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Chain Stretching and Order-Disorder Transitions in Block Copolymer Monolayers and Multilayers¹ EDWARD J. KRAMER, VIND-HYA MISHRA, GILA E. STEIN, KAREN E. SOHN, SUMI HUR, GLENN H. FREDRICKSON, UCSB, ERIC W. COCHRAN, Iowa State University — Both monolayers of block copolymer cylinders and spheres undergo order to disorder transitions (ODT) at temperatures well below those of the bulk. Monolayers of PS-b-P2VP cylinders undergo a "nematic" to "isotropic" transition at temperatures about 20 K below the bulk ODT while monolayers of PS-b-P2VP with P2VP spheres undergo a 2D crystal to hexatic transition at least 10 K below the bulk ODT. Bilayers of each structure disorder at temperatures well above that of the monolayers. While one is tempted to attribute all of the difference to the fact that ordered monolayers are quasi 2 dimensional while bilayers are not, an alternative explanation exists. In the cylinder monolayer the corona PS chains must stretch to fill a nearly square cross-section domain rather than a hexagonal one in the bulk, while the corona PS chains in a sphere monolayer must stretch to fill a hexagonal prism rather than an octahedron in the bulk. The more non-uniform stretching of the chains in the monolayer should increase its free energy and decrease its orderdisorder temperature.

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