Influence of Chain Flexibility on the Self-Assembly of Nanoscale Ionic Aggregates in Ionomers. NICHOLAS BENETATOS, KAREN WINEY, Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pa, 19104 — Rigorously establishing the fundamental physics that govern the morphology of ionomers is essential to continuing the development of this versatile class of materials. To explore how chain flexibility impacts the nanoscale self assembly of ionic aggregates, we have investigated the morphology of Cu neutralized poly(styrene-ran-methacrylic acid) (SMAA) and poly(3-methylstyrene-ran-methacrylic acid) (3Me-SMAA) ionomers with small angle X-ray scattering (SAXS) and real space imaging via scanning transmission electron microscopy (STEM). The copolymer 3Me-SMAA is slightly less flexible on local length scales as evidenced by a shift in the position of the “polymerization” SAXS peak (q ∼ 6 nm$^{-1}$) to lower q compared to that of SMAA (q ∼ 7 nm$^{-1}$). A commensurate shift toward lower q in the position of the ionomer SAXS peak was observed for Cu-3Me-SMAA. Interpreting these SAXS data with a multi-functional model, including that of Yarusso and Cooper, suggests a homogeneous collection of spherical ionic aggregates with diameters of 1.0 nm and 1.2 nm in Cu-SMAA and Cu-3Me-SMAA, respectively. From STEM imaging, the ionic aggregates in both Cu-SMAA and Cu-3Me-SMAA are indeed spherical with a uniform, dense spatial distribution and average diameters of 1.2 ± 0.3 nm and 1.4 ± 0.3 nm, respectively, showing slightly larger size as local chain flexibility decreases.