Anomalous Segregation of Deuterium Labeled PS at hPS:dPS/hPMMA Interfaces as Characterized by SIMS and Mean-Field Theory

SHANE HARTON, FRED STEVIE, HARALD ADE, North Carolina State University — Secondary ion mass spectrometry (SIMS) was used to measure real-space depth profiles of deuterium labeled polystyrene (dPS) in hPS:dPS/poly(methyl methacrylate) (hPMMA) bilayers, with the hPS:dPS blend being well within the single-phase region of the phase diagram. Profound changes in the thermodynamic behavior of this system at the polymer/polymer interface are observed in the form of significant segregation of dPS to the hPS:dPS/hPMMA interface. Furthermore, a depletion hole was observed during the early stages of formation of an equilibrium excess of dPS, implying that the energetic gain at the interface per dPS chain has to be $\Delta \chi > kT$. The observed interfacial excess is quantified by generating theoretical profiles, using self-consistent mean-field theory (SCMF), and fitting an effective interaction energy parameter $\Delta \chi$ as a function of temperature. The temperature dependency of $\Delta \chi$ was found to be a factor of $3-4$ greater than any of those reported for $\chi$ of PS/PMMA. It was also found that SCMF accurately describes the concentration dependency of dPS segregation at a constant dPS molecular weight using a concentration independent $\Delta \chi$, however $\Delta \chi$ was found to be dependent on dPS molecular weight. A novel method of using carbon-13 labeling is demonstrated as an alternative to deuterium labeling, providing a true tracer for investigations of such phenomena as polymer chain mobility near surfaces and interfaces and reactive coupling at polymer/polymer heterogeneous interfaces.

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