

# Chapter. 10

## Polymerization and Depolymerization Equilibria

# Monomer-polymer Equilibria

Ex) PMMA, PTFE, poly( $\alpha$ -methylstyrene), poly(methacrylonitrile), poly(vinylidene cyanide)

**For PS; thermal breakdown produces styrene monomer + products from random chain scission,  $\alpha$ -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**

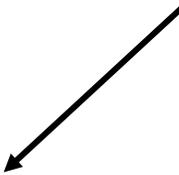
**Absolute entropies at give temp, T (absolute temp.)**

**$C_p$  = 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 >  $\alpha$ -methylstyrene  
steric effect**

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

# Influence of $\Delta H$ and $\Delta S$ 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  $\Delta G_g = \Delta H_g - T\Delta S_g$   
 $\phi$  = weight fraction of chain  
then

Graph  $\ln(1 - \phi)$  vs  $1/T$ ,  
Then  $\Delta H_g$  and  $\Delta S_g$  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  $\Delta G_g$  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  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta H_3^\circ$ , and  $\Delta S_3^\circ$  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  $\pi$  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 (H<sub>2</sub>C-O)<sub>2</sub>  
and cyclic siloxane dimer exist.  
While, (S=N)<sub>2</sub> or [(CF<sub>3</sub>)<sub>2</sub>C-S-]<sub>2</sub> exists.**

# Aromaticity and delocalization

**Delocalization of  $\pi$ -bonding electrons lower the enthalpies  
of the molecules. (ex benzene)**

**d $\pi$ -p $\pi$  overlap does not give 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!**