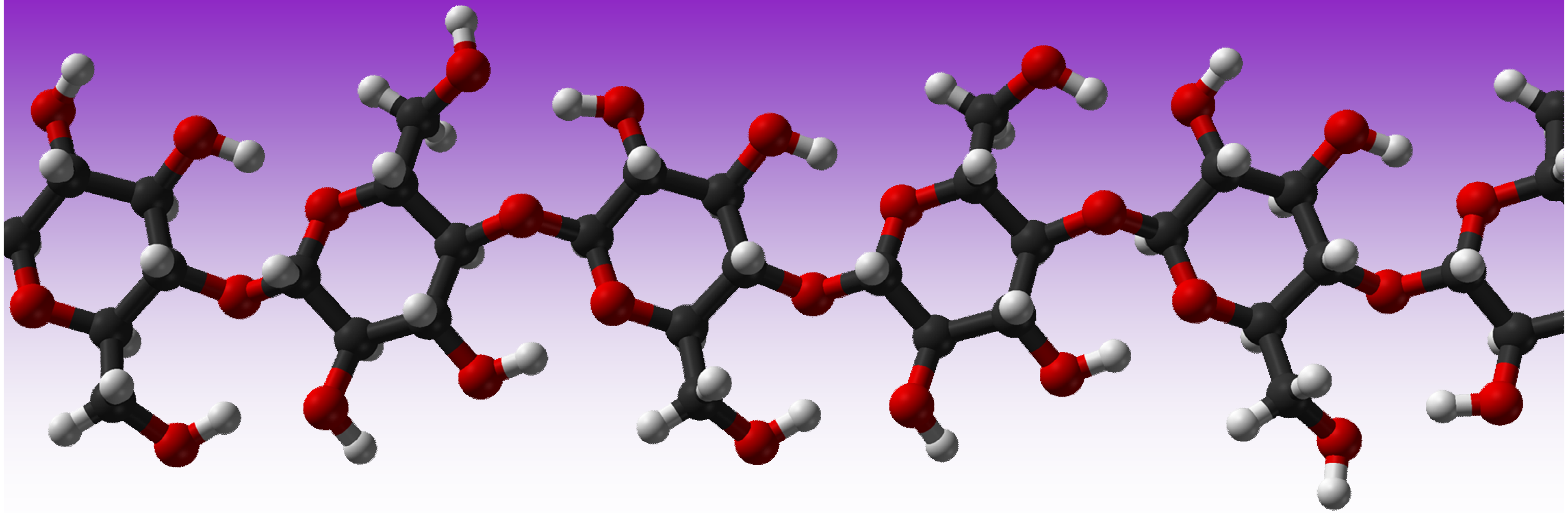


Тема: Поликонденсация

План лекции

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

Поликонденсация

Определение и классификация

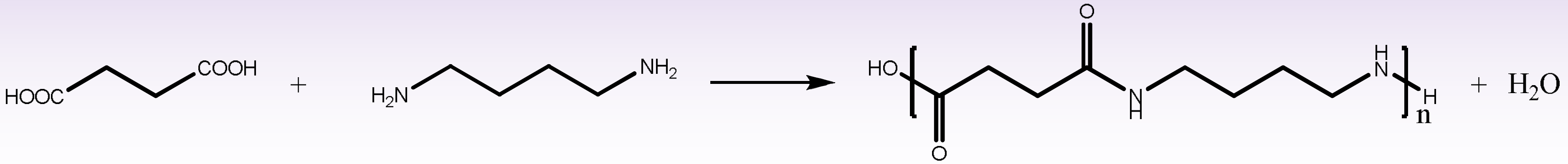
Поликонденсация – разновидность реакции синтеза высокомолекулярных соединений из полифункциональных мономеров, которая обычно сопровождается выделением побочных низкомолекулярных продуктов таких как вода, спирт, хлороводород и т. п.

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

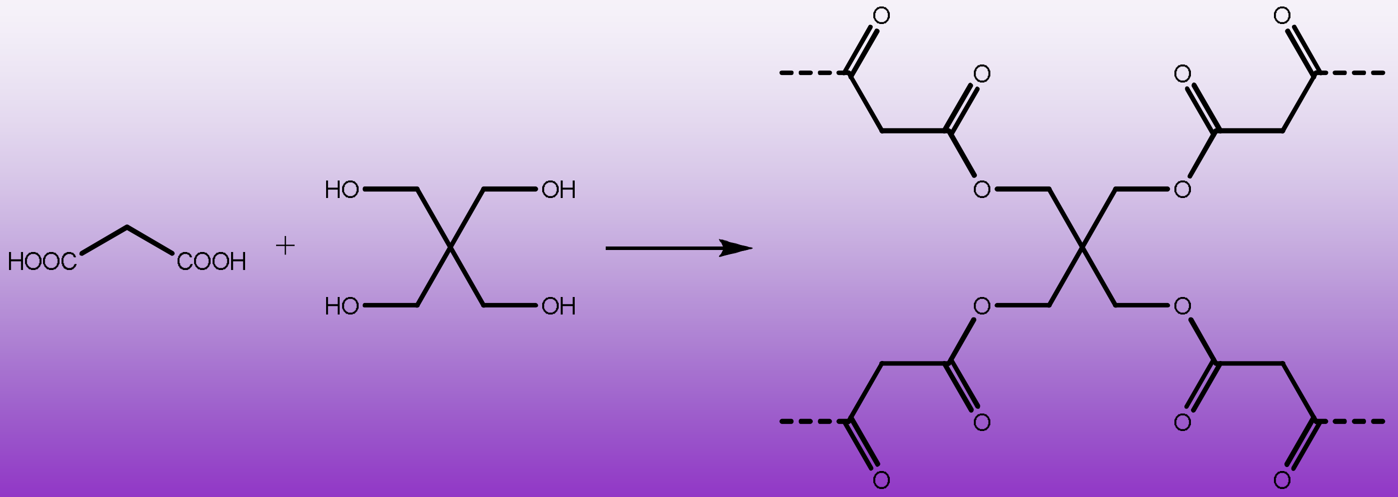
Поликонденсация

Определение и классификация

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



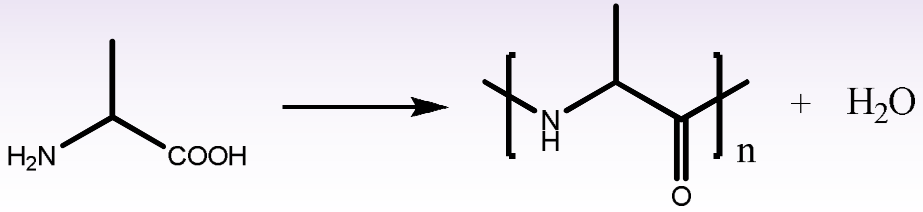
- Если в реакции поликонденсации участвует хоть один мономер, содержащий три и более функциональных групп, такая поликонденсация называется трехмерной и приводит к образованию сетчатых полимеров



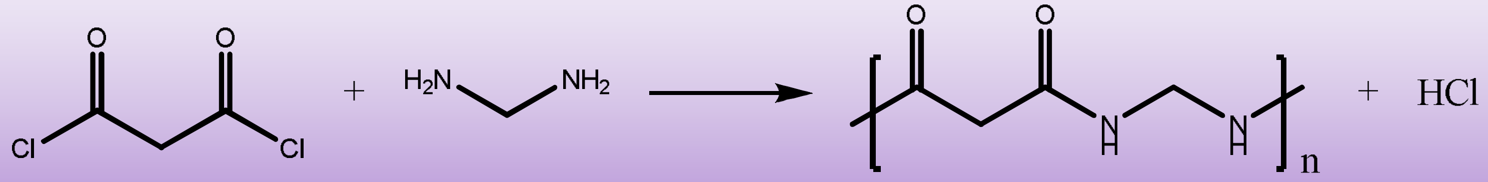
Поликонденсация

Определение и классификация

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



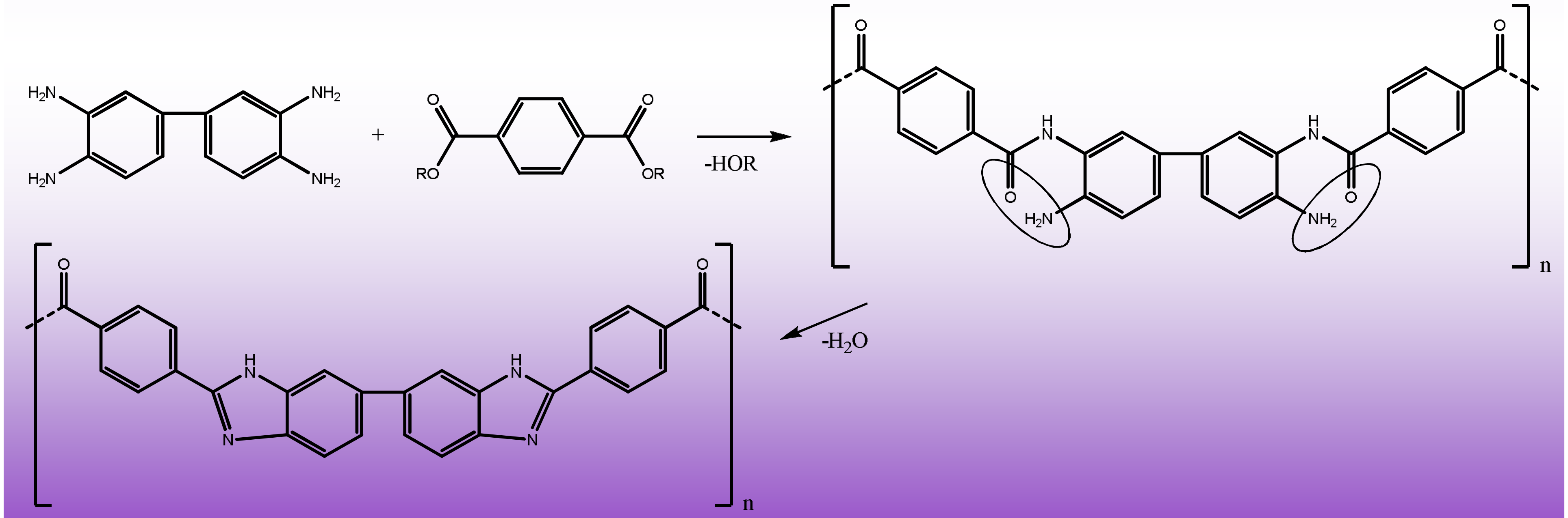
- Поликонденсация, которая идет с участием двух и более мономеров называется гетерополиконденсация (сополиконденсация)



Поликонденсация

Определение и классификация

Отдельным видом реакций поликонденсации является <u>полициклоконденсация</u> – 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:

$$R_1\text{—}COOH + HO\text{—}R_2 \xrightleftharpoons{H^+} R_1\text{—}COOR_2 + H_2O$$

- Неравновесная (необратимая) поликонденсация:

$$R_1\text{—}COCl + NH_2\text{—}R_2 \longrightarrow R_1\text{—}CONHR_2 + HCl$$

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.

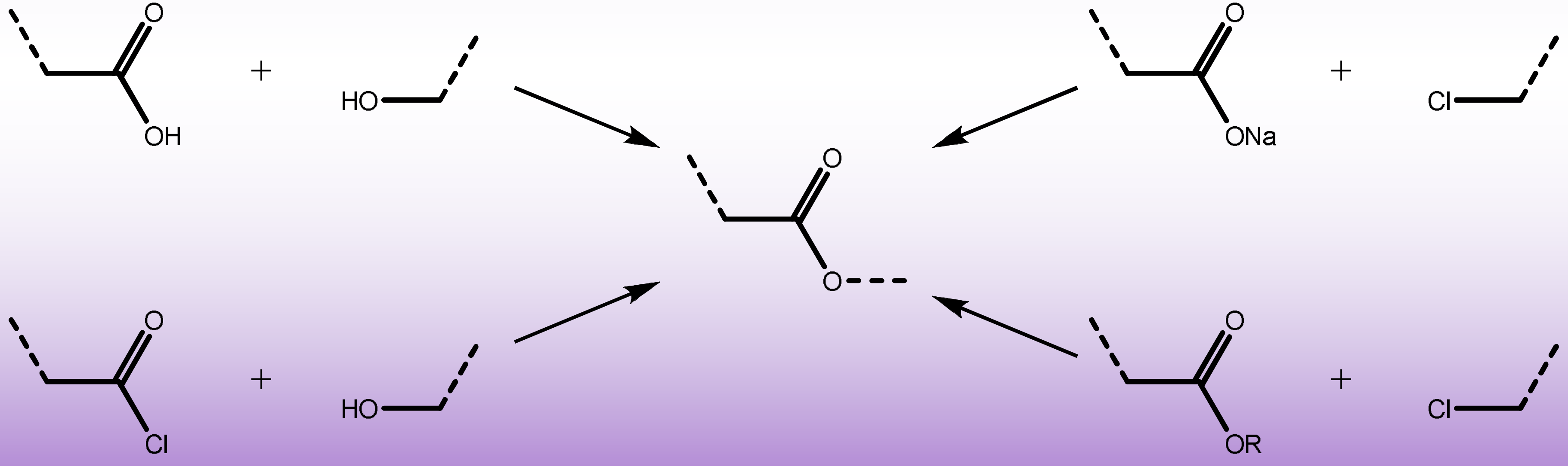
- Макромолекулы целевой молекулярной массы начинают образовываться лишь на завершающих стадиях реакции.

- 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

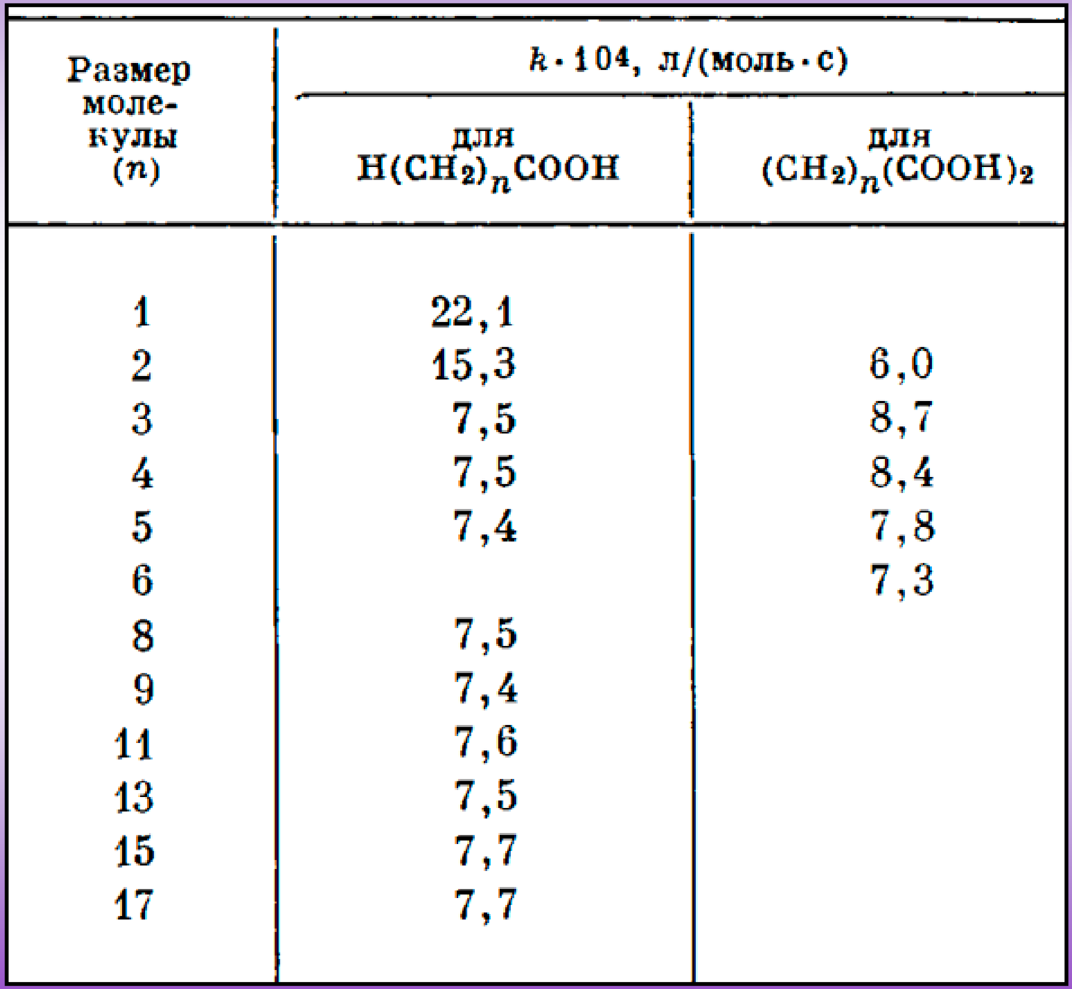
- Реакционная способность функциональных групп бифункционального мономера одинакова.

- 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

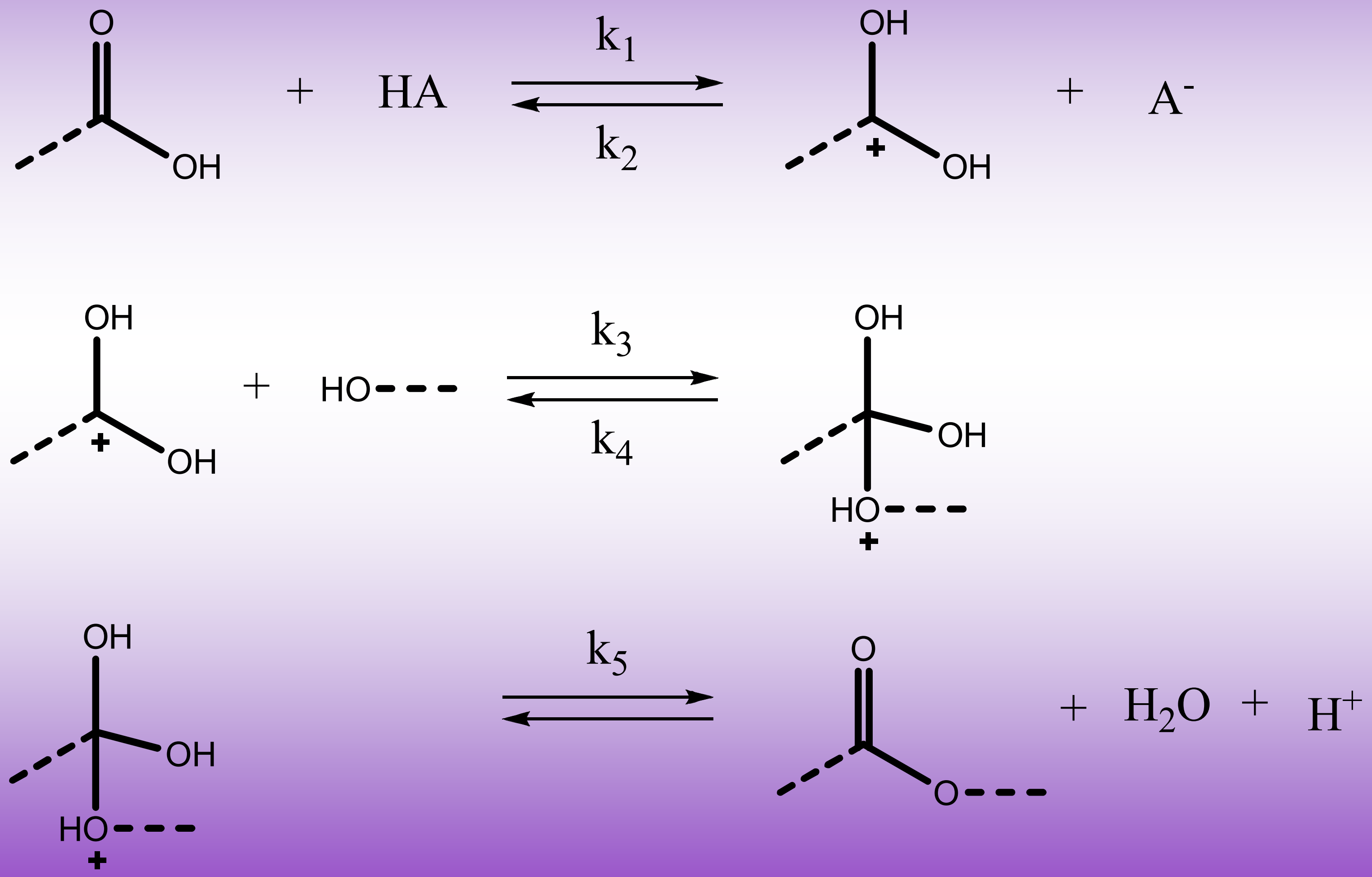
Кинетика



Размер молекулы (n)	$k \cdot 10^4$, л/(моль·с)	
	для $H(CH_2)_nCOOH$	для $(CH_2)_n(COOH)_2$
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

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

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

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

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

Поликонденсация

Кинетика

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

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

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

$$\boxed{V_p = k_p [\mathrm{OH}][\mathrm{COOH}]}$$

Поликонденсация

Кинетика

$$p = \frac{[\mathrm{M}]_0 - [\mathrm{M}]_t}{[\mathrm{M}]_0}$$

p – степень превращения

$$\bar{X}_n = \frac{[\mathrm{M}]_0}{[\mathrm{M}]_t} = \frac{1}{1-p}$$

уравнение Карозерса

$$V_p = k_p[\mathrm{OH}][\mathrm{COOH}] \qquad [\mathrm{OH}] = [\mathrm{COOH}] = [\mathrm{M}]$$

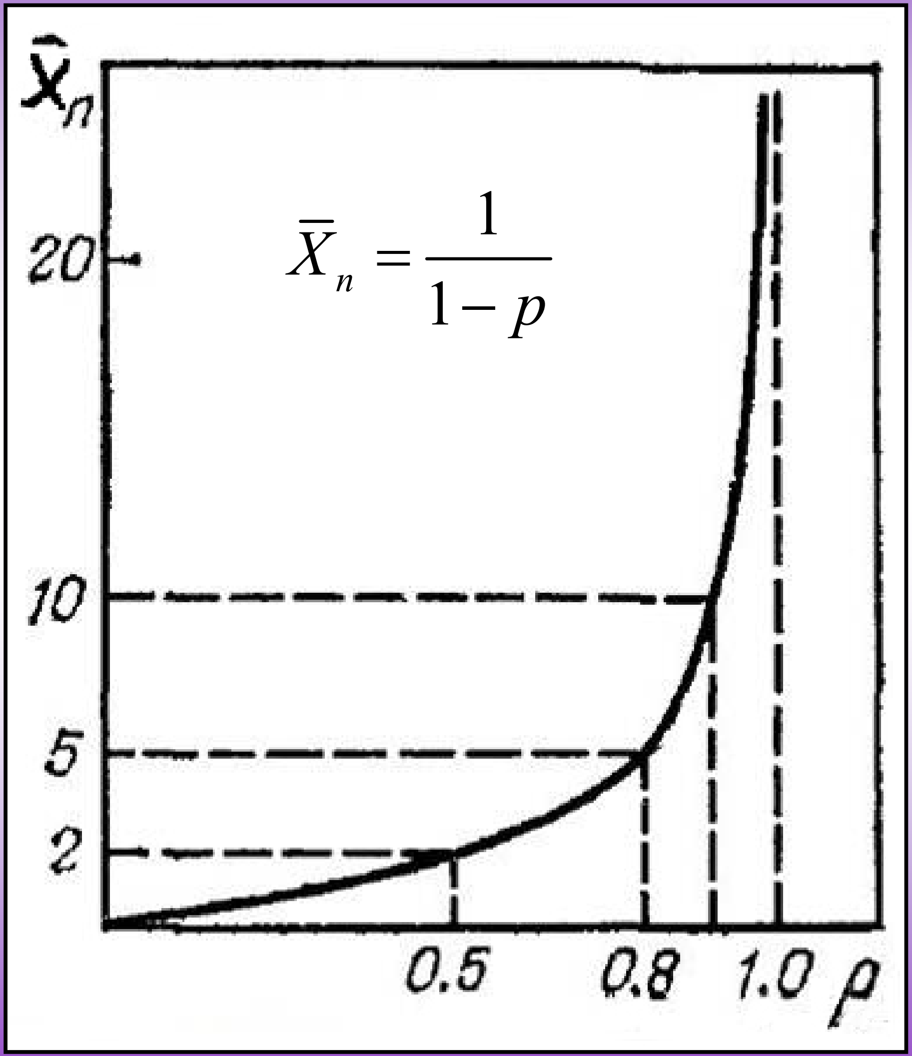
$$-\frac{d[\mathrm{M}]}{dt} = k_p[\mathrm{M}]^2$$

$$\frac{1}{[\mathrm{M}]_t} - \frac{1}{[\mathrm{M}]_0} = k_p t \qquad \frac{[\mathrm{M}]_0}{[\mathrm{M}]_t} - 1 = k_p t[\mathrm{M}]_0$$

$$\boxed{\bar{X}_n = 1 + k_p t[\mathrm{M}]_0}$$

Поликонденсация

Кинетика

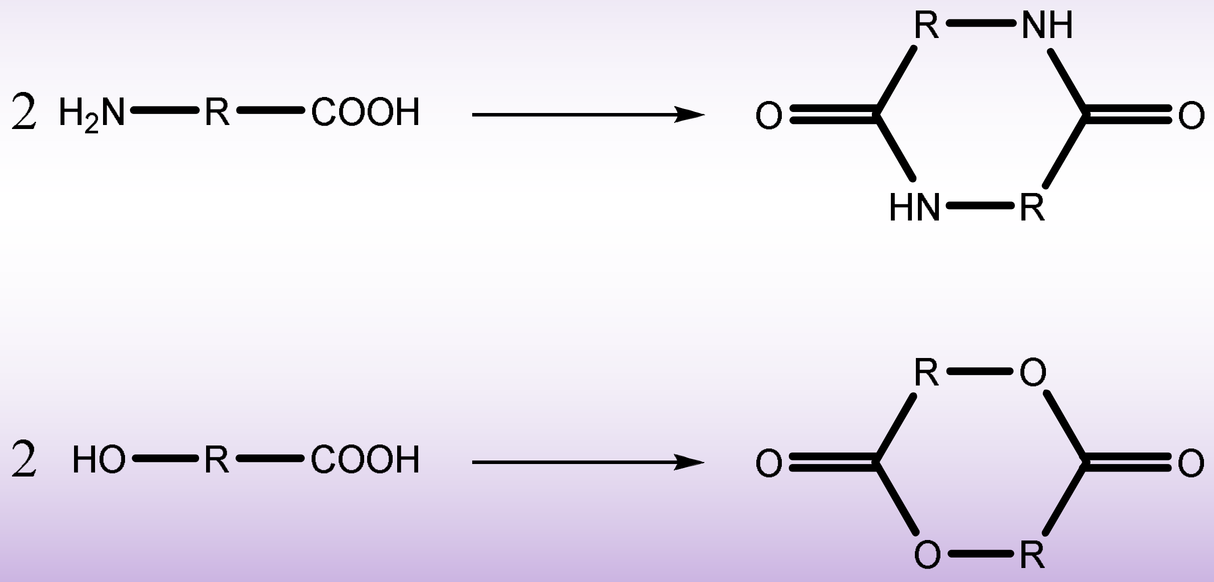


$$\bar{X}_n = \frac{1}{1-p}$$

Поликонденсация

Побочные реакции

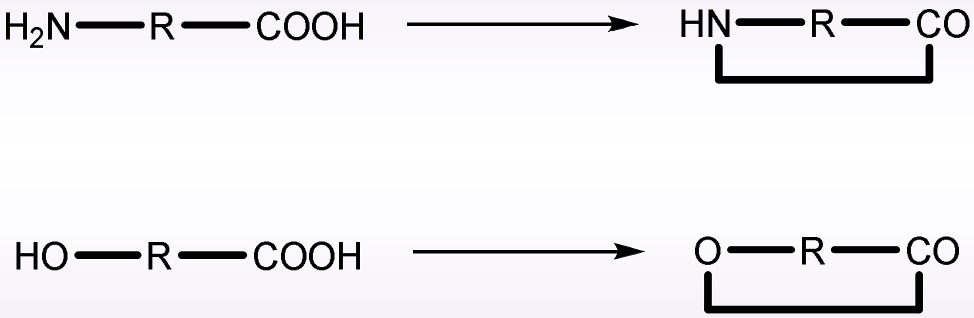
Межмолекулярная циклизация



Поликонденсация

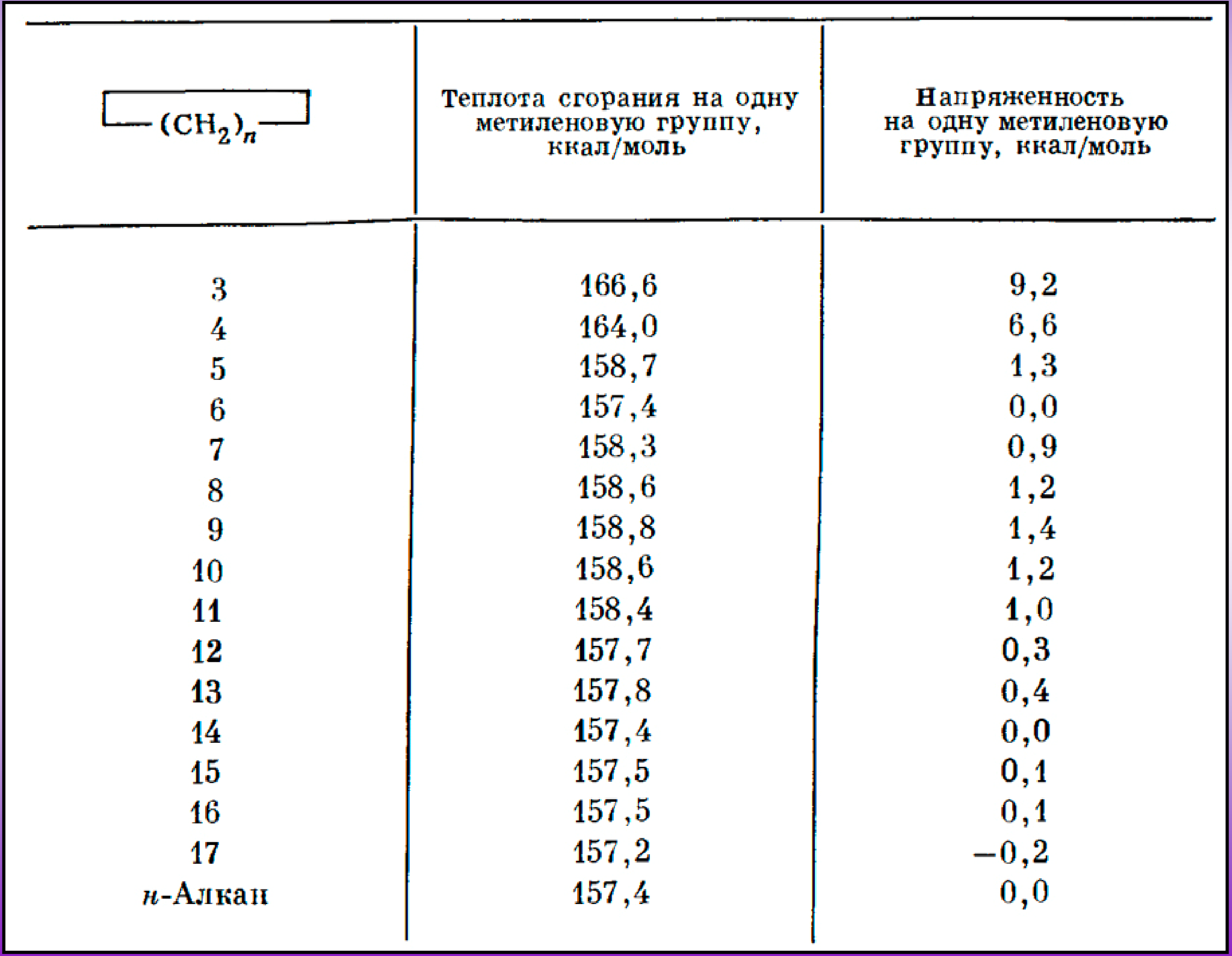
Побочные реакции

Внутримолекулярная циклизация



Поликонденсация

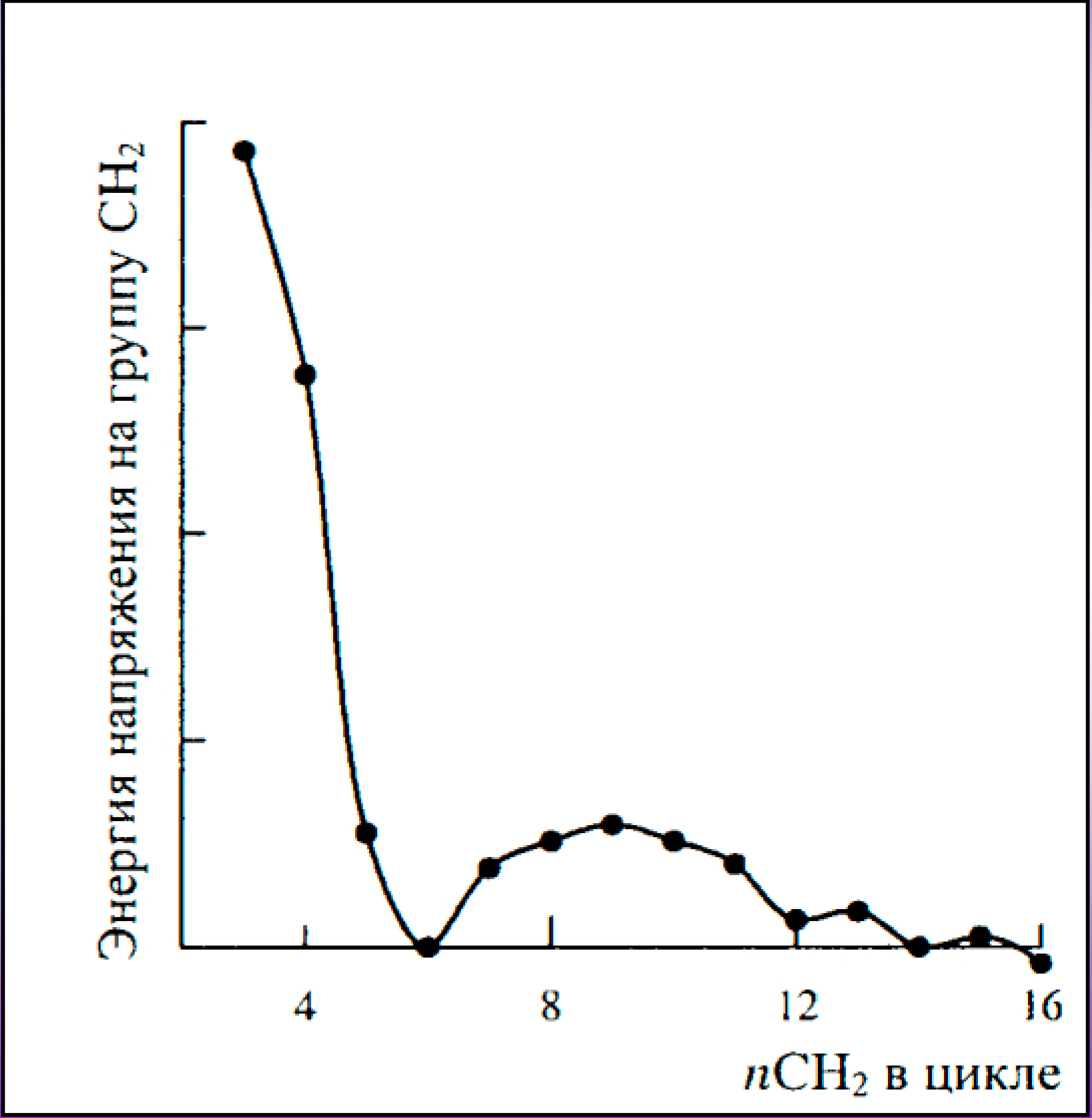
Побочные реакции



$(CH_2)_n$	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
н-Алкан	157,4	0,0

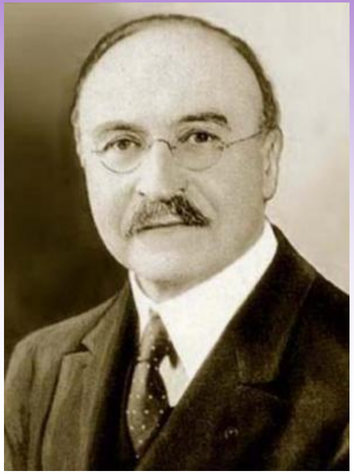
Поликонденсация

Побочные реакции

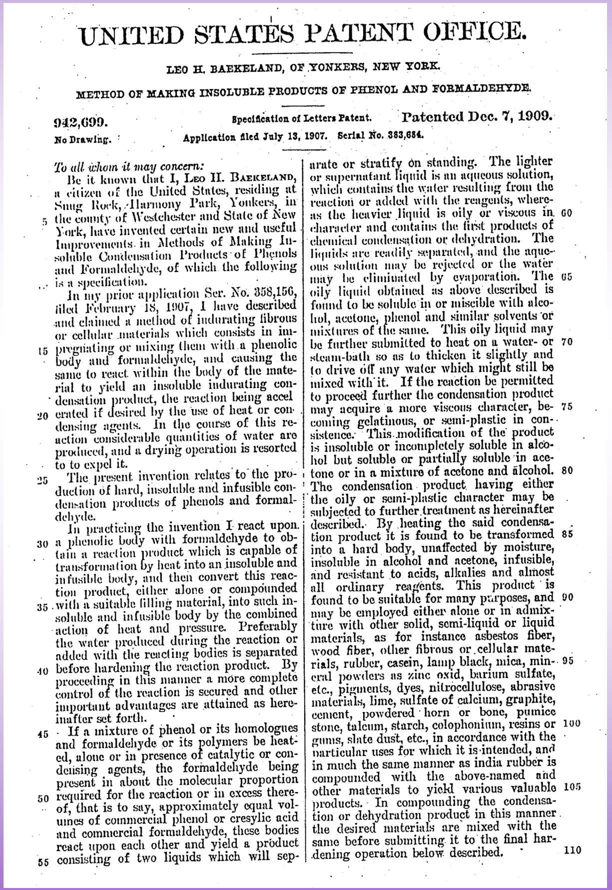


Поликонденсация

Фенопласты



Лео Бакеланд



UNITED STATES PATENT OFFICE.

LEO H. BAEKELAND, OF YONKERS, NEW YORK.

METHOD OF MAKING INSOLUBLE PRODUCTS OF PHENOL AND FORMALDEHYDE.

942,699. Specification of Letters Patent. Patented Dec. 7, 1909.

No Drawing. Application filed July 13, 1907. Serial No. 383,684.

To all whom it may concern:

Be it known that I, Leo H. Baekeland, a citizen of the United States, residing at Snug Rock, Harmony Park, Yonkers, in the county of Westchester and State of New York, have invented certain new and useful Improvements in Methods of Making Insoluble Condensation Products of Phenols and Formaldehyde, of which the following is a specification.

In my prior application Ser. No. 358,156, filed February 18, 1907, I have described and claimed a method of indurating fibrous or cellular materials which consists in impregnating or mixing them with a phenolic body and formaldehyde, and causing the same to react within the body of the material to yield an insoluble indurating condensation product, the reaction being accelerated if desired by the use of heat or condensing agents. In the course of this reaction considerable quantities of water are produced, and a drying operation is resorted to to expel it.

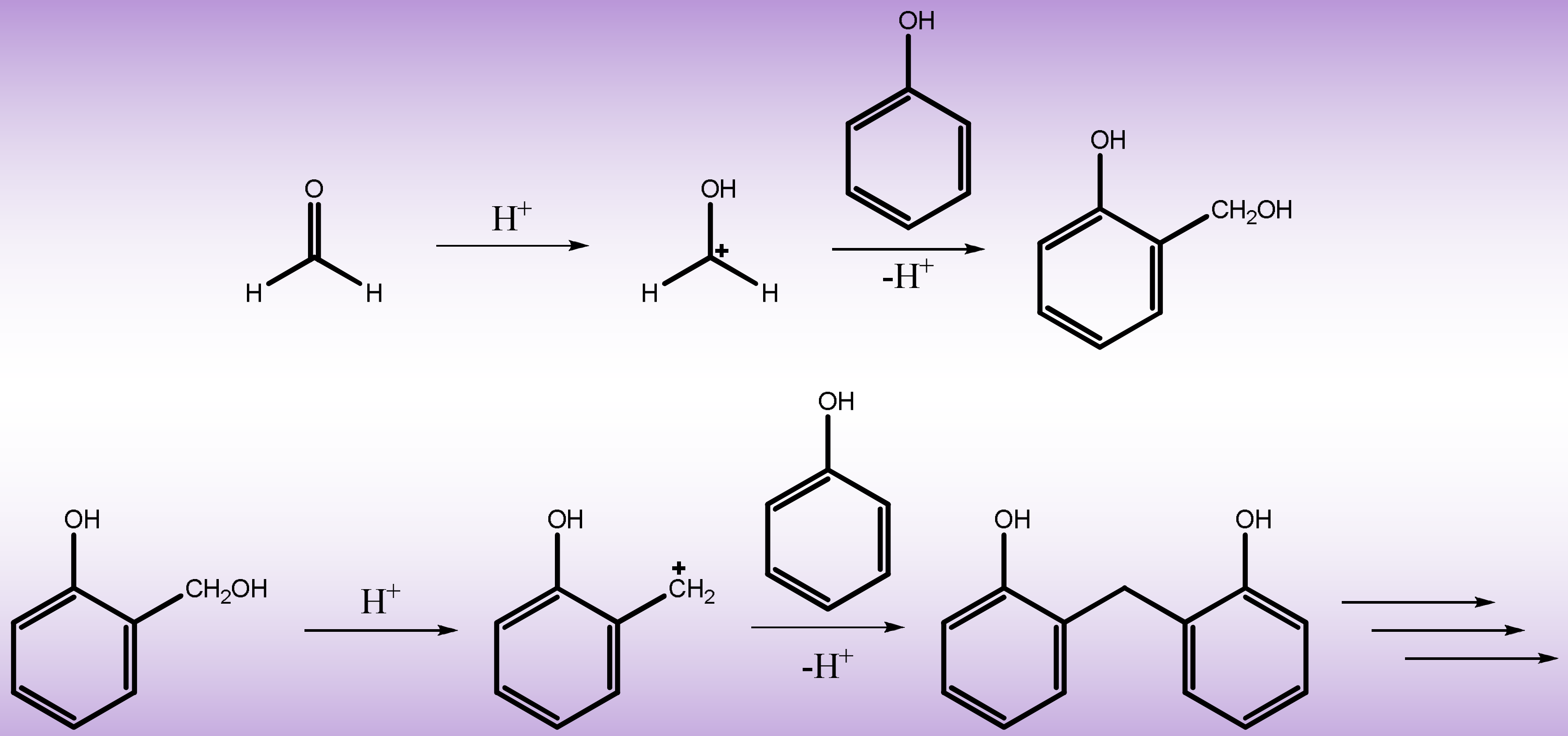
The present invention relates to the production of hard, insoluble and infusible condensation products of phenols and formaldehyde.

In practicing the invention I react upon a phenolic body with formaldehyde to obtain a reaction product which is capable of transformation by heat into an insoluble and infusible body, and then convert this reaction product, either alone or compounded with a suitable filling material, into such insoluble and infusible body by the combined action of heat and pressure. Preferably the water produced during the reaction or added with the reacting bodies is separated before hardening the reaction product. By proceeding in this manner a more complete control of the reaction is secured and other important advantages are attained as hereinafter set forth.

If a mixture of phenol or its homologues and formaldehyde or its polymers be heated, alone or in presence of catalytic or condensing agents, the formaldehyde being present in about the molecular proportion required for the reaction or in excess thereof, that is to say, approximately equal volumes of commercial phenol or cresylic acid and commercial formaldehyde, these bodies react upon each other and yield a product consisting of two liquids which will separate or stratify on standing. The lighter or supernatant liquid is an aqueous solution, which contains the water resulting from the reaction or added with the reagents, whereas the heavier liquid is oily or viscous in character and contains the first products of chemical condensation or dehydration. The liquids are readily separated, and the aqueous solution may be rejected or the water may be eliminated by evaporation. The oily liquid obtained as above described is found to be soluble in or miscible with alcohol, acetone, phenol and similar solvents or mixtures of the same. This oily liquid may be further submitted to heat on a water- or steam-bath so as to thicken it slightly and to drive off any water which might still be mixed with it. If the reaction be permitted to proceed further the condensation product may acquire a more viscous character, becoming gelatinous, or semi-plastic in consistence. This modification of the product is insoluble or incompletely soluble in alcohol but soluble or partially soluble in acetone or in a mixture of acetone and alcohol. The condensation product having either the oily or semi-plastic character may be subjected to further treatment as hereinafter described. By heating the said condensation product it is found to be transformed into a hard body, unaffected by moisture, insoluble in alcohol and acetone, infusible, and resistant to acids, alkalies and almost all ordinary reagents. This product is found to be suitable for many purposes, and may be employed either alone or in admixture with other solid, semi-liquid or liquid materials, as for instance asbestos fiber, wood fiber, other fibrous or cellular materials, rubber, casein, lamp black, mica, mineral powders as zinc oxid, barium sulfate, etc., pigments, dyes, nitrocellulose, abrasive materials, lime, sulfate of calcium, graphite, cement, powdered horn or bone, pumice stone, talcum, starch, colophonium, resins or gums, slate dust, etc., in accordance with the particular uses for which it is intended, and in much the same manner as india rubber is compounded with the above-named and other materials to yield various valuable products. In compounding the condensation or dehydration product in this manner the desired materials are mixed with the same before submitting it to the final hardening operation below described.

Поликонденсация

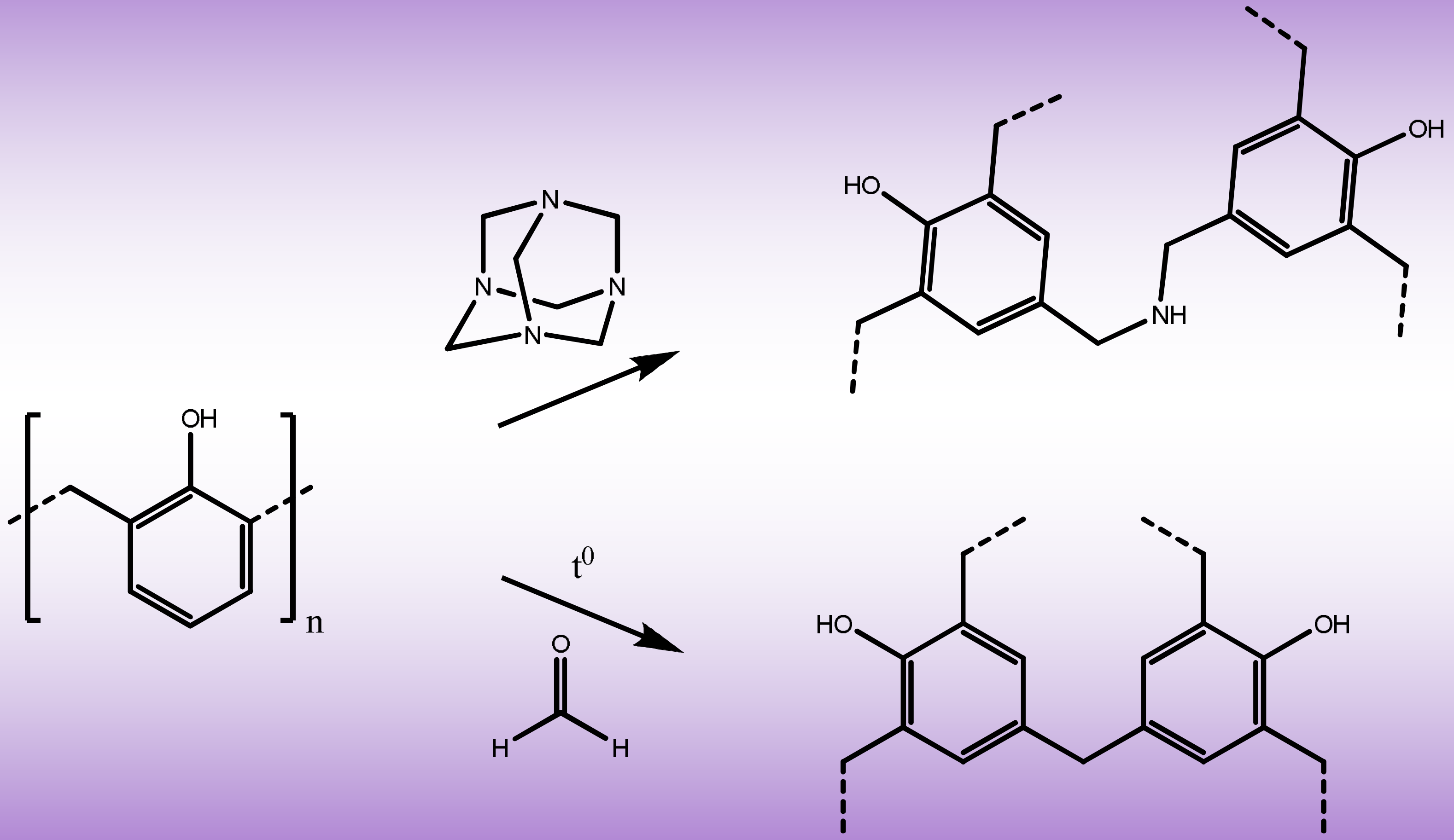
Фенопласты



Олигомеры с M ~ 10^3

Поликонденсация

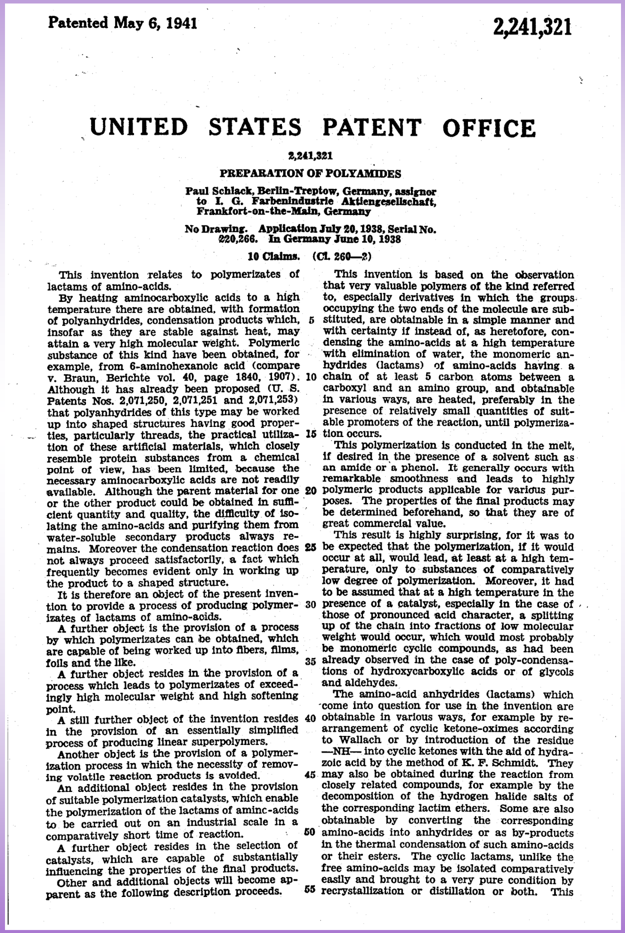
Фенопласты



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 Aktiengesellschaft, Frankfort-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, 1907). 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 aminc-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.

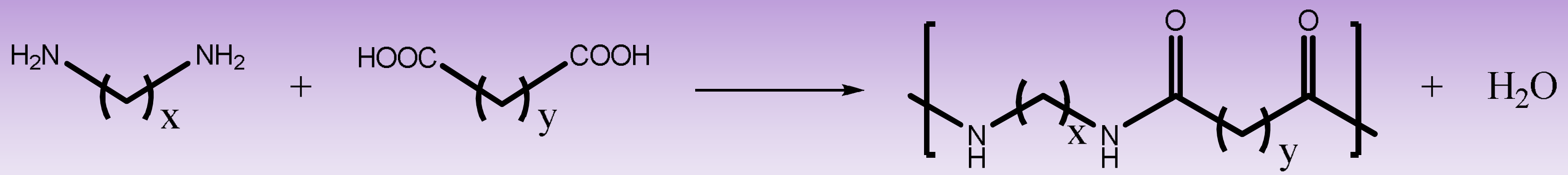
This polymerization is conducted in the melt, if desired in the presence of a solvent such as an amide or a phenol. It generally occurs with remarkable smoothness and leads to highly polymeric products applicable for various purposes. The properties of the final products may be determined beforehand,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

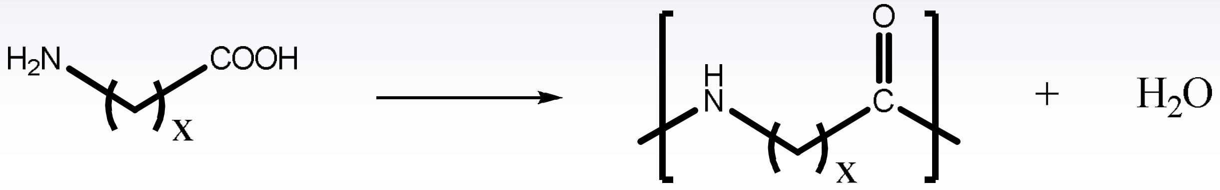
This result is highly surprising, for it was to be expected that the polymerization, if it would occur at all, would lead, at least at a high temperature, only to substances of comparatively low degree of polymerization. Moreover, it had to be assumed that at a high temperature in the presence of a catalyst, 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 poly-condensations of hydroxycarboxylic acids or of glycols and aldehydes.

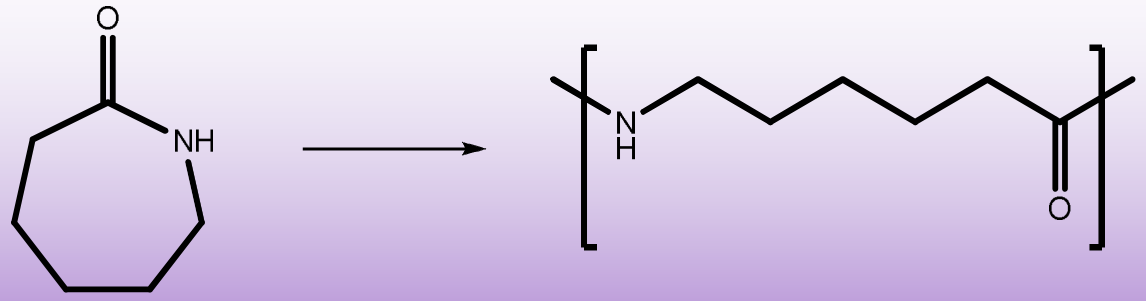
The amino-acid anhydrides (lactams) which come into question for use in the invention are obtainable in various ways, for example by rearrangement of cyclic ketone-oximes according to Wallach or by introduction of the residue —NH— into cyclic ketones with the aid of hydrazoic acid by the method of K. 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

Поликонденсация

Полиамиды



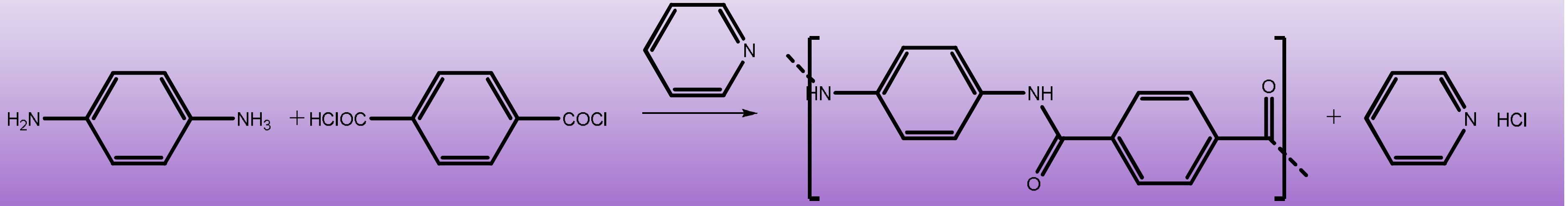




Поликонденсация

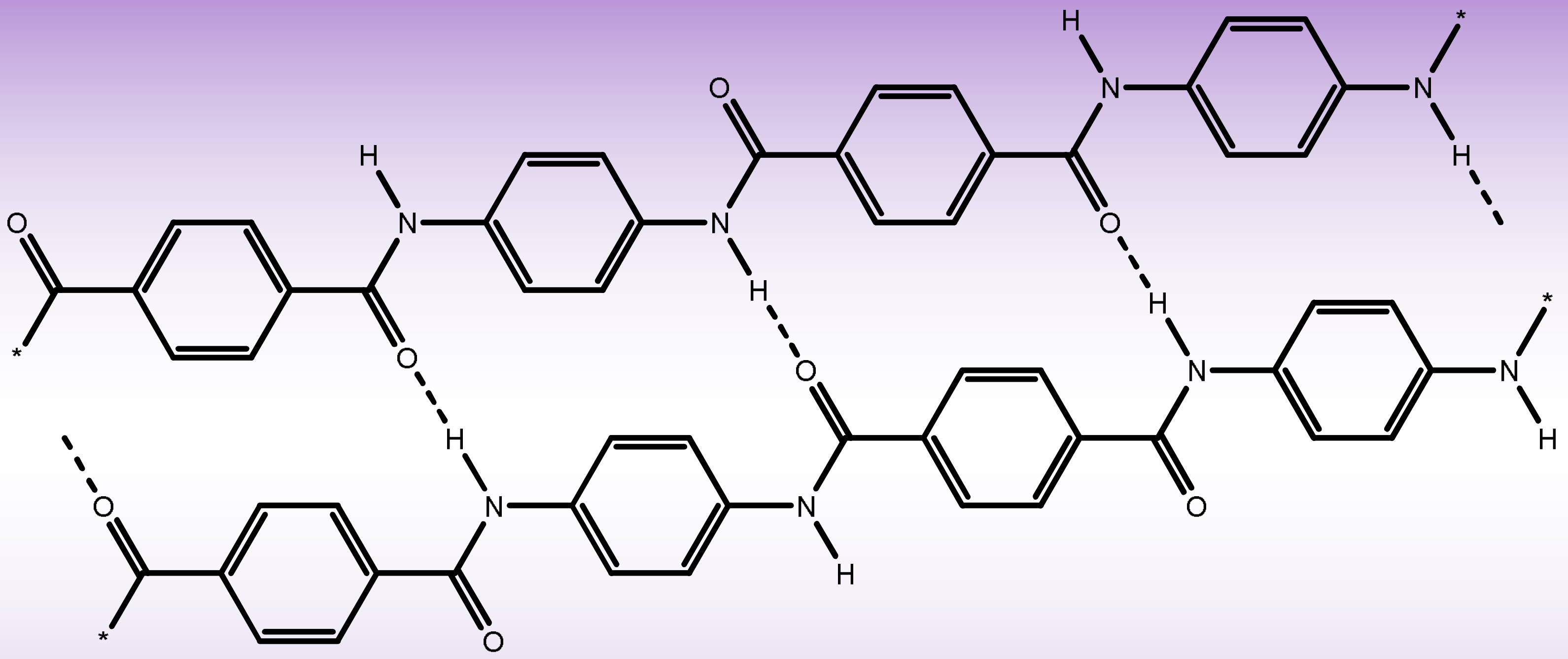
Ароматические полиамиды

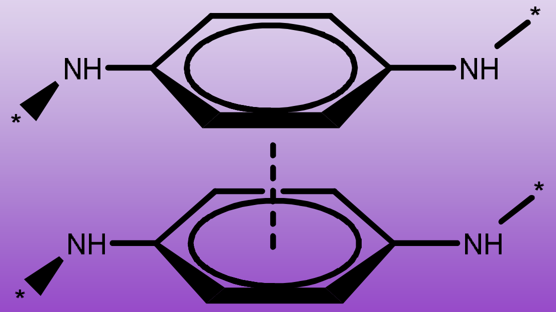
Стефани Кволек



Поликонденсация

Ароматические полиамиды



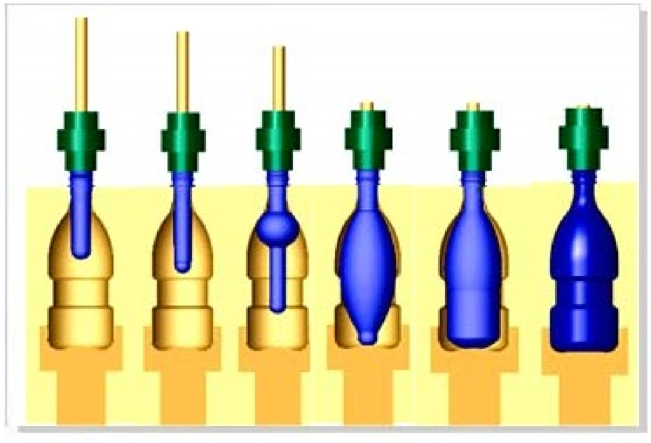


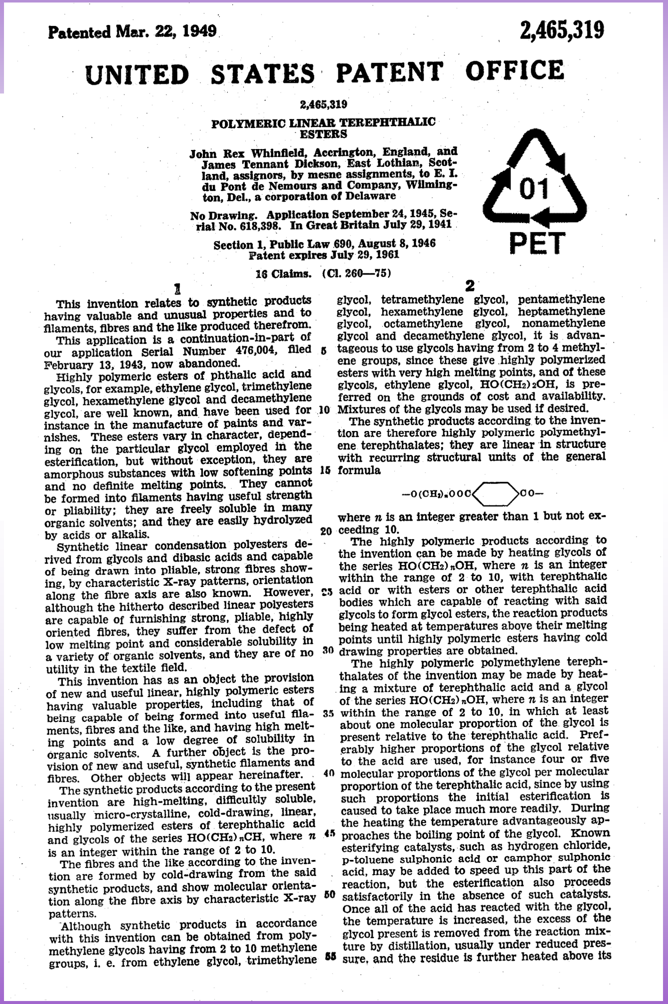
Поликонденсация

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 Whinfield, 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)

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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 $HO(CH_2)_nCH$, 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

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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, $HO(CH_2)_2OH$, 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

$$-O(CH_2)_nOOC\text{⬡}CO-$$

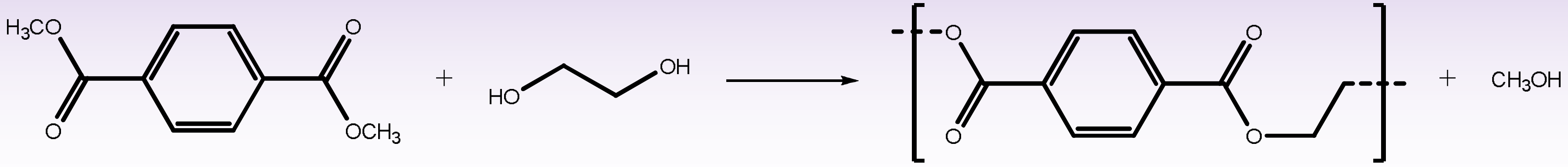
where n is an integer greater than 1 but not exceeding 10.

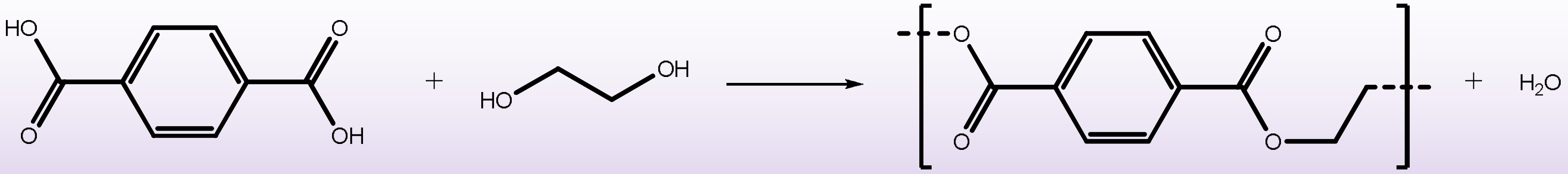
The highly polymeric products according to the invention can be made by heating glycols of the series $HO(CH_2)_nOH$, where n is an integer within the range of 2 to 10, with terephthalic acid or with esters or other terephthalic acid bodies which are capable of reacting with said glycols to form glycol 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 $HO(CH_2)_nOH$, 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

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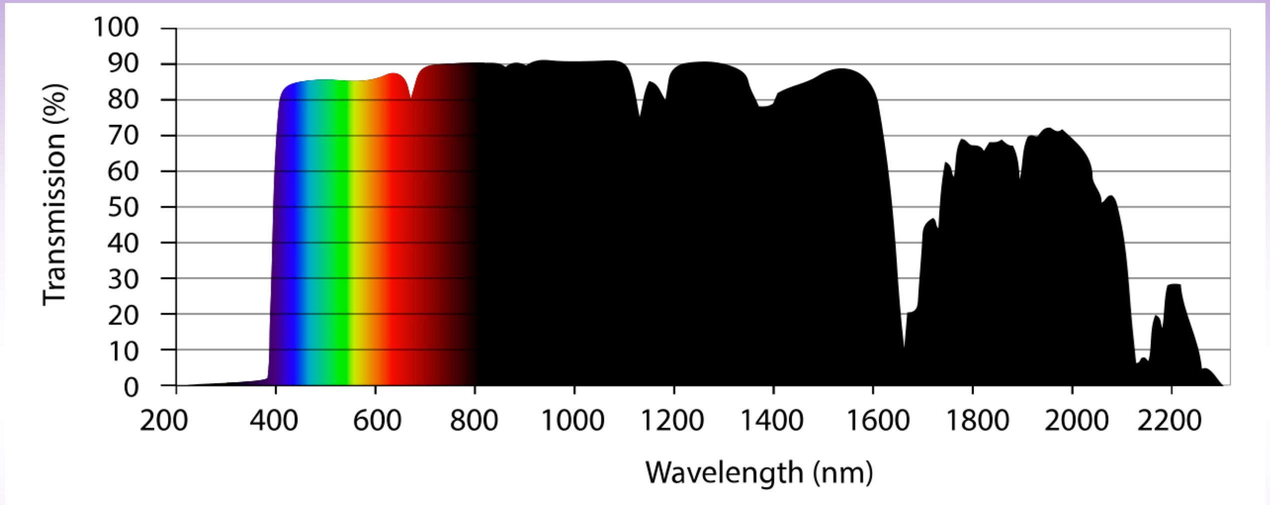
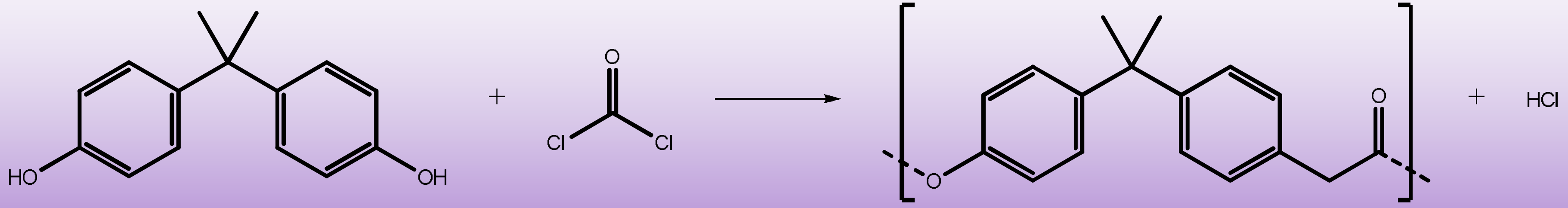
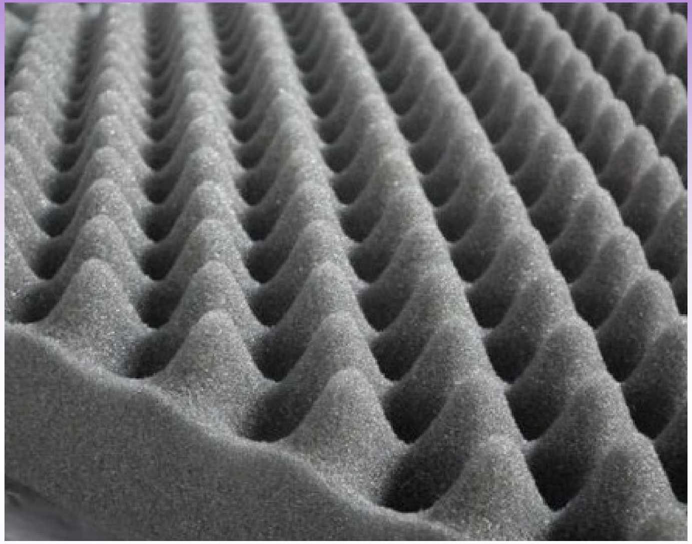


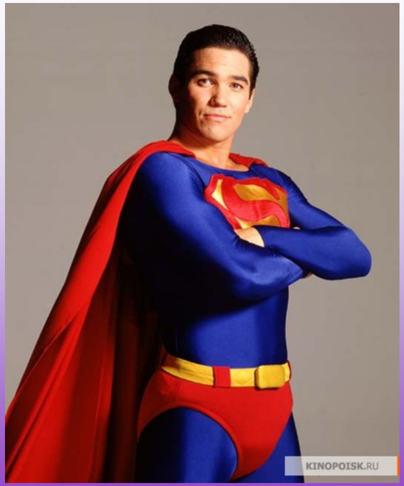


Поликонденсация

Полиуретаны

Отто Байер





Поликонденсация

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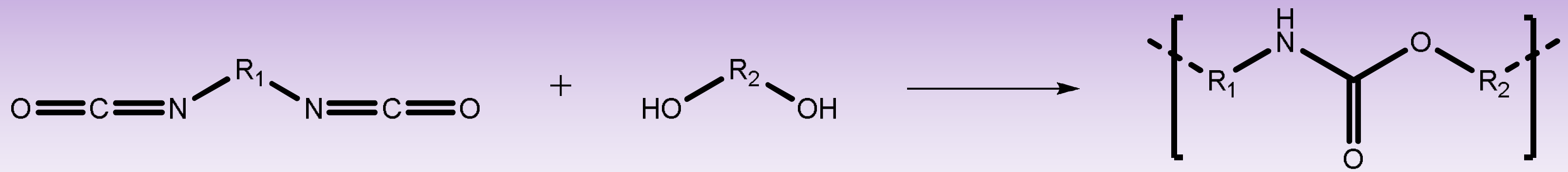
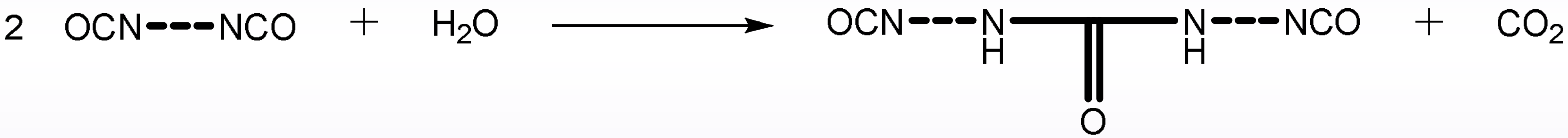
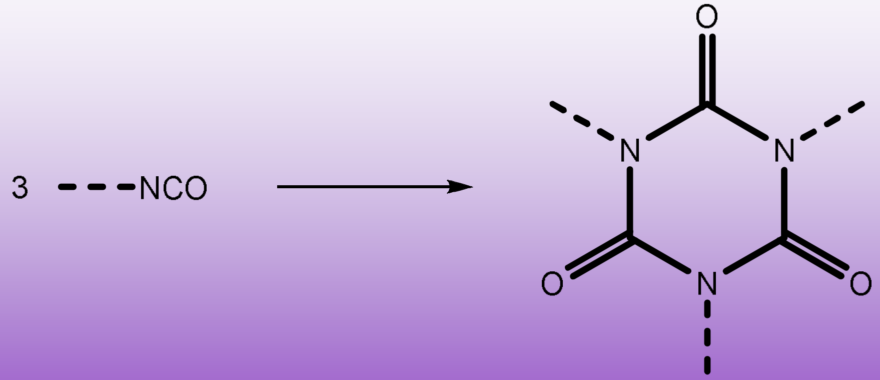




$$2\ OCN{-}{-}{-}NCO + H_2O \longrightarrow OCN{-}{-}{-}\underset{H}{N}{-}\underset{\underset{O}{\|}}{C}{-}\underset{H}{N}{-}{-}{-}NCO + CO_2$$



Продолжение следует…