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**Effect of Confinement in PFSA Ionomer Thin Films** PETER DUDENAS, MERON TESFAYE, University of California, Berkeley, ADAM WEBER, AHMET KUSOGLU, Energy Conversion Group, Energy Technologies Area, LBNL — Ion-conducting polymer (ionomer) behavior in catalyst layers of electrochemical devices is fairly unknown and presents challenges for their characterization in this heterogeneous environment. In order to enable next-generation electrochemical devices, structure-property relationships of these ionomers must be elucidated under confinement. In an effort to do so, model systems of ionomer thin films of varying thicknesses (10 to 200 nm) are utilized to understand effect of confinement on crystallinity, swelling and mechanical properties. Grazing incidence wide-angle x-ray scattering (GIWAXS) is used to determine the relative degree of crystallinity (rDoC) as a function of thickness, which is then correlated to mechanical properties and swelling of thin films, as measured by a cantilever bending method and ellipsometry, respectively. Moreover, factors controlling the thin-film behavior, such as thermal transitions and substrate effects, are explored further through temperature-dependent ellipsometry and GIWAXS. Multiple perfluorinated sulfonic acid (PFSA) ionomer chemistries are used to demonstrate the effect of side-chain length and density on the interplay between the confinement effects and structure-property relationships.

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