

# Silver Nitrate Chemical Ionization for Analysis of Hydrocarbon Polymers by Laser Desorption Fourier Transform Mass Spectrometry

Michael S. Kahr and Charles L. Wilkins

Department of Chemistry, University of California—Riverside, Riverside, California, USA

Addition of silver nitrate to nonpolar hydrocarbon polymer solutions prior to their analysis by laser desorption Fourier transform mass spectrometry is shown to allow efficient silver ion chemical ionization. High-quality mass spectra are thus obtained for polymers, such as polystyrene, polyisoprene, polybutadiene, and polyethylene, that previously failed to yield useful mass spectra using conventional laser desorption. Accurate mass measurement experiments and isotopic ratios verify that the spectra are those of silver-attached oligomer ion distributions. Mass measurement errors for complete oligomer distributions average between 3 and 12 ppm for oligomers with masses between 400 and 6000 D whereas unit mass resolution is maintained throughout the entire spectral range. (*J Am Soc Mass Spectrom* 1993, 4, 453–460)

The class of hydrocarbon polymers poses a difficult challenge to analysis by mass spectrometry. At the heart of this challenge is their chemical inertness, which is the quality that makes them so useful for diverse applications. Because the molecular weight distribution of a polymer is an important factor in determining its properties, it is highly desirable to develop improved methods for determining this distribution. Standard polymer weight determination methods typically involve indirect measurements, such as light scattering, vapor-phase osmometry, and gel permeation chromatography. The primary and obvious advantage of using mass spectrometry is that it provides direct observation of oligomer ion distributions, provided that appropriate sample preparation and soft ionization procedures are used.

A variety of mass spectrometric techniques have previously been applied to analysis of hydrocarbon polymers. Possibly because of the presence of multiple aromatic rings, polystyrene is one of the more tractable hydrocarbon polymers when analyzed using standard volatilization/ionization methods. For example, polystyrenes have been studied by laser desorption/ionization [1, 2], secondary ion mass spectrometry [3–7], field desorption-ionization/mass spectrometry (FD/MS) [8–10], plasma desorption ionization [11], laser desorption/resonance-enhanced multiphoton ionization [12], liquid chromatography/mass spectrometry [13], and thermal desorption electron ioniza-

tion and chemical ionization mass spectrometry [14, 15]. Most recently, polystyrenes have also been characterized by matrix-assisted laser desorption/ionization [16, 17]. Of these techniques, FD/MS has until now been the most successful for obtaining mass spectra for other hydrocarbon polymers. Lattimer and Schulten [8] obtained FD/MS spectra for polyethylene 700 and 1000, several polybutadienes with average weights up to [number-average molecular weight ( $M_n$ ) 2450], and several polyisoprenes with average masses as high as  $M_n$  1070. Craig et al. [18] applied FD/MS to characterize polybutadiene 1000 and 3000, obtaining ions with  $m/z$  up to 3500. Rollins et al. [19] characterized synthetic lubricants, including a polyisobutylene formulation, by FD/MS.

Previously, it has been shown that direct carbon dioxide laser desorption/Fourier transform mass spectrometry (LD/FTMS) is an excellent tool for characterization of heteroatom-containing polymers, providing both accurate molecular weight distribution information as well as high-resolution spectra useful for structural characterization [1, 20, 21]. Ionization is facilitated by alkali metal attachment to oxygen or nitrogen in the analyte. Because of their lack of energetically favorable sites for alkali metal attachment, nonaromatic hydrocarbon polymers give poor results when subjected to LD/FTMS under the conditions that are optimal for polar heteroatom-containing polymers. Generally, only low-mass fragment ions are observed, providing little or no useful information about polymer molecular weight and composition. Thus, it is the goal of the research presented here to develop a gen-

Address reprint request to Charles L. Wilkins, Department of Chemistry, University of California—Riverside, Riverside, CA 92521.

eral laser desorption method that would be applicable to analysis of these otherwise intractable hydrocarbon polymer categories. Specifically, the use of nonalkali metals for cationization, as originally suggested by Grade and Cooks [22] for SIMS applications is investigated. On the basis of earlier studies in our laboratory [23, 24], it was anticipated that admixture of suitable metal salts with analyte samples prior to LD/FTMS would be efficacious.

## Experimental

### Instrumental

Studies were performed using a Nicolet Analytical Instruments (Madison, WI) FTMS-2000 Fourier transform mass spectrometer equipped with a 7-T superconducting magnet, differentially pumped source and analyzer regions separated by a 2-mm-diameter conductance limit, and an automatic solids probe. The Fourier transform mass spectrometer is interfaced to a Tachisto (Boston, MA) 215 pulsed-CO<sub>2</sub> laser for desorption. The CO<sub>2</sub> laser was directed into the mass spectrometer through a ZnSe window in the source flange and was focused to a spot size of approximately 1 mm<sup>2</sup> on the tip of the solids probe by an off-axis paraboloid mirror mounted on the source cell assembly. The laser delivers approximately 10<sup>6</sup>-10<sup>8</sup> W/cm<sup>2</sup> per 80 ± 40-ns pulse.

Spectra were obtained in the direct mode under broadband excitation and observation conditions. All spectra were obtained in the source cell, using a 1-V trapping voltage. Following the laser desorption ionization event, a 10-s delay allowed neutrals to pump away and ions to relax to the center of the cell before excitation. All ions outside the spectral bandwidth were resonantly ejected by a 500-Hz/μs ejection sweep. Ions inside the desired analysis bandwidth were then excited using either swept frequency or the stored waveform inverse Fourier transform (SWIFT) technique [25, 26]. Frequency-swept excitation was from 50 to 200 kHz, with a 180-Hz/μs sweep rate attenuating the excitation so that smooth oligomer ion distributions were observed. For SWIFT excitation experiments, ions were excited to radii of approximately 1.2 cm over the mass range of the distribution, as determined by a preliminary frequency-swept excitation measurement [27]. Ions were detected using a 200-kHz direct-mode receive bandwidth and a 200-kHz low-pass filter to prevent frequencies outside the bandwidth from aliasing into the spectrum. Typically, sixteen 131,072 data-point transients were ensemble averaged to enhance signal-to-noise ratios. The exception to this was for exact mass measurement experiments in which single spectra were obtained and analyzed.

### Data Analysis

Transients were Fourier transformed following augmentation by an equal number of zeros on the basis of

examination of the time domain data to determine where the signal had dropped to baseline level. Thus, 131,072, 65,536, or 32,768 data points were used to produce frequency domain spectra by 256K, 131K or 64K Fourier transforms. The number of data points transformed was chosen to optimize signal-to-noise ratio while preserving adequate mass resolution. The resolving powers (stated in the figure captions) were determined by measuring peak width at half-maximum of magnitude mode spectra. A background spectrum in which no ions were generated was obtained using identical experimental excitation and receive conditions and was subtracted from the sample spectra in the frequency domain to remove electronic noise artifacts.

Number-average ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) values for the polymer standards were obtained for each sample by using the first 4096 data points of the time domain transient to broaden oligomer isotope peaks into a single peak for integration. Peak areas were then measured using the manufacturer's peak area and height (PAH) program. The data file generated by the PAH program was then transferred to a Digital Equipment Corp. (Newton, MA) VAXstation II computer for computation of polymer weight averages using the areas determined and standard  $M_n$  and  $M_w$  formulas:

$$M_n = \sum A_i M_i / \sum A_i \quad (1)$$

$$M_w = \sum A_i M_i^2 / \sum A_i M_i \quad (2)$$

where  $A$  is the measured peak area of oligomer  $i$  with mass  $M$ .

Accurate mass measurements were obtained for the low-molecular-weight standards by using an internal calibrant [poly(ethylene glycol)-1000]. Spectra were calibrated using the automatic calibration program included in the standard Fourier transform mass spectrometer software. This program automatically calibrates using up to 10 peaks read from a user-specified text file. For each spectrum, the 10 internal calibrant peaks were utilized, and this calibration was used to calculate masses of the unknown polymer standard oligomer peaks. Accurate masses were computed using the peak centroid program for the first four peaks of the isotopic distribution for each oligomer molecular ion observed in the mixed calibrant/analyte spectrum. Error in parts per million was calculated by subtracting the theoretical mass for each peak from the appropriate measured mass, dividing by the theoretical mass, and multiplying by 10<sup>6</sup>.

Isotopic ratios were obtained for the low-molecular-weight standards. These ratios were measured by using the PAH program to find the areas of each isotope peak for a given oligomer. Theoretical isotopic ratios were calculated using the isotope distribution program included in the manufacturer's standard software. These

values were compared with measured values to determine the percentage errors.

### Samples

All reagents, solvents, and polymers were obtained from commercial sources and used as received. Silver nitrate [certified American Chemical Society (ACS)] and methylene chloride (certified ACS) were obtained from Fisher Scientific (Fair Lawn, NJ). *n*-Heptane, spectrophotometric grade, was obtained from Mallinckrodt, Inc. (Paris, KY). Ethyl alcohol (200-proof dehydrated alcohol, US Pharmacopeia Punctilious) was obtained from Quantum Chemical Corp. (USI Division, Tuscola, IL). Poly(ethylene glycol), average molecular weight 1000, was obtained from Sigma Chemical Co. (St. Louis, MO). Polybutadiene ( $M_w$  2966), polyisoprene ( $M_w$  2953), polystyrene ( $M_w$  1022), polyethylene ( $M_w$  1214), and polyethylene ( $M_w$  2306) were narrow molecular weight standards anionically polymerized that were obtained from Polymer Laboratories (Foster City, CA). Polymer Laboratories also provided gel permeation data, along with initiation and termination reagent data for its polymers. Molecular weight standard polystyrene ( $M_w$  4140), polybutadiene ( $M_w$  1000), and polyisoprene ( $M_w$  650) were obtained from Polysciences, Inc. (Warrington, PA).

### Sample Preparation


Polystyrene, polybutadiene, and polyisoprene samples were each dissolved in methylene chloride in 0.5-mM concentrations. Polyethylene ( $M_w$  1214) and polyethylene ( $M_w$  2306) were each sonicated in heptane in a 30- $\mu$ g/mL concentration for 1 h to form a saturated solution with suspended solids. The calibration solution, poly(ethylene glycol)-1000 (PEG-1000) was dissolved in methanol in a 0.5-mM concentration with potassium nitrate to ensure potassium cation attachment for calibration. For polyethylene measurements, no potassium nitrate was added, and silver-attached PEG-1000 molecular ions were used for calibration. For silver chemical ionization, a saturated solution of silver nitrate in ethanol was used. To carry out molecular weight and isotopic ratio measurements, all samples

were prepared by spraying 30  $\mu$ L of silver nitrate solution onto a rotating probe via an aerosol spray apparatus. Next, the analyte solution was sprayed onto the same rotating probe tip. Depositions from methylene chloride solutions consumed 300  $\mu$ L of analyte solution. For polyethylene ( $M_w$  1214), 5.0 mL of analyte solution was sprayed, and for polyethylene ( $M_w$  2306), 10 mL of solution was consumed. Exact mass measurement samples were prepared by mixing the silver nitrate, poly(ethylene glycol), and methylene chloride solutions together. Subsequently, the composite solution was sprayed as an aerosol onto the rotating probe tip. For polyethylene, the mixture of silver nitrate solution and poly(ethylene glycol) solution was sprayed together onto the probe tip, followed by the polyethylene solution. For all samples, the prepared probe tip was placed on the direct-insertion probe and inserted into the vacuum system, and the system was pumped down until the pressure was approximately  $5 \times 10^{-8}$  torr before mass spectral analysis.

### Results and Discussion

Polymer samples studied here were chosen to represent a range of types of hydrocarbon polymer, including some that had previously been difficult or impossible to analyze by LD/FTMS. They are listed in Table 1, which includes their structures and functionalities. Polystyrene is representative of aromatic hydrocarbon polymers, which appear to be the most amenable to mass spectral analysis. Polyisoprene and polybutadiene are representative of linear and branched unsaturated hydrocarbon polymers, which are somewhat more difficult to analyze by mass spectrometry. For this type of polymer, low-molecular-weight distributions (averaging less than 1000 D) often readily yield alkali metal-attached molecular ions when analyzed by LD/FTMS. Of interest, for higher mass distributions, conventional laser desorption typically fails, with only fragment ions being detected. Of the current polymer samples, polyethylene, representative of saturated hydrocarbon polymers, represents the most challenging mass spectral analysis problem. Typically, polyethylene yields only low-mass fragments on laser irradiation.

Table 1. Model hydrocarbon polymers

Polymer	Structure	Functionality
Polystyrene	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-(\text{CH}_2\text{CH})_n-\text{H}$ 	Phenyl ring
Polyisoprene	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)-(\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2)_n-\text{H}$	Branched and unsaturated
Polybutadiene	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)-(\text{CH}_2\text{CH}=\text{CHCH}_2)_n-\text{H}$	Linear and unsaturated
Polyethylene	$\text{H}-(\text{CH}_2\text{CH}_2)_n-\text{H}$	Linear and saturated

### Sample Preparation

LD/FTMS of high-mass hydrocarbon polymers has been difficult, owing in part to sample preparation problems. The standard method of sample deposition is application of a dilute solution of sample to the probe tip, followed by evaporation of the solvent. For hydrocarbon polymers, the formation of thin, even sample films is often difficult. Many hydrocarbon polymers are insoluble in solvents that produce ideal sample films by this method, requiring the use of nonideal solvents or sonicated suspensions. The sample films formed under these conditions are usually uneven and heterogeneous. This makes the adjustment of experimental parameters difficult because the sample, and the corresponding mass spectrum, can change from shot to shot. By spraying the sample onto a rotating probe tip with an aerosol spray apparatus, any convenient volatile solvent can be used to produce homogeneous sample films. As a consequence, spectral quality and reproducibility are significantly improved.

### Metal Ion Chemical Ionization

From an analytical standpoint, the ionization procedure is an especially critical parameter. As mentioned above, for a number of the hydrocarbon polymers examined here, direct laser desorption yields alkali ion cationization only for relatively low-mass oligomer distributions and often yields only low-mass fragment ions; however, if the laser desorption event fails to ionize the desired analyte but yields intact neutrals, then a mass spectrum may be obtained by ionizing these neutrals by other means. Chemical ionization is therefore attractive, both because it is a "soft" ionization process and because its combination with laser desorption, which is generally thought to produce significantly more neutrals than ions, should result in sensitivity enhancements. Amster et al. [28] showed that laser-desorbed neutrals can be chemically ionized using a pulsed reagent gas. We, too, have shown that it is possible to chemically ionize low-molecular-weight polybutadiene and polyethylene using this method [29, 30]; however, reproducibility difficulties, combined with an inability to obtain spectra for higher molecular weight distributions prompted us to abandon the use of a reagent gas and to further pursue the use of solid reagents for chemical ionization in conjunction with laser desorption.

Because use of a solid chemical ionization reagent that could be codeposited with the sample and ionized by the laser would not introduce a significant gas load to the vacuum system, such an approach is an attractive possibility. During the laser desorption event, reagent ions would be generated in close proximity to desorbed hydrocarbon neutrals, which would presumably favor chemical ionization reactions. Furthermore, as we observed in our original suggestion of this technique for use of metal salts or metal oxides with

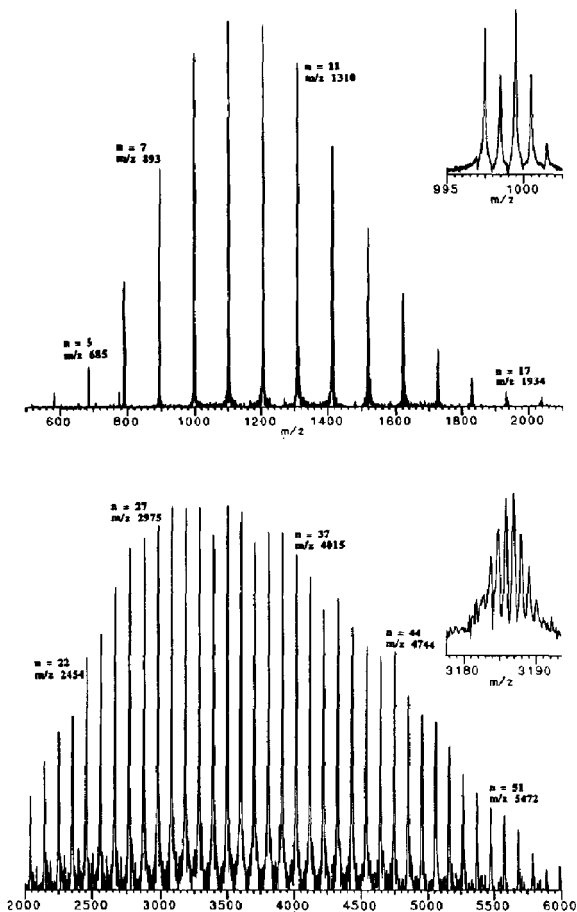
laser desorption [23], the method seems to be general. Further evidence is seen in the more recent work of Wood and Marshall [31] who used ammonium bromide to produce ammonium ions on laser desorption, which then chemically ionized aromatic hydrocarbon analytes that had been codeposited and codesorbed.

Gold was an attractive first choice for a possible chemical ionization reagent because  $\text{Au}^+$  has been shown to effectively chemically ionize alkanes and alkenes [24]. Both gold oxide and gold foil have been used to chemically ionize polybutadienes to obtain their laser desorption mass spectra [17, 32]. The inability of gold oxide or a gold foil substrate to ionize other polymer samples studied prompted the study of gold chloride, which may produce more abundant gold reagent ions. In fact, codeposition of gold chloride and analyte, which are subsequently laser desorbed, does result in chemical ionization of all of the polymers in this study; however, when gold chloride is used, polybutadiene is fragmented significantly, polyisoprene loses end groups, and spectra are not completely reproducible for polyethylene. It seems likely that this behavior results from the high exothermicity of the gold-analyte reactions due to the relatively high ionization energy of gold (9.22 eV). Because silver has a lower ionization energy (7.57 eV), silver nitrate was investigated as a potentially softer chemical ionization reagent for LD/FTMS.

### Polymer Spectra

Spectra obtained for two polystyrene molecular weight standards obtained under silver nitrate laser desorption/chemical ionization (LD/CI) conditions are shown in Figure 1. Although polystyrene can undergo alkali metal attachment under conventional LD/FTMS conditions, it is less efficient compared with the corresponding reactions of heteroatom-containing polymers [1]. As a consequence, lower abundances of molecular ions are produced, spectral quality is inferior, and the upper mass limit is much lower than that seen in spectra of poly(ethylene glycol), for example. Under identical conditions, silver nitrate LD/CI gives polystyrene spectra with a signal-to-noise ratio that is much greater than that obtained in the absence of silver nitrate. This enhancement allows extension of the useful mass range of analysis for polystyrenes. For example, although silver nitrate LD/CI spectra were obtained for the polystyrene ( $M_w$  4140) sample (Figure 1, bottom), identical conventional experimental conditions failed to produce useful spectra.

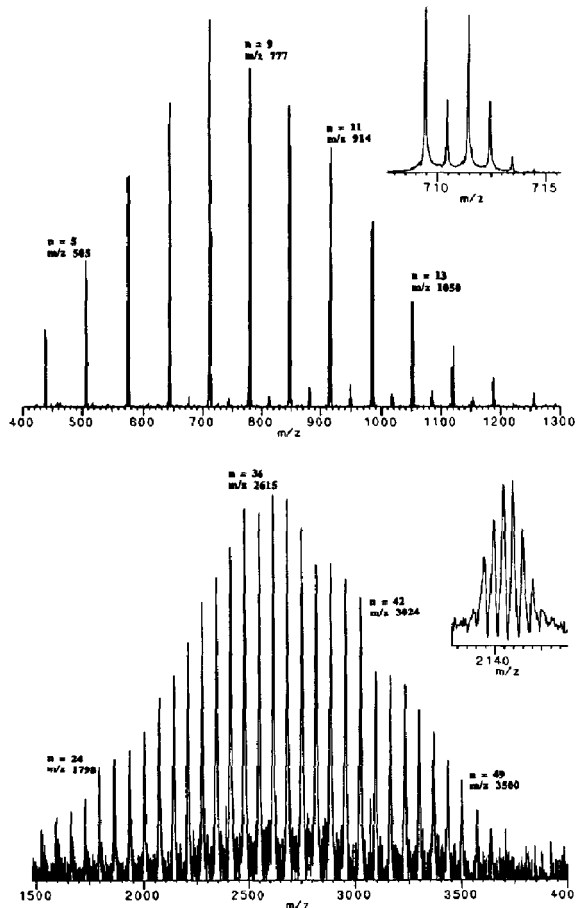
Silver nitrate LD/CI spectra were also obtained for polyisoprene and polybutadiene molecular weight standards (Figures 2 and 3). The spectra show little or no evidence of fragmentation and have better than unit mass resolution, allowing molecular ion isotopic multiplets to be resolved. Lower mass polyisoprene and polybutadiene samples readily yield smooth distributions. For the higher mass representatives of these two



**Figure 1.** (Top) Polystyrene, GPC ( $M_w$  1022). Inset shows the  $n = 8$  silver-attached oligomer molecular ion region with resolving power 6422 at mass 997. (Bottom) Polystyrene, GPC ( $M_w$  4140). Inset shows the  $n = 29$  silver-attached oligomer molecular ion region with resolving power 6245 at mass 3185. This spectrum was obtained using SWIFT excitation.

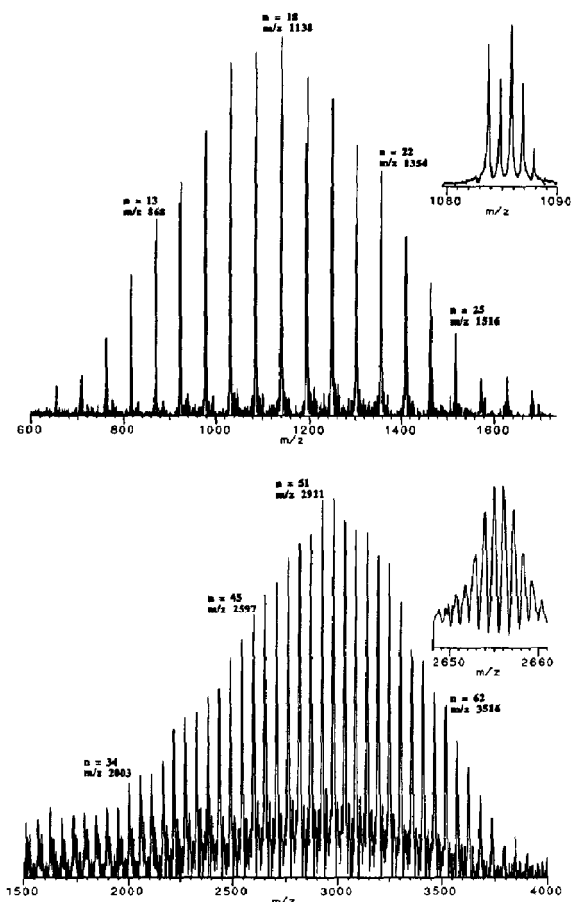
types of polymers, some optimization of the experimental parameters was required. Two means of tuning the spectrometer were used to accomplish this. The polyisoprene spectrum in Figure 2 (bottom) was obtained by attenuation of the frequency sweep excitation by 12 dB at 200 Hz/ $\mu$ s, a sweep rate for the 200-kHz bandwidth that typically produces the expected spectral distributions for conventional LD/FTMS. The polybutadiene spectrum in Figure 1 (bottom) was obtained using SWIFT excitation. Both excitation methods yield regular distributions for these samples, and for these samples either type of excitation may be used.

Polyethylene represents the most challenging polymer studied here. The spectra obtained for polyethylene samples in this study are shown in Figure 4. These spectra were both produced using SWIFT excitation. Spectra also can be obtained using frequency



**Figure 2.** (Top) Polyisoprene, GPC ( $M_w$  650). Inset shows the  $n = 8$  silver-attached oligomer molecular ion region with resolving power 10,082 at mass 709. (Bottom) Polyisoprene, GPC ( $M_w$  2953). Inset shows the  $n = 29$  silver-attached oligomer molecular ion region with resolving power 5180 at mass 2142.

sweep excitation; however, in all cases those spectra were inferior to those produced by SWIFT excitation. It is known that SWIFT is capable of producing much more uniform excitation than frequency sweep [25, 26]. The narrow spacing of the polyethylene oligomers (28 D) accentuates the effect of nonuniform excitation. This spacing results in significantly more oligomers being present in a narrow molecular weight range sample, with a correspondingly greater effect of nonuniformity of excitation over the spectral bandwidth. In addition, the ratio of signal to noise is adversely affected. For example, the polystyrene ( $M_w$  1022) spectrum in Figure 1 (top) contains 15 oligomers distributed over a range of approximately 1400 D. On the other hand, for the polyethylene ( $M_w$  1214) sample spectrum shown in Figure 4 (bottom), there are 40 oligomer ions distributed over a 1100-D range. Thus, to obtain a similar signal-to-noise ratio, approximately

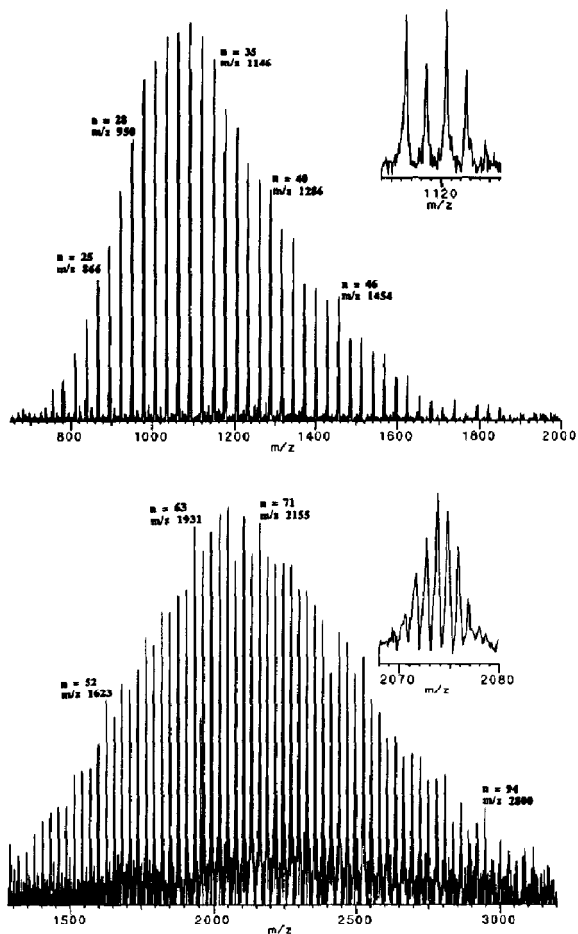


**Figure 3.** (Top) Polybutadiene, GPC ( $M_w$  1000). Inset shows the  $n = 17$  silver-attached oligomer molecular ion region with resolving power 7065 at mass 1084. (Bottom) Polybutadiene, GPC ( $M_w$  2953). Inset shows the  $n = 46$  silver-attached oligomer molecular ion region with resolving power 4773 at mass 2655. This spectrum was obtained using SWIFT excitation.

three times as many polyethylene as polystyrene ions must be trapped, successfully excited, and detected.

### Mass Measurement Accuracy

The low-mass series of hydrocarbon polymer samples was used to evaluate mass measurement accuracy. To obtain the best calibration for the hydrocarbon polymer ions, PEG-1000 was added to the analyte as an internal calibrant. One difficulty encountered when adding such a calibrant is that it is dynamic-range limited. Oligomers of lower abundance are usually not observed for the analyte and cannot be measured, particularly if the calibrant readily yields abundant silver-attached ions and the analyte does not, as is the case for polyethylene. Another problem encountered with use of an internal calibrant is overlap of calibrant ion peaks with those of analyte ions, preventing the



**Figure 4.** (Top) Polyethylene, GPC ( $M_w$  1214). Inset shows the  $n = 36$  silver-attached oligomer molecular ion region with resolving power 7626 at mass 1118. This spectrum was obtained using SWIFT excitation. (Bottom) Polyethylene, GPC ( $M_w$  2306). Inset shows the  $n = 70$  silver-attached oligomer molecular ion region with resolving power 4953 at mass 2073. This spectrum was obtained using SWIFT excitation.

measurement of oligomer ions. Despite these difficulties, the masses of the majority of oligomer molecular ions could be determined. For each peak, the centroid was determined by using a polynomial fitting procedure (see Experimental). Corrections were not made for unresolved isotopic multiplets, such as those arising from the presence of  $^{12}\text{C}$  versus  $^{13}\text{C}$ , for example. Table 2 lists the average error and standard deviation of these errors for the first four isotopes measured for as many oligomers as possible across the spectrum of each hydrocarbon polymer. Mass resolving power ( $m/\Delta m$ ) in excess of 4500 was obtained for all samples evaluated for mass measurement accuracy. It should be noted that calibration (described in Experimental), takes at most a few minutes and is applied to all ions in the spectrum. Thus, 3.32-ppm average mass mea-

**Table 2.** Accurate mass measurements<sup>a</sup>

Hydrocarbon polymer	Average error (ppm)	Standard deviation of errors (ppm)	No. of mass measurements	Mass range of measurements (Da)
Polystyrene ( $M_w$ 1022)	3.32	2.58	20	997-1417
Polyisoprene ( $M_w$ 650)	4.17	3.64	32	505-1121
Polybutadiene ( $M_w$ 1000)	7.76	4.84	52	759-1465
Polyethylene ( $M_w$ 1214)	11.79	7.57	28	950-1205

<sup>a</sup> Weight-average molecular weight ( $M_w$ ) values are those determined by gel permeation chromatography, as provided by the supplier.

surement accuracy is obtained simultaneously for 20 molecular ion species over the mass range 997-1417 D for the polystyrene sample. Even the most difficult sample, polyethylene, yielded an average error of 11.79 ppm over the mass range from 950 to 1205 D.

### Isotope Ratios

It was also of interest to evaluate the capability of the present approach to determine isotopic peak ratios. Therefore, the isotopic peak ratios of the low-mass series of hydrocarbon polymers were determined and compared with the theoretical ratios. Silver has two abundant isotopes, Ag<sup>107</sup> (51.84%) and Ag<sup>109</sup> (48.16%). Thus, identification of silver-attached ions, especially those of lower mass, is straightforward. Visual inspection of the insets for each of the low-mass figures (Figures 1-4) shows the distinct pattern produced by silver attachment. The lowest mass ion in the oligomer molecular ion distribution contains C<sup>12</sup>, H<sup>1</sup>, and Ag<sup>107</sup> isotopes and is predominant at lower masses. The corresponding C<sup>13</sup>-containing peak follows at lower abundance. Next, is the C<sup>12</sup>, H<sup>1</sup>, Ag<sup>109</sup> peak, followed by the C<sup>13</sup>-containing peak at lower abundance. Table 3 summarizes the errors determined by comparing theoretical and measured abundances. The agreement

**Table 3.** Oligomer isotopic multiplet ratio measurements<sup>a</sup>

Hydrocarbon polymer	Average error (%)	Standard deviation of errors (%)	No. oligomers measured
Polystyrene ( $M_w$ 1022)	3.69	3.7	13
Polyisoprene ( $M_w$ 650)	4.21	4.49	10
Polybutadiene ( $M_w$ 1000)	5.51	5.36	13
Polyethylene ( $M_w$ 1214)	7.81	7.39	10

<sup>a</sup> Weight-average molecular weight ( $M_w$ ) values are those determined by gel permeation chromatography, as provided by the supplier.

is reasonable, with average errors ranging between 4% and 8%.

### Molecular Weight Distributions

Of course, average molecular weight information is of particular interest for polymer analysis. To characterize the present procedure of LD/FTMS with silver nitrate chemical ionization, molecular weight standard samples were measured, and the results were compared with gel permeation chromatography (GPC) analyses provided by the manufacturer. Results of molecular weight characterizations for the hydrocarbon polymers used in this study are summarized in Table 4. For the range of polymers studied here, the mass spectral results generally give weight and number averages that are somewhat higher than those obtained by GPC; however, the polydispersity values

**Table 4.** Molecular weight averages<sup>a</sup> of hydrocarbon polymers

Polymer	$M_w$	$M_n$	$M_w/M_n$	Method <sup>b</sup>
Polystyrene	1139	1105	1.03	Ag <sup>+</sup> LDCI
	1022	938	1.09	GPC
	4095	3912	1.05	Ag <sup>+</sup> LDCI
	4140	3970	1.04	GPC
Polyisoprene	645	617	1.04	Ag <sup>+</sup> LDCI
	650	560	1.16	GPC
	2591	2484	1.04	Ag <sup>+</sup> LDCI
	2953	2935	1.05	GPC
Polybutadiene	1195	1153	1.04	Ag <sup>+</sup> LDCI
	1000	833	1.20	GPC
	2967	2916	1.02	Ag <sup>+</sup> LDCI
	2966	2879	1.03	GPC
Polyethylene	1193	1159	1.03	Ag <sup>+</sup> LDCI
	1214	1011	1.20	GPC
	2221	2162	1.02	Ag <sup>+</sup> LDCI
	2306	2015	1.14	GPC

<sup>a</sup>  $M_w$ , weight average;  $M_n$ , number average;  $M_w/M_n$ , polydispersity.

<sup>b</sup> GPC, gel permeation chromatography values provided by supplier; LDCI, laser desorption chemical ionization.

from mass spectra are the same or significantly lower than those derived from GPC.

## Conclusions

Analysis of hydrocarbon polymers poses a significant analytical challenge to mass spectrometry. LD/FTMS using silver cationization is an effective approach to this analytical problem. As demonstrated here, it is possible to obtain rapid, accurate measurements of average molecular weights and polydispersities for a range of representative types of hydrocarbon polymers, including saturated, olefinic, and aromatic samples. Silver-attached molecular ion distributions of oligomers for hydrocarbon polymers with upper masses from 1000 to 6000 D are readily obtained by addition of silver nitrate to the sample solution before carrying out LD/FTMS analysis. SWIFT ion excitation is the method of choice for obtaining Fourier transform mass spectrometry spectra of these polymers, presumably due to the more uniform excitation that this technique affords.

## Acknowledgments

We acknowledge Alan Brookes of Polymer Laboratories, Inc. for providing information regarding the hydrocarbon polymer samples for this study. We gratefully acknowledge support from the National Science Foundation under grant CHE-92-01277.

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