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The proton exchange membranes are synthesized from poly(arylene ether ketone) (PAEK) multi-block copolymers with and without sulfonated groups. The hydrophilic PAEK block is dual – sulfonated at the pendant site to enhance the proton conductivity of the membrane, while the hydrophobic block length is enlarged to reduce its swelling (increase dimensional stability) associated with water accommodation. The chemical structures of the synthesized oligomers and copolymers are identified using 1H– and 19F–NMR, ATR–FTIR, and GPC. The ion cluster dimension of the membrane is analyzed by SAXS. The effect of copolymer composition on the membrane properties is investigated measuring the proton conductivity, water uptake, swelling ratio, and cell performance along with the thermal, mechanical, and oxidative stability. The prepared membrane. Specifically, B.PAEK25–SDPA shows superior cell performance to Nafion115.