

Surface Composition of Polystyrene

RONALD D. GOLDBLATT, GERALD J. SCILLA, and JAE M. PARK, *IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598*, and JULIAN F. JOHNSON and SAMUEL J. HUANG, *Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268*

Synopsis

The physical and chemical properties of bulk polymers are well understood and have been measured exhaustively for numerous systems, but the properties of polymer surfaces are quite often different from those observed in the bulk and are usually not as easily measurable. Since many polymer properties vary with molecular weight, it is of interest to determine whether or not there is any segregation in a homopolymer system based on molecular weight. In particular, does the surface of a polymer sample have the same molecular weight composition as the bulk? The current work answers this question for a polystyrene system. Through the use of secondary ion mass spectrometry and tagged polystyrene, it has been shown that surface and bulk molecular weight composition are indistinguishable within the limits of the experimental method's sensitivity. The sensitivity of the technique is documented using samples artificially created with different surface and bulk molecular weight compositions.

INTRODUCTION

The physical and chemical properties of polymers in the bulk have been measured exhaustively for numerous systems. Surface properties can be drastically different from their bulk counterparts both physically and chemically.

The literature contains a great deal of work done to elucidate surface behavior. Efforts to describe the attractive forces at interfaces^{1,2} and the relative importance of chemical³⁻⁵ vs. physical⁶⁻⁹ factors are abundant. Much of the work done relates the observed surface properties to adhesion strengths. Studies of wettability¹⁰⁻¹² demonstrate the extent to which a single bulk material can exhibit different surface behaviors under various conditions. The role of molecular diffusion¹³ in determining surface behavior has been studied with special attention being paid to surface active agents¹⁴ and various additives,¹⁵⁻¹⁷ which can be exuded from the bulk to yield tailored surface properties. The driving force for these tailored diffusions can usually be found upon consideration of the thermodynamics of the system, especially the surface free energy of the systems components.¹⁸⁻²⁰ The relationship between surface tension and molecular weight²¹⁻²³ is of interest. The molecular weight dependence of polymer surface tension (surface free energy) has been shown to follow²⁴:

$$\gamma = \gamma_{\infty} - K/M_n^{2/3}$$

where γ is the surface tension, γ_{∞} is the surface tension at infinite molecular

weight, and M_n is the number average molecular weight. This relationship leads to a question: Is there or is there not a segregation in a homopolymer system based on molecular weight? The argument that favors segregation, in particular a surface preponderance of lower molecular weight chains, is that any system will strive for lower free energy. Since small chains have a lower surface free energy than large chains they should preferentially populate the surface. However, there is a cost for this in terms of system entropy. A random mixture of low and high molecular weight chains has a greater entropy than a system that orders itself to populate its surface with smaller molecules. The relative magnitude of these competitive effects, and their effect on the total free energy of the system, should determine whether or not segregation by molecular weight occurs.

EXPERIMENTAL

Instrumentation

Chromium sputter deposition was done in a Perkin-Elmer (Norwalk, CT) Randex Sputtering System Model 2400.

Spin coating of sample films was done using a Headway Research, Inc. (Garland, TX) Model AC201 photoresist spinner. Spin speed, spin time, and spin acceleration could all be controlled independently.

Film thicknesses were determined in two ways. For films thicker than $2 \mu\text{m}$ a Sloan Technologies (Santa Barbara, CA) Dektak Model IIA surface profilometer was used. For thinner films either the Dektak or a Gaertner (Chicago, IL) Variable Angle Computer Controlled Laser Ellipsometer was used.

Secondary Ion Mass Spectrometry was done using a Cameca (Courbevoie Cedex, France) IMS 3F and 4F secondary ion mass spectrometer.

Chemicals

Commercial grade polystyrene was purchased from Polysciences Inc. Narrow dispersity polystyrene standards as well as bromine-terminated, deuterium-terminated, and perdeuterated narrow dispersity polystyrenes were purchased from Polymer Labs Inc. Two hundred proof ethanol was purchased from U.S. Industrial Chemical Company. Semigrade acetone was purchased from Mallinckrodt. Semigrade methanol and HPLC grade water were purchased from Aldrich. All chemicals were used as received.

RESULTS AND DISCUSSION

The polymer of choice is polystyrene. The enormous amount of data in the literature that has been gathered for this polymer makes it possible to proceed experimentally without having to gather a great deal of preliminary information. Since polystyrene can be synthesized by anionic chain polymerization, the molecular weight can be tailored to any need, and essentially monodisperse reaction products may be obtained.

It was decided to examine techniques for monitoring Br and D tagged low molecular weight species within a high molecular weight matrix. It was first

necessary to get an idea of spun on thickness as a function of weight percent solids, spin speed, spin time, and spin acceleration. Optimal spin time was observed to be 30 s and medium acceleration was most often used. As a starting point polystyrene of average molecular weight 10,200 and 4,250,000 were spun on and thickness analyzed using Dektak.

The analytical technique investigated was secondary ion mass spectrometry (SIMS). Samples had to be prepared on conductive substrates, and as a starting point 1000 Å sputtered chromium on silicon was used. Solutions of low molecular weight brominated polystyrene in high molecular weight untagged polystyrene were spun onto samples and dried. Various annealing schedules were used. Before SIMS examination, samples were fractured, and a thin (≈ 150 Å) layer of gold was deposited by thermal evaporation. A representative SIMS spectrum of a 2:1 mole ratio of bromine-terminated polystyrene to normal polystyrene, both of average molecular weight 4600 and dispersity 1.05, is shown in Figure 1. The small signal rise initially in both scans was later determined to be a SIMS artifact; however, at this point it was unclear whether this was an artifact or an indication of surface concentration. Initially the concentration of bromine appeared relatively uniform throughout the bulk of the layer (curve 2A: baked 3 h at 85°C), but upon annealing (curve 2B: baked 3 h at 85°C and 186 h at 150°C in nitrogen) a significant loss in intensity was observed. It appeared as if the chromium had catalyzed the debromination of our tagged polymer chains. One should note the spectral change that occurs at approximately 600 s sputtering time is due to the fact that the substrate interface has been reached. This is a typical characteristic of SIMS depth profiles. Before continuing the SIMS work, substrates were switched from 1000 Å chromium sputtered onto silicon wafers to approximately 3000 Å gold *e*-beam evaporated onto silicon wafers, and deuterium tagged low molecular weight chains were used. Solutions and samples were then prepared. Samples were resistive evaporant covered with

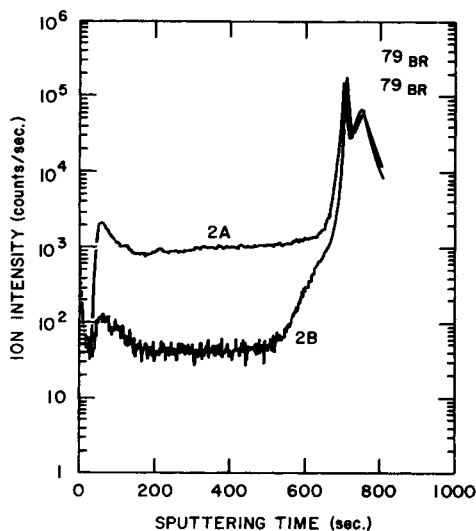


Fig. 1. SIMS depth profile, bromine-terminated low molecular weight polystyrene: (2A) pre-anneal; (2B) post-anneal.

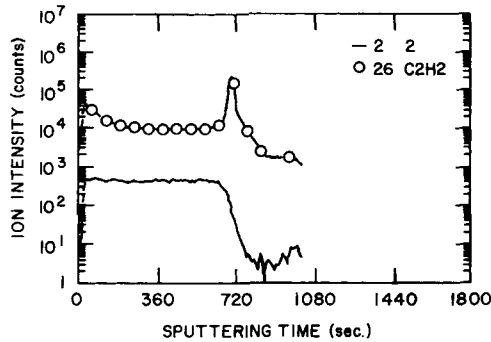


Fig. 2. SIMS depth profile, deuterium-terminated low molecular weight polystyrene.

several hundred angstroms of gold, and SIMS was performed with oxygen positive primary and negative secondary. Four hundred to 1000 nA at 7.5 kV was employed with a 500- μ m raster.

Figure 2 shows a representative scan for a 50/50 weight/weight mixture of deuterium-terminated polystyrene, $\overline{MW} = 4,600$, PDI = 1.05, in normal polystyrene of $\overline{MW} = 4,250,000$, PDI = 1.07. The scan clearly indicates homogeneous concentration of the low molecular weight chains throughout the layer. The intensity changes in the depth profiles at 720 s again result from arrival at the substrate/film interface.

Having achieved good results with the deuterium tagged low molecular weight polystyrene, it was decided that the next attempt to elucidate the molecular weight behavior in polystyrene systems should utilize perdeuterated polystyrene as the tagged species. Stock solutions were prepared and samples were spin cast and baked. The following sample compositions were prepared:

- (i) pure untagged high molecular weight polystyrene (HMWPS-1, $\overline{MW} = 4,250,000$; PDI = 1.07);
- (ii) pure perdeuterated low molecular weight polystyrene (LMW-PSperD, $\overline{MW} = 6,900$; PDI = 1.03);
- (iii) 50/50 w/w LMW-PSperD in HMWPS-1 matrix;
- (iv) 25/75 w/w LMW-PSperD in HMWPS-1 matrix.

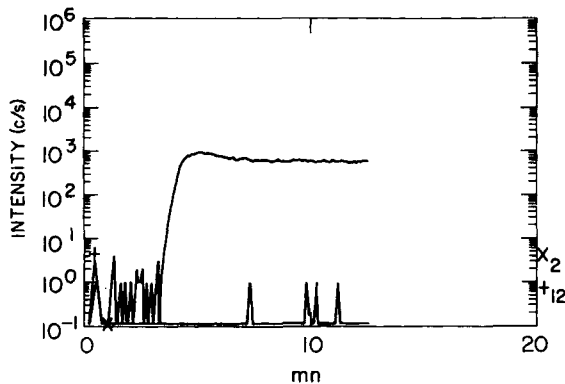


Fig. 3. SIMS depth profile, pure HMWPS-1.

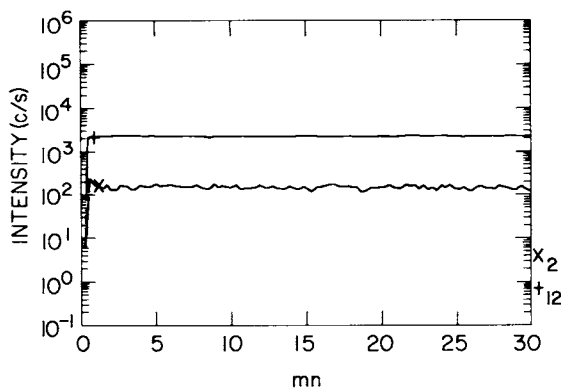


Fig. 4. SIMS depth profile, pure LMW-PSperD.

Samples were then subjected to different bake schedules. SIMS was run with oxygen positive primary and positive secondary ions were monitored.

The first objective was to demonstrate the absence of any appreciable background signal at mass two. Figure 3 shows the scan for a 1- μ m-thick sample of pure HMWPS-1. It is evident that at mass 2, the signal is noisy, but there is no background interference of consequence. Figure 4 shows the scan for a 1- μ m-thick sample of pure LMW-PSperD depth profiled at 2 $\text{\AA}/\text{s}$. One readily sees that the mass 2 signal is constant and very similar in shape to the mass 12 carbon signal.

Now, having established the representative spectra for the pure components, it was appropriate to examine the behavior of binary mixtures. Figures 5 and 6 are spectra for a 50 wt % LMW-PSperD and 25 wt % LMW-PSperD, respectively, in HMWPS-1 that had been annealed for 18 h above the glass transition temperature. The deuterium mass 2 signal, which originates from the low molecular weight chains, appears to remain constant as the layer is depth-profiled. This indicates a uniform distribution of the low molecular weight chains throughout the entire layer.

At this time, investigation of the steady state deuterium to carbon signal intensity ratio provided further encouragement. For the 100% LMW-PSperD

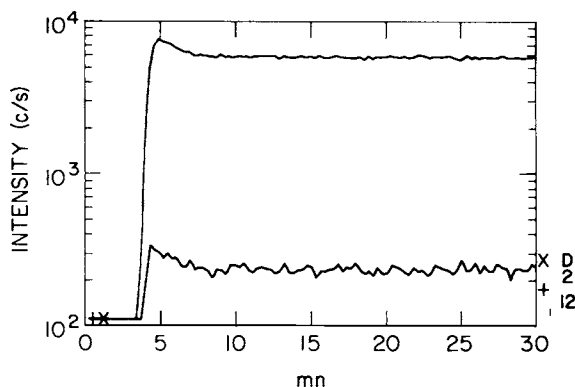


Fig. 5. SIMS depth profile: 50 wt % LMW-PSperD, annealed 3 h at 85°C, then 18 h at 160°C in N_2 .

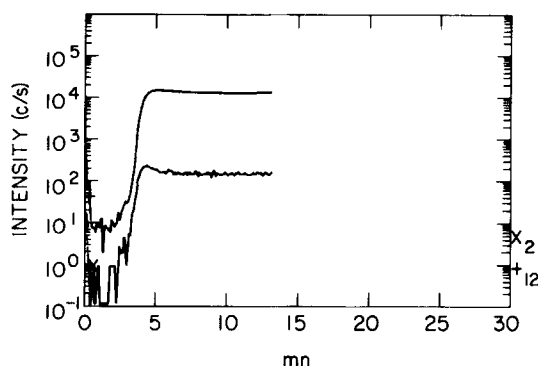


Fig. 6. SIMS depth profile: 25 wt % LMW-PSperD, annealed 3 h at 85°C, then 18 h at 160°C in N_2 .

the deuterium to carbon intensity ratio was observed to be 0.1. For the 50 wt % mixture the intensity ratio dropped to 0.05, and for the 25 wt % mixture the intensity ratio fell to 0.02. These values assured a high degree of self-consistency for the technique.

In order to eliminate any concern about kinetic constraints the 50 and 25 wt % LMW-PSperD mixtures were further annealed for 1 month above T_g (160°C) in nitrogen. The resulting SIMS profiles are presented in Figures 7 and 8. It is clear that, even after annealing above T_g for this extended period of time, no surface segregation was observed.

Before concluding that there was indeed no segregation by molecular weight, it was necessary to demonstrate that the technique used was sensitive enough to detect segregation had it occurred. For this purpose bilayer samples were prepared in the following fashion. Normal polystyrene of $\overline{MW} = 4,400,000$ and $PDI = 1.06$ (HMWPS-2) was cast onto gold-covered silicon wafers and thoroughly dried. The final thickness of these samples was measured to be 2000 Å. The low molecular weight perdeuterated polystyrene (LMW-PSperD) was spun onto clean glass microscope slides at various thicknesses. By scribing the polystyrene film on the glass slide and then inserting the slide into a water

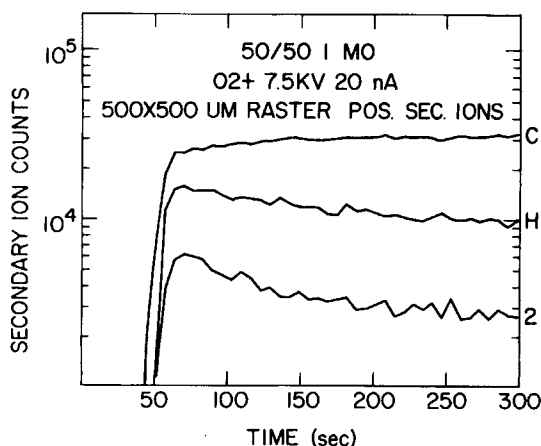


Fig. 7. SIMS depth profile: 50 wt % LMW-PSperD, 1-month anneal at 160°C.

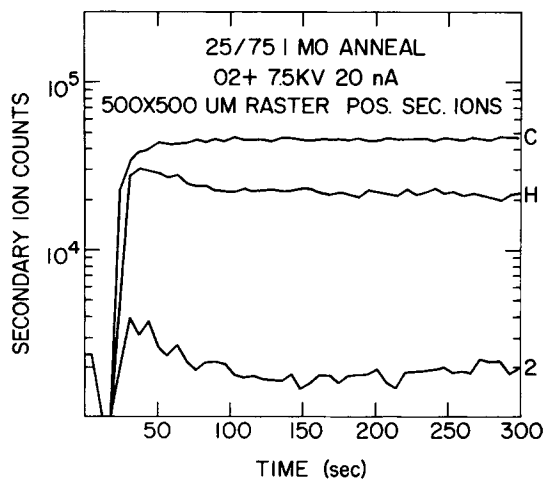


Fig. 8. SIMS depth profile: 25 wt % LMW-PSperD, 1-month anneal at 160°C.

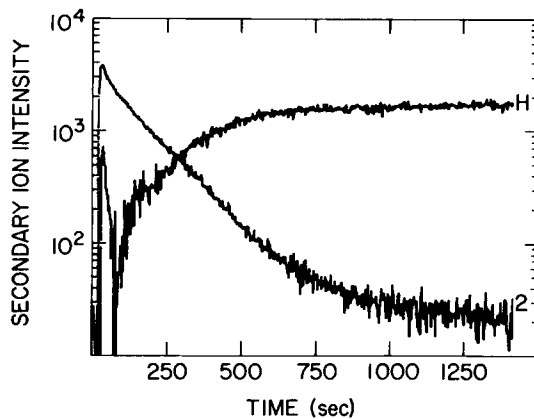


Fig. 9. SIMS depth profile: bilayer sample 1, 225 ± 25 Å LMW-PSperD on top of 2000 Å HMWPS-2.

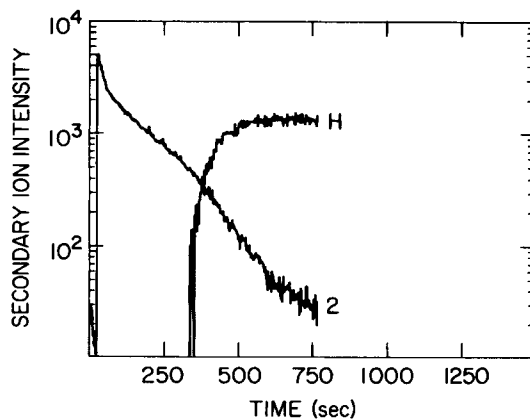


Fig. 10. SIMS depth profile: bilayer sample 2, 105 ± 5 Å LMW-PSperD on top of 2000 Å HMWPS-2.

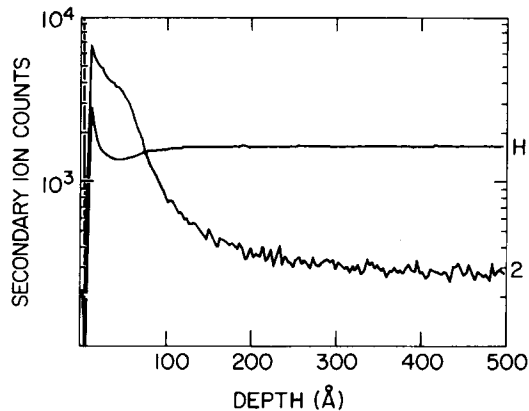


Fig. 11. SIMS depth profile: bilayer sample 3, 62 ± 5 Å LMW-PSperD on top of 2000 Å HMWPS-2.

trough at a 45° angle, a coherent film could be lifted off the slide and floated on the surface of the water. This film could then be transferred to the previously cast samples of high molecular weight polystyrene in the reverse manner.

After perfecting this technique films were deposited at thicknesses as thin as 62 ± 5 Å, as determined by ellipsometry. After drying the bilayer samples below T_g , so that no mixing could occur, SIMS experiments were performed. Figures 9, 10, and 11 show the SIMS spectra for 225 ± 25 , 105 ± 5 , and 62 ± 5 Å layers of LMW-PSperD on top of 2000 Å of HMWPS-2. In each case the detection of two separate layers is readily apparent.

Based upon the work of Yamamoto et al.,²⁵ for atactic polystyrene in cyclohexane at 34.5°C (θ conditions), one can calculate the unperturbed radius of gyration for the low molecular weight (6900) perdeuterated polystyrene to be 24 Å. Having obtained a confidence limit of approximately 20 Å for the SIMS technique used, it is reasonable to conclude that any surface segregation would have been detectable.

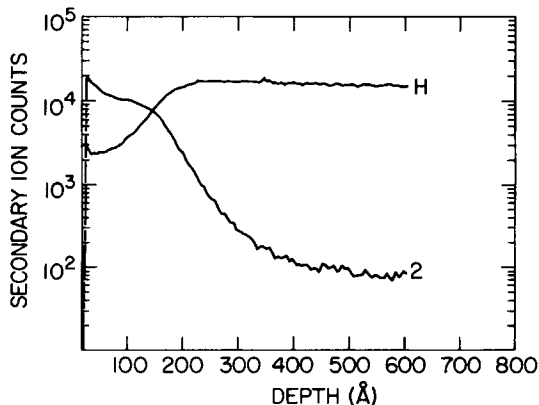


Fig. 12. SIMS depth profile: bilayer sample 4, 169 ± 5 Å LMW-PSperD on top of 2000 Å HMWPS-2, dried below T_g (85°C).

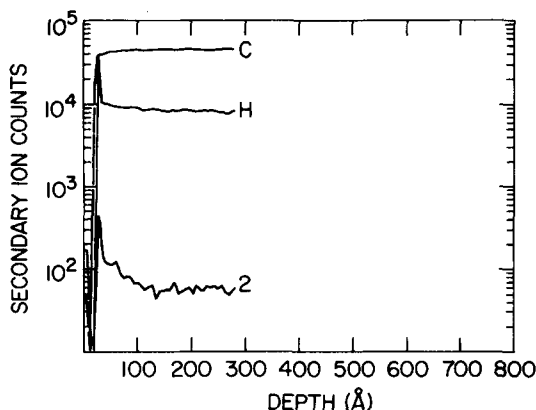


Fig. 13. SIMS depth profile: bilayer sample 4, 169 ± 5 Å LMW-PSperD on top of 2000 Å HMWPS-2, annealed 40 h at 160°C in N_2 .

For the sake of completeness, at this juncture another bilayer sample was prepared. Onto a 2000 Å layer of HMWPS-2, a 169 ± 5 Å layer of LMW-PSperD was cast from a water trough. Figure 12 shows the SIMS spectrum for this sample after drying below T_g . The two layer structure is easily discerned. Figure 13 is a SIMS spectrum of this sample after baking 40 h above T_g (160°C), respectively. The presence of complete desegregation is observed.

CONCLUSION

The original question we asked was: Does the surface of a polystyrene sample have the same molecular weight composition as the bulk? For the system studied the answer to this question is yes. With the aid of secondary ion mass spectrometry, the concentration of perdeuterated narrow dispersity polystyrene of average molecular weight 6900 was depth profiled in a high molecular weight polystyrene matrix for samples cast from bimodally distributed solutions subjected to different thermal histories. No segregation was observed within the resolution limit of approximately 20 Å. To confirm this result, bilayer samples were prepared and analyzed. Two-layer structures were easily discerned using SIMS. We demonstrated a sensitivity (or more appropriately a confidence limit) of approximately 20 Å. A calculation of the size of the low molecular weight polystyrene molecules in bulk yielded a value for the unperturbed radius of gyration of 24 Å. The value stated above for the radius of gyration represents a lower limit; the actual value for the radius of gyration is greater than or equal to this calculated one. This is a clear indication that any surface preponderance of low molecular weight molecules would have been detectable. Therefore, we conclude that, for homogeneous distributions of low molecular weight polystyrene in high molecular weight matrices, segregation does not readily occur nor can it be induced by annealing above the glass transition temperature for long periods of time. It therefore follows that the magnitude of the entropy loss associated with the ordering required to have molecular weight segregation exceeds the magnitude of the system's free energy reduction caused by the decreased surface free

energy that would be associated with a surface preponderance of lower molecular weight chains. This postulated thermodynamic equilibrium was confirmed by the observation of complete desegregation of artificially created bilayer structures upon annealing above T_g .

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