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**Methyl Methacrylate Polymerization in Nanoporous Matrix: Reactivity and Resulting Properties**<sup>1</sup>

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Nanoconfinement is well known to affect the properties of polymers, including changes in the glass transition temperature (T<sub>g</sub>). In this work, the focus is on the influence of nanoconfinement on free radical polymerization reaction kinetics and the properties of the polymer produced. Controlled pore glass (CPG) is used as a nanoconfining matrix for methyl methacrylate (MMA) polymerization with pore diameters of 13 nm, 50 nm, and 110 nm. The reaction is followed by measuring heat flow as a function of reaction time during isothermal polymerization at temperatures ranging from 60 °C to 95 °C using differential scanning calorimetry (DSC). After reaction, the properties of the polymer are measured, including T<sub>g</sub>, molecular weight, and tacticity. Nanoconfinement is found to result in earlier onset of autoacceleration, presumably due to a decrease in the rate of termination arising from decreases in chain diffusivity in the confined state. In addition, T<sub>g</sub> and molecular weight of the resulting PMMA are found to increase. A model of the nanoconfined reaction is able to quantitatively capture these effects by accounting for changes in chain diffusivity, and in native pores, also accounting for changes in intrinsic reaction rates.

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