios, agrees with that observed in the case of PEG-ME [15]. In short, Li^+ and Na^+, among all, provide the most efficient ionization without in-source fragmentation. NH_4^+ and Ag^+ also generate clear spectra, but with slightly lower S/N ratios. Both divalent transition metal ions, Co^{2+} and Cu^{2+}, provide complex and somewhat different spectra. In the case of using Co^{2+}, both $[\alpha\text{-EO}_n\text{-}\omega]CoCl^+$ and $[\alpha\text{-EO}_n\text{-Co}]^+$ (α and ω denote the end groups and EO represents ethylene oxide) were identified, in which the oxidation state of Co remains +2. It is also noted that, the oxidation state of copper is +1 in $[\alpha\text{-EO}_n\text{-}\omega]Cu^+$, although $Cu(NO_3)_2$ was used in the sample preparation. Gianelli et al. [64] showed that Cu(II)→Cu(I) reduction could take place by Cu(II)–ligand complex transferring an electron to solvent methanol in the gas phase. Although there is the possibility that Cu(I) impurity present in $Cu(NO_3)_2$ might contribute to the formation of $[\alpha\text{-EO}_n\text{-}\omega]Cu^+$, more likely the Cu(II) in $Cu(NO_3)_2$ is reduced to Cu(I) in $[\alpha\text{-EO}_n\text{-}\omega]Cu^+$ during ESI. The issue of metal ion reduction in the ESI of polymeric materials will be discussed in a future publication (Talat et al., to be submitted).

Figure 2 shows the MS^2 and MS^3 spectra of sodiated PEG-DBZ. The annotations of the peaks are shown in Scheme **2**. In both spectra, neutral loss of 122 Da results in the main product ions, namely, m/z = 347 in Figure 2a and m/z = 225 in Figure 2b. This neutral loss is attributed to the end group, benzoic acid. In our early study on PEG-ME, no MS/MS spectra were obtained for sodiated species [15]. This was ascribed to the weak electrostatic PEG-Na^+ interaction. The applied collision energy was dissipated preferentially by breaking up this interaction, rather than the PEG backbones. Our results on PEG-DBZ suggest that the ester linkage is even weaker than the PEG-Na^+ interaction. These linkages provide a new energy release channel, hence, a new fragmentation pathway.

Another relevant comparison is the different fragmentation behavior of sodiated PEG-DBZ under high- and low-energy CID conditions. The high energy CID

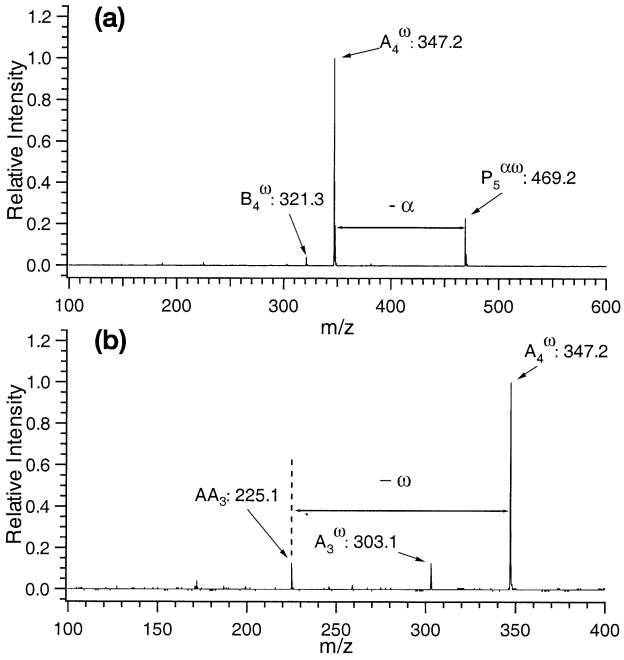
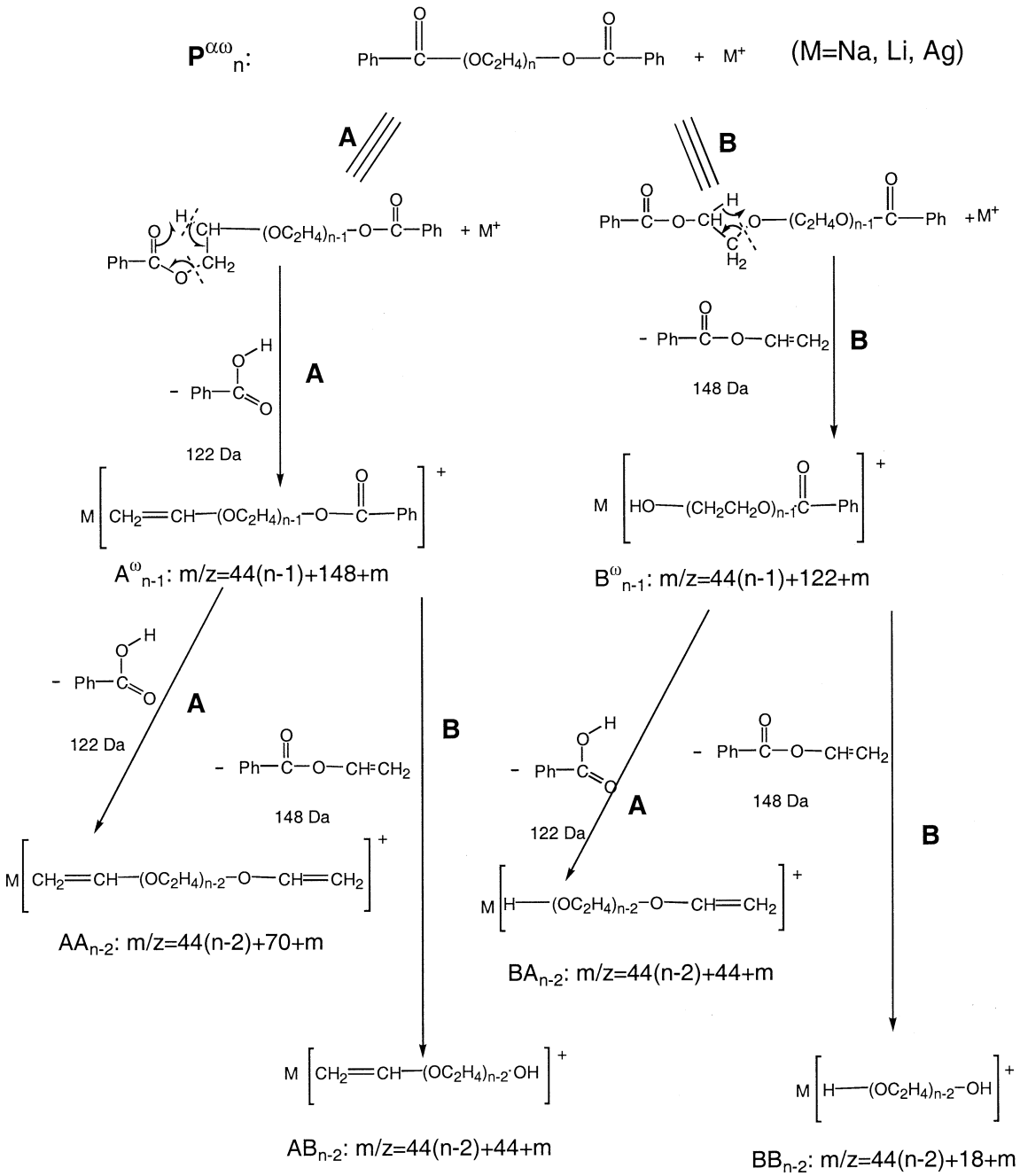


Figure 2. (**a**) ESI MS/MS spectrum of PEG-DBZ pentamer with Na^+ at m/z = 469.2. (**b**) ESI MS^3 spectrum of the product ions at m/z = 347.2 from (**a**).

spectrum of PEG-DBZ contains peaks originating from both end groups and repeating units [5]. However, the end group fragments appear concurrently with those from the internal breakage of repeating units in the low mass region. To distinguish these two types of product ions requires careful interpretation. This lack of specificity may impose challenges in the identification of unknown samples. In the case of low energy CID, a much simpler and more straightforward fragmentation spectrum is generated. However, the information obtained from such spectra is very limited. Only the end group mass can be obtained in the current case of using sodium ion as the cationization reagent.

In light of our early study using Li^+ and transition metal ions to enable fragmentation of PEG ethers [15], a series of experiments using different cations have been performed, with a hope that the resulting MS/MS spectra can provide enriched information on end groups as well as repeating units. Figure 3 shows the MS^2 and MS^3 spectra of lithiated PEG-DBZ. As can be seen, Figure 3a resembles Figure 2a, in which neutral losses of benzoic acid (mass 122 Da) and ethylene benzoate (mass 148 Da) result in the major product ions. However, peaks resulting from consecutive losses of repeating units (i.e., A_n^{ω} series, m/z 331, 287, 243, 199, 155) were observed in Figure 3b, which were not observed in Figure 2b.

Similar spectra were obtained by using Ag^+ (Figure 4). In addition to the improved information content, there are at least two additional advantages of using Ag^+ as the cationization reagent. First, the fragmentation products are shifted towards higher mass, as peaks below m/z 100 are often difficult to obtain in low energy



Scheme 2. Proposed fragmentation pathways for PEG-DBZ with different metal ions.

CID in the ion trap mass spectrometer that has a low-mass cut-off point. The second advantage is that the unique isotope pattern of silver will aid in data interpretation. For example, there is a peak at *m/z* 149 in Figure 4b. Unlike all the other product ions present in the spectrum, this peak does not contain silver, judged by its isotope pattern (see inset of Figure 4b), indicating that this peak is very likely from an internal fragmentation. The implication of this product ion will be discussed in more detail later. It is noted, however, that using Ag^+ would split the ion signals between the two isotopes, and therefore, reduce the overall detection sensitivity. Scheme **2** shows the fragmentation pathways for [PEG-DBZ]M^+ (M=Na, Li, and Ag). A brief description of the nomenclature and mechanism is as follows. α and ω represent two end groups. In the case of PEG-DBZ, α=ω=benzoyl group. Pathway **A** is a McLafferty rearrangement with neutral loss of benzoic acid (mass 122 Da). Pathway **B** involves the neutral loss of ethylene benzoate (mass 148 Da) via a four-member ring intermediate. The product ions resulting from pathways **A** and **B** are identified as **A** and **B** series, respectively. Similarly, ions identified as **AB** series are those resulting from pathways **A** and **B** in a tandem

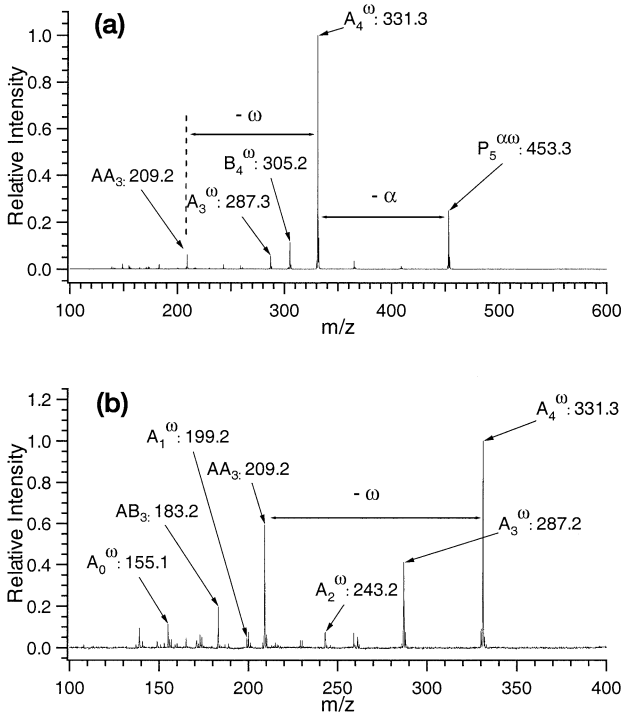


Figure 3. (**a**) ESI MS/MS spectrum of PEG-DBZ pentamer with Li^+ at *m/z* = 453.3. (**b**) ESI MS^3 spectrum of the product ions at *m/z* = 331.3 from (**a**).

manner. The subscripted number denotes the number of the remaining repeating units in the structure, and the superscripted Greek letter signifies the remaining end group. In the mass calculation, ***m*** represents the mass of the involved metal ion.

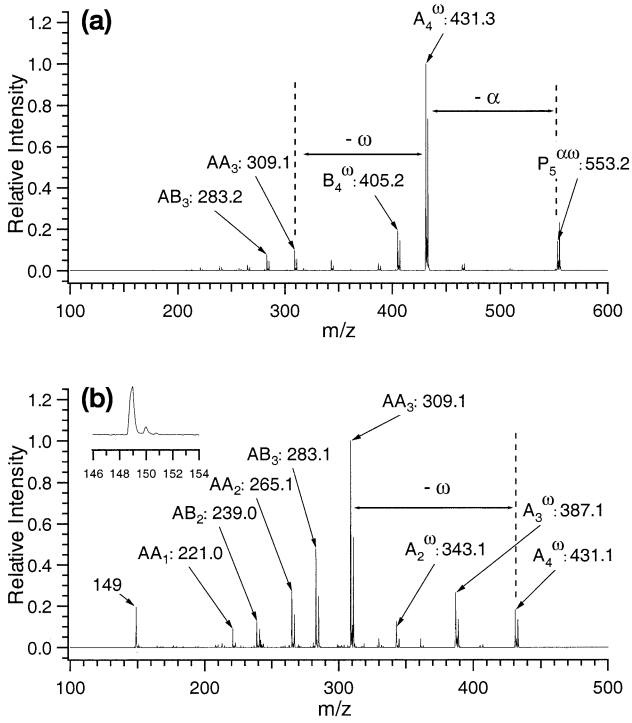


Figure 4. (**a**) ESI MS/MS spectrum of PEG-DBZ pentamer with Ag^+ at *m/z* = 553.2. (**b**) ESI MS^3 spectrum of the product ions at *m/z* = 431.1 from (**a**).

Based on Scheme **2**, the observation of the losses of repeating units by using Li^+ and Ag^+, but not Na^+, can be well explained within the context of our early studies on PEG ethers [15]. The parent ions in all MS^3 spectra (Figures 2b, 3b, 4b) are PEGs containing both ester and ether end groups (i.e., $\mathbf{A}_n^{\omega}$ series). The subsequent fragmentation is still dominated by pathway **A** and **B** from the ester end. However, the PEG-lithium or -silver, but not -sodium, adducts also dissociate from the ether end, in a manner similar to the PEG-ME metal ion adducts, resulting in the observed repeating unit cleavages.

Thus far, we have analyzed the product ions resulting from the neutral loss of end groups, but not any ions containing end groups. This is not sufficient for the end group structure elucidation. Recall that in Figure 4b, the peak at *m/z* 149 is postulated to contain the end group moiety. If, indeed, this ion has the proposed structure, fragmentation on this ion will generate direct end group structural information. Unfortunately, the signal intensity of this ion in the MS/MS spectrum is low. No meaningful MS^3 spectrum could be obtained.

This actually exemplifies one common problem encountered in MS^n study using ion trap. In a conventional ion trap system, the ions of interest are accumulated concomitantly with all other ions that include interfering ions, if any, from the preceding MS/MS stage. If the ions of interest are present at low yield, they often cannot be accumulated to a sufficient number, without causing space charge effect, to endure the next isolation/dissociation stage. Thus an ion trap MS, in principle, has the capability of multiple MS/MS (i.e., MS^n); but in practice, high order MS/MS experiments can be quite difficult.

To circumvent this problem, experiments have been carried out from the following two aspects: (a) to exclude the interfering ions by chemical means, and (b) to increase the ion yield from the previous stage using a different mode of operation. Figure 5a illustrates the use of NH_4^+ to enable fragmentation of the ions at *m/z* 149. Unlike all the metal ions we have used, employing NH_4^+ generates a rather simple MS/MS spectrum with only two product peaks. The peak at *m/z* 447 corresponds to the loss of NH_3, and the peak at *m/z* 149 is the same ions present in Figure 4b. The exclusive formation of the ions at *m/z* 149 is presumably due to the high affinity of H^+ towards the carbonyl oxygen atom in the end group. The ions at *m/z* 447 then undergo charge-driven dissociation to form the product ion. The product ions at *m/z* 149 can be further stabilized by the resonance involving a highly conjugated structure, or charge de-localization. Note that the spectrum shown in Figure 5a was obtained using a mild dissociation condition to demonstrate the presence of protonated PEG (*m/z* 447). In practice, by increasing the collision energy, peaks at *m/z* 447 can be completely eliminated and ion counts of *m/z* 149 can be further increased.

With increased ion counts and decreased interfer-

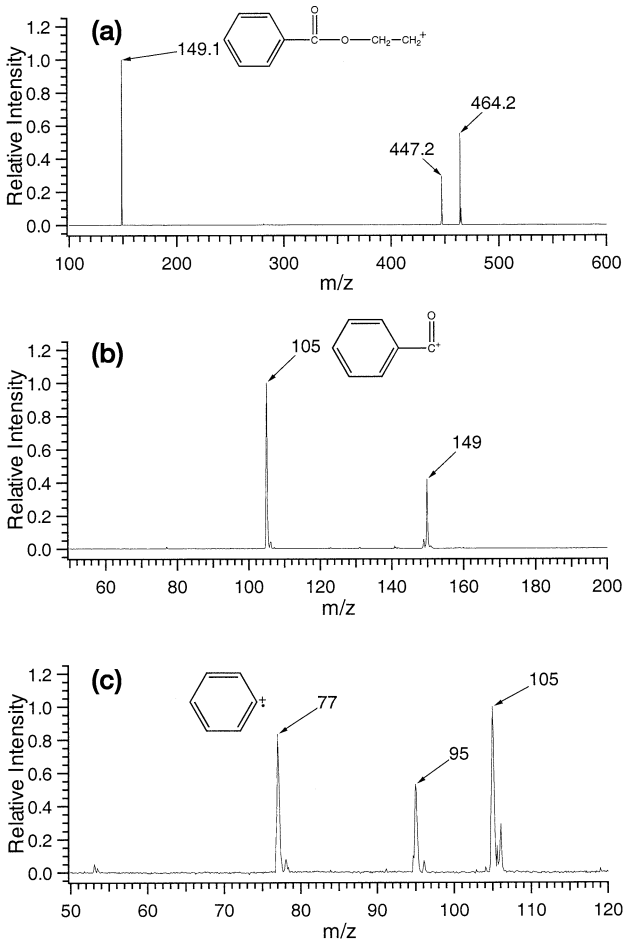


Figure 5. (**a**) ESI MS/MS spectrum of PEG-DBZ pentamer with NH_4^+ at m/z = 464.2. (**b**) ESI MS^3 spectrum of the product ions at m/z = 149 from (**a**). (**c**) ESI MS^4 spectrum of the product ions at m/z = 105 from (**b**).

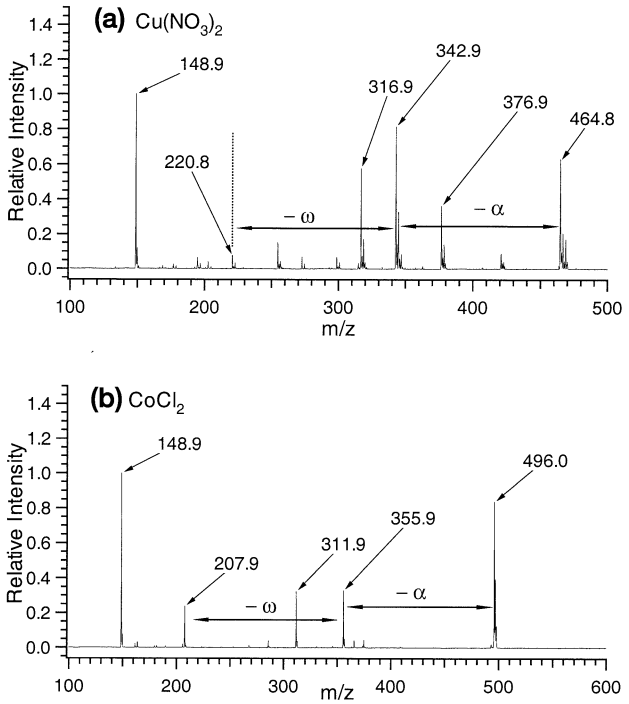


Figure 6. (**a**) ESI MS/MS spectrum of PEG-DBZ quadrimer at m/z = 464.8 obtained using $Cu(NO_3)_2$. (**b**) ESI MS/MS spectrum of PEG-DBZ quadrimer at m/z = 496.0 obtained using $CoCl_2$.

ence, further isolation and fragmentation on m/z 149 were performed. MS^3 on m/z 149 followed by MS^4 on its product ions at m/z 105 are shown in Figure 5b and c, respectively, with proposed structures labeled next to each major peak. The identity of the peak at m/z 95 remains uncertain. Possibly, this is due to ion/molecule reaction between benzene radical ions and water molecules in the trap. Nevertheless, a complete depiction of the end group structure was obtained.

Another way to improve the quality of tandem mass spectra is to increase the precursor ion yield in the preceding stage. Figure 6 shows the MS^2 spectra obtained by using divalent metal ions Co^{2+} and Cu^{2+}. The spectrum obtained using $Cu(NO_3)_2$ (Figure 6a) bears the similar fragmentation characteristics as those using Ag^+, but with greatly increased signal intensity of the peak at m/z 149. This similarity is due to the fact that both transition metals, Ag and Cu, belong to the same IB group, and both ions (+1) have similar d^{10} electronic configuration. The empty ***s*** and ***p*** orbitals can well accommodate the electron pairs from adjacent oxygen atoms and form complex. However, the ionic radius of Cu^+ is smaller than that of Ag^+ (96 pm versus 126 pm). As a consequence, the Cu^+ is more easily coordinated by the surrounding repeating units, giving rise to a stronger complex. Using Co^{2+} (Figure 6b) as the cation results in a somewhat different situation. The parent ion m/z 496 was selected from the $[\alpha\text{-}EO_n\text{-}\omega]CoCl^+$ series. The anion Cl^- participates in the formation of the neutral products, benzoyl chloride. Afterwards, the Co^{2+} ions are linked to the PEG chains via a covalent bonding. This bonding is much stronger than those interactions of electrostatic nature. The increment of the interactions between the metal ions and PEG chains, by means of stronger complex formation or covalent bonding, will promote the likelihood of internal fragmentation to generate ions at m/z 149. In both cases, further fragmentation was enabled and the identical spectra as Figure 5b and c were obtained (data not shown).

It was also found that using in-source fragmentation to generate end group moiety ions (i.e., m/z 149 for PEG-DBZ) in the first MS stage would considerably improve the quality of subsequent tandem MS spectra. The reason is rather straightforward. If the ions are generated by a MS/MS experiment, only those isolated PEGs with one nominal mass will undergo the dissociation and lead to the ions of interest. On the other hand, if they are generated by in-source fragmentation in the first MS stage, all PEGs with the same structure but different chain lengths will collectively contribute to the ion formation. Consequently, ion counts are considerably increased. This is particularly helpful when low-efficiency ionization reagents are used in the first MS

stage. For example, NH_4^+ ionization of PEG often suffers from its low efficiency, especially for real world samples containing large amount of salt. In this case, tandem mass spectrometry does not have sufficient parent ions to begin with under normal operation mode, and to go through $MS \rightarrow MS^2 \rightarrow MS^3$ will not generate satisfactory results. Moreover, skipping one isolation/fragmentation cycle will also alleviate the ion loss during isolation/fragmentation.

Based on the above results and discussion, a MS based approach tailored for PEG ester characterization can be summarized as the following. Molecular mass and its distribution can be estimated from ESI mass spectra obtained using any cations that have reasonable ionization efficiency. By using Li^+ and Ag^+ for ESI, information about the repeat unit and end group mass can be obtained in the second MS stage. Using cations such as NH_4^+, Co^{2+}, and Cu^{2+}, in conjunction with in-source fragmentation, end group structural information can be revealed. All these experiments can be readily carried out in a conventional ion trap mass spectrometer within a short experimental time frame.

Fatty Acid Methyl Ester Ethoxylates (FAMEE)

To demonstrate the general applicability of the proposed protocol, two fatty acid methyl ester ethoxylates were studied. We present our results on these PEG esters obtained using two types of cations, Li^+ and NH_4^+, and the rationale to deduce the structures of these PEG esters.

The MS/MS spectrum of PEG-MOL obtained by using Li^+ is shown in Figure 1b. As pointed out (refer to Scheme **2**), the major products should result from the loss of the end group moiety, via pathway **A** and **B**, respectively. Ensuing products are supposedly separated by 26 Da. Among four major product peaks present in Figure 1b, peak pairs at *m/z* 183 and 157 fit the profile. Therefore, the mass difference between parent ion *m/z* 465 and product ion *m/z* 183 can be tentatively assigned to the end group acid with nominal mass 282 Da. This was further confirmed by the MS/MS spectrum obtained using NH_4^+ (Figure 7c). In Figure 7c, besides the loss of NH_3, the only product ions are the end group acid ethylene esters at *m/z* 309 (282 − 1 + 28 = 309), similar to the case of PEG-DBZ. These ions were also generated by in-source fragmentation (Figure 7b). Figure 7a is the ESI mass spectrum obtained under normal operation mode to reflect the oligomer mass distribution. By increasing the voltage drops between capillary exit and skimmer 1, skimmer 1 and 2, abundant fragment ions at *m/z* 309 are generated to enable further fragmentation.

Fragmentation spectrum of *m/z* 309 is shown in Figure 7d. The foremost products are the carbocations below *m/z* 200 with major peaks separated by 14 Da, reflecting the alkyl nature of the fatty acid. However, pinpointing the double bond position in the end group moiety seems impossible within the current experimental frame, because the loss of H_2O (peak at *m/z* 291) and formic acid, typical for the dissociation of fatty acids and their derivatives, will move the charge onto the alkyl chain and give rise to the observed carbocations. Carbocations are notorious for their ability to isomerize before fragmentation and lead to a complicated spectrum difficult to interpret. The well-established approach to solve this problem is via high-energy charge-remote fragmentation [65–76]. Nevertheless, the resulting spectrum from our approach still contains information from alkyl chain as well as acid proximity. Moreover, in industrial practices, only a handful of fatty acids, including oleic acid, stearic acid, and palmitic acid, are commonly used for PEG ester manufacture. We envision that compiling a reference MS/MS spectrum library can be useful for unambiguous end group identification.

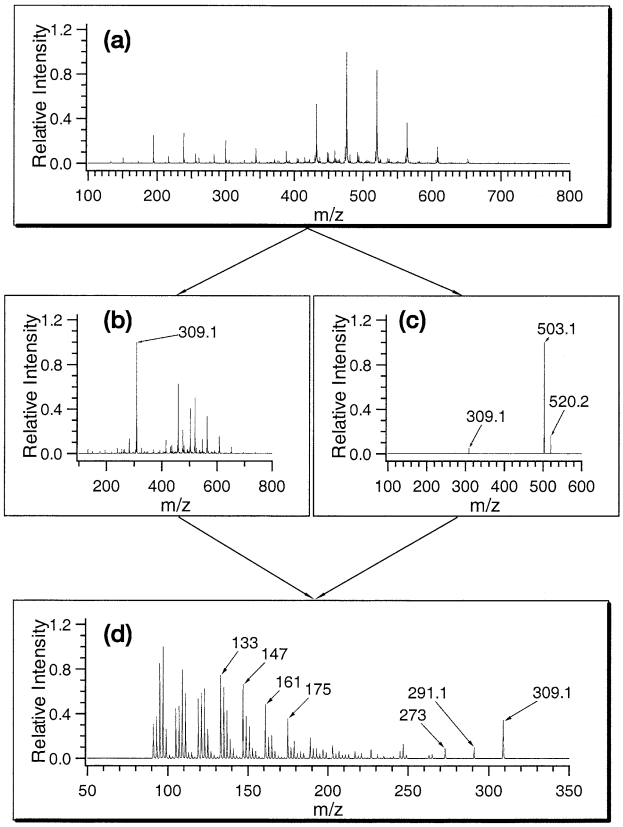


Figure 7. (**a**) ESI mass spectrum of PEG-MOL obtained using NH_4^+ under normal operation mode. (**b**) ESI mass spectrum of PEG-MOL obtained using NH_4^+ with in-source fragmentation. (**c**) ESI MS/MS spectrum of PEG-MOL pentamer at *m/z* = 520.2 with NH_4^+. (**d**) Fragmentation spectrum of product ions at *m/z* = 309.1 from both (**b**) and (**c**).

Figure 8a shows an ESI mass spectrum of sample PEG-DS, obtained by using Li^+ as the cationization reagent. The spectrum is surprisingly complicated with at least three identifiable distributions. The intended product (i.e., *m/z* 953 series, labeled as an asterisk in Figure 8a) is present at the lowest amount. MS/MS spectra of ions from three series are shown in Figure 8b, c, and d. Figure 8b reveals the presence of the expected

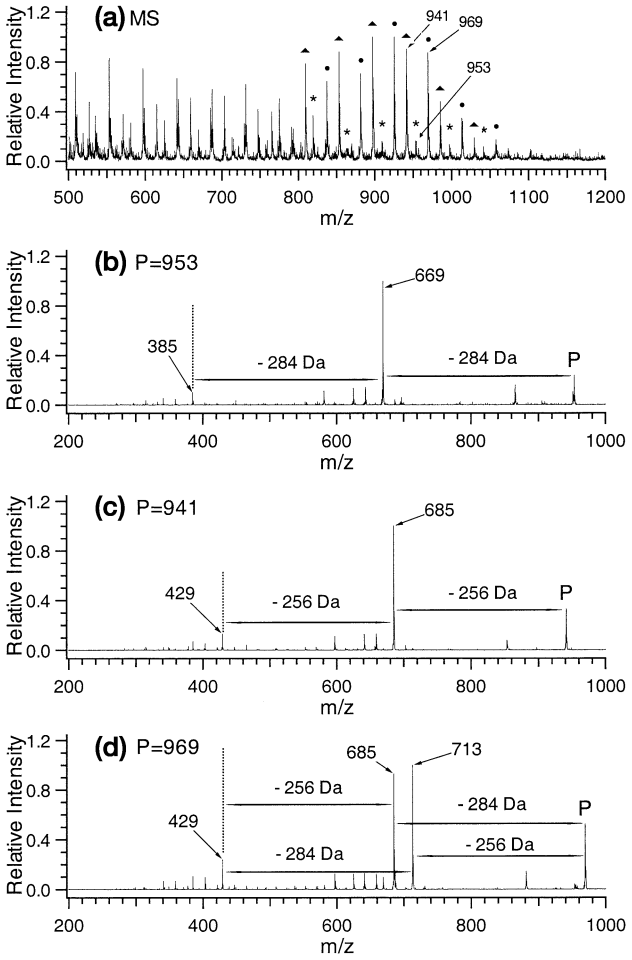


Figure 8. (**a**) ESI mass spectrum of PEG-DS obtained using Li^+ as the cationization reagent. The peaks in the mass range 800–1100 Da were labeled with filled triangle, asterisk, and filled circle, indicating they are from different product series. (**b**) ESI MS/MS spectrum of ions at m/z = 953 with Li^+. (**c**) ESI MS/MS spectrum of ions at m/z = 941 with Li^+. (**d**) ESI MS/MS spectrum of ions at m/z = 969 with Li^+. In (**b**), (**c**), and (**d**), **P** denotes the parent ions of each spectrum.

stearic acid end groups with nominal mass 284 Da. However, Figure 8c suggests that this series of products (labeled as a filled triangle in Figure 8a) have two identical end group acids with nominal mass 256 Da, probably palmitic acid ($CH_3(CH_2)_{14}COOH$) in lieu of stearic acid. Fragmentation spectrum of the ions at m/z 969 (Figure 8d) reveals that the major product ions at m/z 685 and 713 are from the loss of stearic acid and palmitic acid, respectively, indicating that this series of PEGs contain stearic acid at one end, and palmitic acid at the other. Further evidence was obtained by the similar signal intensities of the peaks at m/z 685 and 713, and their common product at m/z 429.

End group moieties from all three series of PEGs were further "isolated" using NH_4^+ and fragmented, with results shown in Figure 9. Both spectra display similar fragmentation patterns, i.e., both spectra consist of peaks from the loss of formic acid (mass 46 Da) and carbocations, indicating their structural similarity.

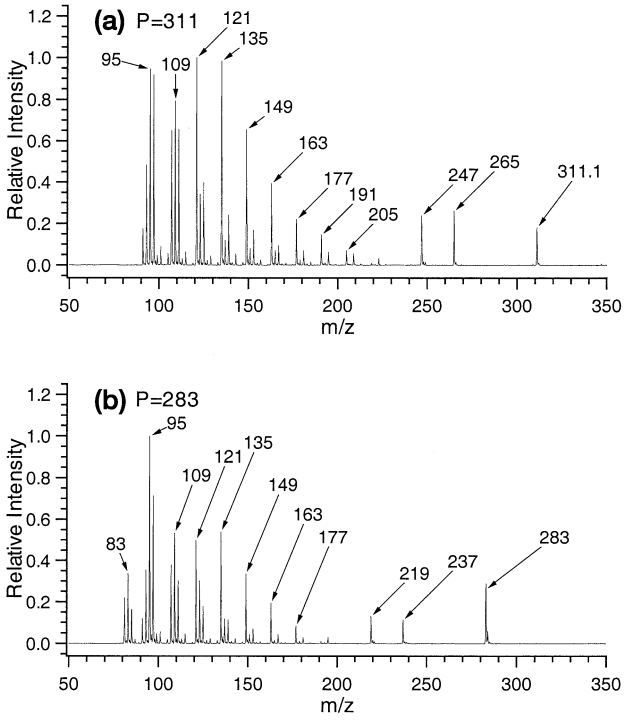


Figure 9. Fragmentation spectra of product ions at (**a**) m/z = 311, and (**b**) m/z = 283. In both cases, product ions were generated by in-source fragmentation of PEG-DS with NH_4^+.

The above results clearly suggest that the starting material stearic acid was contaminated by palmitic acid, hence, resulting in a complicated mixture with three different structures. Palmitic acid is known to be the common impurity present in stearic acid. It is worthy to mention that the carbocations resulting from the fragmentation of unsaturated fatty acid ester (i.e., oleic acid ester, Figure 7d) are slightly different from those from saturated fatty acid esters (i.e., stearic acid and palmitic acid esters, Figure 9). Thus, a library spectral comparison approach should be useful for unambiguous end group identification. We further note that ESI MS does not provide accurate analysis of the relative contents of the individual components. Other techniques such as GC may be used to compare the relative ratio of palmitic acid and stearic acid in the sample.

Conclusion

We have shown that low energy dissociation of PEG esters strongly depends upon the cations involved. PEG ester-sodium adducts can undergo fragmentation, but provide limited information. This can be improved by the use of Li^+, Ag^+, and other transition metal ions. End group containing ions can be generated by using NH_4^+. Fragmentation on these ions leads to end group structural information. Based on these results, we present an integrated MS approach for PEG ester characterization. With the proper choice of cationization reagent and instrumental operation mode, a wealth of structure information can be obtained. Since our approach is

based on the use of a low-energy CID tandem mass spectrometer that is widely available, it should be able to be adapted by others for problem solving in the area related to polyglycol structural characterization. For analytical method development, our current effort is focused on extending this approach to analyze higher mass polyglycols.

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