Hydrocarbon Polymer Analysis by External MALDI Fourier Transform and Reflectron Time of Flight Mass Spectrometry

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The traditional solvent-based matrix-assisted laser desorption ionization (MALDI) preparation method has been used to analyze nonpolar polymers of various molecular weights. High resolution silver cationized oligomers with masses of up to 12 KDa were measured using 9.4 tesla Fourier transform mass spectrometry (FTMS) with an external ionization source. It was observed that when time-of-flight mass spectrometry was used, the spectra of polyethylene polymers showed abundant low mass fragment ions. However, these fragments were absent from the FTMS spectra. (J Am Soc Mass Spectrom 2005, 16, 2009–2016) © 2005 American Society for Mass Spectrometry

Analysis of polymer molecular weight distributions is a valuable tool for understanding the relationships of those distributions to polymer properties. Increasingly during recent years, laser desorption ionization mass spectrometry is being applied to polymer analysis [1–4]. Within this context, analysis of hydrocarbon polymers is one of the most challenging problems. This is a result of their lack of functional groups and their corresponding chemical inertness, which pose problems both for sample preparation and for mass spectral analysis. Among the hydrocarbon polymers, saturated polymers such as polyethylenes and polypropylenes are the most difficult to analyze. For this reason, several years ago as laser desorption ionization mass spectral analysis of hydrocarbons was explored, polyethylene and polyisoprene analyses served as tests of the methodology [5, 6]. Similarly, Chen and coworkers and Yalcin et al. have investigated direct laser desorption and matrix-assisted laser desorption ionization (MALDI) time-of-flight (TOF) mass spectral analysis of low molecular weight polyethylene samples [7, 8] and showed that use of coarse cobalt powder as sample matrix can extend the mass range for polyethylenes up to m/z 5000. In both cases, using TOF-MS, abundant low mass fragment ions were observed.

Two new methods have been introduced to analyze nonpolar hydrocarbon polymers. These techniques involve chemical modification of the hydrocarbon polymer before performing MALDI analysis. The first allows MALDI spectra of polyethylene polymer by chemically modifying the polymer with excess bromine [9]. Although this method results in covalent cationiza-

tion, it is not preferred because of the complications from the bromide ions and possible contamination of the instrument. The second involves sulfonation of olefin end groups to produce more favorable cationization [10]. These methods are time consuming, may involve several steps, and alter the molecular structure of the analyte.

A number of other sample preparation techniques have been introduced for polymer analysis to optimize the signal-to-noise ratio, especially for insoluble polymers [11–16]. Briefly, these methods involve mixing the analyte polymer, the matrix, and the cationizing agent together, in a suitable ratio, and grinding them with either a mortar and pestle or a ball mill. The mixture is then applied to the MALDI plate using double-sided sticky tape, for example [15]. The spectra thereby acquired are similar to those prepared with solvent-based techniques.

In the study reported here, polymer samples are neither brominated nor sulfonated before acquiring polymer spectra. Also, solvent-based methods are utilized to cocrystallize the matrix, using solutions that contain the analyte and silver ions that are used as the cationizing reagent. Furthermore, the issue of fragmentation observed by Chen et al. [7] and Yalcin et al. [8] is addressed and new results are reported. These further establish the relative merits of alternative mass spectral analytical procedures. Interesting basic questions are also raised. In particular, does the mass analyzer that is used (FTMS versus TOF) play any role in determining the appearance of the polyethylene spectrum? Does the laser wavelength affect the extent of fragmentation of polyethylene? In the present paper, a study of mass spectral analysis of narrow distribution polyethylene 2000, polybutadiene 8300, polyisoprene 8000, and polystyrene 10,000 is interpreted in terms of these questions. Furthermore, spectra obtained by reflectron time-of-

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flight mass spectral analysis are compared with those from a 9.4 tesla external ionization source Fourier transform mass spectrometer.

Experimental

Chemicals and Reagents

Polyethylene, PE, (mw ~ 2000) was purchased from Poly-science, Inc. (Warrington, PA). Polyisoprene (mw ~ 8000) and polybutadiene (mw ~ 8300) were purchased from Polymer Laboratories (Amherst, MA). Polystyrene (mw ~ 10,000) was purchased from Fluka (Milwaukee, WI). Silver nitrate and dithranol were purchased from Aldrich Chemical Co. (Milwaukee, WI). 2,5-dihydroxybenzoic acid (DHB) was obtained from Fluka (Milwaukee, WI). Chlorobenzene was purchased from Alfa Aesar (Ward Hill, MA). Tetrahydrofuran (THF) was obtained from J. T. Baker (Phillipsburg, NJ). Ethanol and methanol were obtained from EM Science (Gibbstown, NJ). All reagents were used without further purification.

MALDI-TOF Sample Preparation

Chen et al. [7] observed that dithranol was the best matrix to give an enhanced S/N for polyethylene spectra in the TOF-MS compared with other matrices. Therefore, Chen's sample preparation procedure was followed, as it is essential for reproducible results. Dithranol (the matrix) was dissolved to a concentration of 0.1 M in tetrahydrofuran (THF). Silver nitrate was dissolved in ethanol to make a saturated solution. Polyethylene was dissolved in chlorobenzene to a concentration of 5.0 mg/ml. Thus, 50 mg of PE 2000 was dissolved in a vial containing 20 ml of chlorobenzene in a boiling water bath. This vial was heated until the PE in the solvent became clear (an indication that the PE is in solution). One μL of the matrix was deposited first on the target plate, followed by 0.2 μL of silver nitrate solution. A final layer of 1.0 μL of PE solution was transferred to the target plate on top of the matrix and silver. The sample was allowed to air dry before it was inserted into the TOF mass spectrometer. For the other hydrocarbon polymers, samples were dissolved in THF at a concentration of 5.0 mg/mL. A mixture of 1.0 μL of matrix, 0.5 μL of cation solution, and 1.0 μL of polymer solution was made and 1.0 μL of the resulting mixture was deposited on the MALDI plate and air-dried before it was inserted into the instrument.

MALDI FTMS Sample Preparation

For FTMS measurements, it was found that dithranol matrix gives extensive silver cluster spectra upon desorbing the polyethylene polymer sample. Therefore, an alternative matrix was sought. Use of a DHB matrix results in excellent FTMS spectra of polyethylene polymer. It was also found that, for FTMS polyethylene sample spotting, unless the reverse order of that for

TOF was used, no signal was observed. The matrix (2, 5-dihydroxybenzoic acid) was dissolved in THF to make a 0.5 M solution. A saturated solution of silver nitrate was made by dissolving it in ethanol. The PE was dissolved in chlorobenzene to a concentration of 5.0 mg/ml (the same as for TOF). The other polymer samples were dissolved in THF to a concentration of 5 mg/ml. Deposition of sample on the probe tip was done as follows: 1.0 μL of polyethylene polymer sample was added and allowed to air dry, followed by addition of 0.2 μL of silver nitrate solution, and a final layer of 2.0 μL of DHB matrix solution. The sample was allowed to air dry. The rest of the polymers were deposited on the MALDI plate following the same mixing protocol used for TOF sample preparation.

Instrumentation

MALDI measurements were performed using both a 9.4 tesla Fourier transform (FT) mass spectrometer and a reflectron time-of-flight (TOF) mass spectrometer. The FTMS instrument is an IonSpec Ultima (Lake Forest, CA) with an external ionization source, utilizing a 9.4 tesla superconducting magnet. A Bruker Reflex III reflectron TOF (Billerica, MA) was used for the MALDI-TOF measurements. Separate 337 nm pulsed N_2 lasers (National Electronics, Inc.) were employed with each mass spectrometer. The TOF mass spectrometer is also equipped with a 355 nm pulsed laser Nd-YAG laser. For the Ultima FTMS, ions are created externally by MALDI and guided into the ICR cell using RF quadrupole ion optics. FTMS spectra were acquired in positive ion mode at a pressure of $\sim 5 \times 10^{-10}$ torr. Each spectrum resulted from pulsing the laser 49 times at the same spot on the sample. Ions were gated into the trapping cell after every seventh laser pulse using the procedure documented previously [17]. Spectra measured with the Bruker Reflex III TOF were obtained by operating the instrument in reflectron mode. Each TOF spectrum resulted from 300 laser pulses.

Results and Discussion

As mentioned above, when dithranol was used as matrix with MALDI-FTMS, spectra dominated by silver ion clusters were observed. This occurred even in a series of experiments in which lower concentrations of silver were used. A possible explanation is that the metal ion affinities of dithranol are especially low, leading to inefficient cationization of analyte [18]. Because of the longer reaction time available in FTMS versus TOF, silver cluster formation reactions can compete favorably.

Accordingly, the alternate matrix, 2,5-dihydroxybenzoic acid was chosen for the FTMS measurements. Interestingly, with this new matrix, PE spectra could only be obtained if matrix was added last in the layered sample preparation procedure rather than first as was done for TOF measurements. Although care was taken to use

Figure 1. A 9.4 tesla MALDI-FTMS of polystyrene with an average molecular weight of 10,000 Da. The left inset shows a partial spectrum of the repeat unit of the styrene monomer and the right inset is the partial spectrum of an isotopically resolved oligomer.

similar laser fluence that had previously been found to be important for similar results [19], apparently there was sufficient absorbance from the upper layers when DHB was added first so that the required threshold fluence was not achieved.

Alternative recent MALDI sample preparations aimed at improving resolution and signal-to-noise ratio in MALDI-TOF for nonpolar hydrocarbon polymers have suggested the use of solvent-free over solvent-based MALDI methods. These methods are particularly advantageous for characterizing insoluble polymers [11, 13–16, 20]. Although this approach may be useful in MALDI-TOF to improve the S/N, the resulting spectra do not appear to have an overwhelmingly different resolution from those obtained with solvent-based sample preparation, and in some cases the solventless method produced a more complex mass spectrum [15, 20]. For example, *isotopically* resolved spectra of hydrocarbon polymers with m/z greater than 6000 Da have not been reported by MALDI-TOF regardless of the method used, whether it is with solvent or solventless. Bear in mind that polystyrene polymer with mass of 96 KDa [15] has been analyzed by the solvent-MALDI method, producing a mass spectral hump similar to what is observed by gel permeation chromatography (GPC). Furthermore, polystyrene with molecular weight of 1.5 MDa [21] was analyzed by solvent-based MALDI, producing a similar result. In contrast, when solvent-based MALDI is coupled with the FTMS instrument, high-resolution spectra are easily acquired with m/z of 10,000 Da (isotopically resolved oligomers are observed even up to 12,000 Da). The M_n , M_w , and

polydispersity for all polymer samples were calculated using the following formulas:

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

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

$$PD = M_w / M_n \quad (3)$$

where R is the measured relative abundance of peak i with mass M .

Because silver has been reported to be effective as a cationization reagent [5], it was used to cationize all hydrocarbon polymer samples, and produced the spectra presented in this paper. Figure 1 is a MALDI-FTMS spectrum of polystyrene polymer standard having an average molecular weight of 10,000 Da. The spectrum shows a series of peaks resulting from silver cation attachment. The spacing between two adjacent oligomers is 104 Da, corresponding to the mass of the repeat unit, C_8H_8 . An inset in Figure 1 shows the isotopically resolved m/z 104 oligomer with silver cation attachment. The average resolving power is $\sim 48,103$ and the average mass accuracy is better than 20 ppm. No fragments were observed in the spectrum in the region below m/z 9000. Using eqs 1, 2, and 3, the M_n , M_w , and PD were calculated to be 10,937, 10,965, and 1.003, respectively. Figure 2 is a MALDI-FTMS spectrum of polyisoprene (most probable mass (M_p) = 8000). The spacing between two adjacent oligomers is 68 Da, corresponding to the mass of the isoprene repeat unit C_5H_8 . The inset displays an isotopically resolved

Figure 2. A 9.4 tesla MALDI-FTMS of polyisoprene having an average molecular weight of 8300 Da. The left inset shows a partial spectrum of the repeat unit of polymer and the right inset is the partial spectrum of an isotopically resolved oligomer.

108 repeat unit oligomer with silver ion attachment. The peaks appearing with m/z 4850, 5250, and 5550 are noise peaks. The average resolving power is $\sim 86,190$. M_n , M_w , and PD were calculated to be 6675, 6696, and 1.003 (manufacturer's value is 1.03), respectively. Average mass accuracy is better than 30 ppm. Figure 3 is a

MALDI-FTMS spectrum of a polybutadiene sample ($M_p = 8300$) with partial spectra showing the 54 Da repeat units and the isotopically resolved 137 unit oligomer. The peaks appearing at 4000, 4800, and 5550 are noise peaks. The M_n , M_w , and PD were calculated to be 7229, 7247, and 1.002 (manufacturer's value 1.03),

Figure 3. A 9.4 tesla MALDI-FTMS of polybutadiene having an average molecular weight of 8000 Da. The left inset shows a partial spectrum of the repeat unit of polymer and the right inset is the partial spectrum of an isotopically resolved oligomer.

respectively. Average mass accuracy is better than 10 ppm. Notice the difference in weights acquired by the FTMS result and those reported by the vendor. It is common to observe differences between gel permeation chromatography and mass spectrometric measurements. It is of interest also to point out that the polymers in Figures 2 and 3 display two maxima regions in the distributions. These are referred to as bimodal distributions as opposed to the usually observed unimodal distributions as in Figure 1, for example [22–25]. Of the current polymer samples, polystyrene spectra were the easiest to obtain followed in difficulty by polyisoprene, then polybutadiene. For lower molecular weight polymers, polyethylene was the most challenging to acquire by the solvent-based MALDI preparation due to its low solubility in organic solvents. This low solubility may account for the presence of few results in the literature. Chen et al. [7] reported the analysis of low molar mass polyethylene polymer samples using TOFMS. They concluded that mass spectra of low molecular mass polyethylene with narrow polydispersity can be obtained with conventional MALDI-TOF mass spectrometers equipped with nitrogen lasers [7]. This result is consistent with previously reported work in which direct CO₂ laser desorption was adequate for FTMS analysis of a series of nonpolar hydrocarbon polymer samples [5]. According to Kahr and Wilkins [5], few or no fragment ions were observed in any of the FTMS spectra. Because the present spectra were obtained under similar FTMS conditions (other than the choice of laser), it seems unlikely that the much greater degree of fragmentation seen in the Chen study is attributable to the laser wavelength chosen for the desorption-ionization experiment. Such a conclusion is consistent with other recent results investigating the effect of laser fluence on laser desorption time-of-flight mass spectra [19]. More likely, it is the difference in mass analyzers (FTMS versus TOF) which accounts for the spectral differences between the

Figure 4. A MALDI-TOF spectrum of polyethylene (mw ~ 2000) obtained using a Nd-YAG laser (a) and a nitrogen laser (b). The darker peaks below mass 1200 result from fragmentation.

Figure 5. A MALDI-TOF spectrum of polyethylene (mw ~ 2000) obtained with a nitrogen laser. Here, a suppression function to eliminate fragment masses below 1000 was applied. Still the darker low intensity peaks represent fragment ions separated by 14 mass units (CH₂).

results of Kahr and Wilkins [5] and those of Chen and coworkers [7]. Specifically, the time frame for the TOF measurements, ca. 100 μ s/spectrum as opposed to 100s–1000s of ms for the FTMS measurements. This time frame duration could easily account for the differences in the spectral results. It is proposed that the fragment ions seen in the TOF measurements could well be short-lived ions that do not survive for the requisite length of time to be observed by FTMS. Observation of low mass fragment ions is not uncommon in TOF-MS [26, 27], as “prompt fragmentation” can occur in the ion-source region. Furthermore, in delayed extraction ion sources (employing time-lag energy focusing), fast metastable fragmentation might occur during the delay time before extraction (on the 100 to 1200 ns time scale). This has been referred to as in-source decay (ISD). The increase in ISD fragments has been attributed to the high number of collisions in the expanding plume that increases the amount of collisional activation in the source. In addition, post-source decay (PSD), which occurs on the 10 microsecond time scale, can be attributed to metastable fragmentation that takes place in the field-free region, with fragment ions being detected in the mass spectrum when operating in reflectron mode. Figure 4a is a linear MALDI-TOF spectrum of polyethylene polymer (mw ~ 2000) obtained with N₂ laser, and Figure 4b is the spectrum resulting when a Nd-YAG laser with similar fluence is used. Figure 5 is a reflectron MALDI-TOF spectrum showing the main polymer distribution as the high abundance peaks. These peaks, having spacing of 28 Da (–CH₂–CH₂–) reflect the polyethylene repeat unit. The low intensity peak distribution overlapping the high intensity peak distribution has spacing of 14 Da (CH₂). These peaks result from the fragmentation of polyethylene that was also observed by Yalcin et al. [8] and Chen and coworkers [7]. During acquisition of the polyethylene polymer spectrum with MALDI-TOF, it was observed that by applying a deflection function (below mass 1000) the presence of low mass ions could

Figure 6. A 9.4 tesla MALDI FTMS spectrum of polyethylene polymer ($m_w \sim 2000$). A nitrogen laser was used for the desorption ionization step, silver ions were used as cationizing agent, and DHB was the matrix.

be reduced, therefore minimizing the number of fragments that would otherwise cause interference. **Figure 6** is a full scale MALDI-FTMS spectrum showing the polymer distribution extending from m/z 1625 to m/z 2887. An expanded region of the spectrum revealing the presence of 28 Da repeat units is shown in **Figure 7**. The high-resolution, well in excess of isotopic resolution, is apparent in the expanded scale of this spectrum. For the MALDI-FTMS spectrum, $M_w = 2009$, $M_n = 1993$, and $PD = 1.008$. Mass accuracy was better than 10 ppm. It is of interest to note the same evidence of fragmentation in the MALDI-TOF spectra as noted in references [7] and [8]. As observed above, the MALDI-TOF spectrum of polyethylene (**Figure 5**) has the following parameters: $M_w = 2122$, $M_n = 2070$, and $PD = 1.025$. In contrast to the MALDI-TOF spectrum, this fragmentation is not observed in the MALDI-FTMS spectrum in **Figure 6**. In the low mass region of **Figure 6**, silver ion clusters are also observed and are seen in more detail in the expanded partial spectrum in **Figure 8**. If polymer

Figure 8. Because silver was used as the cationizing agent for the polyethylene polymer, a cluster of the silver cations is shown here. If polyethylene fragments were detected, they would have been observed in this region along with the silver cluster ions.

fragments were to be detected in this region, a spectral signal attributable to the polymer would be seen surrounding the silver cluster. This spectrum provides additional strong evidence of the absence of fragment ions of polyethylene in the FTMS spectrum. Moreover, all oligomers within this polymer distribution are separated by 28 Da (see **Figure 7**), and no overlapping low intensity 14 Da differences between the peaks are seen (i.e., no fragments). The apparent difference between the MALDI-FTMS and MALDI-TOF spectrum further supports the premise that fragmentation behavior is a function of the mass analyzer chosen, not the laser wavelength used. As Kahr and Wilkins [5] showed, when a carbon dioxide laser ($\lambda = 10.6 \mu$) was used for LD of polyethylene and few or no fragments were observed in the FTMS spectrum. Furthermore as shown here, when a nitrogen laser ($\lambda = 337 \text{ nm}$) is used to desorb ions from DHB matrix, polyethylene ions observed are silver cationized polyethylene oligomers in the FTMS spectrum.

An alternative hypothesis is that the source of the 14 Da difference between the mass spectral peaks observed in the TOF experiments results from the presence of two overlapping polyethylene polymer distributions with one distribution having $-\text{H}$ as an end group and the other with $-\text{CH}_3$ as an end group. If such distributions were present, both distributions would have been observed by FTMS. For example, **Figure 9a** is a MALDI-TOF spectrum of polybutadiene ($m_w \sim 2800$) with two distributions. The high intensity peaks belong to the distribution where the end groups of the oligomers have hydrogen at each end, and the low intensity distribution has a hydrogen at one end at a methyl group at the other end. These same two distributions are observed in the MALDI-FTMS instrument as illustrated in **Figure 9b**. The preferred explanation for the 14 Da mass difference series, seen in TOF, is that they result from short-lived ions that are not observed in FTMS. For example, low mass fragment ions are commonly observed in TOF [10, 26–28] even

Figure 7. An expanded region of the polyethylene spectrum in **Figure 6** showing the repeat unit of polyethylene (28 Da) corresponding to the $(\text{CH}_2\text{-CH}_2)$ unit. An example of isotopically resolved peaks is shown with the corresponding peak assignment.

Figure 9. Spectra of polybutadiene (mw ~ 2800) with two distributions having different end groups at each end of the oligomers. These two distributions are observed in both MALDI-TOF spectrum (a) and MALDI-FTMS spectrum (b).

when a polar polymer such as poly(ethylene glycol) is analyzed [11].

Conclusions

The ultraviolet MALDI-FTMS spectra of nonpolar polymers produced superior results compared with those obtained by MALDI-TOF, notably with regard to mass accuracy and resolving power. Because of the mass analyzer time frame of the mass analyzers used, TOFMS showed extensive fragmentation when compared with FTMS polyethylene analysis. Because both TOF and FTMS spectral ions of polyethylene were desorbed with ultraviolet lasers (N_2 , 337 nm), and the FTMS results showed no low mass fragments of compared with TOF, it is appears that the laser choice and the degree of fragmentation are independent. Further evidence is found in the previous CO_2 direct laser desorption results [5]. Accordingly, it is concluded that MALDI-TOF of polyethylene results in significant fragmentation while MALDI-FTMS does not, and that this difference is caused by the much longer time frame of the latter measurements.

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