

# MALDI-TOF MS Characterization of Covalently-Cationized Polymers

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## INTRODUCTION

MALDI-TOF MS generally uses metal salts to cationize synthetic polymers, such as polystyrene. However, reduced analyte signal often results from complications during the metal ionization processes in the gas phase including competition between the analyte and matrix for cationization, self-clustering of the metal salts, and clustering of metal salts with matrix. One approach to increase the polymer ion signal is to apply more aggressive laser power; however, this may result in fragmentation of the polymer leading to molecular mass distribution (MMD) unrepresentative of the true distribution. We have developed a covalent cationization method in which a phosphonium or an ammonium salt is covalently attached to one of the chain ends.<sup>1,2</sup> This will assure singly charged analytes and the competition associated with metal ionization will be eliminated. Better spectra can be generated since the undesirable background noise can also be reduced. Furthermore, polyolefins that cannot be cationized using traditional metal approach can be cationized using covalent cationization to produce successful MALDI spectra. This proceeding will discuss the covalent cationization method used to characterize polyolefins and polystyrenes and compare covalent cationization method to traditional metal cationization for polybutadiene and polystyrene to gain understanding of the mechanisms that govern the desorption ionization processes.

## EXPERIMENTAL

The mass spectrometry was measured using a Bruker Reflex II MALDI-TOF instrument\* equipped with the standard 337 nm nitrogen laser. Dithranol and all-trans retinoic acid were used as matrixes. Narrow mass fractions of polyethylene, LEA-51, Standard Reference Material (SRM) 2885, SRM 1482, and SRM 1483, were covalently attached to an organic cation. Two synthetic steps are involved in the covalent cationization: bromination of the polymer at residual vinyl bonds, followed by conversion of the brominated site to a phosphonium salt that is easily ionized (dissociated) during the MALDI process. Narrowly dispersed Br-terminated polystyrenes (PSty) synthesized via atom transfer radical polymerization and hydroxy terminated polybutadiene (PB) were also chemically modified using a similar approach. The standard uncertainty of the peak position from calibration and repeatability studies is 0.5 u (g/mol) at 5 ku, and the estimated relative uncertainty in overall signal intensity from repeatability studies is 15 %.

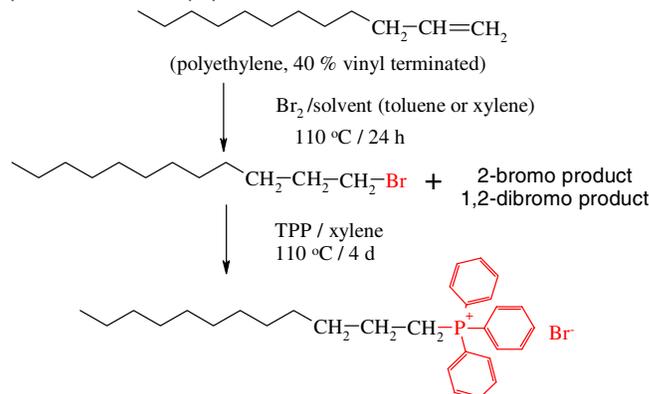
High-resolution, 270-MHz proton NMR spectra were taken on a 6.35 T JEOL GX270 spectrometer. Polyethylene samples dissolved in 1,1,2,2-tetrachloroethane-*d* were sealed in 5 mm tubes under a nitrogen atmosphere whose pressure was slightly below ambient. All spectra were run at 120 °C, 15 Hz sample spinning, 45° tip angle for the observation pulse, and a 20 s recycle delay. The standard uncertainty for molecular mass calculated using <sup>1</sup>H NMR is 12.5 %.

## RESULTS AND DISCUSSION

We have developed a method whereby an amine or phosphine is covalently attached to one of the chain ends on polyethylene forming an organic salt (Figure 1). Successful MALDI spectra can be generated on fractionation products of a commercial polyethylene up to a number

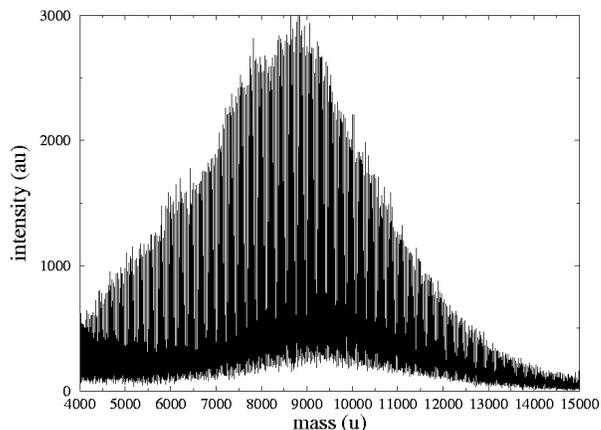
\* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

average molecular mass ( $M_n$ ) of 15,000 g/mol.<sup>1</sup> The vinyl content was found by FTIR and solution <sup>1</sup>H NMR to be independent of the  $M_n$  of the fractionated materials. This is important since the chemical modification uses the population of molecules with terminal double bonds to represent the overall population.



**Figure 1.** Bromination of polyethylene terminal double bond followed by reaction of triphenylphosphine (TPP) with the 1-bromo product.

Figure 2 shows the MALDI-TOF MS for polyethylene fraction, SRM 1482. For all polyethylene spectra, a main series of peaks correspond to (within  $\pm 2$  u) a proton at one terminus and a TPP group at the other. The  $M_n$  and mass average molecular mass ( $M_w$ ) calculated from MALDI were compared with those measured via osmometry, light scattering and <sup>1</sup>H NMR (Table 1). The molecular mass of SRM 1482 determined by <sup>1</sup>H NMR was slightly higher than that measured by osmometry. However, both  $M_n$  and  $M_w$  calculated from MALDI were consistently lower, *i.e.*, 60 % to 75 % of those determined via osmometry, <sup>1</sup>H NMR, and light scattering. Furthermore, singly charged oligomers for SRM 1483 were not detected by MS, although H-NMR confirms sufficient phosphine conversion.



**Figure 2.** MALDI-TOF MS spectrum of polyethylene narrow mass fraction: SRM 1482. The data are shown without smoothing or background subtraction.

**Table 1. Molecular Mass (g/mol) of Polyethylene Fractions Determined by Traditional Methods and MALDI-TOF MS**

	$M_n^1$	$M_w^1$	$M_n^2$	$M_n^3$	$M_w^3$
LEA-51	--	--	4,060	2,510	2,610
SRM 2885	--	6,280	5,720	4,280	4,600
SRM 1482a	11,400	13,600	13,400	8,430	9,080
SRM 1483a	28,900	32,100	32,000	--	--

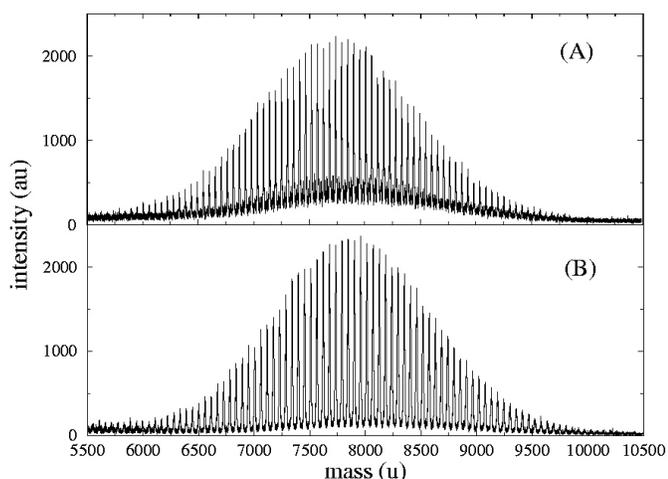
<sup>1</sup> provided by certificate of NIST Standard Reference Materials

<sup>2</sup> calculated using <sup>1</sup>H NMR analysis

<sup>3</sup> calculated using MALDI MS

To explore whether the chemical modification utilized for MALDI was contributing to molecular mass biasing, we compared mass spectra obtained on polymers that could be charged by conventional methods as well as through covalent cationization. A OH-terminated PB and a Br-terminated PSty were used as model compounds to assess the effect of chemical modification on molecular mass biasing. PB and PSty contain double bonds or aromaticities that allow them to be metal cationized by the traditional method. The terminal functionality can also be modified via covalent cationization.

PB was chosen since hydrogenation leads to a linear low-density polyethylene model, which can be compared directly to polyethylene. Figure 3 shows comparison of the MALDI spectra for metal cationized PB and covalently cationized hydrogenated PB. The  $M_n$  and MMD were almost identical for essentially the same source-polymer that was cationized using very different methods. This suggests that in the MALDI analysis any  $M_n$  or MMD biasing in the normal metal cationization method is not different from the covalent cationization method.

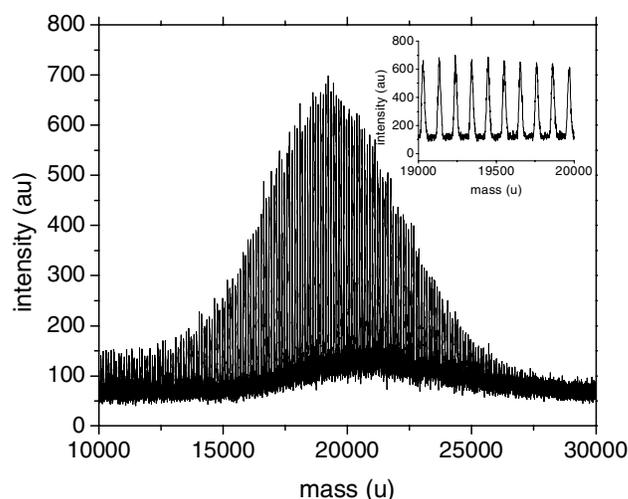
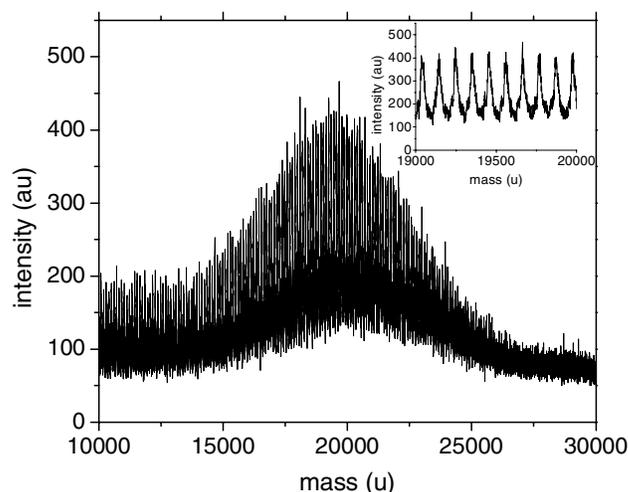


**Figure 3.** MALDI-TOF MS spectra for A) copper metal cationized polybutadiene, and B) hydrogenated analogue of polybutadiene used in A with covalent cationization.

In studying covalent cationization of polystyrene, we address the factors that impose an upper mass limit as well as molecular mass biasing for polyethylene. This study also provides the opportunity to decouple the ionization and desorption process of the MALDI technique. Because the polymer ions are preformed, no ionization bias occurs within the mass spectrometer. Comparison of MALDI analysis of polymer standards ionized using traditional metal cationization and MALDI analysis of the covalently cationized polymers lead to further elucidation of mass discrimination effects found using the traditional metal cationization method in MALDI.

Figure 4 shows the MALDI spectra for silver cationized (upper) and covalently cationized (lower) 20,000 g/mol polystyrene with tributyl phosphine. It is important to note that the  $M_n$  of the model PSty is significantly higher than the "limit" observed for the PE (15,000 u). These results suggest that the inability to observe high  $M_n$  PE (e.g., SRM 1483) by MS does not relate to mass alone. Furthermore, the mass spectra obtained using two very different ionization methods are similar, suggesting that the lower than expected molecular mass moments for PE is not due to chemical derivatization method.

From the PSty mass spectra obtained using different ionization techniques, the intensity was higher for the covalently cationized material. Expansion of the spectra, shown as inserts, revealed that the signal to noise ratio is significantly improved for the covalently cationized sample.



**Figure 4.** MALDI-TOF MS spectra for A) metal cationized PSty, and B) covalently cationized PSty. The baselines are corrected with no smoothing.

Application of covalent cationization method to PSty yields a substantial improvement in mass range and a simultaneous decrease in fragmentation compared to previously reported mass spectra of PE. In addition, the MS of chemically derivatized PSty with higher molecular mass moments than previous reported has been produced with high signal intensities and the similar distribution as obtained from traditional metal cationization. Comparison studies using PB and PSty showed that covalent cationization does not induce  $M_n$  or MMD biasing. Higher signal, less fragmentation, and better reproducibility was achieved using covalent cationization technique.

#### ACKNOWLEDGEMENTS

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