

MALDI MS of Saturated Hydrocarbon Polymers: Polyethylene and other Polyolefins

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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 MALDI 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. A strong MALDI signal results from polymers that give no response by other methods.

Methods

The mass spectrometry was carried out on a Bruker Reflex II MALDI-TOF instrument using the standard 337 nm nitrogen laser. Dithranol and all-trans retinoic acid were used as matrices. An end functionalized PE analogue was prepared from a hydroxy terminated hydrogenated polybutadiene obtained from Polymer Laboratories. It was functionalized by first converting to bromine termination by treatment with PBr₃. Polyethylene NIST standard reference material SRM 2885 was chemically modified by placing bromine groups on the polymer by direct bromination. Charges were placed on the polymers by reaction with trimethylamine or triphenylphosphine producing ammonium and phosphonium groups respectively. *(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)*

Results

A variety of hydrocarbons with single charges were examined. Tetraoctadecyl ammonium bromide contains a single positive charge and has a molecular mass greater than 1000 u. It produces a strong signal under mild conditions both with and without a matrix present as is shown in figure 1. This clearly demonstrates that high molecular mass ammonium compounds remain intact under laser desorption conditions. Chemical modification of 1-bromodocosane was used to produce trimethyl-docosyl ammonium bromide that also produces a strong signal. This suggests that chemical modification of other hydrocarbons such as PE may induce a charge on the polymer that will remain intact and yield high-quality mass spectra.

To this end, a "polyethylene-like" hydrogenated anionically prepared poly(1,4-butadiene) with hydroxy termination was first converted to a bromine terminated "PE" and then to a ammonium or phosphonium terminated polymer. Figure 2 shows the MALDI response of the

end modified “PE” in all-trans retinoic acid. Individual repeat units of 56 u can be easily seen which is consistent with the butadiene repeat unit of 54 u plus 2 u from the hydrogenation.

A NIST standard reference material, SRM 2885, was brominated by adding bromine to a xylene solution at 110 °C. The brominated PE was treated with triphenylphosphine to covalently attach a phosphonium charge. A strong MALDI signal was produced from the modified PE while the unmodified and the brominated PE produced none. Figure 2 shows the MALDI response of the modified SRM 2885 in all-trans retinoic.

All samples show a strong repeating pattern of 28 u; however, some samples also had a pronounced repeat of 14 u. This may be due to fragmentation or may be a consequence of the polymerization chemistry of olefins.

Other polymers such as polystyrene have been modified by this covalent cationization method, both by attachment to an end group and by attachment at sites along the polymer chain. This method not only produces MALDI signals from polymers that otherwise are non-responsive, but also is a complementary method to conventional metal cationization. It also may provide insight into the mechanism of MALDI by offering a material with a controlled amount of cationization.

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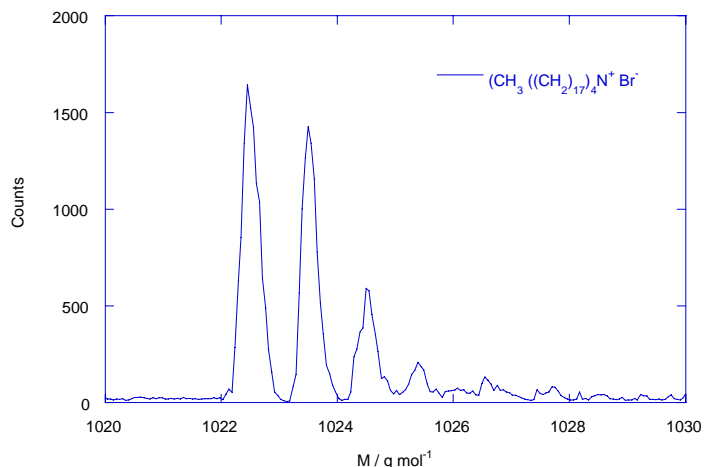


Figure 1. MALDI of tetraoctadecyl ammonium bromide.

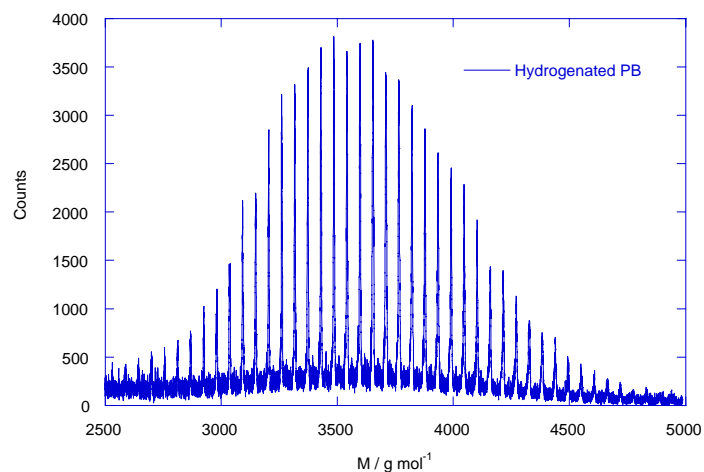


Figure 2. MALDI of trimethyl ammonium terminated hydrogenated polybutadiene.

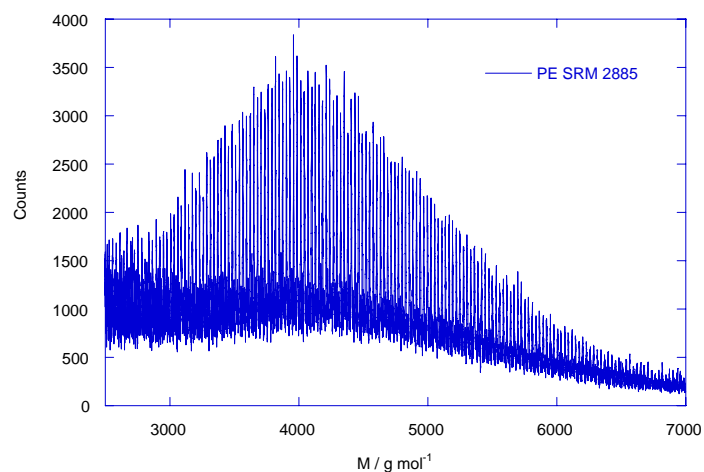


Figure 3. MALDI of triphenyl phosphonium terminated polyethylene