

Reactions of Poly(ethylene glycol) Cations with Iodide and Perfluorocarbon Anions

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Multiply charged poly(ethylene glycol) ions of the form $(M+nNa)^{n+}$ derived from electrospray ionization have been subjected to reactions with negative ions in the quadrupole ion trap. Mixtures of multiply charged positive ions ranging in average mass from about 2000 to about 14,000 Da were observed to react with perfluorocarbon anions by either proton transfer or fluoride transfer. Iodide anions reacted with the same positive ions by attachment. In no case was fragmentation of the polymer ion observed. In all cases, the multiply charged positive ion charge states could be readily reduced to +1, thereby eliminating the charge state overlap observed in the normal electrospray mass spectrum. With all three reaction mechanisms, however, the +1 product ions were comprised of mixtures of products with varying numbers of sodium ions, and in the case of iodide attachment and fluoride transfer, varying numbers of halogen anions. These reactions shift the mass distributions to higher masses and broaden the distributions. The extents to which these effects occur are functions of the magnitudes of the initial charges and the width of the initial charge state distributions. Care must be taken in deriving information about the polymer molecular weight distribution from the singly charged product ions arising from these ion/ion reactions. The cluster ions containing iodide were shown to be intermediates in sodium ion transfer. Dissociation of the adduct ions can therefore lead to a +1 product ion population that is comprised predominantly of $M+Na^+$ ions. However, a strategy based on the dissociation of the iodide cluster ions is limited by difficulties in dissociating high mass-to-charge ions in the quadrupole ion trap. (J Am Soc Mass Spectrom 1998, 9, 957-965) © 1998 American Society for Mass Spectrometry

Electrospray ionization (ESI) has been shown to be effective in yielding gaseous ions from a variety of polymeric species present in solution [1-4]. A hallmark of electrospray is that it tends to yield multiply charged ions with, for a given polymer class, a general correlation between the size of the polymer and the magnitude of the number of charges that it tends to retain as a result of the electrospray process [5]. The nature of the multiply charged ion varies with polymer type and solution composition. For example, proteins are typically observed as multiply protonated species in positive ion ESI [6] and oligonucleotides are typically observed as multiply deprotonated species in negative ion ESI [7]. Synthetic polymers, on the other hand, frequently show the attachment of multiple metal ions, such as sodium cations [2]. Synthetic polymers were the early focus of research in the ionization of high mass species with electrospray [2, 8, 9] and they continue to constitute an important area of application for ESI [10-14].

Poly(ethylene glycols) (PEGs), in particular, have played an important role in the development and understanding of ESI. For example, Fenn and co-work-

ers have made extensive use of PEGs in their pioneering work with ESI [2, 15-17]. PEG ions derived from ESI as massive as 5 MDa have been reported [16, 18], illustrating the remarkable capability of electrospray to form high mass gaseous ions. PEG ions have also been used to illustrate the utility of the high resolving power of Fourier transform mass spectrometry for the characterization of synthetic oligomers [19]. The convolution of a charge state distribution with a broad molecular weight distribution can lead to highly complex spectra that make characterization of the oligomer molecular weight distribution very difficult. Multiple charging therefore limits the oligomer size range amenable to molecular weight characterization by ESI. The upper limit is largely defined by the resolving power of the mass analyzer.

We have pursued the use of ion/molecule [20, 21] and ion/ion reactions [22-27] in the quadrupole ion trap for the manipulation of analyte ion charge to facilitate mass measurements in electrospray mass spectrometry. For example, we have demonstrated the determination of charge states of product ions formed via dissociation of multiply charged parent ions both by ion/molecule reactions [20] and by ion/ion reactions [22]. We have also recently demonstrated the effectiveness of ion/ion chemistry in simplifying electrospray mass spectra of protein mixtures [24, 26] and product

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ion spectra resulting from the dissociation of multiply charged protein parent ions [27]. All of our ion/ion reaction studies to date have involved either multiply protonated positive ions or multiply deprotonated negative ions. We have therefore chosen PEGs to study the ion/ion chemistry of positive ions formed by the attachment of multiple metal ions. We describe herein data that illustrate the phenomenology associated with the reactions of iodide anions and anions derived from glow discharge ionization of perfluoro-1,3-dimethylcyclohexane and perfluoro(methyldecalin) with positive ions derived from PEGs ranging in molecular weight from about 2 to 14 kDa. We compare and contrast the results described here with the ion/ion chemistry associated with multiply protonated positive ions reacting with the same negative ions and comment on the use of these negative ions as reagents to facilitate the molecular weight characterization of synthetic polymers.

Experimental

Materials and Electrospray Conditions

The poly(ethylene glycols) used in this study were purchased from Aldrich and were used directly as supplied. They were dissolved in 90:10 methanol:water to concentrations of 100–200 μM . At these concentrations there was evidence of clustering when relatively gentle vacuum/atmosphere interface conditions were employed. All experiments reported herein were conducted under interface conditions with moderate to high voltage gradients between the sampling orifice and the first interface lens such that clustering was minimized. All solutions were directly infused at flow rates of 0.8–1.0 $\mu\text{L}/\text{min}$ through a 100- μm -i.d. stainless steel capillary held at 3.0–3.5 kV. Perfluoro-1,3-dimethylcyclohexane (PDCH), perfluoro(methyldecalin) (PMD), and iodobenzene were obtained from Aldrich (Milwaukee, WI) and were used directly as supplied.

Mass Spectrometry

All ion/ion reaction experiments were performed using a Finnigan MAT Ion Trap Mass Spectrometer (ITMS, Finnigan MAT, San Jose, CA) modified for ESI, with ion injection through an end-cap electrode, and a glow discharge with ion injection through a hole in the ring electrode [28]. All experiments were controlled by ICMS software provided by N. Yates and the University of Florida. Cations were injected into the ion trap over a period of 0.04–0.4 s. The radio-frequency (rf) sine-wave amplitude applied to the ring electrode during ion injection was 1096 V zero-to-peak (0–p). In all cases, helium was admitted into the vacuum system to a total pressure of 1 mtorr with a background pressure in the instrument of 2×10^{-5} torr without the addition of helium. Anions were formed by sampling the head space vapors of PDCH, PMD, or iodobenzene into the glow discharge operated at 900 mtorr and were injected

into the ion trap after cation accumulation. Anion accumulation times were typically 4–20 ms and anion/cation mutual storage times ranged from 60 to 250 ms.

The typical ion/ion reaction mass spectrometry experiment included a positive ion accumulation period, a desolvation period [20], a negative ion accumulation period, a period of mutual storage of positive and negative ions, a sweep of the amplitude of the rf applied to the ring electrode to eject the negative ions [29], and mass analysis of the positive ions. MS/MS experiments included a positive ion isolation procedure after the desolvation step. Ion isolation steps consisting of two successive stages of resonance ejection were used to eject alternately ions of mass-to-charge ratio greater than and less than those of the parent ions of interest [30]. The ring-electrode rf amplitude during the ion/ion reaction period was held at 1154 V 0–p (low m/z cutoff = 100) for experiments with I^- , whereas ion/ion reaction experiments were conducted at several ring-electrode rf amplitudes with the fluorocarbon anions, as indicated in the text.

Mass/charge analysis was effected via resonance ejection [31, 32] to yield a mass/charge range as high as 16,000 ($q_{\text{eject}} = 0.03651$) using resonance ejection amplitudes of 3–4 V peak-to-peak. In all cases, the rate of change of the amplitude of the rf voltage applied to the ring electrode was the standard rate supplied by the ITMS electronics (128 V p–p/ms). The mass/charge scale for the ion/ion reaction spectra was calibrated using ion/ion reaction data generated from solutions of myoglobin (16,950 Da) and ubiquitin (8564 Da). The mass/charge ratios of the various charge states of these calibration standards were based on the molecular masses provided by the manufacturer and were used to determine a correction for the mass scale provided by the ion trap data system. The spectra shown here were typically the result of an average of 50–400 individual scans.

Results and Discussion

Perfluorocarbon Anions

Figure 1 shows data that illustrate the general observations made when anions derived from perfluorocarbons are used to reduce PEG ion charge states. Figure 1a shows the normal electrospray mass spectrum of PEG 4600, which is largely dominated by the +3 to +5 charge states. Figure 1b shows the spectrum acquired after anions derived from PDCH were allowed to react with the population of ions reflected in Figure 1a for 143 ms at a low m/z cutoff of 150. These are the conditions that we have typically used to deprotonate multiply charged proteins [20–29]. Note in particular the +1 charge state generated from the ion/ion reactions. There appear to be two distributions. One shows the expected 44 Da spacing for the PEG distribution and another shows peaks of lower abundance midway between those of the larger distribution. From these

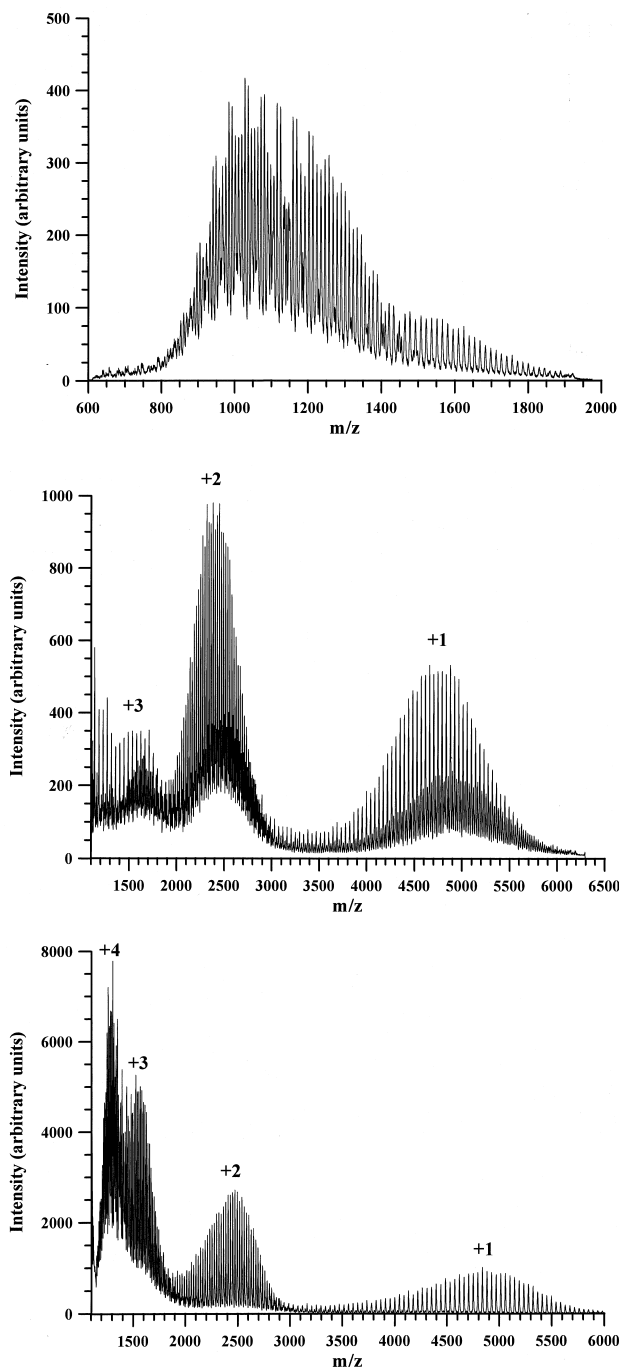


Figure 1. (a) ESI mass spectrum of PEG 4600. (b) ESI mass spectrum obtained after the ions of (a) were subjected to reactions with anions derived from PDCH for 143 ms using a low m/z cutoff of 150 during the reaction period. (c) ESI mass spectrum obtained after multiply charged PEG 4600 ions were subjected to reactions with anions derived from PMD for 205 ms using a low m/z cutoff of 390.

data alone it cannot be determined if the ions of lower abundance are also spaced at 44 Da and are simply shifted in mass from the larger distribution, or if there is a distribution of ions spaced at 22 Da with alternating members of the distribution overlapping in mass with members of the larger distribution. The spectrum of

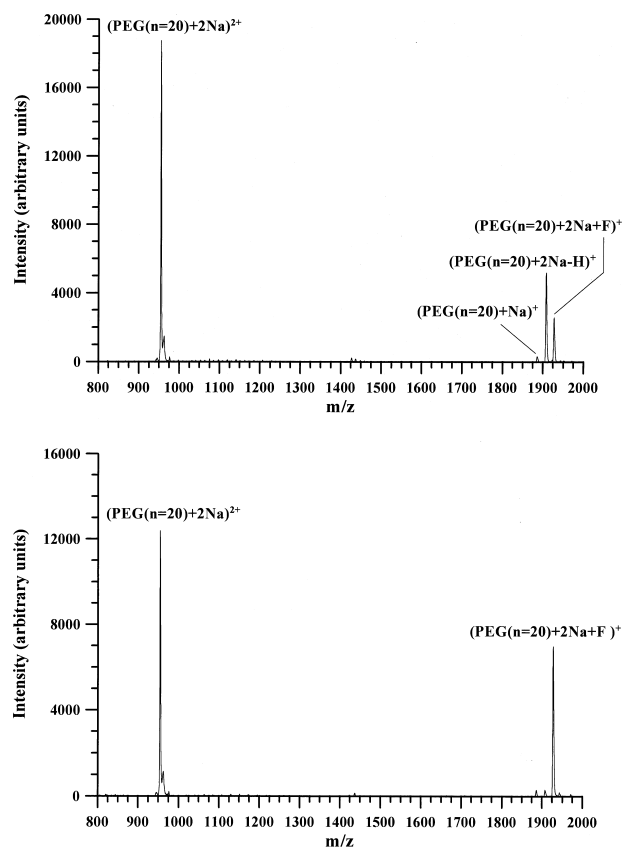
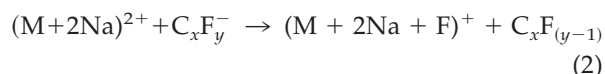
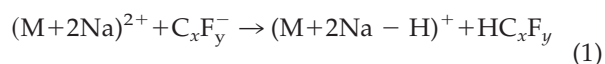


Figure 2. (a) ESI MS/MS spectrum of a mass-selected PEG 2000 $(M+2Na)^{2+}$ parent ion subjected to reactions with anions derived from PDCH using a low m/z cutoff of 100. (b) Results from the same experiment except that a low m/z cutoff of 250 was used.

Figure 1c shows the spectrum obtained when anions derived from PMD are used to reduce the PEG ion charge states using a low m/z cutoff of 390. Note in this case that the distribution of lower abundance in Figure 1b is essentially absent in Figure 1c.

Phenomena underlying the results of Figure 1b, c are revealed by MS/MS experiments as illustrated in Figure 2. Figure 2 shows spectra following an ion/ion reaction period using anions derived from PDCH involving a doubly charged PEG 2000 ion [i.e., $(M+2Na)^{2+}$]. Figure 2a shows the results obtained using a low m/z cutoff of 100 during the ion/ion reaction period and Figure 2b shows the results from an identical experiment except that a low m/z cutoff of 250 was used during the ion/ion reaction period. Figure 2a is remarkable in that it shows that the two major reaction mechanisms that take place for charge state reduction of the $(M+2Na)^{2+}$ ion are proton transfer and fluoride transfer, i.e.:



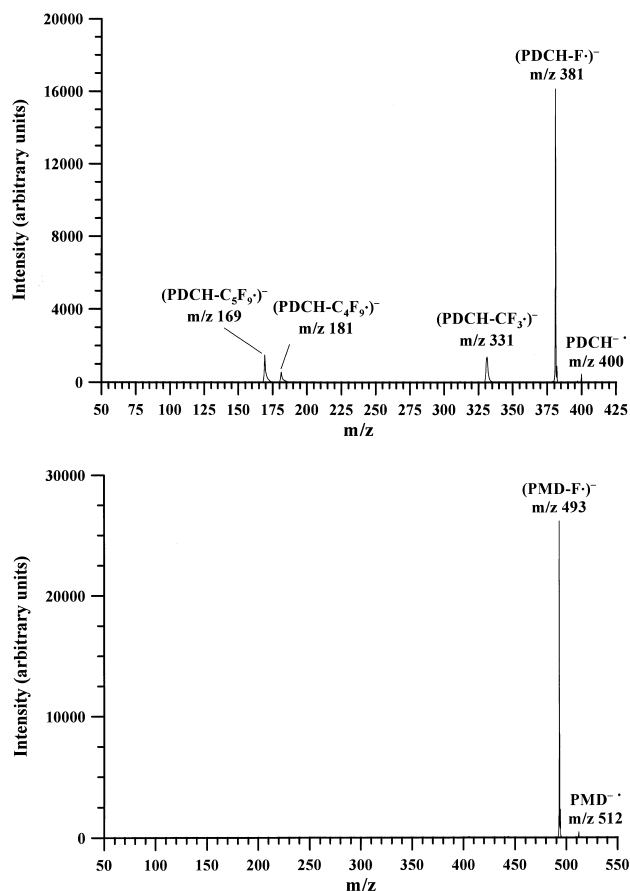


Figure 3. (a) Negative ion mass spectrum obtained via glow discharge ionization of PDCH and injection of the ions through the ring electrode of the ion trap while applying a 577 V 0-p rf potential. (b) Negative ion mass spectrum obtained via glow discharge ionization of PMD and injection of the ions through the ring electrode of the ion trap while applying a 577 V 0-p rf potential.

Although there appears to be a small peak in Figure 2a associated with sodium ion transfer, we were unable to find conditions to make this product increase in abundance. Furthermore, the sodium ion transfer product was often absent in MS/MS spectra derived from PEG cations. We conclude, therefore, that sodium ion transfer is only a very minor reaction channel with the perfluorocarbon anions. Interestingly, the proton transfer channel is almost completely absent when the low mass-to-charge ratio cutoff during the ion/ion reaction period is raised from 150 to 250 (see Figure 2b).

The observations associated with Figures 1c and 2b suggest that reactions (1) and (2) are not competing processes from the same anions but are parallel processes that take place when a mixture of anions is present. The negative ion mass spectra of Figure 3 are consistent with this interpretation. Figure 3a shows the negative ion mass spectrum of PDCH ionized by glow discharge followed by ion injection through the ion trap ring electrode. The major anions correspond to the molecular anion, PDCH⁻, and fragments correspond-

ing to (PDCH - F)⁻, (PDCH - CF₃)⁻, (PDCH - C₄F₉)⁻, and (PDCH - C₅F₉)⁻. Note that the peak heights of Figure 3a do not reflect accurately ion abundances because the (PDCH - CF₃)⁻, (PDCH - C₄F₉)⁻, and (PDCH - C₅F₉)⁻ ion signals are broadened due to space charge [33]. The major difference between the experiments leading to Figure 2a, b is that the (PDCH - C₄F₉)⁻ and (PDCH - C₅F₉)⁻ anions were missing in the experiment leading to the spectrum of 2b. This result implies that one or both of the (PDCH - C₄F₉)⁻ and (PDCH - C₅F₉)⁻ fragments is responsible for proton transfer and that the higher mass anions derived from PDCH react by F⁻ transfer. These conclusions were supported by experiments in which each of the anions observed in Figure 3a were resonantly ejected during the ion/ion reaction period in turn to determine its contribution to the overall ion/ion reaction product spectrum (data not shown). PMD yields a very simple spectrum (Figure 3b) which is dominated by the (PMD - F)⁻ fragment. This ion reacts almost exclusively by F⁻ transfer, as illustrated by Figure 1c, and as confirmed by MS/MS experiments.

Figures 1 and 2 represent the first reported observation of F⁻ transfer as a reaction mechanism leading to charge state reduction of a multiply charged positive ion. Furthermore, this is the first observation of proton transfer from an ion that nominally carries its excess charge in the form of alkali cations. In recognizing that one or both of these mechanisms can be operative in the charge state reduction of multiply charged PEG ions, the behavior observed in the ion/ion reactions involving anions derived from PDCH and PMD can be rationalized. Clearly, the disappearance of the distribution of ions of lower abundance in Figure 1b in the experiment leading to Figure 1c results from the absence during the ion/ion reaction period of the anions that give rise to proton transfer. Obviously, competing reaction mechanisms that lead to different products result in undesirable spectral complexity. For this reason, the use of PMD anions or the use of PDCH anions and a low *m/z* cutoff greater than 181 leads to spectra whereby adjacent peaks are more readily resolved because they are farther apart than those resulting from proton transfer. Figure 4 shows examples of data acquired for PEG 8000 (4a) and PEG 10000 (4b) using PMD anions to reduce charge states to +1. When anions that react by proton transfer are also present, such as the (PDCH - C₄F₉)⁻ and (PDCH - C₅F₉)⁻ fragments, adjacent peaks are more difficult to resolve (data not shown).

It is important to recognize that, although charge state overlap in the ESI mass spectrum of a PEG as large as PEG 10000 can be eliminated by ion/ion reactions with perfluorocarbon anions, the resulting spectrum of the +1 charge state must be interpreted with care in order to extract reliable molecular weight distribution information. The spectra of Figure 4 show good peak definition because of the fortuitous circumstance that the sum of the masses of a sodium cation and fluoride

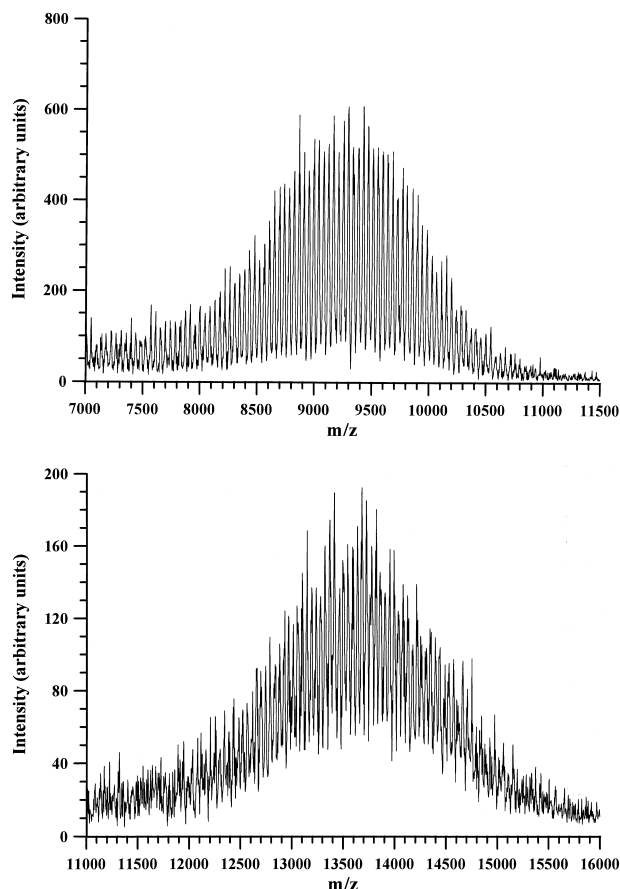
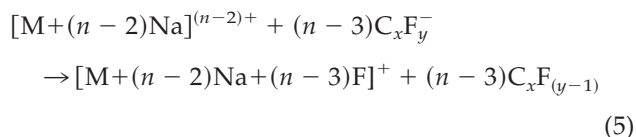
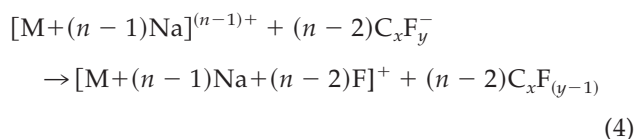
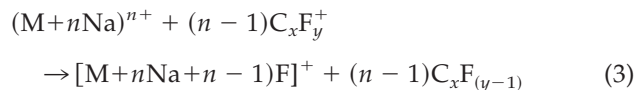


Figure 4. (a) ESI spectrum showing the +1 region of PEG 8000 resulting from ion/ion reactions with PMD anions using a 5-ms anion accumulation pulse and 180-ms reaction time. (b) ESI spectrum showing the +1 region of PEG 10000 resulting from ion/ion reactions with PMD anions using a 5-ms anion accumulation pulse and 200-ms reaction time.

anion is 42 Da, almost the same mass spacing as the n -mer spacing of PEG (44 Da). The final composition of +1 ions is actually a mixture of n -mers with different numbers of sodium and fluoride ions. The complexity of the mixture is determined by the original charge state distribution. Generically, the situation can be presented by listing the initial reactants and the final products, i.e.:



etc.

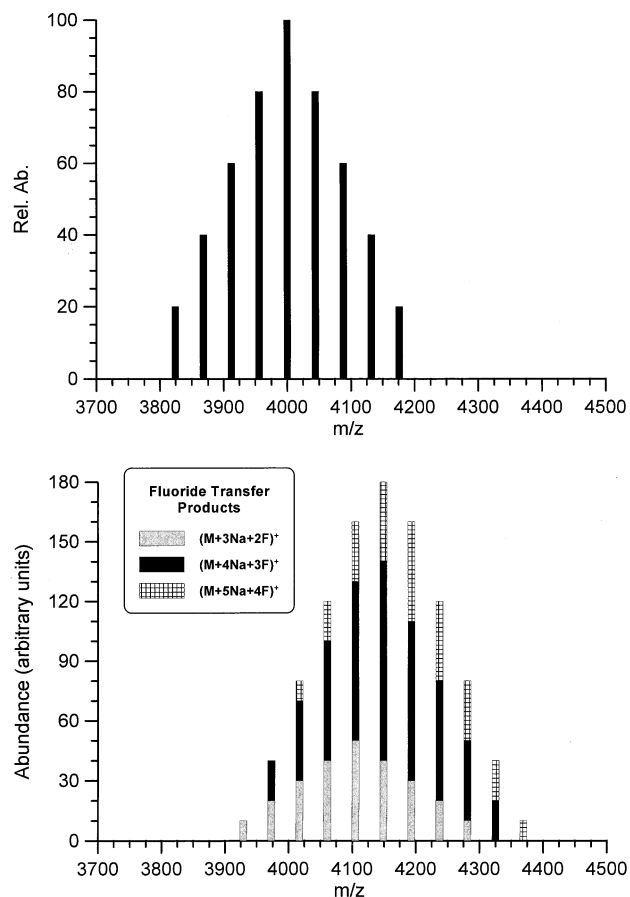
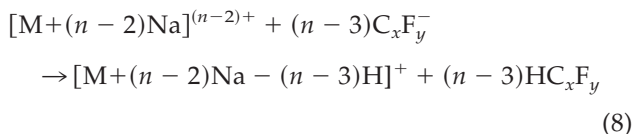
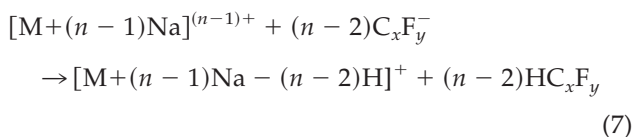
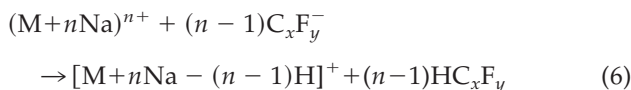


Figure 5. (a) Mass and abundance distribution of a simple hypothetical mixture of PEGs. (b) Singly charged product ion distribution predicted for fluoride transfer to $(M+5\text{Na})^{5+}$, $(M+4\text{Na})^{4+}$, and $(M+3\text{Na})^{3+}$ ions, 1:2:1 abundance ratio, of the mixture of (a).

When charge state reduction occurs via successive fluoride transfers, the oligomer distribution for each initial charge state leads to a final product distribution that overlaps with the final product distributions of the other charge states. The net effect is readily appreciated by considering the simple hypothetical example illustrated in Figure 5. Assuming a very simple PEG mixture with the masses and abundances indicated in Figure 5a and an initial parent ion distribution of $(M+5\text{Na})^{5+}$, $(M+4\text{Na})^{4+}$, and $(M+3\text{Na})^{3+}$ present at a 1:2:1 abundance ratio, the resulting ESI spectrum of the +1 charge ions resulting from successive F^- transfer would look like Figure 5b. Note that there is a 2 Da difference between the products formed from adjacent charge states. In the present system these spacings are not resolved and the net effect is that the different products tend to sum with some broadening of the peak. For simplicity, in Figure 5b we show the contribution from each product ion to the area of a given peak in bar graph form. It is clear from comparison of Figure 5a to Figure 5b that the qualitative effect of successive fluoride transfers to multiply charged PEG ions is to shift the mass distribution to higher mass and to broaden the

distribution. The mass shift is determined by the magnitudes of the initial charges and the broadening is determined by the number of initial charge states (i.e., the distribution is broadened by $m - 1$ peaks, where m is the number of charge states in the initial ESI spectrum). The data of Figure 4, therefore, can be deconvoluted to give a polymer molecular weight distribution but such a deconvolution requires knowledge of the initial charge state distribution and the relative abundance contributions of each charge state. The foregoing discussion assumes no contributions from the kinetics associated with reducing the initial charge states to +1. In fact, the more highly charged ions require slightly longer to be reduced to the +1 charge state. However, we have noted that the charge-squared dependence of the ion/ion reaction rates leads to a situation in which the time frame for reduction to the +1 charge state is relatively insensitive to initial ion charge [34]. Therefore, assuming no differences in the kinetics associated with reduction to the +1 charge state, an error of only a few percent is introduced by the distribution of initial charge states.

A simple hypothetical example similar to that of Figure 5 can also be drawn to show that successive proton transfers from PEG $(M+n\text{Na})^{n+}$ ions also give rise to a singly charged product ion spectrum that does not yield directly the molecular weight distribution. In this case, a final product spectrum with a spacing of 22 Da results from the different numbers of sodium ions in the +1 product ions, the range being determined by the initial charge state distribution. The positive ion reactants and +1 products can be represented generically as follows:



etc.

As with fluoride transfer, conclusions about the molecular weight distribution can only be drawn after correcting for the mass shift and broadening of the distribution associated with multiple sodium ion attachment.

Iodide

Although perfluorocarbon anions have been observed to react exclusively by proton transfer with multiply protonated proteins, the iodide anion has been shown to react largely by attachment to multiply protonated

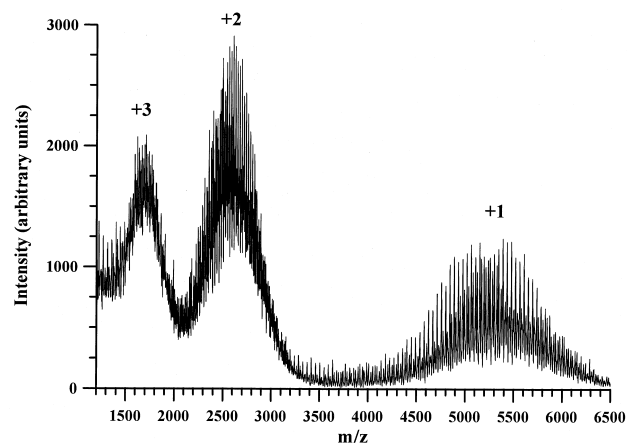
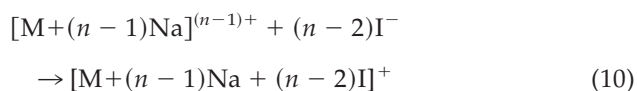
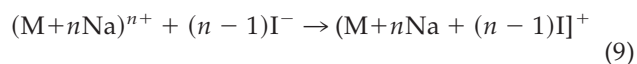


Figure 6. ESI spectrum obtained for PEG 4600 after the initial ESI ion population was subjected to ion/ion reactions with I^- for 196 ms.

proteins [35]. We have found that iodide also reacts by addition to multiply charged PEG cations. Figure 6 shows the ESI spectrum obtained for PEG 4600 after the initial ESI ion population was subjected to ion/ion reactions with I^- for 196 ms. The iodide anion was formed by glow discharge ionization of iodobenzene, which yields I^- exclusively. This spectrum, which can be compared with the spectra of Figure 1b, c, shows what appear to be at least two distinct distributions in the +1 charge state, both of which tend to be somewhat more massive than the distributions shown in Figure 1.

As with the perfluorocarbon anions, the phenomena underlying this observation are revealed by MS/MS experiments. Once again, PEG 2000 cations are used to illustrate the ion/ion chemistry observed with iodide. Figure 7a shows the result of an ion/ion reaction involving iodide in which a doubly charged PEG ion $(M+2\text{Na})^{2+}$ was isolated for study, and Figure 7b shows the result of an ion/ion reaction experiment in which a triply charged ion $(M+3\text{Na})^{3+}$ was isolated for study. These experiments show that the iodide ion reacts almost exclusively by attachment to the PEG positive ions. Furthermore, the triply charged ion reacts by the addition of two iodide ions to form a singly charged ion with very little evidence for any other reaction mechanism. The rather complex mixture of +1 ions in Figure 6, therefore, arises from the multiple attachment of I^- ions with the total number being determined by the initial positive ion charge state. As with fluoride transfer and proton transfer, iodide attachment results in a product ion mixture that reflects the complexity of the initial charge state distribution. Generically, the situation can be represented as follows:



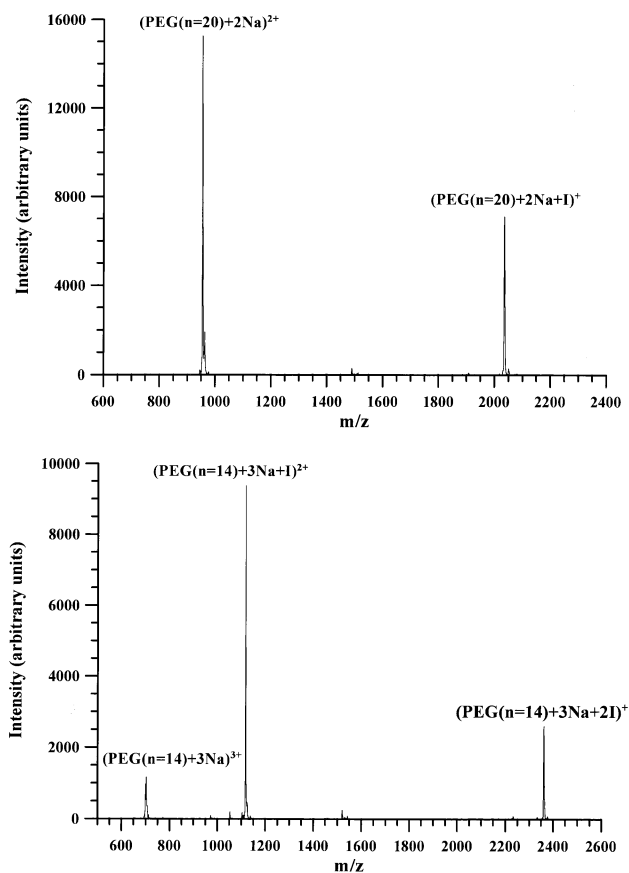
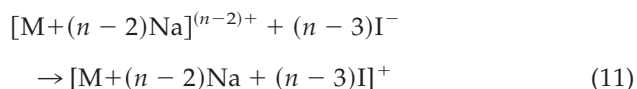


Figure 7. (a) Spectrum obtained after iodide ions were allowed to react with a mass-selected doubly charged PEG ion, $(M+2Na)^{2+}$. (b) Spectrum obtained after iodide ions were allowed to react with a mass-selected triply charged PEG ion, $(M+3Na)^{3+}$.



etc.

This reaction mechanism is highly analogous to the fluoride transfer case whereby a halogen anion is added to the PEG cation. However, in the case of I^- the peak spacing associated with a difference of one sodium cation and one iodide anion (150 Da) is far different from the normal n -mer spacing of 44 Da. Therefore, the mixture of products resulting from iodide attachment to PEG ions of different initial charge state is much more clearly apparent than it is for the fluoride transfer case described above.

It is noteworthy that iodide attachment is the sole reaction channel observed under the ion trap conditions used to conduct these experiments. Mutual neutralization of oppositely charged ions is a highly exothermic process and anion attachment to a multiply charged cation, as opposed to a charge transfer reaction, requires that all of the reaction exothermicity appear as internal energy of the product ion. In spite of this situation, no evidence for fragmentation is observed. That is, there is

no evidence for either fragmentation of covalent bonds of the PEG or break-up of the adduct by loss of either HI or NaI. Recent modeling work [36] has shown that collisional cooling associated with ion/helium collisions in the ion trap can rapidly remove excess internal energy from a highly excited high mass ion before it can fragment. The minimal degree of fragmentation typically associated with ion/ion proton transfer [37] and attachment [35] reactions in the ion trap can be attributed to high collisional cooling rates ($200-2000 \text{ s}^{-1}$) and relatively low unimolecular dissociation rates for high mass ions under these conditions [36].

In light of the observation described above of proton transfer from $(M+nNa)^{n+}$ ions derived from PEGs to some perfluorocarbon anions, the nature of the interaction of I^- with the PEG ions is of interest. For example, collisional activation of iodide adducts of multiply protonated proteins results in the loss of HI [35]. The protein/iodide adducts can therefore be regarded as intermediates in the proton transfer from the multiply protonated proteins to iodide anions. We have therefore subjected PEG/iodide adducts to collisional activation to determine if they are intermediates to proton transfer or sodium ion transfer. Figure 8a shows the results of an experiment in which $(M+2Na+I)^+$ ions formed from iodide attachment to an isolated $(M+2Na)^{2+}$ ion of PEG 2000 were subjected to ion trap collisional activation. Figure 8b shows the results of an experiment in which $(M+3Na+2I)^+$ ions formed from consecutive iodide attachment to an isolated $(M+3Na)^{3+}$ ion of PEG 2000 were subjected to ion trap collisional activation. In the former case, ready loss of NaI was observed and in the latter case, losses of one and two molecules of NaI were observed. The PEG/iodide adducts are therefore intermediates to sodium ion transfer.

Sodium ion transfer is the preferred reaction mechanism for the direct determination of PEG molecular weight distributions when the multiply charged ions are of the form $(M+nNa)^{n+}$. This is because the final singly charged product ion from all initial charge states is the $M+Na^+$ ion. The complex mixture of singly charged product ions that arises from fluoride transfer, iodide attachment, or proton transfer is thus avoided. However, the fact that the PEG/iodide cluster is the intermediate to sodium ion transfer opens the possibility that dissociation of the singly charged product ion mixture formed by iodide attachment could lead to the desired $M+Na^+$ distribution. The concept is illustrated in Figure 9. Figure 9a shows the spectrum acquired after the initial charge states of PEG 2000 were subjected to reactions with iodide anions. Two major distributions are apparent in the singly charged product ions. One is associated with single iodide attachment to the $(M+2Na)^{2+}$ ions and the other is associated with the attachment of two iodide anions to the $(M+3Na)^{3+}$ ions initially present from ESI of PEG 2000. The spectrum of Figure 9b was acquired after adding a collisional activation period after the ion/ion reaction period leading to the product ions of Figure 9a. This collisional activa-

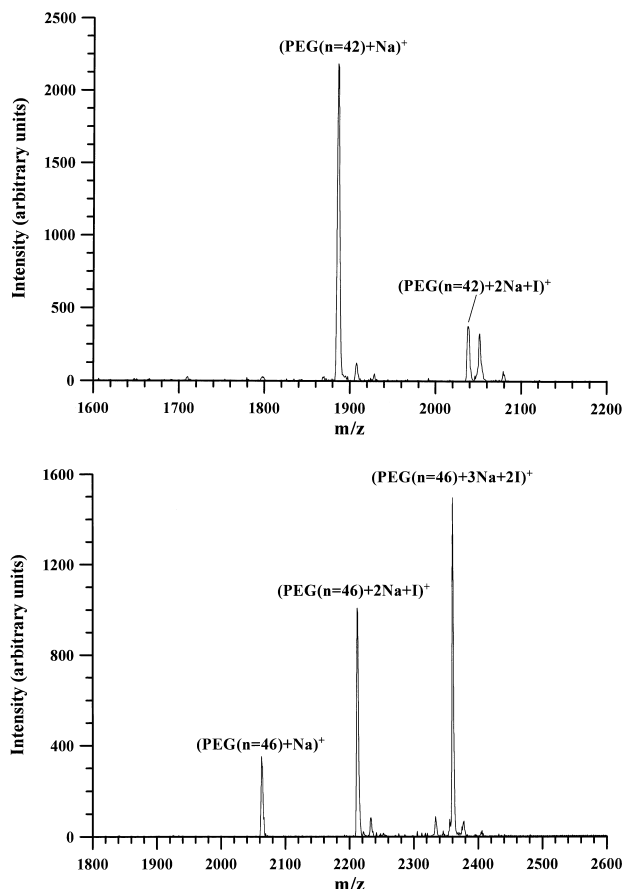


Figure 8. (a) Spectrum acquired after collisional activation of an $(M+2Na+I)^+$ ion formed by I^- attachment to a PEG $(M+2Na)^{2+}$ ion. The peaks to the right of the $(M+2Na+I)^+$ ion are ion/ion reaction products from other parent ions that happened to fall within the mass-to-charge ratio window of ions isolated for ion/ion reaction. (b) Spectrum acquired after collisional activation of an $(M+3Na+2I)^+$ ion formed by consecutive attachment of I^- to a PEG $(M+3Na)^{3+}$ ion.

tion period involved a sweep of the amplitude of the rf applied to the ring electrode while applying in dipolar fashion a 3000 mV p-p amplitude sine-wave to the end-cap electrodes. The amplitude was selected to maximize the collisional dissociation of the singly charged adduct ions while avoiding ejecting them from the ion trap. Note that the doubly charged ions are ejected at this amplitude. Note also that the initial singly charged product ion distribution is largely converted to $M+Na^+$ ions. There is a distribution of relatively low abundance $(M+2Na+I)^+$ ions that arises from either incomplete dissociation of the adducts containing a single iodide or, more likely, from a fraction of the $(M+3Na+2I)^+$ ions that do not fragment by loss of two molecules of NaI (or a combination of both). However, this group of ions could probably be dissociated with a second sweep of collisional activation. In any case, this experiment shows the desirability of reducing PEG ions to singly charged ions via sodium ion transfer. Unfortunately, the technique demonstrated here for the PEG 2000 ions is decreasingly

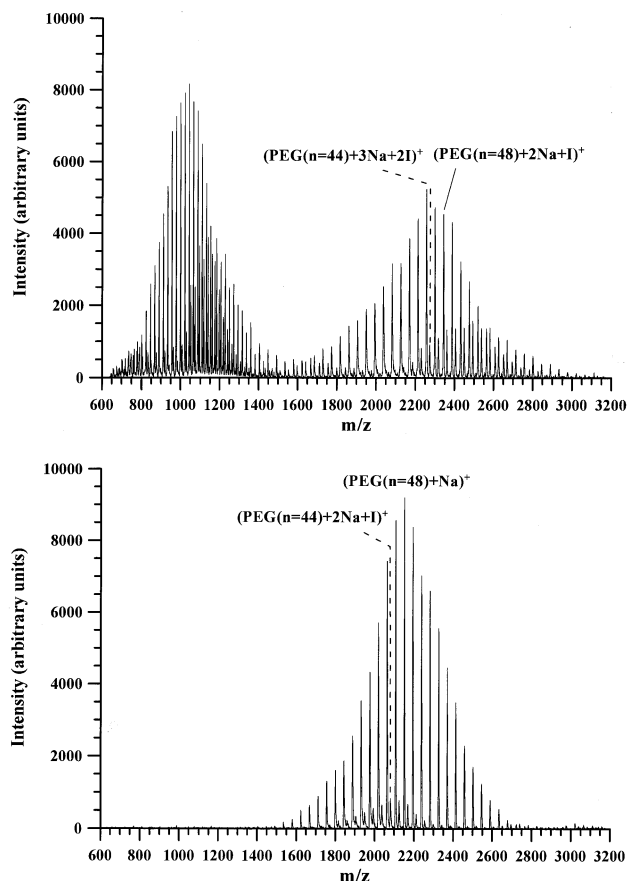


Figure 9. (a) ESI spectrum of PEG 2000 after a 196-ms reaction period with I^- . (b) Spectrum acquired after the ions of (a) were subjected to a rapid collisional excitation period.

effective for larger PEGs because ion ejection becomes increasingly competitive with collisional dissociation as the mass of the PEG ion increases. In the absence of more efficient means for the dissociation of high mass singly charged PEG/iodide adducts, the utility of iodide as a reagent for characterizing PEG molecular weight distributions in the quadrupole ion trap is limited to relatively small oligomers.

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