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Probing Surface Concentration of Cyclic/Linear Blend Films Using Surface Layer MALDI-TOF Mass Spectrometry

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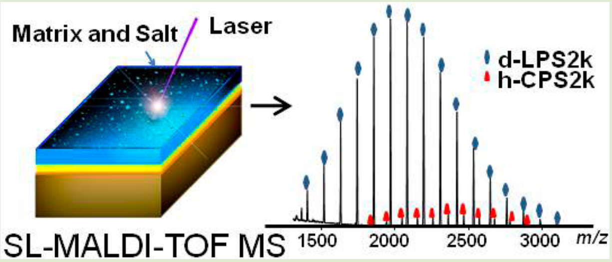
S *Supporting Information*

ABSTRACT: Surface layer matrix-assisted laser desorption ionization time-of-flight mass spectrometry (SL-MALDI-TOF MS) is a powerful new surface sensitive technique to quantify the surface concentration of multicomponent polymer films with enrichment of one component at the surface. Its capabilities are demonstrated for the novel case of a blend of cyclic polystyrene with linear polystyrene, in which we find the composition of linear chains enriched at the surface after annealing, contrary to the expectation of a self-consistent field theory. The probing depth was confirmed to be monomolecular, which for these short chains is less than 2 nm, even though material at a much greater depth is removed by the analysis.



An understanding of surface segregation in polymer systems is crucial for industrial applications in adhesives, coatings, packages, membranes, and biomedical engineering.[1,2] One means for exercising control over the functionality at the surface is the blending of polymers, especially because, in general, one of the two polymers will be preferred at the surface. To maintain excellent mechanical properties, it is essential that the blend film remain a single phase with a gradient of composition from the surface into the film, rather than exhibiting macroscopic vertical phase segregation. One type of blend that shows promise in such uses is that in which the two polymers are of the same repeat chemistry (e.g., polystyrene (PS)), but different chain architecture, so that surface enrichment occurs by virtue of the architectural differences. During the past two decades, experimental and theoretical research on surface segregation phenomena pertinent to this strategy of surface modification has focused on linear/linear[3−5] and branched/linear[6−9] polymer blends. Self-consistent field (SCF) theory[7] predicts that cyclic chains segregate to the surface in a blend with linear chains if one considers only the minimization of free energy due to conformational entropy effects. Here we provide the first experimental test of this prediction.

The segregation is anticipated to occur over a depth that is of the order of the radius of gyration (R_g) of the polymer chain.[3] However, there are few techniques for quantitative measurements of composition within this small depth, particularly when the components being distinguished differ only subtly. Secondary-ion mass spectrometry is directly sensitive to the first molecular layer, but quantitative measurements require complex calibration.[10] Neutron reflectometry is a very high resolution technique for probing the composition depth profile[4,6,9] if a component can be isotopically labeled. However, it is an indirect technique. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) can provide a direct measurement of chemical composition that discriminates among chains with distinct molecular architecture (if these also differ in m/z value),[11,12] without the need for isotopic labeling. Many polymer analytes can be dissolved and mixed with matrix for this technique.[13] Some nonsoluble polymers as well as biological entities have also been analyzed by mechanically mixing the polymer with matrix.[14−18] To extend MALDI-TOF MS to the analysis of the surface specifically, it is necessary to limit the probing depth by modifying the sample preparation method while avoiding any change of the surface composition during sample preparation or measurement. Here an innovative technique we term surface layer MALDI-TOF MS (SL-MALDI-TOF MS) is used to unambiguously identify the species preferred at the surface of a novel blend of cyclic polystyrene with linear polystyrene and quantify its composition.

Molecular characterization data for the hydrogenous cyclic PS (h-CPS2k), hydrogenous linear PS (h-LPS2k), and deuterated linear PS (d-LPS2k) used in this study are summarized in Table 1. The well-defined h-CPS2k was synthesized by anionic polymerization using a new end-coupling method.[19] Deuteration of the linear species provided contrast for study of the blend by other techniques as well as SL-MALDI-TOF MS.

The sample used for SL-MALDI-TOF MS (Figure 1) consisted of four layers from bottom to top (see Supporting Information for preparation): a silicon substrate layer with native oxide, a 10 nm thick chromium adhesion layer, a 50 nm thick gold conductive layer, and a 40 nm polymer blend layer. The conductive gold layer dissipates charges created by the

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Table 1. Molecular Characterization of Polymers Used

polymer	M_n[a] (g/mol)	PDI[a]	T_g[b] (°C)
h-CPS2k	2700	1.03	86.5
h-LPS2k	2300	1.05	61.0
d-LPS2k	2000	1.03	60.0
PS4k	4100	1.03	81.7
PMMA	2800	1.09	80.9

[a] SEC coupled with light scattering (±5%) in THF at 30 °C. [b] Determined by DSC: heating rate, 10 °C/min; recording second run, ±1 °C.

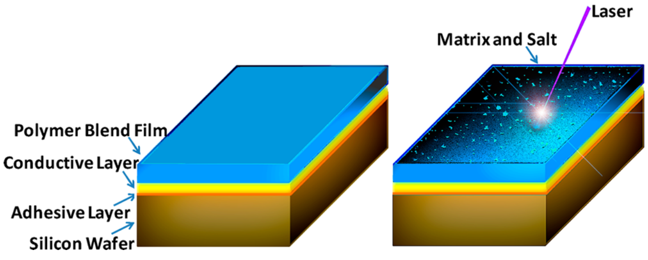

Figure 1. Schematics of the sample for SL-MALDI-TOF MS.

MALDI process.[20] In conventional MALDI-TOF MS, a cationization reagent, silver trifluoroacetate (AgTFA), is carried in a matrix of *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB). This matrix is mixed with PS in solvent to increase the sensitivity. However, placing solvent on the sample surface could change the surface composition. Therefore, in these surface measurements, dry matrix powder and AgTFA were put together in a vial and ground up with a vortexer. The resulting matrix/salt mixture was spread on the film surface using a spatula. The sample was tapped against the table to remove large particles not held onto the surface with van der Waals forces. The layer of matrix and AgTFA was nonuniform, containing particles varying in size from a few to tens of micrometers in diameter (Figure S20).

The sample was held in the standard holder for a Bruker Ultraflex III TOF/TOF mass spectrometer (Nd: YAG laser at a wavelength of 355 nm) using glass slides to ensure good electrical contact and surface flatness (Figure S2). The contact between the matrix and the polymer is *key* to this new approach. Signal can only be detected from the portion of the film in direct contact with the matrix and salt (i.e., the surface layer). After a few hundred laser shots, no signal could be detected, indicating that the thin layer of matrix material had been completely consumed in that spot.

The conventional MALDI mass spectrum from a bulk sample of the h-CPS2k/d-LPS2k blend with 20 wt % h-CPS2k is shown in Figure 2 along with the SL-MALDI spectrum from the surface of a thin film of the same blend before and after annealing 12 h at 120 °C. The relative intensity of the h-CPS2k distribution is a factor of 3 smaller at the surface of the film than in the bulk. The surface concentration of d-LPS2k was quantified[21] using a calibration curve (in Supporting Information) constructed using ratios of the peak area of d-LPS2k (*m/z* 2407.4) to the sum of peak areas for h-CPS2k (*m/z* 2349.4) and d-LPS2k for several standard bulk blends mixed with solvent and measured with conventional MALDI. The d-LPS2k surface concentration of the linear/cyclic blend film was 88.3 (±1.6) wt % even before annealing. The time during which the chains are mobile, while there is sufficient solvent in the film, is less than 1 min, so it is notable that segregation occurs even before annealing. After annealing the film at 120 °C for 12 h, the concentration remains the same within experimental error, 89.3 (±2.8) wt %. Contrary to theoretical prediction,[7] there is a *depletion* of the cyclic chains from the surface compared to the bulk composition. To ensure that this depletion is not due simply to an isotopic effect arising from the deuterium labeling, a blend of h-LPS2k/d-LPS2k with 20 wt % h-LPS2k was analyzed before and after annealing. The data are listed in Table 2 for comparison. The composition at the surface of the h-LPS2k/d-LPS2k blend is 79% d-LPS, as expected. (Details of sample treatment, spectra, and concentration calibration can be found in Supporting Information.) These data confirm that surface segregation due to isotopic labeling alone is not measurable for such short chains.[4]

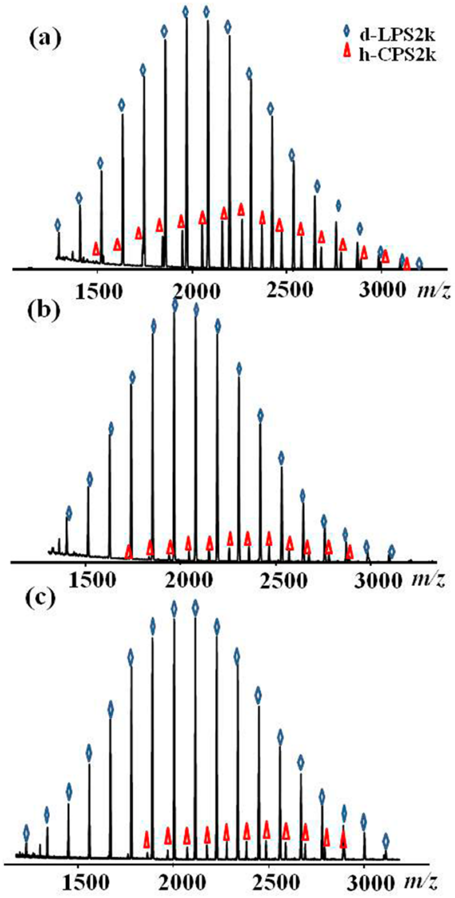

Figure 2. (a) Conventional MALDI-TOF MS spectrum of a bulk sample of h-CPS2k/d-LPS2k blend with 20 wt % h-CPS2k, (b) SL-MALDI spectra from the surface of a thin film of the same blend before annealing, and (c) after annealing at 125 °C for 12 h. The mass difference between pairs of peaks in the distribution for d-LPS2k is 112 Da and that for the distribution of h-CPS2k is 104 Da.

Table 2. Summary of Surface Segregation in Cyclic and Linear Blend Films before and after Annealing

sample type	annealing	SL-MALDI-MS (wt % dPS)	STOF-SIMS signal ratio d/h
h-LPS2k/d-LPS2k (20% h-LPS2k)	no	78.6 ± 2.5	4.4 ± 0.6
	120 °C, 12 h	78.8 ± 2.9	4.2 ± 0.1
h-CPS2k/d-LPS2k (20% h-CPS2k)	no	88.3 ± 1.6	7.3 ± 0.4
	120 °C, 12 h	89.3 ± 2.8	9.8 ± 0.3

The fact that the surface is enriched in *linear* chains, rather than cyclics, was confirmed using static time-of-flight secondary ion mass spectrometry (STOF-SIMS). STOF-SIMS is a direct technique for determining the relative surface concentration of different species. However, calibration to obtain absolute concentrations is very challenging. Adding an internal standard, for example, can alter the surface segregation of the blend under investigation and change the surface composition. We therefore present only ratios of signals in Table 2, which nonetheless confirm our central contention that the surface is enriched in linear chains. The fragmentation spectra for the h-LPS2k/d-LPS2k and h-CPS2k/d-LPS2k blends each containing 20 wt % of hydrogenous PS were analyzed before and after annealing. The surface concentration of deuterated PS relative to hydrogenous PS is related to the ratio of the peak areas for all detectable fragments from the deuterated PS (*m*/*z* 95−98) to the peak area of all detectable fragments for the hydrogenous PS (*m*/*z* 91−92). (Fragmentation patterns and data treatment can be found in Supporting Information.) The linear/linear blend was measured first to obtain an idea of a ratio value one might expect for the overall composition in the cyclic/linear blend in the absence of surface enrichment. The trends observed with SIMS and with SL-MALDI are the same in the following sense. It is clear from the SIMS data that when the ratio of deuterated linear to hydrogenous linear polymer at the surface is of the order of 4, the d/h signal ratio is of order 4. Therefore, even if the SIMS ionization yields for the cyclic and linear chains are somewhat different, the signal ratios of 7.3 and 9.8 suggest that the deuterated *linear* species is already enriched at the surface in the cyclic/linear blend after spin-casting and that this enrichment grows with annealing.

The thickness of the blend films (40 nm) used for the SL-MALDI-TOF MS measurements was much larger than the R_g of d-LPS2k (1.2 nm) or of h-CPS2k (0.8 nm).[22] To experimentally confirm the actual probing depth of SL-MALDI-TOF MS, we tested a model bilayer film. A Langmuir monolayer of poly(methyl methacrylate) (PMMA) was deposited on top of a 100 nm thick layer of PS4k using the Langmuir−Schaefer technique (as described in Supporting Information). The molecular characterizations of the PMMA and PS4k are shown in Table 1. The thickness of the PMMA layer was determined using atomic force microscopy (AFM) at a defect near the film edge. Line cuts through an AFM image (Figure 3) show that the PMMA layer is 1−2 nm thick, which is consistent with the R_g of the PMMA.

The SL-MALDI-TOF MS spectrum from the bilayer surface is shown along with those from the bulk reference films of PS4k and PMMA in Figure 4. The reference PMMA has a number average molecular weight (M_n) of 2800 g/mol, whereas the PS has a M_n of 4400 g/mol as determined by MALDI-TOF MS. The distributions of the two polymers overlap, allowing for a comparison between the two species (Figure S10). A single product was observed on the SL-MALDI spectrum of the bilayer film. The mass difference of those peaks was 100 Da, consistent with sampling of the PMMA. No PS signal was detected, even in the region where PS should give a strong peak if detected (Figure S11). The only signal observed originated from the top PMMA layer, which was only a monolayer thick (1−2 nm), confirming that the probing depth of SL-MALDI-TOF MS is about R_g with these chains. This probing depth was confirmed using two other bilayer samples with a different polymer pair (data in Supporting Information).

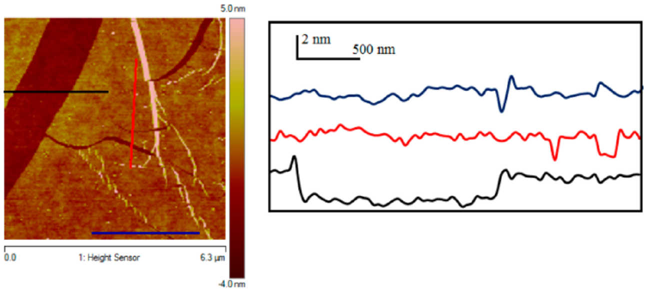

Figure 3. Tapping mode AFM topography image near a defect in the PMMA layer atop the PS film (left) along with corresponding line cuts through the image (right). The line cuts show that the PMMA film is 1 R_g (1−2 nm) thick.

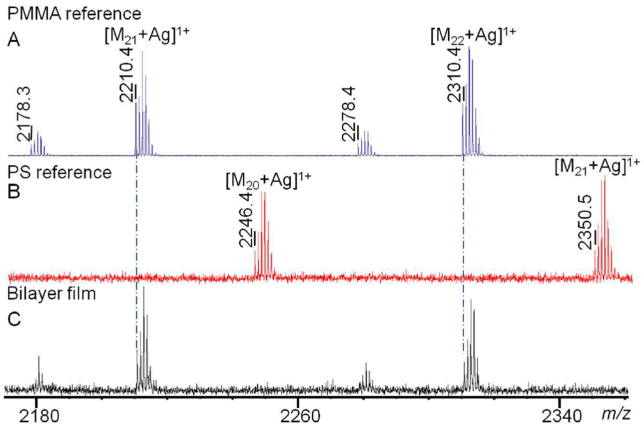

Figure 4. MALDI-TOF bulk reference spectra of (a) PMMA and (b) PS, and (c) SL-MALDI-TOF MS spectrum from the bilayer film surface. Entire spectra are shown in Supporting Information.

The confirmation of the actual probing depth is significant because optical microscopy (Figure S20) shows that the laser penetrates both layers of the bilayer film, ablating all of the polymer in the beam path. This is confirmed with AFM images (Figure S21) showing that the morphology at the bottom of the laser spot is consistent with that of the underlying gold film. However, only the species in direct contact with the DCTB/AgTFA mixture at the surface is detected in the SL-MALDI-TOF MS analysis.

In summary, we have demonstrated the ability of SL-MALDI-TOF MS to determine surface composition of a multicomponent polymer film using a novel cyclic/linear blend. The cyclic chains are *depleted* at the film surface after annealing, contrary to the prediction of a SCF theory.[7] The probing depth of this new surface sensitive technique was shown to be monomolecular (R_g), which for these short chains is 1−2 nm. We anticipate SL-MALDI will be applicable for analysis of surface composition in films of many types of polymers, provided the polymer components are of molecular weights such that the species may be distinguished.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental methods, additional MALDI spectra, and optical and AFM images of the SL-MALDI-TOF sample taken after data were collected. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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