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Effect of chain topology and angular interactions on the competition between crystallization and glass-formation

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We investigate the role of chain topology and angular interactions on the competition between crystallization and glass formation by mapping out the phase diagram of model “soft” colloidal polymers as a function of temperature and bending stiffness k_b , spanning the range from fully flexible to rodlike chains. For small k_b , monomers occupy the sites of close-packed crystallites while chains retain random-walk-like order. For large k_b , for short chains, nematic chain ordering typical of lamellar precursors coexists with a high degree of close-packing, while for longer chains, close-packed chain-folded lamellae separated by amorphous regions are formed. At intermediate values of bending stiffness, the competition between random-walk-like and nematic chain ordering produces glass-formation, as indicated by both dynamical heterogeneity and the growth of icosahedral order near and below T_g . The kinetics of the ordering transition depend strongly on chain flexibility: in the flexible limit chains crystallize at lower temperatures and the disorder-order transition occurs very sharply, while as the rodlike limit is approached, the initial phase of ordering occurs at significantly higher temperatures but the crystallization rate is much slower. We also examine the crystallization behavior of short (unentangled) branched polymers as a function of k_b . Branching points significantly suppress crystallization, especially for stiffer chains, because their preferred bond angles are incompatible with close-packing. Finally, we discuss the degree to which colloidal polymers can serve as proxies for their microscopic counterparts.