Chapter 3
Free-Radical Polymerization

Addition Reactions (Chain reactions)

polyaddition reactions of unsaturated organic compounds induced by

1) Free-radical-forming reagents (radical initiator) (chapter 3)
2) Ionic initiator (chapter 4)

Free-Radical Addition Reactions

the growing chain end bears an unpared electrons

addition of each monomer molecules to the chain end involves an attack by the radical site on the unsaturated monomer

Inhibitor can prevent the polymerization.

Products from the radical polymerization:
LDPE, PMMA, PS, PAN, PVC, …… (Table 3.2)

Mechanism in chapter 12

Initiators for Free-Radical Polymerization

1-4: compounds dissociate into radicals
5,6: physical influences generates free radicals from monomers

Monomers for Free-Radical Polymerization

Solvents and Systems

1. Bulk polymerization
2. Solution Polymerization
3. Emulsion (Suspension) Polymerization

Chain Reactions (↔ Step Reactions)

;Definition based on the mechanism as follows

1. Chain initiation
2. Chain propagation
3. Chain Transfer
4. Chain Termanation

Combination

Disproportionation

Free Radical Initiators

1. Thermal Decomposition of Initiator; peroxides and azo compounds

peroxides

Polymerization temperature (useful initiation temperature) for some peroxides

Di-*t*-bulty peroxides: 100- 120 ^{o}C

Diacylperoxides: 60 - 80 ^{o}C

Phenyl radicals can also initiate the polymerization

Organic hydroperoxides : ROOH

not good for initiation. Why?

Peroxy radicals
are not reactive
for initiation

Azo compounds ; RN=NR

Example; AIBN (azobisisobutyronitrile)

2.Initiation by Redox Reaction;

radical generation through oxidation and reduction reactions

Initiation temperature; 15 – 50 ^{o}C

No side reactions (low temp reaction)

H_2SO_3 (sulfurous acid), HSO_3^- (hydrogen sulfite), SO_3^{2-} (sulfite)
$H_2S_2O_8$ (peroxodisulfuric acid), $S_2O_8^{2-}$ (peroxodisulfuric anion),

Direct Thermal and Photolytic Initiation

1. Thermal Initiation; by heating

2. Photolytic Initiation ; chapter 5

3. Initiation by High E Radiation (X-ray, γ-ray, α-particle, electron, proton); chapter 5

Reaction of Initiator Radicals with Monomer

Efficiency of Initiation (f) = 0.1 -0.8

Radical Chain Propagation

Head to tail addtion (H-T)

Head to Head addtion (H-H)

Tail to tail addtion (T-T)

H-T is major, why?

Example: PVA formation at 25 ^{o}C; H-H 1.1 %
at 100 ^{o}C; H-H 1.8 %

Chain Transfer Reaction

If the chain transfer happens in the middle of the polymer backbone

Free Radical Chain Termination

Termination by the reaction of polymer radicals with initiator radicals would be avoided by keeping the initiation rate low

Termination by Combination and Disproportionation

Combination vs. Disproportionation

Atom Transfer Radical Polymerization (ATRP)

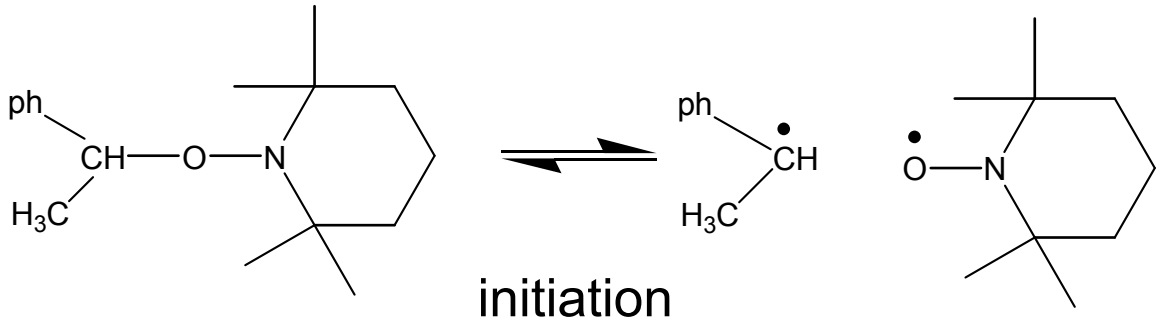
Living Polymerization

Termination can be minimized

Stable Free-Radical Polymerization (SFRP)

Living Polymerization

Styrene monomer



initiation

initiator

nitroxide radical

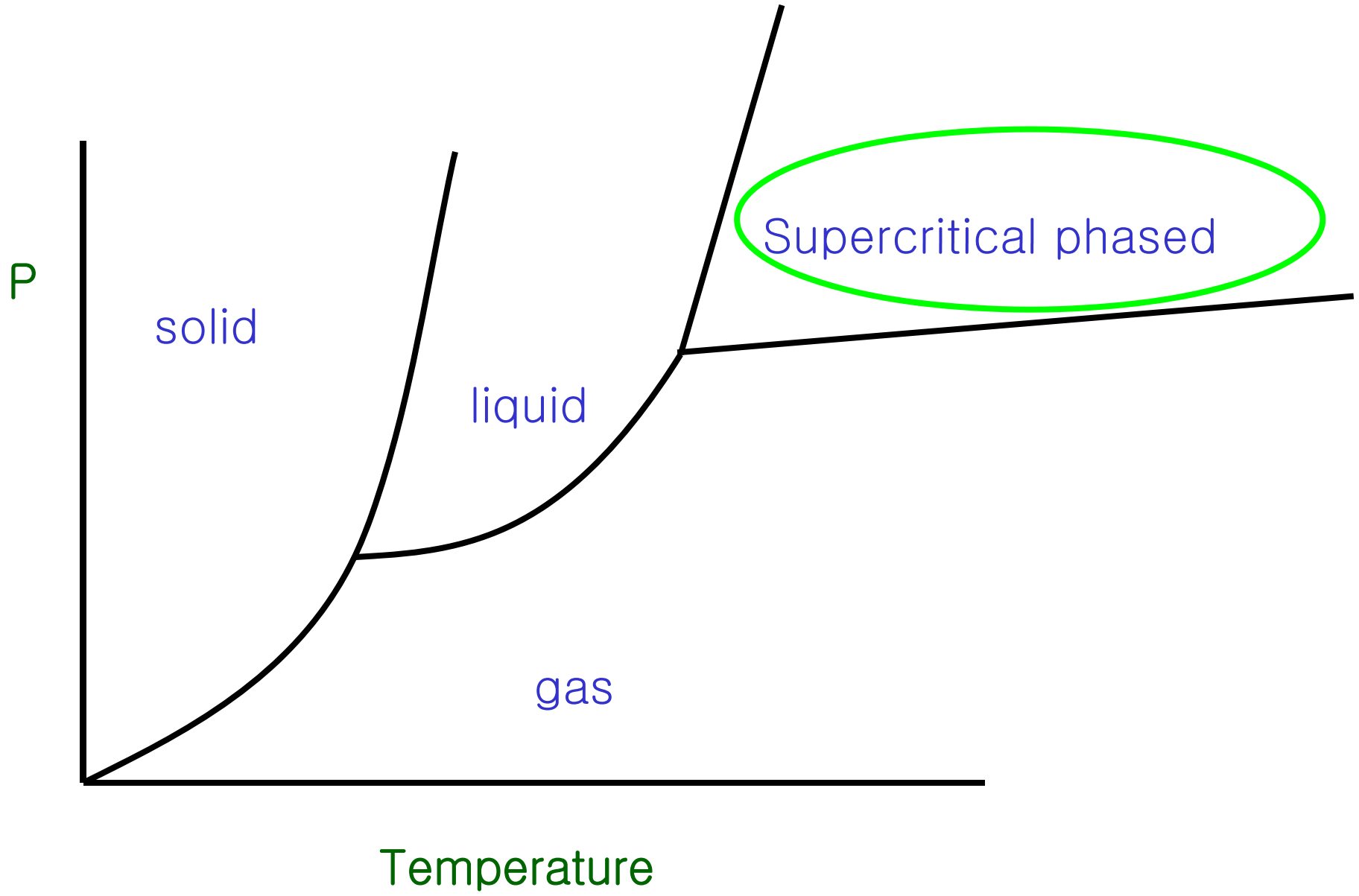
Termination can be minimized

Polymerizations in Supercritical Carbon Dioxide

- No dipole moment
- Quadrupole moment
- Low critical condition

s

- Good solvent for non-polar molecules with low M.W.
- Poor solvent for most of the hydrocarbon polymers
- Good solvent for fluoropolymers and silicone polymers


P
solid
liquid
gas
Supercritical phased
Temperature