

Optimizing the Covalent Cationization Method for the Mass Spectrometry of Polyolefins

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Introduction

Polyolefins such as polyethylene (PE) and polypropylene dominate the market share of synthetic polymer production. However, polyolefins lack polar, unsaturated, or aromatic groups and have not been amenable to mass spectrometric characterization due to the ineffectiveness of conventional methods of cationization and cannot be analyzed by matrix-assisted laser desorption/ionization (MALDI) using existing techniques of metal cationization. Covalent cationization was recently introduced as a new method for the mass spectrometry of these polymers in which an ionic group such as ammonium or phosphonium is covalently bonded to the PE.

Methods

An organic cation is covalently bonded to the polymer to produce the necessary ionization for successful creation of intact gas-phase macromolecules by MALDI. Two synthetic steps are involved in covalent cationization: bromination of the polymer, followed by conversion of the brominated site to a charged ammonium or phosphonium group. Conventional PE contains terminal vinyl groups that can be reacted with Br_2 forming terminal $-\text{Br}$. Anionic polybutadiene (PB) and a hydrogenated, PE-like derivative with terminal $-\text{OH}$ groups were purchased. The $-\text{OH}$ groups were converted into $-\text{Br}$ groups by treatment with PBr_3 . The $-\text{Br}$ terminated polymers were treated with triphenylphosphine to attach a terminal phosphonium ion.

Results

National Institute of Standards and Technology (NIST) Standard Reference Material polyethylenes were chemically modified to produce phosphonium labeled samples. (*Certain commercial materials and equipment are identified in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology*) The resultant polymers were characterized by NMR, FTIR, and DSC to track the reaction. Only a fraction of the polymer chains were found to have functionalization. The PE's with molecular masses up to 20,000 g/mol can be measured using MALDI as shown in figure 1. The averages, however, were systematically below the values determined by other methods as can be seen in the table. Attempts at producing MALDI signals for higher molecular mass PE were not successful, and a general trend of lower signal for higher mass was observed.

Conventional metal cationization of end-functionalized PB and the same materials covalently cationized produced equivalent molecular mass averages for a polymer of greater than 7000 g/mol. Hydrogenation of this PB (HPB) produced a PE type of polymer that also gave an equivalent molecular mass distribution by covalent cationization as can be seen in figure 2. Due to the branch content, the HPB may not be representative of the linear SRM PE. DSC of all of the unmodified PE's and HPB's show that the PE has higher crystallinity. While crystallinity may be an important factor, mass discrimination has been noted in other materials that are non-crystalline.

References

B.J. Bauer, W. E. Wallace, B. M. Fanconi and C. M. Guttman "Covalent cationization method" for the analysis of polyethylene by mass spectrometry", *Polymer* **42**(25) 09949-09953, 2001

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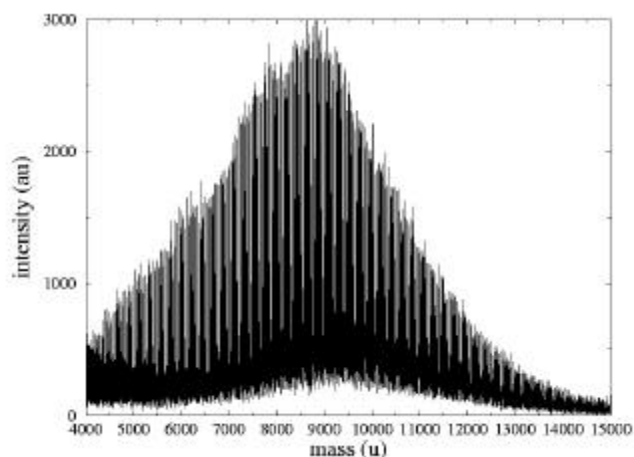


Figure 1. MALDI-MS of SRM1482a

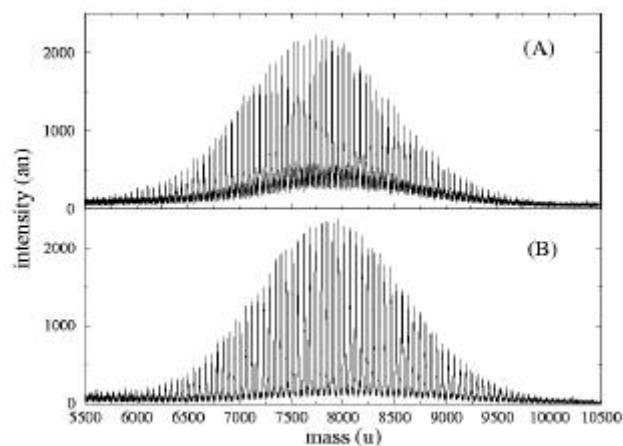


Figure 2. MALDI-MS of PB (A) and HPB (B).

Sample	M_n^*	M_w^*	M_n (1H NMR)	M_n (MALDI)	M_w (MALDI)
LEA-51	--	--	$4,060 \pm 200$	2,510	2,610
SRM 2885	--	6280 ± 560	$5,720 \pm 300$	4,280	4,600
SRM 1482a	$11,400 \pm 300$	13600 ± 1500	$13,400 \pm 800$	8,430	9,080
SRM 1483a	$28,900 \pm 430$	32100 ± 530	$32,000 \pm 4000$	-	--

Table 1, Characterization of PE. * Certified values provided by certificate of NIST Standard Reference Materials. Standard uncertainties are one standard deviation.