

Abstract Submitted  
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**The Nanoconfined Free Radical Polymerization: Reaction Kinetics and Thermodynamics**<sup>1</sup> HAOYU ZHAO, SINDEE SIMON, Texas Tech Univ — The reaction kinetics and thermodynamics of nanoconfined free radical polymerizations are investigated for methyl methacrylate (MMA) and ethyl methacrylate (EMA) monomers using differential scanning calorimetry. Controlled pore glass is used as the confinement medium with pore diameters as small as 7.5 nm; the influence of both hydrophobic (silanized such that trimethylsilyl groups cover the surface) and hydrophilic (native silanol) surfaces is investigated. Propagation rates increase when monomers are reacted in the hydrophilic pores presumably due to the specific interactions between the carbonyl and silanol groups; however, the more flexible EMA monomer shows weaker effects. On the other hand, initial rates of polymerization in hydrophobic pores are unchanged from the bulk. In both pores, the onset of autoacceleration occurs earlier due to the reduced diffusivity of confined chains, which may be compensated at high temperatures. In addition to changes in kinetics, the reaction thermodynamics can be affected under nanoconfinement. Specifically, the ceiling temperature ( $T_c$ ) is shifted to lower temperatures in nanopores, with pore surface chemistry showing no significant effects; the equilibrium conversion is also reduced at high temperatures below  $T_c$ . These observations are attributed to a larger negative change in entropy on propagation for the confined system, with the MMA system again showing greater effects.

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