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Mass spectrometry analysis of poly(styrene sulfonate sodium salt), a polyanionic electrolyte

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ABSTRACT

Electrospray ionization (ESI) of poly(styrene sulfonate sodium salt) (PSS) with a molar mass of 1100 Da (weight average) efficiently produces distributions of $[M+Na]^+$ cations in positive mode and $[M-Na]^-$ as well as $[M-2Na]^{2-}$ anions in negative mode. From these distributions, repeat unit, end groups, and defects in the poly(electrolyte) can readily be determined by quadrupole ion trap mass spectrometry (QiT MS). During MS analysis, sodium/proton exchanges in the SO_3Na substituents of the $[M-Na]^-$ ions take place, with the number of exchanges observed being equal to the number of sulfonate groups present in the analyzed oligomer. Such exchanges are less pronounced for the oligomers with 2− charges and absent in the sodium-cationized oligomers (1+ charge). Collisionally activated dissociation (CAD) of the sodiated cations proceeds via charge-remote homolytic C–C bond cleavages in the polymer backbone, ultimately leading to fragments that contain both or neither of the end groups. The same chemistry is observed for the anions if they have not exchanged sodium ions for protons. In sharp contrast, precursor ions that contain SO_3H (sulfonic acid) groups due to Na/H exchange dissociate mainly by charge-catalyzed SO_3 losses. The number of SO_3 units lost is identical to the number of sulfonic acid pendants in the oligomer. The CAD results suggest that PSS may degrade to polystyrene under acidic conditions.

1. Introduction

Poly(electrolyte)s are polymers containing ionic or ionizable parts in the same macromolecule, either at each of the monomer units or at the end groups [1,2]. In solution, poly(electrolyte)s may form either cations or anions, depending on the ionic/ionizable site present [2]. Compounds with such properties have experienced increased use in polymer electrolyte fuel cells (PEFCs), which are designed to provide energy immediately when needed at ambient temperatures [3–5]. Presently, a highly fluorinated polymer with sulfonic acid groups, manufactured by DuPont under the name Nafion [6], is the sole commercially available poly(electrolyte) for PEFCs. This polymer has the proton conducting properties needed for PEFCs, but it is very expensive. Therefore, considerable industrial effort is devoted to develop alternative polymeric electrolytes, so that PEFCs can become more affordable for commercial applications [1,2,7–13]. Polymers that contain a high level of sulfonic functional groups are suitable candidates. Poly(styrene sulfonate) (PSS) has also shown promise as a replacement for Nafion, especially in combination with other polymers, such as poly(vinyl alcohol) [8,11]. The development of novel poly(electrolytes) at an accelerated pace necessitates fast and accurate methods for the characterization of their structures and degradation pathways. Preliminary data concerning the analysis of higher molecular weight PSS using matrix assisted laser desorption ionization mass spectrometry (MALDI MS) [14,15] have appeared [16–18]. Here, we report the first comprehensive MS and tandem mass spectrometry (MS^2) study of PSS, utilizing electrospray ionization (ESI) [19]. The composition and macromolecular structure of this polymer are characterized and its possible degradation mechanisms are discussed as well.

2. Experimental methods

2.1. Materials

PSS sodium salt, $-[CH_2CH(C_6H_4-SO_3Na)]_n-$, carrying the sodium sulfonate group in *para* position and with $M_w \approx 1100$ Da was purchased from Polymer Standards Service-USA, Inc. (Warwick, RI). End groups and polydispersity were not specified. The solvents and sodium trifluoroacetate (NaTFA) were acquired from Sigma-Aldrich (Milwaukee, WI) or Fisher (Pittsburgh, PA). All substances were used in the condition received without further purification.

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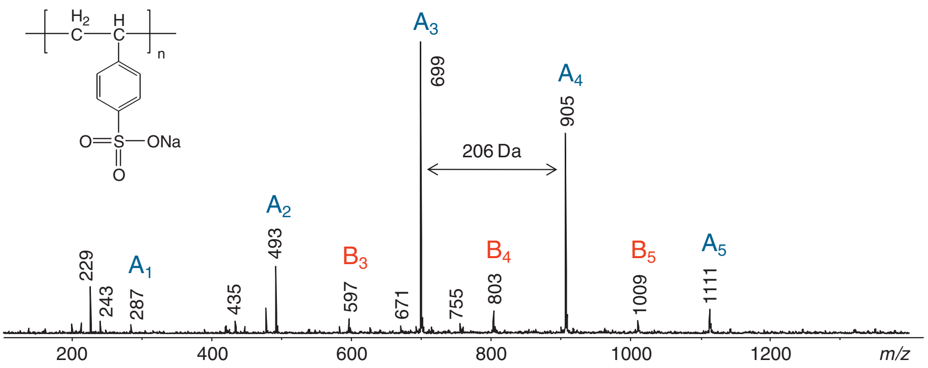


Fig. 1. Positive ion ESI mass spectrum of poly(styrene sulfonate sodium salt). The repeat unit (206 Da) is shown in the inset. All ions observed are sodiated species (ionization by Na$^+$ adduction); the subscripts indicate the number of repeat units.

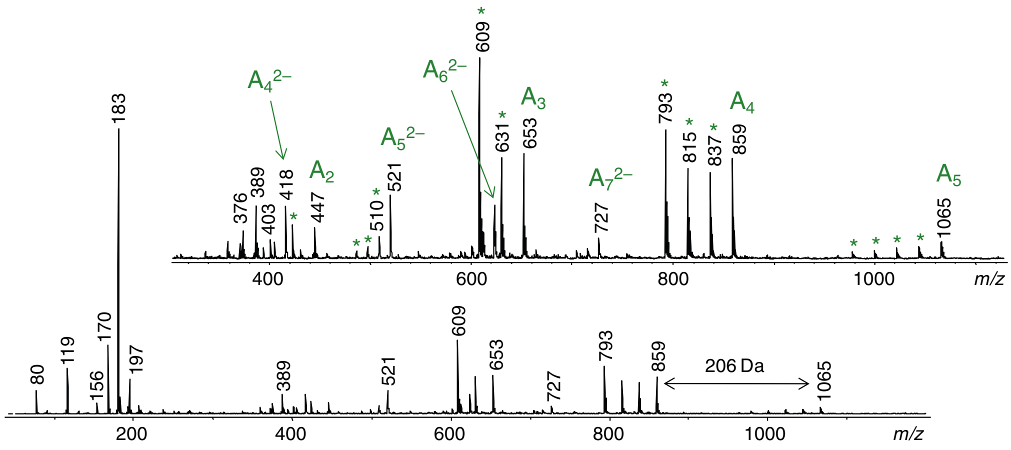


Fig. 2. Negative ion ESI mass spectrum of poly(styrene sulfonate sodium salt), showing both singly (A_n) as well as doubly (A_n^{2-}) charged polymer distributions (ionization by removal of Na$^+$). An expanded view of the m/z 300–1100 region is given in the inset. The asterisks indicate anions that have undergone Na$^+$/H$^+$ exchange which converts the sulfonate (SO_3Na) to sulfonic acid (SO_3H) substituents.

2.2. ESI mass spectrometry

All experiments were performed with a Bruker (Billerica, MA) Esquire LC quadrupole ion trap mass spectrometer (QiT) [20,21]. PSS was dissolved in water to a concentration of 1.0 mg/mL, and a few droplets of methanol were added before introducing the solution into the instrument at a rate of 250 μL/hr using a syringe pump. The spraying needle was grounded and the entrance of the sampling capillary, through which the ions enter the mass spectrometer, was kept at −4 kV or +4 kV in positive or negative ion mode, respectively. Nitrogen was used as the nebulizing gas (10 psi), which flows coaxially with the spray and aids in the formation of charged droplets, and as the drying gas (8 L/min, 300 °C), which heats the sampling capillary to help in the droplet desolvation process. Ions were accumulated for 20 ms before mass-selective ejection through ramping up of the RF potential of the ring electrode for mass-to-charge ratio (m/z) measurement. For MS^2 spectra, the desired ion was mass-selected using resonant ejection and accelerated by an auxiliary RF field on the end caps to undergo collisionally activated dissociation (CAD) with the He bath gas in

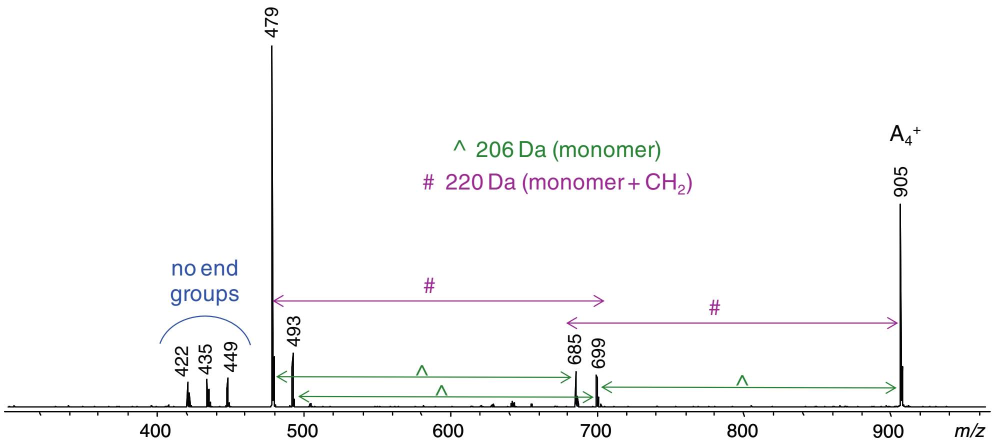
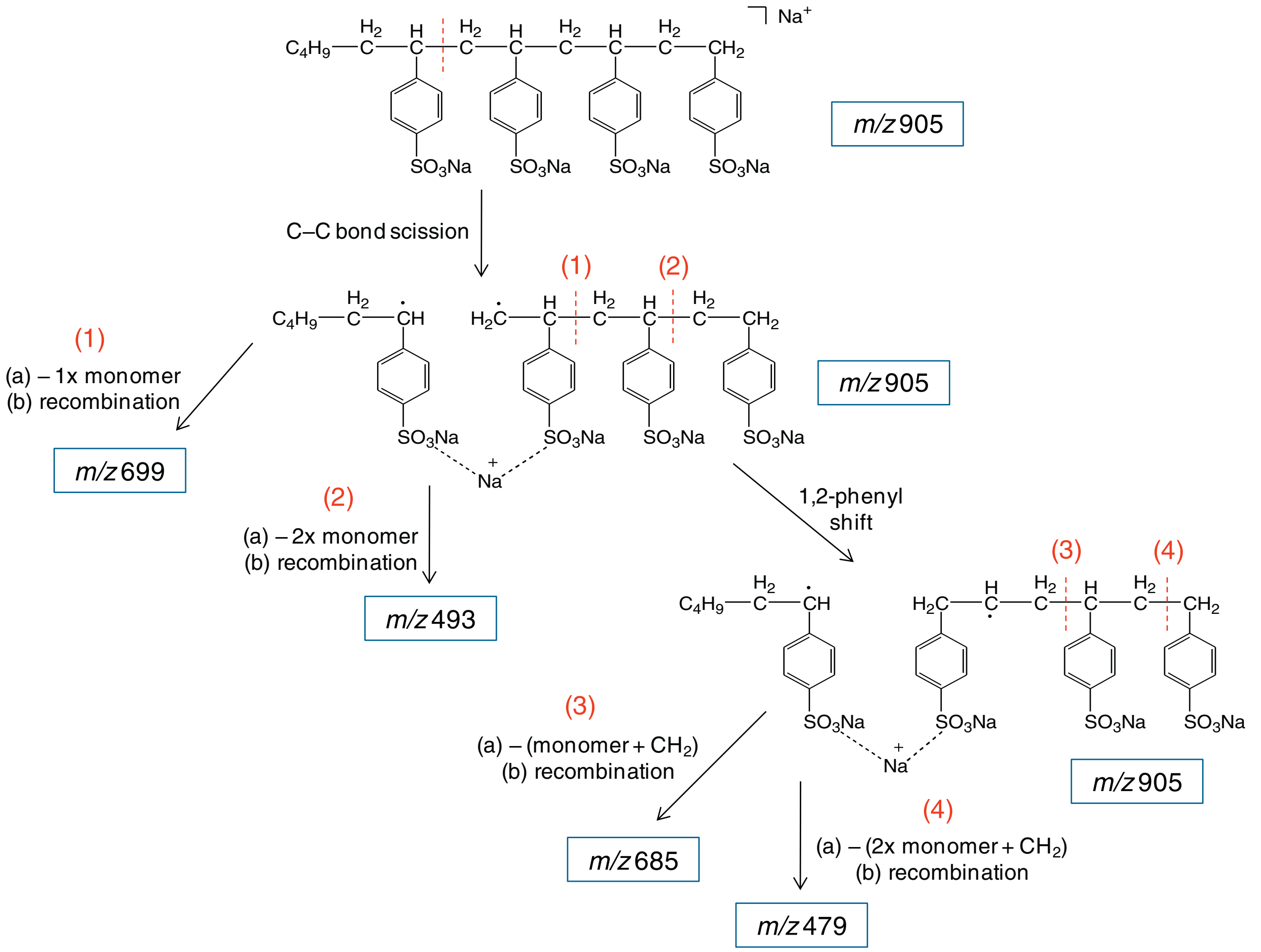


Fig. 3. Positive ion ESI-MS^2 mass spectrum of the sodiated 4-mer from poly(styrene sulfonate sodium salt) (m/z 905).



Scheme 1. Charge-remote elimination of monomer (206 Da) and monomer + CH_2 (220 Da) units from the sodiated 4-mer of poly(styrene sulfonate sodium salt).

the trap (10^{-8} bar). The excitation time was set at 40 ms and the RF amplitude of the auxiliary field at ~1 V. Approximately 20–50 scans were averaged to obtain the spectra shown. All quoted *m/z* values are monoisotopic.

3. Results and discussion

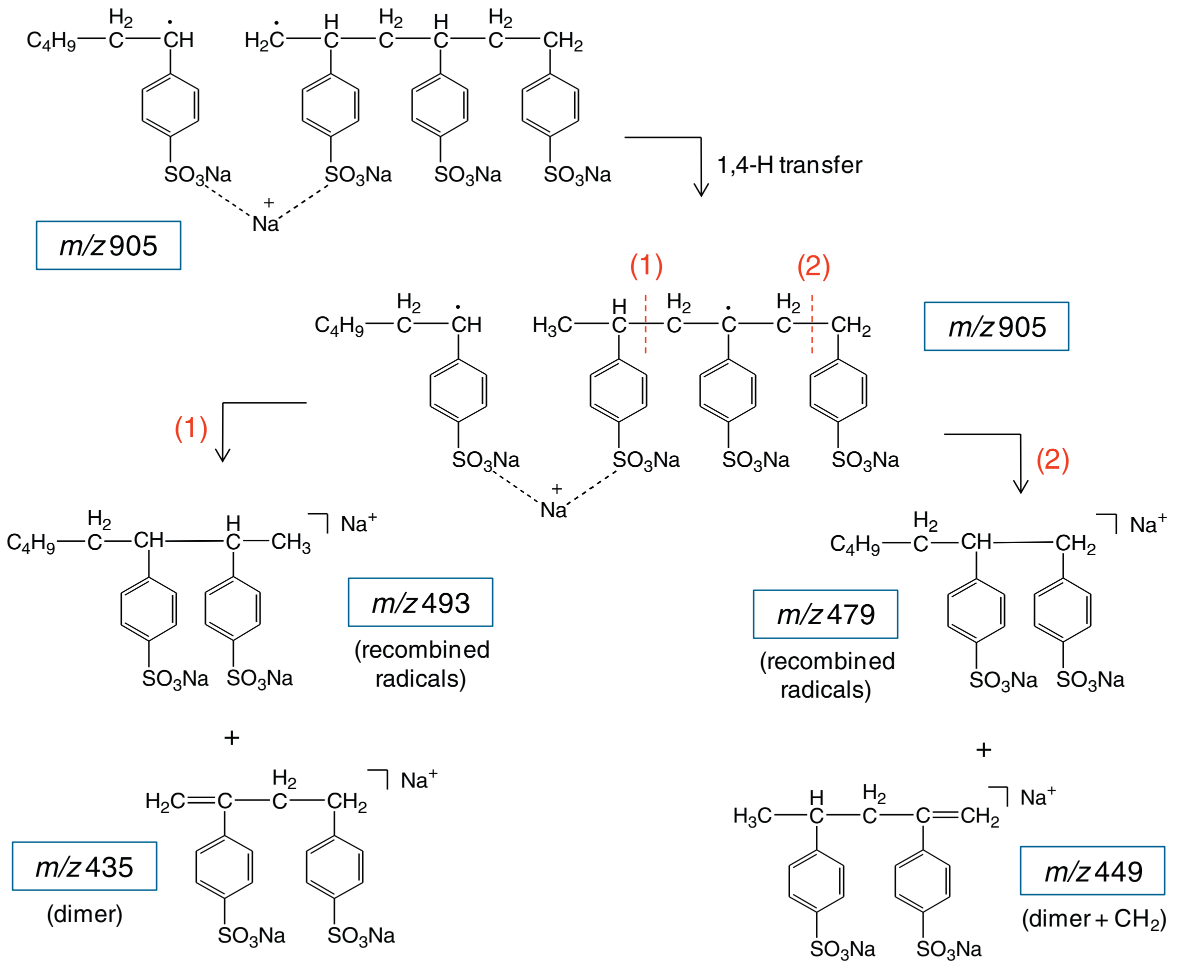
3.1. MS characterization

For the acquisition of the positive mode mass spectrum, PSS was dissolved in H_2O and no cationizing agent (NaTFA) was added. The sodium ions in the backbone are not exchanged by protons under these conditions during MS analysis, resulting in a repeat unit mass of 206 Da, cf. Fig. 1. Singly charged oligomers are observed up to the 5-mer under normal trapping conditions (target mass setting of 800), and up to 9-mer when the instrument is optimized for the detection of higher molecular weights (target mass of 1,200) [22]. The main distribution, viz. series A, agrees well with sodiated PSS ions bearing C_4H_9– (butyl) and –H groups at the α (initiating) and ω (terminating) chain ends, respectively, and a combined end group mass of 58 Da.

A second, minor distribution, viz. series B, appears 102 Da lower than series A. A 102-Da deficit results if one repeat unit lacks the sulfonate substituent (i.e. it carries H instead of SO_3Na in *para* position of the phenyl group). Independent of oligomer size, only one SO_3Na substituent is missing. Because series B is not observed in negative mode (vide infra), it is presumably produced in the ion trap by ion/molecule reactions with background moisture.

The negative mode mass spectrum (Fig. 2) includes both singly and doubly charged anions. The singly charged distributions show a 206-Da repeat unit, verifying that each monomer unit in the polymer chain is sulfonated. The monomer anion (no end groups or sodium), observed at *m/z* 183, gives rise to the most abundant peak in the mass spectrum; in contrast, the sodiated trimer was base peak in positive mode (vide supra). The *m/z* values of the ions with 1− charge confirm that the end groups have a combined mass of 58 Da; they further indicate that no ions are missing a SO_3Na substituent, as was the case in positive mode (vide supra).

The spectrum measured in negative mode shows the occurrence of consecutive Na^+/H^+ exchanges, the number of which depends on the size of the n-mer. For example, five peaks are observed for the pentamer anion: one for the polymer with one SO_3^- and four SO_3Na groups, and four subsequent peaks, arising from sequential SO_3Na/SO_3H exchanges, each causing a 22-Da decrease in mass. Within the singly charged (1−) polymers, the pentamer is the largest oligomer observed. On the other hand, the doubly charged distribution (2−) extends to the heptamer. The mass difference between adjacent doubly charged n-mers is 103 Da, affirming the incorporation of sodium in the doubly charged oligomers. Na^+/H^+ exchanges are also detected in the 2− charge state, each leading to a mass decrease by 11 Da; however, the extent of $SO_3Na \rightarrow SO_3H$ conversions is low for the dianions. The Na^+/H^+ exchanges are attributed to ion/molecule reactions with residual water in the ion trap, with the kinetics of this process being more favorable for the 1− than the 2− charge state, and least favorable for the 1+ charge state.



Scheme 2. Charge-remote elimination of dimer (412 Da) and dimer + CH_2 (426 Da), and formation of sodiated dimer (m/z 435) and sodiated dimer + CH_2 (m/z 449) from the [4-mer + Na]$^+$ of poly(styrene sulfonate sodium salt).

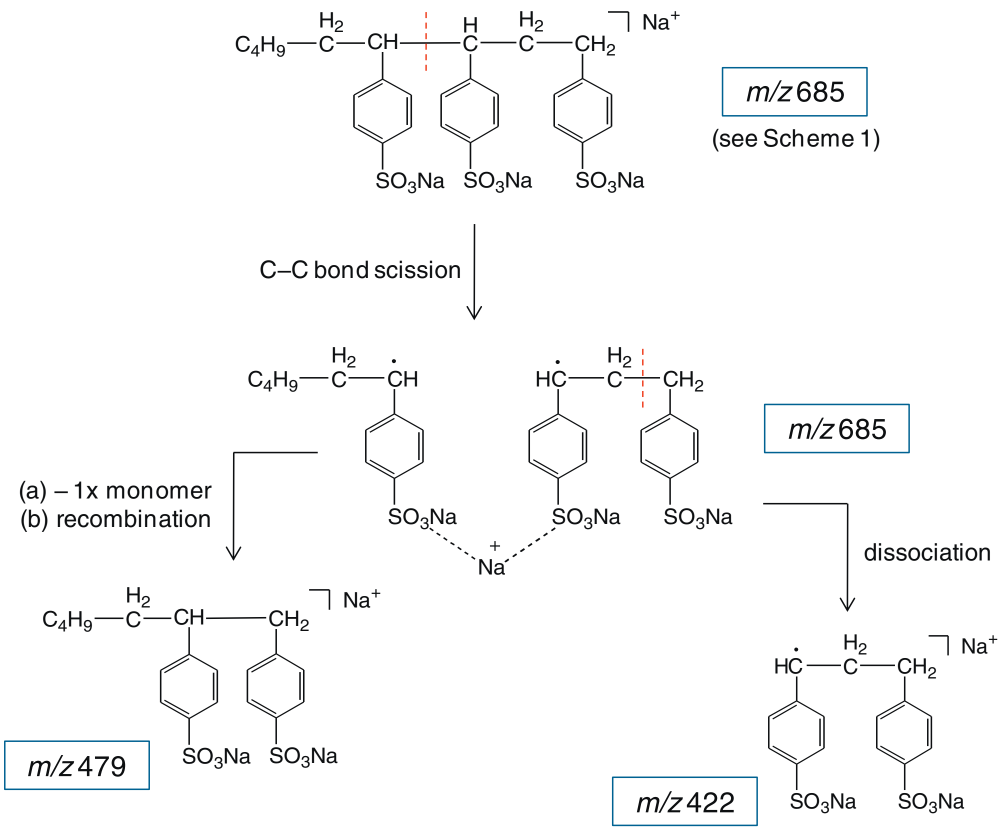
3.2. Tandem mass spectrometry of PSS

CAD of the sodiated tetramer (m/z 905, 1+) gave rise to the dissociation products displayed in Fig. 3. A dominant fragmentation involves evaporation of 1–2 monomer units. In addition, abundant fragments arise from the loss of the elements of one or two monomers plus CH_2, indicating that C–C bond scissions occur at all points along the backbone. Fragments lacking the end groups are observed at the low-mass end of the MS^2 spectrum. The described fragmentation pattern differs dramatically from that of polystyrene, where dissociation products containing one of the end groups (but not both) dominate the tandem mass spectrum [23–27].

The fragments observed can be rationalized by charge-remote [28] homolytic cleavages along the PSS backbone to create radicals that are held together in dimeric Na$^+$-bound complexes (Scheme 1) [25,27,29,30]. The sodium sulfonate groups and the cationizing Na$^+$ ion are capable of building a salt bridge network that keeps the newly formed radicals interconnected, as shown in Scheme 1. Within this complex, radical reactions can take place that generate the observed fragments [25,27]. Schemes 1–3 summarize the reactions possible after initial C–C bond cleavage next to the first repeat unit. Monomer losses from the resulting complex give rise to the fragments at *m/z* 699 and m/z 493 (Scheme 1). Rearrangement of the primary radical by 1,2-phenyl shift to a more stable secondary radical enables the loss of a 220-Da unit (monomer + CH_2), leading to *m/z* 685 or, after consecutive monomer loss, to *m/z* 479. The primary radical may alternatively rearrange to a more stable benzylic radical by 1,4-H atom transfer (Scheme 2). The benzylic radical can lose a dimer (412 Da) or a dimer + CH_2 (426 Da) to generate *m/z* 493 and 479, respectively.

The dimer and dimer + CH_2 units may also keep the Na$^+$ charge instead of being eliminated as neutral losses; this generates m/z 435 and 449, respectively. Note that the monomer and monomer + CH_2 units carry only one SO_3Na group, which prevents them from effectively competing for the Na$^+$ charge; moreover, the *m/z* values of the latter fragment ions are < 1/3 of the *m/z* of the precursor ion (*m/z* 905), which compromises their trapping in the QiT [20–22].

Although the dimer less CH unit ($2 \times 206 - 13 = 399$ Da) is not eliminated from the precursor ion, the corresponding sodiated species (*m/z* 422) is observed in the MS^2 spectrum (Fig. 3). Scheme 3 provides a likely route to this fragment, involving consecutive dissociation of *m/z* 685 (formed as shown in Scheme 1). It is worth noting that *m/z* 422 is a distonic ion and the only MS^2 fragment bearing an unpaired electron. Distonic ions with the 1,3-diphenyl-1-propyl connectivity (as in *m/z* 422) have also been observed in the CAD spectra of lithiated and silverated polystyrenes [27], pointing out that the particular stability of such charged benzylic radicals is a property of the polystyrene frame and not due to the sulfonate groups. Reactions analogous to those summarized in Schemes 1-3 can ensue after initial cleavage of any other backbone C–C bond of PSS; collectively, these pathways would lead to the same fragment ions discussed thus far.



Scheme 3. Consecutive charge-remote dissociation of *m/z* 685 (Scheme 1) by monomer loss to form *m/z* 479 (left) or by radical loss to form *m/z* 422 (right).

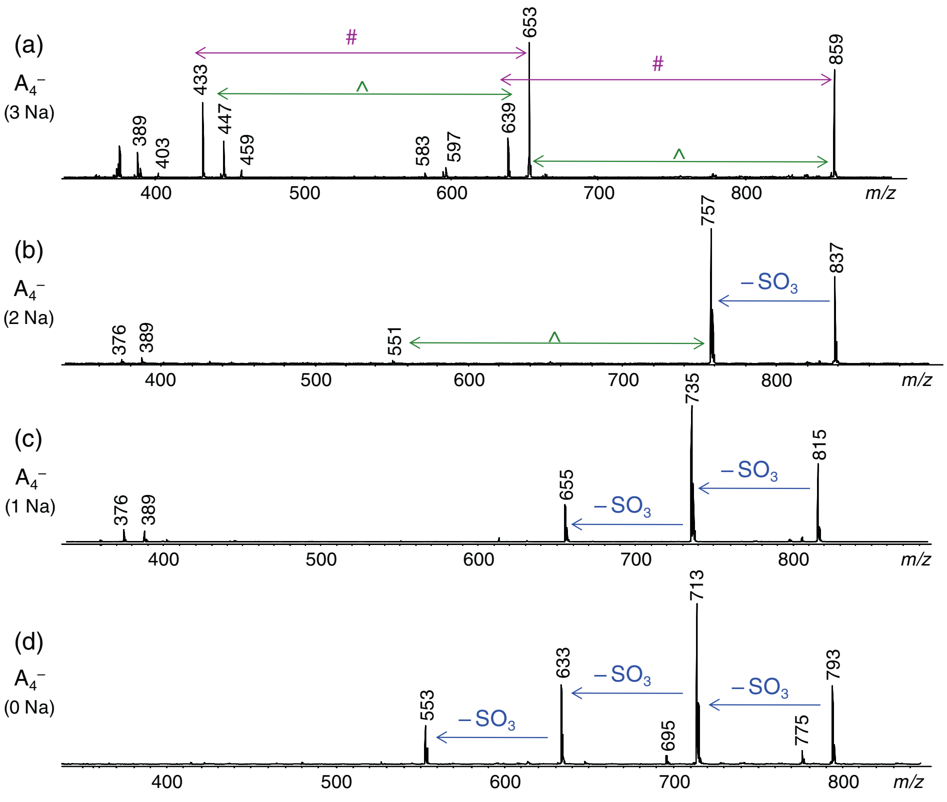
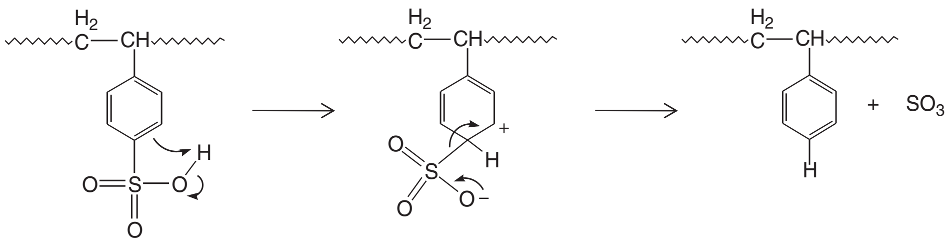


Fig. 4. Negative ion ESI-MS^2 mass spectrum of the singly charged 4-mer from poly(styrene sulfonate sodium salt). All precursor ions contain one SO_3^- anion; (a) oligomer with three SO_3Na groups (*m/z* 859), (b) oligomer one SO_3H and two SO_3Na groups (*m/z* 837), (c) oligomer with one SO_3Na and two SO_3H groups (*m/z* 815), and (d) oligomer with three SO_3H groups (*m/z* 793); the ^ and # signs indicate *m/z* differences corresponding to the masses of one monomer (206 Da) or one monomer + CH_2 (220 Da), respectively.



Scheme 4. Acid-catalyzed SO_3 elimination from poly(styrene sulfonate sodium salt) oligomers that have undergone Na^+/H^+ exchange.

The fragmentation behavior of the polyelectrolyte was also examined in negative mode. Each tetramer ion observed in the mass spectrum (Fig. 2) was subjected to CAD in the QiT; the species investigated include the tetramer with one SO_3^- and three SO_3Na substituents, as well as the tetramers that underwent one, two, or three SO_3Na/SO_3H exchanges. The resulting four MS^2 spectra are given in Fig. 4.

The precursor anion having three SO_3Na groups and no acidic proton (*m/z* 859) shows essentially the same fragmentation pattern as the tetramer in positive mode (cf. Figs. 4a and 3). In both cases, the dominant fragmentations involve evaporation of monomer and monomer plus CH_2 units. In negative mode, the most intense fragment arises by monomer loss, whereas the most abundant fragment in positive mode corresponds to the loss of a dimer plus CH_2 (or a monomer and a monomer + CH_2). All major fragments in Fig. 4a can be accounted for by fragmentation pathways similar to those given in Schemes 1–3. The differences observed in the relative fragment ion abundances of positive vs. negative mode MS^2 spectra are probably due to differences in the relative thermodynamic stabilities of the various fragment cations versus anions as well as to differences in the lifetimes of the radical complexes, in which the radical-induced fragmentations take place.

The fragmentation pattern changes significantly when one Na^+/H^+ exchange occurs. The precursor ion (*m/z* 837 Da) now mainly loses SO_3 (Fig. 4b). After the SO_3 has been lost, peaks representing consecutive monomer evaporation (*m/z* 551) and the dimer with no end groups (*m/z* 389) as well as this dimer less CH (*m/z* 376, a distonic anion) appear just above noise level. This result shows that the presence of an acidic (mobile [31,32]) proton can significantly affect the fragmentation pattern of the polymer. The SO_3H group enables a charge-directed fragmentation, promoted by the SO_3H proton (Scheme 4). Such reactions have lower energy requirements than charge-remote, homolytic bond cleavages and, thus, proceed much more efficiently during the time window available for fragmentation (millisecond time scale in the QiT) [27,28].

In the negative mode MS^2 spectrum of the tetramer with only one sodium ion (Fig. 4c), the fragmentation pattern changes again. In this case, two consecutive SO_3 losses are the main fragments, as expected from the presence of two SO_3H groups in this tetramer. In addition to these SO_3 losses, the dimer and the dimer less CH (both with no end groups) are also seen as minor products.

Lastly, the tetramer without any sodium was fragmented using CAD. The three SO_3H groups in this oligomer cause three consecutive SO_3 losses, cf. Fig. 4d. This time no dimer ion is present in the MS^2 spectrum. The dimer (and dimer less CH) fragments are generated via Na^+-bound radicals, as discussed before. The absence of Na^+ must have disabled their formation. It is noteworthy that the tandem mass spectra of the tetramers with three SO_3Na versus three SO_3H groups show completely different fragmentation patterns (cf. Fig. 4a and d). The former reveals monomer unit and backbone sequence, while the latter the number of sulfonate substituents present. Furthermore, the MS^2 data reveal that the presence or absence of acid plays an important role in the degradation mode of the polymer.

4. Conclusions

ESI of poly(styrene sulfonate sodium salt) renders mass spectra with good signal/noise ratio in both positive and negative mode. Sodium/proton exchange does not occur measurably in charge state 1+. Sodiated PSS cations lose, however, to a small extent one of their SO_3Na substituents, presumably via ion/molecule reactions with residual moisture in the trap. ESI in negative mode leads to singly as well as doubly charged anions for the PSS studied (~1100 Da). The 1− charge state undergoes readily Na^+/H^+ exchange (i.e. $SO_3Na \rightarrow SO_3H$ conversion); the number of Na^+/H^+ exchanges observed is equal to the number of repeat units and, thus, readily reveals the degree of polymerization. Na^+/H^+ exchanges also occur in charge state 2−, but to a much lower extent.

The tandem mass spectra of PSS reveal that in the absence of protons this polyelectrolyte decomposes via charge-remote free radical chemistry, which begins via homolytic C–C bond cleavages in the polymer backbone to produce incipient radicals that are kept together in Na^+-bound complexes sufficiently long to permit radical rearrangements and β C–C scissions to occur before final fragment formation. When protons become available, charge-induced SO_3 eliminations commence and dominate at the expense of the radical-site reactions. If all SO_3Na pendants are converted to SO_3H, the sole significant fragmentation pathway is sequential SO_3 eliminations, with the number of SO_3 lost being equal to the number of SO_3H groups in the polymer.

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