

Abstract Submitted  
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**Kinetic Hindrance during Diffusion-Controlled Reactions at Polymer-Polymer Interfaces** SHANE HARTON, FREDERICK STEVIE, HARALD ADE, North Carolina State University — We have characterized diffusion-controlled (DC) reactions between 75kDa hydroxy-terminated deuterated polystyrene (dPS-OH) and several acyl chloride functionalized poly(methyl methacrylates) (PMMA) using dynamic secondary ion mass spectrometry (DSIMS). When annealed at 393-408K, these systems consistently show a depletion hole at early times, which is indicative of DC reactions, but this depletion hole disappears over time with an apparent reaction extinction. This extinction is characterized by an interfacial excess of block-copolymer ( $Z^*$ ) that is considerably lower than current theories predict. This indicates that reactions at highly immiscible polymer-polymer interfaces, whether inherently DC or reaction-controlled, may actually be controlled primarily by kinetic hindrance at the interface rather than long-range diffusion or reaction mechanisms. To probe this directly, we have measured the extinction excess ( $Z_e$ ) as a function of reactive dPS-OH concentration in the PS matrix ( $\sim 5$ -20 %) and reaction temperature ( $\sim 403$ -433K). The variation of the  $Z_e$  as a function of initial dPS-OH concentration confirms kinetic hindrance as the underlying cause of the reaction extinction, as opposed to loss of reactivity, because the reactive chains are never fully depleted, and the coupling reactions implemented here are extremely robust and completely irreversible. An effective activation energy is determined from the temperature dependency of the  $Z_e$ .

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