

## Optimizing the Covalent Cationization Method for the Mass Spectrometry of Polyolefins

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Received April 22, 2002; Revised Manuscript Received June 13, 2002

**ABSTRACT:** Previously a new method was introduced for the mass spectrometry of saturated polyolefins whereby an organic cation is covalently bonded to the polymer to produce the necessary ionization for the creation of intact gas-phase macromolecules by matrix-assisted laser desorption/ionization (MALDI).<sup>1</sup> In the present study that methodology was further optimized to produce mass spectra for higher molecular mass materials than had been achieved previously. NIST Standard Reference Material polyethylenes were extensively studied and found to give molecular masses that were systematically low, typically about two-thirds of the values determined classically. However, when comparison was made between conventional copper metal cationization of end-functionalized polybutadiene and the same material hydrogenated and subsequently covalently cationized, excellent agreement was found when the molecular mass distributions of these two materials were compared. Reasons for this discrepancy are explored and discussed.

### Introduction

Polyolefins such as polyethylene and polypropylene dominate the market share of synthetic polymer production. While these saturated hydrocarbon polymers have a long production history, new developments in metallocene catalysts have caused a pronounced resurgence of development activities, resulting in a wide variety of new applications and increased raw material production. These new catalysts can provide unprecedented control of polymer molecular mass and molecular mass distribution (MMD), copolymer sequence, stereochemistry, etc. For polyolefins, the molecular mass and molecular-mass distribution in particular are critical in determining performance properties.

Mass spectrometry is currently the most promising method for obtaining accurate molecular mass and absolute MMDs. Matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry (MS) has provided valuable information on the nature of the polymerization process and the resultant structure for many polymer types.<sup>2,3</sup> MALDI-TOF MS offers mass characterization of high molecular mass polymers with minimal fragmentation and also enables determination of polymer repeat units and end-group compositions.

Molecular mass determination by mass spectrometry requires the formation of intact macromolecular ions in the gas phase. Synthetic polymer cationization by elements such as sodium, potassium, silver, and copper, involves association of metal cations with certain functional groups on the polymer. Examples of effective functional groups include the carbonyl groups of methacrylate polymers, the double bonds of diene polymers, and the phenyl groups of styrenics. Polymers that lack polar, unsaturated, or aromatic groups have not been amenable to mass spectrometric characterization due to the ineffectiveness of conventional methods of metal cationization. Thus, saturated polyolefins, e.g., polyeth-

ylene, polypropylene, polyisobutylene, and poly(methylpentene), cannot be analyzed by MALDI using existing techniques of metal cationization. Furthermore, characterization of the molecular mass of these polymers by the conventional solution methods of osmometry, nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), and light scattering is complicated by the need to use aggressive solvents at high temperature. If polyolefins could be routinely analyzed by MALDI, development time for new catalysts and polymers would be greatly reduced.

We recently reported a chemical modification method that allows mass spectrometry to be performed on these materials.<sup>1</sup> In this method an organic cation is covalently bonded to the polymer to produce the necessary ionization for successful MALDI.<sup>4</sup> Ji et al. have also developed a comparable technique using a covalently bonded anion.<sup>5</sup> Two synthetic steps are involved in our covalent cationization method: bromination of the polymer at residual vinyl bonds, followed by conversion of the brominated site to an ammonium or phosphonium salt that is easily ionized (dissociated) during the MALDI process. A strong MALDI signal results from modified polymers with a chargeable group; no response is observed from polymers brominated or in their unmodified form.

In this paper we first describe the optimization of the covalent cationization method. The mass spectra for covalently cationized polyethylene, which produced results for higher molecular mass materials than had been achieved previously, were then compared to results obtained via <sup>1</sup>H NMR and GPC. In the last section we compare covalent cationization vs metal cationization using a polybutadiene as a model compound.

### Experimental Section

**1. Materials.** NIST Standard Reference Materials,<sup>6</sup> SRM 2885, SRM 1482, SRM 1483, and an uncertified material, LEA-51, are fractions of a commercial linear high-density polyethylene, SRM 1475. The fractionation of this material has been

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**Table 1. Molecular Mass (g/mol) of the Polyethylene Standard Reference Materials Determined by Traditional Methods and by MALDI-TOF Mass Spectrometry<sup>a</sup>**

| sample   | $M_n$ (osmometry) | $M_w$ (light scattering) | $M_n$ ( <sup>1</sup> H NMR) | $M_n$ (MALDI) | $M_w$ (MALDI) |
|----------|-------------------|--------------------------|-----------------------------|---------------|---------------|
| LEA-51   |                   |                          | 4060 ± 200                  | 2510          | 2610          |
| SRM 2885 |                   | 6280 ± 560               | 5720 ± 300                  | 4280          | 4600          |
| SRM 1482 | 11400 ± 300       | 13600 ± 1500             | 13400 ± 800                 | 8430          | 9080          |
| SRM 1483 | 28900 ± 430       | 32100 ± 530              | 32000 ± 4000                |               |               |

<sup>a</sup> Membrane osmometry and light scattering values from NIST Standard Reference Material certificates. <sup>1</sup>H NMR  $M_n$  is the number-average molecular mass based on the total number of ends inferred from the integrals of the four bromination product values plus the CH<sub>3</sub> intensity plus the total CH<sub>2</sub> intensity. MALDI values are all ±200 g/mol. MALDI and NMR numbers include only type A (statistical) uncertainty, membrane osmometry, and light scattering numbers include both type A and type B (systematic) uncertainty.

described previously.<sup>7</sup> The number-average molar mass ( $M_n$ ) and mass-average molar mass ( $M_w$ ) of these SRMs are described in the NIST certificates and reports of analysis pertaining to these materials (see Table 1). The  $M_n$  and  $M_w$  for LEA-51 were obtained by gel permeation chromatography at high temperature with columns calibrated using the above-mentioned SRMs. The  $M_n$  of LEA-51 was also determined by <sup>1</sup>H NMR. The uncertainties listed in Table 1 for the certified values of the SRM materials include type A and type B expanded uncertainties.<sup>8</sup> The uncertainty given for LEA-51 is the estimated expanded uncertainty from the repeatability and absolute molecular mass uncertainties estimated for comparable polyethylene.

The hydroxy-terminated polybutadiene (PBDOH) and its hydrogenated analogue (HPBDOH) used in this study were prepared commercially by Polymer Source<sup>20</sup> (Dorval, Québec, Canada). The polybutadiene was prepared via anionic polymerization using a *sec*-butyl initiator and terminated with ethylene oxide to form mainly a -CH<sub>2</sub>-CH<sub>2</sub>-OH end group.

Phosphorus tribromide (1.0 M solution in dichloromethane), triphenylphosphine, xylene, toluene, benzyl peroxide, and bromine were purchased from Aldrich and used as received.

**2. Chemical Modification Procedures. A. Bromination of Terminal Vinyl Substitutions on Polyethylene.** The following procedures are typical of those used for synthetic modifications described in this paper. The mass quantities listed are for reference only and were typically within ±1% of the quoted values. The temperatures given were within the range ± 5 °C unless otherwise noted. Polyethylene (e.g., LEA-51, ≈4000 g/mol, 300 mg,  $7.5 \times 10^{-5}$  mol), benzoyl peroxide (470 mg, 0.002 mol), bromine (40 drops), and *m*-xylene (15 mL) were added to a closed vial at room temperature. The mixture was heated gradually to 110 °C to dissolve the polyethylene and maintained at that temperature for 5 h. The hot solution was then precipitated in cold methanol (≈150 mL). The product was filtered, washed with methanol, and dried in a vacuum oven at room temperature overnight and then at 80 °C for 10 h. <sup>1</sup>H NMR showed that the product consisted of 86% 1-bromo product, 13% 2-bromo product, and less than 1% dibromo product.

**B. Formation of Phosphonium Salts.** This brominated polyethylene (183 mg,  $\approx 4.06 \times 10^{-5}$  mol) and a large excess of triphenylphosphine (400 mg,  $1.53 \times 10^{-3}$  mol) were dissolved in *m*-xylene (5 mL) at 110 °C. The reaction was allowed to proceed for 4 days. Then the hot solution was precipitated in cold methanol (≈200 mL), filtered, and dried in a vacuum oven overnight. Because triphenylphosphine oxide (a contaminant in TPP) tends to concentrate in this precipitated product, the product was redissolved in hot xylene (110 °C), reprecipitated in cold methanol, filtered, and dried in a vacuum at room temperature overnight and then at 80 °C for 10 h.

**C. Modification of Hydroxy-Terminated Polybutadiene and Its Hydrogenated Analogues.** The modification procedures for hydroxy-terminated polybutadiene and hydrogenated polybutadiene analogues are similar. The reaction temperatures are room temperature for polybutadiene and 110 °C for hydrogenated polybutadiene. An example procedure for bromination of polybutadiene is as follows. Hydroxy-terminated polybutadiene (12 000 g/mol, 1.255 g,  $\approx 1.05 \times 10^{-4}$  mol) was dissolved in toluene (10 mL). Then PBr<sub>3</sub> (1.0 M in CH<sub>2</sub>Cl<sub>2</sub> solution, 2 mL) was added. The mixture was stirred at room temperature for 1 day. The product was poured into a large beaker and

purged with nitrogen to evaporate the toluene and then dried in a vacuum oven for 1 h at room temperature. The product was washed four times with methanol and dried under a nitrogen purge.

The end-brominated polybutadiene was dissolved in toluene and then reacted with trimethylamine or triphenylphosphine at room temperature for 3 days. Toluene was evaporated under a nitrogen purge. The product was washed with methanol three times and then dried in a vacuum oven.

**3. Characterization. A. Nuclear Magnetic Resonance.** 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. For polyethylene (PE) samples, all spectra were run at 120 °C, 15 Hz sample spinning, 45° tip angle for the observation pulse, and a 20 s recycle delay. This latter delay was chosen in order to obtain quantitative spectra. For polybutadiene (PBD) samples, the observation temperature was 50 ± 1 °C. Between 100 and 600 scans were averaged, depending on the concentration of end groups. The spectral width of the Fourier transformations was 15 ppm, and the number of complex points in both the free induction decay (FID) and the transforms was 16 384. Up to 0.2 Hz exponential line broadening was applied to the FIDs in order to minimize spectral ringing from data truncation. Baseline correction routines were applied in order to facilitate integration of small peaks that were mainly in the range of  $10^{-2}$ – $10^{-5}$  times the integrals of the larger peaks. Given that TCE has a rather high density (1595 kg/m<sup>3</sup> at 20 °C) compared with solid PE (≈960 kg/m<sup>3</sup>), undissolved PE samples at ambient temperature tended to stratify with the PE floating to the top of the liquid. Since the active sample volume in the NMR experiment lies well below the top of the liquid column, and since polymer mixing from a stratified state upon reaching the dissolution temperature is a very slow process, we needed to minimize this effect on the NMR measurement. Thus, the samples were initially mixed by immersing them in a separate bath at 130 °C and inverting the sample tubes several times until the solution was thoroughly mixed. Then, the sample tubes were quickly cooled in air and subsequently laid on their sides, almost flat, so as to minimize subsequent stratification of the sample to the top of the tube. The resulting dispersion of the crystallites throughout the solution also slowed the rate of stratification. Samples were run as soon as possible after this procedure; moreover, samples were introduced into a preheated probe.

The instrument software automatically places the chemical shift of the residual CHCl<sub>2</sub>CDCl<sub>2</sub> solvent protons at 5.968 ppm; hence, the chemical shifts we measure and cite use that secondary scale instead of the usual tetramethylsilane (TMS) scale. This scale is probably within 0.03 ppm of the TMS scale. We did not deliberately introduce any TMS as a reference because we were interested in leaving the aliphatic methyl region between 0.5 and 1.1 ppm as clear of nearby interfering resonances as possible. To assign resonances to different chemical structures, we made use of literature compilations of spectra (Aldrich catalog of NMR spectra<sup>9</sup>), usually taken on model compounds in CDCl<sub>3</sub> at ambient temperature. We also took spectra of a few model compounds (including

**Table 2. Proton NMR Spectral Positions and Assignments Used in Analyzing the Reaction Products for the Bromination and Subsequent TPP Addition in Polyethylene Samples (Solvent Was Deuterated Tetrachloroethane (TCE); Measurement Temperature Was 120 °C)**

| chemical species         | proton assignment                                                                                 | N <sup>a</sup> | multiplet type                                    | shifts <sup>b</sup> at 120 °C in TCE (ppm)              |
|--------------------------|---------------------------------------------------------------------------------------------------|----------------|---------------------------------------------------|---------------------------------------------------------|
| CH <sub>3</sub> ends     | CH <sub>3</sub> —                                                                                 | N/A            | triplet                                           | 0.908, 0.933, 0.958                                     |
| CH <sub>2</sub> interior | —CH <sub>2</sub> —                                                                                | N/A            | singlet                                           | 1.327                                                   |
| terminal double bond     | CH <sub>2</sub> =CH—                                                                              | 2              | broad triplet                                     | 4.94, 4.99, 5.04                                        |
| 1-bromo                  | CH <sub>2</sub> Br—                                                                               | 2              | triplet                                           | 3.401, 3.426, 3.452                                     |
| 2-bromo                  | CH <sub>3</sub> CHBr—                                                                             | 3              | doublet                                           | 1.720, 1.745                                            |
| 1,2-dibromo              | CH <sub>2</sub> BrCH <sub>2</sub> —                                                               | 2              | 2 quartets                                        | 3.645, 3.679, 3.684, 3.718/3.831, 3.849, 3.870, 3.888   |
| TPP salt of 1-bromo      | (Br <sup>−</sup> )(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P <sup>+</sup> —CH <sub>2</sub> — | 15             | broad, <sup>c</sup> asymmetric <sup>d</sup>       | region: 7.65 to 7.90. maximum: 7.75; shoulder near 7.85 |
| TPP salt of 1-bromo      | (Br <sup>−</sup> )(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P <sup>+</sup> —CH <sub>2</sub> — | 2              | broad, <sup>c</sup> approx symmetric <sup>d</sup> | about 1.2 ppm wide; center varies: 3.45–3.55            |

<sup>a</sup> N = number of protons per original double bond. <sup>b</sup> Chemical shifts are referenced approximately to the TMS scale; however, the actual reference is that of the tetrachloroethane protons assumed to be at 5.968 ppm. Shifts given to three decimal places have standard uncertainties of 0.002 ppm relative to the TCE reference. <sup>c</sup> The main source of line broadening is a large number of unresolved multiplet splittings. <sup>d</sup> These resonances are quite temperature dependent, especially in the upfield region of the aromatic band and the mean shift of the methylene resonance.

1-bromo- and 2-bromoalkanes as well as an alkylated 1-phosphonium bromide) at 120 °C and in TCE in order to verify that any potential solvent and temperature effects were factored in relative to the literature data.

Finally, when one is looking for resonances in 3% solutions at levels as low as 10<sup>−5</sup> times the main resonances, one is bound to have competition from low-level solvent impurities as well as spurious signals generated in the spectrometer and data system. By choosing the spectral window properly, we could avoid most of those latter problems, and by running the spectrum of the solvent alone, we were able to account for the impurities fairly well.

In Table 2 we summarize the spectral features and assignments for those resonances used in the quantitative analysis of the proton spectra. The regions of interest were chosen where there was a minimum amount of overlap with other, conflicting resonances.

**B. Gel Permeation Chromatography.** Gel permeation chromatography (GPC) was performed using an Alliance 2000 GPC liquid chromatograph (Waters Corp., Milford, MA) with a differential refractive index (DRI) detector and with a viscosity detector. Two Styragel 300 mm × 7.5 mm i.d. 10 μm HT6-E columns and one Styragel 300 mm × 7.5 mm i.d. 10 μm HT-2 column (Waters Corp.) were used in this study. The chromatography was run at 1.0 mL/min solvent flow rate.

For the PBDOH and all the derivatized PBDOH materials studies reported in the present study the injector and column compartment of the Alliance 2000 were controlled at 40 ± 1 °C for all measurements. Tetrahydrofuran (Mallinckrodt Specialty Chemicals, Paris, KY) with added antioxidant, 2,6-di-*tert*-butyl-4-methylphenol (commonly known as butylated hydroxytoluene or BHT) or toluene (Mallinckrodt), was used as solvent. Addition of 5 μL of toluene per milliliter of THF was added to the solvent used in preparing solutions as a GPC pump marker. Calibration was done using Easical calibrants (Polymer Labs, Amherst, MA) in combination with SRM 1478 and a polystyrene (*M<sub>w</sub>* = 7190 ± 560 g/mol) that will be soon issued by NIST as SRM 2888.

For the HPBDOH and the PE studies reported in this paper the injector and column compartments of the Alliance 2000 were controlled at 140 ± 1 °C for all measurements. The solvent, 1,2,4-trichlorobenzene (99+%, spectrophotometric grade, TCB), obtained from Aldrich Chemical, was used as received. The antioxidant Santonox (5-*tert*-butyl-4-hydroxy-2-methylphenyl sulfide), also obtained from Aldrich Chemical, was added to the solvent at approximately 0.1 g/L. Hexadecane was added as a pump marker. For the cases where we report a GPC analysis on the HPBDOH or PE, columns were calibrated with SRM 1475, SRM 1482, SRM 1483, SRM 1484, SRM 2885, SRM 2886, and SRM 2887.

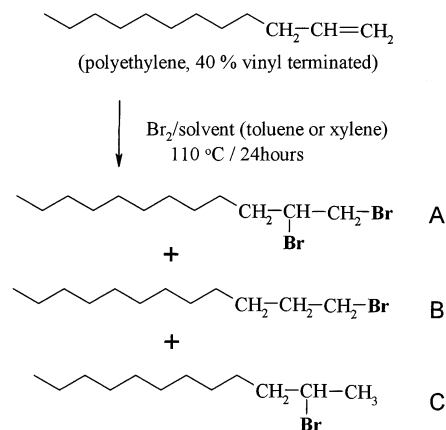
**C. Fourier Transform Infrared Spectroscopy.** The terminal vinyl contents of polyethylene were analyzed by Fourier transform infrared spectroscopy. The infrared samples were

films, approximately 0.015 cm thick, prepared by hot pressing at approximately 130 °C. Spectra were recorded at 2 cm<sup>−1</sup> resolution on a Magna System 550 FTIR (Nicolet Instrument Technologies, Madison, WI) equipped with a DTGS detector. The co-addition of 100 scans gave adequate signal-to-noise to perform spectral subtraction to enhance spectral features resulting from chemical modification of the samples.

Infrared measurements were made on solid-state samples of SRM 1482, SRM 1483, SRM 1484, SRM 2885, SRM 2886, SRM 2887, and the uncertified low mass fraction LEA-51. Determination of vinyl concentration, or content per methylene, requires knowledge of film thickness, density, and extinction coefficient value; however, for intercomparisons one may use an internal standard for methylene, that is, an infrared band that gives the number of methylene groups. Unfortunately, there are no such bands in polyethylene; all are affected somewhat by the degree of crystallinity and/or preferential orientation. However, if one assumes that crystallinity and chain orientation are comparable from sample to sample, there are a number of bands having weak dependencies on these two properties to use as internal standards. An analysis was made of infrared spectra taken on various samples of the same SRM to determine that the integrated absorption between 3738 and 3545 cm<sup>−1</sup> was insensitive to sample preparation method.

**D. Differential Scanning Calorimetry.** Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer (Boston, MA) DSC 7 calorimeter from 40 to 200 °C at 10 °C min<sup>−1</sup> under a nitrogen atmosphere. The first scan was taken on PE or HPBOH samples that had remained at ambient temperature for extended periods of time, typically several months, to allow complete crystallization to occur. Immediately after the first scan was taken, two additional scans were taken to erase previous thermal history and to allow only rapid crystallization processes to occur. The quantities reported are for relative comparisons only, with uncertainties in peak temperatures of about ±1 °C and in heats of fusion of ±10% of the reported value.

**E. Mass Spectrometry.** *all-trans*-Retinoic acid was shown to perform satisfactorily as a MALDI matrix for both polyethylene and polybutadiene. For polyethylene the samples were prepared using the solventless technique described in the literature.<sup>10</sup> The matrix and analyte were ground together with a mortar and pestle in a ratio of approximately 10:1 by mass. The resulting powder was pressed onto the stainless steel target with a laboratory spatula and the excess removed with compressed inert-gas spray. The fine powder that adhered to the plate gave exceptional mass spectra. For polybutadiene, which could not be ground due to its room temperature softness, tetrahydrofuran was used as the solvent to prepare samples for electrospray. Solution concentrations were typically 40 mg/mL for the matrixes, 1 mg/mL Cu(NO<sub>3</sub>)<sub>2</sub>, and 1 mg/mL for the analyte. The three solutions were mixed in a



**Figure 1.** Bromination of the polyethylene terminal double bond leading to (A) the 1,2-dibromo product, (B) the 1-bromo product, and (C) the 2-bromo product.

1:1:1 ratio and electrosprayed at 5 kV onto the stainless steel target.

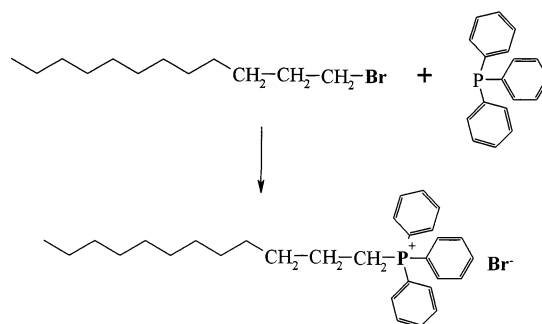
The time-of-flight mass spectrometry was performed on a Bruker (Billerica, MA) REFLEX II in reflectron mode using delayed extraction and low-mass (i.e., matrix-ion) blanking. Typically an accelerating voltage of 25 keV was used. Ions were generated using a 337 nm wavelength nitrogen laser with a pulse duration on the order of 3 ns and an average energy of in the range of 3  $\mu\text{J}$  spread over a spot size of 200  $\mu\text{m} \times 50 \mu\text{m}$ . The laser power used was lower than typically used for other polymers (e.g., polystyrene with silver cationization). Each spectrum shown is the sum of 500 discrete laser shots and is shown without smoothing or background subtraction. All data shown are for positive ions: negative ion spectra produced only matrix ions and their clusters, e.g.,  $\text{M}^-$ ,  $2\text{M}^-$ , etc. The instrument was periodically calibrated with bovine insulin using the  $[\text{M} + \text{H}]^+$  and  $[\text{M} + 2\text{H}]^{2+}$  peaks. The 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%.

## Discussion

**1. Covalent Cationization of Polyethylene.** In addition to fully saturated chains, typical polyethylene contains a percentage of vinyl-terminated chains, which are formed by chain transfer termination during polymerization. These reactive vinyl groups can be chemically modified to form the desired functionalities. For the purpose of this research the vinyl end groups are converted to the bromide salt of a tertiary amine or phosphine, thereby covalently attaching an easily generated cation to the polymer chain ends.

A typical modification procedure follows a two-step reaction. First, the vinyl end group is brominated in a way that optimizes the formation of the 1-Br product (Figure 1, product B). The desirability of 1-Br was established in a series of experiments that showed a strong correlation between 1-Br content in the intermediate product and the level of salt in the final product. In the second step an ammonium group displaces the bromine to form a quaternary ammonium salt, or alternately, triphenylphosphine reacts to form a phosphonium bromide salt. These salts lead to positively charged, intact polymer chains in the plume of the MALDI experiment.

The perspective on optimizing the bromination reaction was to find reaction conditions that simultaneously had the following characteristics: (a) simplicity, (b) optimization of the 1-bromo product, and (c) avoidance



**Figure 2.** Reaction of triphenylphosphine with the 1-bromo-terminated polyethylene.

of the necessity of bubbling toxic HBr into an open high-temperature polyethylene solution or into a closed reaction vessel where the HBr pressure had to be monitored for safety. One important recognition was that HBr could be generated *in situ* as a result of a preferential reaction between  $\text{Br}_2$  and xylene (not between  $\text{Br}_2$  and the double bonds of PE) where a benzylic proton of xylene is replaced with Br and HBr is formed as a byproduct. A second important recognition was the addition of peroxide, as will be discussed presently.

The bromination reaction on terminal polyethylene vinyl groups described herein produced a mixture of three products derived from different reaction mechanisms (Figure 1). 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. It has often been observed that anti-Markovnikov addition of H-Br takes place even when peroxide has not been added because the substrate alkenes absorb oxygen from air, forming small amounts of peroxide.<sup>11</sup> In fact, purification of reaction alkenes is necessary to achieve 100% electrophilic addition. 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 monobromo 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.

The bromination conditions were adjusted to maximize the yield of the 1-bromo product since it reacted most rapidly with triphenylphosphine. Bromine was added to the reaction mixture at room temperature to allow H-Br to be preferentially generated. The amount of bromine was introduced to form sufficient H-Br but not in excess where the direct  $\text{Br}_2$ -vinyl reaction became prevalent. Benzoyl peroxide was also included in the initial reaction mixture. There was no evidence in the brominated product of unreacted double bonds.

Tertiary amines and phosphines displace 1-bromo substituents to form ammonium or phosphonium salts (Figure 2). Triphenylphosphine is a weaker base but a superior nucleophile relative to trialkylamines or phos-

**Table 3. Fraction of 1-Bromo, 2-Bromo, and 1,2-Bromo Products after the Bromination Reaction and the Fraction of Phosphonium Salt after Reaction with Triphenylphosphine<sup>a</sup>**

|              | $f^u$   |      |      |      | TPP (mol/g)           |
|--------------|---------|------|------|------|-----------------------|
|              | dibromo | 1-Br | 2-Br | TPP  |                       |
| LEA-51-Br    | 0       | 0.86 | 0.13 |      |                       |
| LEA-51-TPP   | 0       | 0.04 | 0.10 | 0.86 | $86.0 \times 10^{-6}$ |
| 2885-Br      | 0.73    | 0.21 | 0.06 |      |                       |
| 2885-TPP     | 0.70    | 0.14 | 0.02 | 0.09 | $6.5 \times 10^{-6}$  |
| SRM 1482-Br  | 0.30    | 0.63 | 0.06 |      |                       |
| SRM 1482-TPP | 0.17    | 0    | 0.10 | 0.73 | $25.6 \times 10^{-6}$ |
| SRM 1483-Br  | 0.28    | 0.64 | 0.08 |      |                       |
| SRM 1483-TPP | 0.11    | 0    | 0.16 | 0.73 | $10.1 \times 10^{-6}$ |

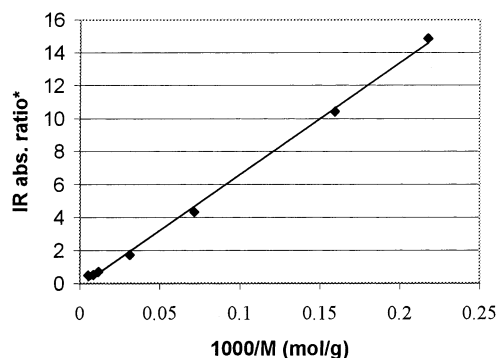
<sup>a</sup>  $f^u$ s are fractions of the original population of terminal unsaturated bonds that reacted, or did not react, in the indicated way. Standard uncertainties in data columns 1–4 are respectively  $\pm 0.03$ ,  $\pm 0.03$ ,  $\pm 0.04$ , and  $\pm 0.05$ .

phines<sup>12</sup> and therefore was used in most chemical modifications. Furthermore, the phenyl groups provided a convenient spectroscopic indicator of extent of reaction. As mentioned previously, the 1-bromo end group is most susceptible to nucleophilic displacement under the described reaction conditions. This was confirmed by <sup>1</sup>H NMR in which the spectral intensities corresponding to the 1-bromo substituent diminished upon reaction with TPP while the intensities corresponding to both the 1,2-dibromo and the 2-bromo structures changed very little throughout the reaction. Competition exists between the nucleophilic substitution reaction and oxidation of triphenylphosphine at high reaction temperatures; therefore, a large excess of triphenylphosphine was used.

The fractions of the original vinyl groups converted to of dibromo, 1-bromo, and 2-bromo end groups are provided in Table 3. Residual double bonds were not detected in these samples. The fraction of TPP-terminated chains in addition to unreacted dibromo, 1-bromo, and 2-bromo terminated chains are listed for polymers after reaction with triphenylphosphine.

In our hands, the bromination reaction was quite reproducible and, after refinement, gives products more typical of the distribution for the brominated LEA-51 sample of Table 3. The other samples were brominated at earlier stages in our optimization of the reaction. The TPP reaction, on the other hand, is one that we understand less well in the sense that the extent of reaction remained variable despite initial conditions, which were, to us, indistinguishable.

**2. Molecular Mass Determinations.** Polyolefins with saturated hydrocarbon chains such as polyethylene and polypropylene cannot be characterized using MALDI via the traditional metal cationization method. The strategy of covalently attaching an ammonium or a phosphonium salt to vinyl-terminated polyethylene has produced successful MALDI spectra.<sup>1</sup> Our current work employs GPC fractionation products of a commercial polyethylene in order to provide a wider and more systematic study. 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  $M_n$ . The vinyl-to-methylene ratio was measured by FTIR as

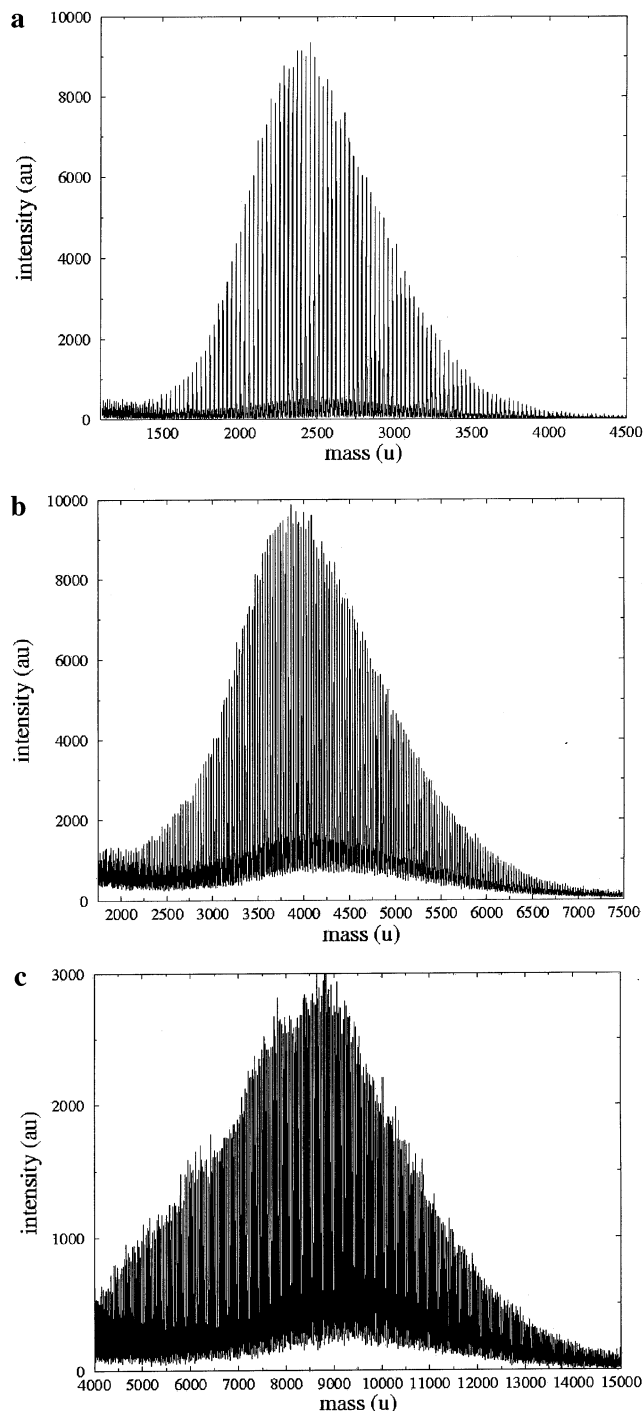


**Figure 3.** FTIR intensity of the vinyl band normalized to a methylene combination band vs reciprocal molecular mass of the polyethylene NIST Standard Reference Materials used.

a function of molecular mass (Figure 3). A linear correlation indicates that the ratio of vinyl end groups to total end groups is quite uniform throughout this molecular range. As an added bit of evidence, solution <sup>1</sup>H NMR analyses of LEA-51, SRM 2885, SRM 1482, and SRM 1483 samples also support the notion that the fraction of molecules with one vinyl end is quite constant; moreover, based on the intensity ratio in the vinyl and methyl regions, this fraction is  $0.39 \pm 0.05$ .

Figure 4 shows the MALDI–TOF MS spectra for LEA-51, SRM 2885, and SRM 1482. The Polymerix software package (Sierra Analytics LLC, Modesto, CA) was used to identify all major peaks in the spectrum as well as to calculate moments of the molecular mass distribution. For all polyethylene spectra the main series of peaks corresponds to (within  $\pm 2u$ ) a proton at one terminus and a TPP group at the other. A secondary series, more prominent at low mass than at high mass, corresponded to a methyl terminus at one end and a TPP group at the other. We attribute the latter series to fragmentation resulting in chains with an odd number of main chain, non-TPP carbons. Presumably, the main series peaks at low mass also have a contribution due to fragmentation; however, since their mass is different from a main series chain by only one proton, they cannot be distinguished from the main series. The number-average molecular mass and mass-average molecular mass 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 than those determined via osmometry, <sup>1</sup>H NMR, and light scattering.

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 28.9 ku and  $M_w$  of 32.1 ku, did not produce good MALDI signals. One possible explanation is insufficient chemical modification on the terminal double bond. As the molecular mass increases, the number of end groups diminishes. The reaction efficiency, therefore, becomes more important in order to achieve the same degree of chemical modification. The number of moles of TPP-terminated chains per gram of material is calculated for all molecular mass fractions based on the NMR data (Table 3). It is apparent that the numbers of TPP-terminated chains per gram are comparable for SRM 2885 and SRM 1483. Considering that the mass fraction of labeled chains is about 6 times



**Figure 4.** MALDI-TOF MS spectra of polyethylene narrow mass fractions: (a) LEA-51, (b) SRM 2885, and (c) SRM 1482. The data are shown without smoothing or background subtraction.

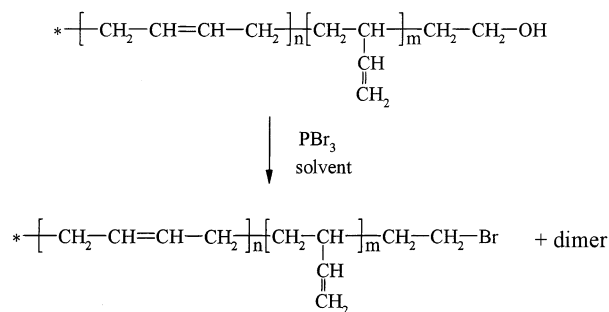
larger for the SRM 1483 than for the SRM 2885, it is notable that the SRM 2885 generated strong MALDI signals yet SRM 1483 did not. This suggests that incomplete chemical modification is not the primary reason for little or no MALDI signal for higher molecular mass polyolefins.

Another explanation for the poor MALDI MS signal for SRM 1483 is that the probability of volatilization of intact polyethylene molecules strongly 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 (not shown), certified  $M_n$  of 28.9 ku, consisted of low-intensity peaks separated by 14 u with a high mass cutoff of 8 ku is entirely consistent with fragmentation. Qualitatively, this pattern was not sensitive to the sample preparation methods that included room-temperature and cryogenic grinding as well as high-temperature electrospraying onto a room temperature target. It was also consistently observed at extremely low laser power, lower than that used to take spectra of the lower mass SRMs. The detection of fragments at their expected masses for TPP conversion confirms 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 15 ku. The extent of fragmentation is related to the laser power; if appreciable volatilization of intact molecules can be achieved at lower laser power, it may be possible to detect higher mass species. 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>13</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 collision with excited matrix molecules. Therefore, higher 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, a noncrystalline polyolefin, demonstrated the very similar mass cut off near 15 ku. Further research is ongoing to optimize sample preparation procedures necessary for polyolefin measurements.

**3. Metal Cationization vs Covalent Cationization.** As noted earlier, the molecular masses obtained by MALDI were consistently lower than those determined by other methods. To explore whether the chemical modification utilized for MALDI was contributing to molecular mass biasing, we compared mass spectra obtained on a polymer that could be charged by conventional methods as well as through covalent cationization. A hydroxy-terminated polybutadiene was used as a model compound to assess the effect of chemical modification on molecular mass biasing. Polybutadiene contains double bonds that allow them to be metal cationized by the traditional method. The terminal hydroxy functionality on our polybutadiene can also be modified via covalent cationization. Furthermore, polybutadiene can be hydrogenated to form a linear low-density polyethylene. Therefore, MALDI measurements on one polymer using three cationization approaches, i.e., metal cationized polybutadiene, covalent cationized polybutadiene, and covalent cationized hydrogenated polybutadiene, were compared and contrasted.

PBr<sub>3</sub> was used to convert hydroxy-terminated polybutadiene to 1-bromo-terminated polybutadiene (Figure 5). One side reaction is the coupling of a hydroxy-terminated polybutadiene and a bromine-terminated polybutadiene, which doubles the molecular mass. The ether-linked dimers, however, are inert to the reaction with tertiary amines or phosphines and therefore will



**Figure 5.** Bromination of hydroxy-terminated polybutadiene.

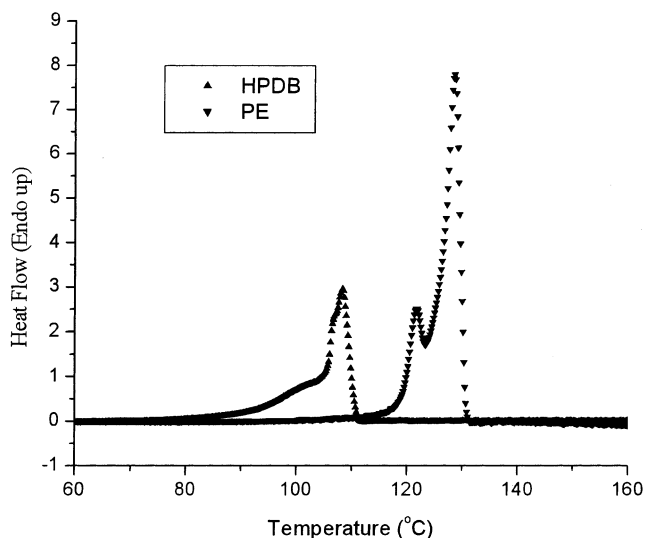
be excluded in the MALDI analysis. The brominated polybutadienes are subsequently converted to covalently bonded ammonium or phosphonium salts.

$^1\text{H}$  NMR showed the original PBDOH to have 7.6% of its butadiene additions to be 1,2; also, we estimated the 1,4 additions to be 55% trans and 37% cis. The hydrogenation of HPBDOH was complete, as determined by  $^1\text{H}$  NMR and FTIR, to the extent that about three of every four molecules were completely hydrogenated. Such fully hydrogenated molecules would be equivalent to a linear, low-density ethylene/butene copolymer with about 4% (mole fraction) butene.

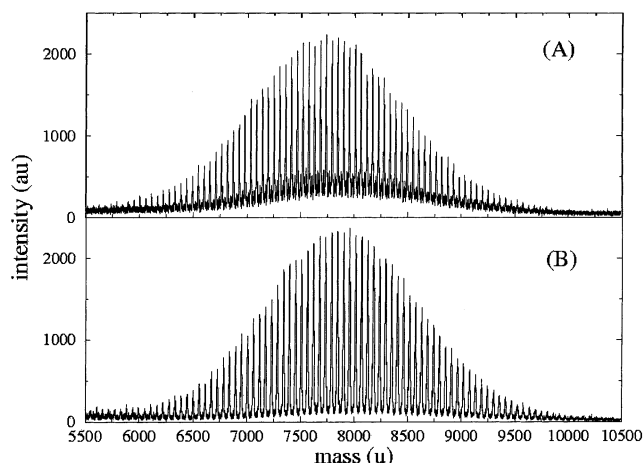
The GPC chromatogram shows a well-shaped symmetric peak for PBDOH. To estimate the mass moments for the PBDOH, we used Mark-Houwink (MH) constants for a PBD with 7% 1,2 additions and 36% cis 1,4 and 57% trans 1,4 in THF of  $K = 0.0256 \text{ dL/g}$  and  $a = 0.715$  assuming universal calibration.<sup>14</sup> This yields an  $M_n = 8400 \text{ g/mol}$  and  $M_w = 8700 \text{ g/mol}$ . We have also run the same polymer in toluene and using MH parameters for PBD 51% trans 1,4 43% cis 1,4 6% 1,2 of  $K = 0.039 \text{ dL/g}$  and  $a = 0.713$  assuming again universal calibration. This yielded  $M_n = 7700 \text{ g/mol}$  and  $M_w = 8100 \text{ g/mol}$ . Thus, we estimate the  $M_n$  of this PBDOH to be about 8000 g/mol. These numbers must be considered to have a large uncertainty (at least 800 g/mol) due to the large variation from solvent to solvent which most likely is due to the fact that the MH parameters are for a polymer of much higher molecular masses, and the extrapolation to these low masses is unreliable.<sup>15</sup>

Because of the branch content, the HPBD may not be representative of crystalline linear PE. DSC thermograms of all of the unmodified PE's and HPBD's were taken to measure the relative crystallinity. Figure 6 illustrates DSC thermograms of a typical PE and HPBD that have comparable molecular mass. The PE and HPBD have peaks at  $128 \pm 1$  and  $108 \pm 1$  °C, respectively, and heats of fusion,  $\Delta H$ , of  $235 \pm 24$  and  $122 \pm 12 \text{ J/g}$ , respectively. By assuming that a PE that is 100% crystalline has a  $\Delta H$  of  $280 \text{ J/g}$ ,<sup>16</sup> the relative crystallinity of the PE and HPBD is  $83 \pm 8\%$  and  $44 \pm 4\%$ , respectively. This range of thermal properties as well as branch content falls within the range reported for commercial PE.<sup>17</sup> Therefore, while there is a significant difference in crystalline content of the two samples, the HPBD still lies in the range of commercial PE's.

Figure 7 shows the MALDI spectra for metal cationized polybutadiene and covalent-cationized hydrogenated polybutadiene. The molecular mass and molecular mass distributions represented in Figure 7 were almost identical for essentially the same source polymer that was cationized using very different methods. This suggests that in the MALDI analysis any molecular mass or molecular mass distribution biasing in the



**Figure 6.** DSC thermograms of polyethylene and hydrogenated polybutadiene.



**Figure 7.** MALDI-TOF MS spectra for (A) copper metal cationized polybutadiene and (B) hydrogenated analogue of polybutadiene used in (A) with covalent cationization.

**Table 4. Number-Average Molecular Mass (g/mol), Mass-Average Molecular Mass (g/mol), and Polydispersity Obtained by MALDI-TOF MS for Copper Metal Cationized Polybutadiene (PBD/Cu<sup>+</sup>), Covalent Cationized Polybutadiene (PBD-TMA), and Covalent Cationized Hydrogenated Polybutadiene (HPBD-TTP)**

| sample              | $M_n$ | $M_w$ | PD   |
|---------------------|-------|-------|------|
| PBD/Cu <sup>+</sup> | 7680  | 7800  | 1.02 |
| PBD-TMA             | 7570  | 7630  | 1.01 |
| HPBD-TTP            | 7570  | 7630  | 1.01 |

normal metal cationization method is not different from the covalent cationization method. In this statement we are also claiming that the bromination and TPP addition reactions on HPBD have negligible mass biases. In terms of the question whether MALDI biasing is significant in this sample, the NMR-determined  $M_n$  (based on one *sec*-butyl terminus per molecule) agrees quite well with the MALDI  $M_n$ . The MALDI-MS-determined  $M_n$ ,  $M_w$ , and polydispersity for polybutadiene, metal cationized and covalently cationized, and covalently cationized hydrogenated polybutadiene are listed in Table 4. All results are comparable regardless of the cationization method. It is interesting to note that the MALDI calculation for covalent cationized polybutadiene is exactly the same (within uncertainty) as the

covalent cationized hydrogenated polybutadiene. The hydrogenated polybutadiene should show a 3.7% increase in molecular mass, but this is very near the uncertainty in the molecular mass calculation. Auto-correlation<sup>18</sup> of the hydrogenated polybutadiene mass spectrum showed a repeat unit of 56.0 u within experimental error of the average mass value of 56.1 u.

These hydrogenated PBD-MALDI results stand in significant contrast to the PE-MALDI results for all linear PE's we examined. In the PE case, MALDI values of  $M_n$  were 60%–75% of those expected from other measurements (osmometry, NMR, GPC, and light scattering). The MALDI values of  $M_n$  reported by Ji et al. for polyisobutylene are also lower than the  $M_n$  determined by classical methods: 67% in the case of a 10.6 ku polymer and 84% for a 6.0 ku polyisobutylene. In contrast, Ji et al. report excellent agreement between MALDI  $M_n$  results and  $M_n$  from GPC or vapor phase osmometry for polyisobutylene below 3 ku. They discuss a possible connection between larger MALDI  $M_n$  biases and higher polydispersities.

We have no clear answers to explain the presence (and absence in the hydrogenated PBD) of the MALDI- $M_n$  mass bias. Nor do we understand the true origin of the strong fragmentation patterns of linear PE at the higher mass. However, fragmentation is, to us, a very important issue to address if one is interested in pursuing the MALDI analysis of linear PE since fragmentation is a property of MALDI at low, as well as high, laser power. There are many facets to explore in the examination of this issue including, but not limited to, (a) whether placing the charge at the end of a chain puts more strain on the accelerating molecule than, say, putting a charge (presumably) closer to the middle of a chain as in metal cationization, (b) whether entanglements arising from crystallization play some role in preventing intact chains from reaching the gas phase, and (c) whether sample preparation methods or different approaches can be found for giving a softer, less-energetic "lift" to the molecules into the gas phase.

## Conclusion

We have optimized a chemical modification procedure for those polyethylene molecules (about 40% of the molecules in our case) that contain residual vinyl end groups. These modified molecules are observed by MALDI mass spectrometry in the range below 15 ku. As with other synthetic polymers the method is limited to polymers of low polydispersity. The samples studied had a polydispersity in the range 1.1–1.2. The method yields a substantial improvement in mass range and a simultaneous decrease in fragmentation compared to previously reported mass spectra of polyethylene.<sup>19</sup>

Moments of the mass distribution,  $M_n$  and  $M_w$ , determined from our MALDI MS data on polyethylene were lower (60%–75%) than values derived by the conventional methods of osmometry, <sup>1</sup>H NMR, and light scattering. The nature of the fragmentation pattern for the 28 ku LPE fraction is noted, especially the fact that extensive fragmentation is seen, even at the lowest laser power. We believe that a true exploration and understanding of the origin of this fragmentation is critical to any future successful applications of MALDI to the analysis of LPE in the range above 15 ku.

**Acknowledgment.** The authors thank W. R. Blair for expert technical assistance and Dr. H. C. M. Byrd for useful discussions.

## References and Notes

- (1) Bauer, B. J.; Wallace, W. E.; Fanconi, B. M.; Guttman, C. M. *Polymer* **2001**, 42, 9949.
- (2) Rader, H. J.; Schrepp, W. *Acta Polym.* **1998**, 49, 272.
- (3) Hanton, S. D. *Chem. Rev.* **2001**, 101, 527.
- (4) Coessens, V.; Matyjaszewski, K. *Pure Appl. Chem.* **1999**, A36, 653.
- (5) Ji, H.; Sato, N.; Nakamura, Y.; Wan, Y.; Howell, A.; Thomas, Q. A.; Storey, R. F.; Nonidez, W. R.; Mays, J. W. *Macromolecules* **2002**, 35, 1196.
- (6) <http://ts.nist.gov/ts/htdocs/230/232/232.htm>.
- (7) Verdier, P. H.; Wagner, H. L. *NBS Special Publication* 260–261, Dec 1978 (also found in *J. Res. Natl. Bur. Stand.* **1978**, 83, 169).
- (8) Taylor, B. N.; Kuyatt, C. E. *NIST Technical Note* 1297, Sept 1994.
- (9) Pouchert, C. J.; Behnke, J. in *Aldrich Library of <sup>13</sup>C and <sup>1</sup>H NMR Spectra*, 1st ed.; Aldrich Chemical Co.: Milwaukee, WI, 1993.
- (10) Przybilla, L.; Brand, J. D.; Yoshimura, K.; Rader, H. J.; Mullen, K. *Anal. Chem.* **2000**, 72, 4591.
- (11) March, J. In *Advanced Organic Chemistry Reactions: Mechanisms and Structures*, 4th ed.; Wiley: New York, 1992.
- (12) Corbridge, D. E. C. In *Studies in Inorganic Chemistry 10: Phosphorus-An Outline of its Chemistry Biochemistry and Technology*; Elsevier: New York, 1990.
- (13) Bauer, B. J.; Byrd, H. C. M.; Guttman, C. M. *Rapid Commun. Mass Spectrom.* **2002**, 16, 1494.
- (14) Brandrup, J.; Immergut, E. H.; Grulke, E. A. In *Polymer Handbook*, 4th ed.; Wiley: New York, 1999; p VII-68.
- (15) McCrackin, F. L. *Polymer* **1987**, 28, 1847.
- (16) Brandrup, J.; Immergut, E. H. In *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989; p V-19.
- (17) Balta Calleja, F. J.; Rueda, D. R. *Polym. J.* **1974**, 6, 216.
- (18) Wallace, W. E.; Guttman, C. M. *J. Res. Natl. Inst. Stand. Technol.* **2002**, 107, 1.
- (19) Chen, R.; Yalcin, T.; Wallace, W. E.; Guttman, C. M.; Li, L. *J. Am. Soc. Mass Spectrom.* **2001**, 12, 1186.
- (20) 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.

MA020619G