

Matrix Clusters and Polymer-Matrix Adducts in the MALDI Analysis of Polystyrene

Robert J. Goldschmidt, Charles M. Guttman

Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8541 USA

Models proposed to describe cation attachment to analyte species in matrix-assisted laser desorption/ionization (MALDI) include those in which precursor ions are directly desorbed and those in which it occurs by interactions during the expansion of material from the sample. In the case of MALDI analysis of polystyrene (PS), it has been shown by use of layered sample preparations that attachment of silver and copper ions during the expansion [1]. Recently, a model has been proposed in which small, charged clusters are directly desorbed [2]. Such clusters decay by loss of neutral species, such as matrix molecules. Cationized analyte molecules are the surviving species from some of the decaying clusters.

In addition to the expected $(PS + M)^+$ series of ions, various secondary series are observed in MALDI mass spectra of PS [3]. The secondary series are largely due to formation and decay of PS-matrix adduct species. In most cases, the most prominent adduct series is $(PS + \text{MaSalt} + M)^+$, where $\text{MaSalt} = [\text{Matrix} - \text{H} + \text{M}]$, and the most prominent decay series is due to loss of MaSalt from such ions, yielding $(PS + M)^+$. Most other adduct decay products observed are also of the form $(PS + M)^+$. It is stressed that the decay products have the same formula as the main series ions. Thus, there is direct evidence that at least some $(PS + M)^+$ ions are formed through a mechanism that involves adduct decay. The question of how PS-matrix adducts are formed therefore has some relevance to the mechanism of cation attachment to PS. One possibility is that adducts are desorbed intact, in a manner similar to that described in reference 2. Alternatively, they could form by combination of species in the selvedge.

Abundant matrix cluster species are often observed in the lower mass portions of MALDI mass spectra of polystyrene [1,3]. Many of these fit the formula $(n\text{Ma} + m\text{MaSalt} + k\text{M})^+$, where Ma = a matrix molecule; $n = 0, 1, 2, \dots$; $m = 0, 1, 2, \dots$; and, at least in most cases, $k = 1$. They also could conceivably be formed either by direct desorption or by combination during expansion. Their composition suggests that they may have some relevance to the formation of $(PS + M)^+$ ions and PS-matrix adduct ions. They may be considered competitors for metal cations and for MaSalt with PS, and they may also transfer those species by collisions with PS.

In this work, layered sample preparations were used to investigate the formation of PS-matrix adduct and matrix cluster ions. Two methods were used to accomplish layering. One was similar to that described in reference 1 and involved deposition of the salt from aqueous solution on top of a dried PS-matrix layer. The second method made use of electrospray sample deposition. Scanning electron microscopy (SEM) experiments indicate that the tiny droplets produced by electrospraying arrive at the target dry or virtually dry [4]. This allows layers to be applied using only organic solvents.

Experiments were performed on a Bruker Reflex II time-of-flight mass spectrometer equipped with dual microchannel plate detectors and with a 3 ns pulsewidth nitrogen laser [5]. PS samples (PS7900 and PS3900) were from Polymer Source, Inc. [5]. The matrices retinoic acid (RA), trans-3-indoleacrylic acid (IAA), and dithranol and the salts silver trifluoroacetate (AgTFA) and copper trifluoroacetate (Cu(II)TFA) were used. Solvents used were tetrahydrofuran (THF) and distilled water. Electrospray sample deposition was performed from a 0.15 mm i.d. stainless steel syringe needle at 5 kV, with a spray tip to target distance of 3 cm to 5 cm and a flow rate of 4 $\mu\text{L}/\text{min}$.

MALDI mass spectra of PS obtained from samples in which a layer of AgTFA or Cu(II)TFA is placed on top of a PS-matrix layer are similar to those obtained from normal, non-layered samples. This is true for either of the layering methods described above. As noted in reference 1, $(PS + M)^+$ ions are readily observed. Also, the PS-matrix adduct and decay species and the matrix cluster species described above are observed. There are some differences in the relative intensities of the cluster species obtained from layered and non-layered samples. Good signal intensity can be obtained from the layered samples, though generally it requires increased laser fluence compared to the non-

layered samples. Thus, MaSalt formation and cation attachment to clusters and adducts both occur during the expansion, though a contribution from precursor species in non-layered samples is not ruled out.

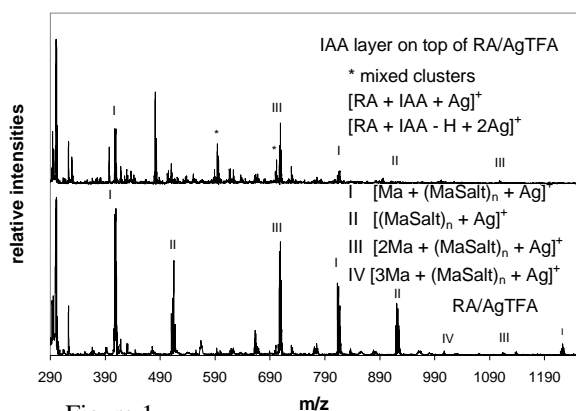


Figure 1.

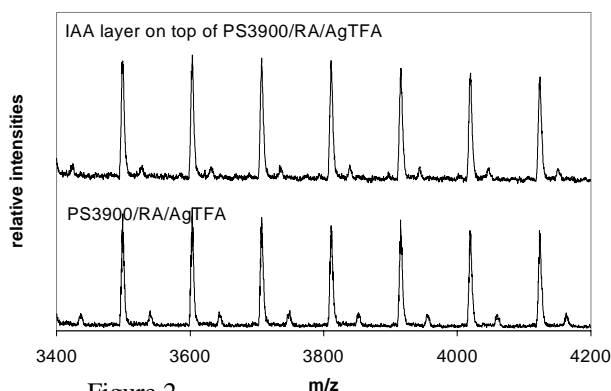


Figure 2.

This still leaves the question of whether PS-matrix adducts and matrix clusters are desorbed intact, with subsequent matrix salt formation and cation attachment, or are formed by combination during expansion. In additional experiments, one layer consisted of a mixture of PS, matrix, and salt deposited by electrospray from a single solution, and a second layer consisted of a second matrix only, electrosprayed on top of the first layer. In Figure 1 the lower mass portion of a mass spectrum obtained from such a layered sample (top) is paired with one obtained from a normal, non-layered sample containing one matrix (bottom). Several of the matrix clusters observed with the sample containing only a PS3900/RA/AgTFA layer are also observed with the sample having an IAA layer on top. Some of the clusters marked in the bottom mass spectrum, however, are not observed in the top one, and the relative intensities of the clusters that are observed are different than those found for the one-layer sample. Similar results are found when the top spectrum is compared to one obtained from a sample containing a single PS3900/IAA/AgTFA layer (not shown). Note also that two mixed matrix clusters have been identified in the top mass spectrum. The mixed clusters and the IAA clusters in the top mass spectrum could only form by combination subsequent to the laser pulse.

The comparison of layered and non-layered results is continued in Fig. 2, where a region containing part of the PS3900 distribution is examined. Post-source decay (PSD) analysis indicates that the smaller series in the mass spectrum obtained from a single PS3900/RA/AgTFA layer (bottom) is due to decay of $(PS + MaSalt + Ag)^+$ adducts by loss of MaSalt, to yield $(PS + Ag)^+$ ions. This series is visible, though not prominent, in the mass spectrum obtained from the sample with the IAA layer on top (top). Comparison to a mass spectrum obtained from PS3900/IAA/AgTFA (not shown) indicates that the top mass spectrum also contains series due to PS/IAA adduct species and their decay products. No PS-mixed matrix adduct species have been identified, though a full PSD analysis of the layered sample has yet to be performed. Note that PS-IAA adduct species could only be formed from the layered sample by combination of PS and IAA species during expansion. Though it can not be ruled out that directly desorbed PS-matrix adducts are produced from the RA layer, such a mechanism can not account for all observed adducts.

References

1. Lehmann, E.; Knochenmuss, R.; Zenobi, R. *Rapid Commun. Mass Spectrom.* 1997, 11, 1483-1492.
2. Karas, M.; Gluckmann, M.; Schafer, J. *J. Mass Spectrom.* 2000, 35, 1-12.
3. Goldschmidt, R.; Blair, W.; Wetzel, S.; Guttman, C. *Proceedings of the 47th ASMS Conference on Mass Spectrometry and Allied Topics*, Dallas, TX, June 13-17, 1999.
4. Hanton, S.D.; Hyder, I.Z.; Stets, J.R.; Owens, K.G. *Proceedings of the 47th ASMS Conference on Mass Spectrometry and Allied Topics*, Dallas, TX, June 13-17, 1999.
5. 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.