

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

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**Introduction.** Mass spectrometry has been used to analyze synthetic polymers for many years. Polyethylene (PE) is commercially one of the most important synthetic polymers, thus detailed PE characterization is of great importance to polymer industry. Traditional characterization methods such as GPC and NMR can be quite involved for analyzing PE, therefore, there is a strong interest in using alternative methods that can provide rapid and accurate information on polymer structure and molecular mass distribution. There are limited reports on mass spectrometric analysis of PE in the literature, however, because PE is only soluble in hot solvents and as a result of the solution cooling upon rapid evaporation, it tends to precipitate out of solution well before the matrix or metal salt do. This in turn makes it difficult to prepare a uniform matrix/analyte/metal-salt mixture, which is crucial step in any MALDI experiment. In addition, polyethylene is highly crystalline and will tend to form spherulites that reject the matrix and the metal salt. This presentation describes the studies of the PE analysis by using metal powder as the matrix where intimate polymer/matrix mixing is not necessary.

**Experimental.** The substrate-assisted LDI experiments were performed on the Bruker Reflex III MALDI-TOF mass spectrometer (Bremen, Germany) having reflectron ion optics. The PE samples were dissolved in toluene at a concentration of 2mM to 3mM. In all cases heating was required to completely dissolve the analyte. Metal powder was suspended in isopropyl alcohol. Silver nitrate was dissolved in ethanol to make a saturated solution.

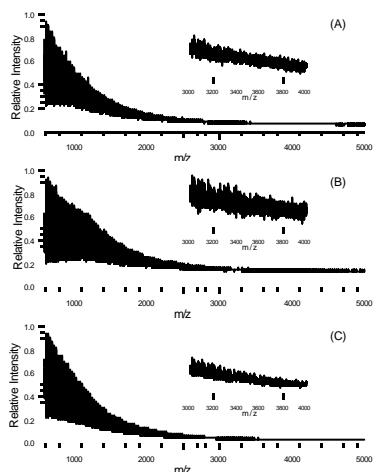
**Results and Discussion.** Figure 1 shows the substrate-assisted LDI mass spectra of PE/wide sample (M<sub>w</sub> 3300 u, polydispersity 1.435, ). A mass spectrum of this material could not be obtained by MALDI with any organic matrix typically used for synthetic polymers; furthermore, direct LDI for this material yielded very poor results. The adjacent peaks in the main series are separated by 28 u, as expected for the polyethylene repeat unit with the appearance of peaks separated at 14 u at the low mass end indicative of fragmentation. Figure 1 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 about m/z 4000. The effect of metal powder size and type of metal powder on the efficiency of PE analysis by substrate-assisted LDI MS were examined. Figure 2 shows the representative results from PE4100 (M<sub>w</sub> 4700 u, polydispersity 1.15). Figure 2B 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 (see in Figure 2A). However, for the experiments using the fine cobalt powder as the LDI substrate, the laser power threshold is generally higher which results in a greater extent of fragmentation, as illustrated in Figure 2B. Figure 2C-E displays the mass spectra of PE4100 obtained by using different metal powders. The size of copper, nickel and iron powders are similar to the coarse cobalt powder. The copper spectrum (Figure 2C) resembles the cobalt spectrum except that the center of the main distribution is shifted to lower mass, due to more extensive fragmentation. In both nickel and iron spectra (see Figure 2D,E), metal ion clusters were detected, which not only reduces the signal to noise ratio, but also interferes with the molecular mass calculation. Figure 3A and B show the image of the fine metal powders layered on a sample target without (A) and with (B) the sample addition. Panels C and D of Figure 3 show the images of coarse cobalt powders without and with sample addition. In Figure 3D, since the particles are loosely dispersed over the target, 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 PE sample. In Figure 3B, a higher laser power is generally required for generating PE signals. The fine cobalt particles are densely packed and white precipitates from PE are clearly visible which can affect the laser penetration to the cobalt powder for rapid heating process.

Figure 4 shows the expanded spectrum of PE4100. In this case each oligomer ion is separated by 28 u in the mass range of between 2000 u to 5000 u as expected. In the mass range from 1000 u to 2000 u,

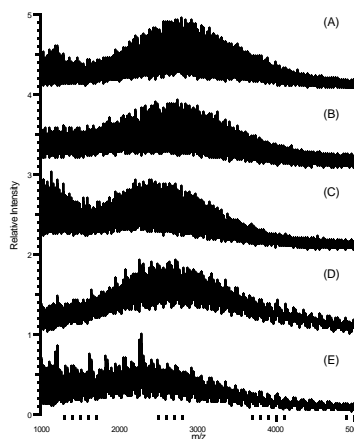
adjacent peaks are separated by 14 u suggesting that many of these ions result from fragmentation of the PE oligomer ions. The average molecular masses of this sample can be calculated as  $M_n=3114$ ,  $M_w=3268$  and  $PD=1.049$  after the correction of the fragment ion contribution to the low mass tail. Compared to the GPC results of  $M_n=4100$ ,  $M_w=4700$  and  $PD=1.15$ , there are some discrepancies in the data. Even for well-characterized polymer standards (e.g., polystyrene), differences between GPC and MALDI data can be observed.

**Conclusions.** It was shown that, using coarse cobalt powder as the substrate and silver nitrate as a cationization reagent, intact PE oligomer ions of up to 5000 u could be produced by LDI. Using this technique, the average molecular masses of low mass PE sample can be determined. Substrate-assisted LDI mass spectrum of a PE sample with moderate polydispersity can be obtained. From a technical development point of view, it remains to be seen how effectively this technique will be for handling even greater mass PE samples.

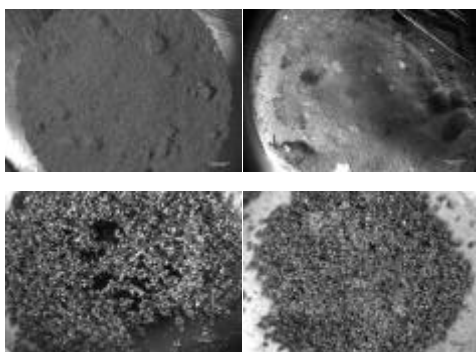
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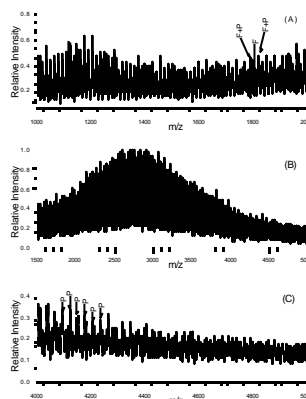
**Figure 1.** Mass Spectrum of PE/wide obtained using coarse cobalt metal powder as the substrate. The laser attenuation reading from the Bruker Reflex III instrument is (A) 55%, (B) 65%, and (C) 70%.



**Figure 2.** Mass spectra of PE4100 using different metal powders (A) Coarse cobalt, (B) fine cobalt, (C) copper, (D) nickel, (E) iron.



**Figure 3.** Microscopic images of (A) and (C) fine and coarse cobalt metal powder layered onto a stainless steel target respectively, (B) and (D) fine and coarse cobalt powder by the addition sample and metal salt.



**Figure 4.** Mass spectrum of PE4100 using coarse cobalt powder as the substrate. Labels "P" and "F" refer to the intact parent and fragment ion peak respectively