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Creating monodisperse polyacrylamide free-radically via thermal frontal polymerization in confined geometries PREETA DATTA, KIRILL EFIMENKO, JAN GENZER, North Carolina State Univ — Bulk free radical polymerization reactions lead to highly polydisperse polymers (polydispersity index, PDI $\gg 1.5$). In the past, researchers have shown that polymerization in porous microreactors can lower polydispersity (PDI ~ 1.5 - 1.7) by promoting gelation. We employ free-radical thermal frontal polymerization reaction of acrylamide (AAm) in DMSO in highly confined reactors (height < 1 mm) to produce high molecular weight (~ 300 kDa) PAAm of relatively low PDI (~ 1.2). In frontal polymerization systems, a localized reaction zone propagates in space along the direction of heat transfer, sustained by the interplay of heat diffusion and Arrhenius reaction kinetics. The directional heat transfer assists in maintaining the uniformity of the front temperature. While convection improves thermal transport, it causes inhomogeneity in the propagating front in horizontal reactors. In highly confined systems, convection is heavily suppressed, as manifested by the “flattening” of the reaction front and the absence of “fingering”. Gelation lowers termination rate and increases the life time of the active reaction centers. Elimination of convection in confined geometries coupled with directional heat transfer and gelation results in polymers with high molecular weights and low PDIs.

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