Matrix-assisted laser desorption/ionization mass spectrometry of covalently cationized polyethylene as a function of sample temperature

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Abstract

A pre-charged, low molecular mass, low polydispersity linear polyethylene was analyzed with matrix-assisted laser desorption/ionization (MALDI) mass spectrometry as a function of sample temperature between 25 °C and 150 °C. This temperature range crosses the polyethylene melting temperature. Buckminsterfullerene (C_{60}) was used as MALDI matrix due to the high volatility of typical MALDI matrices making them unsuitable for heating in vacuum. Starting at 90 °C there is an increase in polyethylene ion intensity at fixed laser energy. By 150 °C the integrated total ion intensity had grown by six-fold indicating that melting did indeed increase ion yield. At 150 °C the threshold laser intensity to produce intact polyethylene ions decreased by about 25%. Nevertheless, significant fragmentation accompanied the intact polyethylene ions even at the highest temperatures and the lowest laser energies.
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1. Introduction

By production volume, saturated hydrocarbon polymers are the most widely used of all synthetic polymers. New developments in metallocene catalysts have resulted in a wide variety of new applications [1] and an ever increasing market share. These new catalysts provide unprecedented control of polymer molecular mass, molecular mass distribution, copolymer distribution, stereochemistry, and other aspects of chain structure which are critical in determining performance properties. Mass spectrometry has proven to be one of the polymer chemist's most versatile tools. Unfortunately polyethylene, polypropylene, and other polyolefins are not amenable to mass spectrometric characterization due to the ineffectiveness of conventional methods of ionization in producing intact, high molecular mass polymer ions in the gas phase. Conventional ionization methods (with selected references for each) that have been applied include electron impact ionization [2], field desorption/ionization [3–5], pyrolysis [6], electrospray ionization [7], laser desorption/ionization [8,9], and matrix-assisted laser desorption/ionization (MALDI) [10–13]. In each case either intact polyolefins could not be produced in the gas phase, or the mass of intact molecules was limited to about 2000 u. Simply put, it is the lack of either polar groups or bond unsaturation that excludes gas-phase metal cationization as it is commonly applied to synthetic polymers from being applied to polyolefins.

In the last few years a new method has been developed to produce the necessary ionization for successful MALDI mass spectrometry (MS) from modified polymers that give no response in their unmodified form. These methods involve replacement of the neutral polymer end group (typically vinyl) with a salt that readily undergoes dissociation during the laser ablation event. Both phosphonium [14,15] and sulfonate [16] salts have been used. Bauer et al. [14] termed this procedure "covalent cationization". Intact macromolecular ions in the gas phase with masses up to 15 000 u for polyethylene [15], and up to 12 000 u for polyisobutylene [16], have been created with this method. In cases where it is known beforehand that mass spectrometry will need to be performed, the method can be applied during polymer synthesis where a pre-charged end-group can be used to terminate the polymerization reaction [17–21].

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Our past experiments on covalently cationized polyethylene demonstrated that it required a large number of laser shots to produce spectra with sufficient signal intensity [15]. Unlike amorphous polymers that are readily analyzed by MALDI, crystalline polymers must overcome their crystallization enthalpy in order to produce single-chains in the gas phase. However, the extra energy to overcome the crystallization enthalpy that could come from increasing the laser intensity only leads to fragmentation of the polyethylene chains. Thus, a lower laser energy had to be used to produce intact chains. In that case an increased number of laser shots was then used to compensate for the lower laser energy in an effort to produce spectra with sufficient ion signal intensity while trying to limit the noise in the spectrum as much as possible.

Using the heated sample stage in our MALDI time-of-flight mass spectrometer our early work indicated that increasing temperature did increase ion yield for a prototypical MALDI matrix, 2,5-dihydroxybenzoic acid (2,5-DHB) [22]. A three-fold increase in total ion intensity was observed by heating the single-crystal samples from room temperature to 150 °C. The increase was attributed to bringing the 2,5-DHB closer to its equilibrium thermodynamic sublimation temperature of 180 °C. Heating caused a decrease in 2,5-DHB cluster ions formed and an increase in both molecular and fragment ions. The increase in fragment ion formation began at 90 °C, while the increase in molecular ion formation began at 120 °C. The experimental results were described using a two-step kinetic model for the laser desorption/ionization process [23]. Heating the sample ablates more material for the same laser energy per pulse as expected. (This has also been confirmed in separate studies by Zhigilei and Garrison [24] using molecular dynamics simulations.) However, ion production decreases at the highest temperatures because the plume expands so rapidly that energy pooling of the excited matrix molecules cannot reach its full extent before the molecules find themselves too far apart to interact in the decreasing time available. So while sample heating may increase ion yield it may also reduce it in cases where ionization reactions taking place in the plume do not reach their maximum extend. In the case of 2,5-DHB with entrained bovine insulin when the sample is melted prior to the laser ablation event, Little et al. [25] found that an infrared pre-pulse that melted the 2,5-DHB before the ultraviolet laser ablation pulse increased both the 2,5-DHB and the bovine insulin ion yields. As the sample cools and refreezes after the infrared pulse the sample regains its former, lower room temperature ion yield.

The issues addressed in this work are whether the melting of the polyethylene sample will produce a similar enhancement of ion yield in a crystalline polymer, whether an increase in sample temperature will decrease the laser threshold intensity, and whether the degree of fragmentation decreases with either increasing temperature or decreasing laser intensity.

2. Experimental

A low molecular mass, low polydispersity linear polyethylene studied previously [15] was used in this work. This material is a size-exclusion chromatography fraction of a commercial Ziegler–Natta linear polyethylene. The polyethylene had an M_n of 4060 ± 200 u (relative expanded uncertainty) from nuclear magnetic resonance measurements of end group composition. The preparation of this material was described in great detail previously [15] (where it was designed 'LEA-51'), so only a brief description of the covalent cationization procedure will be given here. The first step is bromination of terminal vinyl group on the polyethylene to form a 1-bromo end group. This was done by heating a mixture of polyethylene (300 mg), benzoyl peroxide (470 mg), bromine (40 drops) and *m*-xylene (15 mL) in a closed vial at room to 110 °C to dissolve the polyethylene. This temperature was maintained for 5 h. The hot solution was then precipitated in cold methanol (150 mL). The product was filtered, washed with methanol, dried in a vacuum oven at room temperature overnight then at 80 °C for 10 h. Next this brominated polyethylene (183 mg) and a large excess of triphenylphosphine (400 mg) were dissolved in *m*-xylene (5 mL) at 110 °C. The reaction was allowed to proceed for 4 d. Then the hot solution was precipitated in cold methanol (200 mL), filtered and dried in a vacuum oven overnight. Owing to the fact that triphenylphosphine oxide (a contaminant in triphenylphosphine) tends to concentrate in this precipitated product, the product was re-dissolved in hot xylene (110 °C), re-precipitated in cold methanol, filtered, and dried in vacuum at room temperature overnight, then at 80 °C for 10 h. This lead to covalent cationization of 80% of the terminal vinyl groups that are found at the chain terminus of 40% of the polymer chains in the initial sample [15] giving about one-third of the chains in the polymer sample a permanently bound charge.

The MALDI matrix used for these experiments was 98% pure C_{60}. Buckminsterfullerene has sufficient absorption in the near UV [26], and a low enough enthalpy of fusion [27], to ablate under typical MALDI conditions [28]. Furthermore, it has a very low vapor pressure in vacuum [29] even at temperatures well above the 125 °C observed melting point of polyethylene and the 250 °C temperature limit of the heating stage in the mass spectrometer.

Target preparation is critical in achieving good signal to noise in MALDI mass spectrometry experiments on synthetic polymers. To prepare uniform targets a high temperature nebulizer capable of spraying a solution of polyethylene in xylene held at 125 °C was built. It uses a Meinhard Glass Products (Golden, CO) [30] high-solids nebulizer model TL-HEN-170-A0.3. Fig. 1 shows the nebulizer in one-half of a custom-made aluminum heating block. The two parts of the aluminum block sandwich the nebulizer inside and are wrapped with heating tape with insulating tape around the outside of the heating tape. High temperature polytetrafluoroethylene shrink tubing (Zeus Industrial Products Inc., Orangeburg, SC) is used to connect the solution reservoir and the high temperature gas inlet to the nebulizer. The gas is preheated to 150 °C before reaching the nebulizer by a 1 L stainless steel bottle filled with copper ball bearings approximately 3 mm in diameter. The bottle and the stainless steel gas transfer tube are wrapped in heating tape. Thermocouples at the gas heater, gas transfer tube, and nebulizer block are used to monitor process temperature. MALDI samples were prepared by first placing a uniform layer of finely powdered C_{60} onto
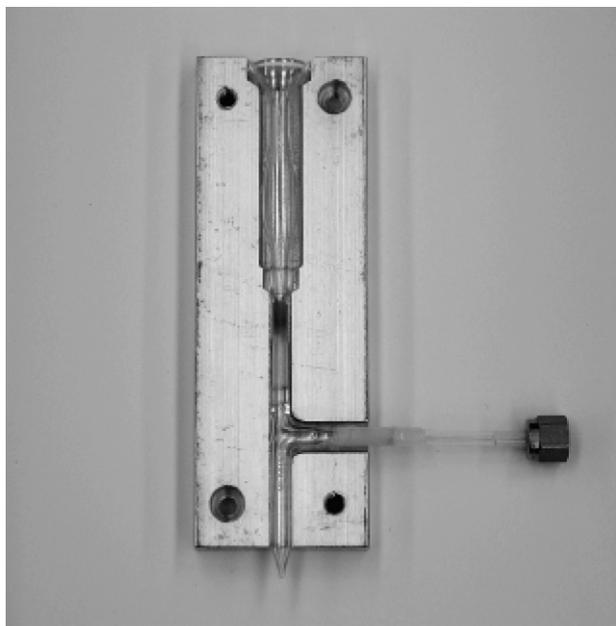
Fig. 1. Photograph of the high temperature nebulizer apparatus used to deposit uniform layers of polyethylene from solution in *m*-xylene held at 125 °C. At the top is the solution reservoir, at the bottom is the nebulizer nozzle, and at the right side is the entrance for the preheated nebulizer gas. For reference, the aluminum heating block is 14.5 cm long and 5 cm wide.

the target surface by applying it from a slurry in acetone. Upon evaporation of the acetone a uniform, finely textured C_{60} layer remained. On top of the C_{60} layer a solution of 1 mg/mL covalently cationized polyethylene in *m*-xylene was sprayed from the high-temperature nebulizer. The target was held approximately 3 cm below the nebulizer nozzle. At this distance the xylene had largely evaporated and the polyethylene was deposited as fine particles onto the C_{60} film.

The MALDI mass spectrometry experiments were conducted on a Comstock Inc. (Oak Ridge, TN) model RTOF-260 reflectron time-of-flight (TOF) instrument. Sample ablation was performed with the typical nitrogen gas laser (337 nm wavelength; ~3 ns pulse width; 175 μJ/pulse maximum energy) that intersects the plane of the sample at an angle of 45° with a spot size of approximately 100 μm in diameter. All laser energies reported are ±0.25 μJ/pulse, which was the typical standard deviation over twenty laser pulses. Each spectrum is the sum of 250 laser pulses. The instrument has several important features. The sample is held at ground potential during laser ablation. The laser strikes the sample along the centerline of the time-of-flight mass separator axis with a lateral deviation of no more than 2 mm. After a delay of 7 μs, a potential of +525 V is applied to the sample plate which repels the (positive) ions through a distance of 1.5 cm to a grounded grid and into the field of the flight tube held at −3675 V. The ions are given −20 000 V post-acceleration before being detected by a dual microchannel plate. The long delay and gentle extraction allow for full plume development. The ion source and entrance to the TOF mass separator, originally designed for gas-phase ionization experiments, have a large ionization volume and wide acceptance angle, respectively. Atom Sciences Inc. (Oak Ridge,

TN) has modified this mass spectrometer to allow resistive heating of the copper sample stage to 250 °C as measured by a thermocouple embedded in it. The copper sample stage that is permanently affixed in the instrument has many times the mass of the removable copper sample holder onto which the MALDI samples are placed. In this way, the temperature of the sample stage is little affected by the introduction of the sample holder (typically at room temperature). The sample holder fits snugly around its circumference into the sample stage allowing for maximum heat transfer.

Differential scanning calorimetry (DSC) to determine the melting temperature of the polymer samples was performed on a TA Instruments (New Castle, DE) model Q1000 instrument. The samples were heated under flowing nitrogen at 10 °C/min from 25 °C to 200 °C. The as-received and covalently cationized bulk samples has masses on the order of 1 mg each; however, the nebulized samples had masses only about 0.1 mg each due to solubility limits of polyethylene in *m*-xylene and the low flow rate of the nebulizer. Nevertheless, even such small amounts of nebulized material yielded usable thermal traces. The instrument manufacturer's software was used to calculate the melting temperatures.

3. Results

Fig. 2 shows a series of mass spectra of a low molecular mass, low polydispersity polyethylene taken at three different temperatures: 25 °C, 100 °C, and 150 °C. Each spectrum is plotted on the same ion intensity scale to allow for direction comparison. At room temperature the laser intensity was set to a value of 14.0 μJ/pulse, or about 25% above the threshold value, threshold being defined as the laser energy where polyethylene ions can be detected just above the instrument noise. Clearly as the sample temperature is increased (and all other instrument values are held constant) the total ion intensity increases significantly. Peak heights of the main series double but total integrated intensity of all main series peaks increases six-fold. This is due in part to high mass peaks being discernable above the instrument
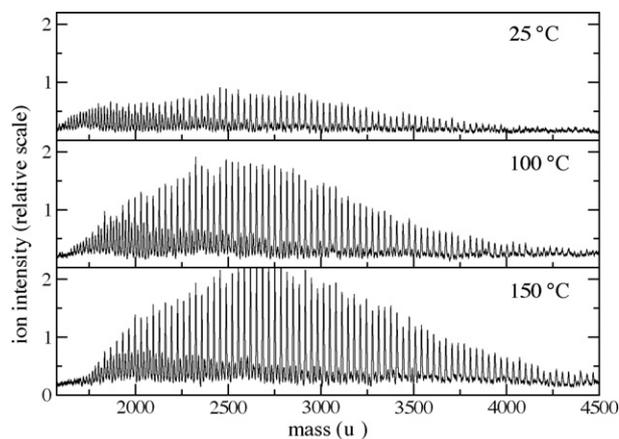
Fig. 2. Representative mass spectra of the covalently cationized polyethylene taken at sample temperatures of 25 °C, 100 °C, and 150 °C, each at 14.0 μJ/pulse. The spectra are plotted on the same intensity scale for direction comparison of ion yield.
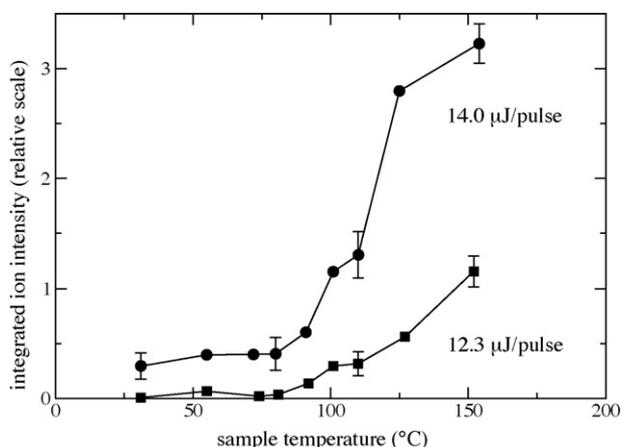
Fig. 3. Covalently cationized polyethylene MALDI ion intensity as a function of sample temperature measured at the laser ablation threshold energy (squares) and at 18% above threshold energy (circles). The solid lines are to guide the eye.

Fig. 4. Buckminsterfullerene (C_{60}) ion intensity as a function of temperature taken at 12.0 μJ/pulse, the laser threshold energy for both C_{60} and polyethylene ion creation. The solid line is to guide the eye.

noise at high sample temperature thereby increasing the total integrated intensity of the main series peaks. For the main series peaks there is no significant change in molecular mass distribution. This means that the value derived from MALDI-TOF mass spectrometry remains below that derived from nuclear magnetic resonance measurements made previously [20]. A slight increase in M_w comes from being able to identify and integrate high mass peaks that appear above the noise at high temperature but are below the noise level at low temperature. One type of fragment in the mass spectra can be identified as peaks that are separated from the main series by 14 u due to the loss of CH_2 units. These fragments would be described as z_n fragments using the proposed unified polymer fragmentation notation [31]. Other fragment peaks can be formed by the loss of multiple C_2H_4 units (y_n fragments) but are indistinguishable from the main series peaks except for a single mass unit due to the terminal proton. This effect leads to the characteristic shape of the mass spectra where a slight increase in main series intensity is observed between 2000 u and 2250 u. This is due to y_n fragments from higher mass molecules, that is, those who have lost an integral number of C_2H_4 units. The fragment peaks constitute the minor series in the spectra and are visible from the lowest masses to approximately the middle of the main series of intact polyethylene ions. Their intensity remains largely unchanged as temperature increases. Thus, they become a smaller percentage of the overall ion intensity but do not decrease in intensity themselves.

Fig. 3 shows two experiments measuring the total ion intensity (fragment and intact ions) as a function of sample temperature. One taken at 14.5 μJ/pulse and the other at the room temperature threshold of 12.3 μJ/pulse. The uncertainties in the graph are the standard deviations of three replicate spectra calculated for selected temperatures. At each temperature the sample was held for 15 min to allow for thermal equilibration. Starting at 90 °C the signal dramatically increases for polyethylene increasing approximately six-fold when the temperature reaches 150 °C. Fig. 4 shows a similar plot for the C_{60} matrix displayed on the same relative scale. Notice that it is flat (within uncer-

tainty) for all temperatures up to 175 °C. The slight decay above 125 °C occurs only on the first heating of the sample and is likely due to annealing out of surface asperities. Surface roughness tends to enhance desorption yield. When the same surface is smoothed, in this case by annealing, the ablation yield would be expected to be lower. The flat C_{60} ion-yield curve indicates that it is not the behavior of the C_{60} matrix that is creating the increase in polyethylene yield. The behavior of the C_{60} stands in contrast to our earlier work on 2,5-DHB that showed a marked increase in ion intensity versus temperature attributed to in plume reactions [22].
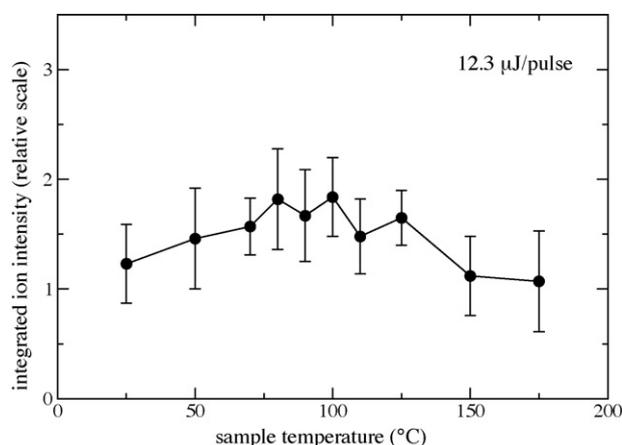
Fig. 5 shows the differential scanning calorimetry plot for the as-received polyethylene as well as for the covalently cationized polyethylene in both its bulk and its nebulized form. Each material shows a well-defined melting transition within ±2 °C of 125 °C. The nebulized material shows a slowly varying baseline due to the small amount of material used (less than 0.1 mg). Replicate sample preparations of nebulized material showed the same melting point within ±2 °C that was consistently lower than the bulk material but with baselines of different slowly
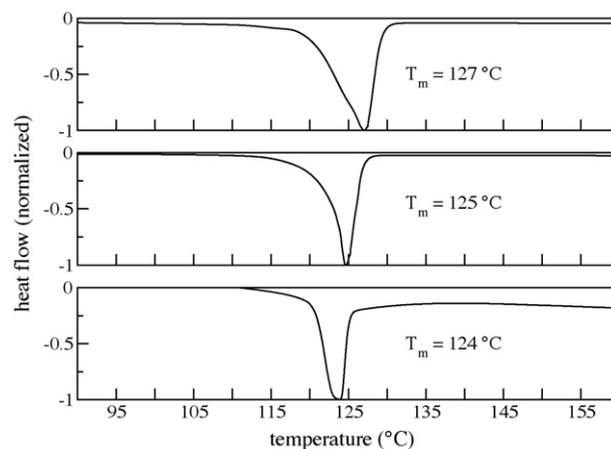
Fig. 5. Differential scanning calorimetry of (from top to bottom) bulk as-received, bulk covalently cationized, and high-temperature nebulized covalently cationized polyethylene.
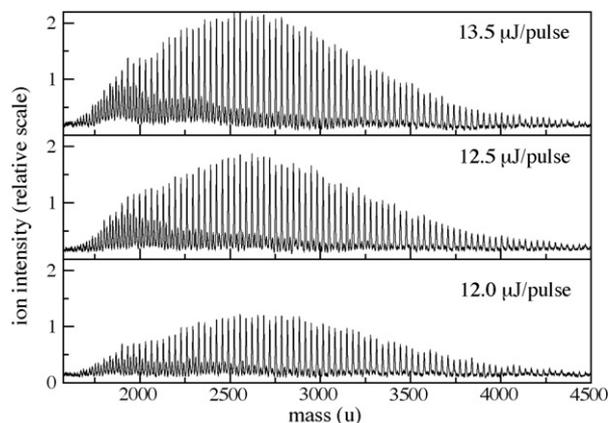
Fig. 6. Representative mass spectra of covalently cationized polyethylene at a sample temperature of 150 °C and at three different laser settings: 13.5 μJ/pulse, 12.5 μJ/pulse, and 12.0 μJ/pulse.

varying shapes. Upon reheating the nebulized material the melting point increases by approximately 1 °C to come more in line with the bulk materials. These results eliminate a spread in melting temperature due to smaller crystallites, or entrained xylene, in the nebulized material as a possible explanation for the onset of MALDI ion production at temperatures well below the bulk melting temperature. It also indicates for the bulk covalently cationized material that the addition of a bulky end-group (triphenylphosphene) does not affect the melting temperature.

Fig. 6 shows a series of mass spectra of a low molecular mass, low polydispersity polyethylene taken at 150 °C and three different laser energies: 13.5 μJ/pulse, 12.5 μJ/pulse, and 12.0 μJ/pulse. The spectrum in the bottom panel of Fig. 2, taken at 150 °C with a laser energy of 14.0 μJ/pulse, is the first spectrum of this series. As the laser energy decreases the overall ion intensity decreases but the ratio of peak heights of fragments ion peaks and intact ion peaks remains virtually unchanged. Calculating the ratio of peak areas becomes difficult at low laser power because the fragments peaks are become difficult to integrate accurately due to noise. Nevertheless, at elevated temperature and low laser power there is still a significant fragment-ion signal.

4. Discussion

While the DSC showed a sharp T_m for the polyethylene in all its forms the MALDI mass spectrometry shows a gradual increase in ion production beginning approximately 35 °C below the melting temperature of 125 °C. This may be due to the crystalline α transition in polyethylene which signals the onset of reorientational motion in the solid [32,33]. The reorientational motions involve the sliding of chains along their axis in the crystalline lattice through a chain twisting mechanism [33]. While the α transition begins near room temperature, linear polyethylene does not reach full reorientational motion until approximately 75 °C [32] or about 50 °C below its bulk melting point. Its gradual onset with temperature is consistent with ion

intensity plotted in Fig. 3 suggesting an increased ability to pull chains from the crystal lattice during the MALDI process. This, in turn, yields a greater number of free-chains in the gas phase and an higher ion intensity. In this way heating increases ion yield significantly.

Fragmentation still exists even though at elevated temperature ion yield is significantly increased and the ablation threshold decreases by about 25%. Earlier work using fast atom bombardment (FAB) [34] or laser desorption ionization (LDI) [35] each with collisionally activated decomposition (CAD) on alkyl phosphonium salts showed both charge remote and charge proximate fragmentation. Proximate fragmentation occurs within two or three carbon atoms of the phosphonium complex by direct chain scission and was found to occur at higher CAD energies, typically 1000 eV and greater. Remote fragmentation can occur anywhere along the alkane backbone and was found to set in at CAD energies of several hundred eV and increased with collision energy [35]. The low energy for charge remote fragmentation was suggested to occur through a six-member transition state via an H_2 1,4-elimination reaction. Charge remote fragmentation would seem to be an unavoidable consequence of having high internal energy alkyl chains in the gas phase.

The results presented here suggest that the balance between sufficient thermal energy to melt the polyethylene to allow for its desorption but not so much thermal energy as to cause gas-phase fragmentation is difficult to achieve. It is possible that this balance could be found if a matrix with a high degree of expansive cooling were used. In that way cooling could be achieved rapidly, that is, contemporaneous with the ablation event. It remains unclear without further study if C_{60} cools the expanding plume any better than a typical MALDI matrix. Plume cooling is exponentially dependent on the ratio of the constant-pressure heat capacity to the constant-volume heat capacity (C_p/C_v) as discussed by Knochenmuss [36]. This is very close to unity for all polyatomic molecules due to their high degree of freedom for internal vibration. This means that all MALDI matrices are poor at expansive cooling of the ablation plume. Ultimately atmospheric pressure MALDI may offer the means sufficient to cool the expanding plume rapidly enough to preserve polyethylene ions intact in the gas phase. This has been demonstrated on polyethylene glycol [37] but without the use of a heated sample stage.

5. Conclusion

Studies on pre-charged low molecular mass, low polydispersity linear polyethylene have shown that while heating the sample to above its melting point greatly increases the MALDI gas-phase ion yield it does not reduce chain fragmentation, nor does it appreciably increase the measured molecular mass distribution. This was true even though the threshold laser energy was decreased by about 25%. The trade off between sufficient energy during the ablation process to produce a significant number of gas phase ions could not be balanced against the need to keep the internal energy of those ions low enough to prevent fragmentation.

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