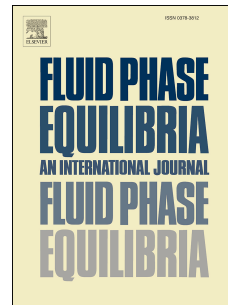# Accepted Manuscript

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Abstract

We perform molecular dynamics computer simulations of free-standing films of symmetric binary linear-cyclic polymer mixtures at equimolar composition. We show that the density of linear polymers at the free-surface is enhanced with respect to the *bulk* value for short chains, but it is depleted for long chains. Our findings suggest that the enhancement of the composition of linear chains reported for polystyrene polymer blends might hold in a more extended composition range than the one considered in previous experiments at the free surface. Focusing on the equimolar regime of the two polymer species with the identical chain length allows us to safely conclude that the observed surface deviations from the *bulk* are driven by the topological differences between the two polymer species, and rule out any role played by the different concentration of the two polymer species.

1. Introduction

Investigation of polymer surfaces using molecular modeling is important in several industrial processes, including for example blending, composites, thin film coatings, paints and adhesives (1; 2). In the past decade, the scientific literature has become populated with a number of papers related to computational (3; 4; 5; 6; 7; 8; 9; 10; 11; 12; 13; 14; 15) and experimental (2; 16; 17; 18; 20; 19) aspects of surface enrichment in polymer melts.

Understanding surface properties of polymeric mixtures has created an interesting challenge in science, especially when such properties are driven by the different topological constraints of the components in the mix. However, little effort has been made in understanding surface adsorption in simple models of polymeric mixtures, such as the ones where polymer chains with linear and cyclic topology are mixed together.

The interest in these investigations is obviously aimed to achieve a fundamental understanding and control of surface segregation of polymeric materials of chosen topology (1), such as polymer blends typically used in photovoltaic applications (21; 22; 23; 24). For example, Wang and coworkers (1) investigated linear-cyclic polymer blends with polystyrene chemistry by means of SL-MALDI-TOFMS spectroscopy, and provided evidence of enrichment of linear chains at the surface in the regime of lower cyclic composition. Very recently, neutron reflectivity (NR) experiments on the same systems showed that the degree of surface segregation of cyclic polymers is dependent on the molecular weight of the polymer chains (25; 26). The evidence is that when chains possess a low molecular

weight ($\approx 2k$), linear polymers enrich the surface and the opposite behavior (cyclic polymers absorbing preferentially to the surface) emerges only in the limit of much longer polymer chains ($\approx 37k$). This experimental evidence was confirmed by us very recently with bead-spring models of linear-cyclic polymer blends (27).

In general, polymer segregation can result from small differences between the components of the blend. For example, in blends of hydrocarbon polymers containing deuterated and hydrogenated components, the weaker component (deuterated) usually segregates at the surface (28; 29). The deuterated component is the weaker one because it is the component with weaker van der Waals interactions. Based on the fact that segregation for those systems is energetic in nature, the component with weaker van der Waals interactions (deuterated) dominates at the surface, while the one with more intermolecular contacts (hydrogenated) stays in the bulk. Since in principle even tiny differences in the composition of the two polymer species could play a role, an important issue is to understand whether the enhancement of one of the two polymer species at the interface is also affected by the composition of the system, or not. In the latter case, the surface deviations of the composition from the *bulk* are truly determined by the topological differences between the two polymer species. To this aim, here we focus on a binary mixture of linear and cyclic chains of same length at equimolar composition. Then, the degree of polymerization is changed in an extended range of chain lengths to observe the effect on the polymers' density at the interface. A number of microscopic properties are also monitored to better understand the details of the structural organization as a function of the distance from the interface.

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