Direct measurement of the counterion distribution within swollen polyelectrolyte films

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A depth profile of the counterion concentration within thin polyelectrolyte films was measured in-situ using contrast variant specular neutron reflectivity to characterize the initial swelling stage of the film dissolution. We find a substantial counterion depletion near the substrate and an enrichment near the periphery of the film extending into the solution. The film expansion extent follows a linear dependence with the segmental degree of ionization. These observations challenge our understanding of the charge distribution and swelling response in polyelectrolyte films and are important for understanding film dissolution in medical and technological applications.