Location-Specific Measurements of The Glass Transition Temperature in Fluorescently Labeled Diblock Copolymers

DANE CHRISTIE, RICHARD REGISTER, RODNEY PRIESTLEY, Princeton University — Block copolymers can self-assemble into periodic structures containing a high internal surface area, nanoscale domain periods, and periodically varying composition profiles. Depending on their components, block copolymers may also exhibit variations in their dynamic properties e.g., glass transition temperature \( T_g \) across the domain period. Measuring the variation of \( T_g \) across the domain period of block copolymers has remained a significant challenge due to the nanometer length scale of the domain period. Here we use fluorescence spectroscopy and the selective incorporation of a pyrene-containing methacrylate monomer at various positions along the chain to characterize the distribution of glass transition temperatures across the domain period of an amorphous block copolymer. The pyrene-containing monomer location is determined from the monomer segment distribution calculated using self-consistent field theory. Our model system is a lamella-forming diblock copolymer of poly(butyl methacrylate - \( b \)- methyl methacrylate). We show that \( T_g \) is asymmetrically distributed across the interface; as the interface is approached, larger gradients in \( T_g \) exist in the hard PMMA-rich domain than in the soft PBMA-rich domain. By characterizing \( T_g \) of PBMA or PMMA interfacial segments, we show that polymer dynamics at the interface are heterogeneous; there is a 15 K difference in \( T_g \) measured between PBMA interfacial segments and PMMA interfacial segments.