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The Effect of Nanoconfinement on Free Radical Equilibrium Polymerization HAOYU ZHAO, SINDEE SIMON, Texas Tech University — Free radical polymerization under nanoconfinement results in changes in reaction kinetics, reaction thermodynamics, and polymer properties. In this work, hydrophilic and hydrophobic nanoporous media ($d < 13$ nm) are employed as the nanoconfined matrix to perform polymerization of acrylate monomer. Differential scanning calorimetry (DSC) is used to study the reaction kinetics and thermodynamics, whereas gel permeation chromatography (GPC) is used to measure the molecular weight of the polymer produced. Although the polymerization is thermodynamically feasible at low temperature, as reaction temperatures increase, the depropagation rates in acrylate polymerization become appreciable resulting in equilibrium polymerization at high temperature. For polymer synthesized in nanoconfined environment, the change in entropy upon propagation becomes a larger negative number resulting in a decrease in equilibrium conversion and a shift of the ceiling temperature to lower temperatures. The results are analyzed in the context of the scaling of the change in confinement entropy of chains on chain length.

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