Analytical Chemistry

Supporting Information

Surface Layer Matrix-Assisted Laser Desorption Ionization Mass Spectrometry Imaging: A Surface Imaging Technique for the Molecular-Level Analysis of Synthetic Material Surfaces

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Contents:

Reference MALDI-MS spectrum of bulk PMMA; replicate SL-MALDI-MSI results; and single scans from intact and defect areas of the polymer films examined

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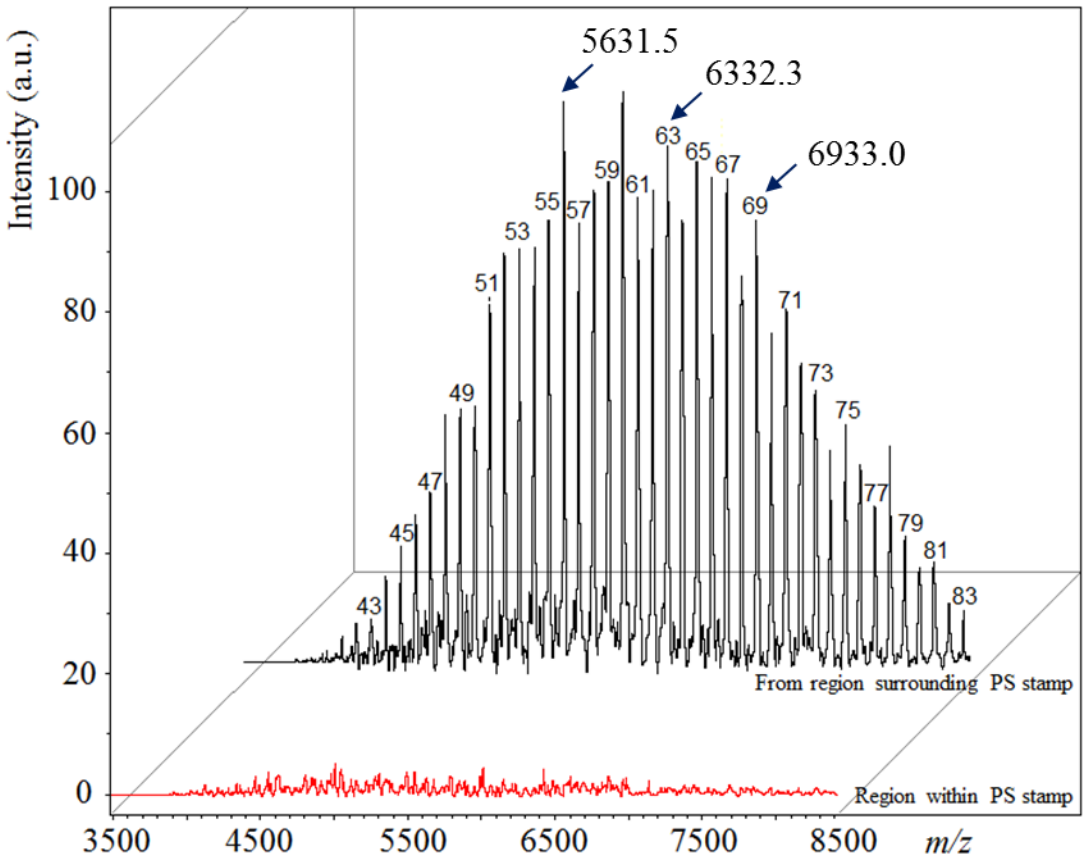

Figure S1. Stacked SL-MALDI-MS spectra extracted from (top, in black) the PMMA region surrounding the PS stamp in Figure 1 and (bottom, in red) the region within the PS stamp. The $[PMMA_n + Na]^+$ oligomers are labelled by their *n*-mer size; select average *m/z* values are given next to the corresponding *n*-mer peaks. The spectrum from the region within the PS stamp is low-level noise and does not contain any distinguishable polymer distribution. These two spectra are examples of similar spectra acquired from their respective regions of the surface. The lack of ions from the ROI of the PS stamp is attributed to the low ionization efficiency of PS by Na^+ adduction (PS is preferentially ionized by Ag^+) and to the rough and uneven surface of the stamp which defocuses any $[PS_n + Na]^+$ ions formed.

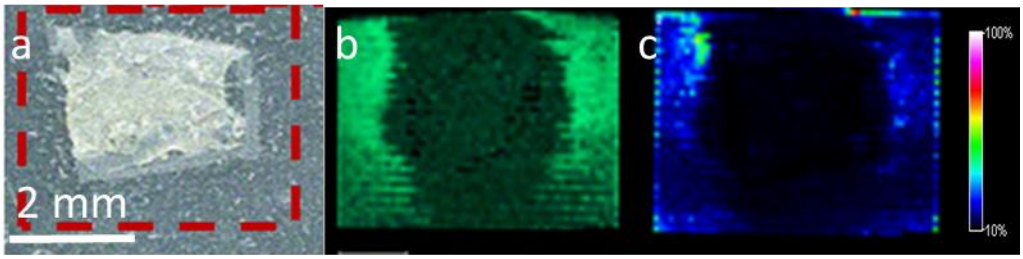

Figure S2. (a) Optical and (b,c) SL-MALDI images of a 6 kDa PS stamp defect on a 7 kDa PMMA thin film. The SL-MALDI images were constructed by summing the intensities of (b) $[PMMA_n + Na]^+$ ($n = 45$-73) ions or (c) all ions within *m/z* 3500-8500. DHB and NaTFA (3:2 w/w) were sublimated onto the entire polymer-air interface. The PS stamped onto the surface hindered the ionization of PMMA underneath it. The SL-MALDI image clearly outlines the foreign material (PS), displaying defects specific to the surface. See Figure 1 for SL-MALDI-MSI of a different PS stamp.

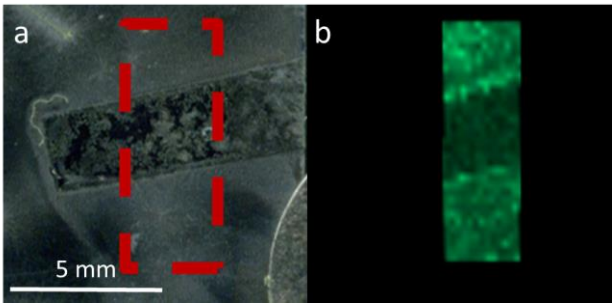

Figure S3. (a) Optical and (b) SL-MALDI images of a 7 kDa PMMA thin film in which PMMA is missing in one region because the tape masking part of the wafer during spin casting was removed. DCTB matrix and NaTFA (3:2 w/w) were sublimated onto the film-air interface after tape removal. The optical image shows the film after matrix/salt sublimation, with the region-of-interest indicated by the red dashed box. The SL-MALDI image was created by summing the intensities of $[PMMA_n + Na]^+$ (n = 50-72) ions and is displayed in green; it documents where PMMA is missing because it was removed when the tape was removed. See Figure 2 for SL-MALDI-MSI of a PMMA film spun cast on a differently masked wafer.

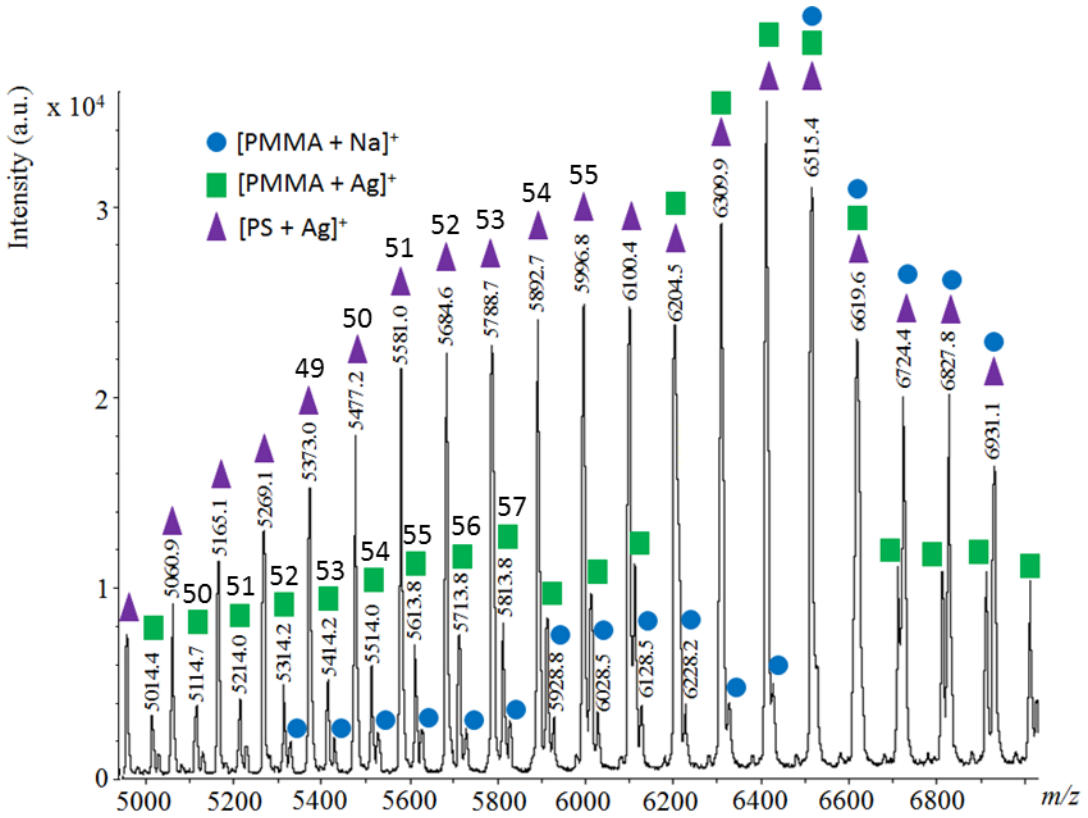

Figure S4. Conventional MALDI-MS spectrum of a 6 kDa PS / 7 kDa PMMA blend (10 mg/mL each in acetonitrile:tetrahydrofuran 9:1 v/v), mixed with sodium and silver trifluoroacetate salts (10 mg/mL each in acetonitrile) and DCTB matrix (20 mg/mL in acetonitrile). PMMA was ionized to $[PMMA + Na]^+$ ions (blue circles) as well as more abundant $[PMMA + Ag]^+$ ions (green squares), whereas PS only formed $[PS + Ag]^+$ ions. Because of the similar masses of the PMMA and PS repeat units (100 vs. 104 Da, respectively, some of these distributions overlap at *m/z* >6100. The number of repeat units in the oligomers used for imaging defects on PS/PMMA bilayer films are marked on top of the corresponding symbols; there is no or minimal isotope cluster overlap in the *m/z* window of these oligomers, all of which appear at *m/z* <6100.

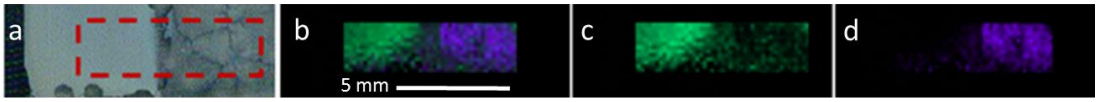

Figure S5. (a) Optical image and (b-d) SL-MALDI-MS images of a bilayer film prepared by spin casting a 6 kDa PS layer onto a spun cast 7 kDa PMMA film, and then removing (from left side) half of the top PS layer by dissolving it in cyclohexane. The optical image is shown after a mixture of matrix and cationizing salts was sublimated onto the film. The area indicated by the red dashed line was imaged using summed $[PMMA_{50\text{-}57} + Ag]^+$ (green) and $[PS_{49\text{-}55} + Ag]^+$ (purple) intensities. A clear interface is observed between the washed region, in which the underlying PMMA layer (green) is uncovered, and the unperturbed PS region (purple). See Figure 4 for the images of a different bilayer film that was partially dipped into cyclohexane.

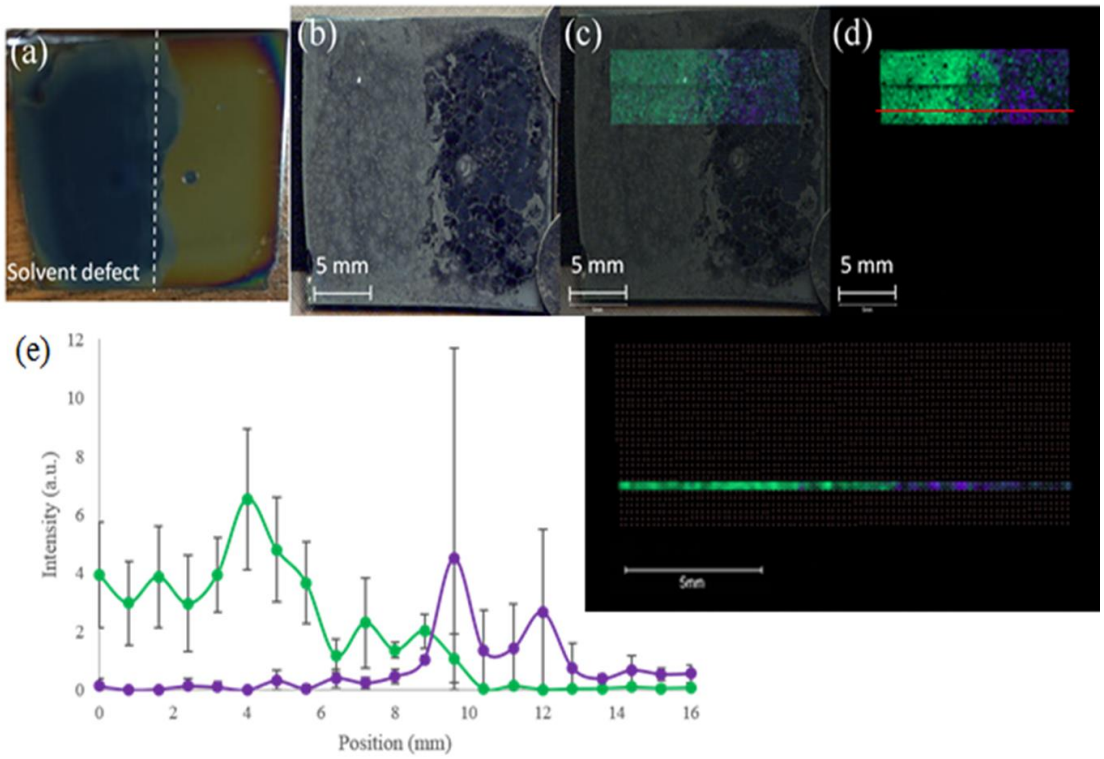

Figure S6. (a) Optical image of a bilayer film prepared by spin casting a 6 kDa PS layer onto a spun cast 7 kDa PMMA film, and then removing (from left side) half of the top PS layer by rinsing it with cyclohexane droplets; (b) optical image after matrix/salt sublimation; (c) overlaid SL-MALDI-MS image; and (d) SL-MALDI-MS image with a red line, along which the intensity profile (e) was measured. Summed $[PMMA_{50\text{-}57} + Ag]^+$ (green) or $[PS_{49\text{-}55} + Ag]^+$ (purple) intensities were used to create the SL-MALDI image and intensity profile, which show a compositional gradient near the rinsed interface between dissolved (perturbed) and native (unperturbed) regions. Mass spectra extracted from the PMMA, PS, and interface regions are included in the following Figures.

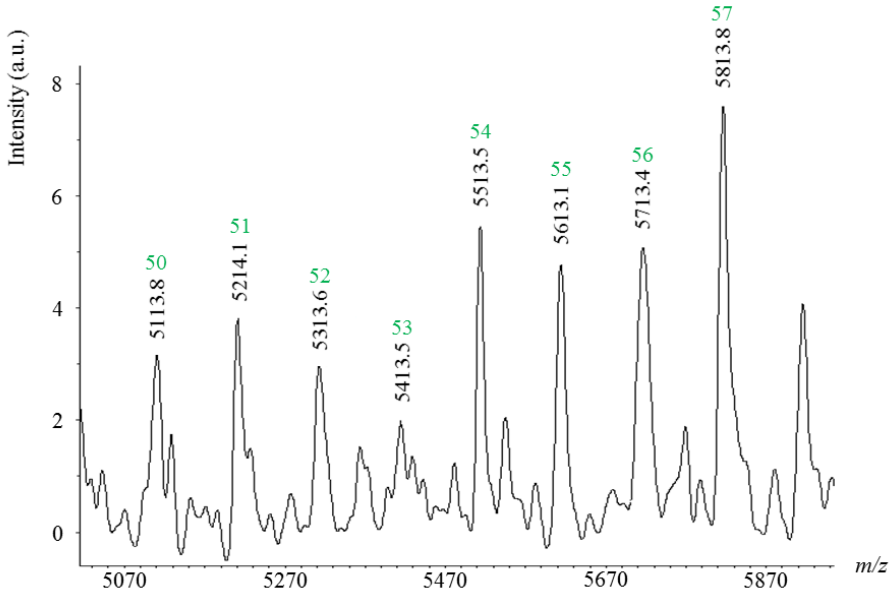

Figure S7. Zoomed in region of a SL-MALDI mass spectrum extracted from the PMMA region on the intensity profile of the cyclohexane-rinsed PS/PMMA bilayer film. The position of extraction was at 5.6 mm along the intensity profile (cf. Figure S6e). The displayed *m/z* range includes the silverated oligomers used to construct the SL-MALDI image in Figure S6 (50-mer to 57-mer); the *m/z* values of these ions are given on top of the corresponding peaks.

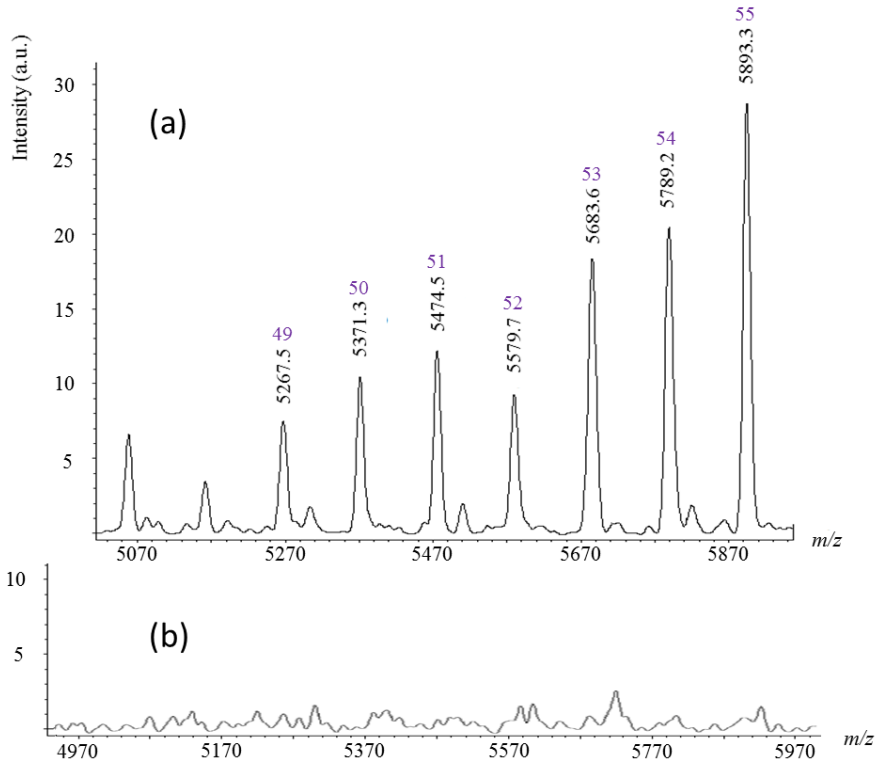

Figure S8. (a) Zoomed in region of a SL-MALDI mass spectrum extracted from the unperturbed PS area on the intensity profile of the cyclohexane-rinsed PS/PMMA bilayer film. The position of extraction was at 9.6 mm along the intensity profile (cf. Figure S6e). The displayed *m/z* range includes the silverated oligomers used to construct the SL-MALDI image in Figure S6 (49-mer to 55-mer); the *m/z* values of these ions are given on top of the corresponding peaks. (b) Zoomed in region of a SL-MALDI mass spectrum extracted from faintly visible green spots within the unperturbed PS area of the cyclohexane-rinsed PS/PMMA bilayer film (cf. Figure S6d). Only noise is detected, with some of the noise spikes accidentally appearing near the *m/z* values of PMMA oligomers and, hence, labelled green by the imaging software.

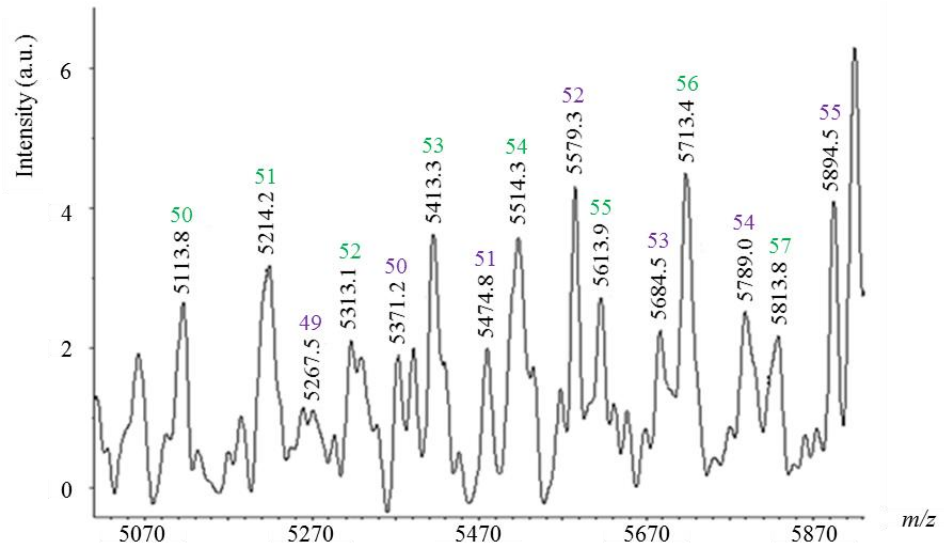

Figure S9. Zoomed in region of a SL-MALDI mass spectrum extracted from the interfacial region between the PS (native) and PMMA (perturbed) area on the intensity profile of the cyclohexane-rinsed PS/PMMA bilayer film. The position of extraction was at 8.8 mm along the intensity profile (cf. Figure S6e). The displayed *m/z* range includes the silverated PS and PMMA oligomers used to construct the SL-MALDI image in Figure S6 (50-57-mer for PMMA and 49-mer to 55-mer for PS).