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Advances in Acceptor-catalytic Polyesterification

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Advances in the synthesis of polymers and copolymers by acceptor-catalytic polyesterification from dicarboxylic acid dichlorides and diols in the presence of tertiary amines are examined. The considerable possibilities of this method are demonstrated. It makes it possible to obtain polymers and copolymers of different composition and structure, including stereoregular polycondensation polymers of a new type—conformationally-regular polyarylates. The study of acceptor-catalytic polyesterification made it possible to establish experimentally the principal characteristics of the formation of polymers containing "head-to-tail" fragments and of copolymers under the conditions of non-equilibrium polycondensation and copolycondensation in a homogeneous system. The bibliography includes 128 references.

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I. INTRODUCTION

As a method of synthesis of polymers, polycondensation was discovered in the past century. Many different polycondensation processes, based on particular substitution reactions, are now known. All these processes can be divided into two types: equilibrium (reversible) and non-equilibrium (irreversible) polycondensation[1].

Analysis and survey of a large number of experimental data made it possible to discover the fundamental features and general characteristics of equilibrium polycondensation[2]. In contrast to equilibrium polycondensation, which has been thoroughly investigated, non-equilibrium polycondensation had been scarcely studied by the 1960s[3]. However, at that time it had already been established that non-equilibrium polycondensation has many useful features, which promoted its subsequent rapid and wide-scale utilisation in laboratory and industrial practice. These features of non-equilibrium polycondensation include the absence of exchange and degradative reactions, high polymer chain propagation rate constants, and many others. Nevertheless many problems of non-equilibrium polycondensation, largely of a fundamental type, have until recently either not been considered at all or have been only slightly touched upon in a few publications. Such exceptionally important problems include those of the kinetics, mechanism, and fundamental characteristics of the formation of macromolecules of homogeneous and mixed polymers, including polymers with different three-dimensional microstructures and containing fragments of the "head-to-tail" type in the macromolecules[3].

Studies on the non-equilibrium polyesterification of dicarboxylic acid dihalides with diols in the presence of tertiary amines [see Eqn. (1)], known previously in the literature as "low-temperature polycondensation in solution"[3], were undertaken to solve these problems:

$$\begin{aligned} &\mathrm{HalOC{-}R'{-}COHal + HO{-}R''{-}OH + 2R_3N \rightarrow} \\ &\rightarrow \mathrm{{-}[{-}OC{-}R'{-}COO{-}R''{-}O{-}]_n{-} + 2R_3N \cdot HHal}\ , \end{aligned} \qquad (1)$$

The study of the mechanism of this reaction established that the tertiary amine plays the role of a reaction catalyst and not merely of a hydrogen halide acceptor. This justified the use of the term acceptor-catalytic polyesterification for this type of polyesterification[3,4].

In the first studies on the synthesis of polyesters by acceptor-catalytic polyesterification it was already shown that this variety of non-equilibrium polycondensation constitutes an extremely convenient method of obtaining polymers which are formed in solution at low temperatures, usually close to 20°C, the reaction terminating over a short period, as a rule within the limits of 30 min. The same factor makes acceptor-catalytic polyesterification a suitable model for the investigation of many fundamental problems associated with the characteristics of the formation of macromolecules under the conditions of non-equilibrium polycondensation.

II. SYNTHESIS OF POLYESTERS BY ACCEPTOR-CATALYTIC POLYESTERIFICATION

As a method of synthesis of polyesters (in the given case, polycarbonates), acceptor-catalytic polyesterification was used for the first time by Einhorn[5] as early as 1898. However, subsequently interest in this procedure lapsed for a long time. Only now, more than fifty years later, have chemists returned to acceptor-catalytic polyesterification[6]. During the 1950s, a vigorous development of acceptor-catalytic polyesterification began on the use of this method for the synthesis of polycarbonates from phosgene and bisphenols in pyridine or mixtures of pyridine and other organic solvents[7,8]. Many carbonates based on bisphenols of different structure have now been synthesised by acceptor-catalytic polyesterification[3,8-10].

In 1961 Sokolov and coworkers[11] synthesised polyarylates from oxalyl chloride or di(hydroxyphenyl)propane in the presence of pyridine. Morgan and coworkers[12,13] obtained polyarylates based on different dicarboxylic acid dichlorides and bisphenols by acceptor-catalytic polyesterification in the presence of tri-ethylamine. By 1965, only about ten papers had been published on the synthesis of polyesters from dicarboxylic acid dihalides and diols in the presence of tertiary amines[11-18]. This enabled Morgan[10] (p.329) to write in 1965, that, with the exception

of polycarbonates, low-temperature polyesterification "has been scarcely used for the synthesis... of polymers".

In recent years acceptor-catalytic polyesterification has begun to be used much more frequently for the synthesis of polyesters, in the first place polyarylates. The studies of Korshak and coworkers made a large contribution to the development of the synthetic possibilities of this method.

Korshak and coworkers[19,24] synthesised a large number of cardo-polyarylates [or 'cross-planar polyarylates' (Ed. of Translation)] based on 9,9-bis-(4-hydroxyphenyl)-10-anthrone and other bisphenols with cardo-groups by acceptor-catalytic polyesterification in the presence of triethylamine. Korshak and coworkers[25] synthesised by the same method cardo-polyarylates based on polycyclic bisphenols such as, for example, bis-(4-hydroxyphenyl)-2-norbornylidene. Morgan[26] reported the properties of many cardo-polyarylates, some of which could be obtained by acceptor-catalytic polyesterification in the presence of triethylamine.

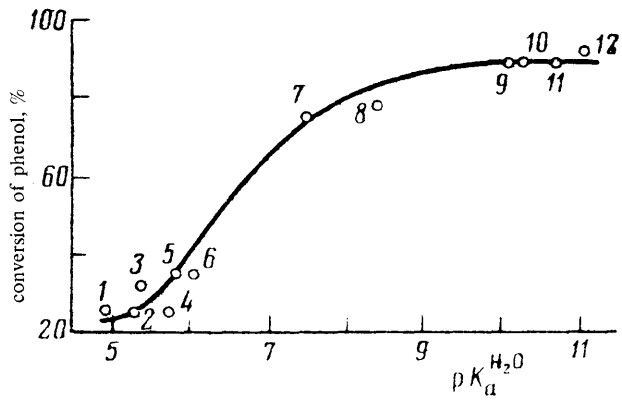


Figure 1. Dependence of the degree of conversion of phenol into phenyl benzoate on the basicity of tertiary amines. Molar ratios of phenol, methanol, tertiary amine, and benzoyl chloride 2.5 : 2.5 : 1 : 1, (dichloroethane, 25°C)[68]; tertiary amines: 1) quinoline; 2) pyridine; 3) isoquinoline; 4) β-picoline; 5) quinaldine; 6) α-picoline; 7) γ-collidine; 8) triallylamine; 9) ethyldimethylamine; 10) cyclohexyldimethylamine; 11) triethylamine; 12) tributylamine.

Numerous communications have been published during the last decade on the synthesis of many polyesters with a wide variety of structures from dicarboxylic acid dichlorides and diols in the presence of tertiary amines[27-36]. Among these, mention should be made of the work of Jedlinski and coworkers[30,31] on the synthesis of interesting, as regards practical applications, polyesters with naphthalene rings in the chain. Korshak and coworkers[33] were the first to obtain by acceptor-catalytic polyesterification polyesters based on bis-β-dicarbonyl compounds reacting in the enolic form.

Acceptor-catalytic polyesterification became very important as a method of synthesis of organoelemental polymers, particularly carborane-containing polyesters[37]. Thus Korshak and coworkers[37-46] were the first to obtain polyarylates with *o*- and *m*-carborane groups in the chain from the dichlorides of 1,2- or 1,7-bis-(4-carboxyphenyl)-carboranes and 1,2-bis-(4-hydroxyphenyl)carborane in the presence of triethylamine. They[37,47-50] used acceptor-catalytic polyesterification for the synthesis of carborane-containing polyesters and copolyesters from the dichlorides of *m*- or *p*-carboranedicarboxylic acids. Soluble and fusible polyester-chelates have also been obtained by acceptor-catalytic polyesterification[51]. Bisphenols, containing copper chelates, for example, bis(acetoacetatohydroquinone)copper, were used for this purpose in the reaction with the dichloride of diphenylphthalide-4,4'-dicarboxylic acid.

Thus studies in this field have now established the considerable synthetic possibilities of acceptor-catalytic polyesterification, whereby polyesters have been obtained with a wide variety of structures and possessing in many instances a set of interesting properties. It appears particularly promising to use this method for the synthesis of polymers which are extremely valuable in practice, namely polyarylates, including polycarbonates.

The problems of the synthesis of mixed polyesters, polyesters based on diols with an asymmetric distribution of hydroxy-groups ("head-to-tail"), and conformationally regular polyarylates by acceptor-catalytic polycondensation are examined in subsequent sections of this review.

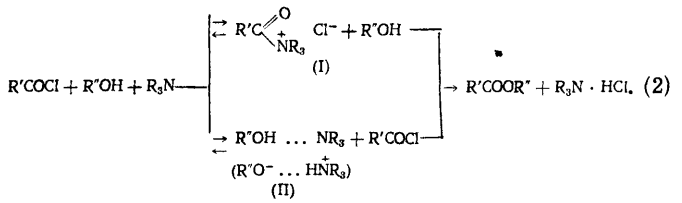
III. THE KINETICS, MECHANISM, AND CHARACTERISTICS OF ACCEPTOR-CATALYTIC POLYESTERIFICATION

Acceptor-catalytic polyesterification is one of the first examples of non-equilibrium polycondensation whose kinetics, mechanism, and principal characteristics have been studied in detail. One of the important results of such research has been the conclusion that the tertiary amine plays a catalytic role in the given reaction. The importance of this conclusion becomes understandable if one takes into account the fact that in 1959 Conix[14] attributed to tertiary amines merely the function of acceptors of the hydrogen halide evolved. Ten years later, in 1969, Billmeyer and Eckard[52] still assumed that tertiary amines behave as acceptors of the acid in the polycondensation of dicarboxylic acid dichlorides with diols, "displacing the equilibrium towards the formation of polyesters".

By 1965 there was virtually no information in the literature about the kinetics of acceptor-catalytic esterification and polyesterification. Nevertheless in his monograph Morgan[10] admitted the possibility of three different reactions under the conditions of acceptor-catalytic polyesterification: the formation of a complex of the tertiary amine and the acid chloride (nucleophilic catalysis), the formation of a complex of the tertiary amine and the phenol (general base catalysis), and simple binding of hydrogen chloride. The majority of investigators concerned with the problems of acylation and polyacylation in the presence of tertiary amines gave preference to the first of the above pathways[8,53,54].

From 1969, Korshak and coworkers[55] began systematic studies on the mechanism of acceptor-catalytic esterification and polyesterification. They established by ^{35}Cl NQR and potentiometric measurements that the interaction of tertiary amines with carboxylic acid chlorides involves the formation of ionic complexes of the type of acylammonium salts (I) [see Eqn. (2)]. The equilibrium complex-formation constant is appreciably influenced by the steric

and resonance factors, while the basicity of the tertiary amine plays a secondary role[56,57]:



At the same time it was found by ^{1}H NMR and infrared spectroscopy that, under conditions close to those in acceptor-catalytic polyesterification, tertiary amines form hydrogen-bonded complexes (II) with phenols [see Eqn. (2)], whose stability increases with increasing acidity of the donor and basicity of the acceptor[58-60]. In many instances it was possible to isolate and investigate the equimolar complexes of bisphenols with trialkylamines[60-62].

Bearing in mind the virtual irreversibility of the reactions of carboxylic acid chlorides with phenols[63,64], the mechanism of acceptor-catalytic polyesterification can be represented on the basis of the results of studies of the initial stages of the reaction[55] by two catalytic fluxes: a nucleophilic flux [the formation of complex (I)] and the general base-catalytic flux [the formation of complex (II)]. The study of the esterification kinetics[65-67] and determination of the relative activities of the starting compounds by the competitive acylation method[68,69] established that, in the absence of steric hindrance at the reaction centre, an increase of the acidity of the hydroxylated compound and of the basicity of the tertiary amine creates conditions for reaction via the general base catalysis. Thus it was found for the competitive benzoylation of phenol and methanol that, in the presence of triethylamine, the degree of conversion of the more acid reagent (phenol) greatly exceeds that of the less acid reagent (methanol) (Fig. 1). This shows that the general base catalysis predominates under the given conditions over nucleophilic catalysis. On the other hand, if the competitive benzoylation is carried out in the presence of a less basic tertiary amine (pyridine), then methanol mainly reacts, i.e. nucleophilic catalysis predominates under these conditions[68].

The kinetic study showed that acceptor-catalytic esterification is of third order overall (of first order with respect to each reactant) and that the rate-limiting stage is the interaction of complex (I) with phenol or of complex (II) with the acid chloride[65-67]. It was found that the rate of benzoylation in the presence of triethylamine (in dioxan at 30°C) is greatly influenced by the acidity of phenols and the plot of the logarithm of the reaction rate constant against pK_a^{DMSO} for phenols (Fig. 2) consists of two linear sections with opposite slopes: $\lg k_3 = -0.40\ pK_a + 4.88$ ($r = 0.996$, $s = 0.05$) for phenols with $pK_a < 14$ and $\lg k_3 = 0.39\ pK_a + 5.99$ ($r = 0.973$, $s = 0.05$) for phenols with $pK_a > 14$. This permitted the conclusion that nucleophilic catalysis is possible when the following conditions are observed: (1) the tertiary amine is more basic than the leaving group in R'COX; (2) the R"–OH nucleophile attacking the acylammonium complex is more basic than the leaving ammonium ion[67]. In the system investigated the first condition is completely fulfilled, while the second apparently holds only for more basic phenols with $pK_a > 14$. For more acidic phenols ($pK_a < 14$), the second condition does not hold and the reaction proceeds via the general base catalysis pathway.

The study of the kinetics of the benzoylation of alcohols in the presence of tertiary amines in a non-polar medium led Bogatkov et al.[70] to the conclusion that, regardless of the formation of complex (I) or (II), the reaction proceeds in this case via a transition state with a five-coordinated carbon atom.

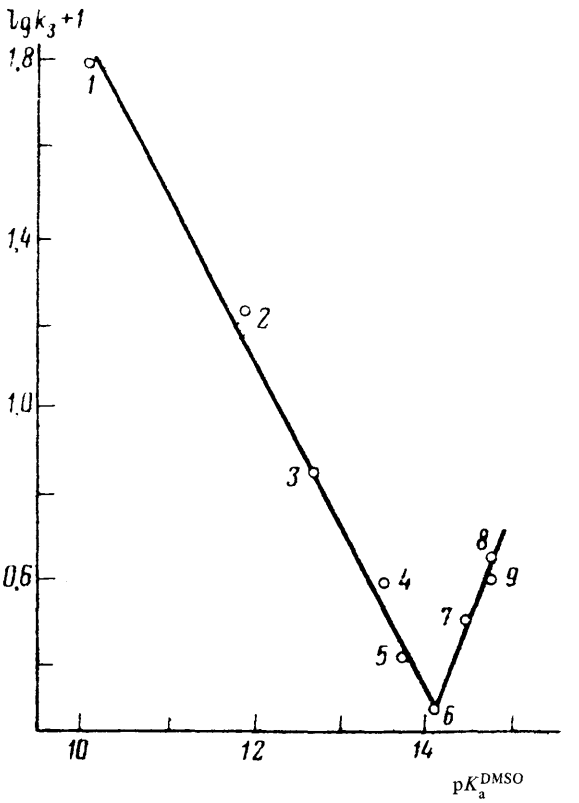


Figure 2. Dependence of the logarithm of the benzoylation rate constant on the acidity of phenols[67]; phenols: 1) *p*-nitrophenol; 2) *p*-acetylphenol; 3) *p*-chlorophenol; 4) *o*-hydroxyphenyl benzoate; 5) phenol; 6) *p*-t-butylphenol; 7) *p*-cresol; 8) *p*-methoxyphenol; 9) hydroquinone.

The solvent and reaction temperature have a marked influence on the rate of acceptor-catalytic esterification[71]. It has been found that an increase of the polarity of the solvent promotes an increase of the rate of reaction. A complex non-Arrhenius temperature dependence of the esterification rate constant (Fig. 3, curve *1*) has been established over a wide temperature range (from −30° to 80°C). The failure of the rate constant to obey the Arrhenius relation was attributed by the authors[71] to the fact that, in a complex reaction of this type, consisting of a series of consecutive stages [Eqn. (2)], temperature can have different effects on the rate of each individual stage. The resulting influence of temperature on the effective rate constant consists of these "partial" influences.

The results of the study of the kinetics and mechanism of acceptor-catalytic esterification enabled Korshak and coworkers to investigate at a qualitatively new level and to interpret the fundamental characteristics of acceptor-catalytic polyesterification as a characteristic example of non-equilibrium polycondensation[57,72]. Only a few aspects of this problem had been examined earlier[11,13,73,74]. In the analysis of the characteristics of acceptor-catalytic polyesterification and copolyesterification, data for the reactivities of diols and dicarboxylic acid dichlorides, first obtained in systematic studies of the above monomers by quantum-chemical[75,76], physical (potentiometry[77,78], ^{1}H NMR, [57,78] ^{35}Cl NQR [79,80]), and kinetic[80-83] methods, were used on a wide scale. It was established that the difference between the activities of the first and second functional groups of the monomer is determined by the distance between them, the structure of the bridge unit, and the structure of the attacking agent. Depending on the above factors, the activity of the second functional group of the monomer can decrease, remain unchanged, or after the first group has reacted, increase.

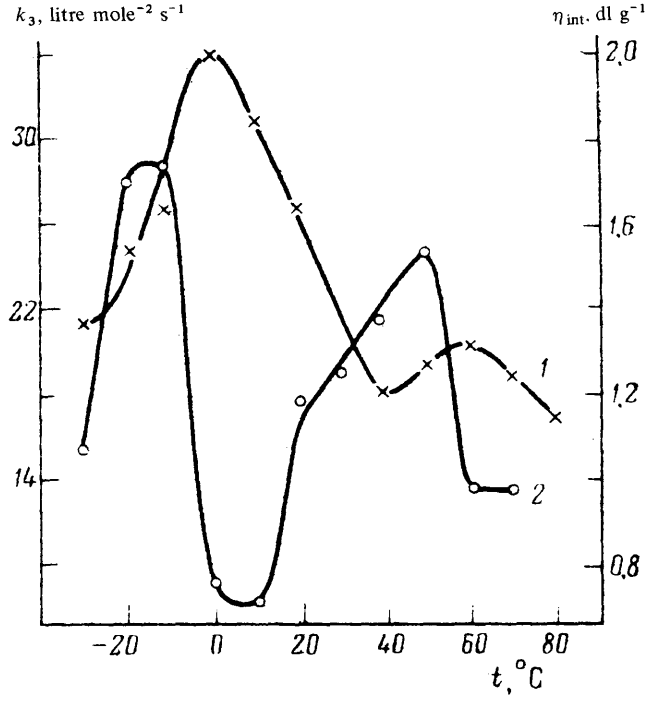


Figure 3. Dependence of the rate constant for the reaction of *o*-chlorophenol with *p*-chlorobenzoyl chloride (curve *1*) and of the intrinsic viscosity of the polyarylate obtained from 2,2-di-(3-chloro-4-hydroxyphenyl)propane and terephthalic acid dichloride (curve *2*) on the reaction temperature (toluene, triethylamine)[71].

Thus the results of the kinetic study of acceptor-catalytic esterification of terephthalic acid dichloride by phenols showed that the rate constants for the first and second COCl groups depend appreciably on the structure of the phenol (Table 1). Enhancement of the electron-accepting nature of the substituent in the phenol molecule increases the reactivity of the second COCl group of the acid dichloride, which actually begins to exceed that of the first COCl group when R = NO_2.[83] In the acceptor-catalytic esterification of di-(4-hydroxyphenyl) ether and 2,2-di-(4-hydroxyphenyl)propane by the chlorides of *p*-substituted benzoic acids, the ratios of the rate constants for the first and second OH groups have virtually the same value, which is independent of the structure of the acylating agent[83].

Table 1. Results of the kinetic study of the reaction of terephthalic acid dichloride with phenols (R––OH) in the presence of triethylamine*[83].

R	k^1, litre^2 mole^{-2} s^{-1}	k^2, litre^2 mole^{-2} s^{-1}	$\varkappa = k^1/k^2$
CH_3	11.5±1.0	4.7±0.3	2.45
H	10.0±1.0	6.8±0.8	1.47
Cl	17±1	15±1	1.13
NO_2	48±2	62±3	0.77

* Here $\overline{k^1}$ and $\overline{k^2}$ are the rate constants for the reactions of phenols with the first and second COCl groups of the dichloride in dioxan at 30°C.

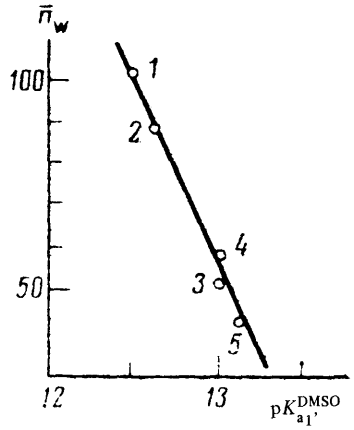


Figure 4. Dependence of the polymerisation coefficients of polyterephthalates $\bar{n}_W$ on the pK_{a_1} of bisphenols[88]; bisphenols: 1) 2,2-di-(3-chloro-4-hydroxyphenyl)propane; 2) 3,3-di-(4-hydroxyphenyl)phthalide; 3) di-(4-hydroxyphenyl)methylphenylmethane; 4) di-(4-hydroxyphenyl)-phenylmethane; 5) 9,9-di-(4-hydroxyphenyl)fluorene.

The study of acceptor-catalytic polyesterification showed that polyesters with the highest molecular weights are formed in high yields for an equimolar ratio of the acid dichloride and diol[57,84]. On the other hand, the optimum amount of tertiary amine is determined by the structure of the initial reactants. Thus, on passing from bisphenols to glycols and with decrease of the basicity of the tertiary

amine, the molar ratio of the acceptor-catalyst and the diol increases from 2 : 1 to 8 : 1.[4,57]

Comparison of the molecular weights of the polymers with the structures of the initial compounds established that, with increase of the acidity (activity) of the bisphenols[55,85,86] (Fig. 4) and the basicity of tertiary amines[87], the molecular weights of the polyarylates increase. The increase of the activity of the acid dichlorides also leads in most instances to an increase of the molecular weight of the polyarylates formed (Fig. 5); however, the increase of the activity of certain acid dichlorides is accompanied by a decrease of the molecular weight of the polymers[85,88].

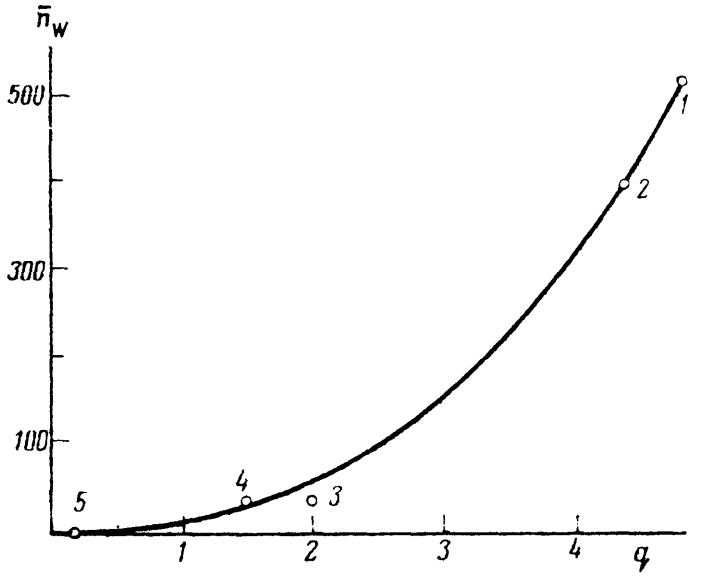


Figure 5. Dependence of the polymerisation coefficients of the polyarylates of 2,2-di-(3-chloro-4-hydroxyphenyl)-propane on the relative activity q of the acid dichloride[88]; dichlorides of different acids: 1) terephthalic; 2) isophthalic; 3) biphenyl-4,4'-dicarboxylic; 4) 1,1'-oxybisbenzene-4,4'-dicarboxylic; 5) tetrachloroterephthalic.

The study of the side reactions accompanying acceptor-catalytic polyesterification showed that the main chain-termination reactions under the conditions examined are hydrolysis and aminolysis of the acid halide groups[88,89], the contribution of these reactions increasing appreciably on passing from strongly basic (general base catalysis) to weakly basic (nucleophilic catalysis) tertiary amines[88]. Thus it has been found that in the presence of triethylamine the reactivity of diethylamine in the reaction with benzoyl chloride exceeds by several orders of magnitude the activity of phenol (Table 2). At the same time, the activity of water under analogous conditions is appreciably inferior to that of phenol. On passing to a less basic tertiary amine (pyridine), the reactivity of water increases and actually begins to exceed that of phenol (Table 2). In the presence of pyridine the role of the chain termination reaction due to the admixture of secondary amines also becomes more marked[88].

These results enabled Korshak and coworkers[88] to demonstrate experimentally for the first time that the molecular weights of the polymers obtained in non-equilibrium polycondensation depend on the ratio of the rates of chain propagation and termination. If an increase of the activity of the monomers (for example, the bisphenols) entails an increase of the contribution of the chain propagation reaction, then the molecular weight of the polymers increases. On the other hand, when an increase of the activity of the monomers (for example, acid dichlorides) is accompanied by an increase of the contribution of the chain termination reaction, the molecular weight of the polymers diminishes.

Table 2. The activities of HO- and NH_2-containing compounds relative to the activity of phenol in the reaction with benzoyl chloride in dichloroethane at 25°C.[88]

RXH	$k_{RXH}/k_{C_6H_5OH}$ **	
	$N(C_2H_5)_3$	NC_5H_5
H_2O*	<0.1	3.4
CH_3OH	0.17	9.5
$C_6H_4NH_2$	3.0	<100
$(C_2H_5)_2NH$	>100	***

*Acylation carried out in dioxan.

**$k_{RXH}/k_{C_6H_5OH}$ is the ratio of the rate constants for the benzoylation of RXH and phenol.

***Too high for determination by the method of competitive acylation.

On the basis of the theory of the heterounit structure of polymers developed by Korshak[90], one must suppose that the occurrence of certain types of reactions leads to the formation of heterounit polyesters. Thus, when acceptor-catalytic polyesterification is carried out in the presence of moisture, there is a possibility of the appearance of anhydride linkages in the macromolecules[33,89].

Interesting data were obtained in the study of the influence of reaction temperature on the results of acceptor-catalytic polyesterification[4,55,91-95]. It was found that, in the presence of highly reactive starting compounds in a homogeneous system, the dependence of the molecular weights of polyesters on the reaction temperature is represented by curves with two maxima (Fig. 3, curve 2). The results of kinetic studies suggested that this dependence is due to the presence of more than one extremum in the relation between the rate constant for the preparation of the polymer chain and the reaction temperature[71].

The study of the influence of the concentration of the initial compounds on the molecular weight of the polyester showed that, for a fairly high activity of the functional groups, the dependence of the molecular weights of the polymers on the concentration of the monomers is represented by a curve with a single maximum at 0.15–0.2 M.[4,91-95] The low activity of at least one of the initial compounds increases the optimum concentration of monomers to 1–2 M.[4]

The nature of the solvent has a major influence on the results of acceptor-catalytic polyesterification. Korshak and coworkers[94] showed that there is a tendency towards a decrease of the molecular weight of the polyester with

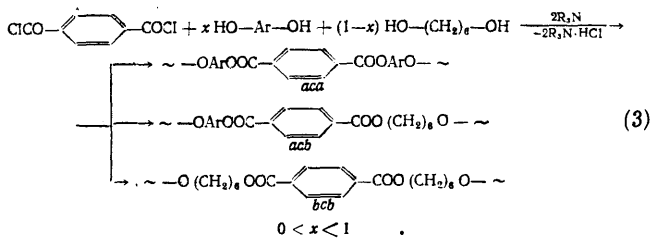
increasing dielectric constant of the medium. When acceptor-catalytic polyesterification is carried out in a metastable solution, the aggregation of macromolecules creates more favourable conditions for the formation of macromolecular compounds than in polyesterification in a thermodynamically stable solution with a similar dielectric constant[94]. Such aggregation of macromolecules apparently leads to a local increase of the concentration of the terminal groups of the polymer chains, which causes, on the one hand, an increase of the rate of propagation of macromolecules, and, on the other hand, diminishes the contribution of side reactions.

The precipitation of the polymer from solution under the conditions of acceptor-catalytic polyesterification does not in principle prevent further increase of its molecular weight, which takes place owing to the interaction of the terminal groups of the macromolecules with one another and with the initial compounds[94,96,97]. The optimum conditions for the synthesis of polyarylates in a heterogeneous system are a high solubility of the initial compounds in the reaction medium, an appreciable swellability of the polymer in a weakly polar medium, or a high polarity of the medium when the swellability of the polymer in the solvent is insignificant[97].

Acceptor-catalytic polyesterification in a heterogeneous system is of considerable practical interest, since the technological scheme of the synthesis of polymers is then significantly simplified.

IV. CHARACTERISTICS OF THE SYNTHESIS OF COPOLYMERS IN A HOMOGENEOUS SYSTEM

The successful discovery of the laws of formation of macromolecules under the conditions of non-equilibrium polycondensation depends in many respects on the extent to which the fundamental rules controlling the formation of fixed polymers have been found. The problems of the composition and structure of both polycondensation and polymerisation copolymers are especially important in this respect. Up to 1972, there were no experimental data for the influence of various factors on the composition and structure of copolymers obtained by non-equilibrium copolycondensation in a homogeneous system. In 1972 Korshak and coworkers[98,99] published for the first time experimental data concerning the rules governing the formation of the macromolecules of mixed polymers under the conditions of non-equilibrium copolycondensation in solution in relation to joint acceptor-catalytic polyesterification of a bisphenol and a glycol (comonomers) with terephthalic acid dichloride (the intermonomer).



(3)

The relative contents of the homo-(*aca*, *bcb*) and hetero-(*abc*) triads in the copolyesters were determined by high-resolution ^{1}H NMR.[98-104] The parameter K_M—the coefficient of the microheterogeneity of the copolymer—was calculated from the results[105,106]. $K_M = 0$ for a mixture of two homopolymers, $K_M = 1$ for statistical copolymers, and $K_M = 2$ for regularly alternating copolymers. Consequently the absolute values of the deviations of K_M from unity may make it possible to infer in quantitative terms the degree of order in the distribution of units, block copolymers being located in the region where $0 < K_M < 1$.

Interesting experimental data were obtained in the study of the structure of copolymers obtained when copolyesterification is carried out in solution by a single-stage method, in which the intermonomer and comonomer are in solution at the beginning of the reaction[98,101-104]. It was established that, regardless of the difference between the activities of the comonomers, copolymers are formed with a nearly statistical distribution of units (Table 3, Nos. 1 and 3). For low degrees of reaction, the composition of the copolymer is enriched in units containing the more active comonomer, but, as the copolyesterification reaction proceeds, the number of units becomes equal to the initial molar ratio of the comonomers[106]. Copolymers with a statistical distribution of units have been obtained also in two-stage copolycondensation, where the second comonomer was introduced into the reaction sphere only after the completion of the polycondensation of the intermonomer with the first comonomer, i.e. under conditions simulating an infinitely large difference between the activities of the comonomers (Table 3, Nos. 2 and 4).[100] It was shown that certain deviations from the statistical distribution of units in the macromolecules are caused by a change in the activity of the second COCl group of the intermonomer after the first COCl group has reacted (Table 1). These results demonstrated the erroneous nature of the view according to which statistical copolymers are difficult to obtain by non-equilibrium copolycondensation of comonomers with different activities[8,10,107].

Table 3. The structure of copolyterephthalates based on a bisphenol and hexamethylene glycol and obtained by joint acceptor-catalytic polyesterification in the presence of triethylamine (dichloroethane, 40°C).

No.	Bisphenol	Copolymerisation constant for comonomers q	Content of triads, mole fraction			K_M
			aca	*acb*	*bcb*	
1	2,2-di-(4-hydroxy-3-methylphenyl)propane*	5,3[103]	0.19	0.62	0.19	1.24
2	ditto**	∞	0.19	0.64	0.17	1.28
3	2,2-di-(3-chloro-4-hydroxyphenyl)-propane*	33[103]	0.22	0.56	0.22	1.12
4	ditto**	∞	0.25	0.54	0.21	1.09

*A solution of terephthalic acid dichloride (0.2 M), the bisphenol (0.1 M), and hexamethylene glycol (0.1 M) was treated with triethylamine (0.4 M) and the copolyesterification was continued for 1 h.[103]

**A solution of terephthalic acid dichloride (0.2 M) and the bisphenol (0.1 M) was treated with triethylamine (0.4 M). After 30 min, hexamethylene glycol (0.1 M) was introduced into the reaction mixture and the reaction was continued for 1 h.[100]

It was found that block copolymers can be obtained under the conditions of single- and two-stage acceptor-catalytic copolyesterification when the intermonomer is gradually introduced into the reaction zone (Table 4).[99-104]

In this case the length of the blocks increases with increasing difference between the activities of the comonomers and with decrease of the rate of entry of the intermonomer into the reaction zone. A convenient method for the synthesis of block copolymers is three-stage copolycondensation, where the acceptor-catalytic polyesterification of the intermonomer with each comonomer is carried out in different reaction volumes. The intermonomer in one reaction volume is introduced in an excess, while in the other it is present in a deficiency in relation to the monomer, the amounts being calculated so that the overall molar amounts of the functional groups of the intermonomer and the comonomers in the two reaction volumes are equal[103]; at the end of the reaction the first and second systems are combined. It was found that the smaller the deviation from equivalence in each system, the greater the length of the blocks in the block copolymers.

By varying the above factors, it is possible to obtain block copolymers with different lengths of the blocks, regulating thereby the structure of the macromolecules of mixed polymers in the required way.

Experimental data for the influence of various factors on the composition and structure of copolymers were confirmed by the fundamental conclusions arising from the quantitative theory of non-equilibrium copolycondensation in a homogeneous system developed by Kuchanov[105, 106, 108]. A satisfactory quantitative correspondence between the experimental and theoretical data was established, the difference between them being within the limits of the experimental error (see, for example, Table 5). This shows that the conclusion reached from the results of the study of joint acceptor-catalytic polyesterification are of general validity and apply satisfactorily to the formation of the macromolecules of copolymers under the conditions of non-equilibrium copolycondensation in a homogeneous system.

Table 4. The structure of copolyterephthalates based on a bisphenol and hexamethylene glycol, obtained by single-stage copolyesterification in the presence of triethylamine with gradual introduction of terephthalic acid chloride into the reaction solution (dichloroethane, 40°C).[99]

Bisphenol	q^{103}	Length of blocks		K_M
		n_{ac}	n_{bc}	
2,2-di-(4-hydroxy-3-methylphenyl)propane	5.3	4.4	4.4	0.46
9,9-di-(4-hydroxylphenyl)fluorene	12.6	5.6	5.6	0.36
2,2-di-(4-hydroxy-3-nitrophenyl)propane	31	8.2	8.5	0.24
2,2-di-(3-chloro-4-hydroxyphenyl)propane	33	9.2	9.2	0.22

Table 5. The values of K_M for copolyterephthalates synthesised by two-stage copolycondensation (dioxan, 40°C)*[83].

X in 2,2-di-(4-hydroxy-3-X-phenyl)propane	x***	K_M (expt.)	K_M (theor.)
CH_3	2.45	1.28	1.33
Cl	1.13	1.09	1.05
NO_2	0.77	0.93	0.91

* See second footnote to Table 3.
** See Table 1.

By surveying the experimental data, it was possible to formulate the fundamental characteristics of the formation of the macromolecules of mixed polymers under the conditions of non-equilibrium copolycondensation in a homogeneous system[98-104, 106].

1. When the entire amount of the intermonomer is introduced at once into the reaction zone at the beginning of non-equilibrium copolycondensation, statistical copolymers are formed regardless of the difference between the activities of the comonomers. The use of a bifunctional compound with dependent functional groups as the intermonomer influences the structure of the copolymers: the decrease of the activity of the second functional group after the first has reacted leads to an increase of the fraction of regularly alternating fragments in the polymer chains; the increase of the activity of the second functional group of the intermonomer promotes an increase in the length of the blocks.

2. The introduction of comonomers into the reaction zone in stages is not a sufficient condition for the synthesis of copolymers with a block structure.

3. The synthesis of block copolymers by single-stage non-equilibrium copolycondensation in a homogeneous system requires that the activities of the comonomers should be different and that the rate of introduction of the intermonomer into the reaction zone should be smaller than the rate of its interaction with the more reactive comonomer.

V. CHARACTERISTICS OF THE SYNTHESIS OF POLYESTERS FROM DIOLS WITH AN ASYMMETRIC DISTRIBUTION OF HYDROXY-GROUPS

The non-equilibrium polycondensation of bifunctional compounds with an asymmetric distribution of functional groups (z–RS–z) gives rise to the problem of the determination of the structure of heterounit polymer chains, and to the possibility of additions of the "head-to-head" ("tail-to-tail") or "head-to-tail" type:

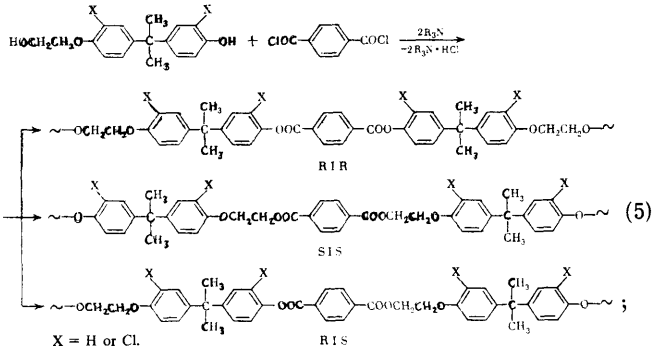
$$z\text{–RS–}z + y\text{–I–}y \rightarrow \begin{cases} \sim\text{–RS–I–RS–I–RS–I–}\sim + 2xy \\ \text{"head-to-tail"} \\ \sim\text{–RS–I–SR–I–RS–I–}\sim + 2xy \\ \text{"head-to-head", "tail-to-tail"} \end{cases} \quad (4)$$

Here z–RS–z and y–I–y are bifunctional monomers with asymmetric and symmetrical distributions of functional groups respectively. This type of problem arises in the polymerisation of asymmetric vinyl monomers, for example, monosubstituted ethylenes, in which heterounit macromolecules with "head-to-head" or "head-to-tail" distributions of units are also formed. This problem has been fairly well investigated in polymerisation and it was established that the "head-to-tail" addition occurs more frequently[109, 110].

There have been a number of studies[111-116] in which the problem of the structure of polycondensation polymers based on the monomers shown in Eqn. (4) is discussed,

and the possibility of "head-to-head" or head-to-tail" additions is considered. The view is expressed in these studies that the different activities of the functional groups in z–RS–z is the decisive factor in the formation of monomers in which "head-to-head" additions predominate.

In 1974 Korshak et al.[117] published the first study where they established the structure of polymers based on monomers with an asymmetric distribution of functional groups, in relation to the acceptor-catalytic polyesterification of the β-hydroxyethyl ethers of bisphenols with terephthalic acid dichloride, and determined the fundamental principles of the formation of their macromolecular structure[117,118]:



(5)

The structure of the polyesters was studied by high-resolution ^{1}H NMR, based on the different chemical shifts of the phenylene protons in the terephthalic acid residue in homo-(RIR, SIS) and hetero-(RIS) triads corresponding to the "head-to-head" ("tail-to-tail") or "head-to-tail" addition respectively[117,118]. The coefficient of microheterogeneity K_M served as a quantitative characteristic of the regularity of the structure of the macromolecules. For regularly alternating polymers of the "head-to-head" and "tail-to-tail" type, $K_M = 0$, while for polymers involving "head-to-tail" additions, $K_M = 2$. $K_M = 1$ corresponds to a statistical distribution of units in macromolecules.

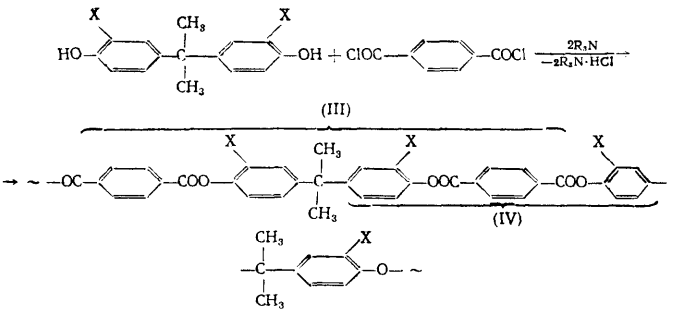
It was established that, when both initial monomers are in solution at the beginning of polycondensation, a polymer with a nearly statistical distribution of units is formed regardless of the difference between the activities of the hydroxy-groups ($K_M = 1.01–1.11$).[117,118] This result showed that, even a considerable difference between the reactivities of the phenolic and alcoholic groups, does not constitute a sufficient condition for preferential addition of the "head-to-head" type. The deviation of K_M from unity is apparently due to the fact that the activity of the second COCl group of terephthalic acid dichloride diminishes after the first COCl group has reacted[83], which leads to a predominance of the "head-to-tail" structures[117]. It has also been established that the formation of polymers with "head-to-head" ("tail-to-tail") structures, predominating under the conditions of non-equilibrium polycondensation, requires a gradual addition of a monomer with a symmetrical distribution of functional groups (terephthalic acid dichloride) to a solution of the monomer with an asymmetric distribution of functional groups (the diol). K_M depends on the rate of addition of the acid dichloride and on the difference between the activities of the OH groups of the diol[117,118].

Analysis[117], has shown that the kinetic mechanism of the above process (and hence its mathematical description) is the same as the mechanism described earlier in connection with calculations on copolycondensation[105,106,108,119]. The experimental and theoretical characteristics of the formation of the structures of the polymer chains based on monomers with a "head" and a 'tail" agree satisfactorily[117].

VI. SYNTHESIS OF CONFORMATIONALLY REGULAR POLYARYLATES

An interesting feature of acceptor-catalytic polyesterification is conformational specificity of this process, which makes it possible to obtain conformationally regular polymers whose conformational tacticity is established in the course of the reaction, and the macromolecules contain regular sequences of one or other (but fully defined) rotational isomer in the monomer residue[120,121].

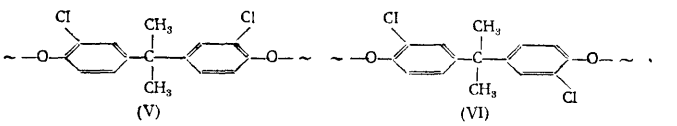
The study of the kinetics, mechanism, and characteristics of acceptor-catalytic polyesterification and of the properties of the polymers obtained enabled Korshak et al.[122] to establish for the first time in 1970 that non-equilibrium polycondensation gives rise to considerable possibilities for the synthesis of stable stereoregular polycondensation polymers of a new type, whose macromolecules contain regular sequences of stable rotational isomers. Conformationally regular polyarylates of the above type were synthesised under the conditions of acceptor-catalytic polyesterification from *o,o'*-disubstituted, 2,2-di-(*p*-hydroxyphenyl)propane and terephthalic acid dichloride[57,123–126]:



(6)

The fundamental novelty of the synthesis of conformationally-regular polymers under the conditions of acceptor-catalytic polyesterification is the fact that their regular three-dimensional microstructure is formed directly during the growth of macromolecules.

Conformational analysis by ^{35}Cl NQR of the polyterephthalates of 2,2-di-(3-chloro-4-hydroxyphenyl)propane (dichlorodian) as well as compounds (III) and (IV) (X = Cl), simulating the fragments of the polymer chain, showed that, depending on the conditions of synthesis, the macromolecules of the given polyarylate contain regular sequences of cisoid (V) or transoid (VI) rotational isomers of the bisphenol residue[57,124,125]:



It was established that the microstructure of conformationally regular polyarylates is influenced by the structure of the initial compounds (bisphenols, dicarboxylic acid dichlorides, and tertiary amines) and by the conditions of acceptor-catalytic polyesterification[121–127].

Comparison of the properties of polyterephthalates based on di-(3-chloro-4-hydroxyphenyl)alkanes with different bridge groups showed that the decrease of the barrier to rotation about the $C_{(1)}-C_{(2)}$ bonds, where $C_{(1)}$ and $C_{(2)}$ are respectively the carbon atoms of the bridge group and the benzene ring, in the sequence $C(CH_3)$. $.(C_7H_{15}) > C(CH_3)_2 > CH_2$ promotes the formation of conformationally regular polyarylates, the high stereotacticity of which in the case of the methylene bridge is apparently caused not so much by the conformational specificity of acceptor-catalytic polyesterification as by the ready crystalisability of such polymers[125,127]. Thus, regardless of the conditions of synthesis, crystalline polyterephthalates of di-(3-chloro-4-hydroxyphenyl)-methane contain only one type of conformational isomer of the bisphenol residue.

The use of sterically hindered bisphenols [di-(5-chloro-2-hydroxyphenyl)alkanes] in acceptor-catalytic polyesterification made it possible to obtain conformationally regular polyarylates with a high degree of order in their structure[125,127]. It has been suggested that the considerable stereotacticity of these polymers is due to the energetic non-equivalence of different conformations in the bisphenol residue, which leads to the formation of macromolecules containing mainly one conformation of the bisphenol fragment.

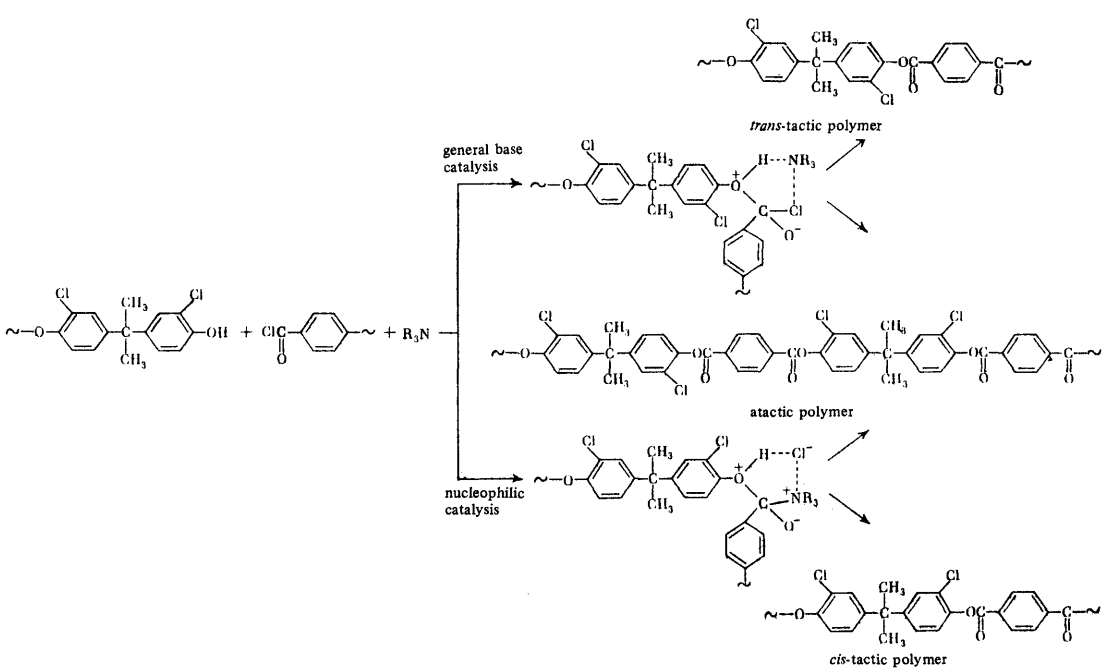
A characteristic example of the conformational specificity of acceptor-catalytic polyesterification is the synthesis of conformationally regular dichlorodian polyarylates based on various dicarboxylic acid dichlorides[126] in the presence of various tertiary amines[57,125,126]. It was established that, depending on the nature of the tertiary amine (primarily depending on its basicity) and hence depending on the reaction mechanism (nucleophilic or general base catalysis)[57,66-68], macromolecules containing one or other type of rotational isomer are formed. In the presence of weakly basic heterocyclic tertiary amines (nucleophilic catalysis) polymers with *cis*-isomers (V) of the bisphenol fragment are formed, whereas in the presence of highly basic trialkylamines (general base catalysis) the products are polymers with *trans*-isomers (VI).[125] Korshak and coworkers[57,125] attribute the cause of this phenomenon to the different geometries of the transition complexes corresponding to the nucleophilic and general base catalysis, which promotes the formation of different rotational isomers in the bisphenol residue [see Eqn. (7)].

A significant factor is that, in the crystallisation of amorphous polyarylates by a secondary treatment, polymers containing only the *trans*-isomers (VI) in the macromolecules are formed, whereas under the conditions of acceptor-catalytic polyesterification polymers with both cisoid and transoid isomeric forms of the dichlorodian residue may be produced. The role of the acceptor-catalyst in the establishment of the conformational tacticity of polyarylates apparently consists in determining the relative contributions of the two catalytic processes competing in the reaction, which leads in its turn to the predominance in the polymer chains of one or other rotational isomer.

Korshak and coworkers[121-127] showed that the presence of regular sequences of isomeric forms in polyarylate macromolecules influences significantly their properties. In particular, an increase of the stereotacticity of the polymers increases the degree of their crystallinity and the softening temperature, and diminishes their solubility.

The study of the influence of the conditions of synthesis and subsequent treatment of conformationally regular polyarylates on their properties showed a fairly high stability, including their state in solution, of the conformations of the bisphenol residue in the polymer chains[27,121,123,124,128]. Under the influence of mechanical, thermal, and other influences, there is a possibility of the conversion of conformationally regular polymers into conformationally atactic polymers[57,121,123,124].

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(7)

Thus the data presented in this review show that acceptor-catalytic polyesterification is of considerable interest as a method of synthesis of homogeneous and mixed polyesters with a definite macromolecular structure, including conformationally regular polyarylates.

Acceptor catalytic polyesterification has acquired particular importance as a model reaction for the investigation of the characteristics of the formation of the macromolecules of copolymers and polymers containing "head-to-tail" fragments under the conditions of non-equilibrium polycondensation in a homogeneous system. There are at present virtually no literature data concerning the characteristics of the formation of macromolecules of this type under the conditions of non-equilibrium polycondensation in a heterophase system. Studies on the characteristics of acceptor-catalytic polyesterification under heterophase conditions may play a definite role in the solution of this problem. The determination of the scope of the synthesis of configurationally regular polymers under the conditions of acceptor-catalytic polyesterification, or in other words, the synthesis by acceptor-catalytic polyesterification of stereoregular polymers (for example iso- or syndio-tactic polymers) from monomers consisting of a mixture of geometrical or optical isomers, is of considerable interest.

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