Post-Source Decay of Polystyrene Ions in Matrix-Assisted Laser Desorption/Ionization

Robert Goldschmidt, Stephanie Wetzel, William Blair, Charles Guttman

NIST Polymers Division, 100 Bureau Drive, Stop 8541, Gaithersburg, MD 20899-8541

Introduction

A polystyrene (PS) sample of nominal molecular mass 7900 was prepared commercially for the NIST polymers division and was expected to consist of oligomers of the form $(CH_3)_3C-(CH_2CHC_6H_5)_n$-H. Matrix-assisted laser desorption/ionization (MALDI) mass spectra of the sample reveal unexpected secondary series of 104 u mass separation in addition to the expected main series ions. The positions of the secondary series ions in relation to the main series ions depend on the choice of matrix and also on the salt added to effect cation attachment to PS. The matrices retinoic acid (RA), trans-3-indoleacrylic acid (IAA), and dithranol were used, and the salts used were silver trifluoroacetate (AgTFA) and copper trifluoroacetate (Cu(II)TFA). Post-source decay (PSD)[1] analysis of the PS7900 sample and also of a PS3900 sample indicate that the secondary series are primarily due to the formation and decay of adducts of PS with matrix molecules and metal cations. Some PSD of main series ions also occurs.

Experimental Notes

Mass spectra were acquired on a Bruker Reflex II time-of-flight mass spectrometer equipped with dual microchannel plate detectors for both linear and reflectron modes and with a 3 ns pulsewidth nitrogen laser.[2] A pulsed deflector allows selection of a mass window for PSD analysis. Delayed extraction was used during the acquisition of all mass spectra. The matrices RA, IAA, and dithranol and the salts AgTFA and Cu(II)TFA were acquired from Aldrich. Solutions were prepared using tetrahydrofuran (THF) solvent. PS7900 was prepared by anionic polymerization using a t-butyllithium initiator. The PS3900 sample, also with butyl and H end groups, was obtained from Polymer Source, Inc. Polymer solutions were prepared at 2.5 mg/mL, matrix solutions at 0.1 mol/L, and silver and copper salt solutions at 0.01 mol/L. These were mixed at a matrix:polymer:salt volume ratio of 20:2:1 prior to deposition on a stainless steel target. PSD fragment mass assignment was performed using the Bruker XTOF software, based on calibration of fragments from the peptide ACTH clip (18-39).

Results and Discussion

When reflectron mode mass spectra of the PS7900 sample are obtained using RA matrix with AgTFA, a small series of ions is observed at +40 m/z relative to the main series $(PS + Ag)^+$ ions. No secondary series is observed in the linear mode mass spectra, suggesting that the +40 series arises from PSD of main series ions. Selection and PSD analysis of a main series ion indicates that four fragment ions emanate from the selected mass window and that these correspond to losses of one, two, three, and four styrene (104 u) repeat units from the main series ion. The fragment peak corresponding to loss of four repeat units is larger than the other three and it is this fragment that gives rise to the +40 series of ions. Similar results are found for the treatments IAA or dithranol with AgTFA and dithranol with Cu(II)TFA, except that the fragment intensity pattern is different in each case (e.g., for the IAA/AgTFA treatment, the fragment corresponding to loss of three repeat units is dominant). When RA or IAA are used with Cu(II)TFA, secondary series are observed in linear mode as well as in reflectron mode. PSD analysis reveals that in these two cases the secondary series in the reflectron mode spectra come not from fragmentation of the $(PS + Cu)^+$ ions, but from the secondary series ions observed in the linear mode spectra.

Experiments were conducted on the PS3900 sample in hopes of improving confidence in mass assignment of the secondary series. Secondary series in the linear mode spectra were found to be consistent with adducts of the form $(PS + salt + Cu)^+$, where salt = (Ma - H + Cu) and Ma signifies a matrix molecule (these could alternatively be of the form $(PS + Ma + 2Cu)^+$). PSD analysis indicated that the main secondary series in the reflectron mode were due to loss of salt (or (Ma + Cu)) from these adducts. A small fragment peak corresponding to loss of Ma was also found.

Improved peak definition at this lower mass range revealed the presence of the $(PS + salt + M)^+$ series, where M = Ag or Cu, also in the linear mode spectra of the dithranol/Cu(II)TFA and IAA/AgTFA treatments. Though no such series have been positively identified in the linear mode spectra of the RA/AgTFA or dithranol/AgTFA treatments, overlapping peaks may obscure them. For all six treatments, PSD analysis supports the loss of salt from $(PS + salt + M)^+$ adducts as a source of secondary series ions observed in reflectron mode. In five of the six treatments, this loss accounts for the most prominent secondary series. The exception is the dithranol/AgTFA treatment, where the most prominent secondary series comes from decay of a different series of ions, also suspected of being adducts, but as of yet not identified. Small fragment peaks corresponding to a loss of M from $(PS + Ma + 2M)^+$ parents are observed for three of the treatments. A series of peaks corresponding to $(PS + 2Cu)^+$ is observed for each of the Cu(II)TFA treatments. PSD of these reveals small fragment peaks that are consistent with losses of Cu, (Cu + 104), and (Cu + 208). The corresponding $(PS + 2Ag)^+$ series or its possible fragments in the AgTFA treatments have so far not been observed, but again overlapping peaks could obscure them.

Although fragments from the main series $(PS + M)^+$ ions do not appear to be major contributors to the secondary series observed in the reflectron mode spectra, PSD from these ions does occur. In each of the three Cu(II)TFA treatments, small peaks corresponding to loss of one and two repeat units are observed. In the three AgTFA treatments, losses may extend to three or more repeat units. At lower mass, PSD fragments are similar for all six treatments. Two series of fragments are observed having approximately equal intensities, with nominal masses given by $[(104)_n + M]^+$ (α series) and $[(104)_n + 70 + M]^+$ (β series). The series are observed from roughly n = 10 to n = 20. Similar series have been observed by others examining fragmentation of PS ions.[3-5] Another group of peaks appears at m/z values lower than the α and β series. Several of them appear to match low mass series described by Jackson, et al (called the A, B, and G series).[4] A few additional low mass peaks are also observed. It should be noted that in order to observe these low mass peaks, and also the α and β series peaks, laser energy and detector gain were increased to levels well past those normally used to acquire MALDI mass spectra of PS. In contrast, the higher mass decay products described above can be observed even at laser intensities close to the threshold for observing the $(PS + M)^+$ ions.

Examination of the low mass portions of mass spectra for the six treatments may offer clues as to how $(PS + salt + M)^+$ adducts, and also $(PS + M)^+$ ions, are formed. Adducts of the form $[Ma_x salt_y M_z]^+$ are prominent. A small amount of Ag^+ and Ag_2^+ signal can be observed for the AgTFA treatments, but the corresponding copper signal is not apparent for the Cu(II)TFA treatments. $(Ma + M)^+$ and $(2Ma + M)^+$ adducts are prominent for all six treatments. Other commonly observed adducts include $[Ma + salt + M]^+$, $(2salt + M)^+$, and $(Ma + 2salt + M)^+$. For RA and IAA, additional adducts can be observed to as high as m/z 1500, but for dithranol there is little or no Ma-M adduct signal past m/z 1000. Interestingly, $(salt + M)^+$ adducts are generally not prominent. They have not been observed at all for the Cu(II)TFA treatments.

Direct collisions involving PS oligomers and bare M cations are one way in which $(PS + M)^+$ ions could be formed; however, the evidence here suggests that collisions with adducts in which M^+ is transferred to PS should also be considered. Likewise, direct collisions between PS oligomers and $(salt + M)^+$ adducts could lead to formation of the $(PS + salt + M)^+$ adducts. However, again the evidence suggests that collisions with larger adducts in which $(salt + M)^+$ is transferred to PS should also be considered. It may also be possible that salt and M^+ are transferred in separate collisions. Note that decay of $(PS + salt + M)^+$ adducts produces $(PS + M)^+$ ions. Thus it is possible that some $(PS + M)^+$ ions are formed by fast (in-source) decay of $(PS + salt + M)^+$ or other adducts.

1. Kaufmann, R.; Kirsch, D.; Spengler, B. *Int. J. Mass Spectrom. Ion Proc.* **1994**, *131*, 355.
2. Certain commercial materials and equipment are identified in order to specify the experimental procedure. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that such materials and equipment are necessarily the best available for the purposes described herein.
3. Jackson, A. T.; Jennings, K. R.; Scrivens, J. H. *J. Am. Soc. Mass Spectrom.* **1997**, *8*, 76.
4. Jackson, A. T.; Yates, H. T.; Scrivens, J. H.; Green, M. R.; Bateman, R. H. *J. Am. Soc. Mass Spectrom.* **1998**, *9*, 269.
5. Craig, A. G.; Derrick, P. J. *Aust. J. Chem.* **1986**, *39*, 1421.