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Oligosaccharide based hybrid block copolymers are a new class of hybrid polymers containing both natural and synthetic polymer components. Due to the large segregation strength between the hydrophilic saccharide block and the hydrophobic synthetic block, the resulting block copolymers are expected to microphase separate at small molecular weights, yielding ordered morphologies with sub-10nm feature sizes. In this work, a series of saccharide-containing hybrid diblock copolymers were prepared by combining maltose with polystyrene chains of different chain lengths. The polymer conjugates were synthesized via copper(I)-catalyzed 1,3-dipolar azide-alkyne cycloaddition of alkyne-functionalized maltose and azido-functionalized polystyrene. Despite the low molecular weights of the diblocks, these polymers were found to microphase separate to form ordered domain morphologies in the bulk. In particular, at a maltose volume fraction of 12.3 vol% and an overall molecular weight of near 2000 g/mol, the diblock copolymer was found to form hexagonally-packed cylinders with long range order, and the domain size is less than 10 nm.