

Тема: Поликонденсация

План лекции

- Определение и классификация
- Отличие полимеризации и поликонденсации
- Кинетика
- Побочные реакции
- Примеры реакций

Поликонденсация

Определение и классификация

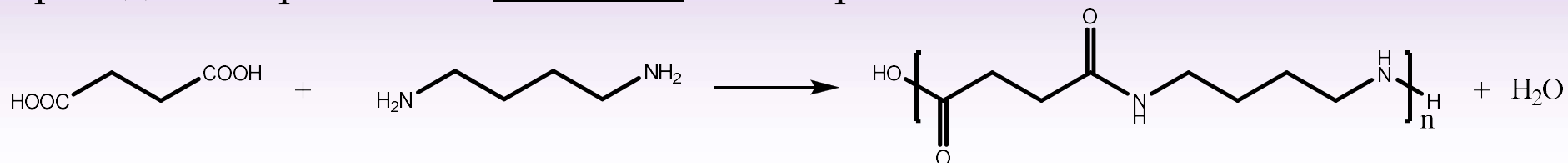
Поликонденсация – разновидность реакции синтеза высокомолекулярных соединений из полифункциональных мономеров, которая обычно сопровождается выделением побочных низкомолекулярных продуктов таких как вода, спирт, хлороводород и т. п.

Полифункциональный мономер – мономер с двумя и более функциональными группами, приходящимися на одну молекулу.

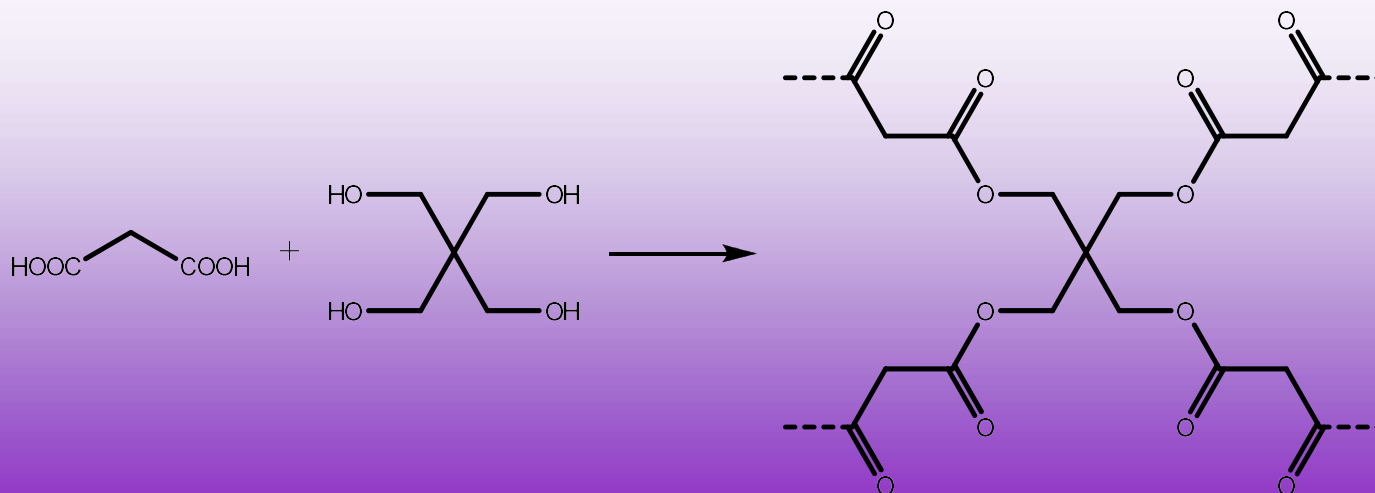
Поликонденсация

Определение и классификация

- Поликонденсация бифункциональных мономеров называется линейной и приводит к образованию линейных полимеров



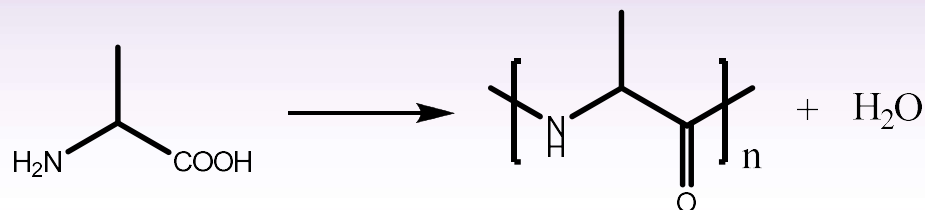
- Если в реакции поликонденсации участвует хоть один мономер, содержащий три и более функциональных групп, такая поликонденсация называется трехмерной и приводит к образованию сетчатых полимеров



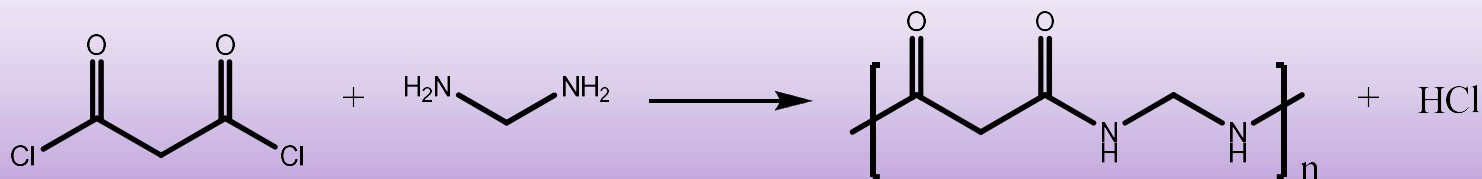
Поликонденсация

Определение и классификация

- Поликонденсация, которая идет с участием одного мономера с различными функциональными группами называется гомополиконденсация



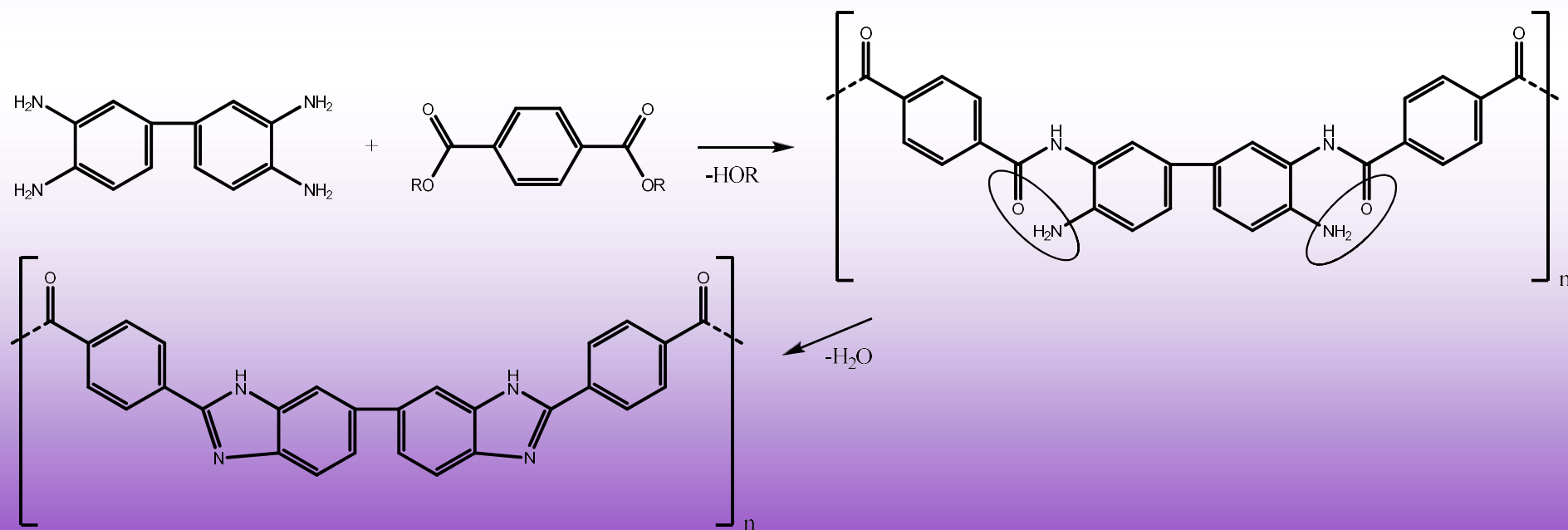
- Поликонденсация, которая идет с участием двух и более мономеров называется гетерополиконденсация (сополиконденсация)



Поликонденсация

Определение и классификация

Отдельным видом реакций поликонденсации является полициклоконденсация — метод синтеза полимеров циклоцепной структуры, механизм которого предполагает наличие двух или нескольких последовательных реакций, первая из которых — поликонденсация, вторая или последующие — циклизация:



Поликонденсация

Определение и классификация

В зависимости от характера взаимодействия между функциональными группами выделяют следующие типы:

- Равновесная (обратимая) поликонденсация:



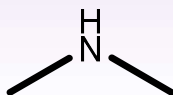
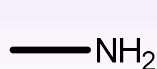
- Неравновесная (необратимая) поликонденсация:



Поликонденсация

Мономеры

- Мономеры, содержащие в молекулах одинаковые функциональные группы, не способные реагировать между собой



- Мономеры, содержащие различные функциональные группы, способные реагировать между собой (гидроксикислоты, аминокислоты)

- Мономеры, содержащие в молекулах одинаковые функциональные группы, способные реагировать между собой в определенных условиях (многоатомные спирты, многоосновные карбоновые кислоты)

Поликонденсация

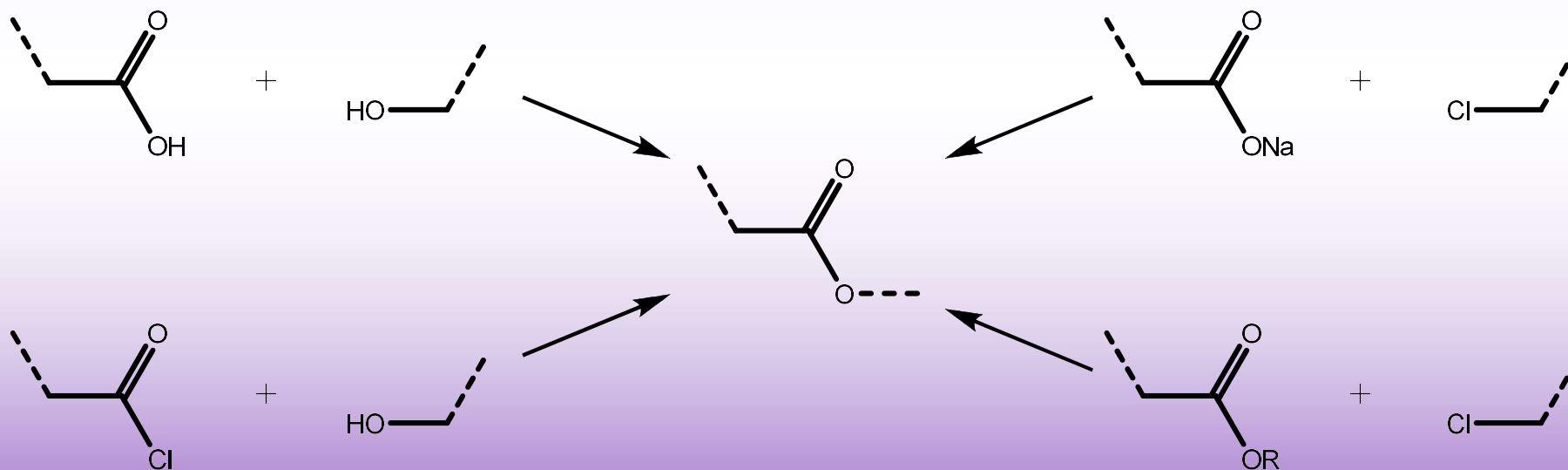
Отличие полимеризации и поликонденсации

- Поликонденсация протекает по ступенчатому механизму в отличие от цепного для полимеризации.
- Поликонденсация подразумевает выделение низкомолекулярного продукта.
- Состав полимерного звена, при поликонденсацией отличается от состава мономера.
- Весь мономер расходуется на ранних стадиях поликонденсации (при малых степенях конверсии), в то время как для полимеризации мономер заканчивается с окончанием процесса.
- Макромолекулы целевой молекулярной массы начинают образовываться лишь на завершающих стадиях реакции.
- Концевые группы полимера (разного типа), сохраняют активность после процесса в отношении дальнейших реакций.

Поликонденсация

Отличие полимеризации и поликонденсации

В отличие от полимеризации, поликонденсационные полимеры одного типа можно получить из мономеров с разнообразными функциональными группами и при различных условиях



Поликонденсация

Кинетика



- Реакционная способность функциональных групп бифункционального мономера одинакова.
- Реакционная способность одной функциональной группы бифункционального мономера не зависит от того, прореагировала вторая группа или нет.
- Реакционная способность функциональной группы не зависит от размера олигомера.

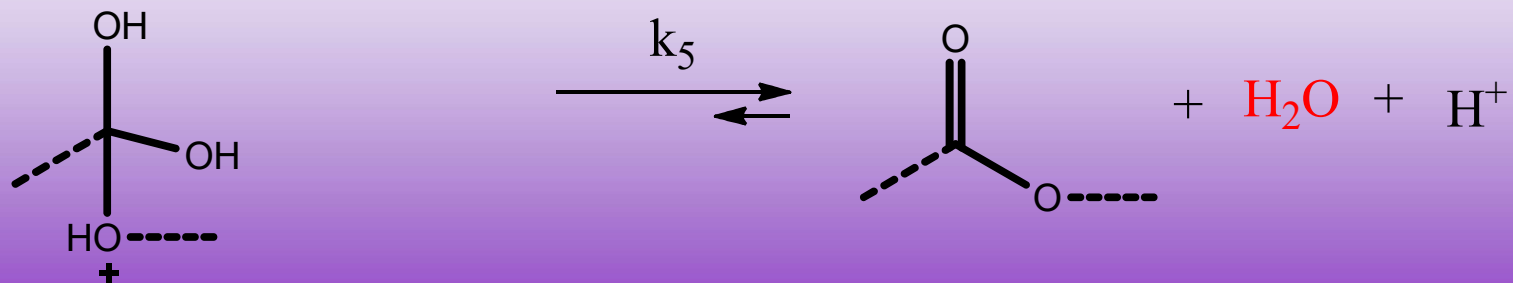
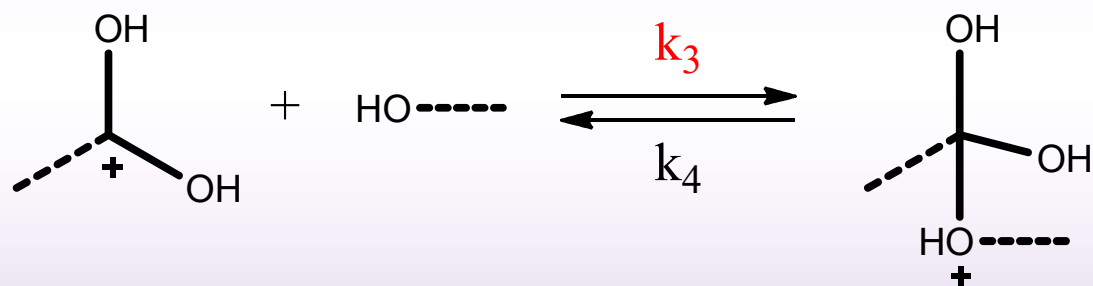
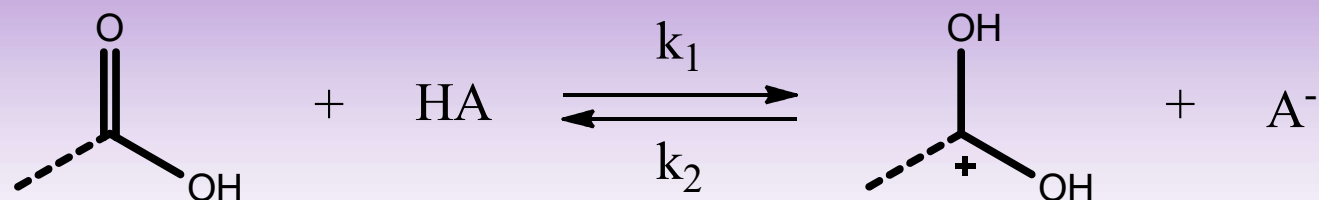
Поликонденсация

Кинетика

Размер моле- кулы (n)	$k \cdot 10^4, \text{ л/ (моль} \cdot \text{с)}$	
	ДЛЯ $\text{H}(\text{CH}_2)_n\text{COOH}$	ДЛЯ $(\text{CH}_2)_n(\text{COOH})_2$
1	22,1	
2	15,3	6,0
3	7,5	8,7
4	7,5	8,4
5	7,4	7,8
6		7,3
8	7,5	
9	7,4	
11	7,6	
13	7,5	
15	7,7	
17	7,7	

Поликонденсация

Кинетика



Поликонденсация

Кинетика

$$V_p = \frac{-d[\text{COOH}]}{dt} = k_3 [\text{C}^+(\text{OH})_2][\text{OH}]$$



$$K = \frac{k_1}{k_2} = \frac{[\text{C}^+(\text{OH})_2][\text{A}^-]}{[\text{COOH}][\text{HA}]}$$

$$[\text{C}^+(\text{OH})_2] = \frac{k_1 [\text{COOH}][\text{HA}]}{k_2 [\text{A}^-]}$$

$$V_p = \frac{k_1 k_3}{k_2 [\text{A}^-]} [\text{OH}][\text{COOH}][\text{HA}]$$

Поликонденсация

Кинетика

$$V_p = \frac{k_1 k_3}{k_2 [A^-]} [OH][COOH][HA]$$

Самокатализ

$HA \sim COOH$

$$V_p = k_p [OH][COOH]^2$$

Внешний катализ

$$K_{HA} = \frac{[H^+][A^-]}{[HA]}$$

$$V_p = \frac{k_1 k_3 [H^+]}{k_2 K_{HA}} [OH][COOH]$$

$$V_p = k'_p [OH][COOH]$$

Поликонденсация

Кинетика

При стехиометрическом соотношении



Самокатализ

$$V_p = k_p [\text{M}]^3$$

$$-\frac{d[\text{M}]}{dt} = k_p [\text{M}]^3$$

$$-\frac{d[\text{M}]}{[\text{M}]^3} = k_p dt$$

$$2k_p t = \frac{1}{[\text{M}]^2} - \text{const}$$

Внешний катализ

$$V_p = k'_p [\text{M}]^2$$

$$-\frac{d[\text{M}]}{dt} = k'_p [\text{M}]^2$$

$$-\frac{d[\text{M}]}{[\text{M}]^2} = k'_p dt$$

$$k'_p t = \frac{1}{[\text{M}]} - \text{const}$$

Слишком тяжело



До свидания

Поликонденсация

Молекулярная масса

$$p = \frac{[M]_0 - [M]_t}{[M]_0} \quad p - \text{степень превращения}$$

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

Уравнение Карозерса

$$\bar{X}_n = \frac{1}{1-p}$$

Внешний катализ

$$\frac{1}{[M]_t} - \text{const} = k'_p t$$

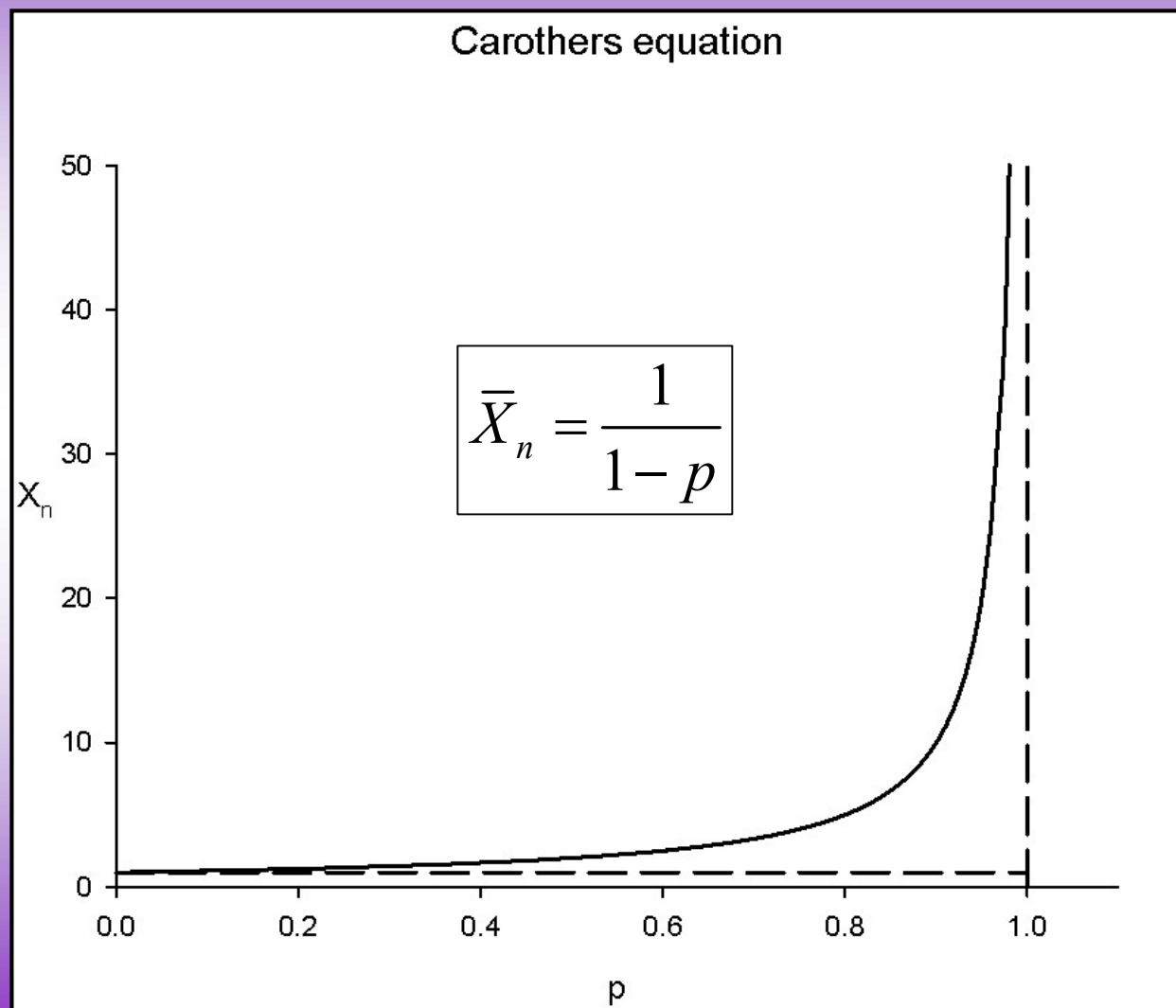
$$\frac{1}{[M]_t} - \frac{1}{[M]_0} = k'_p t$$

$$\frac{[M]_0}{[M]_t} - 1 = k'_p t [M]_0$$

$$\bar{X}_n = 1 + k'_p t [M]_0$$

Поликонденсация

Молекулярная масса



Поликонденсация

Стехиометрический разбаланс

1. Сополиконденсация бифункциональных мономеров

$$r = \frac{N_A}{N_B} \leq 1 \quad A-A \quad B-B \quad r - \text{стехиометрический разбаланс } (N_B \text{ всегда в избытке})$$

2. Сополиконденсация бифункциональных мономеров с добавлением монофункционального вещества

$$A-A \quad B-B \quad B'$$

$$r = \frac{N_A}{N_B + 2N_{B'}}$$

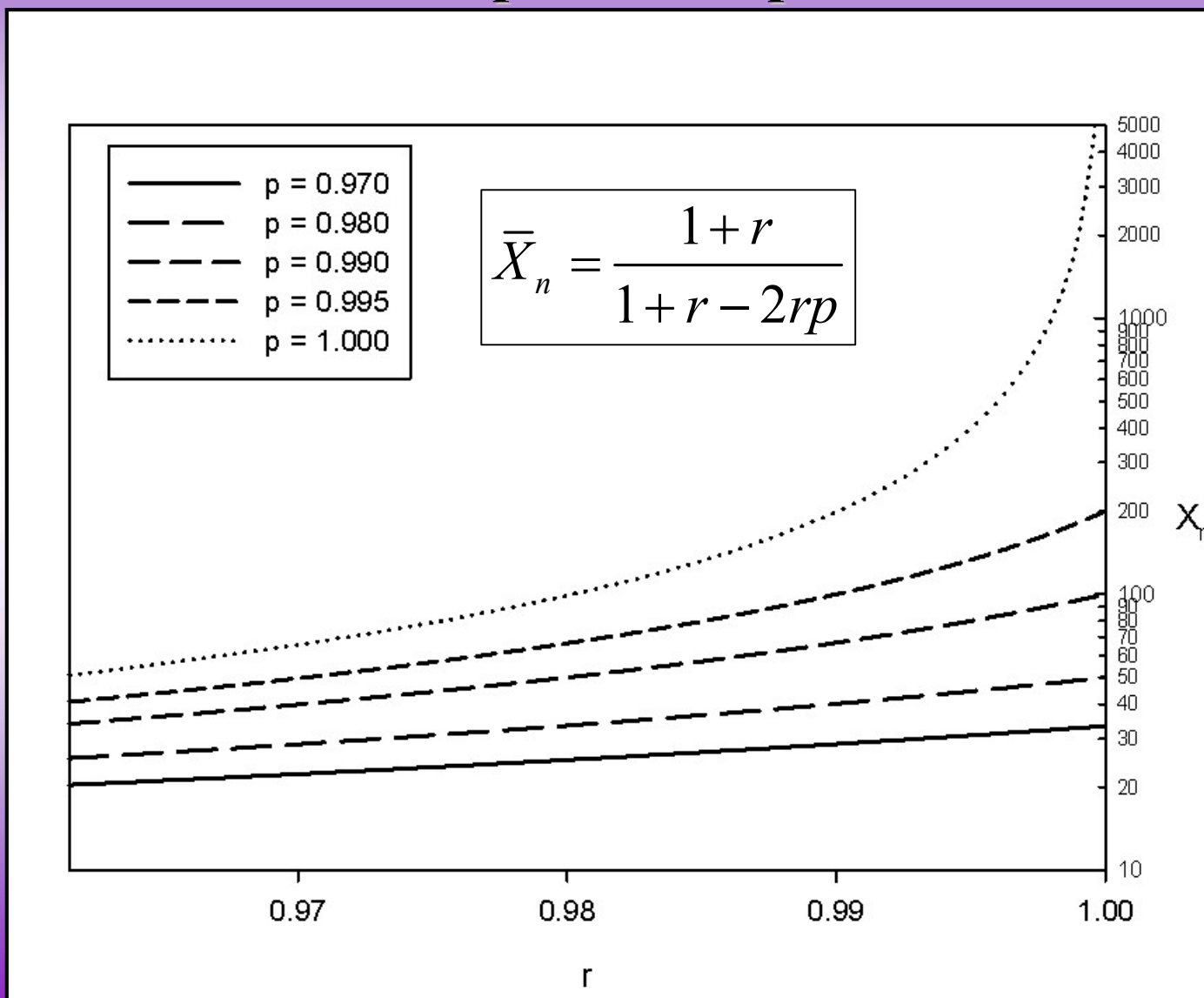
3. Поликонденсация бифункционального мономера с добавлением монофункционального вещества

$$A-B \quad B'$$

$$r = \frac{N_{AB}}{N_{AB} + 2N_{B'}}$$

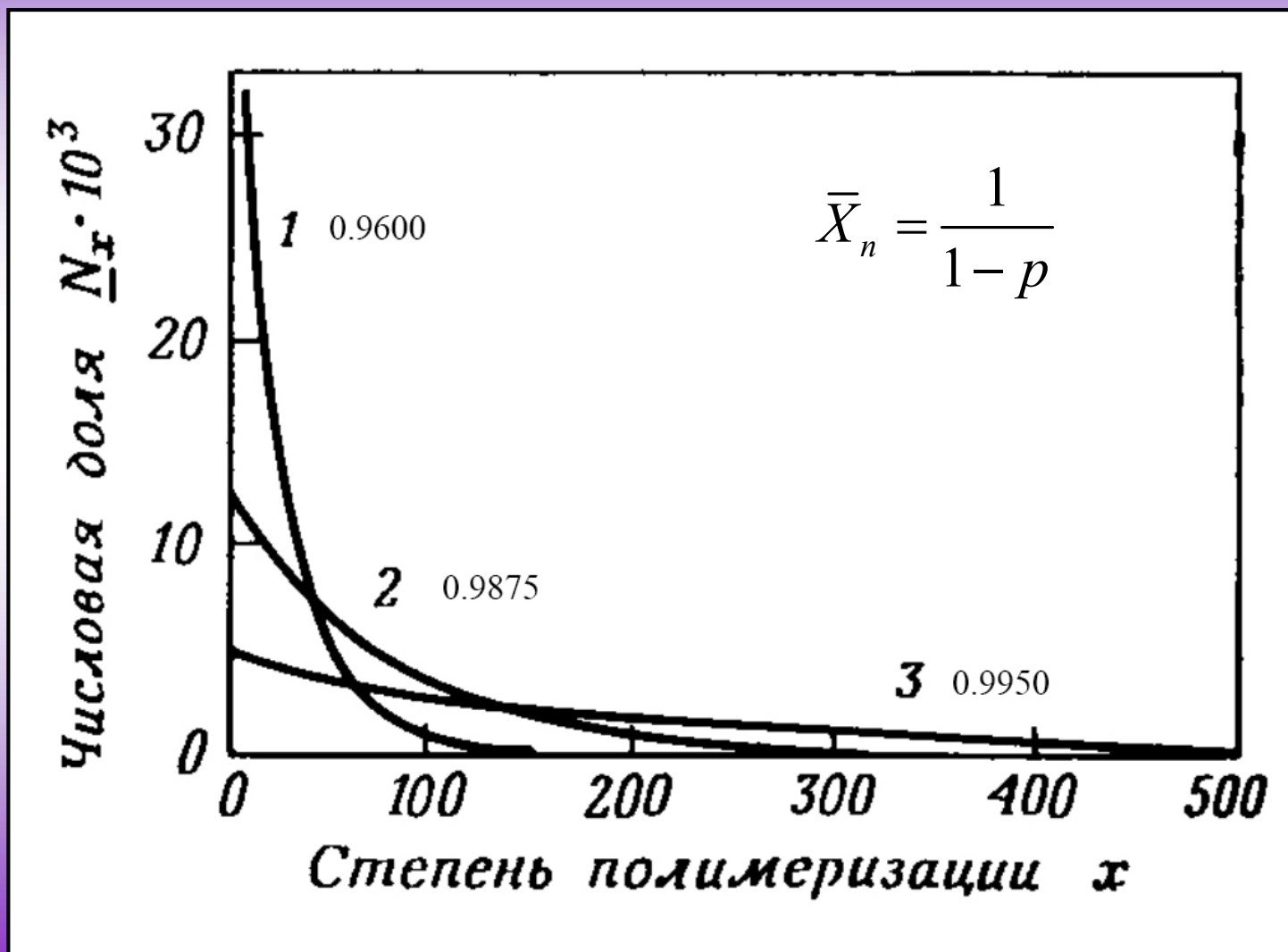
Поликонденсация

Стехиометрический разбаланс



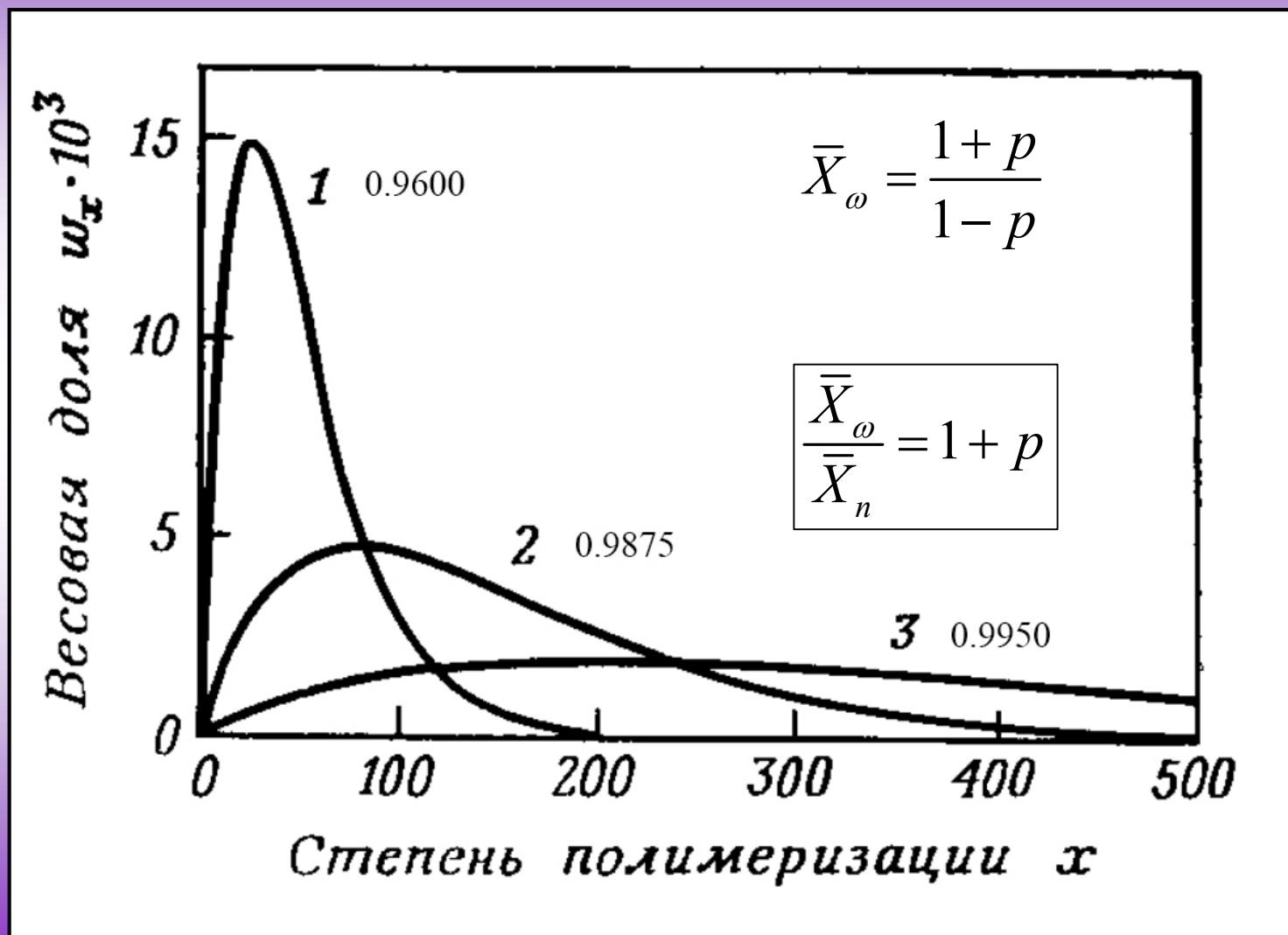
Поликонденсация

Молекулярно-массовое распределение



Поликонденсация

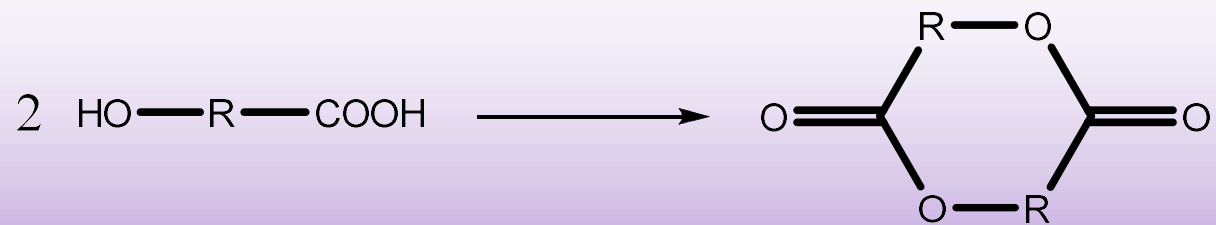
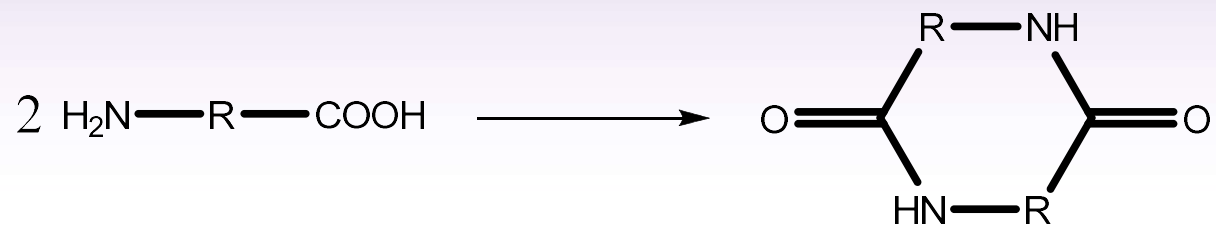
Молекулярно-массовое распределение



Поликонденсация

Побочные процессы

Межмолекулярная циклизация



Поликонденсация

Побочные процессы

Внутримолекулярная циклизация



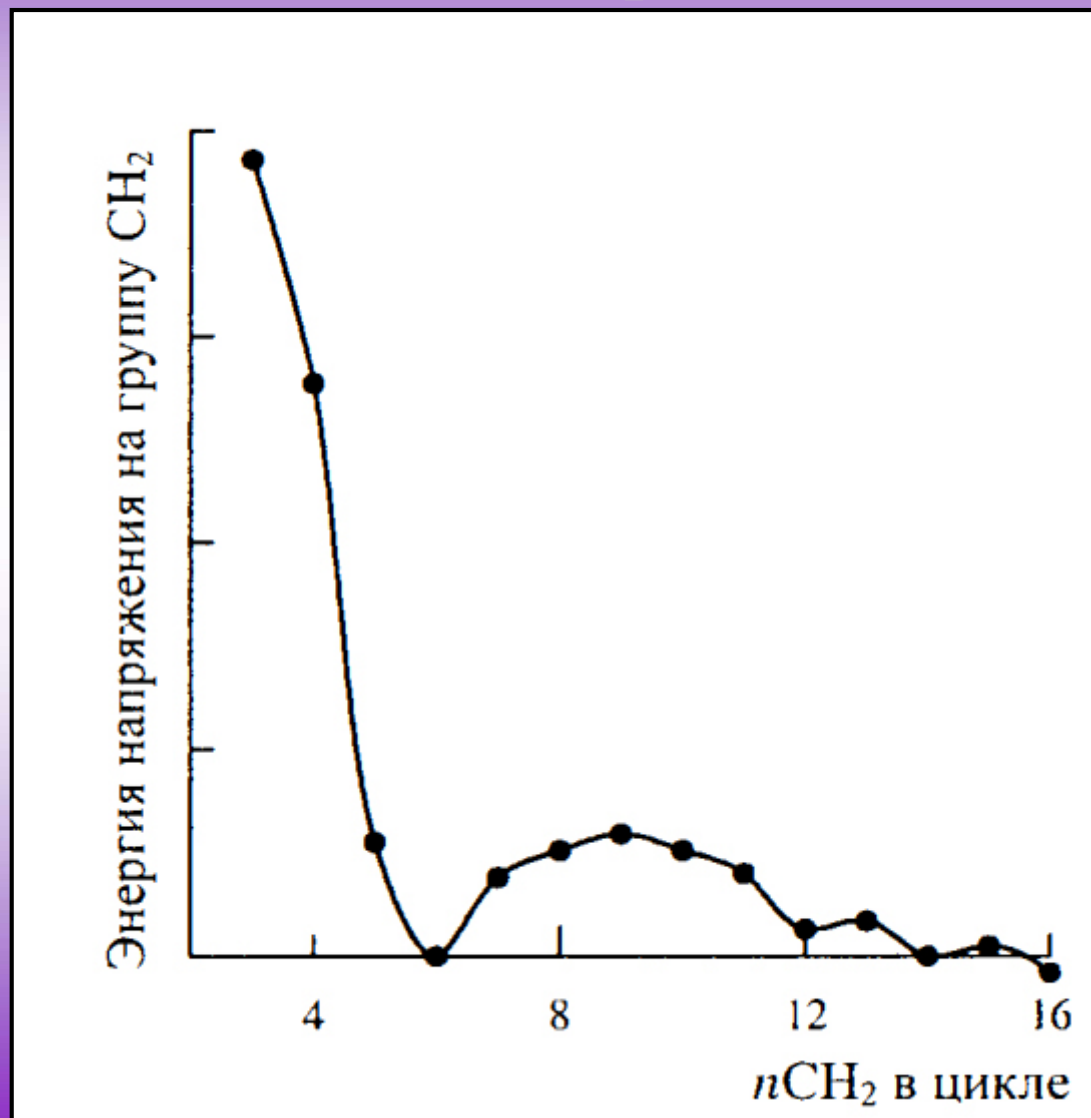
Поликонденсация

Побочные процессы

$\text{—(CH}_2\text{)}_n\text{—}$	Теплота сгорания на одну метиленовую группу, ккал/моль	Напряженность на одну метиленовую группу, ккал/моль
3	166,6	9,2
4	164,0	6,6
5	158,7	1,3
6	157,4	0,0
7	158,3	0,9
8	158,6	1,2
9	158,8	1,4
10	158,6	1,2
11	158,4	1,0
12	157,7	0,3
13	157,8	0,4
14	157,4	0,0
15	157,5	0,1
16	157,5	0,1
17	157,2	-0,2
<i>n</i> -Алкан	157,4	0,0

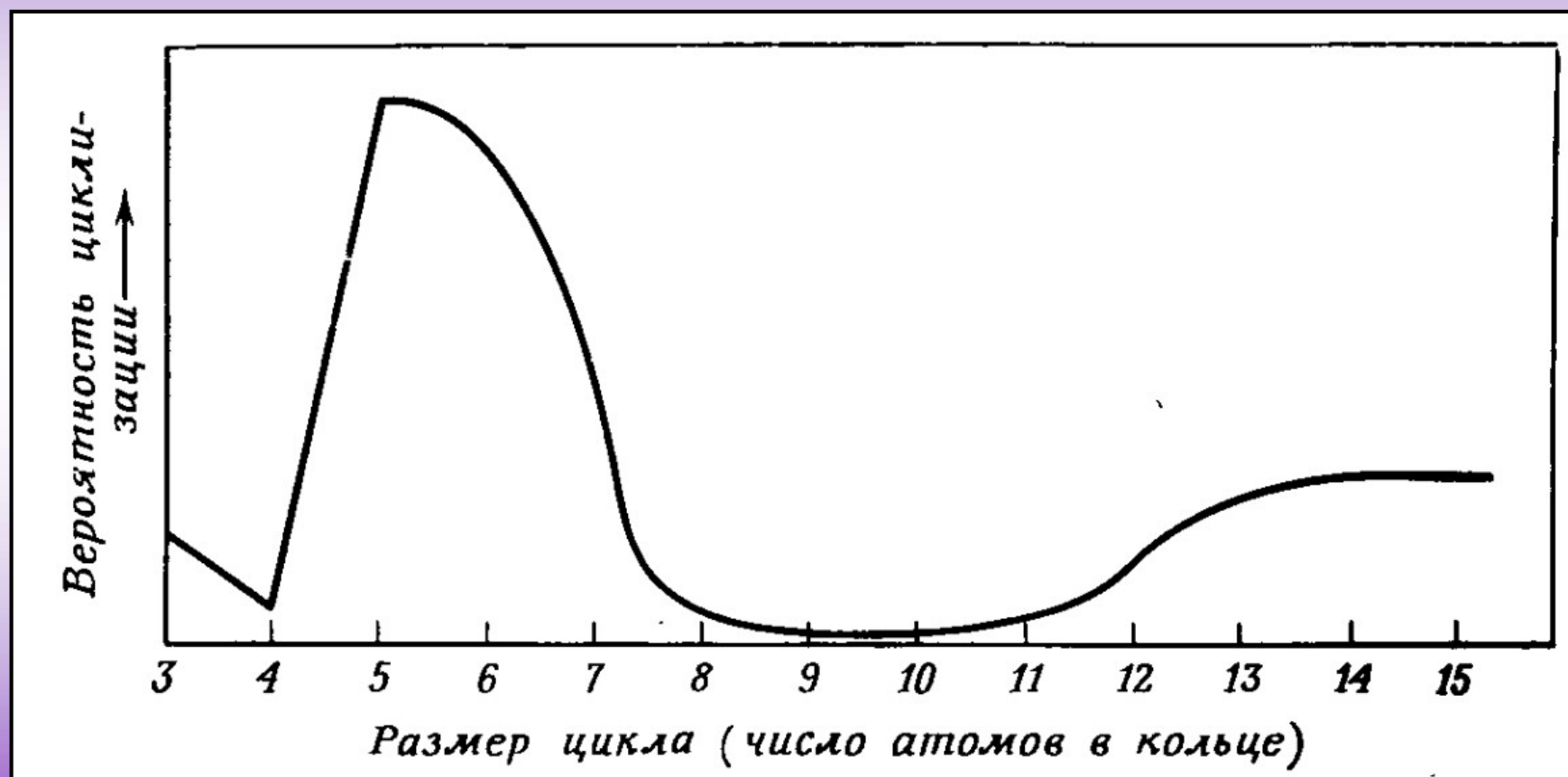
Поликонденсация

Побочные процессы



Поликонденсация

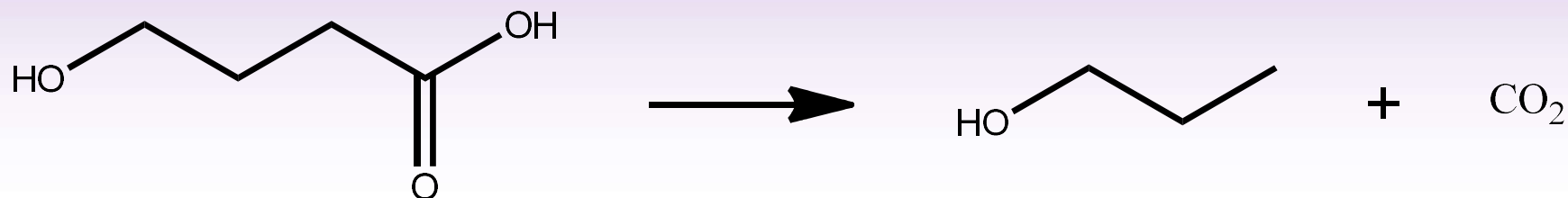
Побочные процессы



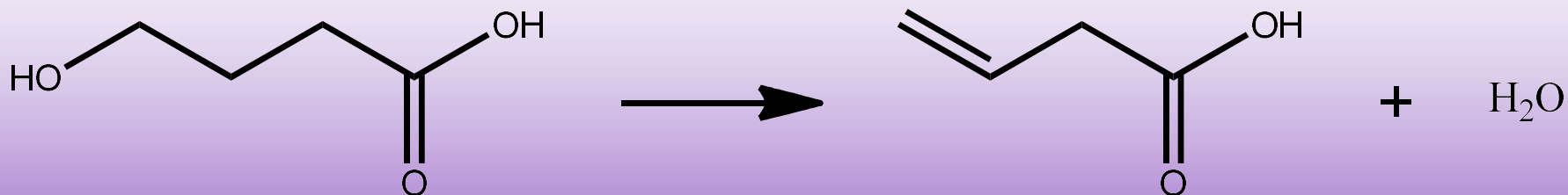
Поликонденсация

Побочные процессы

Декарбоксилирование

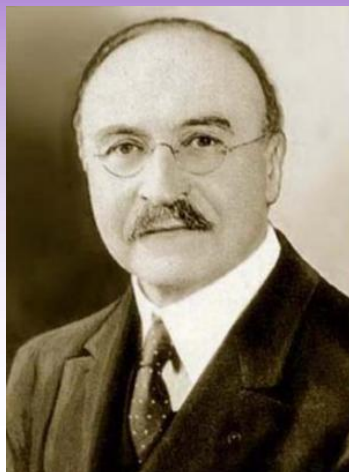


Дегидратация

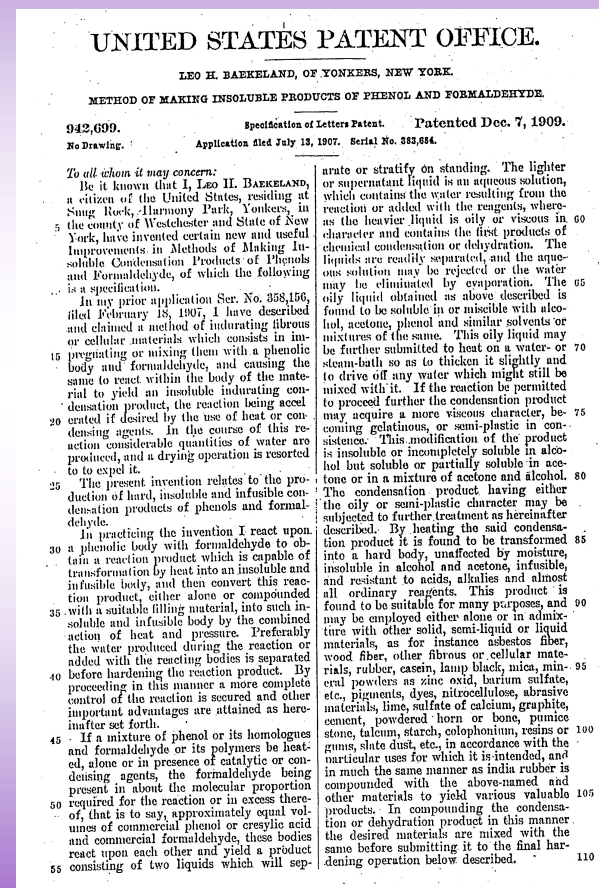


Поликонденсация

Фенопласты

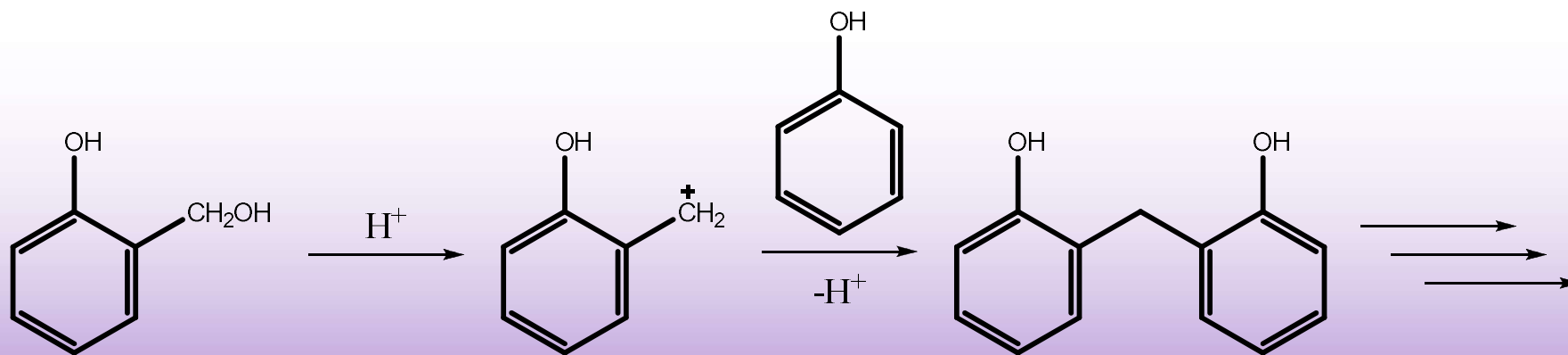
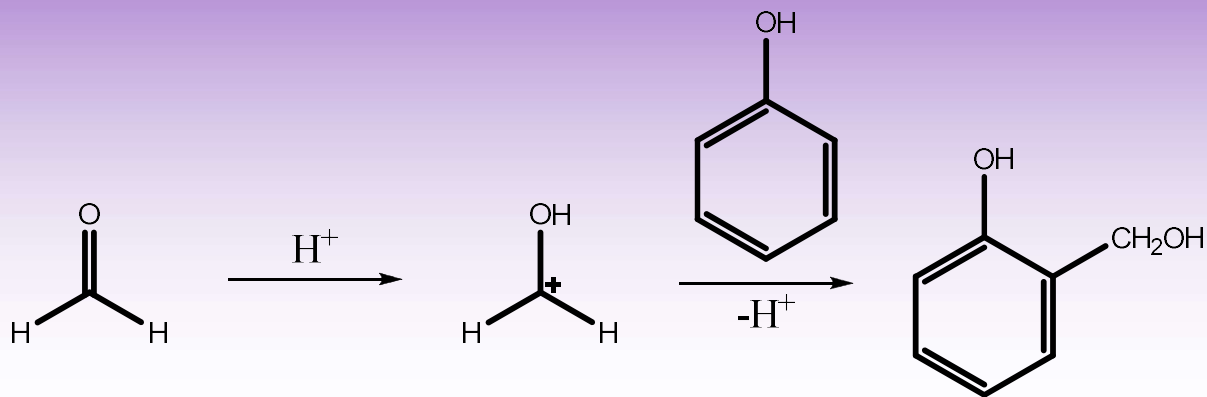


Лео Бакеланд



Поликонденсация

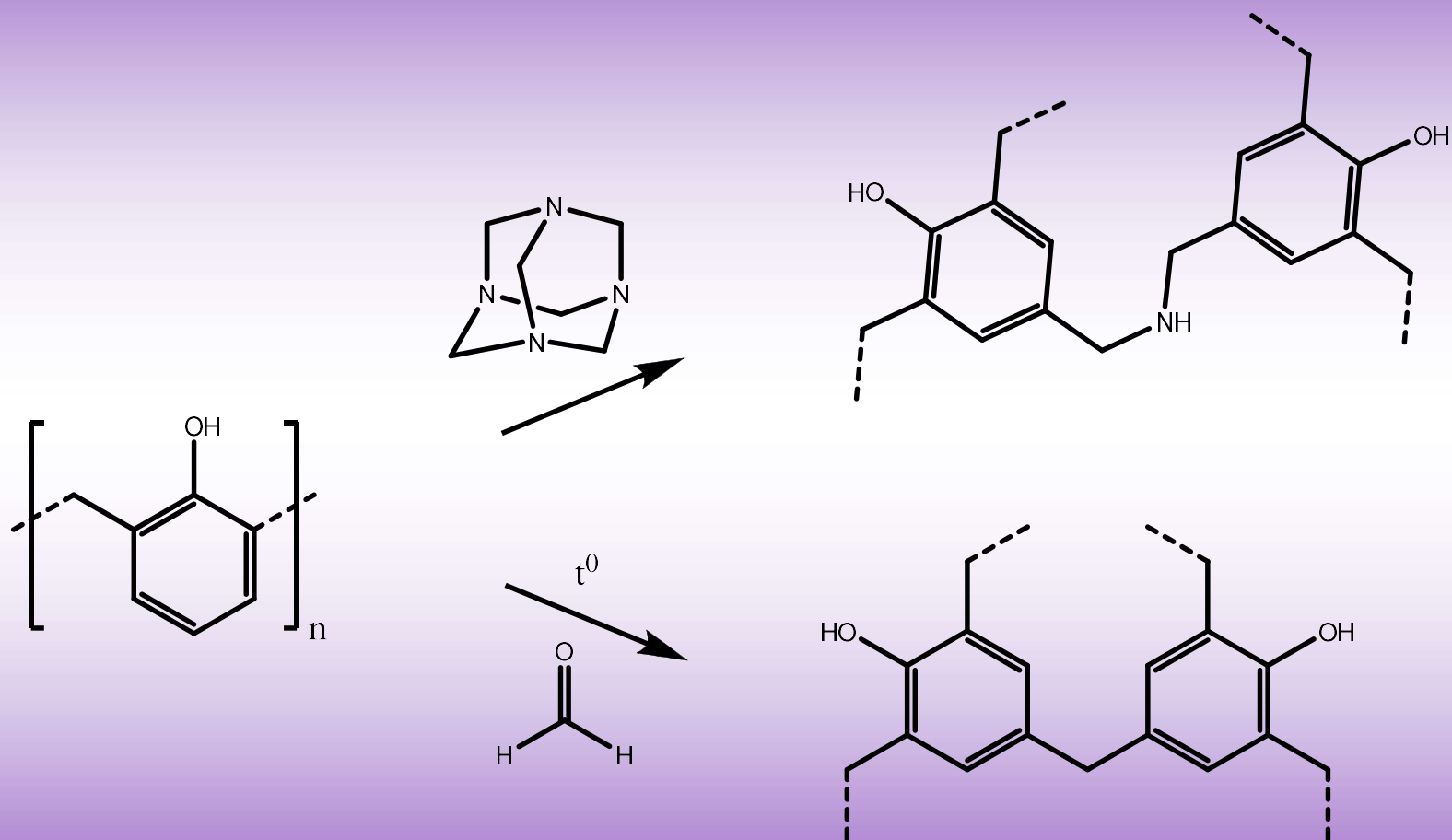
Фенопласты



Олигомеры с $M \sim 10^3$

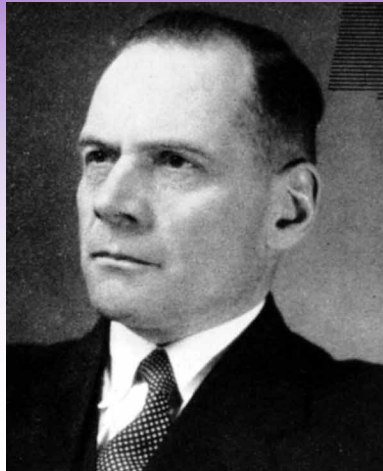
Поликонденсация

Фенопласты



Поликонденсация

Полиамиды



Пол Теодор Шлак



Patented May 6, 1941

2,241,321

UNITED STATES PATENT OFFICE

2,241,321

PREPARATION OF POLYAMIDES

Paul Schlack, Berlin-Treptow, Germany, assignor
to I. G. Farbenindustrie Aktien-Gesellschaft,
Frankfurt-on-the-Main, Germany

No Drawing. Application July 20, 1938, Serial No.
220,266. In Germany June 10, 1938

10 Claims. (Cl. 260—2)

This invention relates to polymerizates of lactams of amino-acids.

By heating aminocarboxylic acids to a high temperature there are obtained, with formation of polyanhydrides, condensation products which, insofar as they are stable against heat, may attain a very high molecular weight. Polymeric substance of this kind have been obtained, for example, from 6-aminohexanoic acid (compare v. Braun, Berichte vol. 40, page 1840, 1897). Although it has already been proposed (U. S. Patents Nos. 2,071,250, 2,071,251 and 2,071,253) that polyanhydrides of this type may be worked up into shaped structures having good properties, particularly threads, the practical utilization of these artificial materials, which closely resemble protein substances from a chemical point of view, has been limited, because the necessary aminocarboxylic acids are not readily available. Although the parent material for one or the other product could be obtained in sufficient quantity and quality, the difficulty of isolating the amino-acids and purifying them from water-soluble secondary products always remains. Moreover the condensation reaction does not always proceed satisfactorily, a fact which frequently becomes evident only in working up the product to a shaped structure.

It is therefore an object of the present invention to provide a process of producing polymerizates of lactams of amino-acids.

A further object is the provision of a process by which polymerizates can be obtained, which are capable of being worked up into fibers, films, foils and the like.

A further object resides in the provision of a process which leads to polymerizates of exceedingly high molecular weight and high softening point.

A still further object of the invention resides in the provision of an essentially simplified process of producing linear superpolymers.

Another object is the provision of a polymerization process in which the necessity of removing volatile reaction products is avoided.

An additional object resides in the provision of suitable polymerization catalysts, which enable the polymerization of the lactams of amino-acids to be carried out on an industrial scale in a comparatively short time of reaction.

A further object resides in the selection of catalysts, which are capable of substantially influencing the properties of the final products.

Other and additional objects will become apparent as the following description proceeds.

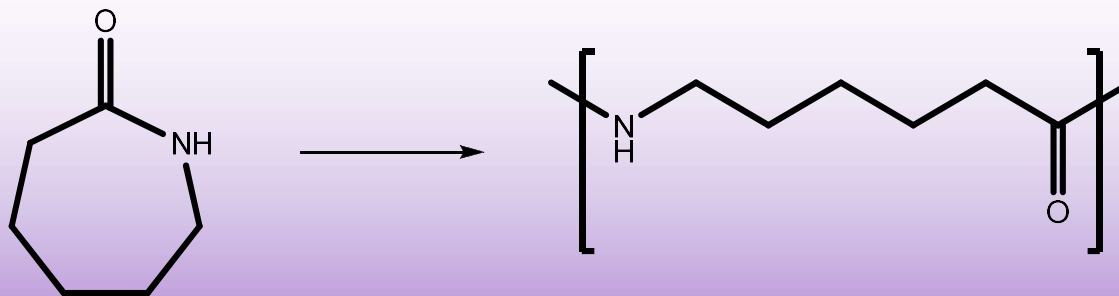
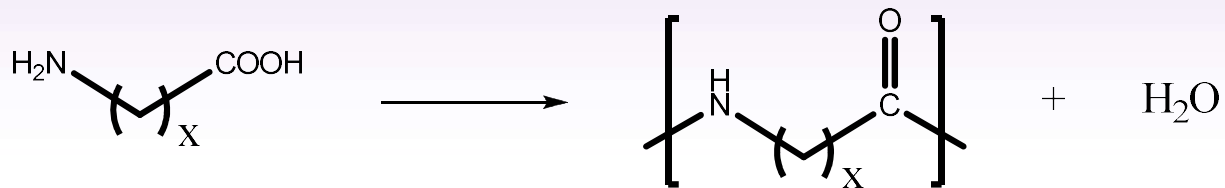
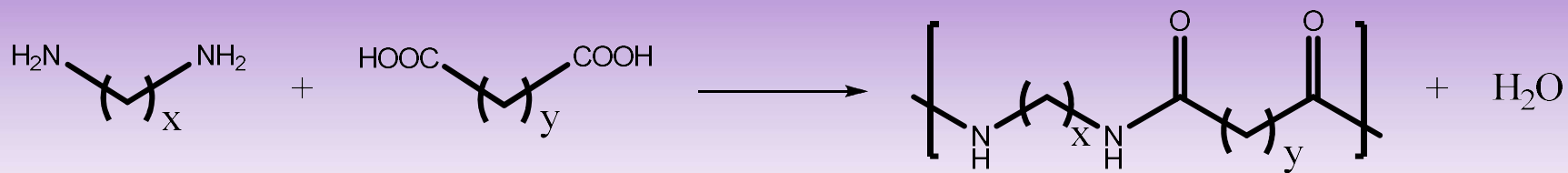
This invention is based on the observation that very valuable polymers of the kind referred to, especially derivatives in which the groups occupying the two ends of the molecule are substituted, are obtainable in a simple manner and with certainty if instead of, as heretofore, condensing the amino-acids at a high temperature with elimination of water, the monomeric anhydrides (lactams) of amino-acids having a chain of at least 5 carbon atoms between a carboxyl and an amino group, and obtainable in various ways, are heated, preferably in the presence of relatively small quantities of suitable promoters of the reaction, until polymerization occurs.

This polymerization is conducted in the melt, if desired in the presence of a solvent such as an amide or a phenol. It generally occurs with remarkable smoothness and leads to highly polymeric products applicable for various purposes. The properties of the final products may be determined beforehand, so that they are of great commercial value.

This result is highly surprising, for it was to be expected that the polymerization, if it would occur at all, would lead, at least at a high temperature, only to substances of comparatively low degree of polymerization. Moreover, it had to be assumed that at a high temperature in the presence of a catalyst, especially in the case of those of pronounced acid character, a splitting up of the chain into fractions of low molecular weight would occur, which would most probably be monomeric cyclic compounds, as had been already observed in the case of polycondensations of hydroxycarboxylic acids or of glycols and aldehydes.

The amino-acid anhydrides (lactams) which come into question for use in the invention are obtainable in various ways, for example by rearrangement of cyclic ketone-oximes according to Wallach or by introduction of the residue —NH— into cyclic ketones with the aid of hydrazoic acid by the method of K. F. Schmidt. They may also be obtained during the reaction from closely related compounds, for example by the decomposition of the hydrogen halide salts of the corresponding lactim ethers. Some are also obtainable by converting the corresponding amino-acids into anhydrides or as by-products in the thermal condensation of such amino-acids or their esters. The cyclic lactams, unlike the free amino-acids may be isolated comparatively easily and brought to a very pure condition by recrystallization or distillation or both. This

Полиамиды

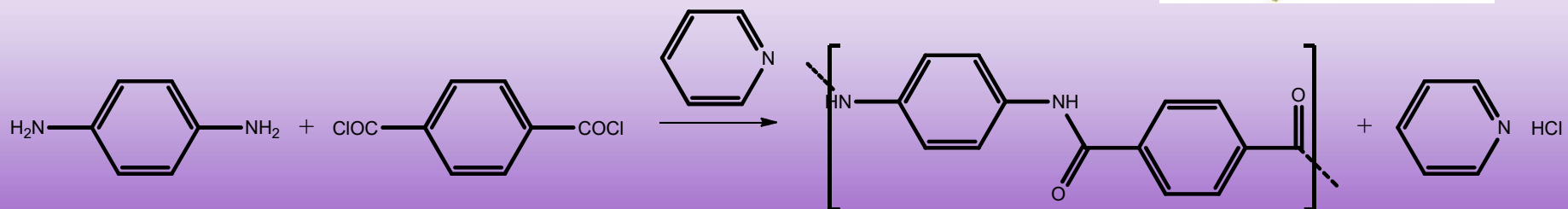


Поликонденсация

Ароматические полиамиды

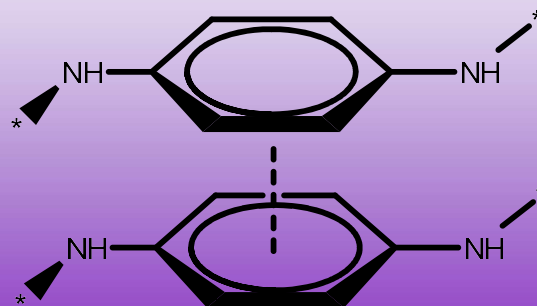
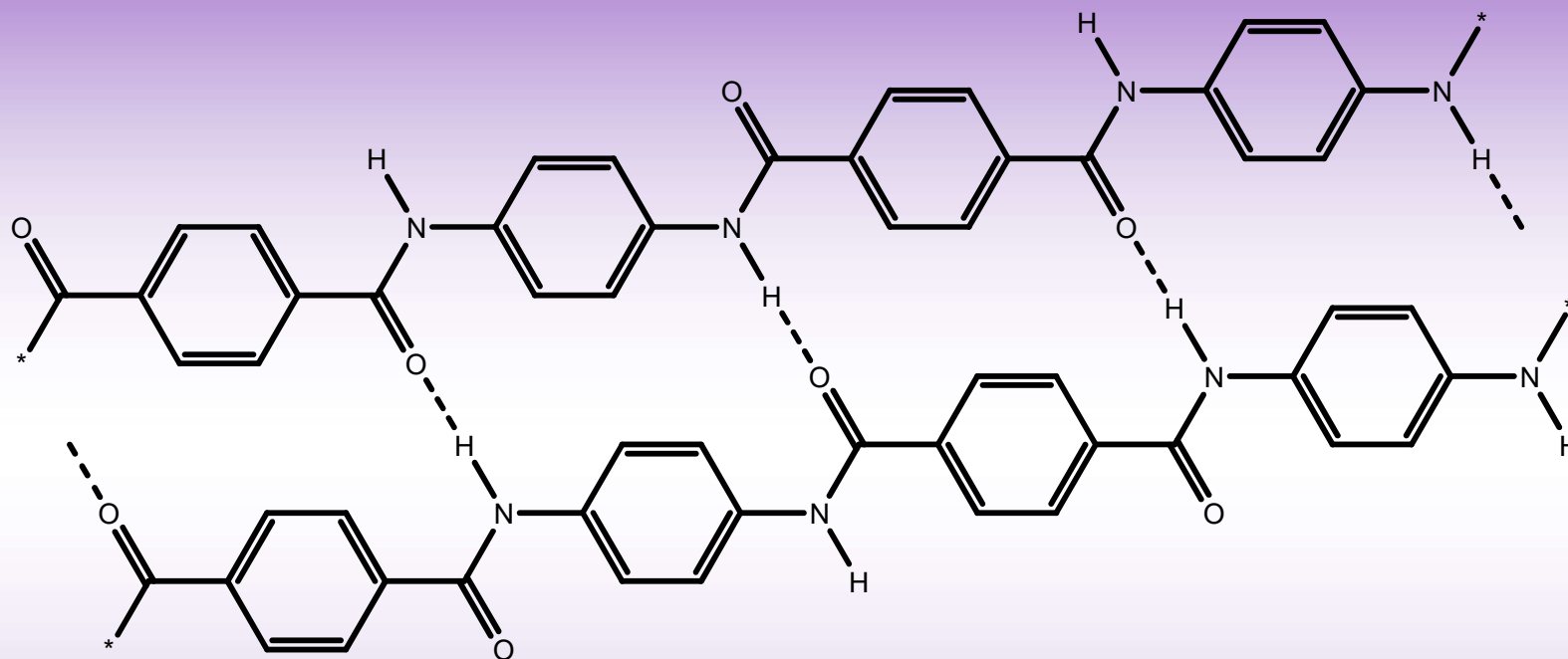


Стефани Кволек



Поликонденсация

Ароматические полиамиды



Поликонденсация

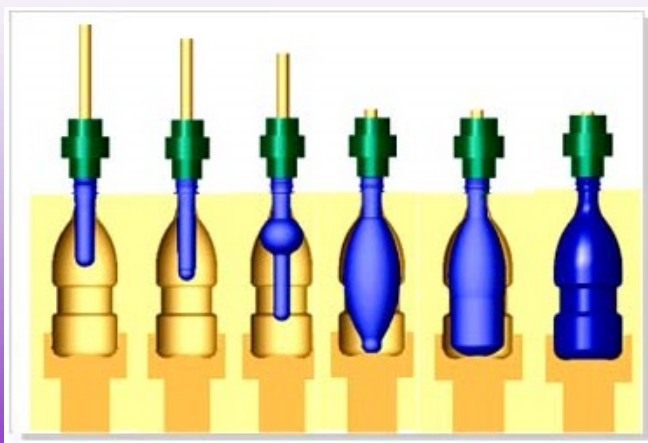
Полиэфиры



Джон Винфилд



Джеймс Диксон



Patented Mar. 22, 1949

2,465,319

UNITED STATES PATENT OFFICE

2,465,319

POLYMERIC LINEAR TEREPHTHALIC ESTERS

John Rex Winfield, Accrington, England, and James Tennant Dickson, East Lothian, Scotland, assignors, by mesne assignments, to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application September 24, 1945, Serial No. 618,398. In Great Britain July 29, 1941

Section 1, Public Law 690, August 8, 1946
Patent expires July 29, 1961

16 Claims. (Cl. 260—75)



This invention relates to synthetic products having valuable and unusual properties and to filaments, fibres and the like produced therefrom. This application is a continuation-in-part of our application Serial Number 476,004, filed February 13, 1943, now abandoned.

Highly polymeric esters of phthalic acid and glycols, for example, ethylene glycol, trimethylene glycol, hexamethylene glycol and decamethylene glycol, are well known, and have been used for instance in the manufacture of paints and varnishes. These esters vary in character, depending on the particular glycol employed in the esterification, but without exception, they are amorphous substances with low softening points and no definite melting points. They cannot be formed into filaments having useful strength or pliability; they are freely soluble in many organic solvents; and they are easily hydrolyzed by acids or alkalis.

Synthetic linear condensation polyesters derived from glycols and dibasic acids and capable of being drawn into pliable, strong fibres showing, by characteristic X-ray patterns, orientation along the fibre axis are also known. However, although the hitherto described linear polyesters are capable of furnishing strong, pliable, highly oriented fibres, they suffer from the defect of low melting point and considerable solubility in a variety of organic solvents, and they are of no utility in the textile field.

This invention has as an object the provision of new and useful linear, highly polymeric esters having valuable properties, including that of being capable of being formed into useful filaments, fibres and the like, and having high melting points and a low degree of solubility in organic solvents. A further object is the provision of new and useful, synthetic filaments and fibres. Other objects will appear hereinafter.

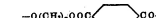
The synthetic products according to the present invention are high-melting, difficultly soluble, usually micro-crystalline, cold-drawing, linear, highly polymerized esters of terephthalic acid and glycols of the series $\text{HO}(\text{CH}_2)_n\text{OH}$, where n is an integer within the range of 2 to 10.

The fibres and the like according to the invention are formed by cold-drawing from the said synthetic products, and show molecular orientation along the fibre axis by characteristic X-ray patterns.

Although synthetic products in accordance with this invention can be obtained from polymethylene glycols having from 2 to 10 methylene groups, i. e. from ethylene glycol, trimethylene

glycol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, heptamethylene glycol, octamethylene glycol, nonamethylene glycol and decamethylene glycol, it is advantageous to use glycols having from 2 to 4 methylene groups, since these give highly polymerized esters with very high melting points, and of these glycols, ethylene glycol, $\text{HO}(\text{CH}_2)_2\text{OH}$, is preferred on the grounds of cost and availability. Mixtures of the glycols may be used if desired.

The synthetic products according to the invention are therefore highly polymeric polymethylene terephthalates; they are linear in structure with recurring structural units of the general formula



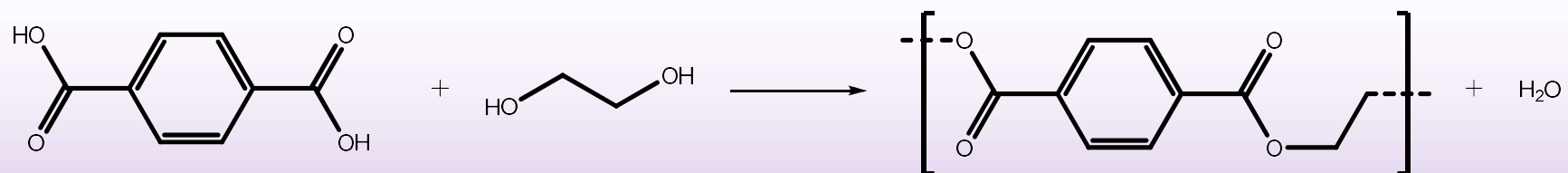
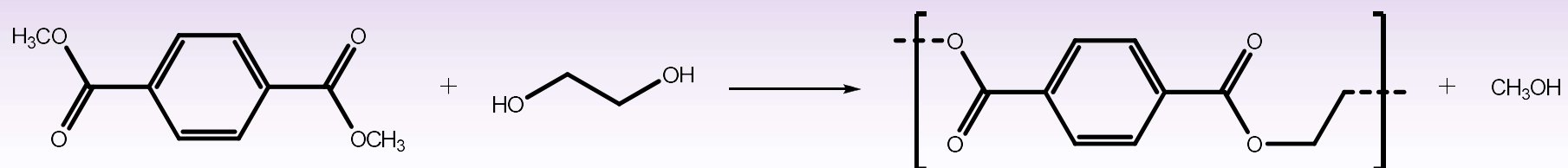
where n is an integer greater than 1 but not exceeding 10.

The highly polymeric products according to the invention can be made by heating glycols of the series $\text{HO}(\text{CH}_2)_n\text{OH}$, where n is an integer within the range of 2 to 10, with terephthalic acid or with esters of other terephthalic acid bodies which are capable of reacting with acid glycols to form glycol esters, the reaction products being heated at temperatures above their melting points until highly polymeric esters having cold drawing properties are obtained.

The highly polymeric polymethylene terephthalates of the invention may be made by heating a mixture of terephthalic acid and a glycol of the series $\text{HO}(\text{CH}_2)_n\text{OH}$, where n is an integer within the range of 2 to 10, in which at least about one molecular proportion of the glycol is present relative to the terephthalic acid. Preferably higher proportions of the glycol relative to the acid are used, for instance four or five molecular proportions of the glycol per molecular proportion of the terephthalic acid, since by using such proportions the initial esterification is caused to take place much more readily. During the heating the temperature advantageously approaches the boiling point of the glycol. Known esterifying catalysts, such as hydrogen chloride, p-toluene sulphonic acid or camphor sulphonic acid, may be added to speed up this part of the reaction, but the esterification also proceeds satisfactorily in the absence of such catalysts. Once all of the acid has reacted with the glycol, the temperature is increased, the excess of the glycol present is removed from the reaction mixture by distillation, usually under reduced pressure, and the residue is further heated above its

Поликонденсация

Полиэфиры



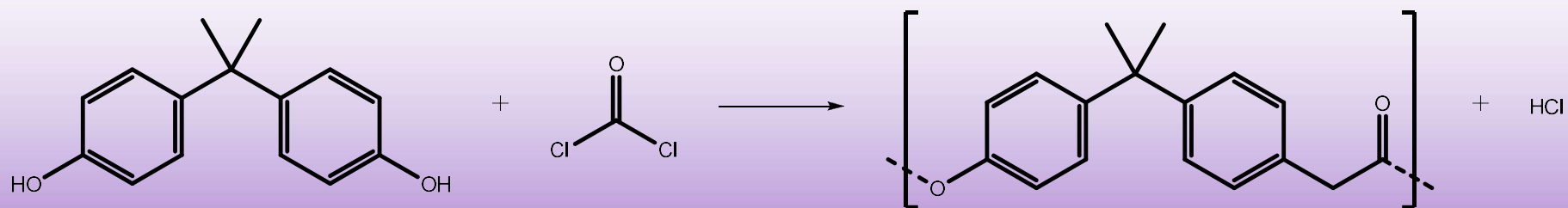
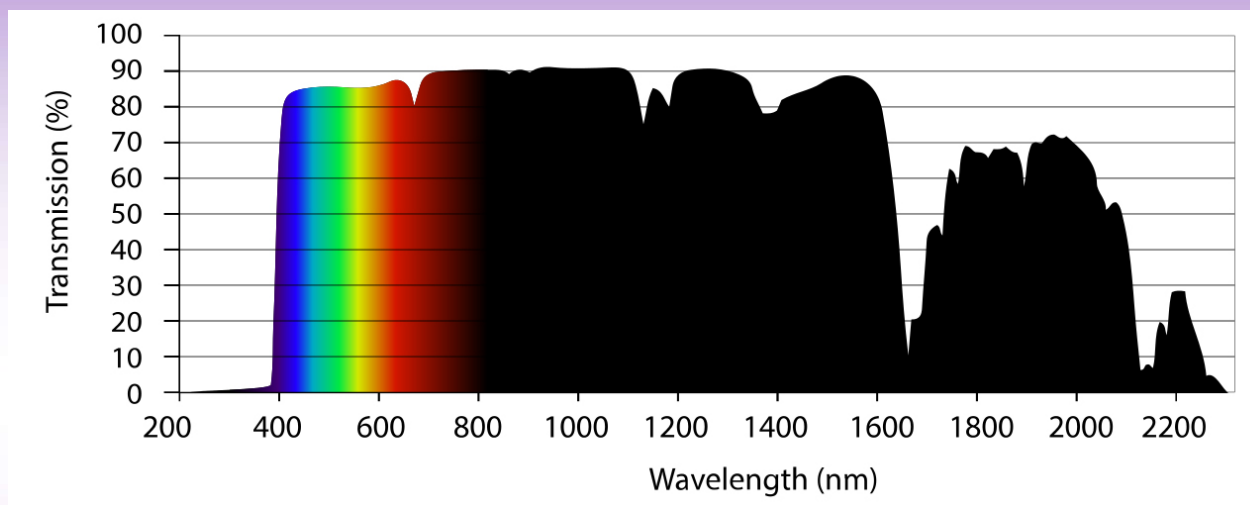
Поликонденсация

Поликарбонаты



Поликонденсация

Поликарбонаты

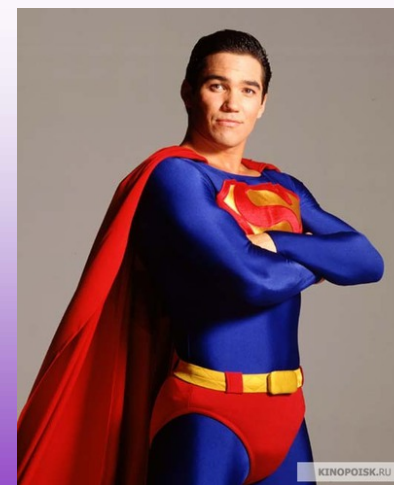
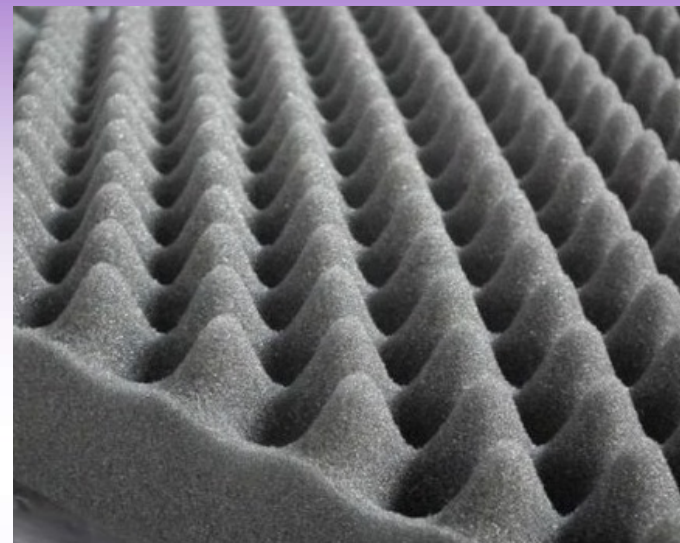


Поликонденсация

Полиуретаны

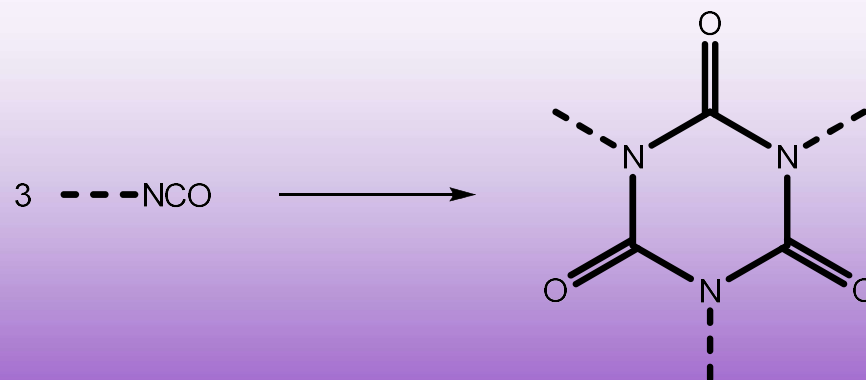
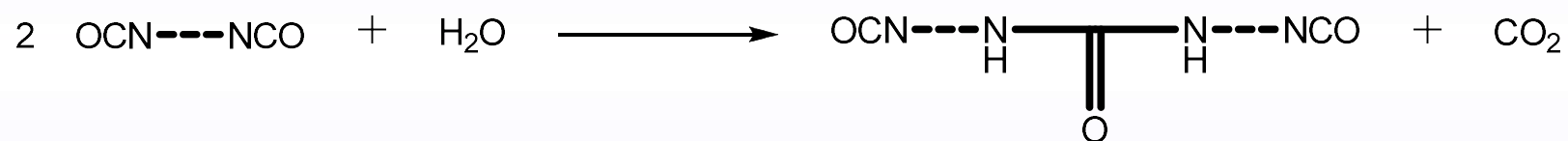
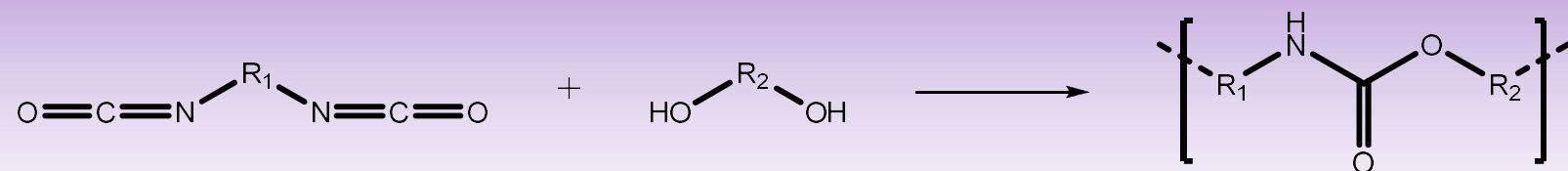


Отто Байер



Поликонденсация

Полиуретаны

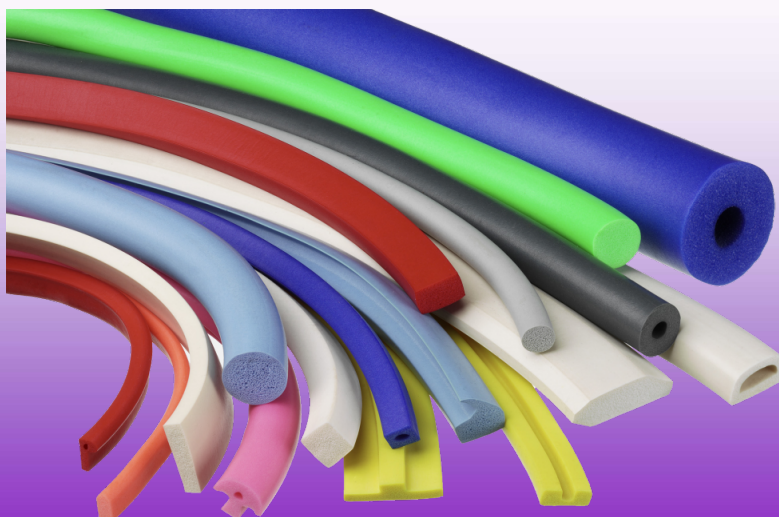


Поликонденсация

Полисилоксаны

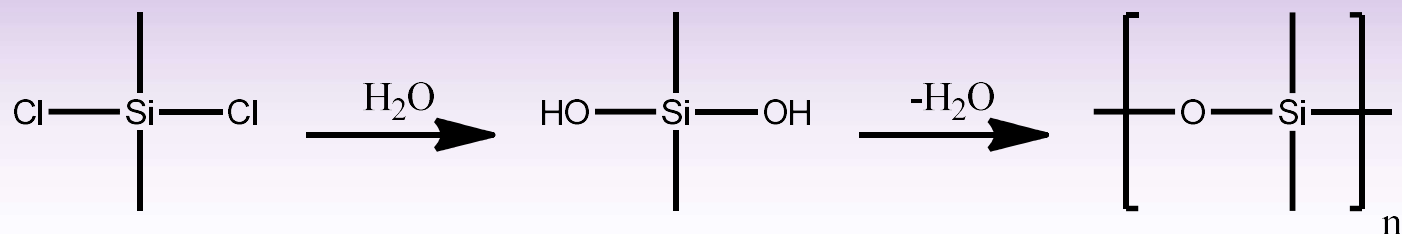


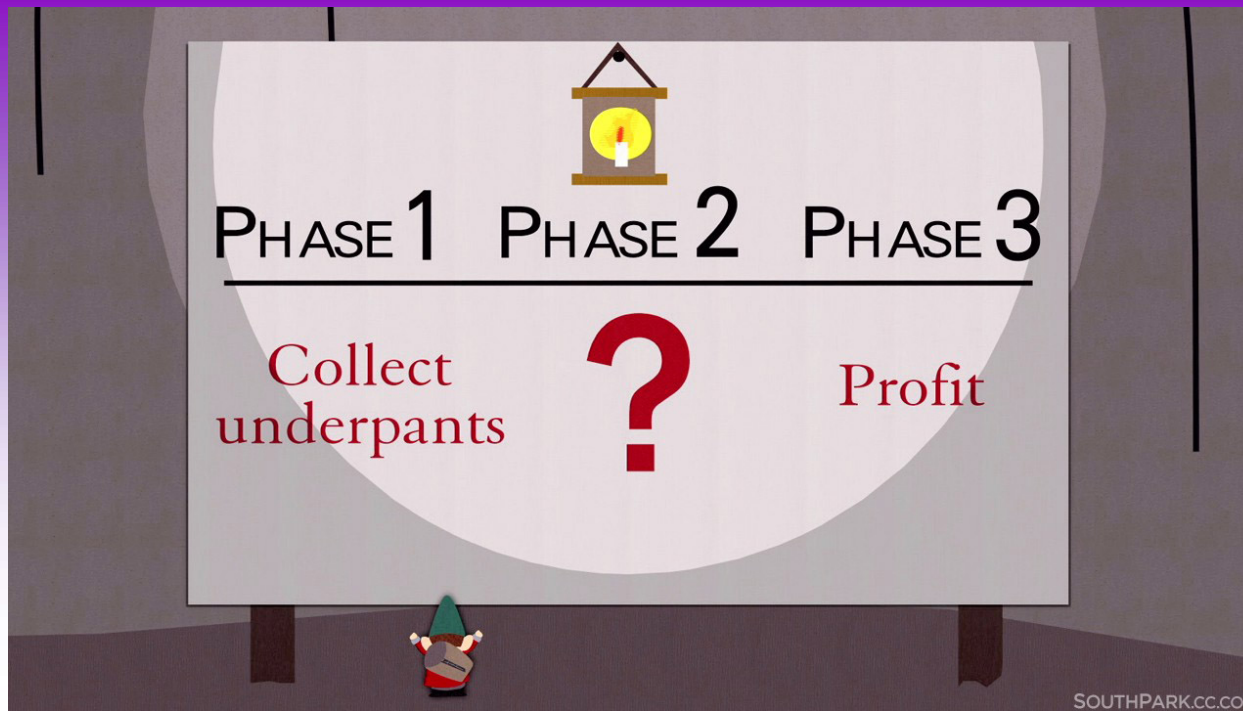
Фредерик Киппинг



Поликонденсация

Полисилоксаны





Продолжение следует...

- 1) Полимеризация с раскрытием цикла
- 2) Сополимеризация
- 3) Полимераналогичные превращения
- 4) Способы проведения полимеризации и поликонденсации
- 5) ????????
- 6) PROFIT Зачет