Metal Powder Substrate-Assisted Laser Desorption/Ionization Mass Spectrometry for Polyethylene Analysis

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Polyethylene is one of the most important industrial polymers and is also one of the most challenging polymers to be characterized by mass spectrometry. We have developed a substrate-assisted laser desorption/ionization (LDI) mass spectrometric method for polyethylene analysis. In this method, cobalt, copper, nickel, or iron metal powders are used as a sample substrate and silver nitrate is used as the cationization reagent. Using a conventional UV LDI time-of-flight mass spectrometer, intact oligomer ions having masses up to 5000 u can be detected. Cobalt is found to produce spectra with the highest signal-to-noise ratio and the lowest level of fragmentation. Cobalt powder size is shown to have some effect on the spectra produced. The best results are obtained with the use of cobalt powders with diameters ranging from 30 to 100 μm. Fragmentation cannot be totally eliminated, but the fragment ion peaks can be readily discerned from the intact polyethylene ions in the substrate-assisted LDI spectrum. Thus, the average molecular masses of low-mass polyethylene samples can be determined by using this method. A rapid heating model is used to account for the effectiveness of using the coarse metal powders to assist the analysis of intact polyethylene molecules by LDI.

For many decades, mass spectrometry in one form or another has been used to analyze synthetic polymers.[1] With the recent advent of matrix-assisted laser desorption/ionization (MALDI), intact oligomers with masses up to 1.5×10^6 u can now be brought into the gas phase,[2] making MALDI a powerful tool for polymer analysis.[3,4] However, polyethylene (PE), one of the most prevalent synthetic polymers, cannot be brought intact into the gas phase, even by MALDI. In a typical MALDI experiment, the polymer analyte, an organic matrix material, and a metal salt are dissolved in a common solvent in a prescribed ratio. This solution is placed on a stainless steel target plate, and the solvent is allowed to

evaporate. The product of this evaporation is laser ablated, putting intact macromolecules into the gas phase. Polyethylene is only soluble in hot solvents, and so as a result of the solution cooling upon rapid evaporation, it tends to precipitate out of solution well before the matrix or the metal salt does. This in turn makes it difficult to prepare a uniform matrix/analyte/metal salt mixture on a MALDI target, which is a crucial step in any MALDI experiment. Furthermore, polyethylene is highly crystalline and will tend to form spherulites that reject the matrix and metal salt. These effects, combined with the chemical inertness of polyethylene, make it all but impossible to perform MALDI in the conventional fashion.

There are limited reports on mass spectrometric analysis of low molecular mass PE in the literature. Intact polyethylene oligomers with masses up to 2000 u were put into the gas phase by Lattimer and co-workers using field desorption mass spectrometry (FDMS).[5−7] Subsequently, Evans and co-workers also observed intact polyethylene oligomers up to 2000 u in the gas phase by FDMS,[8,9] and more recently, Gross and Weidner demonstrated the detection of PE samples up to m/z 3600.[10] They showed that while the end groups can be characterized by FDMS, accurate molecular mass distribution data could not be obtained for PE samples of > 2000 u because strong discrimination against higher masses was observed.[10] PE spectra from secondary ion mass spectrometry consist mainly of fragment ions.[11] Cody and co-workers reported that direct laser desorption/ionization (LDI) of hard wax (unsaturated long-chain hydrocarbons) generated weak signals; but electron impact ionization of the desorbed neutrals produced good results, although fragment ions were also observed.[12] Kahr and Wilkins presented the first report on laser desorption/ionization of PE in an FTMS achieving masses up to 2300 u.[13] In that study, silver salts were sonicated with PE in

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methanol and the sample was desorbed and ionized with a 10.6-μm beam from a CO_2 laser. This work indicated that Ag^+ could cationize intact polyethylene oligomers. Weidner and co-workers reported the analysis of waxes and other low-mass PE samples by IR and UV laser desorption.[14-16] Recently, Li and co-workers presented data on long-chain n-alkanes using conventional MALDI time-of-flight (TOF) mass spectrometers equipped with a 337-nm nitrogen laser[17] including the observation that a variety of transition metal ions can form intact adduct ions.[18] Most recently, Li and co-workers have shown that transition metal ions can attach to polyethylene in the gas phase such that low molecular mass polyethylene can be analyzed using a typical MALDI organic acid matrix;[19] however, ion fragmentation occurred even with use of a matrix that had been shown to work on synthetic polymers at especially low laser power.[20] It has been our objective to extend the technique of LDI for analyzing higher molecular mass polyethylene by optimizing the sample preparation method.

In 1988, Tanaka and co-workers[21] reported that ultrafine cobalt powder (~20-nm diameter) when mixed with glycerol could be used as a LDI matrix to analyze peptides and polymers of 20 000 u and higher. It has also been reported that ultrafine cobalt metal powder mixed in other organic solvents can be used for the analysis of various compounds, such as oligosaccharides, pharmaceuticals, and surfactants.[22] Several groups have reported the use of other types of particles such as graphite, silicon, and titanium nitride as matrixes for LDI with varying degrees of success.[23-25] In the present work, we report a laser desorption/ionization method that uses metal powders substantially more coarse than that used by Tanaka et al. Unlike the Tanaka experiment, where the ultrafine cobalt powder was mixed with the analyte using a suitable solvent, we use a thin-film layering technique to control metal powder/polymer/metal salt phase separation. Thus, the metal powder used in our experiment acts mainly as the LDI substrate. Using the metal powder substrate-assisted LDI method with silver salt as the cationization agent, we are able to create intact polyethylene oligomer ions with masses up to 5000 u, higher than ever produced by any other techniques. In this work, the studies of the effects of laser power, metal powder particle size, and type of metal on the LDI results are reported. PE samples with different polydispersities are used to demonstrate the utility of this technique.

EXPERIMENTAL SECTION

Chemicals and Reagents. Two narrow-polydispersity (PE1100 and PE2100) and a wide-polydispersity polyethylene sample were obtained from the American Polymer Standards Corp.[26] The gel permeation chromatography (GPC) data provided by the supplier indicated that the polydispersity sample has an M_p of 4250 u, an M_n of 2300 u, and an M_w of 3300 u, yielding a polydispersity of 1.435. This material is termed PE/WIDE throughout this paper. Another polyethylene sample was a GPC fraction of a commercial polyethylene (Dupont Alathon[26]). This sample with an M_n of 4100 u and an M_w of 4700 u giving a polydispersity (PD) of 1.15 is termed PE4100 for this study. This material is known to have vinyl termination on approximately half the molecules in the sample.[27,28]

Cobalt metal powder with particles ranging from 30 to 100 μm was purchased from Metron Inc. (Allamuchy, NJ)[26] and was used as received. Cobalt metal powder with a particle size of less than 2 μm was purchased from Aldrich Chemical Co. Inc. (Milwaukee, WI)[26] and was used as received. Nickel metal powder with particles ranging from 50 to 150 μm, iron metal powder with particles ranging from 30 to 225 μm, and copper metal powder with particles ranging 50 to 225 μm were purchased from Fisher Scientific Co. (Fair Lawn, NJ)[26] and were used as received.

Sample Preparation. The polyethylene samples were dissolved in toluene at a concentration of 2-3 mM. In all cases, heating was required to completely dissolve the analyte. PE samples mixed with toluene in a 10-mL glass vial (Fisher) were placed into a water bath (~98 °C) for a few minutes until all samples were dissolved. The vial was then taken off the water bath and allowed to cool to room temperature. During the cooling process, addition of a small amount of toluene in a stepwise fashion (1 μL/step) might be necessary to prevent solidification of the PE samples. The addition of solvent should continue until the solution just becomes cloudy. A micropipet tip (Fisher, 2-μL Redi-Tip) was used to transfer the room-temperature sample solution to the mass spectrometric sample plate. There were no PE signals observed from the control experiment using this sample preparation procedure. For preparing the substrate solutions, metal powder was suspended in isopropyl alcohol at a concentration of ~100-150 mg/mL. Silver nitrate was dissolved in ethanol at room temperature to make a saturated solution.

Sample deposition was done in the following manner: 1 μL of the metal suspension solution was first transferred onto the stainless steel MALDI sample target to form the first layer. Next 0.2-0.3 μL of saturated silver nitrate solution was put down as the second layer, and finally, 1 μL of the analyte solution was deposited to form the third layer.

Instrumentation. The LDI experiments were performed on the Bruker Reflex III MALDI-TOF[26] mass spectrometer operating

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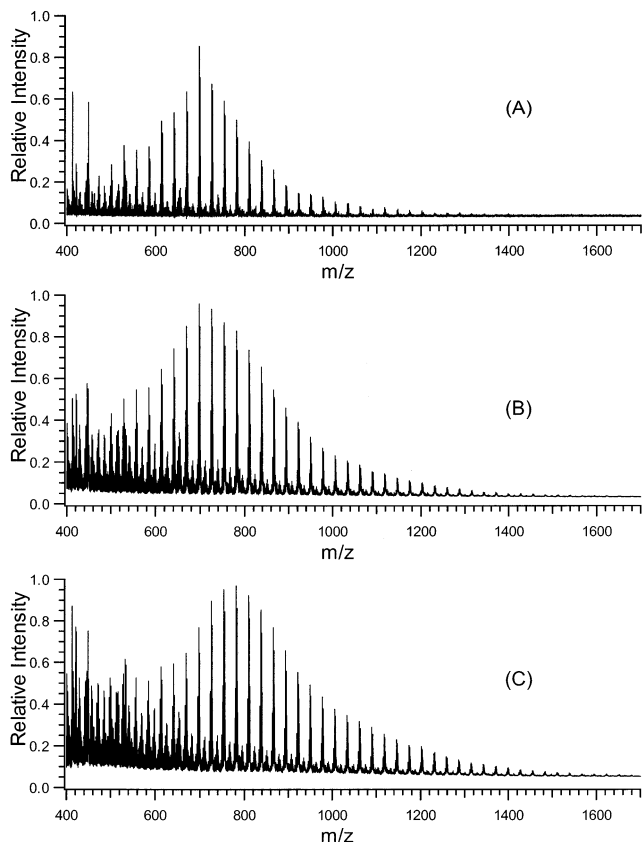
Figure 1. Mass spectrum of PE1100 obtained using coarse cobalt metal powder as the substrate with silver nitrate as the cationization reagent. The laser power reading from the Bruker Reflect III instrument is (A) 50, (B) 60, and (C) 65%.

Figure 2. Mass spectrum of PE2100 obtained using coarse cobalt metal powder as the substrate with silver nitrate as the cationization reagent. The deflection setting is adjusted to deflect low-mass ions with m/z's of (A) less than 500, (B) less than 800, and (C) less than 1000.

in a reflectron mode. This instrument employed a 337-nm pulsed nitrogen laser to generate ions. The laser power was adjusted slightly above the threshold for the desorption/ionization process. All spectra were the result of signal averaging of between 200 and 400 discrete laser shots. A peptide mixture was used for calibration. All data were processed using the Igor Pro Software package (WaveMetrics, Lake Oswego, OR)[26] for presentation. Savitzky−Golay smoothing was applied to the spectra to assist in spectral comparison, particularly for weak signals; but no baseline correction was used for the spectra shown.

RESULTS AND DISCUSSION

Figure 1 shows the LDI mass spectra of PE1100 obtained by using different laser powers for desorption/ionization. The coarse cobalt metal powder was used as the substrate, and silver nitrate was used as the cationization reagent. In all three settings of laser power, very good signal-to-background ratios are observed. The main oligomer distribution corresponds to the expected polyethylene with adjacent peaks separated by 28 u (i.e., the mass of the repeat unit of CH_2CH_2). However, as the laser power increases, fragment ions are produced as shown in the increase of low-mass peaks at m/z <600 from Figure 1A to C. These low-mass fragment ions are separated by 14 u and have a mass distribution that does not significantly overlap with the main distribution. Thus, the average molecular mass of the PE sample can be calculated from the main distribution without the complication caused by the presence of the fragment ions. The average mass results from
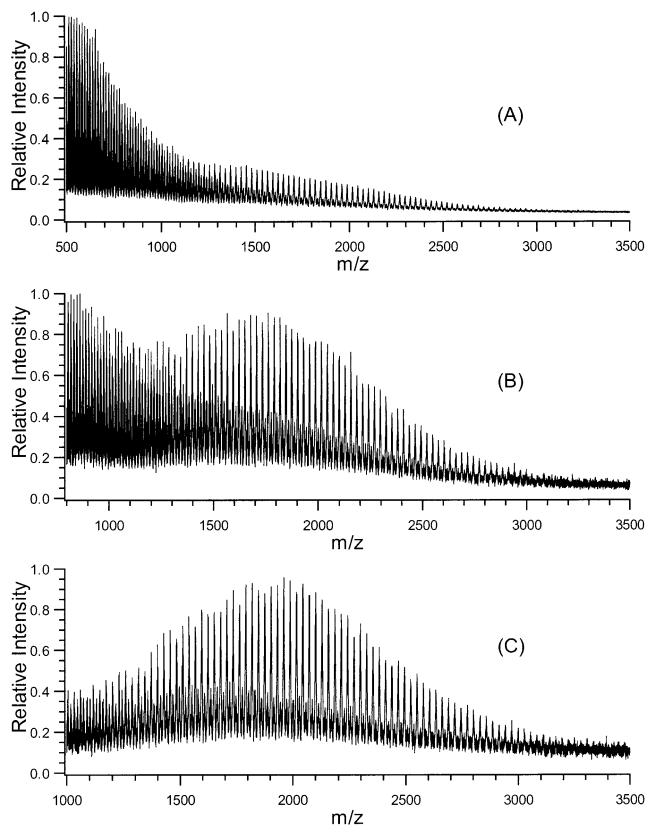
Figure 1A−C are found to be M_n 740, M_w 779, PD 1.053; M_n 813, M_w 876, PD 1.077; and M_n 875, M_w 943, PD 1.078, respectively. It is clear that laser power has some effect on the average molecular mass results. Increasing laser power also extends the high-mass tail of the main distribution from $m/z \sim 1200$ (Figure 1A) to ~ 1600 (Figure 1C). A high laser power shifts the M_p value of the main distribution. In our subsequent experiments, the laser power was adjusted to minimize fragmentation while still observing strong polymer signals (i.e., slightly above the threshold laser power for LDI). The use of near-threshold laser power for LDI also has the benefit that reproducible spectra can be more easily obtained from one sample preparation to another. For a given sample preparation and LDI measurement protocol, the relative standard deviations are generally within ±5% for M_n and M_w from repeat measurements.

As the mass of PE increases, fragment ions can be formed in the metal powder substrate-assisted LDI even at the threshold laser power. It was found that a proper setting for the ion deflector in the reflectron TOF instrument was critical in producing an optimal spectrum. Figure 2 shows the LDI spectra of PE2100 obtained using three different settings of low-mass ion deflection. When the ion gate above the extraction/acceleration ion lenses were set to deflect the ions with m/z <500, very intense low-mass fragment ions were detected and the main distribution from the intact PE ions was relatively less intense, as can be seen in Figure 2A. By setting the ion gate voltage to prevent most ions with m/z <800 from reaching the detector, the intensity of the main
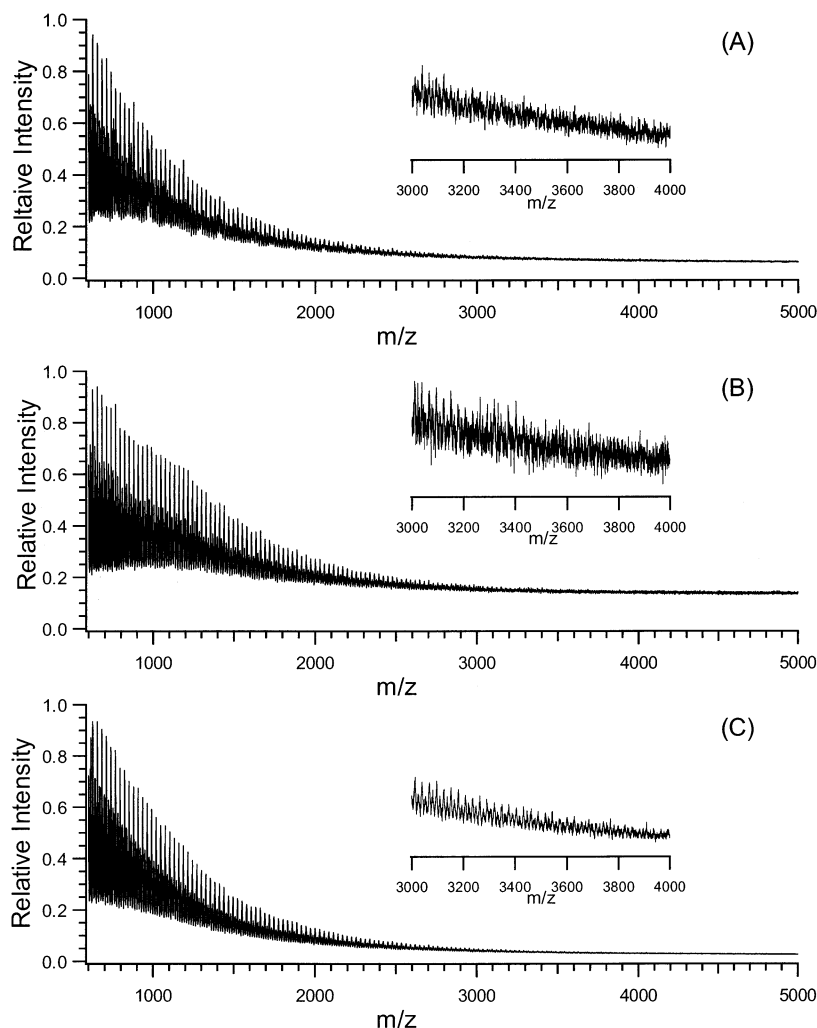
Figure 3. Mass spectrum of PE/wide obtained using coarse cobalt metal powder as the substrate with silver nitrate as the cationization reagent. The laser power reading from the Bruker Reflect III instrument is (A) 55, (B) 65, and (C) 70%.

distribution increases slightly with respect to the fragment ions (see Figure 2B), which will affect the M_n and M_w results. However, as Figure 2C shows, using a setting to deflect ions with m/z <1000, a much cleaner spectrum was obtained. This finding is somewhat surprising and should be related to the detector saturation effect. In our past experiences in working with a variety of polymers using MALDI or LDI in TOF instruments equipped with multichannel plate detectors, including the very same instrument used in this work, we never experienced such a dramatic detector saturation effect. One plausible reason of strong detector saturation effect caused by the presence of fragment ions is due to the high densities of ions packed within a small time window. In the PE experiment, the mass difference between the fragment ions is only 14 u apart, and accounting for the isotope ions, there is a strong peak in almost every mass unit in the low-mass region, which can make the detector recovery less efficient, resulting in poor detector response at the high masses. Neverthe-less, by adjusting the deflection setting to prevent most ions with m/z below the low-mass tail of the main distribution from reaching the detector, the PE intact ions can be detected with reasonably good efficiency, as judged from the well-rounded shape of the main distribution shown in Figure 2C. From Figure 2C, we determine the average molecular masses to be M_n 1982, M_w 2051, and PD

1.035, which is in good agreement with the GPC data (M_n 1890, M_w 2155, PD 1.14). We caution that this level of agreement is perhaps fortuitous. GPC is prone to error in analyzing polymers where a set of accurate polymer standards of the same type is not available. The accuracy of the average masses determined by the LDI MS method remains to be validated.

It should be noted that, besides the laser power and low-mass ion deflection setting, another important experimental parameter related to spectral acquisition is the laser focus. In our experiment, the laser focus setting was optimized (i.e., giving strongest PE signals with minimum fragmentation) to be $49 \pm 10\%$ (the changeable value is from 0 to 100% in the Reflex III TOF instrument, where 100% means the highest laser power). This laser focus setting was kept the same for all samples examined, while laser power and ion deflection settings were adjusted for each sample.

One important example of using metal powder substrate-assisted LDI for polyethylene analysis is shown in Figure 3 for the PE/WIDE sample. A mass spectrum of this material could not be obtained by MALDI with any organic matrix typically used for synthetic polymers; furthermore, direct laser desorption/ionization reported previously for this material[19] yielded very poor results. In Figure 3, the adjacent peaks in the main series are
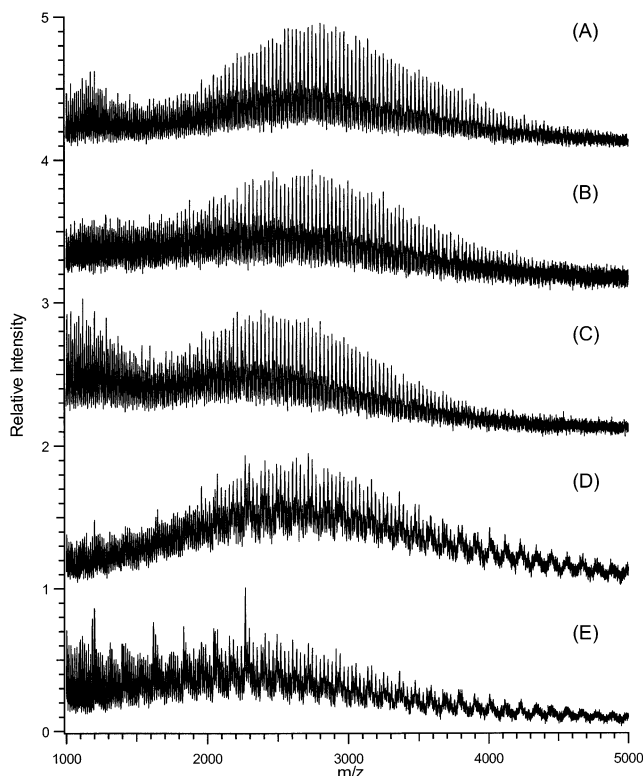
Figure 4. Mass spectra of PE4100 obtained using different metal powders. The metal powder and optimum laser power used are (A) coarse cobalt, 55%, (B) fine cobalt, 75%, (C) copper, 70%, (D) nickel, 70%, and (E) iron, 65%.

Figure 5. Expanded mass spectrum of PE4100 shown in Figure 4A obtained using coarse cobalt metal powder as the substrate with silver nitrate as the cationization reagent. Labels "P" and "F" refer to the intact parent ion peak and the fragment ion peak, respectively.

separated by 28 u, as expected for the polyethylene CH_2CH_2 repeat unit with the appearance of peaks separated at 14 u at the low-mass end indicative of fragmentation. Note that the molecular mass distribution is low compared to the GPC results provided by the supplier. The mass spectrometric method might underestimate the molecular mass by failing to detect the higher mass oligomers in this modestly wide polydispersity material. This effect has been documented in the literature for other polydispersity polymers.[3,29] Figure 3 also shows that, for this polydispersity PE sample, the use of a higher laser power than the threshold power for LDI can extend the high-mass tail from m/z 3000 to ~4000. Further increase in laser power than the one shown in Figure 3C did not result in the detection of any higher mass oligomers.

Figure 4A shows the cobalt powder substrate-assisted LDI spectrum of PE4100 (polydispersity 1.15 by GPC). Despite its narrow polydispersity, previous attempts to use MALDI and direct LDI for analyzing this sample generated very poor mass spectra. With the new method, spectra such as the one shown in Figure 4A can be readily obtained. Figure 5 shows the expanded spectrum of this sample. In this case, each oligomer ion is separated by 28 u in the mass range of between 2000 and 5000 u as expected. In the mass range from 1000 to 2000 u, adjacent peaks are separated by 14 u, suggesting that many of these ions result from fragmentation of the PE oligomer ions. While the fragment ion peaks at the low-mass region overlap with the low-mass tail of the principal distribution, they can be distinguished from the intact PE ions on the basis of the isotope peak fit of the silver ion
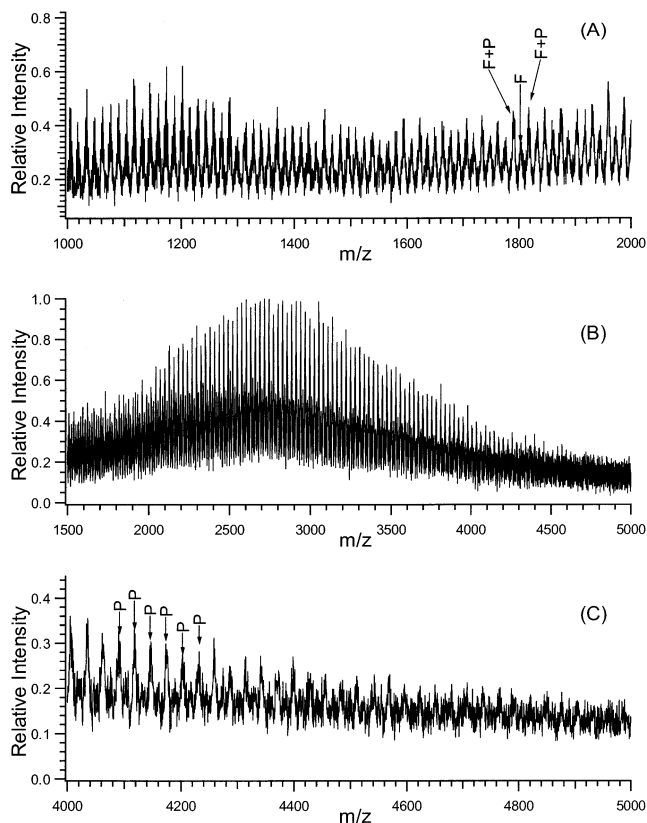
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adduct.[19] With the correction of the fragment ion contribution to the low-mass tail of the Gaussian-like principal distribution, we can calculate the average molecular masses of this sample to be M_n 3114, M_w 3268, and PD 1.049. Compared to the GPC results of M_n 4100, M_w 4700, and PD 1.15, there are some discrepancies in the data. This is not surprising. Even for well-characterized polymer standards such as polystyrenes and polybutadienes, differences between GPC and MALDI data can be observed.

Finally, the effects of metal powder size and type of metal powder on the efficacy of polyethylene analysis by substrate-assisted LDI MS were examined. Figure 4 shows the representative results from PE4100. Similar results were observed for other PE samples. Figure 4B shows the mass spectrum obtained by using the fine cobalt powder as the LDI substrate. The optimal conditions for laser focus and low-mass ion deflection setting were found to be similar to those used in the coarse cobalt powder experiment (i.e., Figure 4A). However, for the experiments using the fine cobalt powder as the LDI substrate, the laser power threshold is generally higher (e.g., laser power setting 55% for Figure 4A vs 75% for Figure 4B), which results in a greater extent of fragmentation, as illustrated in Figure 4B.

Figure 4C−E displays the mass spectra of PE4100 obtained by using different metal powders. The sizes of copper, nickel, and iron powders are similar to the coarse cobalt powder. The copper spectrum (Figure 4C) is similar to the cobalt spectrum except the center of the main distribution is shifted to a lower mass, due to more extensive fragmentation. The laser power required for
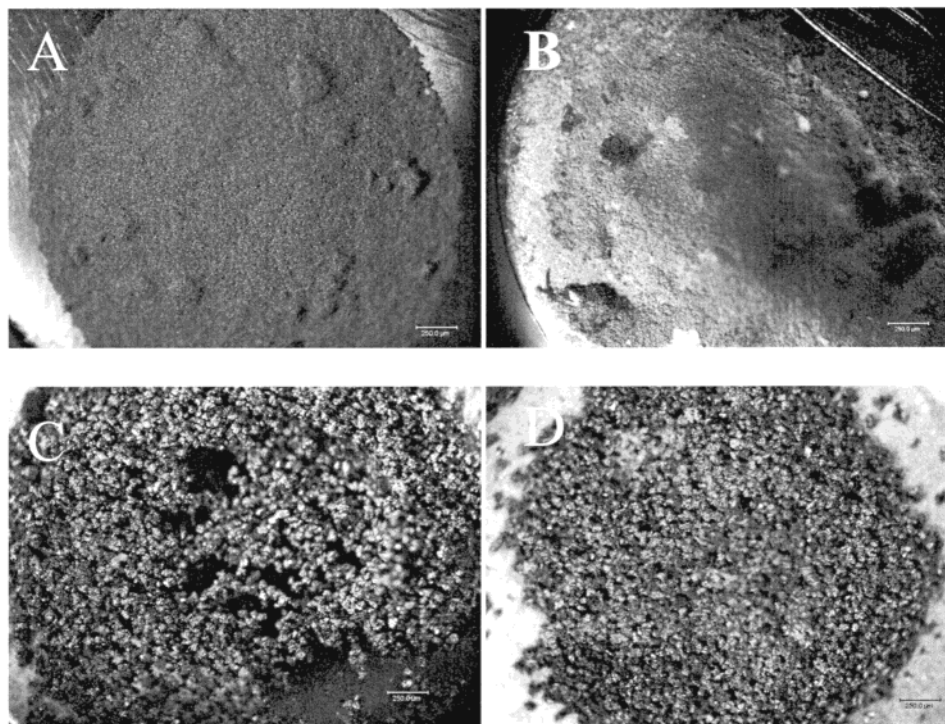
Figure 6. Microscopic images of (A) fine cobalt powders layered onto a stainless steel MALDI target, (B) fine cobalt powders layered onto a stainless steel MALDI target, followed by the additional of a silver nitrate layer and a PE4100 sample layer, (C) coarse cobalt powders layered onto a MALDI target, and (D) coarse cobalt powders layered onto a MALDI target, followed by the additional of a silver nitrate layer and a PE4100 sample layer. The white participates seen in (B) and (D) are from the PE sample. The scale bar represents 250 μm.

the copper powder substrate-assisted LDI is higher than for the cobalt experiment. Nickel produced spectra with lower signal-to-noise ratios than either cobalt or copper. A lower laser power could be used for iron than for any of the other metals; however, the resulting spectra did not show high-mass oligomers and the PE signals were weak. In both nickel and iron spectra (Figure 4D,E), metal ion clusters were detected, which not only reduces the signal-to-noise ratio, but also interferes with the M_n and M_w calculations. In general, cobalt was found to produce the best spectrum likely because signal could be obtained at the lowest laser power without metal cluster ion interference.

The above examples illustrate that using the coarse cobalt powder as the substrate can be quite effective in generating intact gas-phase ions from polyethylene by using LDI. In all cases, silver ion attachment to the oligomer is observed. This is consistent with our earlier observation that silver ion can be more readily attached to the long-chain alkane and the silver−alkane adduct ions are less likely to fragment compared to other transition metal ions during LDI.[18] Since PE does not form adduct ions in the solution or solid phase with the silver ion, PE−silver adduct ion formation most likely occurs during the desorption process. Thus, the major role of the cobalt metal powder is to provide assistance in desorption of PE into the gas phase. The likely mechanism of operation for the substrate-assisted desorption is related to rapid heating.[30,31] We note that, in the Tanaka experiment, the ultrafine cobalt metal powder has a diameter of ∼20 nm, which is smaller than the laser beam wavelength used for LDI. The success of the

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ultrafine powder in assisting the LDI of large and small analyte molecules was believed to be related to the scattering of the laser light between the particles, resulting in high absorption with low reflection.[21,22] The energy dispersion within the particles is low, which promotes the rapid heating critical for generating intact gas-phase molecules.[22]

In our experiment, the coarse powder is in the tens and hundreds of micrometers, which is substantially greater than the laser wavelength, but of a size comparable to that of the focused laser beam. Figure 6A shows the image of the fine metal powders layered on a MALD sample target. No PE sample was added. Figure 6B shows the image of another target prepared by casting the fine cobalt powder as the first layer, followed by depositing a layer of silver nitrate and then the PE sample. Panels C and D of Figure 6 show the images of the coarse powders without and with the sample addition. When a laser light of less than 100-μm diameter in size is directed to the sample target shown in Figure 6D, only a few individual powders will be illuminated. The laser energy will be absorbed by the cobalt particles at the photon/surface interaction sites, and some light will be scattered in the void spaces between the adjacent particles being illuminated. Since the particles are loosely attached to the stainless steel plate, the laser energy quickly absorbed by the particles will not effectively dissipate to the bulk plate. As a result, the particles illuminated by the laser beam are rapidly heated, which in turn vaporizes the polyethylene sample. At the laser power used, silver ions are readily produced during desorption and these ions will interact with the gas-phase polyethylene molecules to form the adduct ions. The fragment ions observed in the LDI spectrum can be from the dissociation of the internally energetic adduct ions or

from the silver ion attachment to the already dissociated polyethylene molecules.

Using the rapid-heating model, we can also explain the results from the fine powder experiments. In this case, a higher laser power is generally required for generating PE signals. As Figure 6B shows, the fine cobalt particles are densely packed and white participates from PE are clearly visible. When the laser is directed to the sample, many particles are illuminated. However, the laser energy absorbed by the particles can be rapidly dissipated to the bulk and adjacent unilluminated particles due to their greater surface contacts with these "cold" neighbors. A nonuniform temperature profile is expected across these fine particles, which can result in overheating in one place (hence fragmentation) and underheating in other place (hence no vaporization). Overall, a higher laser power is needed to vaporize a sufficient number of PE molecules for detection. Regarding the effect of type of metal powder on the LDI spectrum, we do not know the effectiveness of energy absorption of these metals from the laser beam. Thus, we cannot speculate the reason(s) underlying the spectral differences observed in Figure 4.

In summary, we have shown that, using the coarse cobalt powder as the substrate and silver nitrate as a cationization reagent, intact PE oligomer ions of up to 5000 u can be produced by LDI. Using this technique, the average molecular masses of low-mass PE samples can be determined. A substrate-assisted LDI mass spectrum of a PE sample with a moderate polydispersity can be obtained. But the spectrum appears to be biased toward the detection of low-mass oligomers. This finding is consistent with those reported from MALDI analysis of other types of polydispersity polymers. This problem can be addressed by using the combination of GPC fractionation of polydispersity PE with the metal powder substrate-assisted LDI technique. From the technical development point of view, it remains to be seen how effective this technique will be for handling even greater mass PE samples. Unfortunately, to our knowledge, no narrow-polydispersity PE standards with molecular mass of greater than 5000 u are currently available commercially. Future work requires the use of GPC to fractionate and prepare narrow-polydispersity PE standards from a suitable molecular mass polydispersity sample. Until then, we can conclude that the technique described in this work offers a means of analyzing polyethylene samples with masses of up to at least 5000 u.