

Chapter. 10

Polymerization and Depolymerization Equilibria

Monomer-polymer Equilibria

Ex) PMMA, PTFE, poly(α -methylstyrene), poly(methacrylonitrile), poly(vinylidene cyanide)

For PS; thermal breakdown produces styrene monomer + products from random chain scission, α -hydrogen abstraction, and chain transfer process

Why?

Unpolymerizable compounds

**No further polymerization
Why?
Thermodynamics**

The general thermodynamic problem

Possible products from the polymerization of A=B monomer

Thermodynamically stable + kinetic possibility

All of them can exist ?

One or two of them can exist ?

Specific thermodynamic effects

For polymerization, $\Delta G_p < 0$.

Then it is desirable to have $\Delta H_p < 0$ and $\Delta S_p > 0$

Generally in polymerization of monomer (small molecule) to produce high molecular weight polymers, $\Delta S_p < 0$, because of the loss of the number of translational and rotational degrees of freedom.

The to be polymerizable, $\Delta H_p \ll$ to make $\Delta G_p < 0$.

Ceiling temperature (T_c) ; above which no polymer exists

→ at higher temperature $T\Delta S_p$ term is predominant

Floor temperature (T_c) :below which no polymer exists

→ $\Delta H_p < 0$ or very small, $\Delta S_p > 0$

Standard (25 °C) enthalpies, entropies and free energies of polymerizations

One mole of M produces $1/n$ mol of polymer with degree of poly. n

Standard enthalpy for polymerization

Standard entropy for polymerization

Standard enthalpies of formation for the monomer and polymer

Absolute entropies for the monomer and polymer

Absolute entropies at give temp, T (absolute temp.)

C_p = molar heat capacity

Specific monomer-polymer equilibria

At T_c , the tendency of polymerization and depolymerization is equal

$$\Delta G_p = \Delta G_p^\circ + RT \ln K = 0$$

$$\Delta G_p^\circ = \Delta H_p^\circ - T \Delta S_p^\circ = -RT \ln K$$


$-\Delta H_p^\circ$ values vary considerably, while $-\Delta S_p^\circ$ values show much less variations.

**$-\Delta H_p^\circ$ values; ethylene > isoprene
ethylene > styrene > α -methylstyrene
steric effect**

Resonance stabilization and H-bonding also affect the $-\Delta H_p^\circ$

Influence of ΔH and ΔS on ring-chain equilibria (nonrigorous approach)

$$C_{x+y} \approx C_y$$

$$\Delta G_g^\circ = -RT \ln K_g = -RT \ln [R_x]_{\text{eq}}$$

At initial state

If no solvent present, then $[R_x]_{eq}/[R_x]_0 = 1 - \phi$, and $\Delta G_g = \Delta H_g - T\Delta S_g$
 ϕ = weight fraction of chain
then

Graph $\ln(1 - \phi)$ vs $1/T$,
Then ΔH_g and ΔS_g can be obtained

b : $\Delta H_g/\Delta S_g =$ ceiling temperature

c: if $\Delta H_g = 0$, then $R\ln(1 - \phi) = \Delta S_g$, constant

d,e : $\Delta H_g/\Delta S_g =$ floor temperature

If solvent is present, then ring formation is favored.

If R_x is lowered, then ΔG_g increases: left side in eq (8) is favored !

If two or more sizes of ring are in simultaneous equilibrium with the polymer

$$\phi_{x1} + \phi_{x2} < 1$$

The sulfur equilibrium (rigorous approach)

$$\text{If } S_8 = M, S_8^* = M_1^*, S_{8n}^* = M_n^*$$

If P = number-average degree of polymerization,
 $P = [W]/[N]$

The total concentration of S_8 units, $[M_0]$, in monomer and polymer is

$[M_0]$ = moles of S_8 units per
kilogram of sulfur
= 3.90 mol/kg

Then ΔH° , ΔS° , ΔH_3° , and ΔS_3° can be obtained from the determination of K vs 1/T and/or K_3 vs 1/T relationship.

Then [M] and P can be obtained at all temperatures, then K can be obtained

Next page. Experimental and Calculated results are almost identical

We know P vs K

Molecular structural effect (qualitative approach)

1. Skeletal bond energy

2. Skeletal bond angle

3. Aromaticity and delocalization

4. Side group interaction

Skeletal bond energy

Free energy terms are mostly determined by enthalpy changes. Enthalpy changes largely depend on the skeleton bond energy differences of monomer, oligomers, and polymer.

Skeletal bond energy difference exists for monomer, cyclic dimer, cyclic trimer,... and linear polymer due to the ring strain, otherwise the differences are not much.

Olefine-type monomers have a higher enthalpies than the cyclic oligomers and polymers because of the energies stored in the double bond. (energy of π bond in the monomer depend on the shape and type of side group)

Skeletal bond angle

Ring strain affects the changes of the enthalpies.

**Tetrahedral C and Si do not have much angular flexibility.
O, N, S in the skeletal do have more angular flexibility.**

**Ex) in the polymerization no formaldehyde dimer (H₂C-O)₂
and cyclic siloxane dimer exist.
While, (S=N)₂ or [(CF₃)₂C-S-]₂ exists.**

Aromaticity and delocalization

**Delocalization of π -bonding electrons lower the enthalpies
of the moleculs. (ex benzene)**

d π -p π overlap does not gives such delocalization

Side group interactions

For unsaturated monomers

If R is bulky, depolymerization is easier!

The mechanistic aspect

Polymerization depends not only on the free-energy changes but also on the activation energy changes.

So a certain polymerization can be energetically feasible, while kinetically inhibited; catalysts are needed!

Polymerization mechanism for heterolytic ring cleavage system

Initiation

X^+Y^- (catalyst or initiator) is important to overcome the activation E

Propagation

Undesirable reactions

Cyclization; for short chain

backbiting

To minimize this reaction, total removal of the initiator or replacement of end group by nonionic species!