The Micellization of Well-defined Single Graft Copolymers in Block Copolymer/Homopolymer Blends

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A series of well-defined (polyisoprene)$_2$(polystyrene), I_2S, single graft copolymers with similar total molecular weights but different compositions, f_{PS}, were blended with a low molecular weight polyisoprene homopolymer matrix at a constant concentration 2 wt%, and the micellar characteristics were studied by synchrotron small-angle x-ray scattering, in the absence of a lab-based instrument. To investigate the effect of macromolecular architecture on the formation and characteristics of micelles, the results on the single graft copolymers were compared with those of the corresponding linear polystyrene-*b*-polyisoprene diblock copolymers, SI. The comparison reveals that the polystyrene core chains are more stretched in the case of graft copolymer micelles (Figure 1). Stretching turned out to be purely a result of the architecture due to the second polyisoprene block in the corona. The micellization of a (polystyrene)$_2$(polyisoprene), S_2I, graft copolymer was also studied, and the comparison with the results of the corresponding I_2S and SI copolymers emphasizes the need for a critical core volume rather than a critical length of the core-forming block, in order to have stable micelles. Finally, the absence of micellization in the case of the I_2S copolymer with the highest polystyrene volume fraction is discussed. For this sample, macrophase separation occurs, with polyisoprene cylinders formed in the copolymer-rich domains of the phase-separated blends.

Keywords: block copolymers, micellization, shelf assembly, graft copolymers

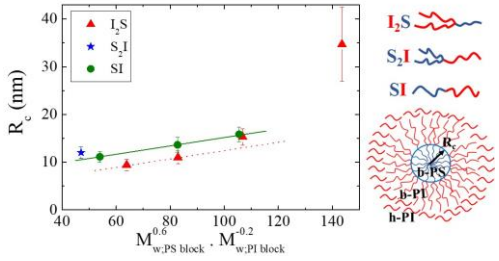

Figure 1. *Core radius of the micelles formed in the 2 wt% blends of the I2S and S2I grafts, and the SI diblock copolymers in the polyisoprene matrix at room temperature, as a function of the particular relations to the molecular weights of the core-forming (PS) and corona-forming (PI) blocks.*

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