Preprint Title	Helium Ion Microscopy with Secondary Ion Mass Spectrometry (HIM-SIMS) for the analysis and quantitation of polyolefins
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Publication Date	18 Jun 2020
Article Type	Full Research Paper
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Helium Ion Microscopy with Secondary Ion Mass Spectrometry (HIM-SIMS) for the analysis and quantitation of polyolefins

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ABSTRACT

Petroleum based polyolefin plastics makeup a large part of the multicomponent/multiphase plastics we use in our daily lives. Multiple plastics are often compounded, laminated or coextruded in these multicomponent systems creating multiple phases and interfaces of varying strengths. Significant opportunity exists in developing strategies for enhancing interfacial properties as well as facilitating disposal of polyolefin plastics by upcycling of polymeric products for reuse. Thus, interfaces and chemically distinct phases in these materials need to be probed structurally and chemically at the relevant length scales. To date, chemical imaging of polymer and polymer blends has been primarily accomplished using time-of-flight secondary ion mass spectrometry (ToF-SIMS) to directly visualize the distribution of components in a complex material with spatial resolution ranging from 100 nm to 5µm. However, in many cases this resolution falls far short of visualizing interfaces directly. To overcome these limitations recent work has focused on developing a SIMS detection system based on the helium ion microscope (HIM) enabling chemical imaging to ~14 nm. Here, we utilize the HIM-SIMS for quantitative differentiation between the olefin-based polymers of polyethylene (PE) and polypropylene (PP). We illustrate both quantitative analysis for separating PE and PP using specific mass fragment ratios as well as demonstrate spatially resolved imaging of phase separated domains within PE thin films with ~14 nm chemical and ~2 nm morphological spatial resolutions. Overall, we demonstrate HIM-SIMS as a multimodal chemical technique for imaging and quantification of polyolefin interfaces, that could be more broadly applied to the analysis of multicomponent/multiphase polymeric systems.

Keywords:

helium-ion microscope, polymer, polyolefins, ToF-SIMS, secondary ion mass-spectrometry

INTRODUCTION

Petroleum based polyolefin plastics make a up a large part of the multicomponent/multiphase plastics we use in our daily lives. Multiple plastics are often compounded, laminated or coextruded in these multicomponent systems creating multiple phases and multiple interfaces of varying strengths, polarity, etc. Creating good/strong inter-facial properties is important for product attributes, but can cause problems when attempting to recycle or upcycle, as the first step is typically separating the products into their component parts. Significant opportunity exists in developing strategies for enhancing interfacial properties as well as facilitating disposal of polyolefin plastics by upcycling of polymeric products to oligomers, original monomers, or other small-molecule products of high value.[1] Many of these multicomponent/multiphase systems have interfaces between chemically distinct phases that need to be probed structurally and chemically at the relevant length scales to develop strategies for enhancement and eventual deconstruction of the interfaces. Currently, time-of-flight secondary ion mass spectrometry (ToF-SIMS) that offers excellent surface sensitivity, high mass resolution, and breadth of mass and fragment detection is the primary tool for chemical visualization of polymeric interfaces.[2-5] As such, research has primarily been focused on characterization of copolymers and polymer blends using ToF-SIMS.[6-11] ToF-SIMS has been used to investigate surface chemistry, interfaces, microscopic phases, and to quantitatively map surface specific polymers in blends including styrene-methyl methacrylate random copolymers, ethylene–propylene–diene terpolymers, and polypropylene/ethylene–propylene copolymer blends[12-15] as well as to determine the molecular weight for a variety of polymers including PE, PP, and polystyrene (PS).[16]

The possibility to analyze and distinguish polymers in a blend with nanosized structures becomes increasingly important as properties and performance of such materials can depend on the interfacial segregation, phase separation, and phase coarsening, which can vary in size down to tens of nanometers. However, the spatial resolution of current commercially available ToF-SIMS systems is on the order of ~100 nm in imaging mode and ~5 μm in high spectral resolution mode.[5] To overcome the spatial resolution limitations of ToF-SIMS, recent work has focused on developing a magnetic sector based SIMS detection system based on the helium ion microscope (HIM) using He^+ or Ne^+ as the primary ions enabling chemical imaging with down to ~14 nm spatial resolution.[17, 18] The HIM uses the gas field ion source (GFIS)[19, 20] that provides a high brightness beam, collimated to ca. 0.5 nm for He^+ and ca. 2 nm for Ne^+,[20-22] and allows ultrahigh-resolution ion generated secondary electron (iSE) imaging with outstanding depth of field even on insulating and biological surfaces without a conductive coating.[22-24]

The implementation of SIMS on the HIM offers the additional benefit of performing multimodal chemical imaging, where the He^+ and Ne^+ beams can be used for both high resolution iSE imaging with down to 0.5 nm resolution as well as sputtering of the surface to generate secondary ions for SIMS detection.[24-27] Therefore, the HIM-SIMS offers the opportunity for *in-situ* correlative imaging combining ultrahigh resolution iSE images with elemental/chemical maps from SIMS. Consequently, the combination of the high-resolution imaging and the chemical sensitivity for the detection of the ion distribution with a lateral resolution of tens of nanometers has been used for the analysis of organic and inorganic systems including chemical segregation of ionic species in hybrid organic inorganic perovskites (HOIPs),[28, 29] impurities in devices,[30] trace element analysis in biological systems.[26] However, all these works focused on analysis of individual elemental species or small molecules. To date, the application of HIM-SIMS for the analysis and quantitation of polymers, in particular polyolefins, has been missing.

In this work, we demonstrate for the first time the HIM-SIMS as an analytical tool for quantitative differentiation between the two polyolefin based polymers, specifically, polyethylene (PE) and polypropylene (PP). We illustrate both quantitative analysis between PE and PP using specific mass fragment ratios as well as spatially resolved imaging of phase separated domains within PE thin films with ~14 nm chemical and ~2 nm iSE spatial resolutions. Furthermore, we validate our results by comparing them with the industry gold standard: ToF-SIMS analysis. Overall, we demonstrate HIM-SIMS as a multimodal chemical technique for imaging and quantification of polyolefin interfaces, that could be more broadly applied to the analysis of multicomponent/multiphase polymeric systems.

RESULTS AND DISCUSSION

To validate the use of HIM-SIMS for polyolefin analysis we benchmarked our results against the ToF-SIMS. Typical ToF-SIMS and HIM-SIMS full range mass spectra in positive ion mode obtained from pure PP and PE thin-film samples are shown in Figure 1. The absolute intensities in each plot were normalized to the highest intensity peak measured in each spectrum for easier comparison between ToF-SIMS and HIM-SIMS data. Polyolefin spectra are composed of peaks of identical hydrocarbon fragments, which is expected, since the only difference between the chemical structures of PP and PE is the presence of a methyl branch (tertiary carbon) instead of a single carbon-carbon bond in the repeating unit of the former. Each group of peaks in Figure 1 corresponds to molecular fragments consisting of the same number of carbon atoms but a varying number of hydrogen atoms. Hydrocarbon fragments containing as much as three carbon atoms can be seen in Figure 1. While ToF-SIMS also allows the peaks of heavier fragments of PP and PE to be detected, HIM-SIMS intensity of the fragments with larger number of carbon atoms is too weak to be resolved for further analysis as the light Ne^+ ion beam breaks the heavier fragments into lighter fragments more so than the heavier Bi_3^+ ion cluster beam in ToF-SIMS as indicated by higher intensity of single (CH_x) and double (C_2H_y) carbon fragments .

Previously, Galuska *et al.*[16] derived a ToF-SIMS methodology for quantitative surface analysis of ethylene-propylene (EP) polymers determining calibration curves to establish the surface content of ethylene and propylene in a mixture. The calibrations were based on the evolution of relative peak intensities of selected fragments ($C_3H_5^+$, $C_4H_7^+$, $C_5H_9^+$, $C_6H_{11}^+$, and $C_8H_{13}^+$) compared to the $C_2H_3^+$ fragment as a function of ethylene content. For quantification of EP concentrations, $C_3H_5^+$and $C_4H_7^+$ ions were evaluated since their enhancement requires only one propylene monomer, which implies that they are independent of the polymer sequence distribution and their intensities should be linearly related to propylene or ethylene concentrations. In a similar way, we focused this research on $C_2H_3^+$ and $C_3H_5^+$ fragments and evaluation of the $C_3H_5^+/C_2H_3^+$ ratio.

It can be seen in Figure 1 that the unique distinction between PP and PE resides in the relative peak intensities. Moreover, from the ToF-SIMS spectra in Figure 1a and 1b, the main difference between PP and PE is indeed the relative intensity of $C_3H_5^+$ fragment compared to $C_2H_3^+$. In order to investigate the ability of the HIM-SIMS to both image and quantitate polyolefin fragmentation, we focused on the analysis of the PE thin films as they have clear chemical phase segregation visible in the HIM iSE images. Pristine PE and PP iSE images can be seen in the Figure 2. PP exhibits mostly uniform surface structure, while PE shows alteration of dark and bright regions. These features can be understood by considering the ability of each polymer to crystallize. Since atactic PP was used during the sample preparation, its methyl groups are randomly aligned and the polymer lacks any regularity, which makes it unable to crystallize,[31] resulting in a uniform appearance of the surface (Figure 2b). On the other hand, PE does not display tacticity, and it is more likely to crystallize resulting in crystallized and non-crystallized domains, where crystallized polymer appears as the darker regions of the surface (Figure 2a) due to more pronounced charging. Therefore, we focused our HIM-SIMS imaging investigation on the PE samples that exhibit different crystallization phase separated domains. HIM-SIMS correlated imaging data of iSE and chemical images of PE polymer fragments CH_3^+, $C_2H_3^+$ and $C_3H_5^+$ are shown in Figure 3a, b, c and d, respectively. Additionally, due to the insulating nature of both the PE and PP thin films, the samples were sputter coated with a 30 nm conductive gold layer for the HIM-SIMS analysis to enable charge compensation. The current HIM-SIMS platform does not allow charge compensation through the use of the electron flood gun when performing SIMS analysis. Despite the insulating nature of most polymers, iSE images of the surfaces of PP (Figure 2b) and PE (Figures 3a and 2a) were directly obtained using the HIM without any coating due to the lower ion flux for iSE imaging as compared to SIMS.

PE exhibits clear surface features (Figure 3) that can be also seen in chemical images when monitoring CH_3^+, $C_2H_3^+$ and $C_3H_5^+$ fragments in both the ToF-SIMS and HIM-SIMS data. Chemical differences are most likely caused by different crystallinity of those regions. However, the higher spatial resolution imaging of the HIM-SIMS allows visualization of chemical variation within the domains that are not resolved when performing ToF-SIMS analysis. Additionally, to investigate the use of HIM-SIMS to depth profile, we performed subsequent SIMS scans of the same area of the PE thin film and revealed buried interfaces inside the film that would otherwise been hidden. Figure 4 a-c shows the iSE images of the PE film morphology, from pristine to after two SIMS scans. As can be seen using the high energy Ne^+ beam, it is possible to sputter through the whole PE film to reveal interfaces and structure within the multiphase domains. The acquired SIMS data of CH_3^+, $C_2H_3^+$ and $C_3H_5^+$ fragments in the PE also reveal unique chemical signatures of buried PE interfaces in the thin film (Figure 4d-4i).

To quantitatively separate PE and PP we collected $C_3H_5^+$ and $C_2H_3^+$ fragment images for both PE and PP thin films and calculated a pixel-by-pixel division of the $C_3H_5^+$ fragment by the $C_2H_3^+$ fragment followed by the extraction of an average value from the resulting image of

$C_3H_5^+/C_2H_3^+$ ratio for both HIM-SIMS and ToF-SIMS acquired data (Figure 5). We performed the calculation across multiple field of views from 50 μm to 250 μm to validate the stability of ratio regardless of the area imaged. We did not do the calculation below 50 μm as there was substantial variability in the PE domains both laterally and horizontally, as seen in Figure 3 and Figure 4, that substantially changed the $C_3H_5^+/C_2H_3^+$ ratio. Results shown in Figure 5a are for HIM-SIMS data and corresponding ToF-SIMS results are shown in Figure 5b. Note that ToF-SIMS does not require a conductive coating of the samples because charge compensation is provided by an electron flood gun. Both methods demonstrate clear separation between PE and PP. For instance, $C_3H_5^+/C_2H_3^+$ ratio from ToF-SIMS ranges from 4 to 4.4 for PP and from 2.6 to 3 for PE (Figure 5b). Similarly, HIM-SIMS revealed ratio in the range 1.8 – 2.2 for PP and 1.2 – 1.5 for PE (Figure 5a). While values of the ratios are different for HIM-SIMS and ToF-SIMS due to different primary ion sources (Ne^+ and Bi_3^+, respectively) and fundamentals of the secondary ion detection process, both techniques demonstrate the possibility of separating PP and PE using relative intensity of $C_3H_5^+$ fragment when compared to $C_2H_3^+$ fragment. Ratios obtained for HIM-SIMS allow clear distinction between the polymers at the all fields-of-view above 100 μm. Variations at lower fields-of-view are most likely related with charging effect.

CONCLUSIONS

In this work, we demonstrate for the first time the use of HIM-SIMS for analytical characterization of polyolefins. We show that using unique mass fragment abundance ratios we are able to quantitatively separate between PE and PP in thin-film samples and validate our results by comparing them to ToF-SIMS data, which is the industry gold standard. Additionality, using HIM-SIMS imaging we are able spatially resolve different chemical phases in the PE thin-films with ~14 nm spatial resolutions and use the HIM-SIMS for depth profiling of the domains to reveal buried interfaces. Overall, we demonstrate HIM-SIMS as a multimodal chemical technique for imaging and quantification of polyolefin interfaces that could be more broadly applied to the analysis of multicomponent/multiphase polymeric systems.

METHODS

Sample preparation.

Polypropylene (PP, atactic, Sigma-Aldrich) and polyethylene (PE, LDPE-type wax, ExxonMobil Chemical Co.) specimens were prepared by dissolving the samples in hot xylene at a concentration of ~ 1 wt%. Approximately 1 mL of hot solution was placed on a silicon wafer, which was then spun at 2000 rpm for 60 seconds. The resulting thin film was allowed to air dry for several hours before storage in a closed container for protection.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS).

ToF-SIMS analysis was performed using an IONTOF TOF.SIMS.5-NSC (IONTOF GmbH, Münster, Germany). The vacuum in the chamber did not exceed 1×10^{-8} Torr during the experiments. The primary source was a Bi_3^+ liquid metal ion source with 30 keV and 31.8 nA current operating in pulsed mode with 5 ns pulse width. Imaging was performed with different fields-of-view (50 – 250 μm) over 256 x 256 grid in random rastering mode. Secondary ions were analyzed in positive ion detection mode with mass resolution $m/\Delta m$ = 1,000 – 7,000. Low energy electron flooding was used for charge compensation.

Helium ion microscopy (HIM) with secondary ion mass spectrometry (HIM-SIMS).

HIM-SIMS analysis of the polymers was performed using Zeiss ORION Nanofab helium ion microscope (Carl Zeiss Microscopy GmbH, Jena, Germany) with a double focusing magnetic sector spectrometer with parallel detection for SIMS. The chamber pressure was $\sim1.2\times10^{-6}$ Torr when using a Ne^+ focused ion beam with an acceleration voltage of 15 kV. The beam current was ca. 10-15 pA with a 40 μm molybdenum aperture. Mass spectra were acquired in positive ion mode by rastering Ne^+ ion beam over a 50×50 μm^2 area using a 128 × 128 pixel density with a magnetic field of 300 mT. Mass calibration was performed using ToF-SIMS spectra of the samples. Chemical imaging was done at specific mass peaks described in detail in the main text. To minimize charging, polymer samples were coated with a 30-nm thick gold layer by sputter deposition. Chemical imaging was done with 500 mT magnetic field. Images were collected at 256 × 256 and 512 x 512 pixels with a dwell time of 1000 μs per pixel.

Gold coating of the samples.

AJA International ATC 2400 sputterer with a gold target at a chamber pressure of 25 mTorr, and an argon flow of 25 cm^3/min was used for coating the samples. The gun was set at 7 watts, and 30 nm of Au was deposited.

Data availability

All data used in this manuscript is available from the lead author on request.

Author Contributions

AAT performed HIM-SIMS experiments. AAT, ML, AVI contributed to the acquisition of ToF-SIMS data. OSO, NB, AVI analyzed HIM-SIMS and ToF-SIMS the results. DA and WL prepared polypropylene and polyethylene samples and contributed to SIMS analysis. STK and NB developed and expended Python scripts for the extraction and processing of HIM-SIMS and ToF-SIMS spectra and chemical images. AVI and OSO supervised the project and analyzed data. All authors discussed the results and co-wrote the manuscript.

Acknowledgements

The research was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy (DOE) Office of Science User Facility. AAT, WL, DA were supported by ExxonMobil Chemical Company. The authors are grateful to Dr. Dale K. Hensley at CNMS for performing gold coating of the samples.

Competing interests: The authors declare no competing interests.

Figures

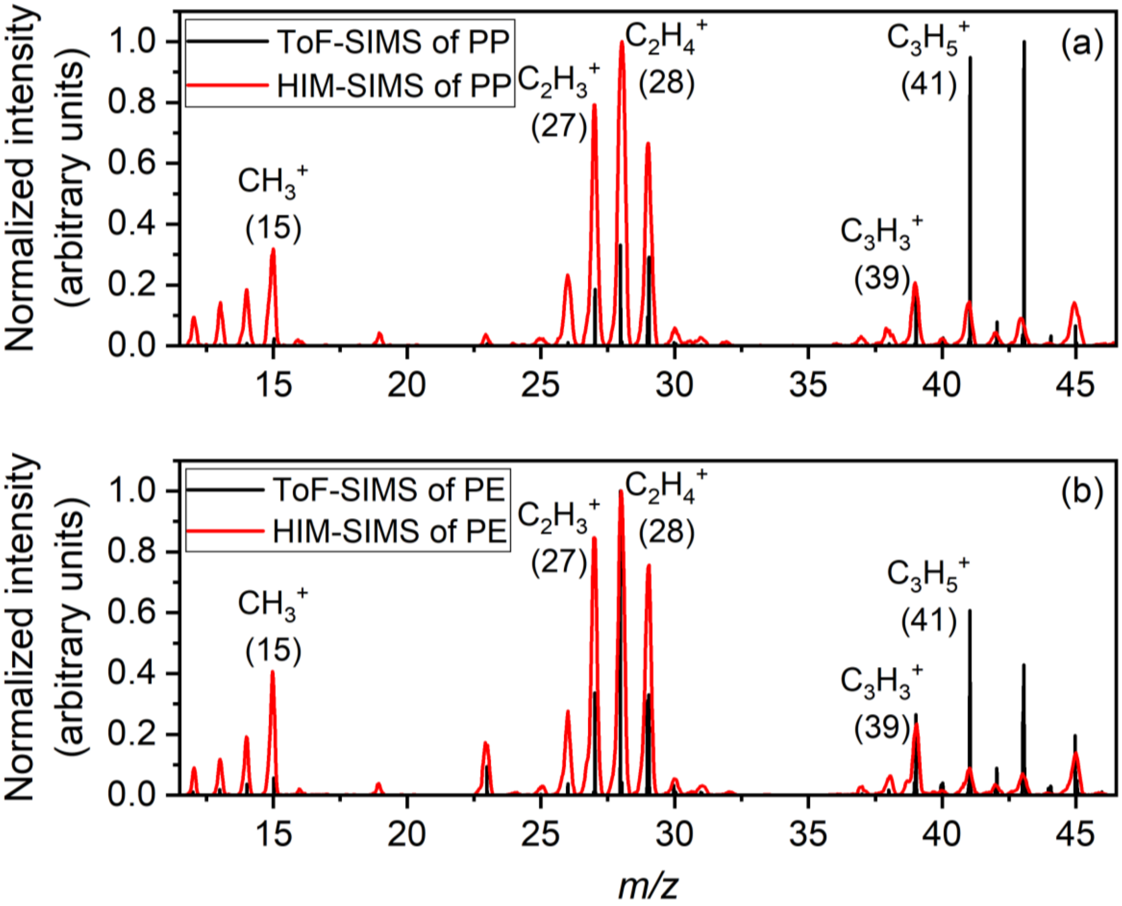

Figure 1. Normalized ToF-SIMS and HIM-SIMS positive mode mass spectra obtained from (a) polypropylene (PP) and (b) polyethylene (PE). HIM-SIMS data had a 30 nm Au-coating sputter coated on the sample for charge compensation. ToF-SIMS data were collected on pristine films with an electron flood gun for charge compensation. The absolute intensities in each plot were normalized to the highest intensity peak measured in each spectrum for easier comparison between ToF-SIMS and HIM-SIMS data.

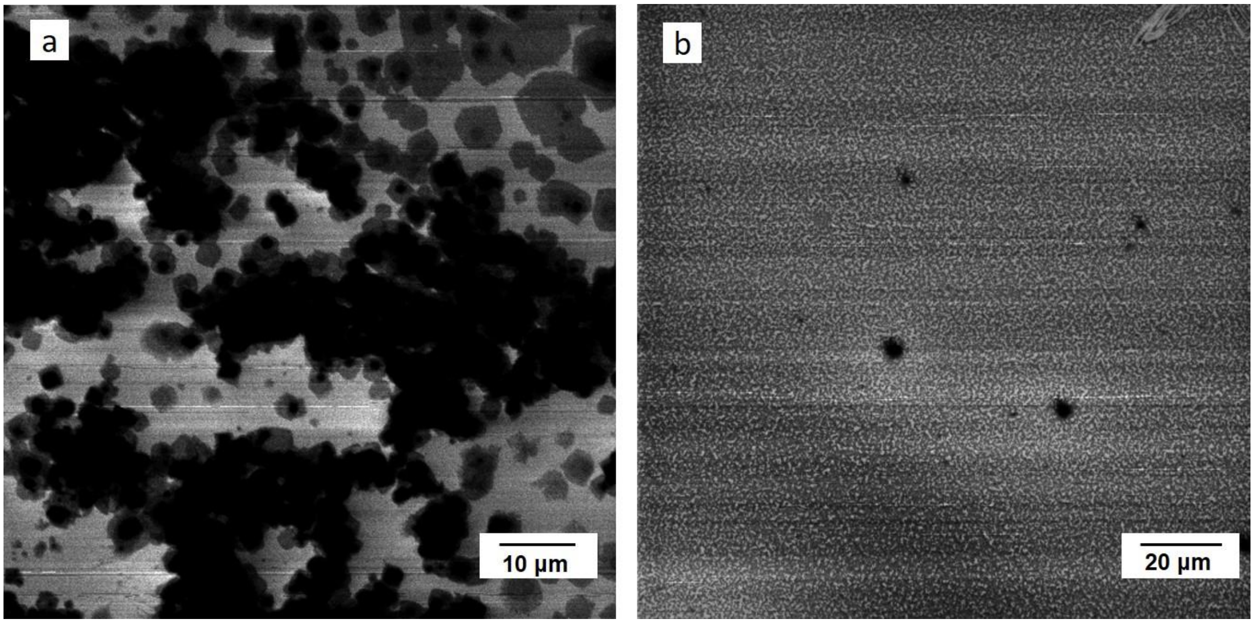

Figure 2. Helium ion microscopy iSE imaging of pristine PE and PP. (a) PE and (b) PP. Dwell time was 50 µm and He+ beam current was at 6.89 pA and 18 pA respectively.

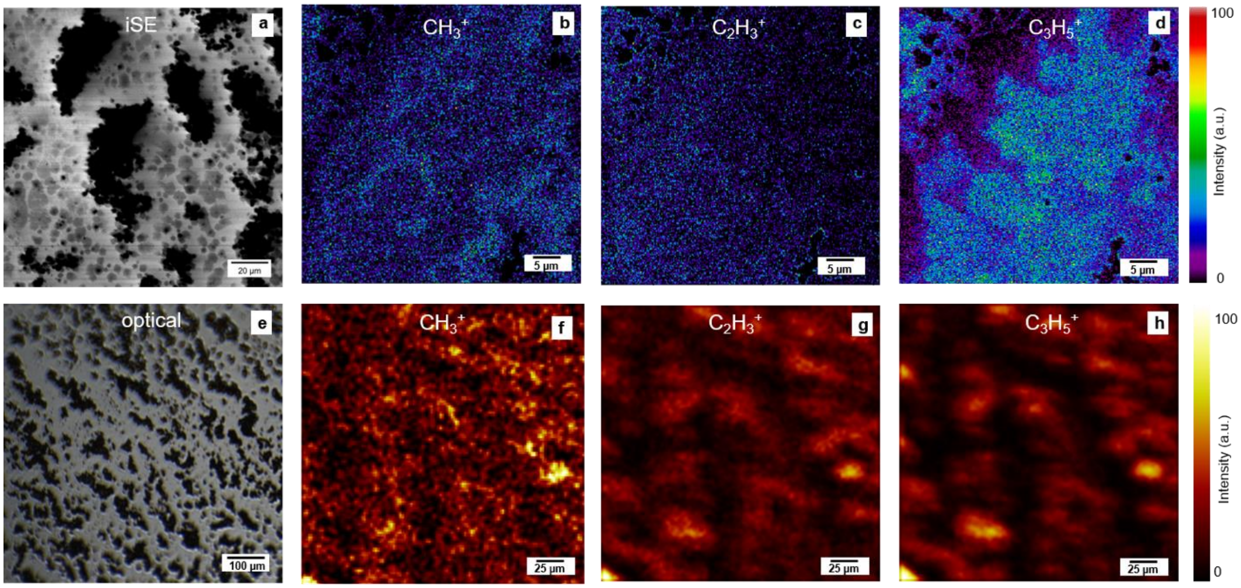

Figure 3. Chemical imaging of polyethylene. (a) HIM secondary electron image of polyethylene. HIM-SIMS chemical images (50 µm FOV) for fragments of (b) CH_3^+ (c) $C_2H_3^+$ (d) $C_3H_5^+$. ToF-SIMS analysis of polyethylene (e) Optical image of polyethylene, ToF-SIMS chemical images (260 µm FOV) for fragments of (f) CH_3^+, (g) $C_2H_3^+$ (h) $C_3H_5^+$. For the HIM-SIMS data in b-d, a 30 nm Au-coating has been sputter coated on the sample for charge compensation. ToF-SIMS data in f-h were collected on pristine films with an electron flood gun for charge compensation.

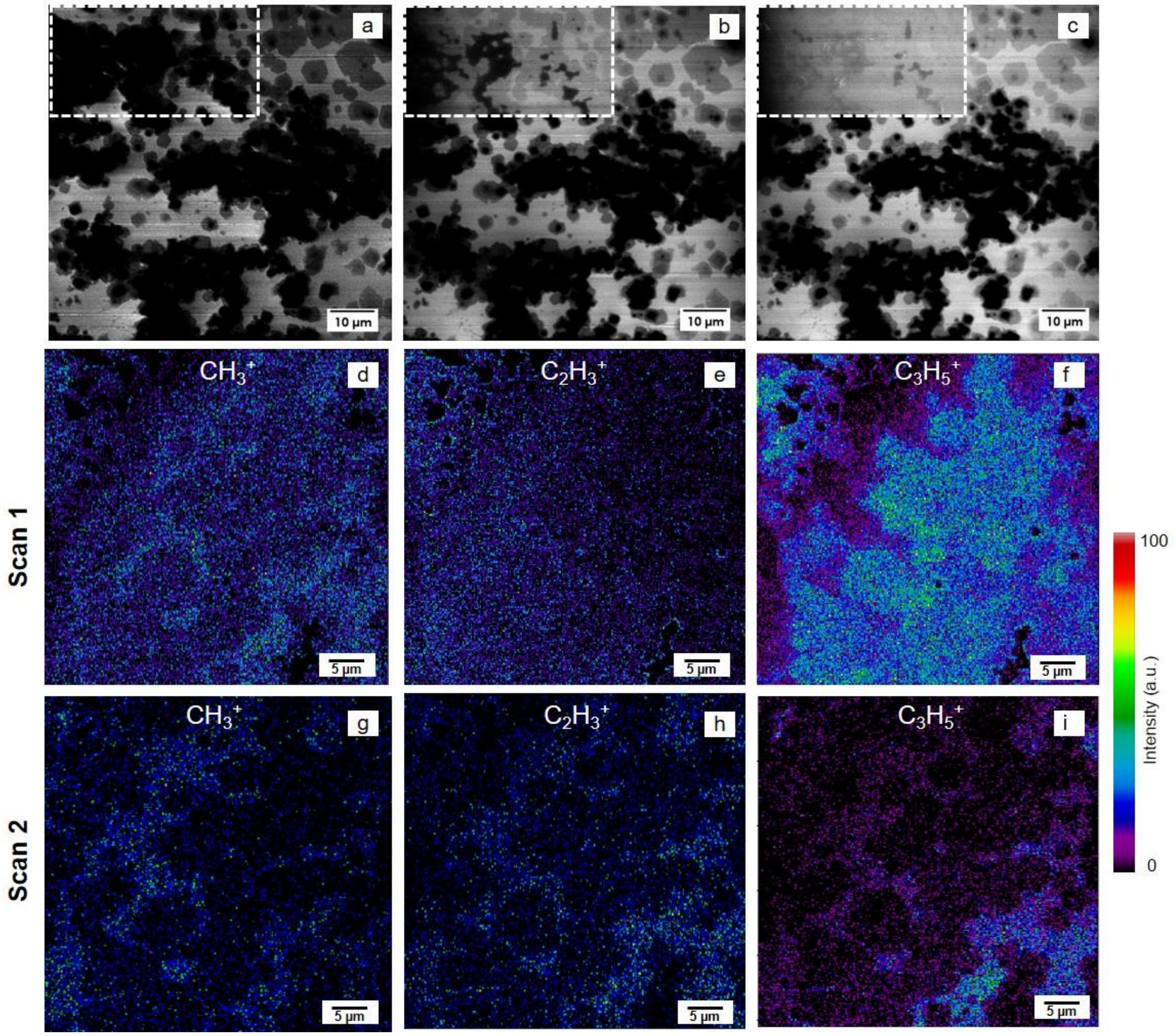

Figure 4. Depth profiling of polyethylene. HIM iSE images of polyethylene, (a) pristine (b) after one SIMS Scan, (c) after two SIMS scans, white dashed box indicates SIMS scanned area. HIM-SIMS chemical images after Scan 1 (d) CH_3^+ (e) $C_2H_3^+$ (f) $C_3H_5^+$ and after Scan 2 (g) CH_3^+ (h) $C_2H_3^+$ (i) $C_3H_5^+$. HIM-SIMS data in d-i has a 30 nm Au-coating sputter coated on the sample for charge compensation.

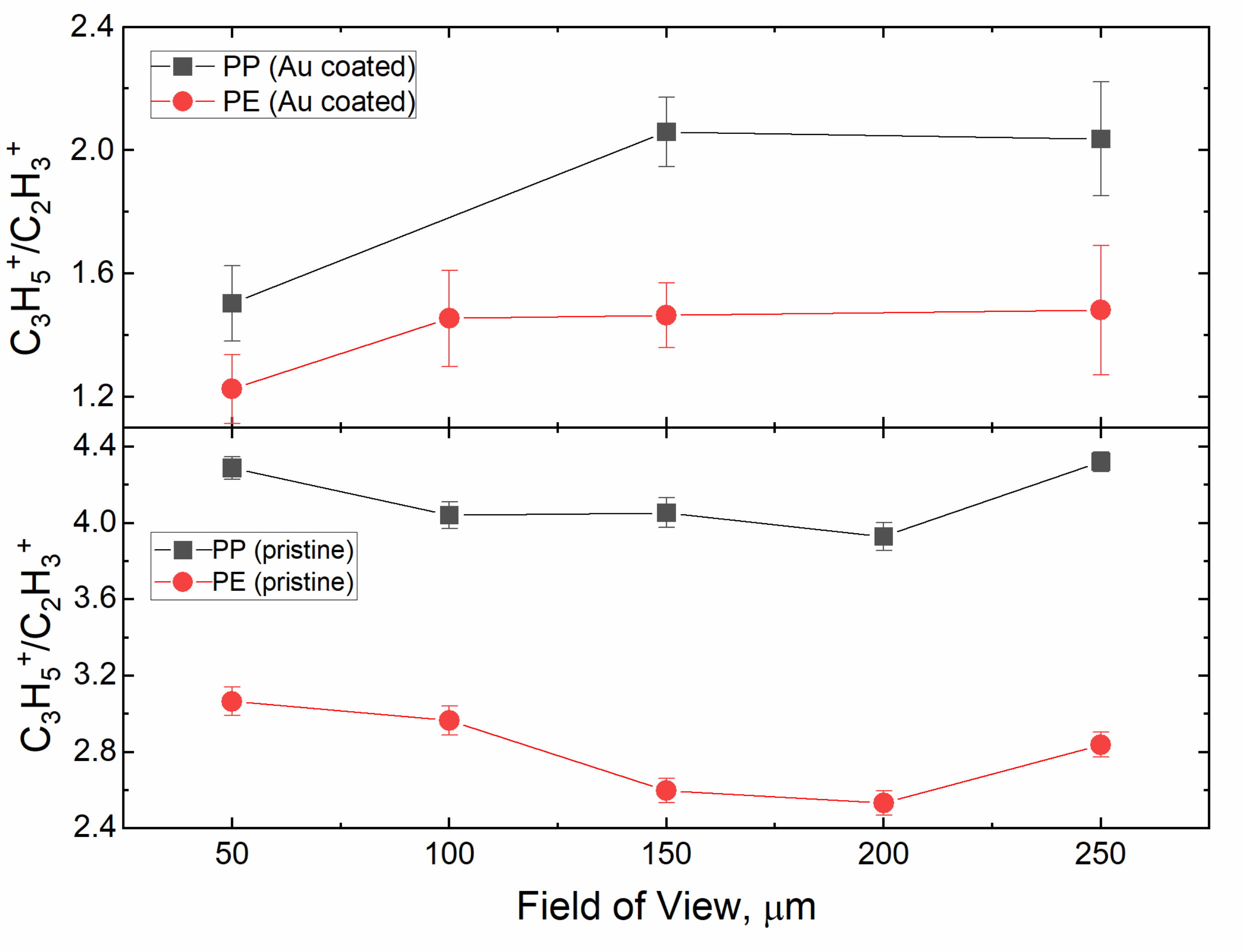

Figure 5. Plot of $C_3H_5^+/C_2H_3^+$ ratio for polypropylene and polyethylene as a function of field of view (FOV) using (a) HIM-SIMS and Au-coating of the sample surface and (b) ToF-SIMS with electron flood gun.

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