

Effective χ and Surface Segregation in Blends of Star and Linear Polystyrene

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SUMMARY: The existence in blends of linear and star branched polystyrenes (PS) of a bulk thermodynamic interaction due to differences in macromolecular architecture has been demonstrated with small angle neutron scattering measurements. It has also been demonstrated that a regularly star-branched polystyrene material segregates preferentially to the surface of a blend of star and linear molecules.

Introduction

In general the surface of a binary polymer blend is enriched in one of the two components, leading to a surface composition which can differ substantially from that in the bulk. This surface segregation presents both a challenge and an opportunity in controlling the surface

properties of polymer blends. Properly understanding the surface segregation behavior requires first understanding the thermodynamic interactions in the bulk of the blend.

In recent years increasingly subtle differences in the components of a binary polymer blend have been shown to lead to measurable interactions in the bulk and/or surface segregation. Thus, miscibility varies not only with differences between components in molecular weight and gross chemistry, but also with differences in chemical microstructure¹⁻³, type of isotopic labeling⁴, and tacticity⁵. Conformational asymmetry can also affect specific interactions⁶. Recent theoretical studies of blends of star and linear polymers⁶⁻⁹ suggest that even the presence of a single branch point in one component can result in a measurable thermodynamic interaction as characterized by χ . Fredrickson *et al.*⁶ argue that even in the absence of enthalpic interactions (an "athermal" blend) a contribution to χ due to architectural differences is present. This athermal component is predicted to increase with number of arms and disparity between the sizes of the linear chains and star arms. Graessley and coworkers^{4,10} have suggested that in weakly interacting polyolefin blends the interactions seen among chains of different short chain random branching can be rationalized on the basis of enthalpic arguments alone, but these differences in enthalpic interactions come as a result of differences in repeat unit microstructure. In this work Small Angle Neutron Scattering (SANS) is used to measure the effective bulk χ parameter for blends of star and linear polystyrenes so that theories predicting the magnitude and character of χ due to architecture differences can be tested.

Surface segregation in these blends has been characterized by Dynamic Secondary Ion Mass Spectroscopy (DSIMS) and other methods. The DSIMS result for a single blend is presented as illustrative. Theoretical studies have predicted that the star chains should be preferred at the surface in the absence of other differences between the two components¹¹. Three mechanisms have been suggested to explain this predicted behavior: the favoring of chain ends at surfaces¹²⁻¹⁵; the lower contact density among stars which leads to an enthalpic driving force for surface segregation; and the connectivity of the stars which causes them to be favored at the surface for entropic reasons. This presentation focuses on providing a measurement of the magnitude of the surface segregation effect.

Experimental

The results from blends containing six arm stars and their linear analogs are considered as illustrative of star/linear blends in general. Linear polystyrene (PS) was purchased from Polymer Source, Dorval, Quebec, Canada and characterized at Polymer Source, as well as at The University of Akron and at Goodyear Tire & Rubber Company. The six arm stars were synthesized *via* living anionic polymerization at The University of Akron by first making narrow molecular weight distribution living poly(styryl)lithium arm precursors and then coupling with 1, 2 *bis*(trichlorosilyl)ethane. The deuterated six arm star (d6s) had a molecular weight of 157,400 g/mol, ($M_w/M_n = 1.01$) corresponding to a chain length (N) of 1405 (segment volume = 100 cm³/mole). The linear analog had a molecular weight of 230,700 g/mol ($N=2218$) and $M_w/M_n = 1.06$.

SANS and DSIMS samples were prepared by dissolving 18wt% star and 82wt% linear material in toluene and solution casting and spin casting films, respectively. Spin casting for DSIMS samples was done on polished silicon wafers, at 2,000 rpm for 2 minutes. The wafers were cleaned in piranha solution and deionized water prior to spin casting. Films for both studies were dried in a vacuum oven (seven days for the SANS studies and 24 hours for the DSIMS studies) to remove excess solvent. Films for surface study were also annealed under high vacuum for 7.8 days at 170 °C and then covered with a sacrificial layer of PS and overcoated with gold. The thickness of the spin coated films was measured with x-ray reflectometry and neutron reflectometry, and always exceeded four times the R_g of the molecules. SANS measurements were conducted on the NG3 30-m SANS instrument at the National Institute for Standards and Technology using neutrons with wavelength 6 Å and $\Delta\lambda/\lambda = 0.150$ FWHM. DSIMS measurements were carried out at the MatNet facility at Case Western Reserve University using a 2kV Ar⁺ ion beam. Selected ions (H⁺, D⁺, CH⁺, CD⁺, O⁺, C⁺, Si⁺) were monitored at a set sputter rate and mass analyzed as a function of charge to mass ratio.

Results and Discussion

Values of the effective bulk interaction parameter, χ , were obtained by fitting the SANS data with a random phase approximation expression incorporating a structure factor for the regularly branched star¹⁶. The value of χ at 165 °C for the blend of d6s with linear analog is 1.5×10^{-4} for

a segment volume of $100 \text{ cm}^3/\text{mol}$. A dPS/hPS linear/linear isotopic blend of the same composition has a value of χ of 0.87×10^{-4} at this temperature. The contribution to χ ascribable to the architecture difference between star and linear molecules is therefore about 6×10^{-5} . This may be compared with the architecturally based contribution to χ of 3×10^{-5} which we have found for a four arm star/linear blend with a four arm star (molecular weights of star and linear both 100k)¹⁷. Thus the contribution to χ due to differences in macromolecular architecture increases with arm number.

DSIMS measurements of a thin film of the same star/linear blend containing the six-arm star revealed preferential segregation of the star to both the surface and substrate interface as shown in Figure 1. The surface excess at the substrate interface ($8 \pm 1 \text{ \AA}$) exceeds that at the surface ($4 \pm 1 \text{ \AA}$). These amounts provide lower bounds on the equilibrium values of interfacial excess, as additional measurements have suggested that the system may not be quite at equilibrium, even after annealing for 7.8 days. DSIMS data show an increased surface excess ($9 \text{ \AA}$) upon annealing for an additional day, supporting this hypothesis. Since it is known that deuterated linear PS is preferred at the interfaces of linear/linear isotopic blends cast on silicon wafers¹⁸⁻²³ one may question if the labeling itself is driving the segregation. However, other measurements²⁴ show that the star still segregates to both surfaces even if the star is not deuterium labeled. Further measurements on blends of polybutadiene and poly(methyl methacrylate) molecules will provide information on the universality of this behavior.

Conclusions

SANS measurements of blends of star and linear polystyrene analogs reveal a bulk thermodynamic interaction which is larger than that due to isotopic labeling alone. Thus, even the presence of a single branch point in a macromolecule leads to a contribution to χ . This interaction manifests itself as well in a preferential segregation of the star polymer to both interfaces of a thin film.

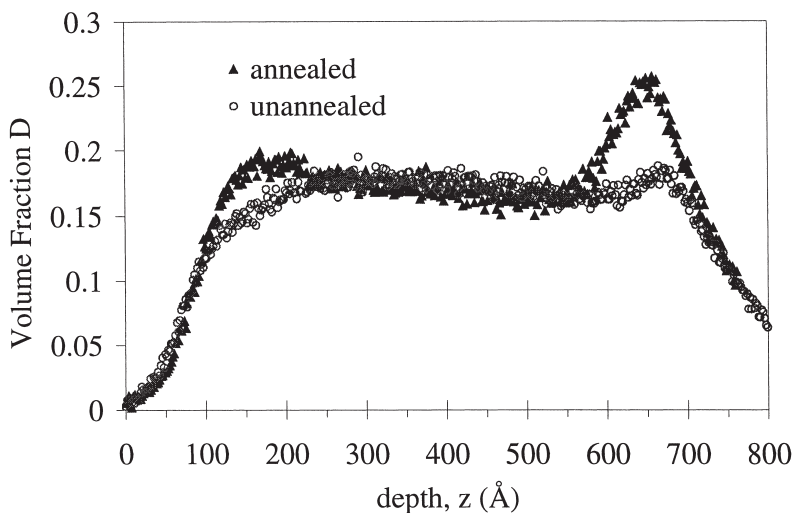


Figure 1. Volume fraction of deuterium as a function of depth for a blend of 18 wt % deuterated six-arm star in a matrix of hydrogenous linear PS (d6s/hPS). Results from unannealed (o) and annealed ($\blacktriangle$) thin films are shown. Annealing was conducted under high vacuum for 7.8 days at 170 °C. Segregation of the star is present at the air surface and at the silicon interface.

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