

Laser Desorption Ionization and MALDI Time-of-Flight Mass Spectrometry for Low Molecular Mass Polyethylene Analysis

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Introduction. Polyethylene (PE) is one of the most important commodity polymers and a detailed PE characterization is of significance for polymer industry. Traditional characterization methods such as GPC and NMR can be quite involved for analyzing PE. There is a strong interest in using alternative method that can provide rapid and accurate information on polymer structure, average molecular mass and molecular mass distributions. This presentation describes our studies of the ionization behavior of several PE samples using conventional MALDI TOF MS.

Experimental. The LDI and MALDI experiments were done in three instruments. The linear time-lag focusing MALDI time-of-flight (TOF) mass spectrometer constructed at the University of Alberta. An Applied Biosystems Voyager LDI TOF mass spectrometer (Framingham, MA) equipped with a reflectron and a Bruker Reflex III TOF mass spectrometer (Bremen, Germany). Samples were dissolved in chlorobenzene at 5 mg/ml. Matrices were dissolved in THF to make a concentration of 0.1 M. Silver nitrate was dissolved in methanol to make a saturated solution.

Results and Discussion. Figure 1 shows the LDI mass spectra of three PE samples from American Polymer Standards Cooperation. These spectra were obtained in a linear TOF mass spectrometer. In all cases, the mass difference between two adjacent peaks from the main distribution is 28 Da. From the masses and peak intensities of the main distribution, with the removal of the low mass fragment ion contributions, the Mn, Mw and polydispersity can be calculated and are found to be consistent with those from GPC for PE1100 and PE2100. Figure 1C resembles MALDI spectra of many broad polydispersity polymers. No reliable average molecular mass information can be obtained for this sample.

The effect of the type of cationization reagent on PE detectability was studied. Figure 2 shows the LDI spectra of PE500 and PE1000 obtained by using copper cationization. For PE500, the quality of the spectrum is comparable to that obtained by silver cationization. However, copper cationization is not as effective as silver cationization for analyzing higher mass PE samples. For example, for PE1000, with copper cationization, the signal to noise ratio for the principal distribution is not as high as in the case of silver cationization (see Figure 3D). Many known polymer MALDI matrices have been tested for PE analysis. *All-trans* retinoic acid, *trans,trans*-1,4-diphenyl-1,3-butadiene and dithranol are found to be useful to enhance signal intensities and/or reduce fragmentation (see Figure 3). The use of matrix reduces the laser threshold required for LDI in all three cases. Figure 3 also shows that matrix can influence the shape of the principal distribution, resulting in different average molecular masses. More work is still needed to understand the roles that the matrix molecules play in MALDI of PE.

Searching for an optimal matrix and sample preparation method for MALDI analysis of PE is currently underway. Figure 4 shows the MALDI spectra of PE4000 with silver cationization and cobalt powder as the matrix. The principal distribution spans from 1000 to 5000 Da with adjacent peaks separated by 28 Da. The low mass peaks separated by 14 Da (see Figure 4B) are from fragment ions of the PE oligomers. This is the highest molecular mass PE sample analyzed by MALDI to date.

Conclusions. LDI and MALDI mass spectra of narrow polydispersity polyethylene with molecular masses of up to 5000 Da can be obtained in conventional time-of-flight mass spectrometers equipped with a nitrogen laser. Silver cationization generally provides better results than copper cationization. Low

mass fragments are observed. Addition of some commonly used polymer matrices to the sample preparation assists in enhancing signal intensity and/or reducing the extent of fragmentation.

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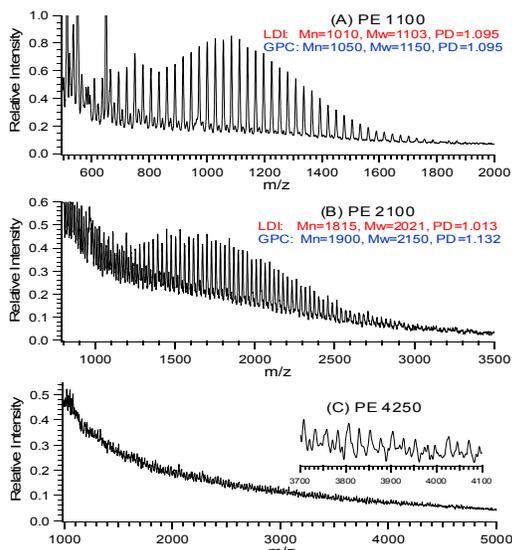


Figure 1. LDI mass spectra of (A) PE1100, (B) PE2100, and (C) PE4250. These samples were from American Polymer Standards Corporation.

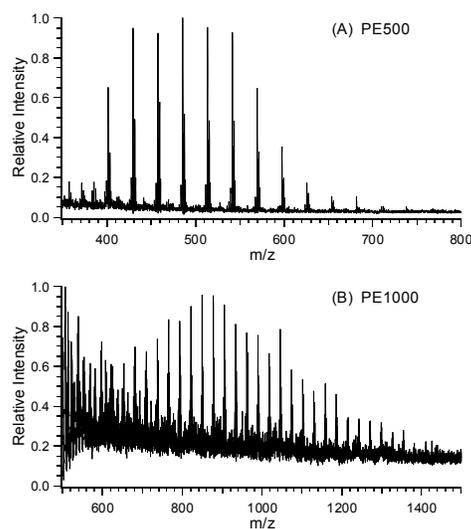


Figure 2. LDI mass spectra of PE500 and PE1000 obtained by using copper cationization.

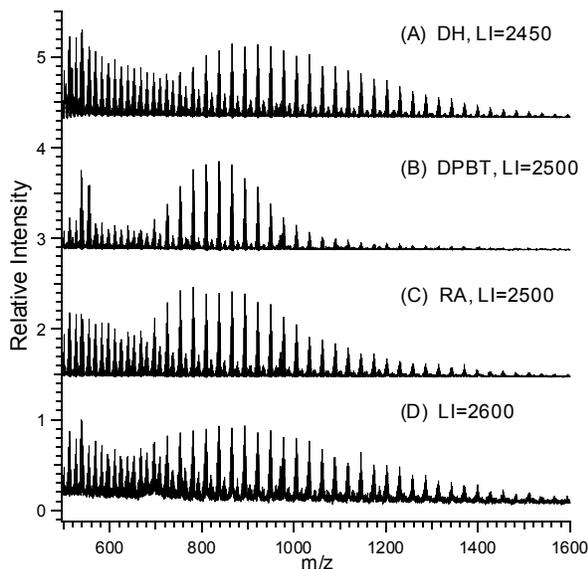


Figure 3. MALDI mass spectra of PE1000 obtained by using silver cationization with (A) dithranol, (B) *trans,trans*-1,4-diphenyl-1,3-butadiene (DPBT), (C) *all-trans* retinoic acid (RA), and (D) no matrix. LI is laser power index.

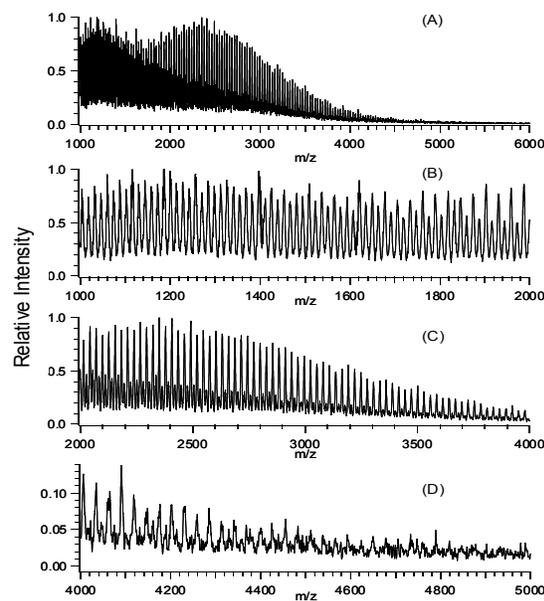


Figure 4. (A) MALDI mass spectrum of PE4000 from NIST and (B), (C) and (D) expanded mass spectra. Cobalt powder was used as the matrix. However, similar spectra can be obtained with organic matrices as well.