

MALDI-TOF MS Characterization of Covalent Cationized Polymers

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INTRODUCTION

MALDI-TOF MS generally uses metal salts to cationize synthetic polymers, such as PMMA and polystyrene. However, complications arise from the metal ionization processes in the gas phase including competition between the analyte and matrix as well as self-clustering of the metal salts and clustering of metal salts with matrix may lead to reduced signals. One approach to increase the polymer ion signal is to apply more aggressive laser power, however, fragmentation of the polymer may result leading to erroneous MMD. We, and others, have developed a covalent cationization method in which a phosphonium or an ammonium salt is covalently attached to one of the chain ends. This will assure singly charged analytes and the competition associated with metal ionization will be eliminated. Better spectra can be generated since more reproducible results can be obtained under general conditions and 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.^{1,2} 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* using the standard 337 nm nitrogen laser. Dithranol and all-trans retinoic acid were used as matrices. Polyethylenes, LEA-51, NIST standard reference materials 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. Narrow dispersed Br-terminated polystyrenes (PS) synthesized via ATRP and hydroxy terminated polybutadiene (PB) were also chemically modified using a similar approach. Estimated standard uncertainty of the peak position from calibration and repeatability studies is 0.2 u (g/mol), and the estimated standard 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 ¹H NMR is 12.5 %.

RESULTS AND DISCUSSION

We have developed a method whereby an ammonium or a phosphonium salt is covalently attached to one of the chain ends on polyethylene (Figure 1). Successful MALDI spectra can be generated on fractionation products of a commercial polyethylene up to a number average molecular mass (M_n) of 15,000 g/mol.¹ The MMD for the

molecules with double bonds was found by FTIR and solution ¹H NMR to be an accurate representation of the overall MMD in each 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.

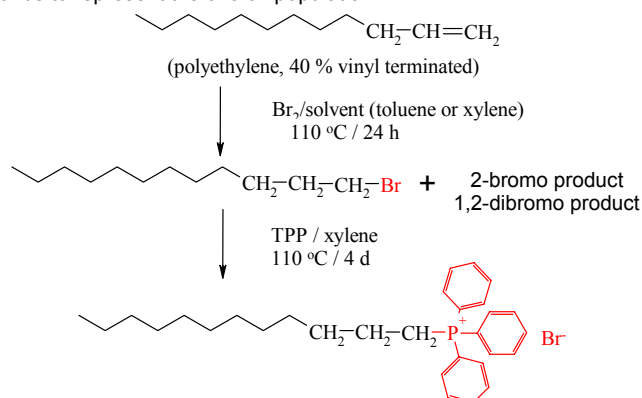


Figure 1. Bromination of polyethylene terminal double bond followed by reaction of triphenylphosphine with the 1-bromo product.

Figure 2 shows the MALDI-TOF MS for the highest detectable polyethylene fraction, SRM 1482. For all polyethylene spectra, a main series of peaks correspond to (within ± 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 ¹H NMR (Table 1). The molecular mass of SRM 1482 determined by ¹H 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, ¹H NMR, and light scattering. Moreover, higher M_n PE could be detected even with sufficient chemical modification.

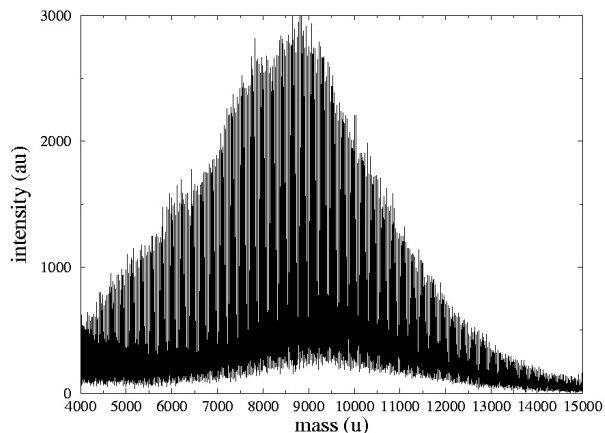


Figure 2. MALDI-TOF MS spectrum of polyethylene narrow mass fraction: SRM 1482. The data are shown without smoothing or background subtraction.

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	--	--

¹ provided by certificate of NIST Standard Reference Materials

² calculated using ¹H NMR analysis

³ calculated using MALDI MS

* 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.

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 PS were used as model compounds to assess the effect of chemical modification on molecular mass biasing. PB and PS 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

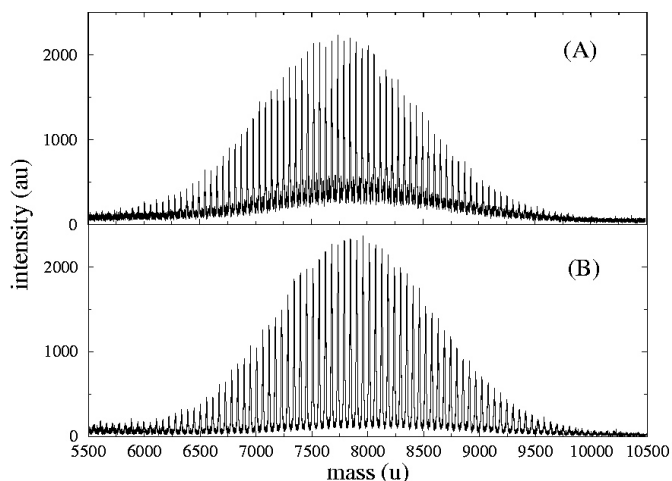


Figure 3. MALDI-TOF MS spectra for A) copper metal cationized polybutadiene, and B) hydrogenated analogue of polybutadiene used in A with covalent cationization.

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. This is important to note that the M_n of the model PS 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 by MS relates to sample preparation or crystalline aggregates. Furthermore, the M_n and MMD obtained using two very different ionization methods are the same, suggesting that the lower than expected molecular mass moments for PE is not due to chemical derivatization method.

From the PS 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.

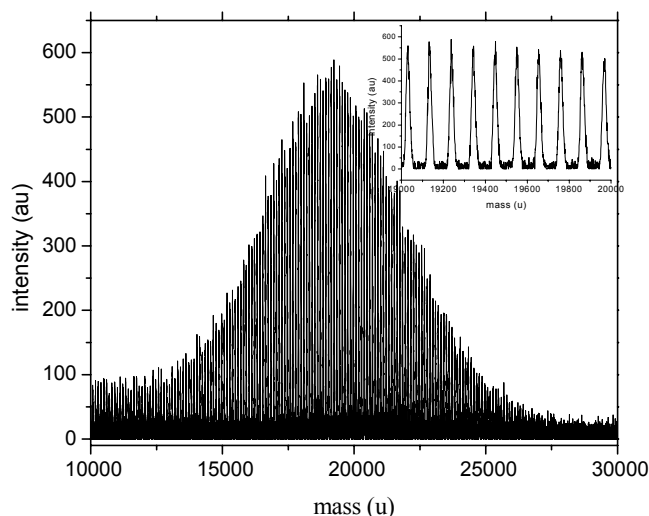
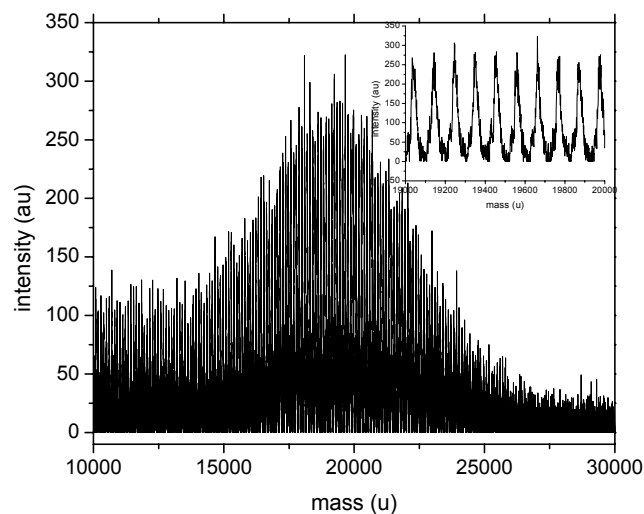


Figure 4. MALDI-TOF MS spectra for A) metal cationized PS, and B) covalently cationized PS. The baselines are corrected with no smoothing.

The covalent cationization method 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 PS with higher molecular mass moments than previously reported has been produced with high signal intensities and the same M_n and MMD as obtained from traditional metal cationization. Comparison studies using PB and PS 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

The authors would like to thank W.R. Blair for expert technical assistance.

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