A New Method for Mass Spectrometry of Polyethylene Waxes: The Chloride Ion Attachment Technique by Atmospheric Pressure Photoionization

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Received March 11, 2008
Revised Manuscript Received April 23, 2008

Introduction. Polyethylenes (PE) with differing molecular weights and structures, including linear or branched, are produced in the largest quantity all over the world. Low molecular weight polyethylenes (LP-PE) represent a particular segment of the PE industry.[1−4] LP-PE can potentially be utilized in many important applications, such as surface coatings, lubricants, or additives, for improving the flow and molding properties of plastics during processing.[1−3]

Mass spectrometry (MS) methods that utilize soft ionization processes for polymer characterization are superior to the most generally used techniques, since MS methods allow not only the determination of end groups and average functionality (F_n) but also the detection of intact polymer chains. However, MS combined with soft ionization sources, such as matrix-assisted laser desorption/ionization (MALDI)[5,6] or electrospray ionization (ESI),[7] are less suitable for the analysis of nonpolar polymers, e.g. PE, given the lack of effective ionization sites. On the contrary, it has been shown that fully saturated PE can be analyzed using laser desorption ionization (LDI) or MALDI through the formation of silver adducts or the use of coarse cobalt powder matrices.[8−10] However, in some cases, MS showed extensive fragmentation of PE chains, as in the case of silver cluster formation caused by silver cationization. In that study, the peaks of the silver clusters coincided with those of oligomers and thus created difficulties for the mass spectral interpretation. To overcome these problems, several methods have been suggested, including chain modification with bromine or introduction of readily ionizable polar groups into PE.[11,12] Since these methods involve chemical reactions performed in several steps prior to MALDI sample preparation, they are time-consuming. Also, they may suffer from incomplete chain-end transformations. Very recently, a sophisticated, but not readily available, matrix "solid C_{60} intercalated with cobalt cyclopentadienyl dicarbonyl" was proposed for the MALDI characterization of PE. Therefore, the ionization of PE with minimal or no fragmentation prior to chemical modification is highly desired, along with the avoidance of interfering agents, such as silver salt/matrices, and the easy online coupling of the ionized PE source to the liquid chromatography.

The recently introduced APPI technique[14,15] has been shown to enable the ionization of nonpolar compounds such as steroids,[16,17] lipids,[18,19] and polyaromatic hydrocarbons.[20,21] In this study, we report the characterization of saturated PE samples by APPI-MS using the chloride attachment technique (CAT).

Experimental Section. Chemicals. Polyethylene standards with H,H (M_n ∼1000 g/mol) and H,OH (M_n ∼700 g/mol) termini, CCl_4, and HPLC grade toluene were received from Sigma-Aldrich (Steinheim, Germany). LP-PE was obtained via extraction of high-density polyethylene (HDPE) with hexane (TVK, Tiszaújváros, Hungary).

Instrumentation. APPI quadrupole time-of-flight mass spectrometric (APPI-Qq-TOF MS) measurements were performed in the positive and negative ion modes with a MicroTOF-Q type Qq-TOF MS instrument (Bruker, Bremen, Germany), which was equipped with an APPI source (PhotoMate, Kr discharge lamp, VUV photons of 10.0 and 10.6 eV in an intensity ratio of 4:1) (Syagen Technology, Inc., Tustin, CA). PE was dissolved at a concentration of 0.2 mg/mL in hot toluene dopant. The PE solutions were introduced directly into the APPI source with a syringe pump (Cole-Parmer Ins. Co., Vernon Hills, IL) at a flow rate of 20 μL/min. The carrier flow rate of CCl_4 was 200 μL/min through a T-piece. The APPI source heater was kept at 350 °C. End-plate offset and capillary voltage were set to −500 and 2500 V, respectively. All of the spectra were recorded by a digitizer at a sampling rate of 2 GHz. The spectra were calibrated externally with the APCI/APPI calibrant mixture from Bruker in the *m*/*z* range of 600−1600. The accuracy of the *m*/*z* was determined to be within ±0.01. The recorded MS results were evaluated using the DataAnalysis 3.1 software from Bruker.

Results and Discussion. The positive ion mode of the APPI-MS of PE revealed significant fragmentation of the PE chains. This was determined from intensity distributions of the PE chains (not shown) skewed to the lower *m*/*z* values and the appearance of 14 Da mass spacing between the adjacent PE peaks (instead of 28 Da mass spacing that can be expected for polyethylene, i.e., corresponding to the mass of ethylene repeat unit). In APPI(+)-MS, protonated molecules, i.e., $[M + H]^+$, were formed by the dissociation of successive PE chains. These observations clearly demonstrate that APPI(+)-MS is not suitable for the investigation of intact PE chains, but it may be utilized for gathering information on the chain structure. The negative ion mode of APPI-MS showed minimal or no fragmentations of PE chains. Figure 1 shows the APPI(−)-MS spectrum of a PE standard of molecular weight ∼1000 g/mol. As is indicated in Figure 1, the mass spacing between the adjacent peaks is 28 Da, corresponding to the mass of the repeat unit of ethylene.

The formation of $[M + Cl]^-$ ions was supported by accurate mass measurements and by the isotopic pattern. For example, the measured/calculated monoisotopic *m*/*z* values for the $[M + Cl]^-$ ions with $n = 34$, 38, 42, and 46 which correspondedtocompositionsof$C_{68}H_{138}Cl$,$C_{76}H_{154}Cl$,$C_{84}H_{170}Cl$, and $C_{92}H_{186}Cl$ were found to be 990.049/990.054, 1102.174/1102.185, 1214.300/1214.309, and 1326.425/1326.435, respectively. It is also evident from the accurate mass measurements that the end groups of PE are hydrogen atoms as indicated in Figure 1. This corresponds to the fully saturated PE chains that do not contain any heteroatoms (PE-H). To study the effect of the LP-PE end groups on the APPI(−)-MS, the LP-PE standard with a molecular weight of ∼700 g/mol and −H and −OH termini (PE-OH) was chosen. A representative APPI(−)-MS spectrum of the PE-OH standard is shown in Figure 2.

As seen in Figure 2, mass spacing between the neighboring peaks corresponds to the mass of the ethylene repeat unit, as expected. On the basis of the accurate masses and isotopic patterns, it can be shown that adduct $[M + Cl]^-$ was formed and consistent with the end groups indicated in Figure 2.

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10.1021/ma8005476 CCC: $40.75
Published on Web 05/06/2008

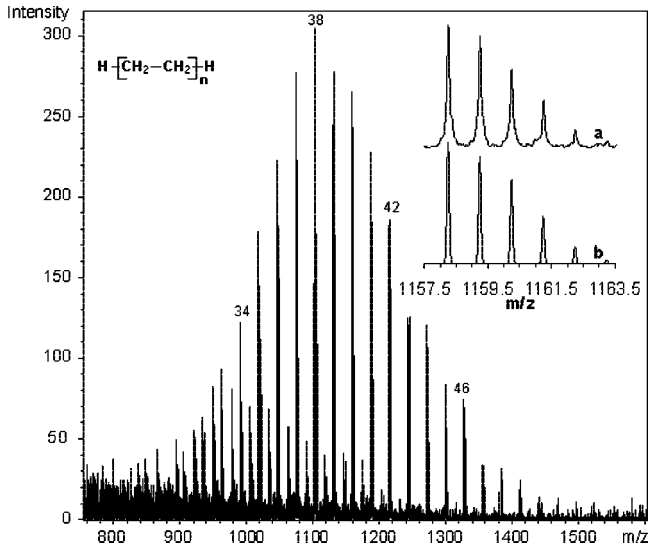


Figure 1. APPI(−)-MS of the PE standard [H−(CH_2−CH_2)$_n$−H]. Experimental conditions: PE concentration, 0.2 mg/mL in toluene; sample flow rate, 25 μL/min (toluene); CCl_4 flow rate, 200 μL/min. The numbers at the top of the peaks represent the number of repeat units. The inset shows the measured (a) and the calculated (b) isotopic distribution for PE oligomer with $n = 40$. The minor, low-intensity series is presumably due to a sample impurity. Based on the accurate mass measurements, the mass differences between the main and the second series of peaks (weaker) is 16 Da (accurate mass 15.997 Da), which corresponds to the mass of an oxygen atom; i.e., the second series may be due to the presence of polyethylene with hydroxyl group.

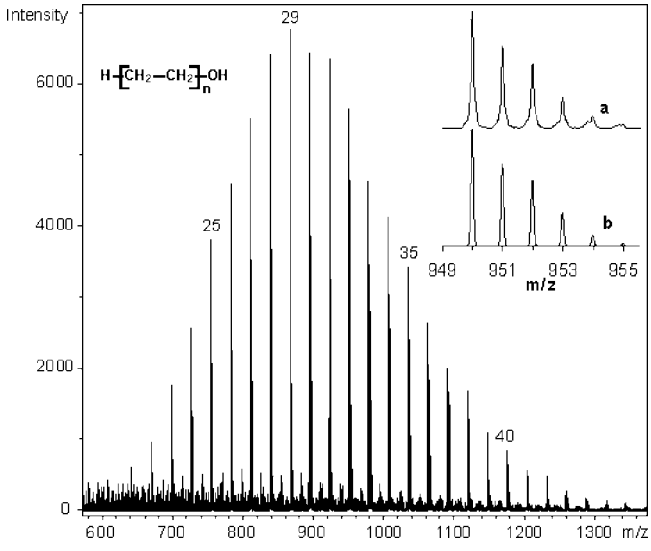
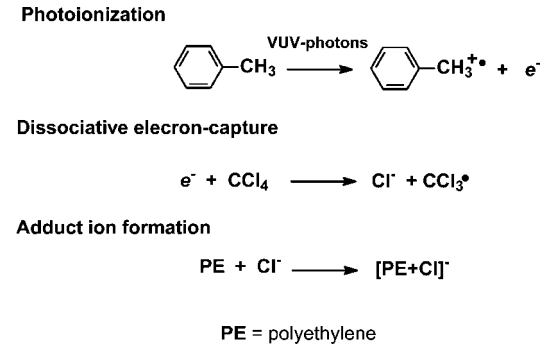


Figure 2. APPI(−)-MS of the hydroxyl-terminated PE standard [H−(CH_2−CH_2)$_n$−OH]. Experimental conditions: see Figure 1 captions. The numbers at the top of the peaks represent the number of repeat units. The inset shows the measured (a) and the calculated (b) isotopic distribution for PE-OH oligomer with $n = 32$.

For example, the measured/calculated monoisotopic m/z values for the $[M + Cl]^-$ ions with $n = 25$, 29, 35, and 40, which corresponded to compositions of $C_{50}H_{102}OCl$, $C_{58}H_{118}OCl$, $C_{70}H_{142}OCl$, and $C_{80}H_{162}OCl$, were found to be 753.762/753.764, 865.888/865.883, 1034.075/1034.071, and 1174.232/1174.226, respectively.

However, using toluene as a dopant was necessary to obtain MS in each case. In the presence of toluene, photoionization yields thermal electrons that are captured by the solvent CCl_4, which donates chloride ions as depicted in Scheme 1. This assumption is supported by earlier works from other laboratories.[20,22]

Scheme 1. Proposed Mechanism for the Formation of PE Adduct with Chloride Ions in the Presence of a Toluene Dopant



The chloride ions formed most likely ligate with the partially positively charged H atoms of the PE backbone and end groups. Thus, the end groups may affect the ionization efficiency as shown by the signal intensity of PE-H and PE-OH (see Figures 1 and 2). PE-OH has a signal intensity significantly higher than that of PE-H. Since the positive charge on the end group of

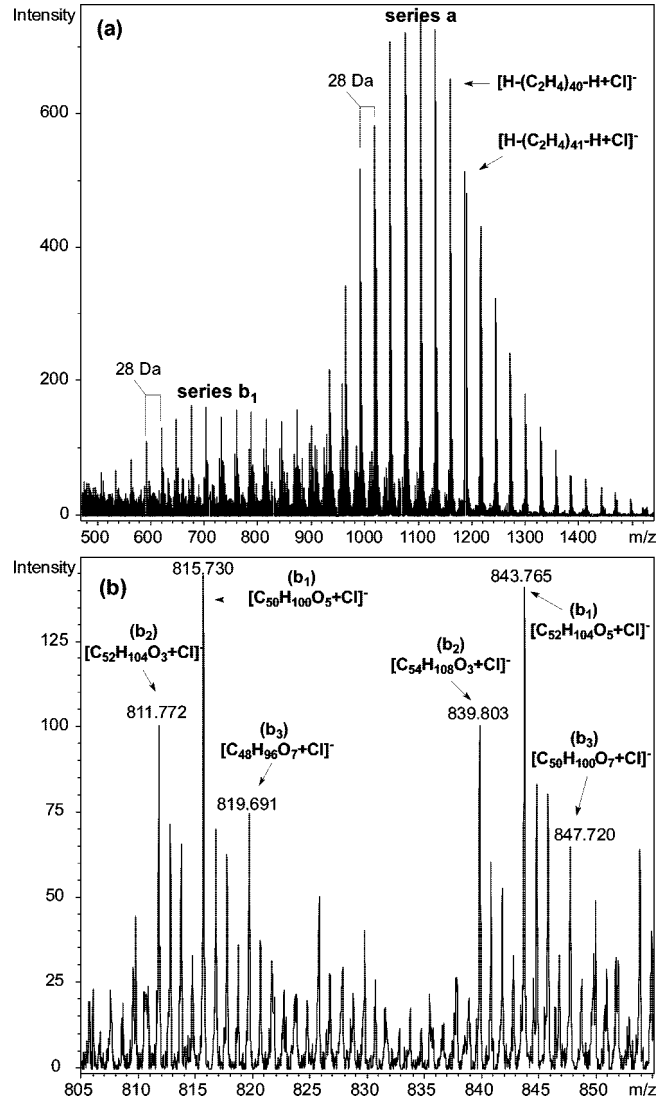


Figure 3. APPI(−)-MS spectrum (a) and zoomed APPI(−)-MS spectrum (b) of LP-PE wax extracted from HDPE. In (b) the compositions of the oligomers proposed together with their accurate masses are also indicated. Experimental conditions: see Figure 1 captions.

PE-OH is higher than on the ethylene backbone units, it is expected that the Cl^- ion will predominantly attach to the H atoms of the PE-OH end group. Our conclusion may supported by the fact that carbohydrates known to contain several OH groups readily form adducts with chloride ions under negative ion electrospray.[23]

The next sample is a side product of industrial HDPE manufacturing and processing. The APPI(−)-MS spectrum of the HDPE extract is presented in Figure 3. As is evident in Figure 3a, two different main series (**a** and $\mathbf{b_1}$) are present in the APPI(−)-MS spectrum of the HDPE extract. Series **a**, appearing at higher *m*/*z* values, is caused by the presence of $[H-(C_2H_4)_n-H + Cl]^-$ adduct ions, i.e. polyethylene oligomers with H end groups ionized by a chloride ion. The identification of series $\mathbf{b_1}$ is not straightforward. One can realize from Figure 3b that besides the series $\mathbf{b_1}$, there are two additional series denoted by $\mathbf{b_2}$ and $\mathbf{b_3}$. The mass spacing (28 Da) between the adjacent peaks in each series indicates PE oligomers; however, the end groups of these oligomer series are not consistent with olefin or H termini. In addition, it seems unlikely that series $\mathbf{b_1}$, $\mathbf{b_2}$, and $\mathbf{b_3}$ were formed by thermal degradation of PE under APPI conditions, since in that case the oligomer mass spacing should be 14 Da. On the basis of the accurate masses, we found that the compositions of the series $\mathbf{b_1}$, $\mathbf{b_2}$, and $\mathbf{b_3}$ are $C_{2n}H_{4n}O_5Cl$, $C_{2n}H_{4n}O_3Cl$, and $C_{2n}H_{4n}O_7Cl$, respectively. Taking into account the low unsaturation index of formula obtained for series $\mathbf{b_1}$, $\mathbf{b_2}$, and $\mathbf{b_3}$, it can be postulated that these series should contain mostly hydroperoxide and/or alcoholic groups. This is in line with the studies obtained on the oxidation of polyethylene that oxidation yields predominantly hydroperoxide, aldehyde, ketone, and secondary alcoholic groups.[24] It can be postulated that oligomers $\mathbf{b_1}$, $\mathbf{b_2}$, and $\mathbf{b_3}$ were formed from reactive LP-PE during HDPE manufacturing and processing.

Conclusions. As demonstrated, LP-PE can be analyzed by APPI(−)-MS using the chloride ion attachment technique. In the negative ion mode of APPI-MS, LP-PE molecules do not suffer from fragmentations, thereby allowing the determination of their repeat unit and end groups. In addition, it is postulated that the chloride ion attachment technique in the APPI-MS practice can be applied to the analysis of other nonpolar polymers and compounds, which are typically very difficult to ionize using different soft-ionization methods.

Acknowledgment. This work was financially supported by grants K-62213 and K-72524 given by OTKA (National Scientific Research Fund, Hungary) and grants RET-006/2004 and GVOP-3.2.1.-2004-04-0152/3.0.

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MA8005476