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## Chapter 4. Ionic and coordination (addition) polymerization

4.1. Similarities and contrast on ionic polymerization

4.2. Cationic polymerization

4.3. Anionic polymerization

4.4. Coordination polymerization

4.5. Ring-opening polymerization

## 4.1. Similarities and contrasts in ionic polymerization

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**Similarities** between the radical and ionic polymerizations  
There are 3 steps: initiation, propagation, and termination.

**Differences** between the radical and ionic polymerizations  
**In radical polymerization involves**

- radicals
- reactions between two growing chains

**In ionic polymerization involves**

- carbanions ( $C^{\ominus}$ ) in anionic polymerization and carbonium ions ( $C^{\oplus}$ ) in cationic polymerization.
- unimolecular reactions of a chain with its counterion or a transfer reaction leaving a species too weak to propagate.

TABLE 4-1. Types of Chain Polymerization Suitable for Common Monomers<sup>a</sup>

Monomer Type	Polymerization Mechanism <sup>b</sup>			
	Radical	Cationic	Anionic	Coordination
Ethylene	+	+	-	+
Propylene and $\alpha$ -olefins	-	-	-	+
Isobutylene	-	+	-	-
Dienes	+	-	+	+
Styrene	+	+	+	+
Vinyl chloride	+	-	-	+
Vinylidene chloride	+	-	+	-
Vinyl fluoride	+	-	-	-
Tetrafluoroethylene	+	-	-	+
Vinyl ethers	-	+	-	+
Vinyl esters	+	-	-	-
Acrylic and methacrylic esters	+	-	+	+
Acrylonitrile	+	-	+	+

<sup>a</sup>Lenz (1967).

<sup>b</sup>+ = high polymer formed; - = no reaction or oligomers only.

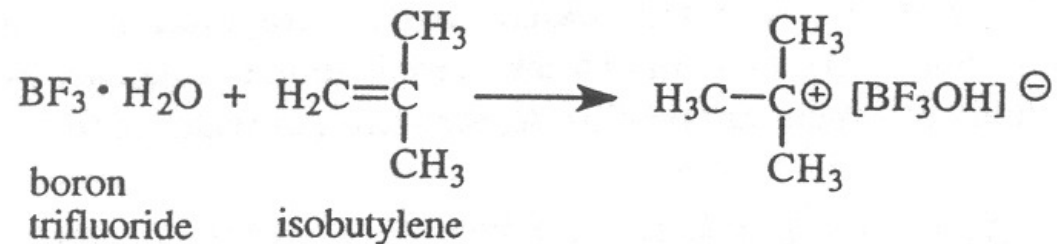
## 4.2. Cationic polymerization

The initiation applies a true catalyst that is restored at the end of the polymerization and does not become incorporated into the terminated polymer-chain.

Example of a catalyst is a strong Lewis acid, such as  $\text{BF}_3$ .

In a commercial isobutylene polymerization, water is used as a cocatalyst.

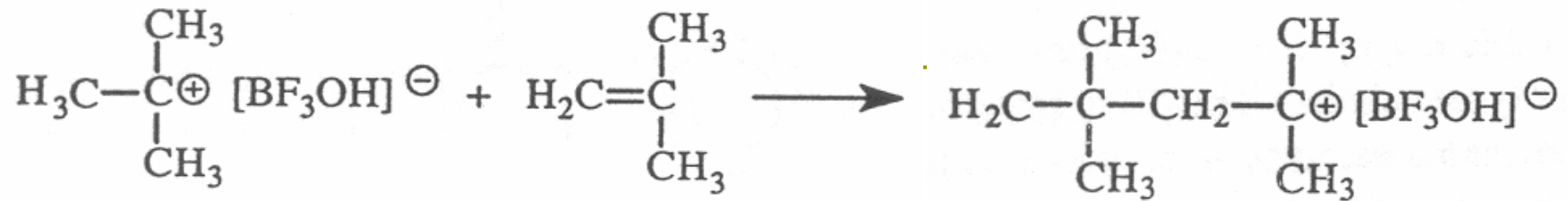
### Initiation



Isobutylene carbonium ion

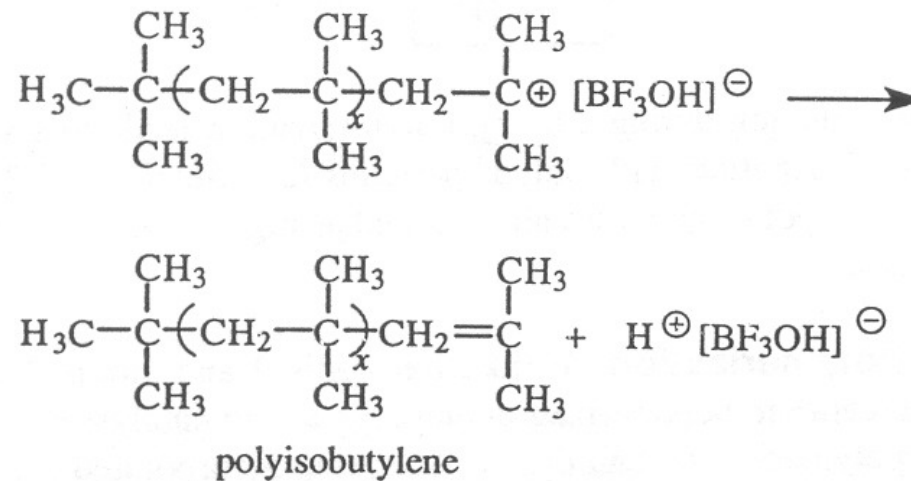
counterion or gegen ion

## Propagation



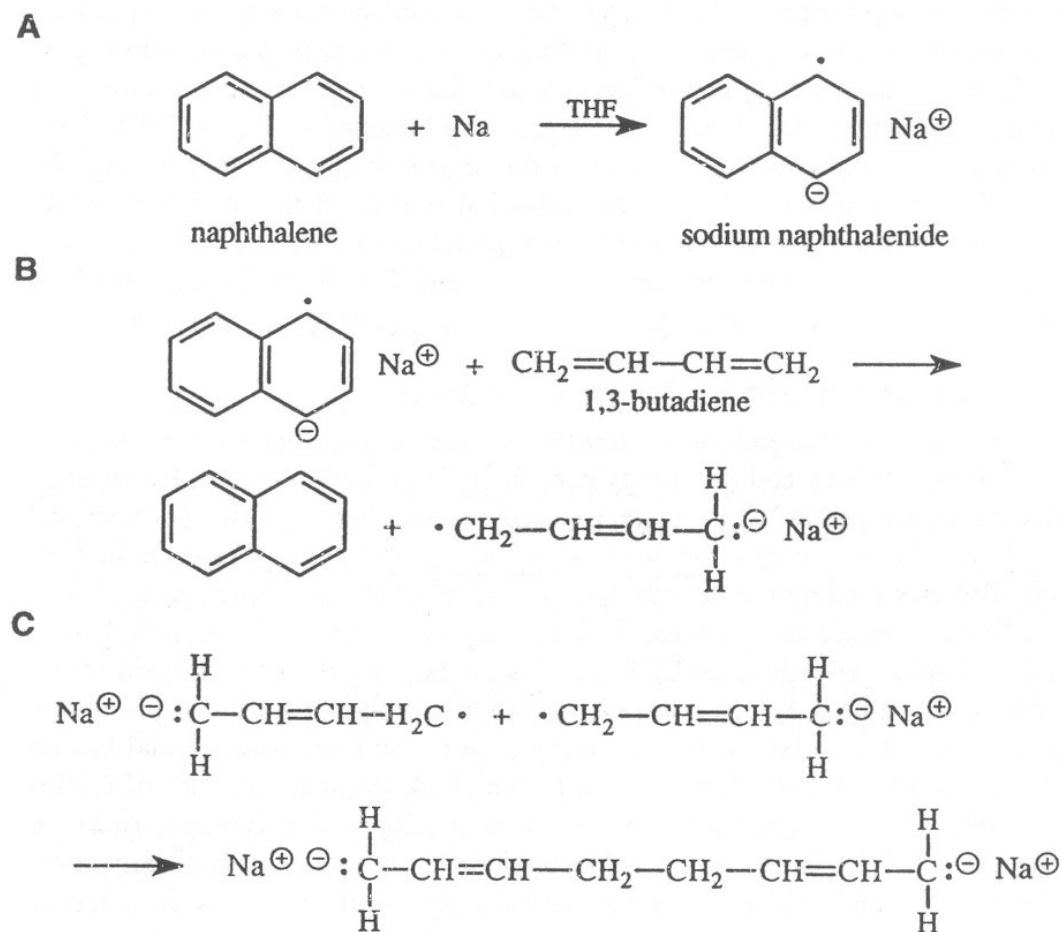
## Termination

Chain transfer to a monomer or counterion process occurs



Cationic polymerizations are usually conducted in solution and often at low temperature (-80 °C to -100 °C).

Typically, there is a linear increase in polymer chain-length and an exponential increase in polymerization rate as the dielectric strength of the solvent increases.

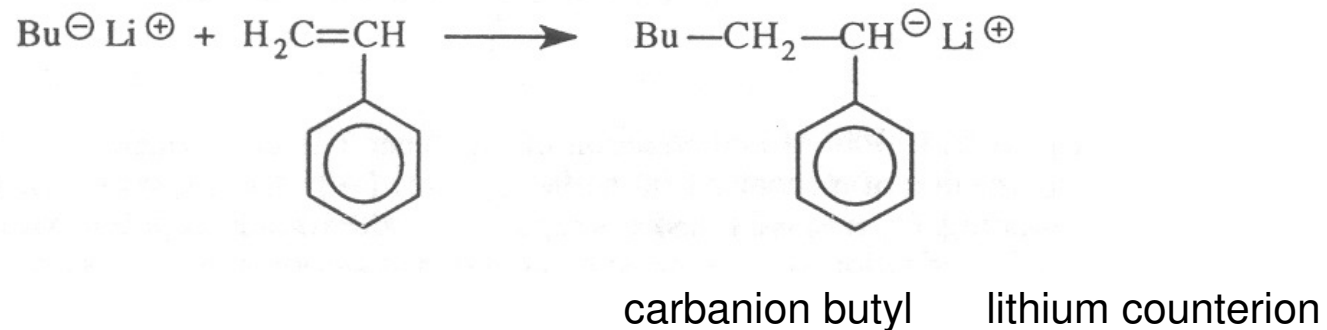


**Figure 2.5.** Use of sodium naphthalenide in the synthesis of a SBS triblock copolymer. **A.** Formation of sodium naphthalenide from naphthalene and sodium. **B.** Reaction of sodium naphthalenide with butadiene monomer. **C.** Combination of radicals to give the dianion available for anionic polymerization at both ends.

## 4.3. Anionic polymerization

### Initiation

The initiation involves a strong nucleophile, for example Grignard reagents and other organometallic compounds, such as n-butyl (n-C<sub>4</sub>H<sub>9</sub>) lithium.



### Propagation

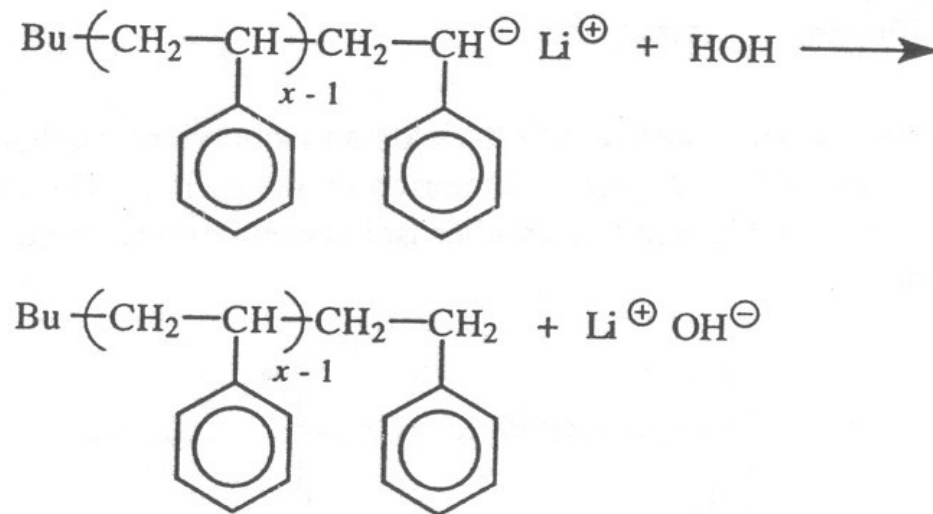
The chain propagates by insertion of additional styrene monomers between the carbanion and counterion.

If the reagents are pure and if the polymerization reactor is purged of water and O<sub>2</sub>, the propagation proceeds indefinitely or until all monomer is consumed.

## Termination

Termination occurs only by the deliberate introduction of O<sub>2</sub>, CO<sub>2</sub>, methanol, or water.

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In the absence of a termination mechanism and the growing chains remain active indefinitely, transfer process occurs → living polymerization. This leads to a molecular-weight distribution:

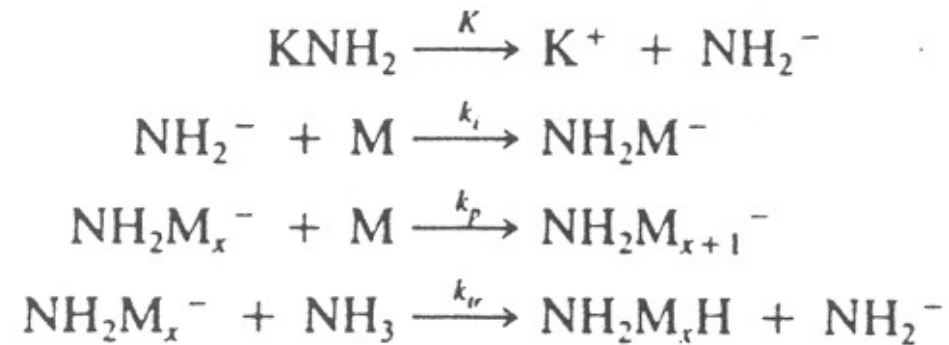
$$\bar{X}_n = \frac{[\text{M}]_0}{[\text{I}]_0}$$



Example:

The polymerization of styrene with potassium amide in liquid ammonia

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The rate of propagation: 
$$R_p = \frac{Kk_p k_i}{k_{tr}} \frac{[\text{NH}_2^-]}{[\text{NH}_3]} [\text{M}]^2$$

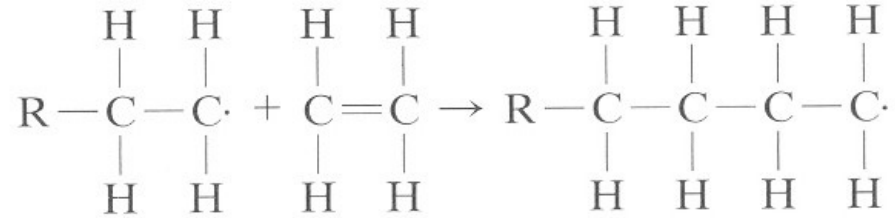
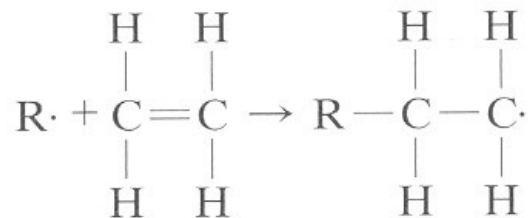
The number-average degree of polymerization: 
$$\bar{X}_n = \frac{k_p [\text{M}]}{k_{tr} [\text{NH}_3]}$$

## 4.4. Coordination polymerization

Coordination polymerization applies a novel class of transition-metal catalysts, called the Ziegler-Natta catalysts and produced of polymers with unusual stereospecific structures. The mechanism and the kinetics are complicated and the catalysts are usually solids to form heterogeneous polymerization systems.

### History

**1939** : a high-pressure free-radical polymerization of ethylene was developed by ICI. PE has some short and long alkane branches, moderate crystallinity, thermal and mechanical properties. This product is called LDPE.



1954:

**Giulio Natta** (Italy) developed a stereochemical process to polymerize isotactic PP (i-PP). This i-PP had degree of crystallinity comparable to LDPE and exhibited good mechanical properties in a wide range of temp.

**Karl Ziegler** (Germany) developed a similar process to polymerize ethylene at lower temp & pressure to produce HDPE. This HDPE had fewer branches and a higher degree of crystallinity.

Polymer	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	Repeating Unit
Polyethylene	H	H	H	H	$[-\text{CH}_2-\text{CH}_2-]$
Polypropylene	H	H	H	CH <sub>3</sub>	$[-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-]$

**TABLE 4-2. Components of Typical Ziegler–Natta Catalysts\***

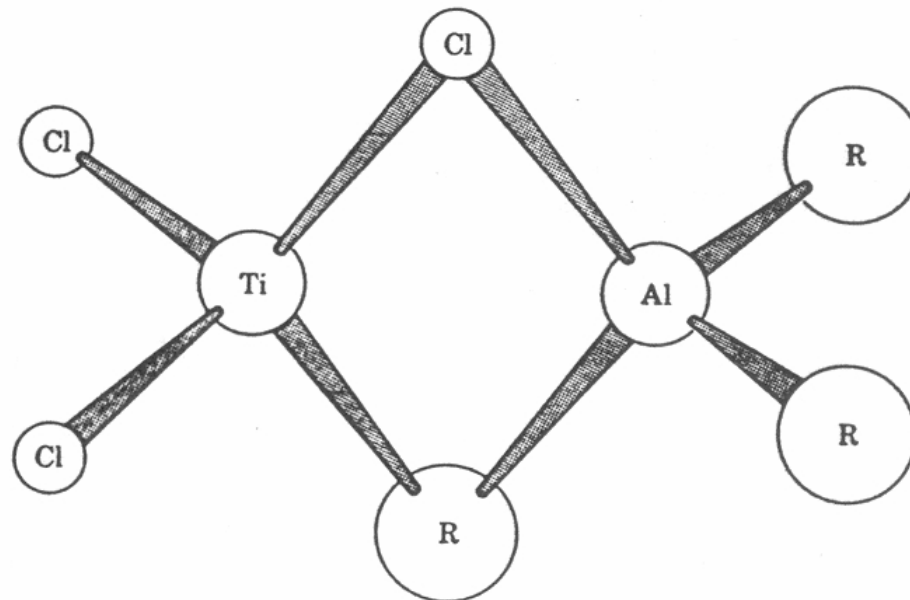
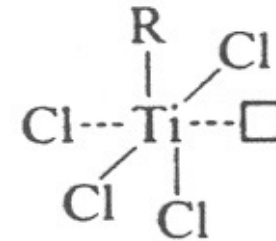
Organometallic Compound	Transition-Metal Salt
Triethyl aluminum	Titanium tetrachloride
Diethyl aluminum chloride	Vanadium trichloride
Diethyl aluminum chloride	Triacetyl acetone vanadium
Diethyl aluminum chloride	Triacetyl acetone chromium
Diethyl aluminum chloride	Cobalt chloride–pyridine complex
Butyl lithium	Titanium tetrachloride
Butyl magnesium iodide	Titanium trichloride
Ethyl aluminum dichloride	Dichlorodicyclopentadienyl titanium

\*Henrici-Olivé (1969).

A Ziegler-Natta catalyst is usually a metal-organic complex of a metal cation from groups I – III  $\{Al_2(C_2H_5)_3\}$  and a metal compound from groups IV – VIII  $\{TiCl_4\}$ .

## Ziegler-Natta catalyst: $\text{TiCl}_4$

The Ti has been reduced from Ti(IV) to Ti(III) and the chlorine bridge is called three-center bond.



#### 4.4.1. Mechanism of coordination polymerization

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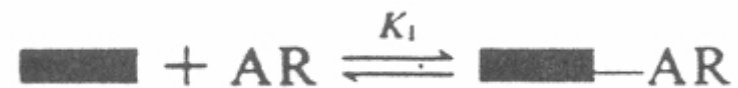
The exact mechanism of coordination polymerization is still unclear. However, it is believed that the transition metal is the active site. The ethylene is coordinated to the free site at the transition metal and inserted between metal and the alkyl group R. The coordination process results in the stereospecificity of the polymerization. The rate of the reaction can be influenced by the nature of the other ligands present.

## 4.4.2. Kinetics of coordination polymerization

A case of heterogeneous polymerization.

It is defined :  $\blacksquare$  is the surface of the transition-metal compound,  
AR is the metal alkyl,  
M is the monomer,  
 $M_x$  is the polymer.

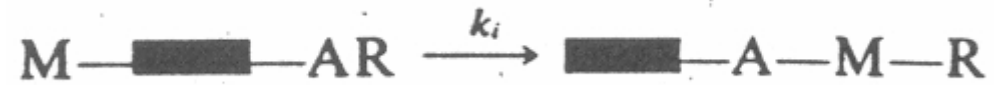
Adsorption of metal alkyl from solution to form the active site



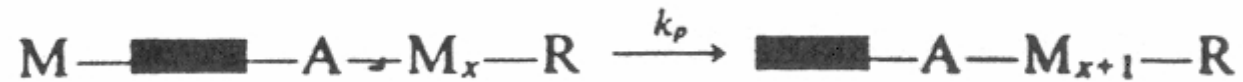
Adsorption of M from solution



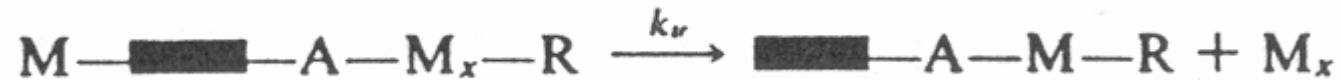
## Initiation



## Propagation



## Termination (transfer)



## Termination (monomer forms an inactive site)





It is assumed that the process occurs in Langmuir isotherm condition and it is defined that :

$\theta_A$  and  $\theta_M$  are the fractions of the available surface covered by AR and M respectively,

$[C^*]$  is the concentration of growing chains,

Then the overall rate can be determined.

$$\theta_A = \frac{K_1[AR]}{1 + K_1[AR] + K_2[M]} \quad \theta_M = \frac{K_2[M]}{1 + K_1[AR] + K_2[M]}$$

The overall rate: 
$$R_o = -\frac{d[M]}{dt} = (k_p + k_{tr})\theta_M[C^*]$$

Assume that  $[C^*]$  reaches steady state so that the initiation rate is similar to the termination rate.

$$k_i\theta_A\theta_M = k_t[C^*]\theta_M$$

The overall rate:

$$R_o = -\frac{d[M]}{dt} = \frac{(k_p + k_{tr})k_i}{k_t} \frac{K_1 K_2 [AR][M]}{(1 + K_1 [AR] + K_2 [M])^2}$$

## 4.5. Ring-opening polymerization

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The ring-opening polymerization consists of both chain and step polymerization as far as kinetics and mechanisms are concerned. Most of ring-opening polymerizations are very rapid and involve cyclic compounds by ionic mechanisms in the presence of strong acids or bases when water and alcohols are excluded.

The commercial products are caprolactam, ethylene oxide, and 3,3-bis-(chloromethyl)oxetane.

**TABLE 4-3. Typical Ring-scission Polymers**

Type	Example
Lactone	$\text{O}(\text{CH}_2)_x\text{CO} \longrightarrow -[\text{O}(\text{CH}_2)_x\text{CO}-]_y$
Lactam	$\text{HN}(\text{CH}_2)_x\text{CO} \longrightarrow -[\text{HN}(\text{CH}_2)_x\text{CO}-]_y$
Cyclic ether	$(\text{CH}_2)_x\text{O} \longrightarrow -[(\text{CH}_2)_x\text{O}-]_y$
Cyclic anhydride	$\text{CO}(\text{CH}_2)_x\text{CO} \longrightarrow -[\text{CO}(\text{CH}_2)_x\text{COO}-]_y$
<i>N</i> -Carboxyanhydride	$\text{COCHR}\text{NHCO} \longrightarrow -[\text{COCHR}\text{NH}-]_y + \text{CO}_2$