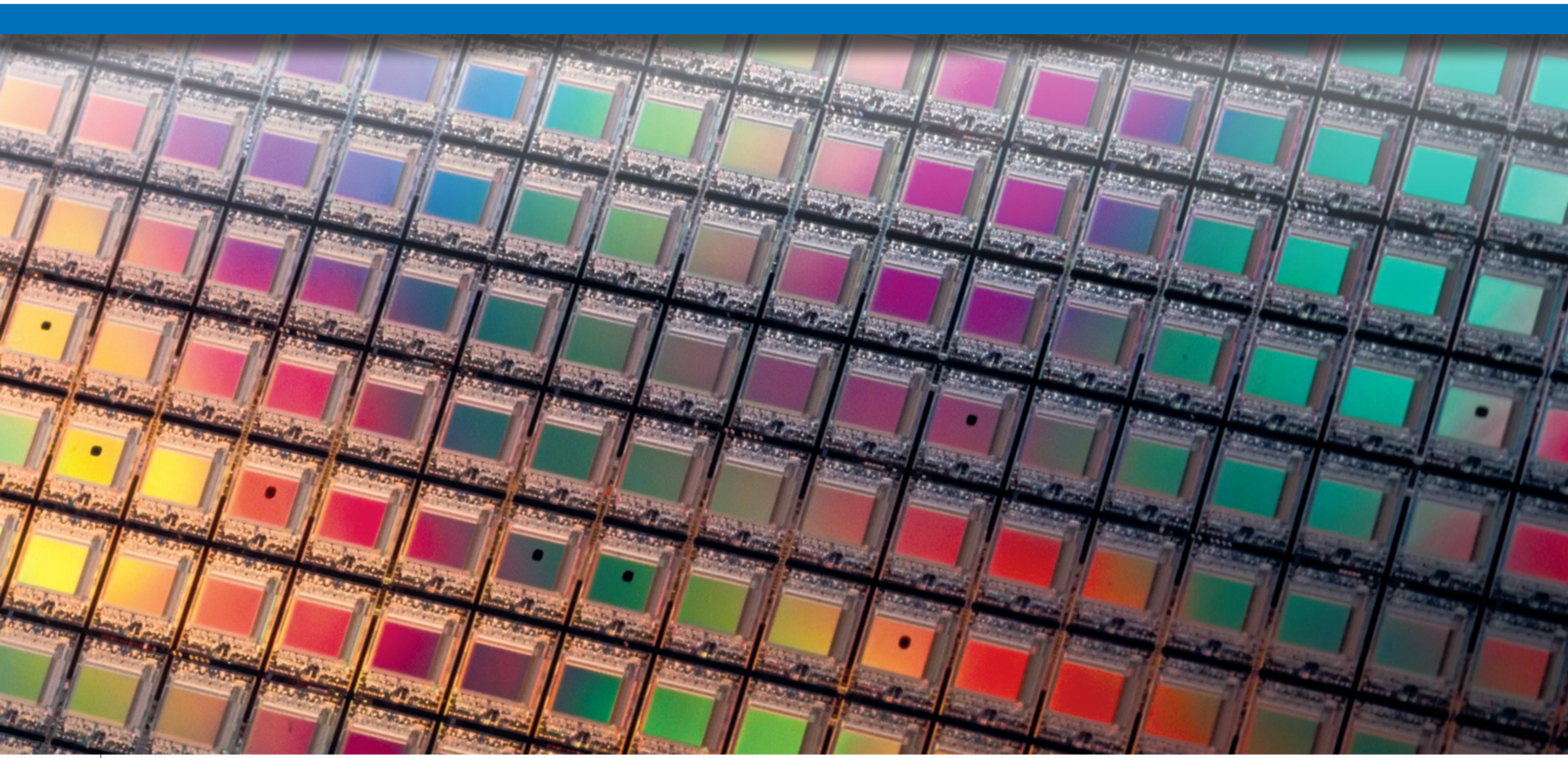

Surface Layer MALDI-MSI of Synthetic Materials on a Molecular Level

A surface-layer matrix-assisted laser desorption ionization mass spectrometry imaging technique (SL-MALDI-MSI) is developed to study the chemical composition of multicomponent polymer surfaces.

Abstract

Using this technique, four different types of surface defects caused by contamination, masking, abrasion, and solvation at the surface of poly(methyl methacrylate) and polystyrene thin films are analyzed. An UltrafleX-III MALDI-TOF/TOF MS with a Nd/YAG laser and a rapifleX MALDI-TOF/TOF MS with a smartbeam 3D laser are used for the analysis.

Introduction

Synthetic material surfaces play an important role in several industrial and medical processes such as catalysis, adhesion, printing, coatings, biomedical device applications and more. These processes depend on the consistency of the chemical composition across the surface on a molecular level. However, this consistency is easily disrupted by the synthesis and/or processing techniques of the material which

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can impart various types of surface defects such as abrasion, degradation, contamination with other materials, and many more.

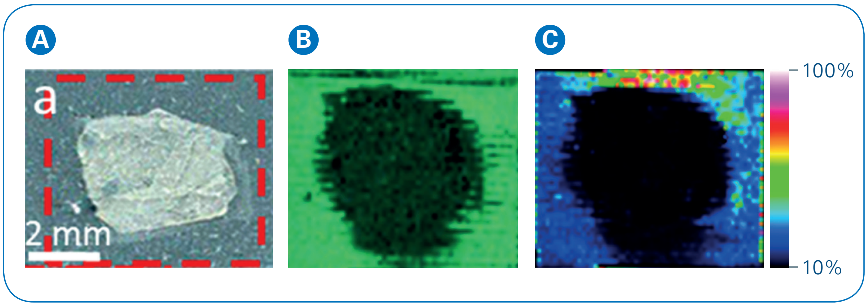

Figure 1: Ⓐ Optical image of the PS stamp defect on a PMMA thin film. Ⓑ and Ⓒ SL-MALDI images constructed by summing the intensities of Ⓑ [PMMAn + Na]+ (n = 45-73) ions or Ⓒ all ions within m/z *3500-8500. Reprinted with permission from Anal. Chem. 2018,* ***90*** *(22), 13427-13433. © 2018 American Chemical Society.*

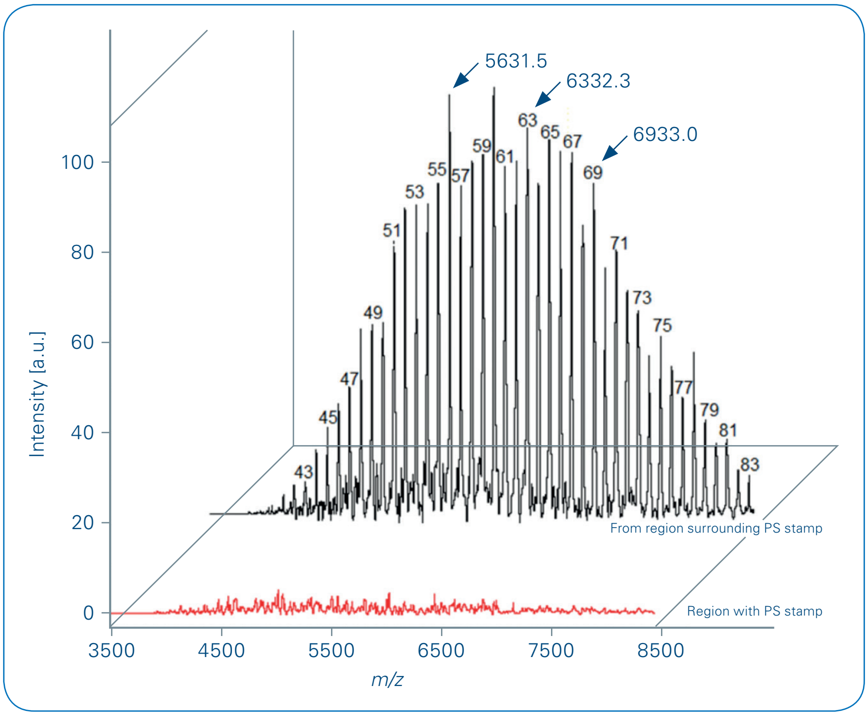

Figure 2: Stacked SL-MALDI-MS spectra extracted from (top, in black) the PMMA region surrounding the PS stamp in Figure 1a and (bottom, in red) the region within the PS stamp. The [PMMA$_n$ + Na]$^+$ oligomers are labelled by their n-mer size; select average m/z *values are given next to the corresponding n-mer peaks. Reprinted with permission from Anal. Chem. 2018,* ***90*** *(22), 13427-13433. © 2018 American Chemical Society.*

To date, several analytical techniques have been developed to characterize the chemical composition of synthetic material surfaces. Among these are time-of-flight secondary ion mass spectrometry (ToF SIMS), surface-assisted laser desorption ionization mass spectrometry imaging (SALDI-MSI), laser desorption ionization mass spectrometry (LDI-MS), X-ray photoelectron spectroscopy (XPS), and more. Each technique has its own advantages and disadvantages; however, none of these techniques provides direct information on the actual composition of specific molecules at the surface. But rather, these techniques probe compositions of segments, molecular fragments, and/or atoms. In contrast, matrix-assisted laser desorption ionization mass spectrometry imaging (MALDI-MSI) produces intact molecular ions, generating less convoluted spectra in a timely manner [1].

MALDI-MSI has been extensively used in the study of biological samples, such as in the localization of peptides, proteins, drugs and metabolites within biological tissues. The use of MALDI-MSI in industrial applications is still limited, although similar information on the spatial distribution of additives, copolymers or degradation products in synthetic polymers is also highly desired. A few examples where MALDI-MSI has been used in industry include the study of polystyrene film changes as they were UV-irradiated [2], the investigation of the degradation of polycaprolactone diol exposed to different wastewater treatments [3], the study of molecular level changes in ultrahigh molecular weight polyethylene joint implants in correlation with lipid adsorption [4], and others. In all these examples, however, the sample preparation procedure utilized involve solvent-based matrix and cationizing salt application methods that can penetrate and perturb the surface composition.

Herein, a surface-layer MALDI-MSI technique that uses a solvent-free matrix application procedure is presented. In this technique, MALDI matrices and cationizing salts are sublimed onto the synthetic material surface to be analyzed. Based on intact molecular ion detection, surface-specific analysis with a depth resolution of about 2 nm was achieved. To demonstrate the usefulness of this technique, surface defects on polystyrene (PS) and poly(methyl methacrylate (PMMA) thin films caused by contamination, masking, scratching/abrasion, and solvation were generated and analyzed.

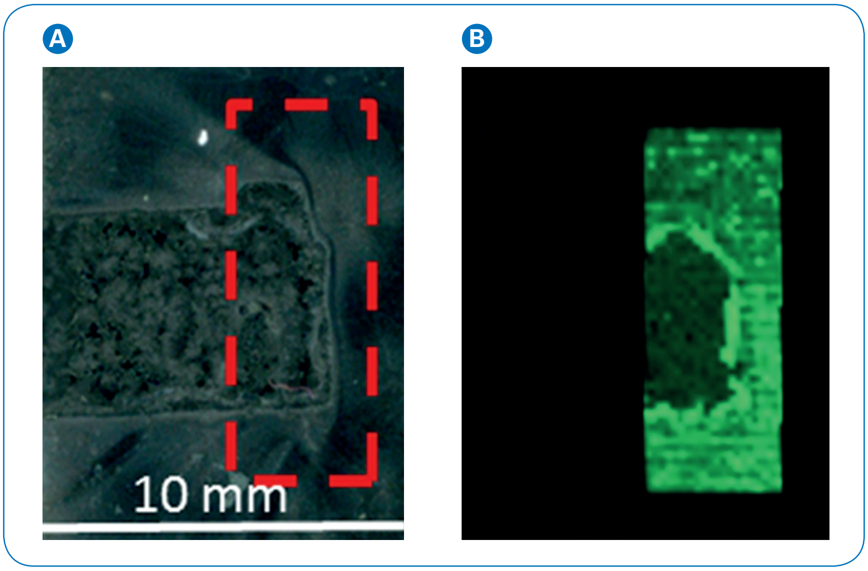

Figure 3: Ⓐ Optical and Ⓑ SL-MALDI MS images of a PMMA thin film in which some PMMA is missing because of the tape masking that part of the wafer during spin-casting was removed. The region-of-interest is indicated by the red dashed box. Reprinted with permission from Anal. Chem. 2018, ***90*** *(22), 13427-13433. © 2018 American Chemical Society.*

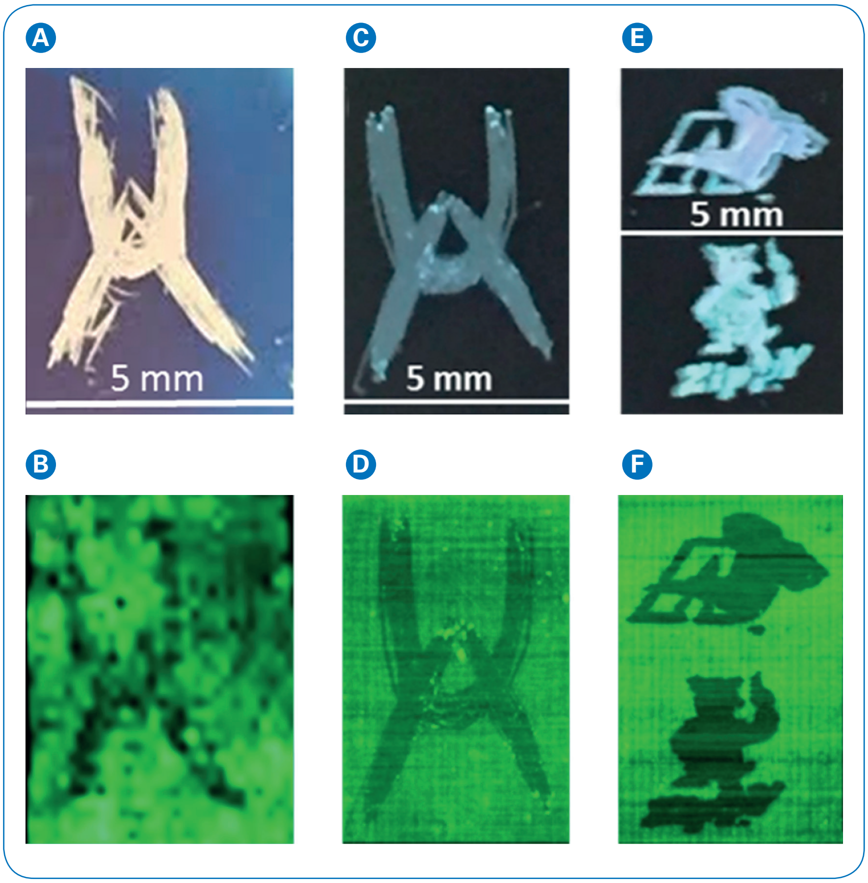

Figure 4: Ⓐ and Ⓒ Optical image of the UA logo scribed on the surface of a PMMA film and Ⓑ and Ⓓ corresponding 200 µm resolution SL-MALDI-MS images acquired with the UltraFlex mass spectrometer and the RapifleX mass spectrometer, respectively. Ⓔ Optical images of "Akron Zips" logo (top) and "Zippy" mascot (bottom) laser-etched on the surface of a PMMA film and Ⓕ corresponding SL-MALDI-MS images acquired with the RapifleX mass spectrometer. Reprinted with permission from Anal. Chem. 2018, ***90*** *(22), 13427-13433. © 2018 American Chemical Society.*

Methods and Materials

Instrumentation

A Bruker Ultraflex-III MALDI-TOF/TOF mass spectrometer, equipped with a Nd/YAG laser, and a rapifleX MALDI- TOF/TOF mass spectrometer, equipped with a smartbeam 3D laser, were used for analysis. All spectra were recorded in the linear positive mode. A polystyrene standard (Mn: 6.1 kDa, PDI: 1.05) from Scientific Polymer Products in in Ontario, NY, USA, was used for external calibration of the instrument prior to analysis. Optical images were recorded with an Epson optical scanner. Film thicknesses were determined with a spectroscopic ellipsometer (VASE, M-200 UV-Visible-NIR 240-1700 nm, J. A. Woollam Co., Inc., Lincoln, NE, USA).

Sample Preparation

Thin film fabrication

Using a PMMA (~ 7 kDa) sample purchased from Polymer Source Incorporated and a PS (~ 6 kDa) sample synthesized at the University of Akron, PS and PMMA thin films were prepared by spin-casting from toluene solutions of 1-3 wt % polymer at a rate of 2000 rpm onto silicon wafers cleaned in piranha solution.

Matrix and Cationizing Agent Sublimation

The matrix and cationizing agent were applied by sublimation for 3-4 h at 90°C. Using double-sided scotch tape, samples were attached to the condenser portion of the sublimation apparatus facing the bottom of the apparatus, where the matrix and cationizing agents were located. DHB (2,5-dihydroxybenzoic acid) and DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile) were used as matrices and NaTFA (sodium trifluoroacetate) and AgTFA (silver trifluoroacetate) as cationizing salts.

Data Analysis

For the profiling of the PS and PMMA thin films, the obtained spectra were processed using the flexImaging software version 2.1 (Bruker Daltonik GmbH). Peak series corresponding to each polymer were selected and assigned a color, green for PMMA and purple for PS.

Results

Analysis of surface defects caused by contamination

Surface defects by contamination were created by stamping pure molten PS on a PMMA thin film using a polydimethylsiloxane stamp, and subsequently cooling it to allow vitrification of the stamped material (Figure 1A). A layer of DHB matrix and NaTFA salt was sublimed on the entire surface of the PMMA film, and the sample was imaged.

As can be seen in Figure 1B, the collected images showed lack of ionization in the area where the PS stamp was located, even when the entire *m/z* 3500-8500 range was scanned (Figure 1C). The SL-MALDI images display $[\text{PMMA} + \text{Na}]^+$ ions which contour the PS stamps. Each PMMA oligomer was selected and color labelled in green to contrast the negative image from the PS stamp defect. The SL-MALDI-MS spectra collected from the PS stamp region did not show any noticeable signal resembling a PS or PMMA distribution (Figure 2).

Analysis of surface defects caused by masking

Surface defects by masking were achieved by placing scotch tape on a silicon wafer substrate in two separate locations before spin-casting a PMMA thin film. After spin-coating, the tape was removed to ensure that no PMMA was deposited on the wafer in those locations, and a layer of DCTB matrix and NaTFA salt was sublimed onto the entire surface of the film prior to imaging.

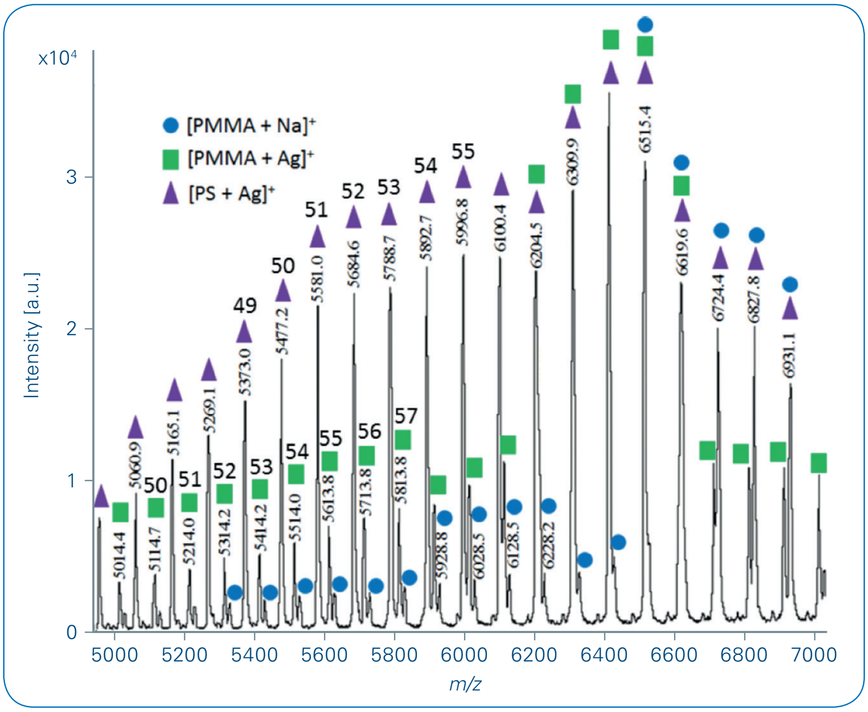

*Figure 5: Conventional MALDI-MS spectrum of a PS and PMMA mixture in presence of the AgTFA and NaTFA cationizing salts along with DCTB matrix. Reprinted with permission from Anal. Chem. 2018, **90** (22), 13427-13433. © 2018 American Chemical Society.*

The resulting SL-MALDI-MS image of the thin film (Figure 3), constructed from sodiated PMMAn oligomers with *n* = 50-72, revealed the regions where the PMMA film was removed when the tape was removed.

Analysis of surface defects caused by scratching

In order to create mechanical surface defects, a stacked UA (University of Akron) logo and/or the university's kangaroo mascot were either scratched or laser etched into a PMMA film, and the film was imaged.

The defects caused by mechanical scratching or laser-etching of the film surfaces are clearly visible in the corresponding SL-MALDI-MS images generated by displaying the summed intensities of the sodiated PMMA_n oligomers with *n* = 50-72 in green (Figure 4). For a clearer SL-MALDI-MS image of the scratch defect, the rapifleX MALDI-TOF/TOF mass spectrometer with higher spatial resolution was used and allowed for better and more uniform signal as compared to the older Bruker Ultraflex-III MALDI-TOF/TOF mass spectrometer (Figure 4B vs Figure 4D&F).

Analysis of surface defects caused by solvation

Finally, surface defects were created by spin casting a PS layer onto an underlying spun cast PMMA film and exposing the resulting bilayer films to cyclohexane. In one case, PS was washed off the film using cyclohexane from a syringe, while in the other case the PS and PMMA bilayer film was dipped in a bath of cyclohexane four times. A mixture of DCTB matrix with AgTFA and NaTFA cationizing salts was used, as Ag^+ and Na^+ are the cationizing species commonly used for PS and PMMA respectively.

Similarly to a conventional MALDI MS analysis performed on a PS and PMMA mixture in presence of the two salts, PMMA was found to ionize more efficiently by Ag$^+$ adduction (Figure 5). As a result, [PMMA + Ag]$^+$ ions, displayed in green, and [PS + Ag]$^+$ ions, displayed in purple, were used for SL-MALDI imaging of the partially washed bilayer film.

As anticipated, [PMMA + Ag]$^+$ ions (n = 50-57) are detected only in the solvent perturbed region (green area in Figure 6B,D), whereas [PS + Ag]$^+$ ions (n = 49-55) are found only within the unperturbed region (purple area in Figure 6C,D). This result is consistent with the fact that cyclohexane, as a nonpolar solvent, selectively dissolves the relatively nonpolar PS without affecting the underlying polar PMMA.

Furthermore, an intensity profile measured laterally to determine the composition of each raster position across the bilayer film exhibited an immediate shift from PMMA to PS from one raster point to the adjacent point, distinctively defining the interface between washed and unwashed surface (Figure 6E). Ion signals from each polymer type are distinctively representative of the regions they are detected from and no PMMA ions were observed in the unperturbed part of the surface, substantiating the surface specificity of the imaging method.

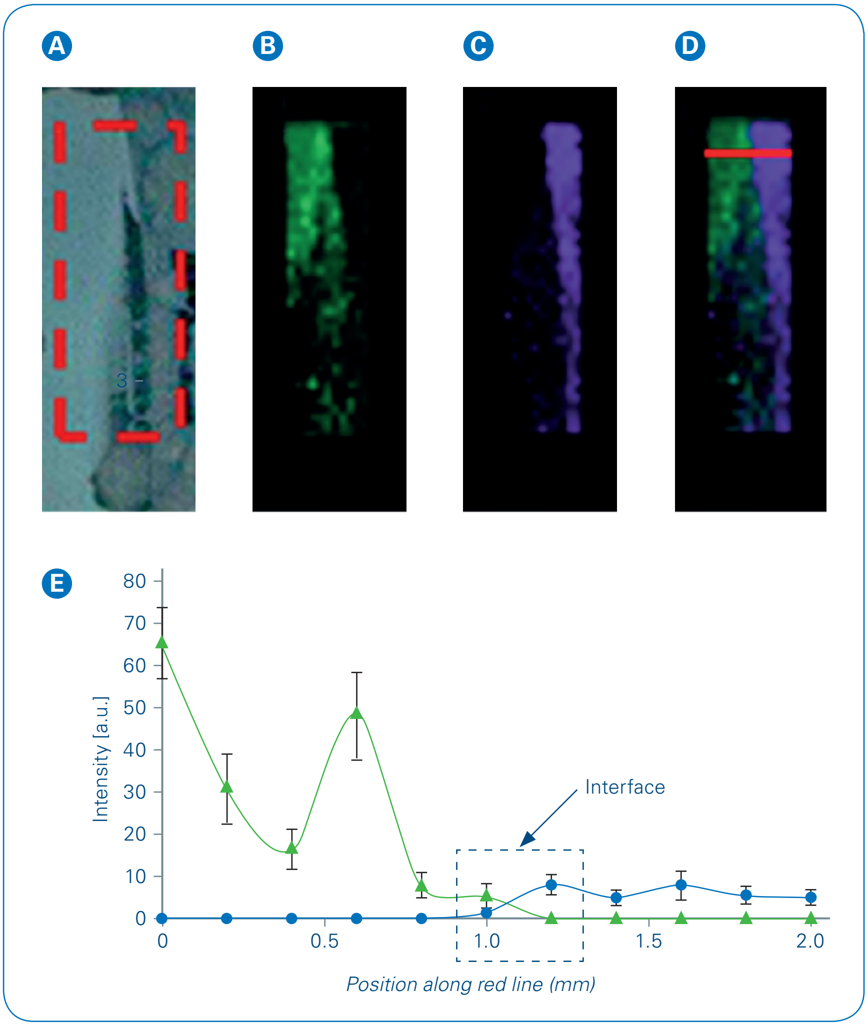

*Figure 6: Ⓐ Optical image and (Ⓑ-Ⓓ) SL-MALDI-MS images of a PS/PMMA bilayer prepared by spin casting a PS layer onto a spun cast PMMA film, and then removing (from the left side) half of the top PS layer by dissolving in cyclohexane. Ⓔ Intensity profile along the red line in Ⓓ showing the uncovered PMMA from the washed region (left, in green) and the PS surface in the unperturbed part (right, in purple). Reprinted with permission from Anal. Chem. 2018, **90** (22), 13427-13433. © 2018 American Chemical Society.*

Conclusion

- In this study, SL-MALDI-MSI, a novel surface imaging technique is used to achieve conclusive chemical analysis of material surfaces with high sensitivity and specificity. For the first time, a mixture of MALDI matrix and cationizing salt was sublimed onto the surface of a multicomponent sample of synthetic polymers. The data presented establish SL-MALDI-MSI as the first analytical technique capable of providing surface images from intact molecular ions obtained from the sample within 2 nm of the surface.

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