Detection of Surface Enrichment Driven by Molecular Weight Disparity in Virtually Monodisperse Polymers

Jacob A. Hill[1,‡], Kevin J. Endres[1,‡], Pendar Mahmoudi[3], Mark W. Matsen[3,4], Chrys Wesdemiotis[1,2*], Mark D. Foster[1*]

[1]Department of Polymer Science, University of Akron, Akron, OH 44325
[2]Department of Chemistry, University of Akron, Akron, OH 44325
[3]Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada ON N2L 3G1
[4]Department of Physics & Astronomy, University of Waterloo, Waterloo, Ontario, Canada ON N2L 3G1

KEYWORDS: Surface enrichment, entropy, MALDI, surface, surface layer MALDI-ToF, mass spectrometry

ABSTRACT: The preference for a shorter chain component at a polymer blend surface impacts surface properties key to application specific performance. While such segregation is known for blends containing low molecular weight additives or systems with large polydispersity, it has not been reported for anionically polymerized polymers that are viewed, in practice, as monodisperse. Observations with surface layer matrix-assisted laser desorption ionization time-of-flight mass spectrometry (SL-MALDI-ToF-MS), which distinguishes surface species without labelling, and provides the entire molecular weight distribution, demonstrate that entropically driven surface enrichment of shorter chains occurs even in low polydispersity materials. For 6 kDa polystyrene the number average molecular weight (M_n) at the surface is ca. 300 Da (5%) lower than that in the bulk and for 7 kDa poly(methyl methacryalate) the shift is ca. 500 Da. These observations are in qualitative agreement with results from a mean-field theory that considers a homopolymer melt with a molecular-weight distribution matched to the experiments.

The enrichment of a component of a polymer blend at its surface is a general phenomenon which can be controlled to tailor surface properties. Surface segregation that leads to the formation of a complex single phase containing a concentration gradient rather than a macroscopically phase separated surface layer provides surface properties that differ from bulk properties without the loss of mechanical strength that accompanies phase separation.[1,2] Improved methods for elucidating this segregation will allow advances in many applications such as adhesives, coatings, membranes, and biomaterials.[1,3-7]

In general, surface segregation is difficult to quantify.[8-12] Several methods that are sensitive to gradients in composition with depth require labelling of one species that could alter the segregation behavior.[9] These include techniques, such as reflectometry, that sometimes require deuteration to achieve contrast between components. X-ray photoelectron spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS) are sensitive to composition at or near the surface, but only in terms of atomic composition or molecular fragments, respectively.[8,13] Complimentary information can be obtained with the surface layer matrix-assisted time-of-flight mass spectrometry (SL MALDI-ToF-MS) technique described by Wang et al.[17] that analyzes entire molecules within a probing depth of ca. 2 nm from the surface and reveals the entire molecular weight distribution. Many subtle differences among polymer chains can be distinguished with MALDI-ToF MS,[10,11,14-17] with the focus of this study being differences in number average molecular weights (M_n) of the chains at the surface and those in the bulk of a pure, unlabeled homopolymer.

Chain length disparity is a ubiquitous driver of surface enrichment.[18-28] The enrichment of shorter chains affects

properties such as surface tension[21,24], wall slip[22,23], and glass transition of thin films.[25,26] This entropically driven enrichment has been studied experimentally for systems in which the disparity in chain sizes is large.[18,19,28,29] Hariharan et al.[20] first described such segregation theoretically for two lengths using lattice self-consistent field theory (SCFT). Van der Gucht et al.[30] extended that approach to melts with several chain lengths. Mahmoudi and Matsen[31] have recently applied the SCFT to off-lattice bead-spring models, and derived semi-analytical approximations. Three experimental studies[18,19,28] attempted to confirm the theoretical predictions for mixtures of short and long polymers, but to do so they had to distinguish the two species by deuterium labelling. However, this labelling introduced a small χ parameter between the blend components that was comparable in magnitude to a contribution to χ due to the entropic effect being studied. The ultimate conclusion was that it is impossible to separate out the entropic effect.[32] We have now overcome this experimental challenge with a method that is able to detect surface segregation without the need for isotopic labelling.

Here we demonstrate that even for homopolymer melts of narrow molecular weight distribution surface enrichment by lower molecular weight species occurs and the average molecular weight at the surface can be more than 10% lower than that in the bulk. SL-MALDI-ToF-MS can simultaneously resolve the surface segregation of many species in a distribution, even for cases for which heretofore even the segregation of some single average species has been too subtle to experimentally detect and quantify. Calculations from an off-lattice SCFT treatment using freely-jointed chains agree qualitatively with the experimental results.

EXPERIMENTAL DETAILS

Samples of anionically polymerized 2.5k polystyrene (PS), 3k poly(methyl methacrylate) (PMMA), and 7k PMMA were purchased from Polymer Source™ Incorporated. Analysis of conventional MALDI-ToF-MS measurements yielded values of M_n in the bulk of 2680 ± 30 Da for the 2.5k PS, 3050 ± 90 Da for the 3k PMMA, and 6850 ± 50 Da for the 7k PMMA. One additional anionically polymerized PS synthesized at The University of Akron was found to have a bulk M_n of 6030 ± 130 Da. All samples had polydispersities (PDIs) less than 1.1, with the PDIs for the PMMA samples being larger (Table 1). Thin PS films were prepared by spin casting from toluene solutions to obtain smooth and laterally uniform films. Films were spun cast onto silicon wafers covered with a 20-25 nm coating of Ag deposited using thermal evaporation in a home-built physical vapor deposition system, to minimize charging during SL-MALDI-ToF-MS analysis. Thicknesses determined with ellipsometry were 90 ± 5 nm for those films spun from 2 wt. % solution and 42 ± 5 nm for those spun from 0.2 wt. % solution. "Annealed" films were heated overnight (12-24 hours) under high vacuum (<10^{-3} Pa) at a temperature more than 30°C above that polymer's glass transition temperature (T_g) (Table S1). Other samples that will be referred to as "dried" were heated to 30°C below the T_g to remove residual solvent after the spin coating process.

Table 1. Sample Polydispersities Determined by MALDI-ToF Mass Spectrometry.

	2.5k PS	6k PS	3k PMMA	7k PMMA
PDI	1.02	1.01	1.09	1.03

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 account for the low intensity produced in the SL-MALDI-ToF-MS technique. This lower intensity limits the molecular weight range over which chains can be analyzed as compared to conventional MALDI-ToF-MS. Bulk MALDI-ToF-MS samples were prepared in tetrahydrofuran (THF). A solution of *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) matrix (20 mg/mL) and a solution of silver trifluoroacetate (AgTFA) ionization agent (10 mg/mL) in THF were spotted before and after spotting the polymer sample solution on a standard MALDI plate. Polymer film surfaces were analyzed using SL-MALDI-ToF-MS[17], a variant of solvent free MALDI mass spectrometry[33-35]. With the SL-MALDI-ToF-MS technique only the analyte at the sample surface that is in direct contact with the matrix is ionized and mass analyzed.[17] For experiments with chains of molecular weight 2k – 7k the probing depth is less than 2 nm.[17] PS molecular weights up to 21k can be studied (Figure S2).

After determining the end groups manually, the polymer spectra were entered into Polymerix™ software to determine number average molecular weight. Enrichment was calculated as an average of results from at least three samples. Reported errors represent a standard deviation of three or more measurements.

THEORETICAL DETAILS

The polymer chains are modeled as a sequence of N beads (i.e. monomers) connected by freely-jointed bonds of fixed length, a. In the spirit of mean-field theory, we represent the non-bonded interactions by a field, $w(z)$, which in our case depends only on the coordinate, z, normal to the polymer surface. Additive constants to the field have no effect, which allows the field to be adjusted to zero in the bulk. With this choice, the dimensionless concentration of chains of length N is

$$\phi_N(z) = \frac{P_N^{bulk}}{N_n h(z)} \sum_{i=1}^{N} G_i(z) G_{N+1-i}(z),$$

where P_N^{bulk} the bulk molecular weight distribution as provided by the experiment and N_n is the number-average polymerization. The function

$$h(z) \equiv \exp\left(-\frac{w(z)}{k_B T}\right)$$

is the Boltzmann weight of the field, and $G_i(z)$ is the partition function for a chain fragment of *i* monomers with one end fixed at *z*. For rigid bonds, the partition function is evaluated with the recursive relation

$$G_{i+1}(z) = \frac{h(z)}{2a}\int_{-a}^{a} G_i(z+Z)d\mathrm{Z},$$

starting from $G_1(z) = h(z)$.[7] In principle, the surface is created by solving an appropriate equation-of-state relationship between the field and the total concentration,

$$\phi(z) \equiv \sum_N \phi_N(z).$$

However, we take the simpler approach of adjusting $w(z)$ so as to produce a sigmoidal concentration profile,[36]

$$\phi(z) = \frac{1}{2}\left[1 + \tanh\left(\frac{2z}{\xi}\right)\right],$$

with a chosen width of ξ=5a. Once the field is determined, the molecular weight distribution at *z* is given by

$$P_N(z) = \frac{N\phi_N(z)}{\sum_N N\phi_N(z)}.$$

From this, we estimate the surface molecular weight distribution by $P_N^{sur} = P_N(-\xi/2)$.

RESULTS AND DISCUSSION

SL-MALDI-ToF-MS was first used to observe the entropically driven enrichment of the shorter chains to the surfaces in a blend made with two homopolymers with readily resolved differences in M_n, as done in earlier studies with other techniques.[18,19] However, a much smaller absolute difference in M_n was considered here than has been done before and here the surface segregation of every species in the distribution was probed simultaneously. The results for a blend of 2.5k and 6k PS are shown in Figure 1. The blend contained 12 wt % 2.5 kDa PS and 88 wt % 6 kDa PS. This ratio is not the ratio seen in the raw data because the ionization efficiencies of 2.5 kDa PS and 6 kDa PS are different enough that the correction for ionization efficiency variation with molecular weight would have to be made to quantify the bulk composition.

Notwithstanding this complexity due to variation in ionization efficiency with *M* and small movement of the M_n for the 6kDa chain distribution between bulk and surface spectra, it is clear that the surfaces are substantially enriched in chains from the 2.5kDa distribution. For the dried film surface the ratio of the intensities of the distribution due to 2.5kDa chains to that of the distribution due to 6kDa chains is about 0.7:1.0 (±0.2) rather than 0.6:1.0 (±0.1), as it is in the bulk. For the annealed film the ratio is higher, about 1.4:1.0 (±0.2), indicating further enrichment with annealing (Figure S2). The surface segregation of short chains in polymer blends has not been previously observed for blend components of such low molecular weight, or for cases in which the disparity in average molecular weights of the two molecular distributions is this small. The smallest molecular weight studied earlier was 30 kDa.[18] The smallest disparity investigated before was that between 104 kDa and 96 kDa PS.[18] That study with neutron reflectometry faced the complexity of isotopic labelling.

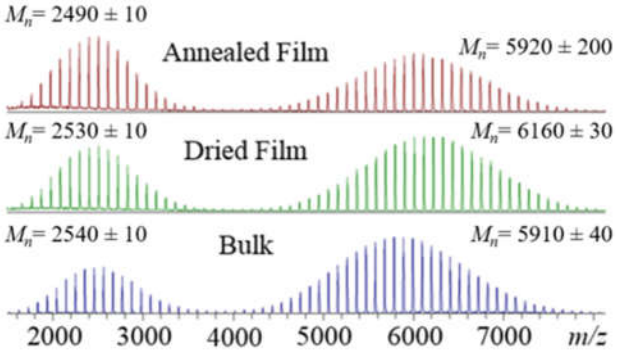


Figure 1. Spectra representative of the 'bulk', dried film surface, and annealed film surface of 2.5 kDa/6 kDa PS blend films. The x-axis represent the ratio of the mass (m) to charge (z), with all molecules having only a single charge.

Further measurements revealed that enrichment of smaller chains could be observed even within all four "single component" samples of low molecular weight chains with very low PDI (for synthetic polymers) considered here. Comparison of spectra from "dried" and "annealed" samples for the homopolymers showed identical ratios of distribution intensities, indicating that the surface enrichment with shorter chains occurs rapidly, in just the time required for spin casting. This contrasts with blends of decidedly different molecular weights, in which further enrichment is seen to occur with annealing. Annealing of the homopolymer samples above T_g brought no change in the spectra. Therefore, in the following figures comparing bulk MALDI-ToF-MS spectra with SL-MALDI-ToF-MS spectra from surfaces, only spectra from annealed samples are used.

The behavior of the narrow dispersity 2 kDa PS melts is revealed in Figure 2 with spectra representative of the results observed from three samples. The spectrum labelled "bulk" is representative of spectra collected with conventional MALDI MS. The spectrum labelled "surface" is representative of the spectra collected with the SL-MALDI MS methodology. The value of M_n for the surface spectrum is 280 ± 70 Da lower than that for the bulk

spectrum. This corresponds to a difference of nearly three repeat units. For 6k PS films, the value of M_n for the surface is 340 ± 185 Da smaller than that for the bulk, as shown in the supporting information Figure S3.

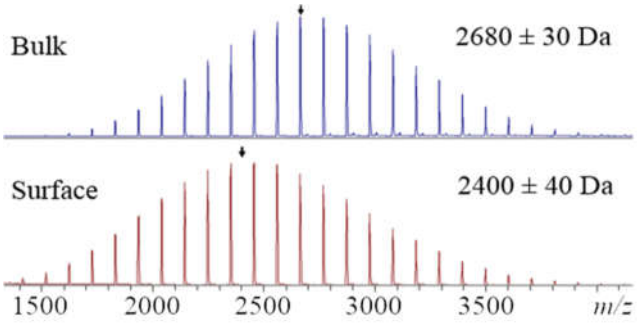


Figure 2. Representative spectra for the 'bulk' (top) and surface (bottom) of 2.5 kDa PS films, with the corresponding values of M_n and error noted. The arrow marks the m/z value corresponding to the value of M_n from an average over three samples.

This shift in M_n from the bulk to the surface spectra is not unique to PS. For two molecular weights of PMMA, 3k and 7k, the shift in M_n from bulk to surface is larger than for the somewhat stiffer PS chains, as shown in Figure 3. In general, anionic polymerization of acrylates is less well controlled than that of styrene, resulting in larger PDI values, which makes surface enrichment by short chains more evident. For 3k PMMA the difference is 680 ± 160 Da, or nearly seven repeat units, while for 7k PMMA it is 550 ± 200 Da. The range of m/z data shown corresponds to the range over which the analysis was done. Analysis for still lower values of m/z was complicated by the appearance of silver clusters and therefore was avoided. If that portion of the spectrum could have been included in the analysis without artifacts due to the clusters, the calculated shifts in M_n value from bulk to surface would have been even larger. Another complication that arises with the PMMA samples is the presence of a second distribution resulting from backbiting during synthesis.[37] The backbiting changes the end group, polarity and possibly the ionization efficiency of about 20% of the chains. The complications from the second distribution in the 3kDa PMMA are more serious than with the second distribution in the 6kDa PS because the second PMMA distribution shifts so much that a substantial portion of it moves below the m/z value at which analysis was stopped to avoid including Ag clusters. Most important to note is that enrichment at the surface by the shorter chains is obvious in the spectra for both the primary species as well as for the species resulting from backbiting.

Theoretical calculations qualitatively capture the trends observed experimentally. Figure 4 compares representative experimentally obtained bulk and surface spectra for 2.5kDa PS with the theoretical prediction. Expressing the molecular weight shifts in terms of monomer units, the experimental shift for the single spectrum used for comparison was 2.0 (0.08%) while the theoretical estimate of the shift is 0.93 (or 0.04%), so the theory significantly underestimates the strength of the surface segregation phenomenon. Furthermore, the shape of the theoretical molecular weight distribution for the surface is narrower than the experimental distribution. We could use a broader surface width, ξ, in the calculations to improve the agreement, but the more likely reason for the discrepancy is the rigidity of short PS chains, which the freely-jointed chain model does not represent well. For the 6 kDa PS melt, the agreement in the shapes of the experimental and theoretical spectra, shown in Figure S4, is better. This may be because longer chains are better approximated by the freely-jointed chain model. However, the discrepancy between the means of the experimental and theoretical distributions is larger for 6 kDa PS. The experimental shift is 2.3 (0.04%) and the theoretical shift is 0.65 (0.01%). Nevertheless, both the experiment and theory find reductions in the relative shift compared to the 2.5kDa PS, which can be attributed to the narrower molecular weight distributions (i.e., smaller PDI).

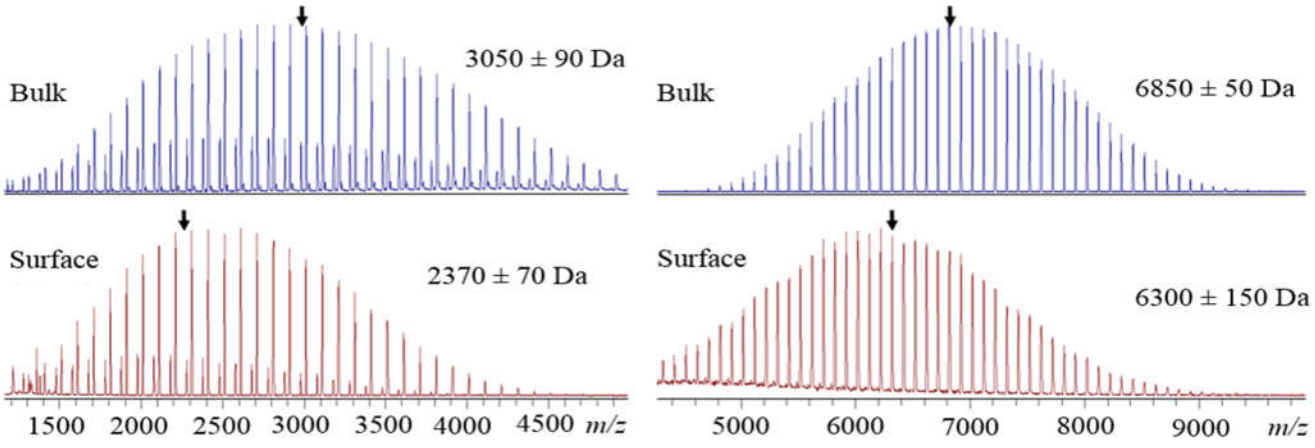


Figure 3. Spectra representative of the 'bulk' (top) and surface (bottom) of 3 kDa and 6 kDa PMMA. Arrows mark the m/z values corresponding to the values of M_n averaged over three samples. Baselines for the surface spectra of PMMA were higher than those for PS due to less overall intensity, but analysis still produced a reliable M_n.

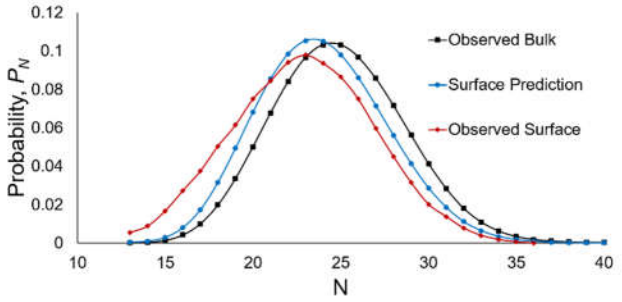


Figure 4. Comparison of experimental and theoretical distributions of chain length, *N*, for the surface of the 2.5 kDa PS melt. The experimental distribution for the bulk serves as input for the calculations of the surface distributions.

Comparison between the experimental and theoretical distributions for 7 kDa PMMA is shown in Figure 5. No calculation for the 3 kDa PMMA was attempted due to complications from the second distribution caused by backbiting. The agreement in the magnitude of the shift is better for 7 kDa PMMA than for PS. The experimental shift was 4.2 (0.06%) and the theoretical shift is 1.94 (0.03%). The shapes of the theoretical and experimental distributions do not agree quite so well as for the 6 kDa PS case. This is probably due to the greater noise in the experimental PMMA distributions. Enhanced background in the low *m*/*z* portion of the experimental bulk spectrum, in the low *N* range, caused noise in the theoretical distribution. Furthermore, noise is also evident in the distribution around N = 50-70. Nonetheless, both experimentally and theoretically, the surface enrichment of short chains is more pronounced with 7 kDa PMMA than with 6kDa PS. This could be due to PMMA's somewhat greater flexibility, the larger polydispersity for PMMA, or perhaps differences in the relative importance for PS and PMMA of enthalpic effects due to differences between the precise chemistry of the chain end and that of the repeat units.

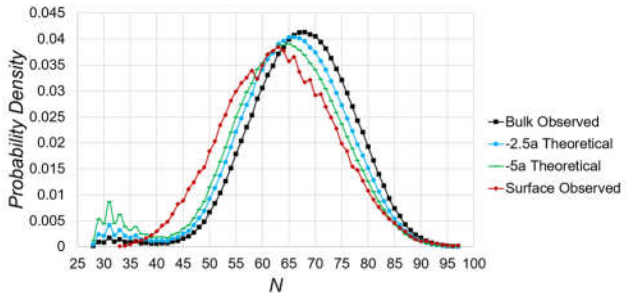


Figure 5. Comparison of experimental and theoretical distributions of chain length, *N*, for the surface of the 7 kDa PMMA melt. The experimental distribution for the bulk serves as input for the calculations of the surface distributions.

In summary, enrichment of a surface by shorter chains occurs even for anionically polymerized materials considered in many practical situations as monodisperse. Though subtle, the segregation for every n-mer in the distribution can be precisely quantified using SL-MALDI-ToF-MS in a single measurement. Since the technique requires no labelling, results are readily compared with a self-consistent field theory using a freely-jointed chain model that provides a description consistent with the experimental trends, but underestimates the magnitude of the effect, possibly due to chain stiffness. The ability to quantify such effects and model them without perturbing systems with labelling has potential for improving tailoring of surface properties with low molecular weight components such as additives.

ASSOCIATED CONTENT

Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

* E-mail: mdf1@uakron.edu; wesdemiotis@uakron.edu.

Author Contributions

‡These authors contributed equally.

Funding Sources

The authors acknowledge support from the National Science Foundation (CHE-1308307) and the University of Akron Research Foundation.

ORCID

Mark D. Foster: 0000-0002-9201-5183
C. Wesdemiotis: 0000-0002-7916-4782
Kevin J. Endres: 0000-0002-0857-6966
Jacob Hill: 0000-0001-7019-1779
Mark W. Matsen: 0000-0003-2099-0892
Pendar Mahmoudi: 0000-0001-7280-5594

ACKNOWLEDGEMENTS

The authors acknowledge Dr. Ahlam Alalwait for early contributions in refining the measurement methodology and MM thanks Jamie Forrest for useful discussions.

REFERENCES

1. Wu, S., *Polymer Interface and Adhesion*. Taylor & Francis: 1982; p 630.
2. Schmidt, I.; Binder, K. Model Calculations for Wetting Transistions in Polymer Mixtures. *J. Phys. France* **1985,** 46, 1631-1644.
3. Briggs, D. New Developments in Polymer Surface Analysis. *Polymer* **1984,** 25, 1379-1391.
4. Russell, T. P.; Hadziioannou, G.; Warburton, W. Phase Separation in Low Molecular Weight Polymer Mixtures. *Macromolecules* **1985,** 18, 78-83.

5. Jones, R. A. L.; Kramer, E. J.; Rafailovich, M. H.; Sokolov, J.; Schwarz, S. A. Surface Enrichment in an Isotopic Polymer Blend. *Phys. Rev. Lett.* **1989,** 62, 280-283.
6. Wightman, J. P.; Lin, T. D.; Webster, H. F. Surface Chemical Aspects of Polymer/Metal Adhesion. *International J. Adhes. Adhes.* **1992,** 12, 133-137.
7. Matsen, M. W.; Mahmoudi, P. Segregation of Chain Ends to the Surface of a Polymer Melt. *Eur. Phys. J. E* **2014,** 37, 78-86.
8. MacDonald, R. J.; King, B. V., SIMS — Secondary Ion Mass Spectrometry. In *Surface Analysis Methods in Materials Science*, O'Connor, D. J.; Sexton, B.; Smart, R. C., Eds. Springer Berlin Heidelberg: 1992; Vol. 23, pp 117-147.
9. Russell, T. P. X-Ray and Neutron Reflectivity for the Investigation of Polymers. *Mater. Sci. Rep.* **1990,** 5, 171-271.
10. Hanton, S. D. Mass Spectrometry of Polymers and Polymer Surfaces. *Chem. Rev.* **2001,** 101, 527-570.
11. Fouquet, T.; Mertz, G.; Desbenoit, N.; Frache, G.; Ruch, D. TOF-SIMS/MALDI-TOF Comination for the Molecular Weight Depth Profiling of Polymeric Bilayer. *Mater. Lett.* **2014,** 128, 23-26.
12. Jin, Y.; Wong, K. H.; Granville, A. M. Enhancement of Localized Plasmon Resonance Polymer Based Biosensor Chips Using Well-Defined Glycopolymers for Lectin Detection. *J. Colloid Interface Sci.* **2016,** 462, 19-28.
13. Hollander, J. M.; Jolly, W. L. X-Ray Photoelectron Spectroscopy. *Acc. Chem. Res.* **1970,** 3, 193-200.
14. Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F. Characterization of Polymers by Matrix-Assisted Laser Desorption Ionization-Time of Flight Mass Spectrometry. End Group Determination and Molecular Weight Estimates in Poly(ethylene glycols). *Macromolecules* **1995,** 28, 4562-4569.
15. Räder, H.; Schrepp, W. MALDI-TOF Mass Spectrometry in the Analysis of Synthetic Polymers. *Acta Polymerica* **1998,** 49, 272-293.
16. Li, L., *MALDI Mass Spectrometry for Synthetic Polymer Analysis*. Wiley: 2009.
17. Wang, S.-F.; Li, X.; Agapov, R. L.; Wesdemiotis, C.; Foster, M. D. Probing Surface Concnetration of Cyclic/Linear Blend Films Using Surface Layer MALDI-TOF Mass Spectrometry. *ACS Macro Letters* **2012,** 1, 1024-1027.
18. Hariharan, A.; Kumar, S. K.; Russell, T. P. Reversal of the Isotopic Effect in the Surface Behavior of Binary Polymer Blends. *J. Chem. Phys.* **1993,** 98, 4163-4173.
19. Hariharan, A.; Kumar, S. K.; Russell, T. P. Free Surfaces of Polymer Blends. II. Effects of Molecular Weight and Applications to Asymmetric Polymer Blends. *J. Chem. Phys.* **1993,** 99, 4041-4050.
20. Hariharan, A.; Kumar, S. K.; Russell, T. P. A Lattice Model for the Surface Segregation of Polymer Chains due to Molecular Weight Effects. *Macromolecules* **1990,** 23, 3584-3592.
21. Dee, G. T.; Sauer, B. B. The Cohesive Energy Density of Polymers and its Relationship to Surface Tension, Bulk Thermodynamic Properties, and Chain Structure. *J. Appl. Polym. Sci.* **2017,** 134.
22. Sabzevari, S. M.; McGraw, J. D.; Wood-Adams, P. Short Chains Enhance Slip of Highly Entangled Polystyrene During Thin Film Dewetting. *RSC Advances* **2016,** 6, 91163-91170.
23. Ebrahimi, M.; Ansari, M.; Inn, Y. W.; Hatzikiriakos, S. G. Surface Fractionation Effects on Slip of Polydisperse Polymer Melts. *Phys. Fluids* **2016,** 28, 093101.
24. Qian, Z.; Minnikanti, V. S.; Sauer, B. B.; Dee, G. T.; Kampert, W. G.; Archer, L. A. Surface Tension of Polystyrene Blends: Theory and Experiment. *J. Polym. Sci. Part B: Polym. Phys.* **2009,** 47, 1666-1685.
25. Mayes, A. M. Glass Transistions of Amorphous Polymer Surfaces. *Macromolecules* **1994,** 27, 3114-3115.
26. Tanaka, K.; Kajiyama, T.; Takahara, A.; Tasaki, S. A Novel Method to Examine Surface Composition in Mixtures of Chemically Identical Two Polymers with Different Molecular Weights. *Macromolecules* **2002,** 35, 4702-4706.
27. Stark, R.; Kappl, M.; Butt, H.-J. Interaction of Solid Surfaces Across Binary Mixtures of Polymer Melts. *Macromolecules* **2007,** 40, 4088-4091.
28. Composto, R. J.; Stein, R. S.; Felcher, G. P.; Mansour, A.; Karim, A. Surface Enrichment and Evaporation in a Polymer Mixture of Long and Short Chains in *Polymer Based Molecular Composites*, Schaefer, D.W., Mark, J.E., Eds.; MRS Symposia Proceedings 171; Materials Research Society: Boston, 1989.
29. Hong, P. P.; Boerio, F. J.; Smith, S. D. Effect of Annealing Time, Film Thickness, and Molecular Weight on Surface Enrichment in Blends of Polystyrene and Deuterated Polystyrene. *Macromolecules* **1994,** 27, 596-605.
30. Van der Gucht, J.; Besseling, N.; Fleer, G. Surface Segregation in Polydisperse Polymer Melts. *Macromolecules* **2002,** 35, 6732-6738.
31. Mahmoudi, P.; Matsen, M. Entropic Segregation of Short Polymers to the Surface of a Polydisperse Melt. *Eur. Phys. J. E* **2017,** 40, 85.
32. Russell, T.P. The Characterization of Polymer Interfaces. *Annu. Rev. Mater. Sci.* **1991**, *21*, 249-268.
33. Skelton, R.; Dubois, F.; Zenobi, R. A MALDI Sample Preparation Method Suitable for Insoluble Polymers. *Anal. Chem.* **2000,** 72, 1707-10.
34. Trimpin, S.; Rouhanipour, A.; Az, R.; Räder, H. J.; Müllen, K. New Aspects in Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry: A Universal Solvent-Free Sample Preparation. *Rapid Commun. Mass Spectrom.* **2001,** 15, 1364-1373.
35. Hanton, S. D.; Parees, D. M. Extending the Solvent-Free MALDI Sample Preparation Method. *J. Am. Soc. Mass Spectrom.* **2005,** 16, 90-93.
36. Mahmoudi, P.; Matsen, M. W. Segregation of Chain Ends to the Surface of a Polymer Melt: Effect of Surface Profile Versus Chain Discreteness. *Eur. Phys. J. E* **2016,** 39, 78.
37. Jacobs, C.; Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jerome, R.; Teyssie, P. Termination Mechanism in the Anionic Copolymerization of Methyl Methacrylate and *tert*-Butyl acrylate. *Macromolecules* **1990,** 23, 4024-4025.

TABLE OF CONTENTS GRAPHIC

