Chapter 6

Polymerization of Cyclic Organic Compounds

Introduction

Two main difference from other polymerizations

1. **No loss of small molucules (condensation)**
2. **No loss of multiple bonding enthalpy (addition)**

Cyclic compounds that resists polymerization

- **No suitable catalysts have not been found yet**
- **The absence of ring strain; thermodynamically stable**

Cyclic compounds that be polymerizable

Two general mechanisms of classical ring-opening polymerization

1. Initial ring cleavage through the attack of catalysts

2. The attack of catalysts generates a coordination intermediates (generally oxonium ion)

Cyclic ethers

Trioxane

Polymerization using

1. Lewis acid or acid,
2. during sublimation,
3. through γ-irradiation of the crystalline monomer.

Protonic acid

ring cleavage

Lewis acid

Trithian and Tetrathiane

Cationic type catalysts

BF_3 or SbF_3

Tetrahydrofuran

Vigorous purification is required

1. **Polymerization using trifluoromethanesulfonic acid, CF_3SO_3H**

High molecular weight polymer

or

Crown ethers

coordination intermediates

2. Polymerization using Lewis acids with a small amout of water

ring cleavage

3. Polymerization using Lewis acids without water;

$2PCl_5 \rightarrow PCl_4^{+}PCl_6^{-}$ or $2PF_5 \rightarrow PF_4^{+}PF_6^{-}$

ring cleavage

4. Polymerization using Lewis acids without a cocatalysts

coordination intermediates

Oxetanes and Oxepanes

Oxetanes

Oxepanes ; polymerization is reversible (97-8% of 29, 2-3% of 28)

Polymerizability; Oxetanes >Tetrahydrofuran>Oxepanes

Epoxides; ethylene oxide, propylene oxide,

Both cationic and anionic mechanisms are possible

Epichlorohydrin; epoxy resins can be prepared

Further polymerization

Linear polymers can be formed ←

Anionic mechanism; using alkoxides, hydroxides, metal oxides, organometallic species

ring cleavage

Termination may not occur unless protonic reagents are added

Chain transfer; lower the MW

Cationic mechanism; strong protonic acid *(change)*

coordination intermediates

Lactones; *polyesters are produced*

Ring size effect ?

γ –butyllactone (5-membered ring); non-polymerizable

δ-valerolactone (6-membered ring); polymerizable

Glycolides and Lactides;

poly(glycolic acid) and poly(lactic acid) are produced;
biologically acceptable and biodegradable polymers

Condensation polymerization

Low MW Polymer

Cationic ; stannous chloride, antimony trifluoride….

High MW Polymer

Mechanism ?

Cyclic anhydrides

Biodegradable (bioerodable) polymers

Polymerization using anionic, cationic, coordination initiators

Cyclic carbonates

PC from condensation polymerization; side-products

PC from ring opening polymerization; no side-products, then polymerization in mold or extruder is possible

Lactams; nylons are produced through ring opening

caprolactam

Strong base catalyzed polymerization

Water catalyzed polymerization

Amino acid zwitterion attack the ring

Polymer

Ethyleneimine

Cationic initiator

Carcinogenicity

Oxazoline

Non vinyl oxazoline

No-catalyst copolymerization

Two cyclic monomers of one a nucleophile and the other an electrophile can undergo a ring opening polymerization to produce a 1:1 alternating copolymer

Free-radical ring-opening polymerization

Ring opening polymerization; mostly ionic mechanism

Vinylcyclopropane, byclobutane can undergo radical polymerization due to the ring strain.

(How? Solve by yourself !)

In some cases, unstrained cyclic monomers can undergo radical polymerization

A free-radical ring-opening polymerization with a volume expansion

Cyclopolymerization

The addition reactions of nonconjugated dienes that generate rings during the polymerization.

Normally this occurs through an alternating intra-intermolecular propagation process

Cyclopolymerizaton through γ *–ray irradiation*

(How? Solve by yourself !)

Production of DIVEMA

polyanions derived from this polymer are interferon-inducing agents and pocess anitumor activity

Poly(*para*-xyrene)