第二章　　逐 步 聚 合

Stepwise Polymerization

本节重点

1、逐步聚合是制备高分子材料的重要方法

2、几个重要概念

- 官能团和官能度
- 反应程度P和转化率C
- 官能团等活性

3、缩聚反应特征

- 逐步进行：聚合度/分子量逐步增加
- 可逆平衡：平衡常数 K

2.1 引 言

- 链式聚合：活性中心
  - 自由基、正离子、负离子、配位聚合
- 逐步聚合：官能团的反应
  - 缩(合)聚(合)反应；
  - 逐步加成聚合；
  - 部分开环聚合；
  - 氧化耦合；
  - Diels-Alder加成反应

部分重要的逐步聚合物

尼龙－66

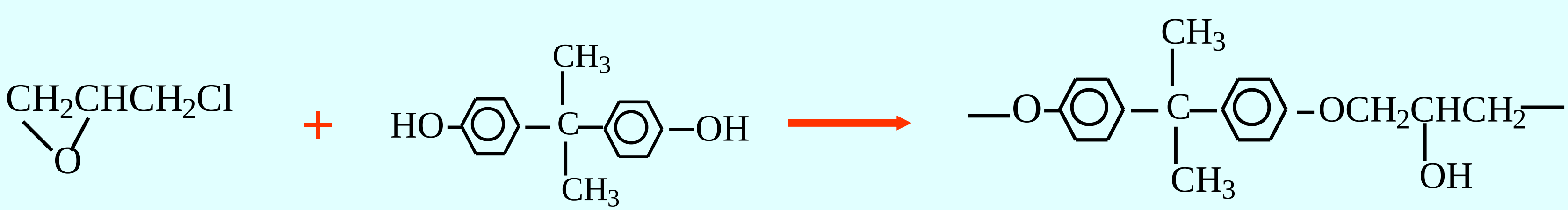
$$H_2N(CH_2)_6NH_2 + HOOC(CH_2)_4COOH \longrightarrow \text{—}NH(CH_2)_6NHOC(CH_2)_4CO\text{—}$$

聚氨酯

$$HOR'OH + OCNRNCO \longrightarrow \text{—}\underset{\|}{\overset{}{C}}\text{—}NHRNH\text{—}\underset{\|}{C}OR'O\text{—}$$

$$\quad\; O \qquad\qquad\qquad O$$

环氧树脂



尼龙—66，Nylon66

$$\underset{\text{己二胺}}{H_2N-(CH_2)_6-NH_2} + \underset{\text{己二酸}}{HO-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_4-\overset{\displaystyle O}{\overset{\|}{C}}-OH}$$

$$\rightleftharpoons$$

酰胺基团

Amide Group

$$\left[-\underbrace{\underset{\displaystyle H}{\underset{|}{N}}-(CH_2)_6}_{6}-\underset{\displaystyle H}{\underset{|}{N}}-\underbrace{\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_4-\overset{\displaystyle O}{\overset{\|}{C}}}_{6}-O-\right]_n$$

华莱士·卡罗瑟斯(1896–1937)

◆1930年，用乙二醇和癸二酸缩合制取聚酯

◆1935年，用戊二胺和癸二酸合成聚酰胺

◆1935年2月，合成出聚酰胺66。耐磨、强度高，成本低，杜邦公司决定进行商品生产开发

纽约先驱论坛报,
Oct. 30 1938

"I am making the announcement of a brand new chemical textile fiber ---derivable from coal, air and water -- and characterized by extreme toughness and strength --"
Charles Stine V.P. for research, Du Pont, 1938

Du Pont Announces for the World of Tomorrow...

a new word and a new material

NYLON

NO BETTER EXAMPLE of the fruits of research could be found than nylon—so new a material that a name had to be coined by Du Pont for it—so vast in the number of its possible uses that no list, however farseeing at present, can include them all—so promising in its first uses that Du Pont will spend $8,000,000 on a plant employing approximately 1,000 people.

Nylon is the generic name for all materials defined scientifically as synthetic fiber-forming polymeric amides having a protein-like chemical structure; derivable from coal, air and water, or other substances, and characterized by extreme toughness and strength and the peculiar ability to be formed into fibers and into various shapes, such as bristles, sheets, etc.

This is the newest of the synthetic materials. In its development a group of Du Pont chemists have been occupied for years. Nylon, though it springs from common raw materials that exist in abundance, can be fashioned into filaments possessing a beautiful luster, strong as steel, delicate as the fiber of a spider's web, yet more elastic than any of the natural fibers.

Toothbrushes with "Exton" bristles made from nylon are now available. Soon other forms of this new product will reach the public as a result of experimental work in progress.

Out of continued research in synthetic chemistry has come this development, as will others, to aid in the building of the World of Tomorrow.

Jobs...Jobs...

Still another important result comes from this contribution—as from other chemical developments. From these fruits of chemical research spring jobs for the men who build plants and machinery—jobs for the men who make the raw material—jobs for the men who convert it into numerous articles for everyday service. Thus science doubly aids man in his search for better living.

The Past Gives a Clue to the Future

During the past ten years, Du Pont developments have included (among many other uniquely useful products) such contributions as these:

Moistureproof "Cellophane" cellulose film to protect foodstuffs from dirt and germs, and to preserve freshness and flavor.

"Cordura" rayon yarn, the super-tough fiber for truck and auto tires.

Nitrogen compounds made from the air, to return vital elements to the soil.

Neoprene chloroprene rubber with the resilience, strength and toughness of natural rubber, yet superior in its resistance to gasoline, oils, sunlight, heat and aging.

Improved fire retardants to reduce fire hazards in home and industry.

"Zerone" anti-rust anti-freeze to protect automobile radiators from freezing in winter . . . from rusting and corroding in summer.

"Dulux" enamels, the tough, long-lasting finishes now used on automobiles, trucks, streamlined trains, ships, bridges, home appliances, interior walls, refrigerators.

Higher Wages...Lower Prices

Since 1929, Du Pont has developed scores of new products. Today Du Pont employs more people than in 1929, pays higher wages, and sells its goods in greater quantities and at lower prices. Last year, forty percent of Du Pont's entire sales was on twelve lines of products developed or improved since 1929.

Scientists believe this record of accomplishment, these contributions to better living, are a promise of things to come—a promise for the World of Tomorrow and for those who will inherit it.

Your Preview of a Better World

At the New York World's Fair, Du Pont's "Wonder World of Chemistry" exhibit will present some of the more spectacular chemical achievements. Here will be shown, for the first time, many of the intricate processes used in the development and manufacture of Du Pont products. Here those who look hopefully to the future will find proof of what orderly research has done to contribute to better living and more continuous employment for everyone.

Where to Tomorrow, Mr. Chemist?

And the chemist answers: "To a thousand untouched shores. To a land of tomorrow where rain won't wet your clothes, where everyone gets his vitamins, where fire won't burn your home, where insects won't steal your wealth, where life is easier, happier, and more complete in ways that can't even be dreamed of today."

How soon, Mr. Chemist? And the chemist answers: "Just as soon as I can make it come true. I build for the tomorrow that will be yours, and your children's and your grandchildren's. And when each of these tomorrows becomes a 'today'—there will still be tomorrows to work for!"

Such is the spirit and the meaning of the Du Pont pledge: "Better Things for Better Living . . . through Chemistry."

When you visit New York's World Fair in 1939, you will find nothing more fascinating than a tour through this building—The Wonder World of Chemistry, presented by Du Pont to give you a glimpse of the world of tomorrow.

DU PONT
REG. U.S. PAT. OFF.

E. I. du Pont de Nemours & Company, Inc., Wilmington, Delaware

BETTER THINGS FOR BETTER LIVING...THROUGH CHEMISTRY

部分重要的逐步聚合物

- 涤纶（PET）
- 聚碳酸酯（PC）
- 聚氨酯（PU）
- 环氧树脂（Epoxy）
- 不饱和聚酯（UP）
- 酚醛树脂
- 脲醛树脂
- 有机硅树脂
- 芳纶
- 聚酰亚胺
- PBO
- ……

2.2 缩聚反应

2.2.1 缩合与缩聚

2.2.2 缩聚反应分类

2.2.3 线型缩聚反应特征

2.2.3.1 反应程度P与聚合度关系

2.2.3.2 平衡常数与平均聚合度Xn关系

2.2.1 缩合（Condensation）与缩聚（poly-condensation）

- 几个概念：
  - 官能团和官能度
  - 缩聚反应和缩合反应：
  - 自缩聚和混缩聚
  - 线型缩聚和体型缩聚
  - 平衡缩聚和不平衡缩聚

2.2.2　缩聚反应分类

- 按不同的分类原则有多种分类方法，常见的有如下三种
  - 按参加反应的单体种类分类:
    - 均缩聚（自缩聚）　混缩聚（杂缩聚）　共缩聚
  - 按缩聚产物的分子结构分类:
    - 线型缩聚反应;　　体型缩聚反应
  - 按反应的热力学特征分类:
    - 平衡缩聚;　　不平衡缩聚

2.2.3 线型缩聚反应特征

线型缩聚的反应特征：

- 1）大分子链增长是逐步进行的

- 2）反应的可逆平衡性

1） 大分子链增长是逐步进行的

以 aAa 代表二元醇，以bBb代表二元酸，聚酯反应历程如下：

- 首先由两种单体分子相互反应生成二聚体

$$aAa + bBb \rightleftharpoons a\text{-}[A\text{-}B]\text{-}b + ab$$

- 二聚体还可以与单体、二聚体等继续反应
- 不同链长的聚合物间也可进行反应……

n－聚体 ＋ m－聚体 ⇌ (n+m)聚体 ＋ 水

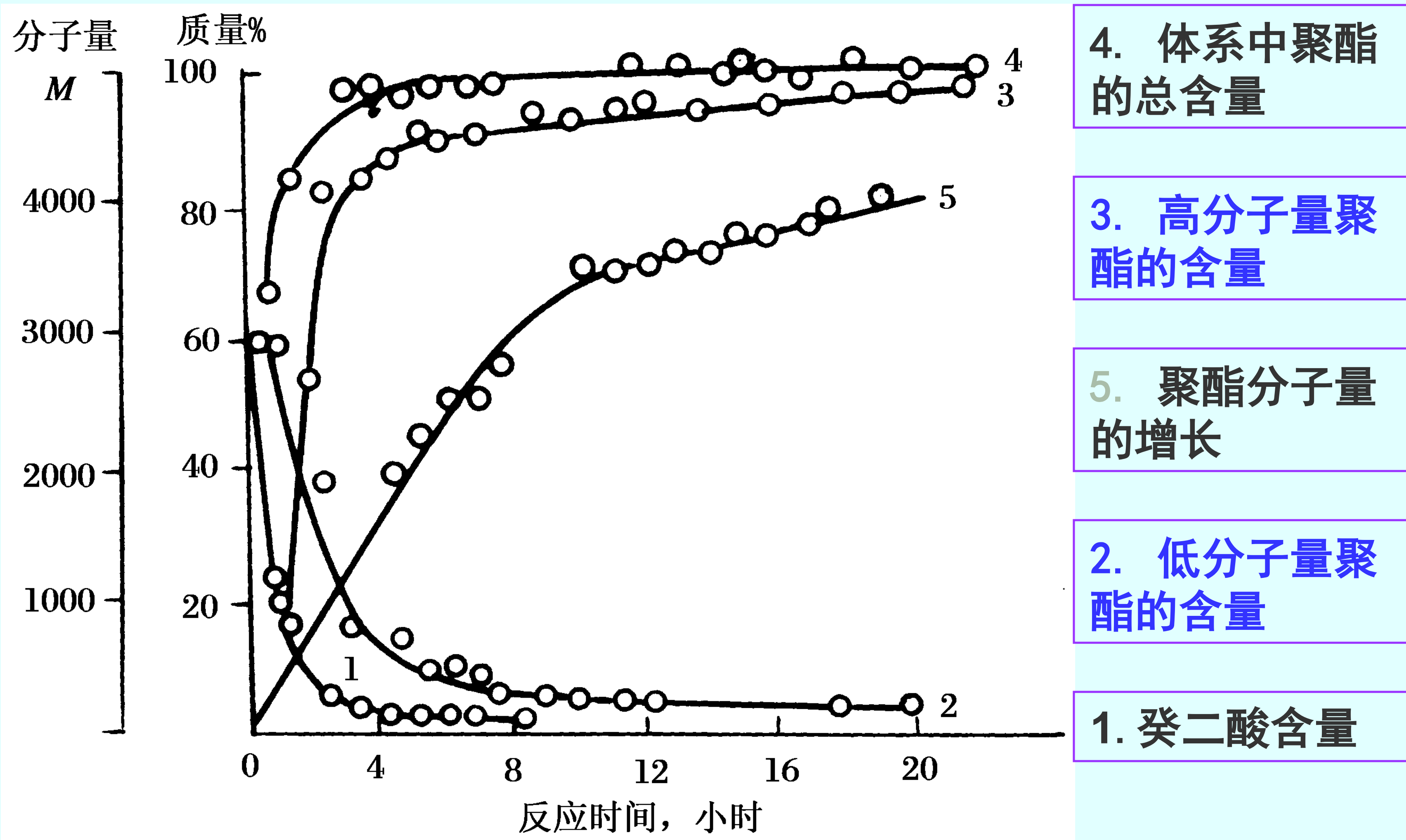


图2—1 癸二酸与乙二醇聚酯反应体系缩聚大分子的生成过程

2） 反应的可逆平衡：存在平衡常数K

$$-COOH + -OH \rightleftharpoons -OCO- + H_2O$$

$$K = \frac{k_1}{k_{-1}} = \frac{[-OCO-][H_2O]}{[-COOH][-OH]}$$

反应的可逆平衡：平衡常数K

- ① K小(K=4--10)
  - 聚酯类，小分子存在对聚合度影响很大，应除去
- ② K中(K＝300--400)
  - 聚酰胺类，小分子存在对聚合度有所影响
- ③ K很大（K≥10^3）
  - 可视为不可逆，苯酚--CH_2O 体系
- 可见，K的大小，在合成工艺上很有差别。

$$nH_2N(CH_2)_6NH_2 + HOOC(CH_2)_4COOH \rightarrow [NH(CH_2)_6NHOC(CH_2)_4CO]n + (2n-1)H_2O$$

- 封闭体系中进行缩聚反应时，由于产物和小分子副产物的逆反应，往往使聚合物分子量难以提高
- 为了提高分子量，一般采用减压除去副产物小分子，使平衡向着有利于生成大分子的方向移动

2.3　缩聚反应平衡

- 2.3.1　官能团等活性概念
- 2.3.2　反应程度、平衡常数与平均官能度的关系
- 2.3.3　影响缩聚平衡的因素

2.3.1 官能团等活性概念

- 缩聚反应是逐步进行的官能团之间的反应，大多数常见的缩聚反应均为可逆平衡反应。
- 等活性理论：Flory提出，官能团的反应活性基本上是等同的，与链的长短无关
- 根据等活性理论，整个缩聚过程可以用两种官能团之间的反应来表征。

例如：

聚酯：$-COOH + -OH \rightarrow -OCO- + H_2O$

聚酰胺：$-COOH + -NH_2 \rightarrow -CONH- + H_2O$

P·J·Flory 等作过不少研究

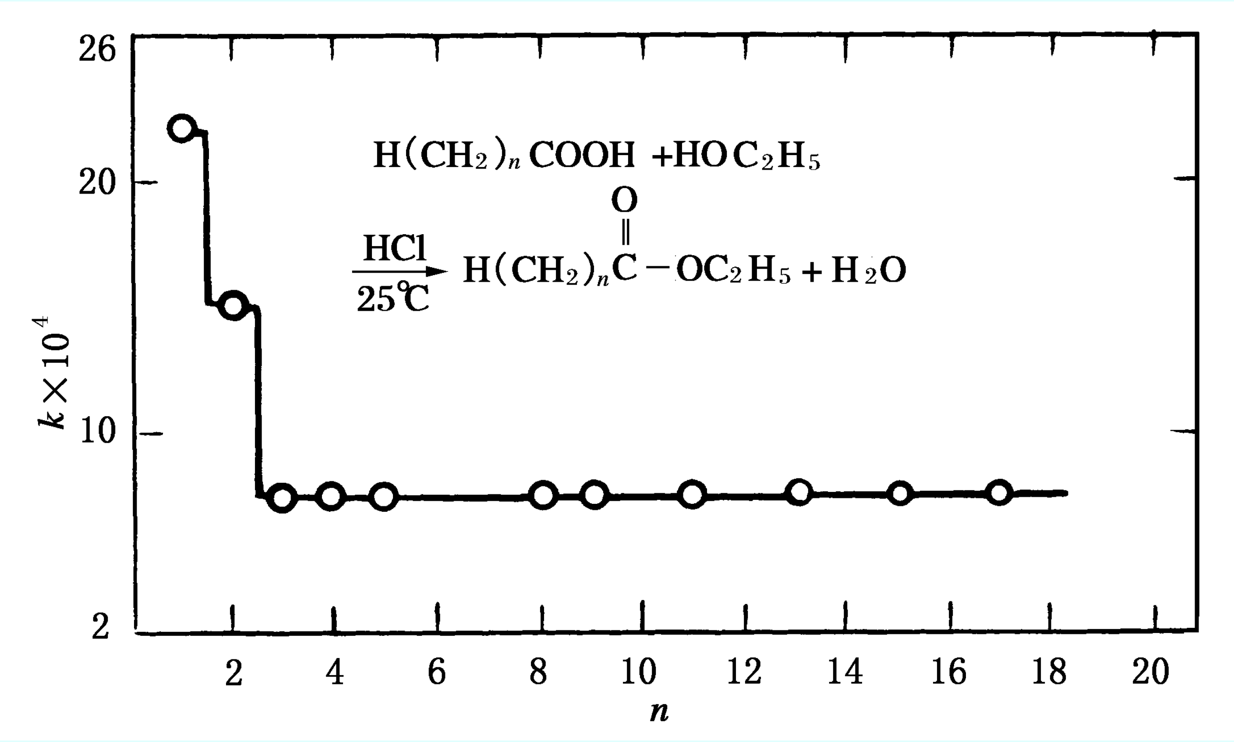


图2-2A 官能团的反应活性与分子大小的关系

- 反应速率常数k随n增大而减小
- 但n≥3后趋于定值

说明：

- 1) 当 n =1, 2, 3时， 速率常数 k 随 n 增大而迅速减小
  - 诱导效应引起的。只沿着碳链传递1-2个碳原子，随着链增长，影响作用减弱，因而n≥3后，速率常数均趋向于定值，说明官能团的活性与链长无关。
- 2) 官能团的反应活性与基团的碰撞频率有关，而与整个大分子的扩散速率关系不大。
  - 端基的活动能力大，而大分子的低扩散速率反而可保证端基能有较多的碰撞次数

- 3）聚合后期，体系粘度很高时，碰撞频率降低，聚合速率变成**扩散控制**，此时活性和速率才有所减小
- **4）在粘度不很大的情况，官能团等活性概念是正确的，**即“不同链长的官能团，具有相同的反应能力及参与反应的机会”

2.3.2 反应程度(P)、平衡常数(k)与平均聚合度(Xn)的关系

（1）转化率、反应程度、与聚合度的关系

转化率 C：已转化为聚合物的单体量占起始单体量的百分率

$$\boxed{C\% = \frac{[M]_0 - [M]}{[M]_0}}$$

转化率不适合表征缩聚反应进行的程度 ？？！

反应程度 P

- **反应程度 P**：某一特定官能团，在缩聚中已参加反应的官能团数与起始官能团数之比值。

$$P=\frac{N_0-N}{N_0}=1-\frac{N}{N_0}$$

($P\leq1$)

N_0：初始时某官能团总数

N ：时间为 t 时，未反应的官能团数

反应程度 P 与聚合度 $\overline{X}_n$ 关系？？

- **反应程度 P：** $$P=\frac{N_0-N}{N_0}=1-\frac{N}{N_0}$$

- **聚合度 $\overline{X}_n$**：进入每个大分子链的结构单元总数。平均每个大分子中含有的结构单元数命名为**数均聚合度**

P ?? $\overline{X}_n$

- 举例：聚酯化反应：

$$nHO-R-COOH \rightarrow \text{-}[ORCO]_n\text{-} + (n-1)H_2O$$

设t=0时，　　起始官能团数：—COOH：N_0

t=t时，　未反应官能团数：—COOH：N

- $$P_{-OH}=P_{-COOH}=\frac{N_0-N}{N_0}=1-\frac{N}{N_0}=P \qquad (2-2)$$

$$\overline{X}_n=\frac{\text{结构单元总数}}{\text{大分子数}}=\frac{N_0}{N} \qquad (2-3)$$

由(2—3)可知：$\frac{1}{\overline{X}_n}=\frac{N}{N_0}$　　代入(2—2)得：

$$P=1-\frac{1}{\overline{X}_n}$$

$$\boxed{\overline{X}_n=\frac{1}{1-P}} \qquad (2-4)$$

反应程度 P 与聚合度 $\overline{X_n}$ 关系

P	0	0.5	0.8	0.9	0.95	0.98	0.99	0.995	0.999
$\overline{X}_n$	1	2	5	10	20	50	100	200	1000

$$\overline{X_n} = \frac{1}{1-P}$$

（2）平衡常数与平均聚合度Xn的关系

- 平衡缩聚是由一系列的相继进行的平衡反应构成
- 根据等活性理论的概念，各步反应都可用同一个平衡常数 K 来表示，如：

$$-COOH + -OH \rightleftharpoons -OCO- + H_2O$$

$$K = \frac{k_1}{k_{-1}} = \frac{[-OCO-][H_2O]}{[-COOH][-OH]}$$

分两种情况讨论(封闭体系/非封闭体系)：

i ）封闭体系

$$-COOH + -OH \rightleftharpoons -OCO- + H_2O$$

$t=0$	C_0	C_0		
$t=t$	$C_0(1-P)$	$C_0(1-P)$	C_0P	C_0P

$$K = \frac{C_0P \bullet C_0P}{C_0(1-P) \bullet C_0(1-P)} = \frac{P^2}{(1-P)^2}$$

$$\sqrt{K} = \frac{P}{1-P}$$ 同时：$$\overline{X}_n = \frac{1}{1-P}$$

$$P = \frac{\sqrt{K}}{\sqrt{K}+1}$$

$$\boxed{\overline{X}_n = \sqrt{K} + 1}$$

对于聚酯： K＝4， P(平衡时)＝2/3， $\overline{X}_n$ ＝3

对于聚酰胺：K＝400，P(平衡时)＝0.95， $\overline{X}_n$ ＝21

当 K＝10^4，P(平衡时)＝0.99 $\overline{X}_n$ ＝100

- 平衡与分子量：对于缩聚反应，封闭体系，尤其是 K 值比较小的体系，难以制得高分子量聚合物。为了提高聚合物的分子量，必须设法除去反应体系中的小分子物。

ⅰⅰ） 非封闭体系：随反应进行，把小分子副产物除去

$$-COOH + -OH \rightleftharpoons -OCO- + H_2O$$

t = 0　　C_0　　C_0

t = t　　$C_0(1-P)$　　$C_0(1-P)$　　C_0P　　n_w

$$K=\frac{[-OCO-][H_2O]}{[-COOH][-OH]}=\frac{(1-C)\cdot n_\omega}{C^2}=\frac{P\cdot n_\omega}{(1-P)^2C_0}$$

可知： $$\bar{X}_n=\sqrt{\frac{KC_0}{P\cdot n_\omega}}$$ (2 – 10)

当 P→ 1，（P＞0.99） $$\bar{X}_n\approx\sqrt{\frac{C_0K}{n_\omega}}$$

（2—10）称为缩聚平衡方程，反映了非封闭体系中Xn与K、nw间的定量关系

为排除低分子物，常采用下列方法：

①减压；②提高反应温度；③通入惰性气体

例如：聚酯 K＝4，欲使$\overline{X_n}$≥100，要求nw≤4×10^{-4}（mol/l）

聚酰胺 K＝400，欲使$\overline{X_n}$≥100，要求nw≤4×10^{-2}（mol/l）

小结

1、重要的基本概念

- 缩聚反应和缩合反应
- 官能团和官能度
- 线型缩聚和体型缩聚
- 平衡缩聚和不平衡缩聚
- 反应程度P 和 转化率 C

2、缩聚反应特征

缩聚反应特征：官能团等活性概念

1. 逐步进行：聚合度/分子量逐步增加

2. 可逆平衡：平衡常数 K

3、缩聚反应平衡

- 平衡——平均聚合度Xn的关系
  - 封闭体系
  - 非封闭体系

$$\overline{X_n} = \sqrt{K} + 1$$

$$\overline{X}_n = \sqrt{\frac{KC_0}{P \cdot n_\omega}}$$