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Confinement effects on thermal frontal polymerization PREETA DATTA, KIRILL EFIMENKO, JAN GENZER, NCSU — Frontal polymerization systems belong to the broader class of reaction-diffusion systems. In thermal frontal polymerization, the interplay of heat diffusion and Arrhenius reaction kinetics gives rise to a moving reactive front; propagation occurs through a positive feedback mechanism. We seek to understand how spatial confinement can change the system dynamics and cause to deviate the system from bulk behavior. In highly confined systems, the front propagates slower and the front profile is flatter than in bulk. The polymerization product shows a decrease in polydispersity index (<1.5) for high confinement. The molecular weights of the samples do not exhibit simple unimodal distributions, unlike bulk. In specimens at the highest degree of confinement the molecular weight of the resultant polymer decreases with increasing distance from the external heating source. In highly confined systems a smaller number of radicals are generated, resulting in a slower propagation step and polymer chains of more uniform length; front propagation is slow as it is reaction-limited. In contrast, for bulk or unconfined systems, higher heat generation rates, leading to faster polymerization with higher polydispersity in molecular weight; front propagation is fast as it is diffusion-limited.

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