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Internal Structure of Ultrathin Diblock Copolymer Brushes BULENT AKGUN, WILLIAM J. BRITTAIN, MARK D. FOSTER, The University of Akron, Akron, OH, 44325, CHARLES F. MAJKRZAK, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, XUEFA LI, JIN WANG, Argonne National Laboratory, Argonne, IL 60439 — Diblock copolymer brushes (DCBs) have garnered enormous interest in recent years due to their stimuli-responsive behavior. Although the synthesis of DCBs has been widely studied, the internal brush structure of these films is still not clear. We have resolved the internal structure of ultrathin DCBs using neutron reflectivity and grazing incidence small-angle X-ray scattering (GISAXS). DCBs of deuterated polystyrene (dPS) and poly(methyl acrylate) (PMA) with dPS adjacent to the substrate (d-PS-b-PMA) or with PMA adjacent to the substrate (PMA-b-dPS) and having different thicknesses were synthesized using atom transfer radical polymerization. It was found that internal brush structure depends strongly on the block sequence and the value of XN. For the thinnest films a model of two layers with an interfacial region of finite width provides a good description of the data. For dPS-b-PMA films that are thicker and of sufficiently asymmetric composition, a third layer must be included. The necessity of including a third layer is consistent with the presence of a lateral ordering of some type in the center of the brush, as evidenced by correlation peaks in the GISAXS data. The interface width is found to be smaller for PMA-b-dPS than for dPS-b-PMA brushes.

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