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An interplay between self-organization and interfacial modification of diblock copolymers in bilayered thin film laminates

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We study the interfacial partitioning of poly(styrene-*b*-methyl methacrylate) (SM) diblock copolymers at interfaces between thin planar films of polystyrene (PS) and poly(methyl methacrylate) (PMMA) homopolymers. SM copolymers with constant PS and varying PMMA block lengths are incorporated into the top PS layer and the resulting dewetting kinetics of the top PS film decrease by reducing the length of the PMMA block and increasing the molecular weight of the host PS homopolymer. Similar behavior is observed when the SM copolymers are added to the bottom PMMA homopolymer. Systems incorporating SM copolymers possessing short PS blocks and long PMMA blocks exhibit dewetting rates that are higher than those of the copolymer-free PS/PMMA bilayer. This behavior is attributed to the segregation of SM aggregates at the PS/PMMA interface, which migrate to and roughen the interface and destabilize the film. The dewetting kinetics of systems with mixtures of asymmetric copolymers (stabilizing and destabilizing) added in the PS homopolymer lie between those of the individual copolymers pure copolymers. Using block copolymer mixtures rather than single copolymers to tune stabilizing/compatibilizing efficacy provides an unexplored route to achieving property control in thin polymer films.