ACS Macro Letters

Letter

Cite This: ACS Macro Lett. 2018, 7, 795−800

pubs.acs.org/macroletters

Subtle End Group Functionalization of Polymer Chains Drives Surface Depletion of Entire Polymer Chains

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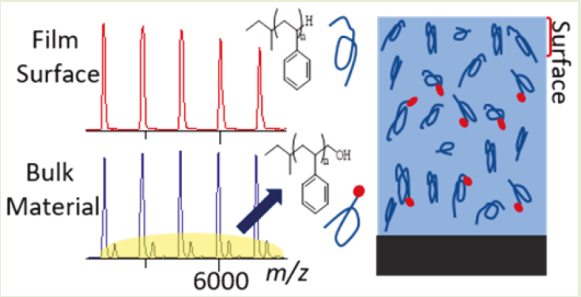
Supporting Information

ABSTRACT: The surface of a blend of 6 kDa polystyrene and 6 kDa polystyrene functionalized with hydroxymethyl ends not only is depleted of the higher energy end groups but also is depleted of any segments belonging to the functionalized chains. This is demonstrated using the emerging technique of surface layer matrix-assisted laser desorption ionization time-of-flight mass spectrometry (SL-MALDI-ToF-MS), which detects entire chains that have any repeat unit at the outer surface, and requires no labeling. Detecting entire chains provides information about the relationship of chain functionalization to surface segregation behavior of entire chains. That the surface is depleted of interior segments of functionalized chains as well as of the ends is remarkable, since the functionality at the single chain end involves less than 0.5 wt % of the functionalized polymer chain.



Surface segregation is critical to the ultimate performance of devices fabricated from polymeric blends[1−5] and can be tailored to provide surface properties that differ from bulk properties without the loss of mechanical strength that accompanies phase separation.[1,6] Improved methods for quantifying surface segregation in polymers will enable design of materials for applications as diverse as adhesives, coatings, membranes, and biomaterials.[1,7]

An important question concerning the formation of solid films from blends is the degree to which end group functionalization can influence surface segregation. Surface segregation driven by chemical functionality is one way to create desirable surface properties related to adhesion and wetting.[8,9] It has been shown that functionalization with groups of lower surface energy, such as fluorinated units, can drive enrichment of the fluorinated units at air and substrate interfaces.[10−15] Conversely, high surface energy groups are depleted from the surface to lower the overall free energy of the system.[10,16] Theoretical studies predict that the surface depletion of higher energy functionalities is less pronounced than the surface enrichment by low energy groups.[11,14,17,18]

In commercial applications a subtle functionality difference between a single end unit and repeat units interior to the chain is sufficient to significantly alter surface properties. However, systematic research of the impact of such subtle differences on surface segregation is challenging. Labeling strategies used to create contrast for characterization can complicate tests of theoretical claims regarding surface characteristics.[4,17] Nonetheless, to investigate the phenomena of, for example, wetting dependence upon surface composition of chain end groups, researchers have resorted to using multiple fluorinated units to represent low energy functionalities and carboxyl chain ends to represent high energy functionalities to obtain an extent of segregation sufficient to be experimentally resolved.[2,10,16,19,20]

Having several adjacent functional units, rather than just one, is an important difference, since placing functionality on consecutive units increases the enrichment.[2,4,17] In other studies, isotopically labeled components have been used to obtain contrast, but this introduces complexity as well.[10,19,21−24] The isotopic effect alone can induce segregation.[21] The complexity that additional functional units or labeling creates and the difficulty of synthesizing model systems lead to a need for techniques that can readily distinguish surface segregation driven by subtle chemical differences between chains.

Determining the specific location of end groups and also connecting end group behavior with overall chain behavior has been a challenge. Previous studies have been limited to determining the atomic percentages of elements at the surface or segment concentration depth profiles.[2,10,16,19,21−24] X-ray photoelectron spectroscopy (XPS) probes the atomic percentages of elements in the vicinity of the surface.[25] Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is extremely

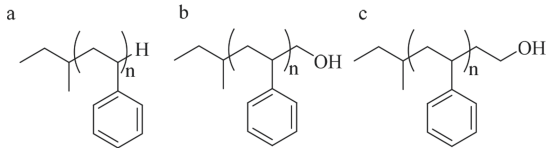
Received: May 22, 2018
Accepted: June 13, 2018
Published: June 21, 2018

DOI: 10.1021/acsmacrolett.8b00394
ACS Macro Lett. 2018, 7, 795−800

sensitive to the outer surface functionality but provides complex fragmentation spectra.[7,26] Neutron reflectivity (NR), dynamic secondary ion mass spectrometry (SIMS), forward recoil spectroscopy (FRES),[27] and nuclear reaction analysis (NRA)[28] are among those techniques providing segment concentration depth profiles.[26,29] None of these techniques is able to quantify the composition of specific chains at the surface. MALDI-ToF-MS is unique in its capability to provide the composition in a sample of polymer chains as a composition of entire chains rather than as a concentration of chain segments.[30]

The emerging technique of surface layer matrix-assisted laser desorption ionization time-of-flight mass spectrometry (SL-MALDI-ToF-MS) probes only the top molecular layer of a sample (within a depth $\leq$ 2 nm) and can provide the concentration of the chains of a particular blend component at the surface for any polymer ionizable by MALDI.[31,32] An additional feature that makes this technique powerful is the ability to distinguish blend components differing only in the identity of one end group (<0.5 wt % of the entire chain).[33] Using this capability we demonstrate that when the majority blend polystyrene component is terminated with hydrogen (PS-H) while the minority (9 ± 4 mol %) component is terminated with a hydroxymethyl (PS-MeOH) group (Scheme 1), all parts of the chains containing the hydroxymethyl end groups are depleted from the surface.

Scheme 1. Structures of (a) Hydrogen-Terminated Polystyrene, (b) Hydroxymethyl-Terminated Polystyrene, and (c) Hydroxyethyl-Terminated Polystyrene



A conventional, bulk mass spectrum of a 6 kDa PS sample and a SL-MALDI-ToF-MS spectrum from a dried 90 nm thick film cast from the same solution are shown in Figure 1. The bulk and surface spectra differ in three ways. One difference is in the mean molecular weights. This shift has been discussed elsewhere.[34] A second difference is in the peak breadths. This is discussed in the Supporting Information. Of central interest is the third difference. A distribution associated with end-functionalized chains appears in the bulk mass spectrum but does not appear in the surface mass spectrum. The primary distribution corresponds to chains having one hydrogen terminal end group (−H, 1 Da) and an α-end group of *sec*-butyl (C_4H_9−, 57 Da). The secondary distribution corresponds to chains with one hydroxymethyl end group (−CH_2OH, 31 Da). Quantitative spectrum analysis reveals that in the bulk sample 9 ± 4 mol % of the chains are functionalized with a hydroxymethyl end group. However, no mass-to-charge (m/z) distribution resulting from hydroxymethyl-terminated chains was detectable above background noise (signal-to-noise ratio is 330) in the SL-MALDI-ToF-MS spectra from films of thicknesses 16, 42, and 90 nm. If there were any peaks corresponding to hydroxymethyl-terminated chains, they would have appeared between the peaks from −H terminated chains.

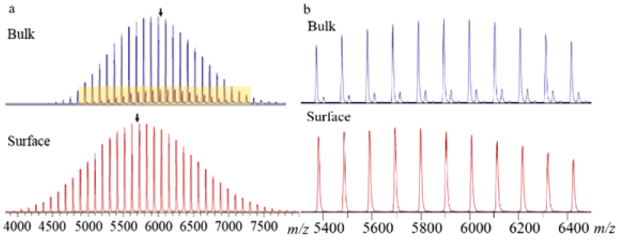


Figure 1. MALDI mass spectra of 6 kDa PS samples. Two distributions are observed in the conventionally obtained spectrum of the bulk material in (a). The distribution corresponding to PS-MeOH is present in the bulk spectrum (highlighted in yellow) but not the surface spectrum of a 90 nm thick annealed film. An arrow marks the value of M_n for each spectrum. An expanded spectrum from 5300 to 6500 m/z in (b) more clearly shows the second distribution.

Since no functionalized chains are observed in the SL-MALDI spectra of the PS/PSMeOH blends of any thickness, very few functionalized end groups must be present at the surface, and, in fact, nearly all segments of chains with functionalized ends must be depleted from the surface. If any segments from end-functionalized chains are present at the surface, their composition must be less than 0.2 mol %. We determine this by comparing the intensity of the noise in the end-functionalized chain m/z region adjacent to the most intense peak for H-terminated PS oligomer to the intensity of that most intense peak in the SL-MALDI spectrum. It is important to note that if any segment of an end-functionalized chain were present in the outermost layer of a film, there would be a high probability of that chain being ionized and detected. The ionization agent Ag^+ complexes with phenyl groups on the PS backbone, and it has been shown[35] that it is the phenyl groups that are primarily at the surface. This situation is very favorable for ionization. The degree of surface depletion in functionalized chains for higher values of bulk blend composition is under investigation.

The absence of segments from end-functionalized chains at the surface cannot be rationalized as resulting from a saturation of the surface by the butyl groups found at the α chain ends. No prior studies suggest that surfaces of anionically polymerized PS samples are saturated with butyl end groups.[20,36] Indeed, if the surface were saturated with butyl groups, no chains of either type would have been detected at all, since the Ag^+ ionizes chains by interacting with double bonds. Nonetheless, we cannot exclude the possibility that there may be a few functionalized chains that are very close to the surface, each having only one segment at the outermost surface and with that segment being the butyl end group.

Spectra from dried, but not annealed, thin films (Figure S1) are consistent with the contention that segregation of the functionalized chains away from the surface occurs rapidly during film deposition. Those spectra were the same, within uncertainties, as those from annealed films. The segregation develops within only 2 min during spin coating. Surface depletion in dried samples was confirmed by analyses of three or more samples of each thickness, for a total of 10 samples. Data were collected from various points on each sample surface to obtain spectra representative of the entire film.

Further measurements confirmed that the absence of hydroxymethyl-terminated chains at the surface is not due to chains lost from the sample during casting or sequestered at the substrate interface by adsorption. The *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) matrix and silver trifluoroacetate (AgTFA) ionization agent

DOI: 10.1021/acsmacrolett.8b00394
ACS Macro Lett. 2018, 7, 795−800

were dissolved in tetrahydrofuran (THF), and one droplet of the solution was placed at each of the three locations on the surface of a 90 nm thick blend film. The diameter of the perturbed surface area was about 1 mm. In the regions where the solution of matrix and ionization agent was applied, portions of the film below the surface were penetrated with matrix and ionization agent. Other regions of the film located away from these spots were left unperturbed and were analyzed using the solvent-free application of matrix and ionization agent. The SL-MALDI-ToF-MS spectra from these other locations with solvent-free application were identical to those in Figure 1. Figure 2 shows a spectrum obtained by summing

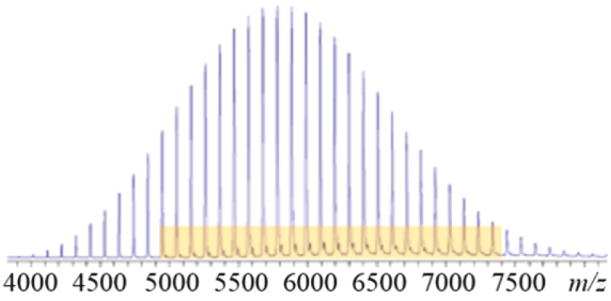


Figure 2. Sum of MALDI-ToF-MS spectra collected from three spots on the 90 nm thick film treated with DCTB/AgTFA/THF solution. The peaks of the secondary distribution (highlighted in yellow) correspond to hydroxymethyl-terminated chains present beneath the surface. Expanded portions of the spectra are available in Figure S3.

spectra from all three perturbed regions of the film. Spectra from the surface and DCTB/AgTFA/THF perturbed regions are compared side by side in Figure S2. A plot enlarging the same m/z region in both spectra, shown in Figure S3, makes even clearer the presence of peaks from functionalized chains in each spectrum from a perturbed spot.

The spectra from the three spots were summed to obtain better statistics, but the secondary distribution was evident in data from each spot. Peaks from hydroxymethyl-terminated chains corresponding to a composition of 4.6 ± 0.5 mol % appear when the application of solvent has allowed matrix and ionization agent to penetrate beneath the surface layer. Since this spectrum represents a sampling of both the surface composition (which is zero) and the composition of some region beneath the surface, we can deduce that the composition in the bulk of the film is at least 4.6 ± 0.5 mol %. A more precise discussion of the observed secondary distribution intensity is not possible because the contribution of each component from the bulk and surface of the sample has not been defined. However, it is important to note that we are certain that any functionalized chains that may have been sequestered at the substrate by adsorption cannot be represented in the spectrum in Figure 2. The very thin layer of chains adsorbed to the substrate,[37−41] which most likely contains both types of chains, was studied after rinsing away loose chains using a protocol developed by Koga et al.[37] MALDI-ToF MS analysis of that layer would have been an ideal means of quantifying the amount of functionalized chains there, but none of the adsorbed chains could be ionized, as shown in the Supporting Information (Figure S4). So the spectrum in Figure 2 demonstrates clearly that though the surface is depleted of chains with higher energy end groups, the interior of the film still contains a substantial composition of hydroxymethyl-terminated chains.

Two additional experiments probed how important sequestration of functionalized chains to the substrate might be in determining the surface composition. Since the quantity of the MeOH functionalized material available for study was very limited, these comparisons were performed using blends containing 5.3 ± 0.4 mol % EtOH functionalized chains with the same length as the MeOH terminated chains. The driving force for depleting the EtOH functionalized chains from the surface was similar to that for PS-MeOH chains but somewhat weaker. Surface compositions of PSEtOH for 90 nm films on Ag coated substrates and hydrogen-passivated silicon (H−Si) substrates were identical at 1.0 ± 0.1 mol %. If adsorption of functionalized chains to the substrate were pulling a large fraction of chains from the film interior, the surface depletion for these two substrate types should have been different. In addition, the PSEtOH surface compositions of 90 and 430 nm PS/PSEtOH blend films on Ag coated substrates were the same within experimental uncertainty, as shown in Figure 3. Any depletion of the surface composition by sequestration at the substrate alone should have differed by a factor of 5 for these two films, so sequestration of functionalized chains from the whole film is not the dominant mechanism for the surface depletion.

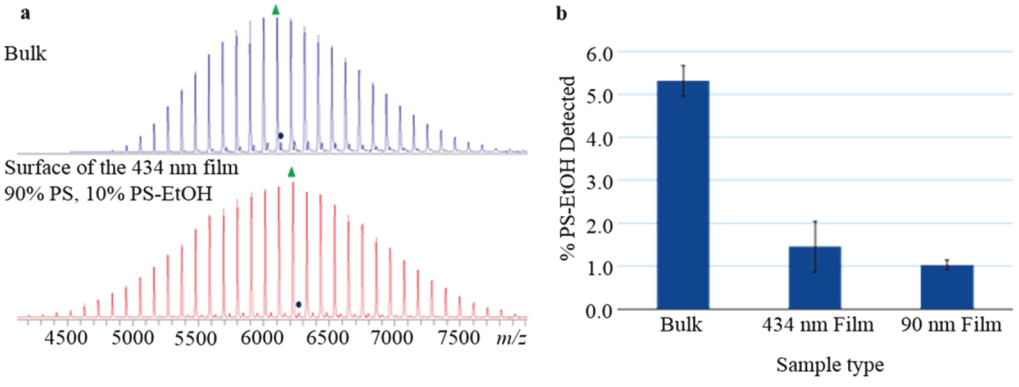


Figure 3. Analysis of a blend film with hydroxyethyl functionalized chains (PS-EtOH) and unfunctionalized PS chains. In (a) are spectra collected from the bulk and surface of the 430 nm film. The peaks from unfunctionalized chains used for analysis are marked with triangles, and those for functionalized chains are marked with blue circles. In (b) are the percent abundances of PS-EtOH calculated from a conventional MALDI spectrum for bulk and from SL-MALDI spectra for a 430 nm film and 90 nm film.

DOI: 10.1021/acsmacrolett.8b00394
ACS Macro Lett. 2018, 7, 795−800

We have shown that entire 6k end-functionalized chains are rapidly depleted from a blend surface during its formation, with that depletion driven primarily by the character of a single segment, which constitutes less than 0.5 wt % of the functionalized chain. This phenomenon is resolved without requiring labeling, eliminating the need to extrapolate from the behavior of "similar" systems to the behavior of systems of interest. Avoiding these extrapolations offers great potential for studying segregation phenomenon in functionalized materials. For example, the methodology can be used to elucidate the effects on surface segregation of changing the polarity of end groups.[17] Better understanding the impact of functionalized chain design on surface segregation in blends has implications for improving adhesives, release films, antifouling surfaces, and biomedical devices, among other applications.

EXPERIMENTAL DETAILS

Anionically polymerized PS with number-average molecular weight, M_n, of 6030 ± 130 Da, as determined by conventional MALDI-ToF-MS, was found to include 9 ± 4 mol % chains having $-CH_2OH$ termination (PS-MeOH) with the remainder having conventional −H termination (Scheme 1).[42] The value of M_n for the hydroxymethyl chain terminated chain distribution was 6310 ± 210 Da.[42] Smooth, uniform PS thin films were spun cast from toluene solutions of three concentrations (0.02−2.0 wt %) at 2000 rpm. To minimize charging during SL-MALDI-ToF-MS analysis, films were cast onto silicon wafers coated with 20−25 nm of Ag deposited using thermal evaporation in a home-built physical vapor deposition system and study focused primarily on thinner films. The ellipsometrically determined thicknesses for these thin films were 90 ± 5 nm, 42 ± 5 nm, and 16 ± 5 nm. Separately, bulk, 90 ± 5 nm, and 430 ± 10 nm thick samples of a blend of PS-H and PS-EtOH (Scheme 1) were also studied. The PS had a M_n of 6090 ± 20 Da while that of PS-EtOH was 6120 ± 10 Da.

"Annealed" films were heated overnight (12−24 h) under high vacuum ($<10^{-3}$ Pa) at 150 °C, well above the glass transition temperature (T_g) of ca. 80 °C. "Dried" films were only heated to T_g - 30 °C overnight to remove residual solvent. Spectra from annealed films and dried films showed the same M_n and degree of segregation for the thicknesses of 90 and 42 nm. For the 16 nm annealed films, AFM revealed slightly greater roughness, possibly due to the onset of dewetting. Therefore, only results from dried 16 nm films are reported here, but for the other two thicknesses the surface compositions of dried and annealed samples were the same. Atomic force microscopy (AFM) measurements indicated a typical root mean squared (RMS) roughness of 0.6 ± 0.3 nm, consistent with values expected for spun cast films. Representative images in the Supporting Information (Figure S5) show no signs of dewetting and show that the surfaces are free of features that could obscure the surface segregation behavior.

Both bulk and surface MALDI-ToF-MS experiments were performed in positive linear mode using a Bruker Ultraflex-III MALDI-ToF/ToF mass spectrometer (Bruker Daltonics Inc., Billerica, MA) equipped with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (355 nm). Linear mode was chosen to address the low intensity characteristic of the SL-MALDI-ToF-MS technique, which limits the molecular weight range over which the analysis can be done. All ionization source and instrumental parameters (see the Supporting Information) used for solvent-free and solvent based MALDI acquisitions were identical. Bulk MALDI-ToF-MS samples were prepared using THF. A solution of DCTB matrix (20 mg/mL) in THF and a solution of AgTFA ionization agent (10 mg/mL) in methanol (10:1) v/v were spotted with PS sample solution onto a standard MALDI plate. Samples for SL-MALDI-ToF-MS[22] were made by dusting the film surface with dry matrix and ionizing agent (solventless technique).[31,43−45]

After determining the masses for the end groups manually, the polymer spectra were entered into Polymerix software to determine M_n and the relative amounts of each species. When only one species was observed by visual inspection of the surface spectrum, the absent blend component was not included in the surface spectrum analysis. Enrichment was calculated based on measurements of at least three samples. Reported errors represent a standard deviation of three or more measurements.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge via the Internet at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.8b00394.

Spectra of dried films, films treated with solvent to verify the presence of hydroxymethyl terminated PS in the films, testing the presence of functionalized chains at the substrate surface, film properties, MALDI mass spectrometry parameters (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge support from the National Science Foundation (CHE-1808115) and the Defense University Research Instrumentation Program (DURIP) (W911NF-10-1-067).

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