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Catalysis in Polycondensation Reactions

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The importance of catalysis in polycondensation processes is considered. It is suggested that the catalytic processes in polycondensation reactions be divided into four groups: cationic, anionic, ionic-coordination, and free-radical. Examples of catalysts for a number of reactions are presented and the mechanisms of the catalytic action in various types of catalysis in polycondensation processes are considered. Such types of catalytic reactions are cationic and anionic catalysis and catalysis with the aid of tertiary amines, stereoregular polycondensation and polycondensation in the presence of catalysts of the Friedel-Crafts type, and oxidative polycondensation. The side reactions due to the presence of catalysts and their influence on the properties of the polymers obtained are examined.
The bibliography contains 60 references.

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I. INTRODUCTION

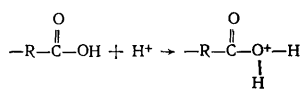
Since polycondensaton is an important method of synthesis of polymers, studies on polycondensation processes are vigorously developing at the present time. Many polymers obtained by polycondensation methods are nowadays manufactured in amounts running into millions of tonnes: these are phenol-formaldehyde and carbamide polymers as well as polyurethanes, polyamides, and polyesters[1,2]. Many polymers obtained by polycondensation are manufactured in amounts of thousands of tonnes: these include polycarbonates, unsaturated polyesters, polysiloxanes, polyoxides, and others. Finally the third group of numerous polycondensation polymers includes those whose manufacture is on a small scale but which are irreplaceable since they possess a set of valuable properties. These include thermostable polymers such as polyimides, polyarylates, polybenzimidazoles and other polyheteroarylenes, and also various semiconducting and light-sensitive polymers, etc. The great variety and wide range of properties of the polymers account for the vigorous development of studies on the polycondensation reaction, which is also reflected in the numerous articles, reviews, and monographs[1-10].

Catalysis plays a major role in polycondensation processes and the application of catalysts of all kinds is extremely widespread. The aim of the present review is to consider the literature data on catalysis in the polycondensation reaction[1,11,12].

II. TYPES OF POLYCONDENSATION PROCESSES

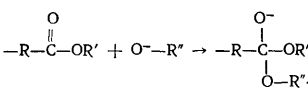
Depending on the nature of the catalyst and the starting materials employed, the polycondensation reaction can proceed as a cationic, anionic, polycoordination and even a free-radical process[3].

Thus the polycondensation of carboxylic acids with glycols in the presence of strong acids proceeds via a cationic mechanism with the intermediate formation of the product of the addition of a proton to the hydroxyl group of the acid:



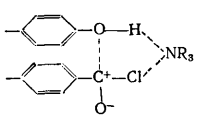
(1)

An example of anionic polycondensation is provided by the reaction of dicarboxylic acid esters with glycols in the presence of alkali metal glycolates, which proceeds in accordance with the equation



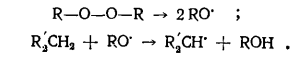
(2)

The polycondensation of dicarboxylic acid chlorides with bisphenols in the presence of catalysts such as tertiary amines is an example of the ionic-coordination polycondensation. This reaction leads to the formation of stereoregular polyarylates. Its mechanism can be accounted for by the formation of the following complex in its intermediate stage:



(3)

The formation of free radicals is an elementary step in the polyrecombination reaction [see reaction (4)], which is one of the instances of free-radical polycondensation[11]:



(4)

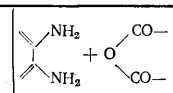
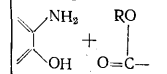
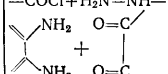
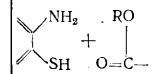
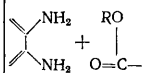
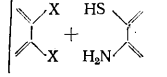
The examples presented illustrates the differences in the elementary step in polycondensation for each of the four types of polycondensation processes indicated above.

III. REACTIONS USED IN POLYCONDENSATION

An extremely significant feature of polycondensation processes, which has an appreciable influence on the process mechanism, is the great variety of types of initial monomers and hence differences between the structures of their active end groups whose reaction determines the course of the polycondensation process[1].

Table 1 lists the most important end groups and types of reactions used in polycondensation processes[12].

Table 1. The most important end groups and types of reactions used in polycondensation.

—COOH+HO—	>SiOH+HOAl<	—CO(CO)O+H₂N—	
—COOH+H₂N—	>BH+HB<		
—COOR+HO—	>BH+HN<		
—COOR+H₂N—	=CH(OH)+M(OCOCR)₂*	—RX+Na+XR—	
—COCl+HO—			
—COCl+H₂N—	—COCH₂X+H₂N—CS—	—RX+Na₂S+XR—	
—CONH₂+H₂N—	—COCl+H₂N—NH—	—RX+H₂N—	
>C=O+H₂N—		—ArH+HAr—	
		≡CH+HC≡	
≥CH+OC<			
—RX+M+XR—		—ArH+XR—	
—ArX+M+XAr—		—Ar+O=C<	
		—ArH+O₂+HAr—	
—ArX+HO—		>SiOH+HOSi<	

*M = metal.

Table 2. The elements whose various compounds have been used as catalysts of the polyesterification reaction.

Periods	Groups							
	1	2	3	4	5	6	7	8
I	H	—	—	—	—	—	—	—
II	Li	Be	B	C	N	O	—	—
III	Na	Mg	Al	Si	P	S	Cl	—
IV	K	Ca	—	Ti	—	Cr	Mn	Fe, Co, Ni
	Cu	Zn	—	Ge	As	—	—	—
V	—	Sr	—	Zr	—	Mo	—	Pd
	Ag	Cd	—	Sn	Sb	—	—	Pt
VI	—	Ba	Ce	—	Ta	—	—	—
	—	Hg	—	Pb	Bi	—	—	—
VII	—	—	—	Th	—	U	—	—

IV. CATALYSTS FOR THE POLYCONDENSATION REACTION

Among the catalysts for the polycondensation reaction involving an ionic mechanism, one encounters a wide variety of compounds such as oxides, salts, inorganic and organic bases, alkalis, complexes, inorganic and organic acids, amines, etc[13–15]. As an illustration, Table 2 lists the elements whose various compounds have been used as catalysts in the polycondensation reaction[13,15–19].

It is noteworthy that the polyesterification reaction is a process for which catalytic problems have been studied in greater detail compared with other reactions. It was established that both the nature of the metal and the nature of the anion of the catalyst used play a significant role. Table 3 presents the catalysts employed in polyesterification processes.

Table 3. Polyesterification catalysts.

Catalyst		References
cation	anion	
H^+	Cl^-, $H_2PO_4^-$, HSO_4^-, $CH_3C_6H_4SO_3^-$, BO_3^{3-}, $C_6H_5COO^-$	[13, 16, 20, 21]
Li^+, Na^+, K^+	Cl^-, Br^-, HSO_4^-, OH^-, RO^-, $RCOO^-$, H^-, SbO_4^{3-}	[16, 17, 22, 23]
Zn^{2+}, Mn^{2+}, Co^{2+}, Mg^{2+}, Cd^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Ti^{4+}, U^{6+}	$RCOO^-$, Cl^-, Br^-, SO_4^{2-}	[15, 16, 17, 20, 24]
R_3N		[17, 25–28]
R_4N^+	OH^-, Cl^-	[17]
Pb^{2+}, Zr^{4+}, Al^{3+}, Ge^{4+}, Mg^{2+}, Ti^{4+}, Th^{4+}, Ta^{5+}, U^{6+}	O^{2-}	[16, 17, 22]
Ion-exchange resins		[29]

Table 4. Dependence of the rate constant k for the polycondensation of bis(β-hydroxyethyl) terephthalate on the nature of the catalyst.

Catalyst	$10^{-2}k$, g mmol^{-1}s^{-1}	Catalyst	$10^{-2}k$, g mmol^{-1}s^{-1}
GeO_2	326	$Co(Ac)_3$	61
$Sb(Ac)_3$	156	$Mn(Ac)_3$	32
$Al(Ac)_3$	131	Without catalyst	0.156

In order to characterise the dependence of the activity of the catalyst on its structure, we present as an illustration Table 4, which shows how the activity of the catalyst in the polyesterification reaction of bis(β-hydroxyethyl) terephthalate depends on the polarity of the metal ion[24]. The Table shows that the rate constant for this reaction increases sharply under the influence of the catalyst and there is a significant variation in the presence of different metals[24].

The activity of the catalyst in a specific process also depends on the nature of the reaction investigated. Thus in the synthesis of polyamides the activity of the catalyst is much lower than in the polyester synthesis. However, substances such as boric acid[30], zinc chloride[31], phosphoric acid[31], magnesium oxide[30], tetraethyl pyrophosphate[32], and other compounds[12] were nevertheless shown in many instances to be catalytically active in the synthesis of polyamides.

The polycondensation of α-aminoacid esters is known to be very sensitive to the action of catalysts[33]. Various acids, among which carbon dioxide is particularly active, are active catalysts for this reaction. The mechanism of the catalytic action of carbon dioxide on the polycondensation of α-aminoacid esters has been explained by the formation of *N*-carboxyaminoacid esters in the first stage, the esters subsequently giving rise to carbamates,

$$R'OOCCHRNH_3 \cdot HOOCNHCHRCOOR' , \qquad (5)$$

which decompose at 55 °C with formation of polypeptides[33].

A large group of polycondensation reactions includes the interactions of aldehydes with phenols, amides, and other derivatives. All these reactions are sensitive to the pH of

the medium and to the action of catalysts of different kinds. Table 5 lists the catalysts used in the reactions of phenols with aldehydes[11,34].

Table 5. Catalysts used in the reactions of phenols with aldehydes.

HCl	$CH_3C_6H_4SO_2NH_2$	$Zn(NO_3)_2$
H_2SO_4	$BeCl_2$	$Th(NO_3)_2$
H_3BO_3	$CuCl_2$	$UO_2(NO_3)_2$
$H_2C_2O_4$	$FeCl_3$	$Hg(NO_3)_2$
$HClO_4$	$SnCl_2$	$AgNO_3$
CCl_3COOH	$Ba(NO_3)_2$	NH_4NO_3
$(NaO)_2Zn$	$Al(NO_3)_3$	$NaNO_3$
$(NaO)_3Al$	$Mn(NO_3)_2$	KNO_3
NH_3	$Fe(NO_3)_3$	$Ca(NO_3)_2$
NaOH	$Ce(NO_3)_4$	$Mg(NO_3)_2$
KOH	$Ni(NO_3)_2$	$Co(NO_3)_3$
NR_3	$Cu(NO_3)_2$	$Cd(NO_3)_2$
$NH(CH_3)_2$	$Pb(NO_3)_2$	$Fe(SO_4)_2$
		I_2

In many polycondensation reactions alkylation or acylation takes place in the presence of Friedel-Crafts catalysts such as aluminium chloride, aluminium bromide, zirconium chloride, boron fluoride, and others[11,12].

The above examples of catalysts illustrate fairly clearly their great variety in different instances of polycondensation. As will be shown below, a common property of all the catalysts is their ability to form intermediates with reactants and hence to increase their chemical reactivity. It is also noteworthy that in many instances the initial monomers act as catalysts and the reaction can then be regarded as an example of self-catalysis.

V. THE MECHANISM OF THE ACTION OF CATALYSTS

The great variety of the structures and types of catalysts complicates the consideration of the mechanism of their action from a single standpoint. We shall therefore attempt to consider mechanisms common to each group of reactions.

In considering catalysis in polycondensation processes as a general phenomenon we must, on the one hand, deal with specific instances of catalysis in individual processes, and, on the other hand, an attempt must be made to survey its overall importance. The polycondensation process can be represented by the equation

$$x\,aAa + x\,bBb \rightarrow a\text{—}(\text{—}AB\text{—})_x\text{—}b + (2x-1)\,ab \quad . \qquad (6)$$

The role of catalysis can be represented in general form as a process involving the formation of an intermediate active compound of the catalyst (K) with one of the monomers via the mechanism

$$\begin{aligned} &a\text{—}A\text{—}a + K \rightarrow (a\text{—}A\text{—}a)\,K \quad ; \\ &b\text{—}B\text{—}b + K \rightarrow (b\text{—}B\text{—}b)\,K \quad , \end{aligned} \qquad (7)$$

followed by the reaction of the intermediate with a molecule of the second monomer;

$$\begin{aligned} &(a\text{—}A\text{—}a)\,K + b\text{—}B\text{—}b \rightarrow a\text{—}A\text{—}B\text{—}b + ab + K \quad ; \\ &a\text{—}A\text{—}a + (b\text{—}B\text{—}b)\,K \rightarrow a\text{—}A\text{—}B\text{—}b + ab + K \quad . \end{aligned} \qquad (8)$$

A version is also possible in which both monomers form compounds with the catalyst and subsequent reaction takes place between these two active intermediate molecules via the mechanism

$$(a\text{—}A\text{—}a)\,K + (b\text{—}B\text{—}b)\,K \rightarrow a\text{—}A\text{—}B\text{—}b + ab + 2K \quad . \qquad (9)$$

These considerations apply to the general character of the action of the catalyst. Considering the mechanism of the latter in greater detail, we shall attempt a more detailed consideration of the mechanism of the action of catalysts of different chemical types in a wide variety of polycondensation reactions. In view of the fact that all ionic polycondensation processes take place with formation of ions and ionic systems, all the catalysts of such reactions can be divided into three groups[11,12].

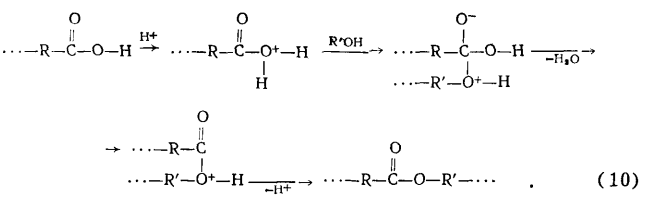
1. Catalysts which form reactive cations (cationic polycondensation).

2. Catalysts which form reactive anions (anionic polycondensation).

3. Catalysts which form reactive salt-like compounds (acceptor-catalytic polycondensation or stereospecific catalysis).

VI. CATIONIC CATALYSIS IN POLYCONDENSATION

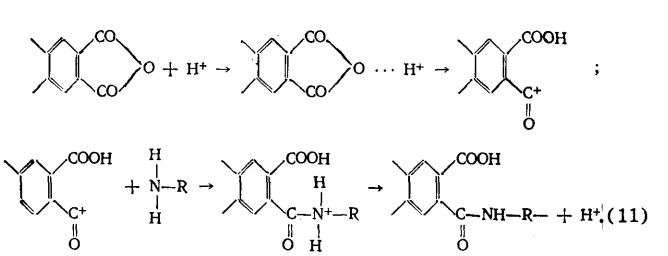
We shall now proceed to a more detailed consideration of the individual examples of the action of catalysts in each of the groups indicated above. In the equilibrium polycondensation of dicarboxylic acids and glycols in the presence of acid catalysts, the cationic reaction mechanism can be represented schematically as follows:



(10)

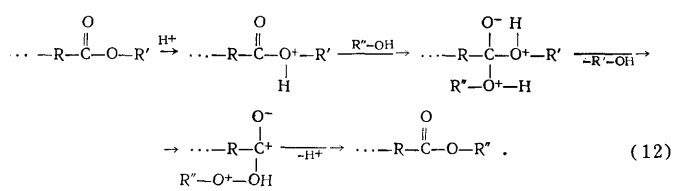
It is clearly seen from the above scheme that in the formation of oxonium compounds the addition of the acid proton to the hydroxyl group is an intermediate reaction in this process.

The carbonyl carbon atom becomes positively charged as a result and combines with the oxygen atom of the alcohol in consequence of nucleophilic attack. The reaction is accelerated in the presence of strong acids, since the initial glycol is a weak nucleophile and the initial dicarboxylic acid is a weak electrophile. However, the reaction can proceed via the above scheme also in the absence of a strong acid. Flory showed[35] that in this case the initial dicarboxylic acid plays the role of the catalyst. The catalytic action of carboxylic acids has also been demonstrated in the reactions of diamines and tetracarboxylic acid anhydrides, leading to the formation of polyamidoacids[36]. We believe that the reaction mechanism [see reaction (11)] can be represented schematically as follows:



(11)

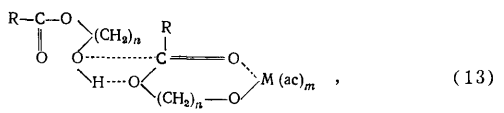
The mechanism of cationic polycondensation can be also illustrated in relation to the formation of a polyester via the transesterification of a dicarboxylic acid ester with a glycol in accordance with the equation



(12)

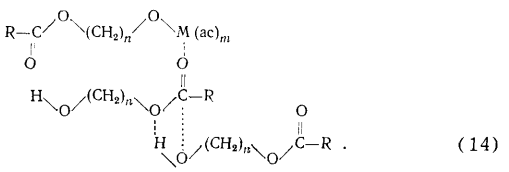
This reaction was investigated in particularly great detail in the synthesis of poly(ethylene terephthalate).[8,15,19,24,37,38]

Reinisch and coworkers[24] proposed the following mechanism of the action of catalysts in this reaction based on the formation of cyclic complexes:



(13)

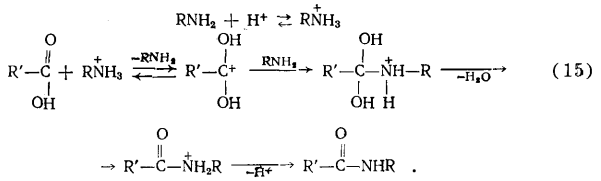
where M is a metal ion. There is a possibility of the simultaneous formation of linear complexes having the structure



(14)

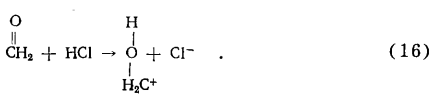
Here it is assumed that the activity of the catalyst is proportional to its ability to form complexes of this kind[24].

In the formation of polyamides the catalysis involves protons[39] [see reaction (15)]. The following mechanism, which explains the action of the acid, has been proposed:



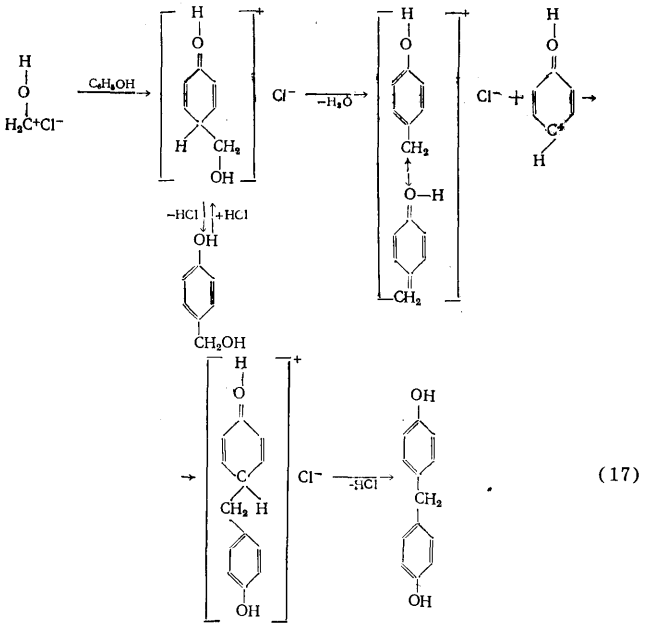
(15)

The reaction of phenols with aldehydes can proceed via a cationic mechanism in the presence of acids in accordance with the equation[40,41]



(16)

The ion pair formed in this process reacts further in the following manner:

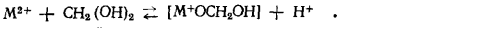


(17)

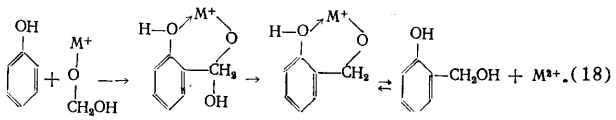
The first product is a quinone derivative, which is subsequently transformed into dihydroxydiphenylmethane. For this reason, phenol-alcohols are formed extremely rarely in an acid medium.

Bivalent metal ions accelerate the reaction of phenol with formaldehyde and at the same time exhibit a directing effect driving the hydroxymethyl groups in the *o*-positions relative to the hydroxy-groups. This results in the formation of phenolformaldehyde oligomers which contain predominantly *o*-substituted phenolic residues. These products are known as *ortho*-novolak or *ortho*-resol and are of interest as rapidly hardening materials.

Fraser et al.[42] described the catalytic action of bivalent metal ions in terms of the following scheme. The product of the reaction of the metal ion and methylene glycol is formed initially:

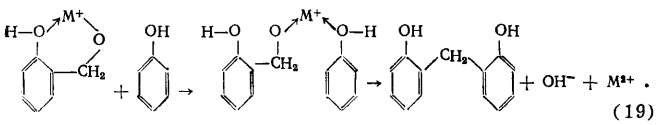


It then interacts with phenol to form *o*-salicyl alcohol



(18)

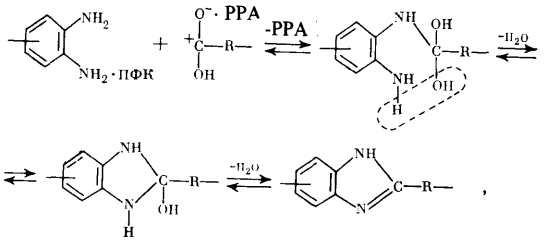
The last stage is the formation of di(*o*-hydroxyphenyl)methane:



(19)

The catalytic action of polyphosphoric acid has been explained by the formation of an intermediate complex in the synthesis of polybenzimidazoles in accordance with the

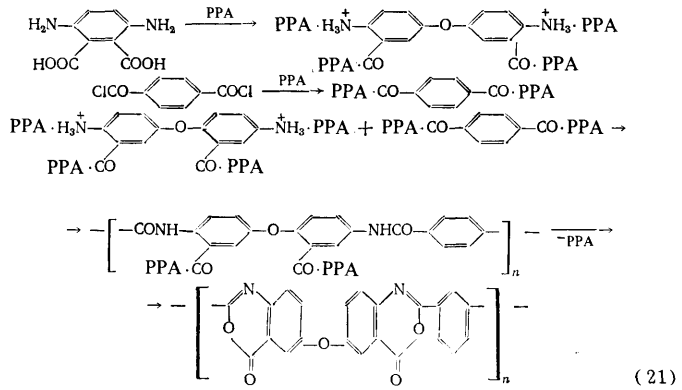
scheme[43]



(20)

where PPA is polyphosphoric acid.

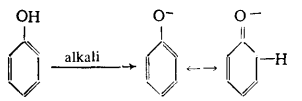
The formation of intermediate compounds with polyphosphoric acid has been demonstrated in relation to the formation of polybenzoxazinones from bisanthranilic acids[44]:



(21)

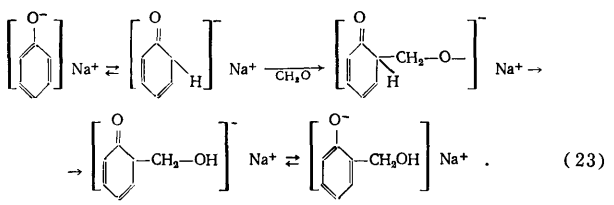
VII. ANIONIC CATALYSIS IN POLYCONDENSATION

The alkaline catalysts used in ionic polycondensation are extremely active, since in their presence phenol is converted into the phenoxide anion, which is accompanied by a redistribution of electron density in accordance with the following scheme:



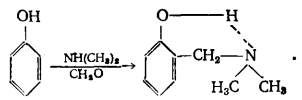
(22)

As a result of this, alkaline catalysts facilitate the reaction of phenols with aldehydes[40]. Accordingly, the action of an alkaline catalyst in the polycondensation of phenol with formaldehyde can be represented schematically as follows:



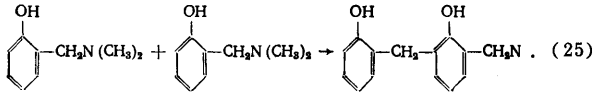
(23)

When dimethylamine is used, the reaction of phenol with formaldehyde proceeds with formation of an intermediate Mannich base[45] via the mechanism



(24)

The Mannich base thus produced decomposes on heating into dimethylamine and a phenol-formaldehyde polymer in accordance with the equation

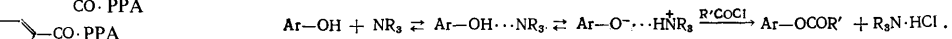


(25)

VIII. CATALYSIS WITH THE AID OF TERTIARY AMINES

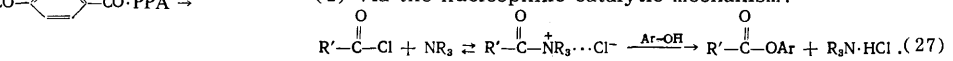
The acylation of alcohols and phenols by carboxylic acid chlorides in solution is frequently carried out in the presence of tertiary amines (pyridine, triethylamine, etc) as catalysts. Depending on the nature of the tertiary amine and the initial phenol and acid chloride, the reaction can then proceed via one of the following two mechanisms:

(1) Via the general base catalytic mechanism:



(26)

(2) Via the nucleophilic catalytic mechanism:



(27)

The result of the reaction of a dicarboxylic acid chloride with a bisphenol depends on the amount of catalyst—triethylamine. Fig. 1 illustrates the variation of the yield and molecular weight of the polyarylate obtained by the polycondensation of terephthalic acid dichloride (AC) in solution in dichloroethane with the amount of triethylamine (TEA).[46] The maximum in the plot of the viscosity against the amount of the catalyst is also observed for the reaction of dian with terephthalic acid chloride at a catalyst concentration of 20 wt.% (Fig. 2).[47]

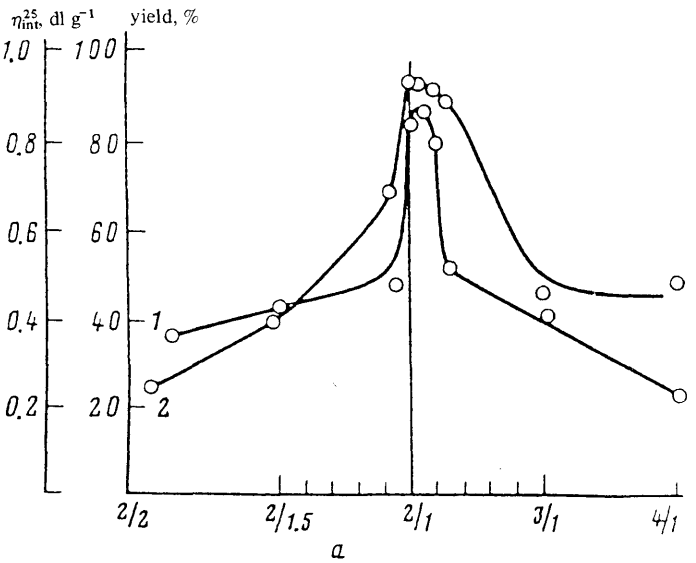


Figure 1. Dependence of the intrinsic viscosity (curve *1*) and the yield (curve 2) of the polyarylate on the molar ratio TEA : AC (*a*).

Tertiary amines not only accelerate the acylation reaction (for example, in the benzoylation of *p*-nitrophenol in the presence of triethylamine, the rate constant was higher by two orders of magnitude than for the same reaction in the presence of pyridine[48]) but also influence the steric structure of the polyester formed, as will be shown below[27,28,49].

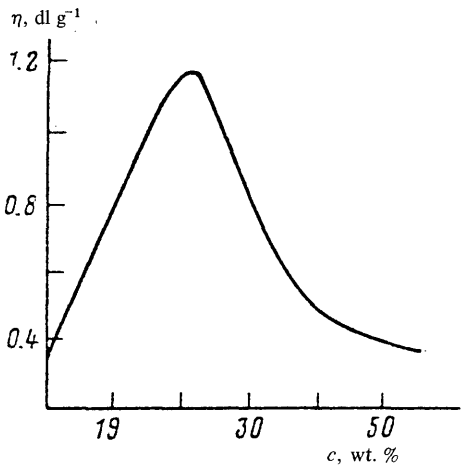


Figure 2. Dependence of the logarithmic viscosity of a solution of dian polyarylate and terephthalic acid on the amount of tetraethylammonium chloride (*c*) in the interfacial polycondensation reaction.

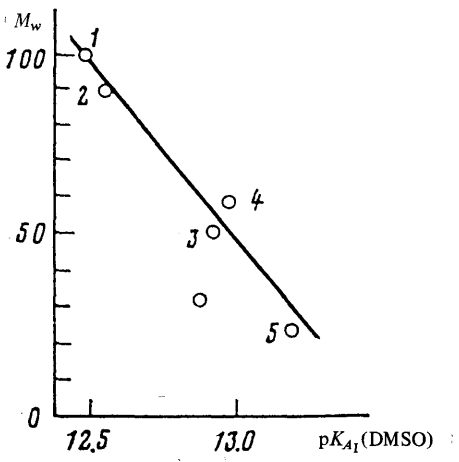


Figure 3. Dependence of the molecular weights of polyterephthalates M_W on the acidity of the bisphenol; bisphenol: *1*) 2,2-bis(3-chloro-4-hydroxyphenyl)propane; *2*) 3,3-bis-(4-hydroxyphenyl)phthalide; *3*) bis (4-hydroxyphenyl)methylphenylmethane; *4*) bis(4-hydroxyphenyl)phenylmethane; *5*) 9,9-bis(4-hydroxyphenyl)fluorene.

A characteristic feature of general base catalysis is also that, as can be seen from Fig.3, an increase of the acidity of the bisphenols entails an increase of the molecular weight of the polyarylates obtained from terephthalic acid chloride. Eqn.(26) shows that more favourable conditions for the acylation reaction are created with increase of the acidity of the phenol. Indeed an increase of the acidity of the hydroxy-component should entail an increase in its capacity for complex formation with the tertiary amine[48]. The increase of the activity of the hydroxy-component with increase of its acidity is indicated by the results of the joint acylation of a mixture of phenol and methanol with benzoyl chloride in the presence of triethylamine; it was found that the yield of phenyl benzoate was nine times greater than that of methyl benzoate. On the other hand, the reaction in the presence of a weak base such as pyridine led to the reverse ratio of the yields of phenyl and methyl benzoates, which was 0.35. This means that in the former case the general base catalysis predominates [reaction (26)], since the more acidic phenol is more reactive, whilst in the latter case nucleophilic catalysis predominates. This dependence of the rate of benzoylation of the mixture of the aliphatic alcohol and phenol on the basicity of the catalyst was confirmed by investigating the reactions using tertiary amines with different basicities as catalysts[49a]. It was found that the relative reactivity of the phenolic component increases with increasing basicity of the tertiary amine as can be seen from the curve in Fig.4.

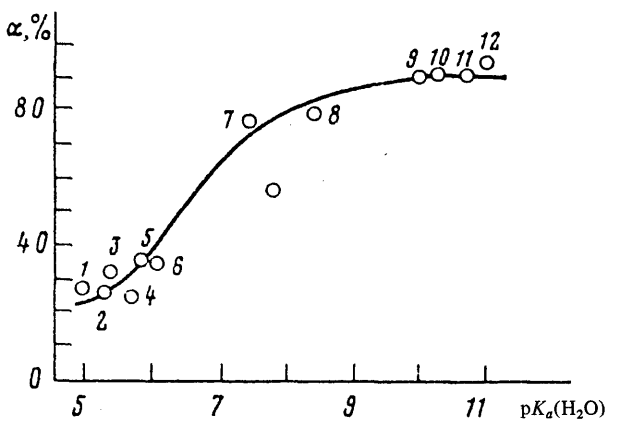


Figure 4. Dependence of the degree of conversion of phenol α on the basicity of the amine: *1*) quinoline; *2*) pyridine; *3*) isoquinoline; *4*) β-picoline; *5*) quinaldine; *6*) α-picoline; *7*) γ-collidine; *8*) triallylamine; *9*) ethyldimethylamine; *10*) cyclohexyldimethylamine; *11*) triethylamine; *12*) tributylamine.

These results confirm the above hypothesis that two catalytic processes can occur in acylation: general base catalysis and nucleophilic catalysis [reactions (26) and (27)].[49] The predominance of a particular catalytic process depends on the nature of the starting material and the tertiary amine[49]. The rate constants for the benzoylation of various phenols in the presence of triethylamine are presented in Fig.5. The left-hand part of the plot corresponds to phenols with pK_a ranging from 10 to 14. The sharp alteration in the form of the

plot starting from $pK_a > 14$ can be accounted for as a consequence of the change in the mechanism of the catalysis from the general base type to the nucleophilic type, as suggested above.

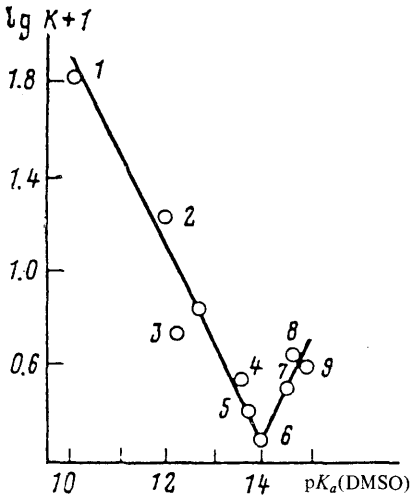


Figure 5. Dependence of the logarithms of the rate constants for the benzoylation of phenols on their acidity; phenol: *1*) *p*-nitrophenol; *2*) *p*-acetylphenol; *3*) *p*-chlorophenol; *4*) hydroquinone benzoate; *5*) phenol; *6*) *p*-t-butylphenol; *7*) *p*-cresol; *8*) *p*-methoxyphenol; *9*) hydroquinone.

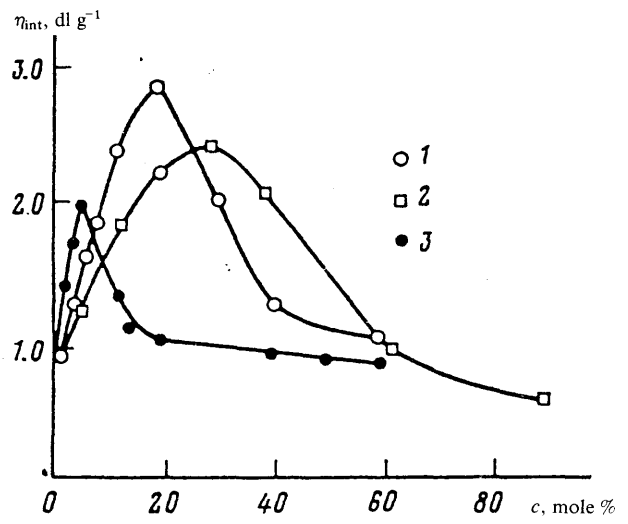
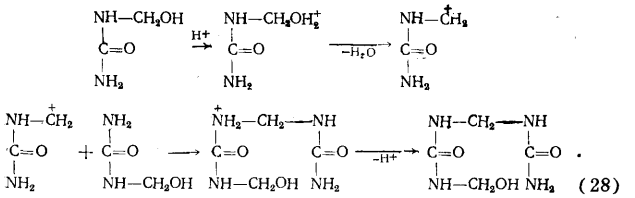


Figure 6. Dependence of the viscosity of the polyimide obtained by the reaction of the dianhydride of tricyclo [4.2.2.0]dec-10-ene-3, 4, 7, 8-tetracarboxylic acid with di(4-aminophenyl) ether on the catalyst concentration *c*: *1*) triethylamine; *2*) trimethylamine; *3*) tributylamine.[52]

The reactions of diamines with dicarboxylic acid dianhydrides are extremely sensitive to the catalytic action of tertiary amines such as pyridine, triethylamine, and trimethylamine[50]. A maximum is then observed in the curves relating the viscosity of the product to the amount of the catalyst, as shown in Fig. 6.

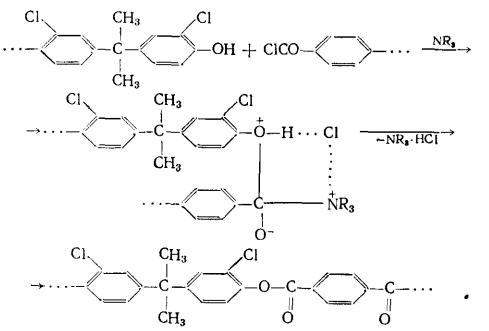
The role of the acid catalyst in the reactions of amines and acid amides with aldehydes consists, according to Smets[51], in the formation of a carbonium ion in accordance with the equation



(28)

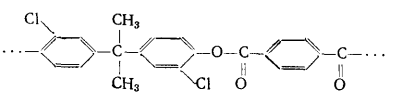
IX. CONFORMATIONALLY REGULAR POLYCONDENSATION

Stereoregular polycondensation was observed in the study of the polycondensation reaction in the presence of tertiary amines[27,28]. It proceeds as conformationally regular polycondensation on interaction of monomers capable of existing in several stereoisomeric forms [see reaction (29)]. The catalytic action of tertiary amines is manifested in the formation of polyarylates from bisphenols and dicarboxylic acid chlorides, which leads to the preferential formation of the *cis*- or *trans*-form of the polyester in accordance with the mechanism



(29)

In the presence of a weak base, for example, pyridine, the cisoid form of the polymer is formed. The use of a tertiary amine with strongly basic properties, for example, triethylamine, as the catalyst leads to the formation of the transoid form of the polyarylate:



(30)

The probable cause of the formation of conformationally regular polymers is the formation of stable conformations of the complexes of the starting materials with the tertiary amines.

X. POLYCONDENSATION IN THE PRESENCE OF FRIEDEL–CRAFTS CATALYSTS

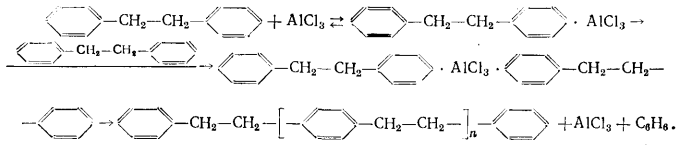
The polycondensation of aromatic hydrocarbons with halogen atoms in the side chain as well as the polycondensation of dihalogenoalkanes with aromatic hydrocarbons proceed only

in the presence of Friedel–Crafts catalysts. Aluminium chloride or the halides of cerium, boron, and other elements are most frequently used for this purpose.

A ternary complex of the halogenohydrocarbon with aluminium chloride and the aromatic hydrocarbon is formed as the first reaction product in this instance. The formation of such a complex in the polycondensation of dichloroethane with benzene can be described by the equation[53]:

$$ClCH_2CH_2Cl \cdot Al_2Cl_6 + 2C_6H_6 \rightleftarrows ClCH_2CH_2Cl \cdot Al_2Cl_6 \cdot 2C_6H_6 \qquad (31)$$

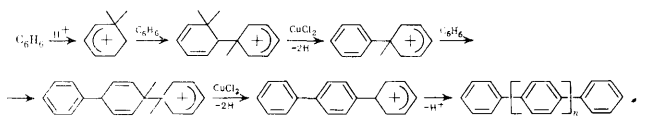
Catalysts act similarly in *trans*-arylation[54]. This type of polycondensation leads to the formation of polyarylenealkyls in the following reaction accompanied by the formation of benzene[54]:



(32)

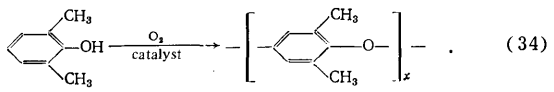
XI. OXIDATIVE POLYCONDENSATION

The oxidative polycondensation of benzene and other aromatic hydrocarbons, which leads to the formation of polyphenylenes according to Kovacic and Lange[55], takes place in the presence of iron(III) chloride or a mixture of copper(II) chloride and aluminium chloride[55]. The intermediate stage in this reaction is the formation of a σ-complex and the benzenium ion in accordance with the equation



(33)

An important instance of oxidative polycondensation is the synthesis of poly(2,6-dimethylphenylene oxide) by the oxidation of 2,6-dimethylphenol with atmospheric oxygen via the reaction



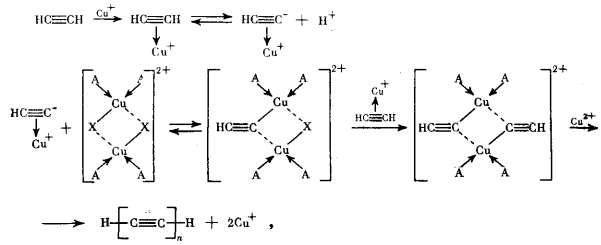
(34)

The reaction proceeds in the presence of various catalysts, among which the most important is the copper complex of pyridine[56]. The activity of this catalyst in the reaction depends on the ratio of the concentrations of pyridine and copper. With increase of this ratio, the number of ester linkages increases and the number of carbon–carbon bonds diminishes; when the ratio of the pyridine and copper concentration is 10:1, carbon–carbon bonds are not formed at all[57].

The copper complex of ammonia also proved to be an active catalyst of the oxidative polycondensation of acetylene, leading to the formation of a "carbyne"—a linear form of carbon—via the reaction[58]

$$HC \equiv CH \xrightarrow{+Cu^{2+}} -(-C \equiv C-)-_x \qquad (35)$$

The mechanism of the action of the catalyst in this reaction can be described by the equation



where A = complexone residue.

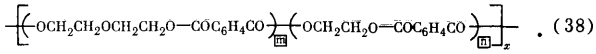
XII. SIDE REACTIONS INDUCED BY THE PRESENCE OF CATALYSTS

In considering the problem of the action of catalysts, one must bear in mind the fact that catalysts can influence not only the main reaction involving the synthesis of polymers but can also induce or accelerate various side reactions, which can involve both the initial monomers and the polymer formed and this can be reflected in the molecular weight and structure of the reaction product and can influence the entire set of its physical and chemical properties. In certain cases catalysts accelerate the decomposition of the polymer in the course of its synthesis, impairing its properties[16].

As an example of the negative influence of side reactions, one may quote the synthesis of poly(ethylene terephthalate) from ethylene glycol and terephthalic acid in the presence of sulphuric acid[11]. A side reaction involving the elimination of water and the formation of diethylene glycol then takes place:

$$2HOCH_2CH_2OH \rightarrow HOCH_2CH_2-O-CH_2CH_2OH + H_2O \qquad (37)$$

In addition, acetaldehyde and ethylene acetal are also formed. The diethylene glycol produced reacts with terephthalic acid, which results in the formation of a hetero-unit polymer containing diethylene glycol units:



(38)

Acetaldehyde can be readily removed from the reaction mixture, which alters the ratio of the starting materials and has a negative effect on the molecular weight of the polymer.

The use of certain catalysts, such as, for example, titanium and aluminium compounds, leads to the formation of dark-coloured products[16]. The occurrence of such reactions necessitates caution in the selection of catalysts[15]. It has been noted that even the material of the reactor can influence the process and the polycondensation product[19].

In addition, one should point out that in certain cases the presence of the catalyst influences the mode of reaction. Thus Murochochi et al.[32] observed that *N*-(γ-aminobutyryl)-γ-aminobutyric acid gives rise to the cyclic γ-pyrrolidinone on heating. However, if this monomer is heated to 100 °C in diethylphosphinic acid in the presence of tetraethyl pyrophosphate, polybutanamide is formed.

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In conclusion of the review, we should like to emphasise that catalysis is a positive factor in polycondensation processes, since it accelerates the reaction, makes it possible to carry it out under mild conditions, and determines the microstructure of the polymer obtained. However, one should

note that theoretical studies of catalysis in polycondensation reactions fall short of the importance which they have for the development of this field. Therefore the problem of the selection of catalysts is still solved mainly empirically. The most important task for the future is the determination by extensive studies of the effective factors in the catalysis of polycondensation reactions, which should lead to the raising of the level of the relevant research and to advances in this field of polymer chemistry.

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