

## MALDI MS CHARACTERIZATION OF CATIONIZED COVALENT POLYETHYLENE

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### Introduction

Polyolefins, saturated hydrocarbon polymers such as polyethylene (PE) and polypropylene, are, by production volume, the most widely used of all synthetic polymers. Their molecular mass and molecular mass distribution (MMD) are critical in determining performance properties. There is no technique currently available to perform mass spectrometry on saturated hydrocarbon polymers above molecular mass of about 1000 u that leaves intact polymers. Polyolefins have not been amenable to Matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry (MS) characterization of MMD due to the ineffectiveness of conventional methods of cationization. The lack of polar groups, unsaturation, and aromaticity excludes cationization methods that are used for other common synthetic polymers. A new method is introduced in which an organic cation is covalently bonded to the polymer to produce the necessary ionization for successful MALDI.<sup>1</sup> A strong MALDI signal results from polymers that give no response by other methods.

### Experimental

The mass spectrometry was carried out on a Bruker Reflex II MALDI-TOF instrument<sup>†</sup> 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. Estimated standard uncertainty of the peak position from calibration and repeatability studies is 0.2 u, and the estimated standard uncertainty in overall signal intensity from repeatability studies is 15%.

The terminal vinyl contents of polyethylene were analyzed by Fourier transform infrared spectroscopy. The infrared samples were films,  $\approx$  0.015 cm thick, prepared by hot pressing at  $(130 \pm 5)^\circ\text{C}$ . Spectra were recorded at  $2\text{ cm}^{-1}$  resolution on a Nicolet Magna System 550 FTIR equipped with a DTGS detector. 100 scans were recorded for each sample. The standard uncertainty associated with IR measurements is 2%.

High-resolution, 270-MHz proton NMR spectra were taken on a 6.35 T JEOL GX270 spectrometer manufactured by JEOL, Ltd. (Akishima, Japan). Samples were sealed in 5 mm tubes under a nitrogen atmosphere whose pressure was slightly below ambient. Deuterated 1,1,2,2-tetrachloroethane (TCE) was used as a solvent and the polymer concentrations varied between 2.5 % and 3.0 % by mass fraction. All spectra were run at  $120^\circ\text{C}$ , 15 Hz sample spinning,  $45^\circ$  tip angle for the observation pulse, and a 20 s recycle delay. The standard uncertainty for molecular mass calculated using  $^1\text{H}$  NMR is 12.5 %.

### Results and Discussion

Polyolefins with saturated hydrocarbon chains such as polyethylene and polypropylene cannot be characterized using MALDI via the traditional metal cationization method. A method whereby an ammonium or a phosphonium salt is covalently attached to one of the chain ends on polyethylene has produced successful MALDI spectra.<sup>1</sup> Our current study uses the fractionation products of a commercial polyethylene. Since the chemical modification uses the population of molecules with terminal double bonds to represent the overall population, it is critical to verify that the molecular mass distribution for the molecules with double bonds is an accurate representation of the overall molecular mass distribution in each of the fractionated materials. This was verified by determining the concentration of double bonds as a function of number average molecular mass,  $M_n$ . The vinyl to methylene ratio was measured by FTIR as a function of molecular mass (Figure 1). A linear correlation indicates that the ratio of vinyl to total end groups is uniform throughout this molecular range. Solution  $^1\text{H}$  NMR analyses also support the notion that the fraction of molecules with one vinyl end is quite constant and has a value of  $0.39 (\pm 0.05)$ .

\* 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.

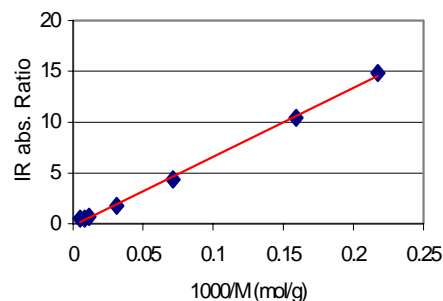


Figure 1. FTIR intensity of vinyl band normalized to a methylene combination band of SRMs vs. reciprocal molecular mass of PE SRMs.

The bromination reaction on terminal polyethylene vinyl groups described herein produced a mixture of three products derived from different reaction mechanisms (Figure 2). HBr was generated *in situ* under the described reaction conditions and therefore both  $\text{Br}_2$  and HBr were available for reaction. Direct addition of  $\text{Br}_2$  across the terminal polyethylene double bond leads to the 1,2-dibromo product. Addition of hydrogen halides such as H-Br to vinyl-terminated olefins in the absence of peroxide takes place by an electrophilic mechanism according to Markovnikov's rule and the product is 2-bromo. In the presence of peroxide, addition of H-Br occurs via a free-radical mechanism, and the orientation is anti-Markovnikov, i.e., 1-bromo. For our reaction, the ratios of reaction products thus depend on the precise reaction conditions. For example, adding bromine to the reaction mixture at high temperatures after the polymer has been dissolved favors the production of the 1,2-bromo product while adding bromine at room temperature before polymer dissolution promotes the formation of H-Br which leads to mostly mono-bromo additions. In the latter scenario, adding a free radical initiator, such as a peroxide, into the initial reaction mixture increases the 1-bromo over the 2-bromo product. In the second step the triphenylphosphine (TPP) preferentially reacts with the 1-bromo product. An excess of TPP was added since this reaction competes with the oxidation of TPP.

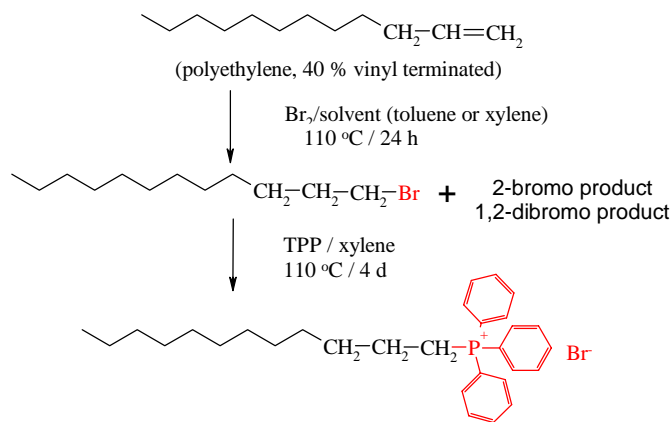
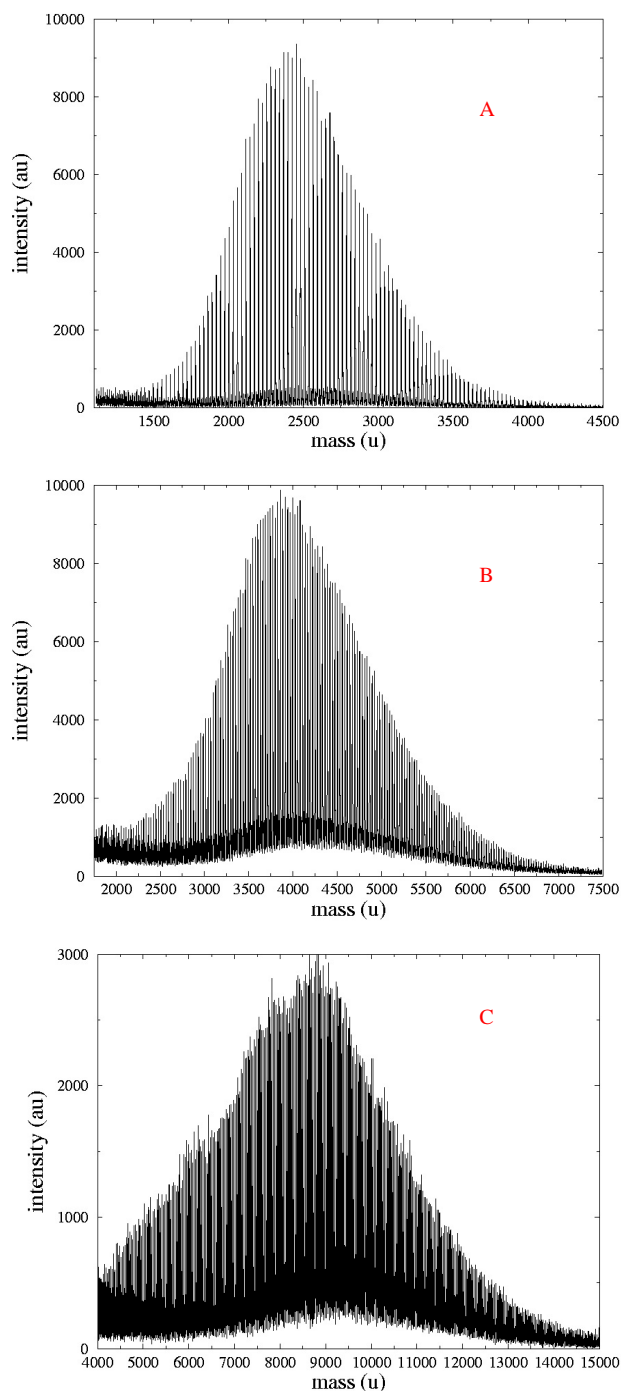


Figure 2. Bromination of polyethylene terminal double bond followed by reaction of triphenylphosphine with the 1-bromo product.

Figure 3 shows the MALDI-TOF MS spectra for LEA-51, SRM 2885 and SRM 1482 respectively. For all polyethylene spectra a main series of peaks corresponds to (within  $\pm 2\text{ g/mol}$  or 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  $^1\text{H}$  NMR (Table 1). The molecular mass of SRM 1482 determined by  $^1\text{H}$  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,  $^1\text{H}$  NMR, and light scattering.



**Figure 3.** MALDI-TOF MS spectra of polyethylene narrow mass fraction: a) LEA-51, b) SRM 2885 and c) SRM 1482. The data are shown without smoothing or background subtraction.

Strong signals were observed for LEA-51 and SRM 2885 and the signals remained high for SRM 1482. However SRM 1483, a higher molecular mass polyethylene with certified  $M_n$  of 28900 g/mol and  $M_w$  of 32100 g/mol, did not produce good MALDI signals. SRM 2885 and SRM 1483 had comparable numbers of TPP-terminated chains per gram; yet, SRM 2885 generated strong MALDI signals whereas SRM 1483 did not. This suggests that incomplete chemical modification is not the primary reason for little or no MALDI signal for higher molecular mass polyolefins.

**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	--	--	$4060 \pm 200$	2,510	2,610
SRM 2885	--	$6280 \pm 560$	$5720 \pm 300$	4,280	4,600
SRM 1482a	$11400 \pm 300$	$13600 \pm 1500$	$13400 \pm 800$	8,430	9,080
SRM 1483a	$28900 \pm 430$	$32100 \pm 530$	$32000 \pm 4000$	--	--

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

<sup>2</sup> calculated using  $^1\text{H}$  NMR analysis

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

The probability of laser-induced volatilization of intact polymer molecules diminishes with increasing molecular mass. Furthermore higher laser power is necessary for increasing molecular mass for all polymers. Although successful MALDI MS signals are obtained on other high mass polymers, polyethylene may be more susceptible to fragmentation. Our observed MALDI mass spectrum of SRM 1483, with a certified  $M_n$  of 28900 g/mol (not shown), which consisted of low intensity peaks separated by 14 g/mol with a high mass cutoff of 8000 g/mol (even at low laser power), which is consistent with fragmentation. The fragment mass values confirm the presence of chemical modification in SRM 1483. However, we should not conclude from these observations that MALDI MS of polyethylene is limited to masses lower than 15000 g/mol. It is known that the choice of matrix material and how the sample is prepared for MALDI MS analysis affect signal intensity and the measured mass distribution. Sample preparation is critical in obtaining strong MALDI signals.<sup>2</sup> For linear polyethylene an added complication may arise from sample morphology that is increasingly dominated by crystallization as the molecular mass increases. Longer chains could participate in multiple crystallites and therefore might not be "lifted" into the gas phase by the laser and the subsequent collisions with excited matrix molecules. Modifications to laser power may be necessary not only because of the higher analyte mass, but to extract individual molecules from the crystalline morphology. On the other hand the work of Ji *et al.* on polyisobutylenes,<sup>3</sup> a non-crystalline polyolefin, demonstrated a very similar mass cut off near 14000 g/mol. Further research is needed to optimize sample preparation procedures necessary for polyolefin measurements.

### Conclusions

We have optimized a chemical modification procedure for polyethylene of a sort containing residual vinyl groups that produces spectra by MALDI mass spectrometry in the range below 15000 g/mol. The samples studied had a polydispersity in the range 1.1 to 1.2. The method yields a substantial improvement in mass range and a simultaneous decrease in fragmentation compared to previously reported mass spectra of polyethylene. Moments of the mass distribution,  $M_n$  and  $M_w$ , determined from our MALDI MS data on polyethylene were lower (60% to 75%) than values derived by the conventional methods of osmometry,  $^1\text{H}$  NMR and light scattering.

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