

Thermodynamics of Polymerization

- Thermodynamics of polymerization determines the position of the equilibrium between polymer and monomer(s). Thus, it impacts both polymerization, depolymerization, and degradation. The thermodynamics of polymerization of most olefins is favorable due to the exothermic nature of converting π bonds into σ bonds. For cyclic compounds, the driving force for polymerization can vary over a much wider range, and one observes a variety of behaviors ranging from completely unreactive to spontaneously polymerizable under all conditions.
- The well known thermodynamic expression:

$$\Delta G = \Delta H - T\Delta S$$
 yields the basis for understanding polymerization/depolymerization behavior.
- For polymerization to occur (i.e., to be thermodynamically feasible), the Gibbs free energy of polymerization $\Delta G_p < 0$.
- If $\Delta G_p > 0$, then depolymerization will be favored.
 - Thus:** Any factor that lowers the enthalpy, H (i.e., makes ΔH_p more negative), or raises the entropy, S (i.e., makes ΔS more positive), will shift the equilibrium towards polymerization.
- Standard enthalpy and entropy changes, ΔH_p° and ΔS_p° , are reported for reactants and products in their appropriate standard states. Generally:
 - Temperature = 25°C = 298K
 - Monomer – pure, bulk monomer or 1 M solution
 - Polymer – solid amorphous or slightly crystalline
- Polymerization is an association reaction such that many monomers associate to form the polymer
 - Reaction is enthalpically favored. It's a large loss in the total number of rotational and translational degrees of freedom, so the total system as the monomers associate.
 - The monomer has a large loss in entropy upon polymerization.
 - If $\Delta S_p < 0$, then polymerization processes are almost always entropically disfavored.
- Since depolymerization is almost always entropically favored, the ΔH_p must then be sufficiently negative to compensate for the unfavorable entropic term. Only then will polymerization be thermodynamically favored by the resulting negative ΔG_p .
- In practice,
 - Polymerization is favored at low temperatures: $T\Delta S_p$ is small
 - Depolymerization is favored at high temperatures: $T\Delta S_p$ is large
- Therefore, thermal instability of polymers results when $T\Delta S_p$ overrides ΔH_p and thus $\Delta G_p > 0$; this causes the system to spontaneously depolymerize (if kinetic pathway exists).

Thermodynamics Of Polymerization

David Baud



Thermodynamics Of Polymerization:

Unveiling the Magic of Words: A Overview of "**Thermodynamics Of Polymerization**"

In some sort of defined by information and interconnectivity, the enchanting power of words has acquired unparalleled significance. Their capability to kindle emotions, provoke contemplation, and ignite transformative change is truly awe-inspiring. Enter the realm of "**Thermodynamics Of Polymerization**," a mesmerizing literary masterpiece penned by way of a distinguished author, guiding readers on a profound journey to unravel the secrets and potential hidden within every word. In this critique, we shall delve to the book is central themes, examine its distinctive writing style, and assess its profound effect on the souls of its readers.

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