## Section Question 10

Polymerization reactions typically exhibit negative entropies of reaction (ΔS^0) that result from incorporating many monomer molecules into single polymer molecules. You might imagine that these negative ΔS^0 values would also be reflected in the activation entropies ($\Delta S^{\ddagger}$) of typical polymerizations, the sign and magnitude of $\Delta S^{\ddagger}$ for a catalyzed polymerization can depend on both the rate-determining step of the polymerization cycle and the resting state of the catalyst. For this problem, imagine that our catalyst is always bound to the end of the polymer, and that it operates by a simplified, two-step mechanism: (1) complexation of the monomer to the catalytic center; and (2) connection of the monomer to the polymer.
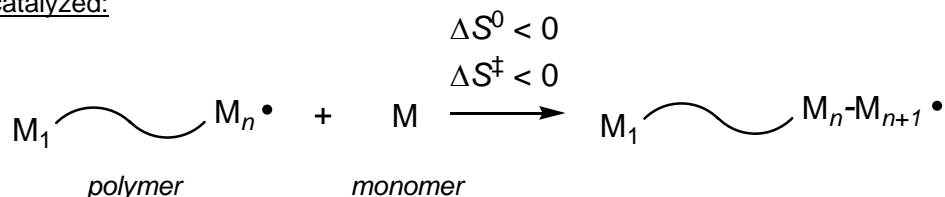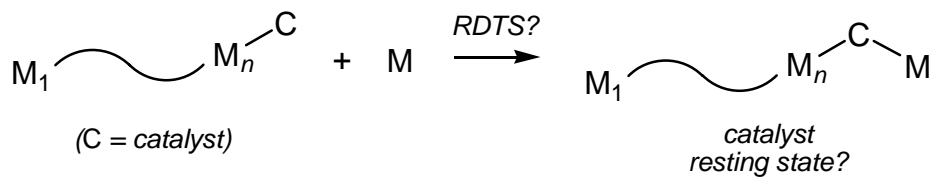
Draw potential energy diagrams for polymerizations in which each of the two steps above is rate-determining, and each of the two product states is the "resting" (thermodynamically most stable) state of the polymerization. What would you expect for $\Delta S^{\ddagger}$ in each of these four cases?